SYNTHESIS AND STRUCTURAL STUDIES OF GROUP 16 *PERI*-SUBSTITUTED NAPHTHALENES AND RELATED COMPOUNDS

Fergus Ross Knight

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SYNTHESIS AND STRUCTURAL STUDIES OF GROUP 16 *PERI*-SUBSTITUTED NAPHTHALENES AND RELATED COMPOUNDS

by

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A thesis submitted in partial fulfilment for the award of

DOCTOR OF PHILOSOPHY

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Declaration

I, Fergus R. Knight, hereby certify that this thesis, which is approximately 69,000 words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

I was admitted as a research student in September, 2006 and as a candidate for the degree of PhD. in July, 2007; the higher study for which this is a record was carried out in the University of St Andrews between 2006 and 2009.
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Abstract

Understanding how atoms interact is a fundamental aspect of chemistry, biology and materials science. There have been great advances in the knowledge of covalent and ionic bonding over the past twenty years but one of the major challenges for chemistry is to develop full understanding of weak interatomic/intermolecular forces. This thesis describes fundamental studies that develop the basic understanding of weak interactions between heavier polarisable elements. The chosen methodology is to constrain heavy atoms using a rigid naphthalene backbone.

When substituents larger than hydrogen, are positioned at close proximity at the *peri*-positions of a naphthalene molecule they experience steric strain; the extent of which is dictated by intramolecular interactions. These interactions can be repulsive due to steric hindrance or attractive due to weak or strong bonding.

In efforts to understand the factors which influence distortion in sterically crowded naphthalenes and study possible weak intramolecular interactions between *peri*-atoms, investigations focussed on previously unknown mixed 1,8-disubstituted naphthalene systems. Mixed phosphorus-chalcogenide species were initially studied; three mixed phosphine compounds of the type Nap[ER][PPh_2] were prepared along with their chalcogenides and a series of metal complexes.

The study of interactions between heavy atoms was progressed by investigations into a series of mixed chalcogenide compounds of the type Nap[EPh][E'Ph] (E = S, Se, Te). Subsequent reaction of the chalcogenide systems with the di-halogens, dibromine and diiodine, afforded a mixture of charge transfer and insertion adducts displaying an array of different geometries around the chalcogen atom.

From molecular structural studies, a collection of intramolecular *peri*-interactions were found, extending from no interaction due to repulsive effects, weak attractive 3c-4e type interactions and one example containing a strong covalent *peri*-bond. Further weak intramolecular interactions observed include CH-π and E···E' type interactions plus π-π stacking between adjacent phenyl rings. It was discovered that the bulk of the *peri*-atoms is influential on the distance between them, but this is not the only factor determining the naphthalene geometry. Inter- and intramolecular interactions can also have an impact and furthermore the number, size and electronic properties of substituents attached to the *peri*-atoms can determine molecular distortion.

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Abbreviations

Fig.	Figure
dman	1,8-bis(dimethylamino)naphthalene
dmpn	1,8-bis(dimethylphosphino)naphthalene
dppn	1,8-bis(diphenylphosphino)naphthalene
rac-	racemic
dmeopn	1,8-bis[(dimethoxy)phosphino]naphthalene
DAN	8-dimethylaminonaphth-1-yl
Nap	naphthalene-1,8-diyl
HSAB	hard soft acid base
TCNE	tetracyanoethylene
TTN	tetrathionaphthalene
TTL	'tetrathiolene' ligands
TCTTN	tetrachlorotetrathionaphthalene
TTT	tetrathiotetracene
3c-4e	three centre-four electron
4c-6e	four center-six electron
cod	cyclooctadiene
aq	aqueous
cg	centroid
J	coupling constant (Hertz, Hz)
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphine)propane
^{p}Cy	*para*-cymene
MO	molecular orbital
WBI	Wiberg bond index
mCPBA	*meta*-chloroperoxybenzoic acid
TMEDA	tetramethylethylenediamine
C.-T.	charge-transfer
χ	electronegativity
TBP	trigonal bipyramidal

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Chapter 1 - Introduction

The structure and properties of *peri*-disubstituted naphthalenes

Naphthalene.

Naphthalenes are members of a class of aromatic bidentate ligands with rigid C_3-backbones. Substituted naphthalenes have potential significance as ligands in transition metal-catalysed reactions.[1] Unsubstituted naphthalene is known to be rigidly planar with the bond lengths and bond angles having been accurately determined (Figure 1.1).[2] In contrast to benzene, the C-C bond lengths in naphthalene are not all equal, giving naphthalenes a unique geometry.[2]

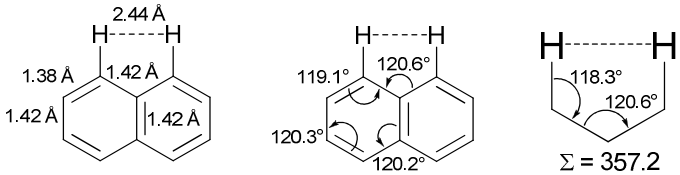

Fig. 1.1 *Unsubstituted naphthalene is known to be rigidly planar with unequal bond lengths and angles.*[2]

The *peri*-carbon atoms (1- and 8- positions) of naphthalene are separated by a distance of between 2.4 and 2.5 Å. This is considerably less than in other aromatic molecules where the non-bonded substituent distance is approximately 3 Å.[2] This *peri*-distance is sufficient to accommodate two hydrogen atoms but it is reasonable to expect that with larger substituents at the *peri*-positions there will be considerable steric hindrance.[3]

Substituted naphthalenes – intramolecular interactions.

Despite the presence of steric hindrance between the *peri*-atoms, chemists have encountered no difficulties in synthesising a large and diverse collection of *peri*-disubstituted naphthalenes. As early as 1969, Franck and Leser succeeded in synthesising 1,3,6,8-tetra(*t*-butyl)naphthalene (Figure 1.2).[4]

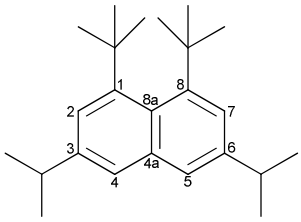

Fig. 1.2 *The structure of 1,3,6,8-tetra(t-butyl)naphthalene as reported by Franck and Leser in 1969.*[4]

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The ability to synthesise *peri*-substituted naphthalenes, despite the presence of *peri*-atom steric hindrance, can be explained by intramolecular or transannular interactions between the *peri*-substituents caused by their close proximity to one another.[3] These interactions can be repulsive steric effects caused by crowding of substituents, or attractive effects caused by weak or strong bonding.[5] Consequently steric interactions in *peri*-substituted naphthalenes has received a large amount attention.[3,6]

Strain relief – naphthalene distortion.

Steric strain between *peri*-atoms is relieved via naphthalene distortions which effectively change the geometry observed in unsubstituted naphthalene. Relief can be accomplished by stretching of the *peri*-atom bonds **(a)**, in-plane **(b)** or out-of-plane **(c)** deflection of the *peri*-substituents or distortion or buckling of the naphthalene ring **(d)** (Figure 1.3). Large amounts of energy are associated with even a small change in bond length so few examples of *peri*-atom bond stretching are known. The most common form of naphthalene distortions are in-plane and out-of-plane deviations of the exocyclic bonds with few examples of buckled naphthalene ring systems reported. This can be accounted for because relatively large relief of steric interaction is accomplished by minor molecular distortions.[3]

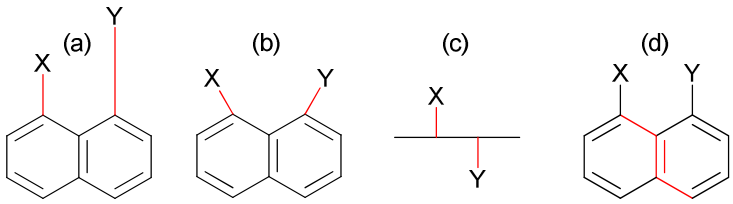

Fig. 1.3 *Steric strain relief via stretching of bonds, in-plane and out of plane distortion and buckling of the naphthalene plane.*[3]

In 1974, Roberts *et al.* determined the structure of 1,8-bis(bromomethyl)naphthalene (Figure 1.4). They reported the non-bonding distance between the methylene carbon atoms to be 3.05 Å which is 0.55 Å larger than the *peri*-distance in naphthalene and evidence for steric hindrance forcing the naphthalene skeleton into distortion.[7]

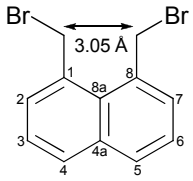

Fig. 1.4 *1,8-bis(bromomethyl)naphthalene reported by Roberts et al. in 1974.*[7]

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Similarly, a planar model of 1,8-dinitronaphthalene results in a very short non-bonded O···O distance of ~0.5 Å, much shorter than the normal distance [2.7 Å]. The incredible steric strain which would result is avoided in a number of ways. Firstly the C-N bonds are rotated about their axis by 45° and the N···N distance is increased from 2.42 Å (as in the planar model) to 2.93 Å by the splaying apart of the C-N bonds (in-plane distortion) and the deviation of the C-N bonds away from the aromatic plane in opposite directions by 0.37 Å (out-of-plane distortion). A slight nuclear distortion also occurs with the *peri*-carbon atoms forced out-of-plane in the direction of the nitro groups.[3,8]

Assessing intramolecular interactions and strain relief

X-ray structural data is central in assessing the crowding of *peri*-substituents and therefore quantifying the repulsive steric effects in substituted naphthalenes. Various concepts are used to describe the extent of steric strain occurring in these compounds. However the *peri*-distance is the primary parameter. To give a greater idea of the overall naphthalene distortion taking place in a given molecule, the amount of in-plane distortion, out-of-plane distortion and buckling of the naphthalene plane can also be measured and compared to the geometry of naphthalene (Figure 1.5).[9]

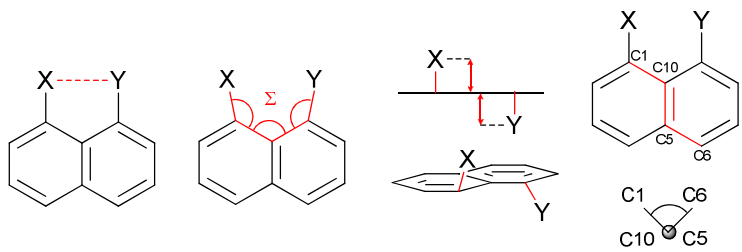

Fig. 1.5 *Measuring steric interactions and naphthalene distortions: peri-distance, sum of the bay region angles, distance of the peri-atoms from the mean naphthalene plane and torsion angles around the C5-C10 bond.*

The distance of the *peri*-atoms above and below the naphthalene mean plane indicates the degree of out-of-plane deformation and by comparing the sum of the angles in the bay region (splay angles) the amount of in-plane distortion can be deduced. Torsion angles show the level of planarity in the molecule and give an insight into the degree of buckling taking place in the naphthalene ring system (as depicted by the C(1)-C(10)-C(5)-C(6) angle in Figure 1.5). In naphthalene the splay angles sum to 357.2° and torsion angles are either 0° or 180° depicting total planarity.[2,9]

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Uses of *peri*-substituted naphthalenes.

The unique geometry and steric strain responsible for the appearance of transannular interactions gives *peri*-disubstituted naphthalenes distinctive properties, which have resulted in a great deal of attention.[3,6] The rigid C_3-backbone of the naphthalene molecule strictly defines the locations of the *peri*-substituted atoms in space. However by attaching bulky or electronically dissimilar substituents around the ring system the properties of the molecule can be altered leading to many different uses.[6]

For example Maruoka *et al.* reported a novel non-catalysed allylation of aldehydes and ketones using 1,8-bis(allylstannyl)naphthalene derivatives as neutral, bidentate, chelation-induced Lewis acids (Figure 1.6).[10]

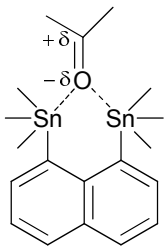

Fig. 1.6 *Non-catalysed allylation of aldehydes and ketones using 1,8-bis(allylstannyl)naphthalenes.*[10]

Zoltewicz *et al.* reported the synthesis of five new atropisomerically chiral, cofacial 1,8-diheteroarylnaphthalenes which mimic stacked/cofacial heteroaromatic ring systems found in a number of natural products, most importantly in nucleic acids (Figure 1.7).[11]

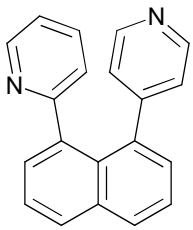

Fig. 1.7 *The 1,8-diheteroarylnaphthalenes which mimic heteroaromatic ring systems found in many natural products.*[11]

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Whiting *et al.* reported the first preparation of bifunctional Lewis acid-Lewis base derivatives, based up aryldifluoroborane and arylamine functions using the 1,8-naphthalene backbone (Figure 1.8).[12]

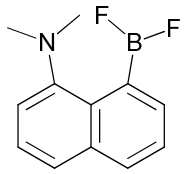

Fig. 1.8 *Bifunctional Lewis acid-Lewis base derivatives based on a 1,8-naphthalene backbone.*[12]

A literature study of *peri*-substituted naphthalenes

Peri-substituted bis-borane and bis-amino naphthalenes.

In 1985, Katz reported the synthesis and hydride-abstracting ability of 1,8-naphthalenediylbis(dimethylborane), the first example of a multidentate Lewis acid that was both rigid and uncharged.[13] This novel borane may be viewed as the electron-deficient counterpart of the non-nucleophilic base 1,8-bis(dimethylamino)naphthalene (dman) known as 'proton sponge' (Figure 1.9).[14,15]

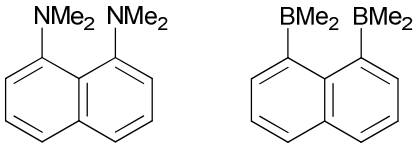

Fig. 1.9 *1,8-bis(dimethylamino)naphthalene ('proton sponge') and its electron-deficient counterpart 1,8-naphthalenediylbis(dimethylborane).*[13,14]

Katz demonstrated that the 'hydride sponge' (1,8-naphthalenediylbis(dimethylborane)) forms stable, bridged complexes by abstracting H^-, F^- and OH^-. However NMR data suggested that the interaction of the hydride sponge with Cl^- is weak or nonexistent.[16]

Driven by the importance of Cl^- chelation by organotin[17] and organomercury[18] bidentate Lewis acids and the catalytic significance of chloride-abstracting Lewis acids in Friedel-Crafts reactions,[19] Katz went on to prepare a bis(borane) that forms chelated complexes with Cl^-. It was evident from previous studies that such a compound would have to be a stronger Lewis acid than the hydride sponge and so 1,8-naphthalenediylbis(dichloroborane) was synthesised and its interaction with Cl^- was investigated (Figure 1.10).[20]

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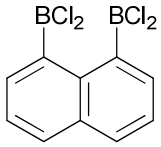

Fig. 1.10 *1,8-naphthalenediylbis(dichloroborane) reported by Katz.*[20]

Lewis acid-carbonyl group interactions have long been investigated due to their dramatic effect on reactivity and selectivity in a variety of reactions.[21] One recent development has been in the area of asymmetric catalysis by Lewis acids.[22] In 1995, Reilly and Oh reported the simultaneous coordination of a carbonyl group **(a)** by the bimetallic chiral Lewis acid 1,8-naphthalenediylbis(dichloroborane) and coordination of a chiral ligand and a carbonyl group **(b)**. Each boron atom (Lewis acid) was shown to play an organizational role doubly activating the substrate (Figure 1.11).[23]

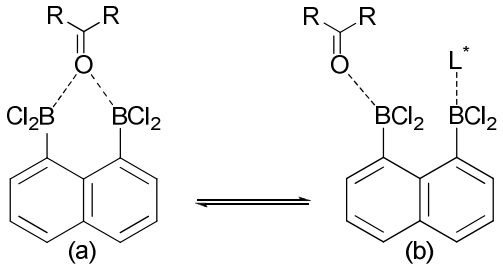

Fig. 1.11 *The simultaneous coordination of a carbonyl group by a bimetallic chiral Lewis acid.*[23]

***Peri*-substituted bis-phosphine naphthalenes.**

Over the last 30 years, a novel class of bidentate bis-phosphine ligands has been developed and reported. These compounds utilise a rigid C_3-backbone by placing phosphino groups *peri*-substituted on a naphthalene ring. The first of this new type of 1,8-bis(phosphino)naphthalene to be published, 1,8-bis(dimethylphosphino)naphthalene (dmpn) was reported by Costa and Schimdbaur in 1982 (Figure 1.12).[24]

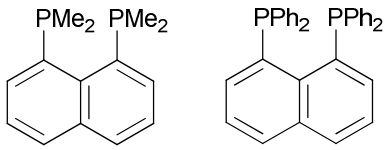

Fig. 1.12 *1,8-bis(dimethylphosphino)naphthalene (dmpn) and 1,8-bis(diphenylphosphino)naphthalene (dppn).*[24,25]

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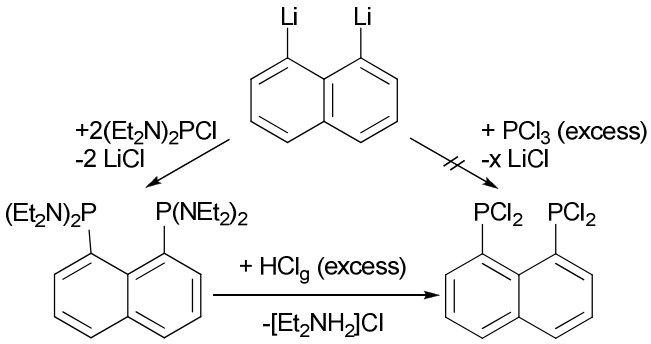
Roughly a decade later whilst working on 1,8-bis(phosphino)naphthalene ligands, Pringle's group reported the preparation of 1,8-bis(diphenylphosphino)naphthalene (dppn) by a similar route to dmpn, along with its X-ray structure and some preliminary results on its reaction chemistry (Figure 1.12).[25] An easier route to dppn was later reported by Brandsma *et al.* in 1994 starting from commercially available 1-bromonaphthalene and avoiding the painstaking synthesis of 1,8-dibromonaphthalene.[26]

These 1,8-bis(phosphanyl)naphthalene compounds, which can be regarded as phosphorus analogues of the 'proton sponge' (dman), have received great attention because they form six-membered palladium(II) chelates active for catalytic CO/ethylene co-polymerisation.[25,27]



Scheme 1.1 *The first synthesis of a 1,8-bis[(dialkylamino)phosphanyl]naphthalene.*[28]

Schmutzler *et al.* have been highly active in this field of research over the last decade and in 1997 reported the first synthesis of a 1,8-bis[(dialkylamino)phosphanyl]naphthalene (Scheme 1.1).[28] This compound is important because it provides a starting material for the synthesis of the previously unknown 1,8-bis(dichlorophosphanyl)naphthalene which is not accessible via the direct reaction of 1,8-dilithionapthalene with phosphorus dichloride (Scheme 1.1).[28]

With the emphasis on introducing bulky alkyl substituents in the *peri*-positions, Schmutzler *et al.* went on to synthesise and characterise a series of 1,8-bis(phosphino)naphthalene ligands which included the previously reported 1,8-bis(diphenylphosphino)naphthalene (dppn) and 1,8-bis(dimethylphosphino)naphthalene (dmpn) (Scheme 1.2).[24-26,29] The *rac*-isomer of 1,8-bis(phosphino)naphthalene **e** has the potential to act as a rigid, P-chiral, C_3-ligand in asymmetric synthesis so deserves special interest.[30]

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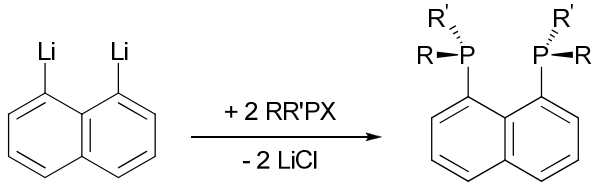
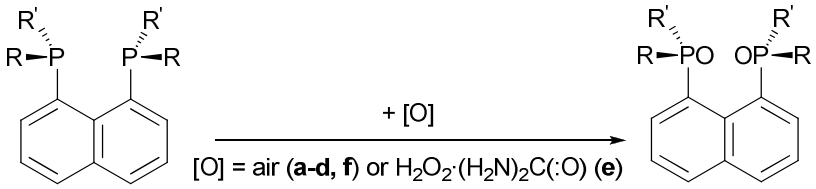
Schmutzler *et al.* continued their study of 1,8-bis(phosphino)naphthalene ligands by investigating the behaviour of their previously prepared series of phosphines (Scheme 1.2) towards oxygen, sulfur, selenium and tellurium.[31]



	a	b	c	d	e	f	g
R	Me	Et	*i*Pr	Cy	*t*Bu	Ph	*t*Bu
R'	Me	Et	*i*Pr	Cy	Ph	Ph	*t*Bu

Scheme 1.2 *Synthesis of 1,8-bis(phosphino)naphthalenes* **a-g** *reported by Schmutzler et al..*[29]

In 2001 they reported a series of naphthalenediyl-1,8-bis(phosphine oxides) prepared by oxidation of the corresponding bis(phosphine) with either molecular oxygen or $H_2O_2{\cdot}(H_2N)_2C(:O)$ (Scheme 1.3).



	a	b	c	d	e	f	g
R	Me	Et	*i*Pr	Cy	*t*Bu	Ph	*t*Bu
R'	Me	Et	*i*Pr	Cy	Ph	Ph	*t*Bu

Scheme 1.3 *The behaviour of the 1,8-bis(phosphino)naphthalene ligands towards oxygen.*[31]

During their studies they tested the behaviour of 1,8-bis(diphenylphosphino)naphthalene (dppn) towards the heavier chalcogens and found that reactivity decreased as the atomic size grew (Scheme 1.4). Whilst reaction with excess sulfur afforded the bis(phosphine sulfide), the corresponding reaction with selenium, even under forcing conditions (reflux), did not afford the bis(phosphine selenide). Instead the product formed contained two different phosphorus moieties with only one 4 co-ordinate phosphorus due to the P=Se bond. Due to the increased size and inherent instability of tellurophosphinyl groups no reaction was observed between dppn and tellurium and neither the bis- nor mono- telluride were formed (Scheme 1.4).[31,32]

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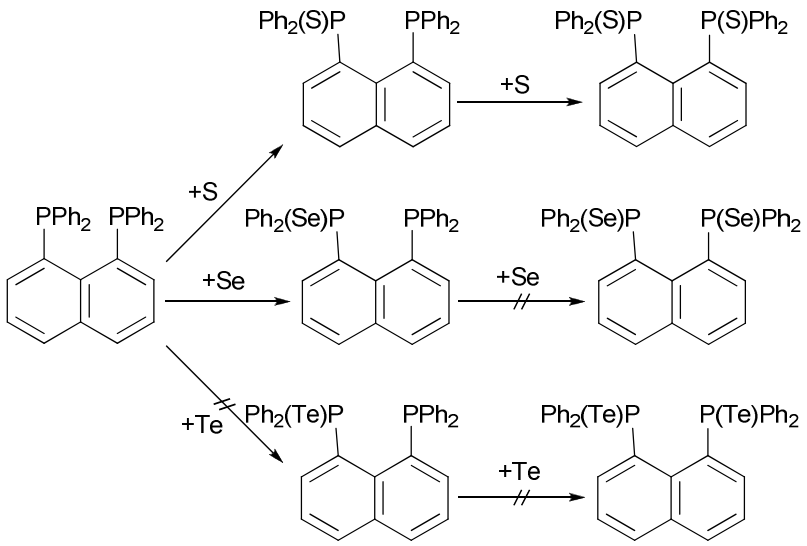

Scheme 1.4 *The behaviour of the 1,8-bis(diphenylphosphino)naphthalene towards sulfur, selenium and tellurium.*[31]

In 2001 Schmutzler *et al.* reported the synthesis of 1,8-bis[(dimethoxy)phosphino]naphthalene (dmeopn) (Figure 1.13), the first example in a series of bis-phosphonite naphthalene ligands.[33] The electron-withdrawing nature of the oxygen substituents in phosphites weakens their σ-donor characteristics but results in a stronger π-acceptor ability compared with corresponding phosphines.[34] Bis-phosphonites have intermediate properties between bis-phosphines and bis-phosphites and form electron-poor transition metal complexes exhibiting shorter bonds between the metal centre and the phosphorus atom compared to corresponding phosphines.[35] Schmutzler *et al.* went on to study the oxidation and ligand capabilities of 1,8-bis[(dimethoxy)phosphino]naphthalene (dmeopn) towards Mo^0 and Pd^{II} metal centres.[33]

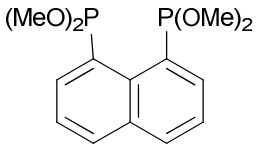

Fig. 1.13 *The structure of 1,8-bis[(dimethoxy)phosphino]naphthalene (dmeopn).*[33]

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A leading topic of research in *peri*-disubstituted naphthalenes is the controversial discussion by Chuit, Corriu and Schiemenz among others regarding the possible occurrence of intramolecular bond formation and hypercoordination.[67-82] This will be discussed fully, later in the introduction. The initial work was carried out on compounds containing the 8-dimethylaminonaphth-1-yl (DAN) fragment (Figure 1.14) including phosphorus compounds containing a possible N→P interaction.[71-82]

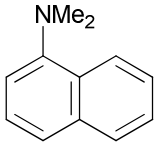

Fig. 1.14 *The structure of 8-dimethylaminonaphth-1-yl (DAN).*

The potential for hypercoordination occurring across the *peri*-space should be greatly enhanced in 1,8-diphosphorus-substituted naphthalenes forming a P→P donor-acceptor interaction. The fact that both P-C_{Nap} bonds are of equal length and both interacting atoms are of the same size means the two phosphorus atoms have an easier approach compared to two different atoms. Phosphorus-phosphorus bond lengths are also nearer to the ideal *peri*-distance [2.5 Å] than the P-N bonds in equivalent DAN compounds.[36] Also, from hard soft acid bases (HSAB) principles a P→P interaction is more favourable than a N→P interaction. The potential for hypercoordination by P→P donor-acceptor interaction across the *peri*-space is therefore greatly enhanced.[37]

Schmutzler *et al.* carried out protonation and alkylation reactions of dppn to prepare unsymmetrical phosphine-phosphonium substituted systems of the type [1-$Ph_2P(C_{10}H_6)$-8-$PRPh_2]^+X^-$ (R = H, alkyl group, X = non-coordinating anion) (Figure 1.15).[36]

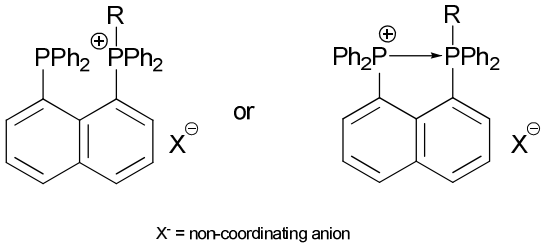

Fig. 1.15 *Unsymmetrical systems of the type [1-$Ph_2P(C_{10}H_6)$-8-$PRPh_2]^+X^-$ investigated by Schmutzler et al. for the occurrence of P→P hypercoordination.*[36]

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The greater electrophilic acceptor character of a phosphonium phosphorus atom compared to a phosphorus atom in phosphines means these mixed cations should be better models for studying intramolecular dative $P \rightarrow P^+$ interactions.[36] The two possible structures for these types of compounds are shown in Figure 1.15. From X-ray crystal structure analysis Schmutzler *et al.* concluded that repulsive steric effects predominated and there was no evidence to confirm the existence of a dative $P \rightarrow P^+$ type interaction.[36]

***Peri*-substituted bis-thio/seleno/telluro naphthalenes.**

Naphtho[1,8-*cd*]-1,2-dithiole (Figure 1.16) was first reported by Lanfrey in 1911, after interacting naphthalene and sulfur within a hot iron tube.[38] Seventeen years later, Price and Smiles reported a new route, starting with 1-aminonaphthalene-8-sulfonic acid.[39]

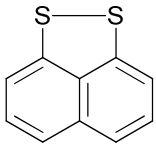
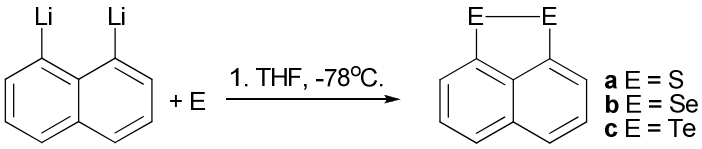


Fig. 1.16 *The structure of naphtho[1,8-cd]-1,2-dithiole.*[38,39]

In 1965 Zweig and Hoffman re-examined the synthesis of naphtho[1,8-*cd*]-1,2-dithiole by repeating the method reported by Price and Smiles. Investigations of its polarographic oxidation and reduction potentials were carried out and charge-transfer compounds were prepared with donor molecules such as tetracyanoethylene (TCNE) and *p*-chloranil.[40]

Later in 1977, Meinwald *et al.* reported a more efficient one-step synthesis of naphtho[1,8-*cd*]-1,2-dithiole by the reaction of 1,8-dilithionaphthalene with sublimed sulfur. Comparable reactions with elemental selenium and tellurium led to the formation of a series of naphthalene derivatives containing a pair of identical Group 16 atoms bridged at the *peri*-positions (Scheme 1.5).[41]



Scheme 1.5 *The one-step synthesis of the group of peri-bridged naphthalene 1,8-dichalcogenides.*[41]

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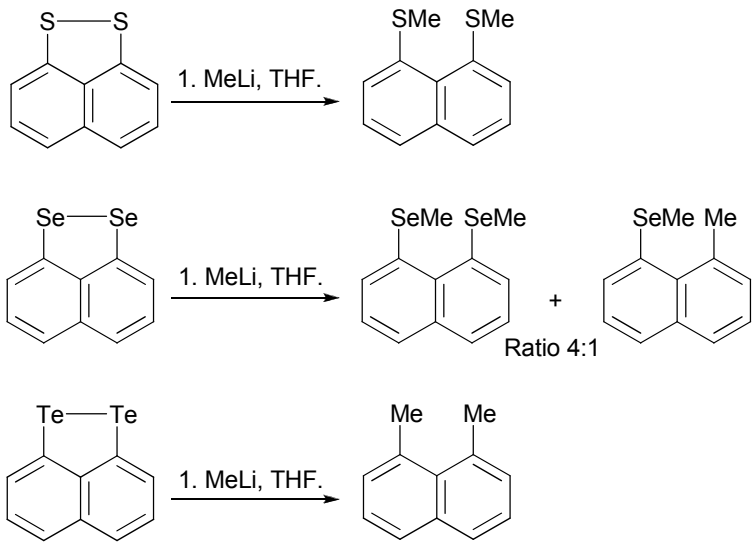
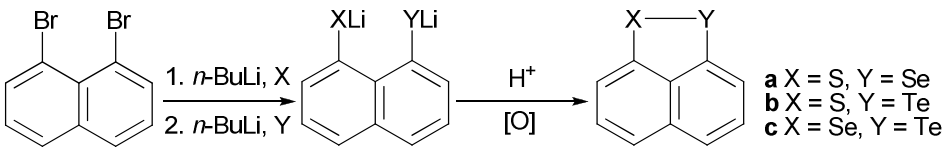
The bridged compounds react readily with methyllithium in tetrahydrofuran to produce a range of different alkylation products. Naphtho[1,8-*cd*]-1,2-dithiole reacts to form 1,8-bis(methylthio)naphthalene as the sole product. However under the same conditions naphtho[1,8-*cd*]-1,2-diselenole yields 1,8-bisselenomethylnaphthalene and 1-selenomethyl-8methylnaphthalene in a ratio of 4:1. The alkylation of naphtho[1,8-*cd*]-1,2-ditellurole results in the formation of 1,8-dimethylnaphthalene (Scheme 1.6).[41]



Scheme 1.6 *The alkylation of the bridged naphthalene 1,8-dichalcogenides by reaction with methyllithium.*[41]

In a subsequent paper, Meinwald *et al.* developed their ideas by reporting the synthesis of three unsymmetrical members of the series, naphtho[1,8-*cd*]-1,2-selenathiole, naphtho[1,8-*cd*]-1,2-tellurathiole and naphtho[1,8-*cd*]-1,2-telluraselenole (Scheme 1.7).[42]



Scheme 1.7 *The synthesis of the unsymmetrical chalcogen bridged naphthalenes.*[42]

Following their synthesis of the six naphthalene dichalcogenides, Meinwald *et al.* developed the series of compounds to include the acenaphthalene analogues (Figure 1.17).[43]

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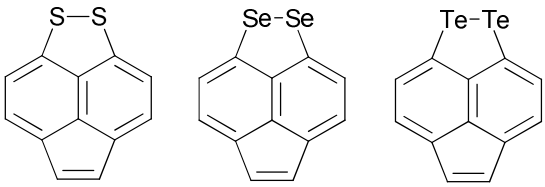

Fig. 1.17 *The synthesis of the unsymmetrical chalcogen bridged acenaphthalenes.*[43]

The doubly bridged analogue of naphtho[1,8-*cd*]-1,2-dithiole, namely tetrathionaphthalene (TTN), is a member of a group of 'tetrathiolene' ligands (TTL). These planar compounds with extensive π-delocalization are attractive ligands in organometallic chemistry. Each compound contains two S-S bonds which can simultaneously coordinate to two metal complexes, therefore accommodating up to four electrons.[44]

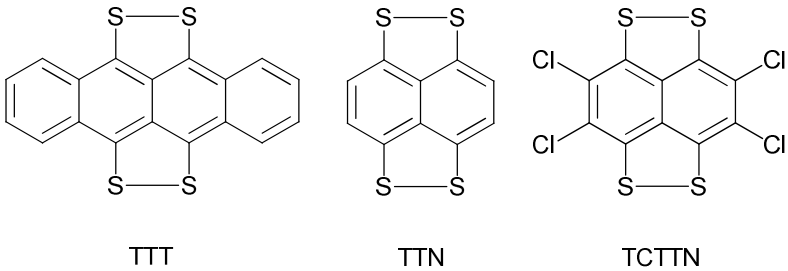

Fig. 1.18 *Tetrathiotetracene (TTT), tetrathionaphthalene (TTN) and tetrachlorotetrathionaphthalene (TCTTN).*[44]

In 1979, Teo and Robinson prepared a set of bridging transition metal complexes containing a delocalized π-system from oxidative addition reactions of low-valent platinum complexes with tetrathiotetracene (TTT), tetrathionaphthalene (TTN) and tetrachlorotetrathionaphthalene (TCTTN) and their selenium analogues (Figure 1.18).[44]

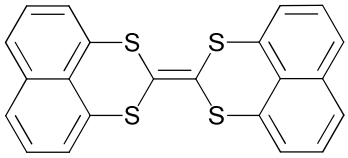

Fig. 1.19 *The electron donor binaphtho[1,8-de]-1,3-dithiin-2-ylidene.*[45]

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Binaphtho[1,8-*de*]-1,3-dithiin-2-ylidene (Figure 1.19) can be thought of as an extended form of a 1,8-dichalcogen-bridged naphthalene containing an ethylene conjunction. The synthesis and electrochemical properties were reported in the 1980s by Ogura *et al.* along with those of its selenium analogue which was expected to have enhanced electron transfer capabilities due to the more polarisable chalcogen atom.[45] Cyclic voltammetry studies however, revealed that these symmetrical compounds are actually poor donors, but unsymmetrical compounds (Figure 1.20) possess considerable donor abilities capable of forming crystalline charge-transfer complexes.[46]

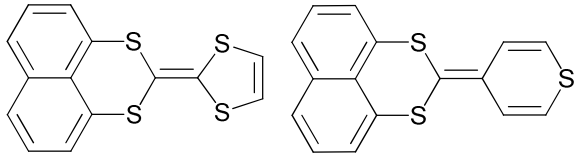

Fig. 1.20 *Unsymmetrical analogues of binaphtho[1,8-de]-1,3-dithiin-2-ylidene with considerable donor abilities.*[46]

Attractive interactions in *peri*-substituted naphthalenes

Intramolecular transannular interactions in *peri*-naphthalenes.

Transannular interactions are intramolecular interactions between two atoms in a monocyclic ring. If the interaction between the two atoms is strong enough, bond formation will occur and a bicyclic molecule will be created. Transannular intramolecular interactions occurring in organic compounds bearing two or more heteroatoms in close proximity has received considerable attention.[47,48] Since the pioneering works of Musker and Asmus who employed the reaction systems of 1,5-dithiacyclooctane and related cyclic and acyclic sulfur compounds, the research of transannular interactions between two sulfur atoms has developed.[48] Musker showed that 1,5-dithiocane is easily oxidized to form an unusually stable radical cation and dication due to the presence of destabilization as a result of transannular lone-pair lone-pair repulsion and stabilization of the oxidized products by neighbouring-group participation, *i.e.* bond formation between two sulfur atoms (Figure 1.21).[48]

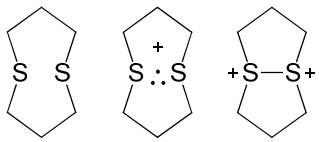

Fig. 1.21 *The unusually stable radical cation and dication from the oxidation of 1,5-dithiocane.*[48]

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Glass *et al.* proposed that a geometrically constrained derivative of 1,5-dithiocane, naphtho[1,8-*b,c*]-1,5-dithiocin (Figure 1.22) would enhance the effects seen in 1,5-dithiocane. The geometry and rigidity of the naphthalene ring places the sulfur atoms in close proximity with greater overlap of the p type lone pair orbitals subsequently increasing the lone-pair lone-pair interaction.[49]

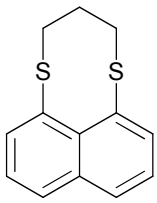

Fig. 1.22 *Naphtho[1,8-b,c]-1,5-dithiocin, a geometrically constrained derivative of 1,5-dithiocane.*[49]

Furukawa *et al.* reported the structure of dinaphtho[1,8-*b,c*]-1,5-diselenocin (Figure 1.23), a selenium compound containing the same structural motif as naphtha[1,8-*b,c*]-1,5-dithiocin. This compound, along with 1,8-bis(methylselanyl)naphthalene prepared for structural comparison, places selenium atoms in close contact allowing for possible *peri*-interactions to take place (Figure 1.23).[50]

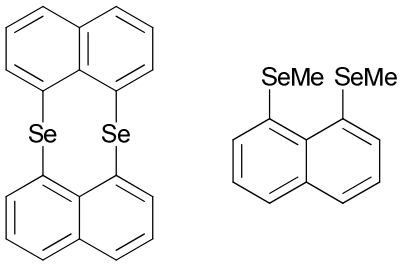

Fig. 1.23 *Dinaphtho[1,8-b,c]-1,5-diselenocin and 1,8-bis(methylselanyl)naphthalene.*[50]

Oxidation with concentrated H_2SO_4 revealed distinct differences in the reactivity of the two selenium compounds. Upon work up with ice-H_2O, the dication formed from dinaphtho[1,8-*b,c*]-1,5-diselenocin afforded the mono-selenoxide depicted in Scheme 1.8.[50]

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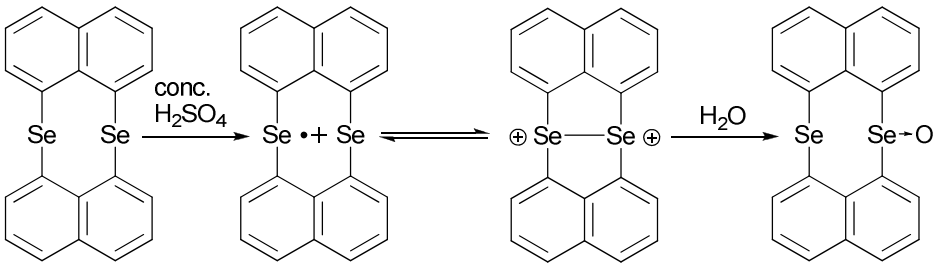
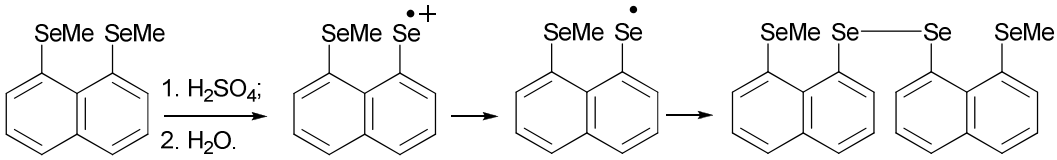


Scheme 1.8 *Reaction of dinaphtho[1,8-b,c]-1,5-diselenocin with concentrated H_2SO_4 via cation radical and dication species.*[50]

In contrast the addition of concentrated H_2SO_4 to 1,8-bis(methylselanyl)naphthalene produced the demethylated cation radical which after reaction with water converted to the radical species. Two radical species subsequently dimerised to generate demethylated coupling product (Scheme 1.9).[50]



Scheme 1.9 *Reaction of 1,8-bis(methylselanyl)naphthalene with concentrated H_2SO_4 via cation radical and radical species to form a demethylated coupling product.*[50]

The group of Furukawa developed their series of selenium compounds by synthesising a group of new macrocyclic polyselenides including the selenium analogue of naphtha[1,8-*b,c*]-1,5-dithiocin previously reported by Glass *et al.*[49] (Figure 1.24). In these compounds the trimethylene bridges help to align the selenium orbitals which enhances the possibility for *peri* Se-Se interactions.[51]

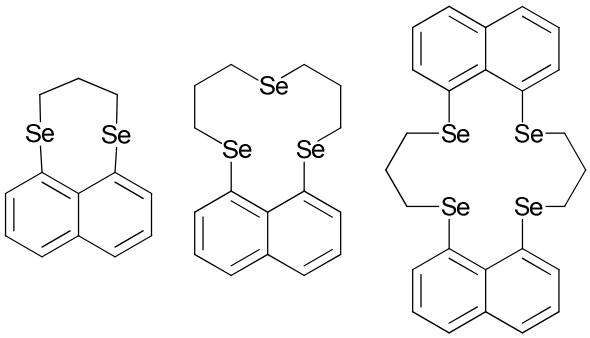


Fig. 1.24 *Macrocyclic polyselenides have the potential for peri Se-Se interactions due to the alignment of selenium orbitals by the presence of trimethylene bridges.*[51]

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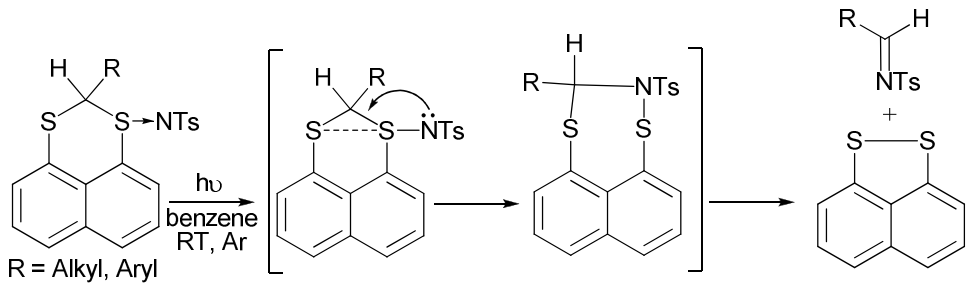
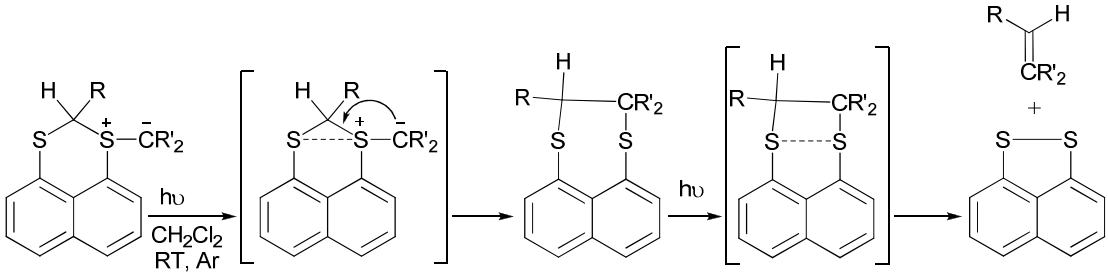
1,8-dithia- and 1,8-diselena- naphthalene derivatives have been utilized for generating active species and developing new reactions which are initiated by the transannular interactions between sulfur or selenium atoms. The majority of work done in this field of research has been developed by the group of Furukawa *et al.*. In 1994 they reported the photo-oxygen rearrangement of naphtho[1,8-*de*]dithiin monoxides which released carbonyl compounds quantitatively together with naphthalene-1,8-dithiole.[52]

Continuing their research they prepared a series of *N-p*-tosylsulfilimines of naphtho[1,8-*de*]dithiin and demonstrated their ability to afford the corresponding *N*-sulfonylaldimines upon photolysis (Scheme 1.10).[53]



Scheme 1.10 *Photolysis of N-p-tosylsulfilimines of naphtho[1,8-de]dithiin via intramolecular imino group rearrangement affords the corresponding N-sulfonylaldimines.*[53]

In an extension to this work, Furukawa *et al.* prepared a range of naphtho[1,8-*de*][1,3]dithiin-1-bis(ethoxycarbonyl)methylides which undergo similar photo-rearrangements to yield olefins and naphthalene-1,8-dithiole in quantitive yields (Scheme 1.11).[54]



[a] R = Ph, R' = CO_2Et; [b] R = *p*-Tol, R' = CO_2Et; [c] R = CH_3, R' = CO_2Et; [d] R = $CH_3(CH_2)$, R' = CO_2Et

Scheme 1.11 *Photo-rearrangement of naphtho[1,8-de][1,3]dithiin-1-bis(ethoxycarbonyl)methylides.*[54]

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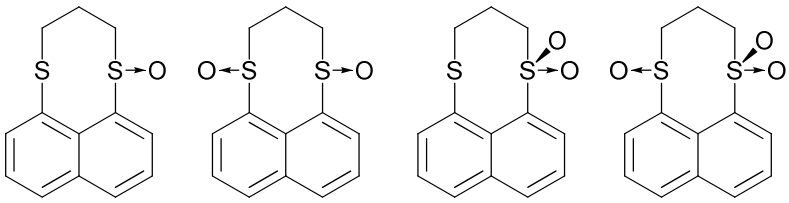

Fig. 1.25 *Geometrically constrained derivatives of 1,5-dithiocane.*[55]

In 1991, Glass *et al.* studied the nature of non-bonded S···S transannular interactions in geometrically constrained derivatives of 1,5-dithiocane (Figure 1.25).[55] They proposed that lone pairs of sulfur atoms in naphtho[1,8-*b,c*]-1,5-dithiocin derivatives interact directly with each other since the two orbitals lie on the naphthyl plane **(a)**, whilst those in the unconstrained 1,8-bis(methylsulfanyl)naphthalene mainly interact with its π-system **(b)** (Figure 1.26).[49,55]

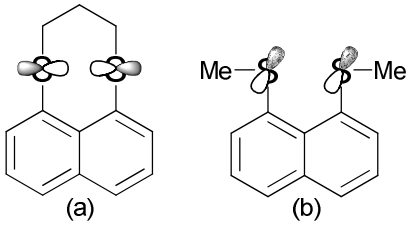

Fig. 1.26 *Lone-pairs of sulfur atoms in naphtho[1,8-b,c]-1,5-dithiocin and 1,8-bis(methylsulfanyl)naphthalene.*[49,55,56]

Non-bonded interactions of sulfur are especially interesting with known S···X distances ranging from no interaction (where the S···X distance is greater or equal to the sum of the van der Waals radii) through to strong covalent bonding. The trend observed experimentally is that for interacting atoms S···X distances are less than the sum of the van der Waals radii for the respective interacting atoms and R-S···X angles approach 180°.[55]

Non-bonded intramolecular interactions across the *peri*-gap.

Non-bonded intramolecular interactions can also occur across the *peri*-gap where interacting atoms are constrained only by the naphthalene ring system, i.e. non-transannular. Non-bonded lone-pair lone-pair interactions can be fundamental in determining the geometry, reactivity and biological properties of organic molecules containing heteroatoms.[57]

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When heteroatoms are located at positions in rigid organic molecules where the distance between them is less than the sum of their van der Waals radii (for instance the *peri*-positions in naphthalene), non-bonded interactions take place between overlapping orbitals leading to steric compression.[48,49,56-58] There is particular interest in intramolecular interactions between chalcogen atoms in naphthalene compounds containing group 16 elements at the *peri*-positions. Current research in this area has been mainly led by the group of Nakanishi *et al.*.[56-58,60,62-65]

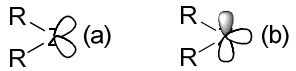

Fig. 1.27 *Chalcogen lone pair orbital representations.*[56]

The lone-pair orbitals of chalcogen atoms can be portrayed by either two sp^3-hybrid orbitals **(a)** or p- and s-type orbitals (p- and sp^2-hybrid orbitals) **(b)** (Figure 1.27).[56] Interactions can occur between chalcogen lone-pair orbitals and orbitals of other atoms or other lone-pair orbitals. When two p-type lone-pair orbitals overlap, σ-bonds can be formed.[56,59] If the orbitals are closely located and align linearly then it is possible to form a weak unsymmetrical hypervalent bond between a lone-pair orbital of a heteroatom (Z) interacting with a σ*(E-C) (Figure 1.28). This σ-type (Z)···σ*(E-C) bond is known as a three center-four electron (3c-4e) interaction.[60] When all the orbitals taking part are filled with electrons, non-bonded interactions are repulsive. However, if all the orbitals are not filled with electrons, for example in the σ-type 3c-4e interaction, then the interactions can be attractive.[48,56,57,60,61]

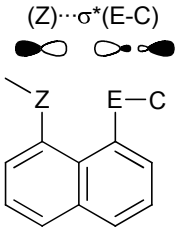

Fig. 1.28 *Lone-pair orbital of a heteroatom (Z) interacting with a σ*(E-C) orbital.*[56,59]

Nakanishi *et al.* focused their initial studies on organoselenium compounds which showed typical examples of the lone-pair lone-pair interactions described previously. Bis[8-(phenylselanyl)naphthyl]-1,1'-diselenide and 1-(methylselanyl)-8-(phenylselanyl)naphthalene were prepared as the first step in their investigation (Figure 1.29).[56,62] The molecular structure of bis[8-(phenylselanyl)naphthyl]-1,1'-diselenide revealed a quasi-linear arrangement of four selenium atoms whilst in 1-(methylselanyl)-8-(phenylselanyl)naphthalene the Se-C(Me) and Se-C(Ph) bonds were shown to lie at 50° and 40° from the naphthyl plane, respectively.[56,62]

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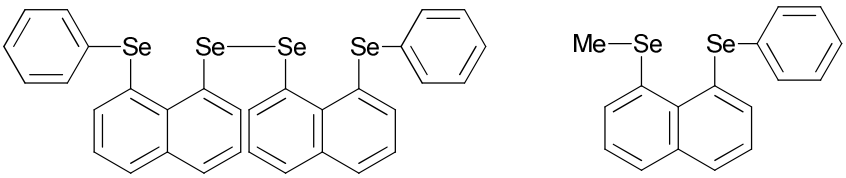

Fig. 1.29 *Bis[8-(phenylselanyl)naphthyl]-1,1'-diselenide and 1-(methylselanyl)-8-(phenylselanyl)naphthalene.*[56,62]

To help rationalise the two structures, Nakanishi *et al.* performed *ab initio* MO calculations and proposed the linear alignment of four selenium atoms was a result of an energy lowering effect due to the construction of a four center-six electron bond (4c-6e).[56,62]

In a subsequent paper Nakanishi and co-workers revealed the structure of 8-fluoro-1-(*p*-anisylselanyl)naphthalene (Figure 1.30) exhibiting a linear alignment of the type F···Se-C(An) with an F-Se-C angle of 175.0°. From *ab initio* MO calculations the linear arrangement was found to result from a charge-transfer from the fluorine atom to the σ*-orbital of selenium.[63]

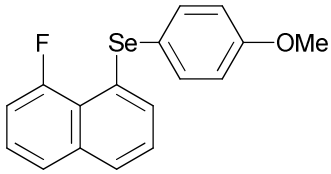

Fig. 1.30 *8-fluoro-1-(p-anisylselanyl)naphthalene exhibits a linear F···Se-C(An) arrangement.*[63]

Expanding their research, Nakanishi *et al.* went on to study a wide range of compounds with the same 8-G-1-(*p*-$YC_6H_4Se)C_{10}H_6$ structural motif (Figure 1.31). Both the Y dependence and G dependence on the 'type' of structure adopted were investigated.[57,64]

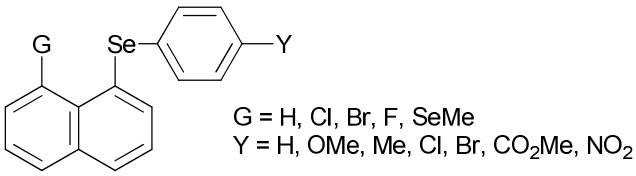

Fig. 131 *A new array of (arylselanyl)naphthalenes of the type 8-G-1-(p-$YC_6H_4Se)C_{10}H_6$.*[57,64]

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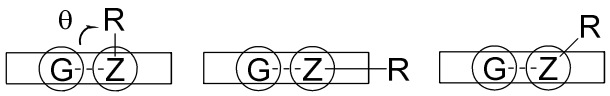
Each structure was classified as either type A, B or C depending upon the position of the Se-C_{Ar} bond relative to the mean naphthalene plane. In type A the Se-C_{Ar} bond lies almost perpendicular to the naphthalene plane whilst in type B the bond is located on the plane. The type C structure is intermediate between type A and type B (Figure 1.32).[57,64]



type **A**: $\theta \leq 90^{o}$ type **B**: $\theta \approx 180^{o}$ type **C**: $\theta \approx 135^{o}$

Fig. 1.32 *Types of structures in 8-G-1-(p-YC_6H_4Se)$C_{10}H_6$ naphthalenes.*[57,64]

Nakanishi *et al.* concluded that naphthalene systems with Z-R = Se-C at the 1-position and G = halogens at the 8-position satisfy the conditions for non-bonded interactions to take place. Compounds where G = Cl or Br were found to always adopted the type B structure irrespective of what occupied the Y position and thus contain the linear non-bonded G···Se-C arrangement. From *ab initio* MO calculations Nakanishi *et al.* concluded that *'the linear alignment of the three atoms must be the result of the non-bonded G···Se-C 3c-4e type interaction'*.[57,64]

Nakanishi *et al.* have recently reported the linear alignment of four sulfur atoms in bis[8-(phenylthio)naphthyl]-1,1'-disulfide the sulfur analogue of bis[8-(phenylselanyl)naphthyl]-1,1'-diselenide. The linear S_4 alignment is accounted for by the 4c-6e model with the linear form shown to be substantially more stable than the zig-zag conformer (Figure 1.33).[65]

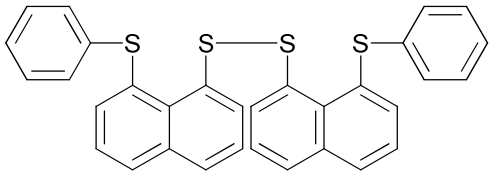


Fig. 1.33 *The linear alignment of four sulfur atoms in bis[8-(phenylthio)naphthyl]-1,1'-disulfide.*[65]

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Intramolecular dative (coordination) bond formation and hypercoordination.

Intramolecular interactions occurring between *peri*-heteroatoms in rigidly constrained naphthalenes could be strong enough for bond formation to occur. A leading topic of current research and one which has seen much controversy, concerns the possible occurrence of intramolecular dative bond formation leading to hypercoordination.[67-71,75-82] Most of the pertinent work in this field has been investigated using 8-dimethylaminonaphth-1-yl (DAN) compounds where the nitrogen atom can donate a pair of electrons for the formation of a coordination bond with acceptor heteroatoms such as Si or P.[66] Upon bond formation the acceptor species finds itself with a greater than normal co-ordination number and is termed hypercoordinate.[66]

8-dimethylamino-naphth-1-yl silanes (DAN-silanes).

It is widely recognised that silicon can obtain a greater than normal coordination number and in many cases this can be achieved by the intramolecular coordination of a donor group.[67] In 1989, Corriu and co-workers reported the molecular structures of three novel DAN-silanes where the nitrogen lone pairs were directed towards the silicon central atom in each case (Figure 1.34). The formation of a hexacoordinated silicon complex due to the presence of dative N→Si bonds was proposed for each compound based on their experimental N···Si bond lengths.[68,69]

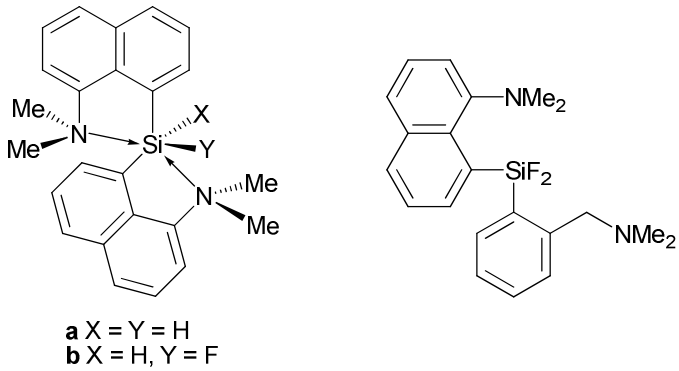

Fig. 1.34 *Bis(8-(dimethylamino)-naphthyl)silane, bis(8-dimethylaminonaphthyl)fluorosilane and (2-((dimethylamino)methyl)phenyl)(8-(dimethylamino)-naphthyl)difluorosilane.*[68]

In a subsequent paper Corriu and co-workers found the ^{1}H NMR study of bis(8-(dimethylmino)naphthyl)fluorosilane and related compounds (Figure 1.35) was in agreement with previous findings and gave evidence for hexacoordination in solution.[70]

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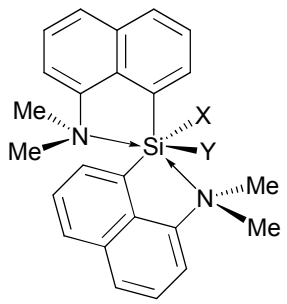

a X = H, Y = OCH_3
b X = H, Y = CH_3
c X = CH_3, Y = C_6H_5

Fig. 1.35 *The series of DAN-silanes studied by ^1H NMR spectroscopy by Corriu and co-workers to determine the existence of hexacoordinated silicon.*[70]

In 1998, Schiemenz *et al.* reexamined the DAN-silanes which Corriu and co-workers described as hexacoordination at silicon.[70,71] When comparing their own results of the DAN-silanes with a closely related carbon analogue, bis(8-dimethylamino-naphth-1-yl)carbinol (Figure 1.36), Schiemenz *et al.* discovered that the bonding of Si and C was essentially the same with the carbon compound exhibiting a similar structure.[71]

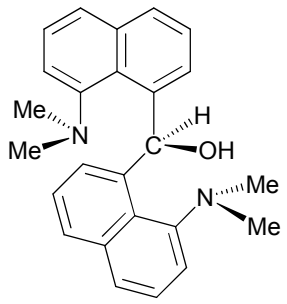

Fig. 1.36 *Bis(8-dimethylamino-naphth-1-yl)carbinol was found to exhibit similar bonding characteristics to the DAN-silanes reported by Corriu and co-workers.*[70,71]

From their findings Schiemenz *et al.* were left with two conclusions. Either to accept the interpretation by Corriu and co-workers[67,68,70] and present 'proof' of a hexacoordinated carbon atom or to remain with the acknowledged theory of carbon tetracovalency, thus disproving the hypervalency of silicon in the DAN-silanes.[71]

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DAN-phosphorus compounds.

The debate on dative bond formation and hypercoordination in *peri*-naphthalenes between Schiemenz and Corriu later developed to incorporate DAN-phosphine (Figure 1.37) and its derivatives; phosphorus conceivably becoming hypercoordinate as a consequence of electron donation from nitrogen.

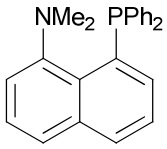

Fig. 1.37 *(8-dimethylamino-naphth-1-yl)diphenylphosphine (DAN-phosphine).*[71]

As early as 1974, Hellwinkel *et al.* had concluded from ^{31}P NMR signal positions that no dative N→P bond existed in DAN-phosphorus compounds.[72] This was later corroborated by Day and Holmes who determined the P···N distance [2.81 Å] and concluded that although shorter than the sum of the two interacting atoms [3.4 Å] this was not conclusive of a bonding interaction.[74] Nevertheless, Corriu and co-workers re-opened the debate by studying the structure of DAN-phosphine and related compounds (Figure 1.38) and reaching a similar conclusion to their view of DAN-silanes.[75]

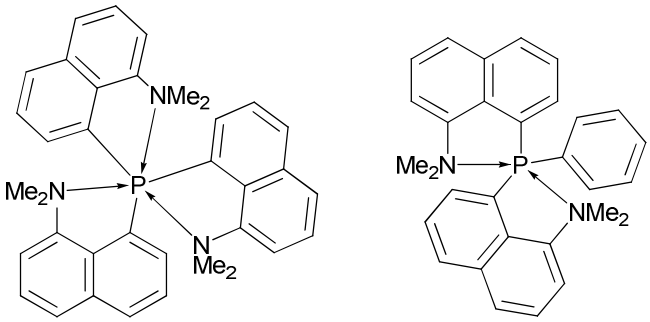

Fig. 1.38 *DAN-phosphorus compounds investigated by Corriu and co-workers for the occurrence of hypercoordination at phosphorus.*[75]

They found that intramolecular donor-acceptor interactions exist between the nitrogen and phosphorus atoms in DAN-phosphine without the deformation of the naphthyl group. Corriu and co-workers also indicated the ability of the phosphorus atom to undergo an extension of coordination in bis(DAN)(phenyl)phosphine and tris(DAN)phosphine (Figure 1.38).[75] In $(DAN)_3P$ the phosphorus is claimed to be "*pseudo-seven-coordinate due to three P-C bonds, three dative N→P interactions and to the lone pair acting as a pseudo-substituent*".[75]

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In 1998, Chuit and Reyé reviewed a series of phosphanes, phosphane derivatives and phosphenium salts based on the DAN-phosphine motif (Figure 1.39). In all cases the rigid geometry of the naphthalene strategically fixes the NMe_2 groups close to the phosphorus centre. This close proximity was the explanation for hypercoordination at the phosphorus centre by intramolecular coordination.[76]

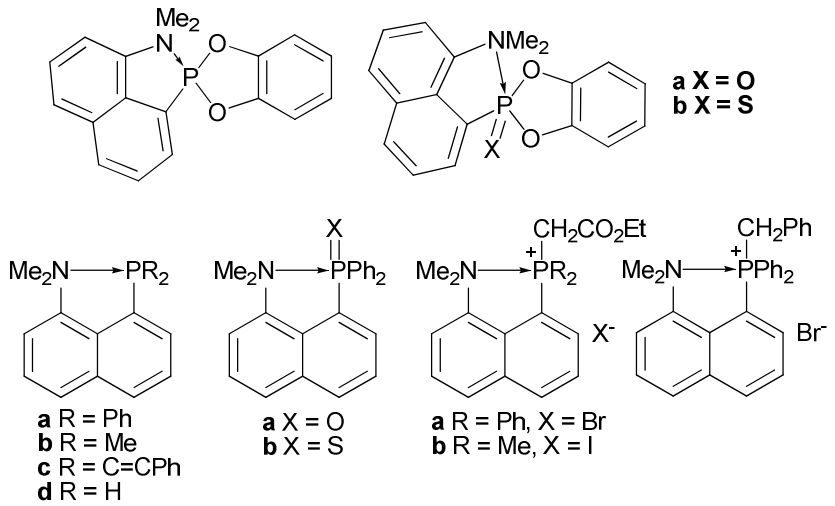

Fig. 1.39 *Dan-phosphorus compounds reviewed by Chuit and Reyé during their studies into hypercoordination.*[76]

Over the last decade Schiemenz *et al.* have been highly active in the field of DAN-phosphorus chemistry in an attempt to draw a conclusion to the controversial debate of hypercoordination. Sceptical of the claims made by Corriu, Chuit and others, they investigated the structure of DAN-phosphine and its related compounds (Figure 1.40).[77]

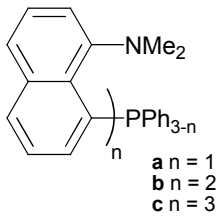

Fig. 1.40 *Dan-phosphorus compounds re-examined by Schiemenz.*[77]

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Several structural and chemical properties of the DAN-phosphorus compounds led them to conclude that an intramolecular dative bond was highly unlikely and no hexacoordination would be anticipated.[77] Firstly the dimethylamino group in DAN compounds is a poor nucleophile compared with organo lithium compounds; it is widely accepted that the positively charged phosphorus in tetraarylphosphonium cations is sufficiently electrophilic to react with only very strong nucleophiles such as aryl lithium reagents.[77,78] Schiemenz also believed that the rigid structural geometry of naphthalene was detrimental for hypercoordination in these compounds. The *peri*-substituents in an 'ideal' DAN-phosphorus compound lie at a distance of ~2.5 Å, much longer than the sum of the covalent radii [N 0.74 Å, P 1.1 Å], and therefore too long for any appreciable bonding.[71] For a dative bond to occur, the *peri*-distance would have to be considerably reduced requiring distortion of the C_{10} skeleton. The cost in energy for this to occur could only be achieved by forming a strong *peri*-bond such as a C-C or an amide N-CO bond.[79,80]

Schiemenz *et al.* developed their investigation to elucidate whether Helliwinkel or Corriu had the correct interpretation.[72,75] The ^{31}P NMR data for a series of *peri*-substituted diphenylphosphines (Figure 1.41) was studied and compared with DAN-phosphorus compounds.[77] The conclusion they drew was that the chemical shifts in (8-(dimethylamino-naphth-1-yl)phosphines are the result of the *"high field ortho-effect"* and *"a low field peri-substituent effect"* of about the same magnitude.[77] ^{31}P NMR therefore does not support the claim that dative N→P interactions are present in DAN-phosphines.[77]

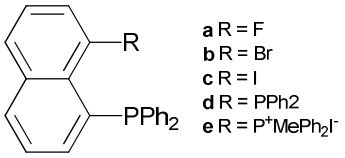

Fig. 1.41 *Peri-substituted diphenylphosphines investigated in a ^{31}P NMR study by Schiemenz.*[77]

In an attempt to definitively answer the question of the presence of hypercoordination in DAN-phosphorus compounds, Schiemenz *et al.* strived for a *peri*-N,P-substituted naphthalene which unambiguously contained both hypercoordinate phosphorus and a dative N→P bond. Such a compound, DAN-$P(O_2C_6H_4)_2$, was synthesised by the reaction of chloro-bis(1,2-phenylenedioxy)phosphorane with 8-dimethylamino-naphth-1-yl-lithium (Figure 1.42).[81]

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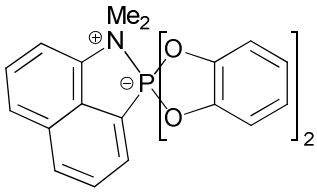

Fig. 1.42 *DAN-P($O_2C_6H_4$)$_2$ exhibiting a hypercoordinate phosphorus and a dative N→P bond reported by Schiemenz et al..*[81]

The short N-P distance [2.13 Å] although not much shorter than the 'ideal' *peri*-distance [2.50 Å] is much closer to known N-P distances in phosphatanes and evidence for bond formation and hypercoordination.[81] Furthermore the distance matches the value found in a similar compound exhibiting certain features of phosphatanes (Figure 1.43).[74] As a consequence of the N-P distance being shorter than the ideal *peri*-distance the three bay region angles have been reduced and are significantly shorter than 120°.[81]

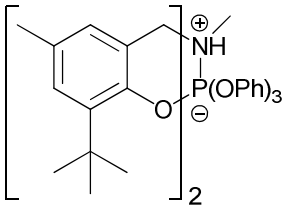

Fig. 1.43 *A compound exhibiting similar features to DAN-P($O_2C_6H_4$)$_2$ and a similar N-P distance.*[74]

Schiemenz *et al.* concluded that under favourable conditions DAN-phosphorus compounds can form dative N→P bonds and hexacoordination at phosphorus can occur. The N-P distance is found to be 0.6-0.9 Å, shorter than other DAN-phosphorus compounds and the naphthalene skeleton is forced into distortion. DAN-phosphines and their derivatives are found to act normally with steric repulsion dominating the structures and no dative bonds forming. From these results, Schiemenz *et al.* extended their findings to the DAN-silanes and found that most exhibit N-Si distances greater than the ideal *peri*-distance and contained substantial splay angles, the criteria for steric hindrance.[81-82]

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Metal coordination and hemilability in *peri*-substituted naphthalenes

Transition metal complexes.

A significant property of *peri*-disubstituted naphthalenes is their ability to form complexes with transition metals (ML_x). Coordination occurs when metal ions acting as Lewis acids accept lone pairs of electrons donated by ligands (Lewis bases), as defined by the original acid-base definition as stated by Lewis.[83] When the two *peri*-substituents are both electron pair donors the ligand becomes bidentate and can form ring complexes (chelates) with the metal. The enhanced stability of a system containing chelate rings compared to the stability of a system that is similar but contains no or fewer rings is known as the 'chelate effect'.[84]

Many transition metal complexes are important tools in organic synthesis allowing apparently unfeasible reactions to occur without difficulty. Complexes of the platinum group metals (Ru, Os, Rh, Ir, Pd, and Pt) have been shown to act as active homogeneous catalysts in reactions of industrial importance, including hydrogenation,[85] hydrosilylation,[86] hydroformylation,[87] oxidative hydrolysis of olefins[88] and the carbonylation of methanol.[89]

Hemilability.

A class of chelate ligand of great interest and one which has become a popular topic of research, places two or more donor atoms with very different electronic properties close to the metal atom. These mixed donor, hemilabile ligands possess two types of bonding groups which differ in their hard and soft characteristics based on Pearson's HSAB principle.[37,90] Hard metal ions are small in size with closely held orbitals with high oxidation states (Cr^{3+}, Al^{3+}) are low in electron density and require good σ donors such as NH_3, H_2O, or F^- (hard ligands). Large low oxidation state (soft) metals (Ag^+, Hg^{2+}) with less closely held orbitals, having excess electron density from their reduced state form strong complexes with unsaturated polarisable (soft) ligands (I^-, PPh_3, or C_2H_4).[37]

For hemilabile ligand-metal complexes to be thermodynamically stable, one group of the hemilabile ligand must be a substitutionally inert soft donor which binds strongly to the (soft) transition metal atom. However the second bonding group is a hard donor atom which binds less strongly and is thus coordinatively or substitutionally labile.[90,91] The ability of this hard donor group to equilibrate between a coordinated 'closed' and a dissociated 'open' form with the metal centre ('windscreen wiper action'),[134] is the key property of this special type of chelating ligand and ideal for inducing changes in the properties of the metal centre.[90,91]

The ability of metal complexes to catalyse reactions of organic substrates is dependent on the ease with which the substrate (S) can enter the coordination sphere of the metal ion.[92] In complexes containing hemilabile ligands the hard donor atom (Z) dissociates from the metal, on the request of a competing substrate, forming a free coordination site where the substrate can bind. This dissociative ability of one arm of the chelate is referred to as the 'arm off' mechanism (Figure 1.44).[91]

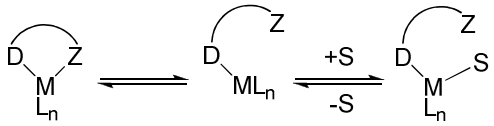

Fig. 1.44 *The hemilabile character of the hybrid bidentate ligand D-Z.*[90,91]

Hemilabile ligands were first described in 1979 by Jefferey and Rauchfuss while investigating the chemistry of phosphine-amine and phosphine-ether ligands.[90] They envisaged that these ligands would bind well enough to allow isolation but would readily dissociate the 'hard' ligand component, thus generating a vacant site for substrate binding.[90]

Since the conception of using hemilabile ligands in coordination chemistry and homogeneous catalysis was established at the end of the 1970s, there has been continuous interest in mixed donor ligands.[93] Mixed donor hemilabile chelating ligands are of great interest owing to the increased catalytic activity of their transition metal complexes in certain homogeneously catalysed reactions. The most commonly employed hemilabile ligands are bidentate phosphines.[94]

Phosphines are neutral two electron donors and as such are one of the most versatile ligands that can bind to late transition metals. They produce stable metal-phosphorus bonds via sigma donation of the lone pair to an empty metal orbital and back-donation from a filled orbital on the metal to an empty orbital on the phosphine ligand.[95] The steric characteristics of the ligand can be easily controlled allowing the reactivity of the metal complex to be tuned. Increasing the electron-withdrawing capability of the groups surrounding the phosphorus atom decreases the σ-donating capacity whilst lowering the π-acceptor (σ*) of the phosphorus, thus increasing its back-bonding ability. Phosphines can therefore exhibit a range of σ-donor and π-acceptor capabilities and the electronic properties of the metal centre can be altered by the substitution of electronically differing phosphines.[95,96]

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The group of Scmutzler has developed compounds of the type 1-$Ph_2P(C_{10}H_8)P(:E)PPh_2$ (E = O, S, Se, NR") containing the rigid 1-P-$C_{10}H_8$-8-P naphthalene backbone (Figure 1.45).[97] Compared to the parent diphosphines which form coordinatively stable six-membered chelates with the catalytically active transition metal centres,[25] these compounds containing diphosphine mono-chalcogenides should form more labile seven-membered chelates, advantageous for certain catalytic reactions.

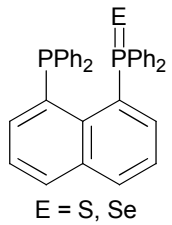

Fig. 1.45 *Ligands investigated by Schmutzler containing the rigid naphthalene backbone.*[97]

Previous work on *peri*-substituted naphthalenes in the Woollins Research Group

In 1987, the Woollins Group reported the first example of a six-membered organothiophosphate heterocycle containing a C_3P_2S ring at the *peri*-positions on naphthalene (Figure 1.46).[98]

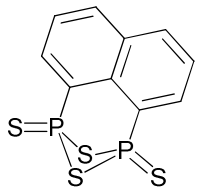

Fig. 1.46 *The structure of 1,3-epithionaphtho[1,8-cd][1,2λ^5,6λ^5]thiadiphosphine-1,3-dithione, the first example of a six-membered organothiophosphate heterocycle.*[98]

Since then numerous analogues have been prepared and the subsequent P_2S_2 ring cleavage reactions these compounds undergo have been reported (Scheme 1.12).[99]

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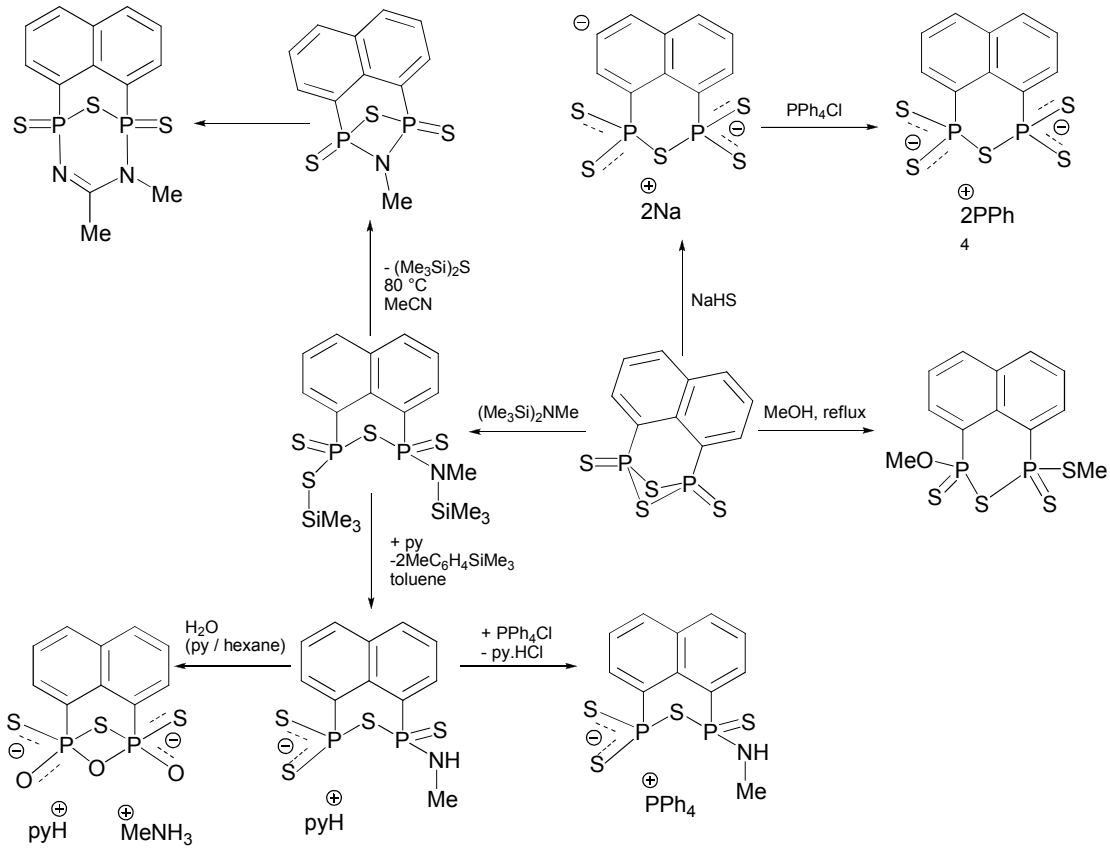

Scheme 1.12 *A few of the reactions of 1,3-epithionaphtho[1,8-cd][1,2λ^5,6λ^5]thiadiphosphine-1,3-dithione reported by the Woollins Group.*[99]

Of particular interest was the reaction of $NapP_2S_2$ with chlorine gas due to the versatile synthons such a reaction could produce. At the time of writing, only two methods were known for introducing two phosphorus moieties at the *peri*-positions of naphthalene, one starting from 1,8-dilithionaphthalene and the other as described from P_2S_4.[98,100] The initial reaction of $NapP_2S_2$ with chlorine gas afforded $Nap(PCl_2)(PCl_4)$] containing a very rare σ^4P-σ^6P bond (Figure 1.47).[101] Further refluxing this compound in toluene with a slight excess of methyldichlorophosphite ($MeOPCl_2$) afforded $Nap(PCl_2)_2$ known to be a versatile synthetic intermediate in organophosphorus chemistry.[28] Further reactions of $Nap(PCl_2)(PCl_4)$] were also reported.[102]

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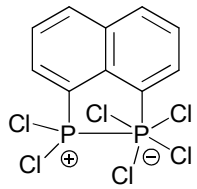

Fig. 1.47 *Reaction of $NapP_2S_2$ with chlorine gas gave a novel naphthalene compound containing a rare σ^4P-σ^6P bond.*[101]

The investigation into sterically constrained bis-phosphorus naphthalene systems was developed further with the synthesis of 1,8-bis(dimethylphosphonito)naphthalene, $Nap[P(E)(OMe)_2]_2$, along with a complete series of mono- and di-oxidised phosphonato counterparts (Figure 1.48).[103]

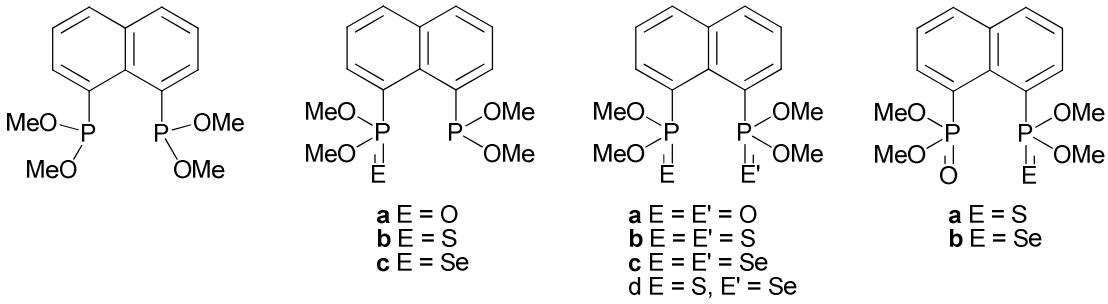

Fig. 1.48 *Sterically constrained $Nap[P(E)(OMe)_2]_2$ (E = O, S, Se) (Nap = naphthalene-1,8-diyl) systems.*[103]

Whilst carrying out investigations on phosphorus-based naphthalene systems a parallel study was undertaken on chalogenide-based systems. A preliminary study of the coordination chemistry of some chalcogenides was initially undertaken by reacting a collection of chalcogen containing naphthalenes with a range of platinum bisphosphine complexes (Scheme 1.13).[104] A more comprehensive structural study was then performed on a range of disubstituted systems including [1,8-*cd*][1,2]dithiole, naphtho[1,8-*cd*][1,2]diselenole, naphtho[1,8-*cd*][1,2]ditellurole and some oxidised species (Figure 1.49). Comparison of the molecular structures showed a variation in the E-E distance loosely indicating the degree of distortion imposed by the naphthalene backbone and the extent of oxidation at the sulfur (Figure 1.49).[105]

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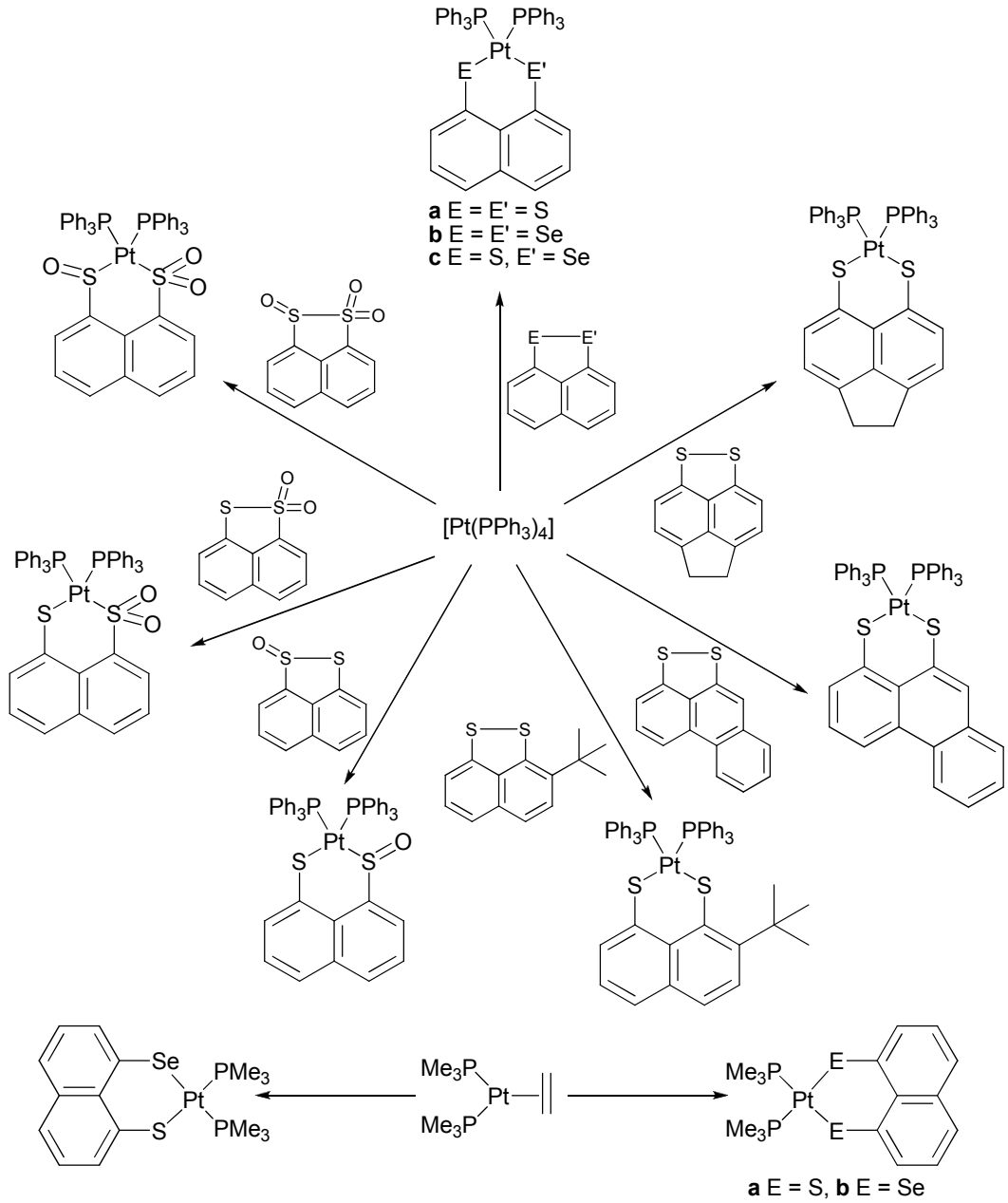

Scheme 1.13 *Initial coordination reactions of chalcogenide-based systems with platinum bisphosphine complexes.*[104]

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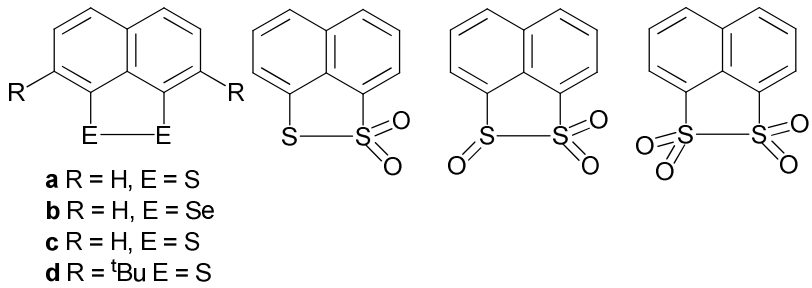
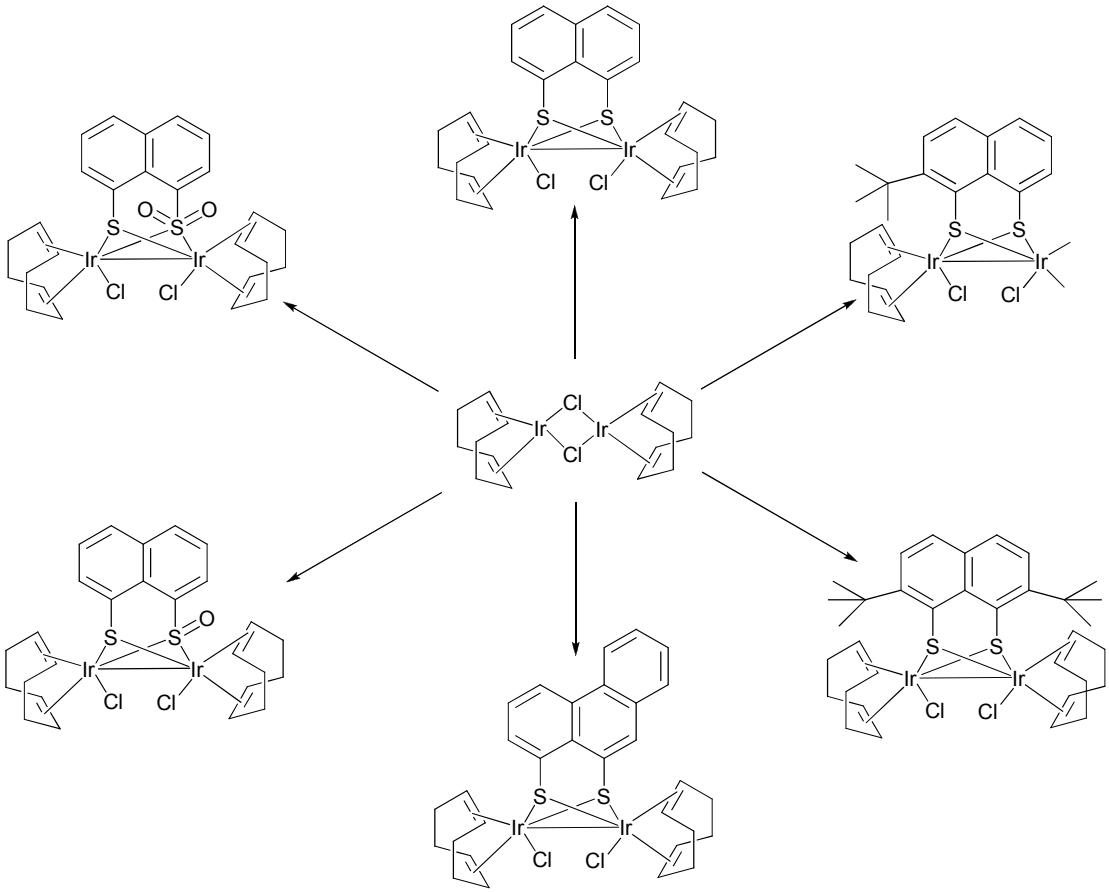


Fig. 1.49 *A structural study of chalcogen-substituted naphthalenes revealed a variation in E-E length.*[105]

As a extension, a number of dinuclear Ir(III) dimers containing an Ir-Ir bond were prepared via the oxidative addition of naphtha[1,8-*cd*][1,2]dithiole (and a series of related compounds) to [{Ir(μ-Cl)(cod)}$_2$] (Scheme 1.14).[106]



Scheme 1.14 *Oxidative addition reactions of naphtha[1,8-cd][1,2]dithiole (and a series of related compounds) to [{Ir(μ-Cl)(cod)}$_2$].*[106]

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Studying distortion in sterically crowded 1,8-disubstituted naphthalenes

As an extension of the work previously carried out in the Woollins group, this thesis reports on the synthesis and characterisation of two novel series of mixed sterically crowded *peri*-substituted naphthalenes. As discussed previously, extensive work has been carried out on bis-phosphines[24-33] as well as DAN-phosphorus compounds[71-82] containing nitrogen and phosphorus at the *peri*-positions on naphthalene. To date there are very few examples of phosphorus-oxygen, phosphorus-sulfur and phosphorus-selenium *peri*-substituted naphthalenes in the literature.

In efforts to understand the factors which influence the degree of distortion in sterically crowded 1,8-disubstituted naphthalenes, investigations focussed on phosphorus-chalcogenide species and a series of mixed chalcogenide systems (Figure 1.50).

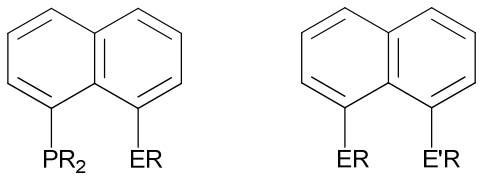

Fig. 1.50 *Investigations focussed on phosphorus-chalcogenide ligands and a series of mixed chalcogenide systems.*

The availability of X-ray structural data has played a crucial role in assessing substituent effects on steric strain and naphthalene distortion. To quantify the extent of naphthalene distortion taking place the geometry of the naphthalene compounds was compared with that of unsubstituted naphthalene. In-plane distortion was calculated by observing the sum of angles in the bay region (splay angles); in the 'ideal' geometry these angles sum to 357.2°.[2] If the sum of the splay angles is greater than this value we can conclude the bonds have moved apart, indicating steric repulsion, but if the sum is lower, then the atoms have come closer as a result of favourable interactions. Likewise, out-of-plane distortion can be measured from the distance the *peri*-substituents reside above and below the naphthalene plane; in 'ideal' naphthalene the *peri*-hydrogens lie on the naphthyl plane.[2] Lastly, torsion angles can indicate the move away from planarity by buckling of the naphthyl plane. For clarity, two torsion angles have been used as a guide to planarity; C(6)-C(5)-C(10)-C(1), C(4)-C(5)-C(10)-C(9) (Figure 1.51). The three types of distortion are expressed cumulatively by the value of the *peri*-distance which is used as the primary parameter when describing the distortion away from 'ideal'.

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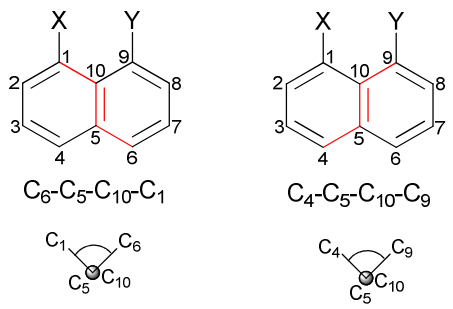

Fig. 1.51 *Torsion angles C(6)-C(5)-C(10)-C(1) and C(4)-C(5)-C(10)-C(9) are used as a guide to the naphthalene planarity.*

The size of *peri*-atoms as well as the number and size of substituents attached to them are important factors influencing the degree of strain. The mixed phosphorus-chalcogenide and mixed chalcogenide systems offer a good model with which to study substituent affects on steric repulsion, favourable intramolecular interactions and the possibility of bond formation and hypercoordination and hypervalency. Furthermore the bidenticity and rigid C_3 backbone these ligands possess makes them suitable candidates for metal coordination and the design of ligands for catalysis.

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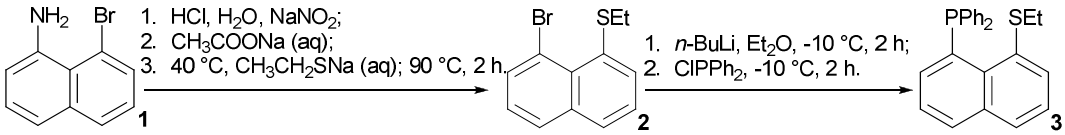
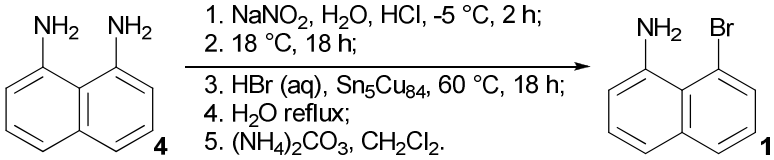
Chapter 2

Preparation and chemistry of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine 3



Scheme 2.1 *The reaction scheme for the preparation of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine* **3** *from 8-bromonaphthalen-1-amine* **1**.

Initial attempts to synthesise (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** revolved around 8-bromonaphthalen-1-amine **1** as the key starting point for this reaction sequence (Scheme 2.1). Our first attempts to synthesise **1** used the procedure of Fieser and Seligman from 1939.[1] This synthesis converts commercially available 1,8-diaminonaphthalene **4** to **1** via the Sandmeyer reaction (Scheme 2.2).[1]



Scheme 2.2 *Synthesis of 8-bromonaphthalen-1-amine* **1** *from 1,8-diaminonaphthalene* **4**.[1]

We found that the reaction proceeded in 21% yield and **1** was fully characterised by melting point determination, elemental analysis, infra-red spectroscopy, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.[1] The black crude product was recrystallized from 40:60 petroleum ether to afford pink crystals which were characterised by single crystal X-ray crystallography (Figure 2.1).[2]

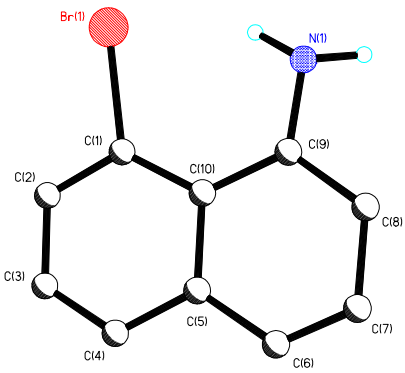


Fig. 2.1 *The crystal structure of 8-bromonaphthalen-1-amine* **1**.[2]

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Compared to other 1,8-disubstituted naphthalene compounds,[3] **1** exhibits a somewhat unstrained intramolecular non-bonded Br(1)···N(1) distance of 3.070(3) Å. An intramolecular hydrogen bonding interaction between the N(1)-H(1a)···Br(1) enables a close non-bonding Br(1)···N(1) distance and at the same time leaves the molecule relatively unstrained. The other NH proton is involved in an intermolecular hydrogen bond (Table 2.1) N(1)-H(1b)···N(1) and forms an infinite zigzag chain. These chains have normal hydrophobic contact to each other with the naphthalene units arranged in a herring-bone stacking motif (Figure 2.2).

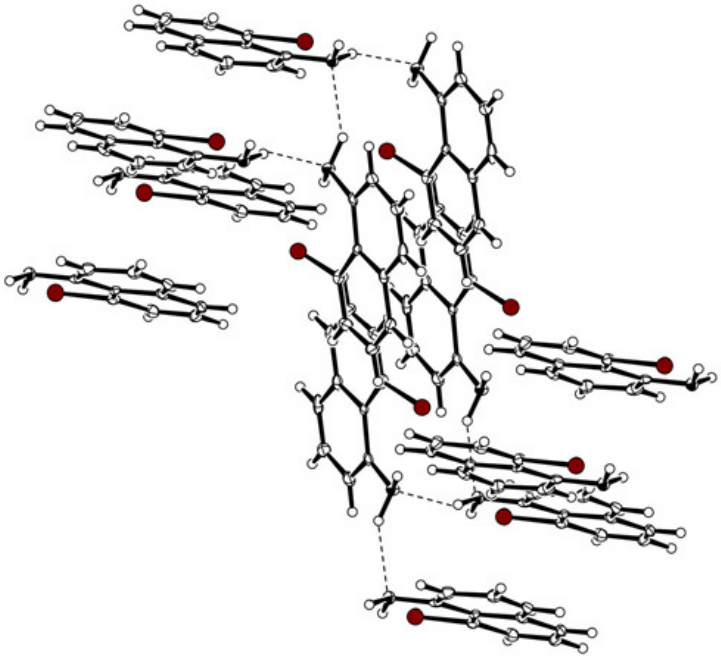

Fig. 2.2 *The crystal structure of 8-bromonaphthalen-1-amine* **1** *showing the intra- and intermolecular hydrogen bonding and the herring-bone stacking motif of the naphthalene units.*[2]

The *peri*-atoms display a minor out-of-plane distortion, N(1) lying 0.02(1) Å above the plane of the naphthalene ring and Br(1) lying -0.16(1) Å below the plane. Bond angles and distances (Table 2.1) also confirm the existence of in-plane distortion with all three *peri*-area angles being greater than those expected for the ideal naphthalene geometry [in naphthalene these angles are 118.3(1)°, 120.6(1)°, 118.3(1)° with a sum of 357.2°].[4] The two torsion angles associated with the central C10-C5 naphthalene bond show only a slight buckling of the naphthalene backbone with angles only varying from a planar geometry by 1.6-2.0°. Further details of the crystal structure can be found in Appendix 1.

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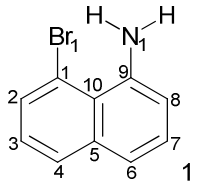
Table 2.1 Selected bond lengths [Å] and angles [°] of 8-bromonaphthalen-1-amine **1**.[2]



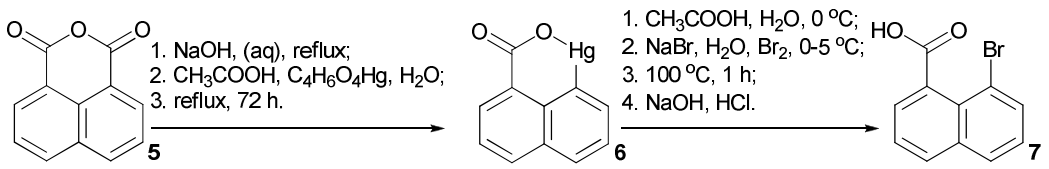
Br(1)···N(1)	**3.070(3)**	Br(1)-C(1)-C(10)	123.4(4)
Br(1)-C(1)	1.939(4)	C(1)-C(10)-C(9)	124.1(4)
N(1)-C(9)	1.400(5)	N(1)-C(9)-C(10)	121.2(4)
			Σ = 368.7(8)

Distance from naphthalene mean plane	
Br(1)	-0.16(1)
N(1)	0.02(1)

Torsion angles			
C(6)-C(5)-C(10)-C(1)	-178.0(5)	C(4)-C(5)-C(10)-C(9)	-178.4(5)

Hydrogen bond geometry [Å, °]				
***D*-H···A**	***D*-H**	**H···A**	***D*···A**	***D*-H···A**
N(1)-H(1a)···Br(1)	0.98	2.27	3.070(3)	138
N(1)-H(1b)···N(1^1)	0.98	2.2	3.073(5)	148

Concerns with the relatively low yield for the synthesis of 8-bromonaphthalen-1-amine **1** from 1,8-diaminonaphthalene **4** led to the investigation of new routes to the target compound. In 1987 Herbert, Woodgate and Denny published a synthesis starting from 8-bromo-1-naphthoic acid **7** (Scheme 2.3).[5]



Scheme 2.3 *Synthesis of 8-bromo-1-naphthoic acid* **7**.[6]

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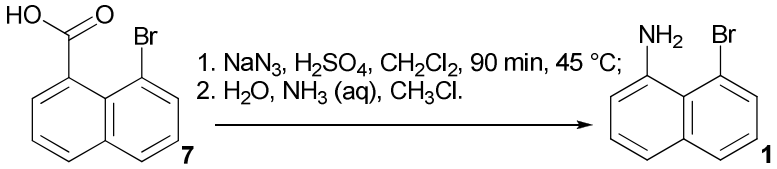
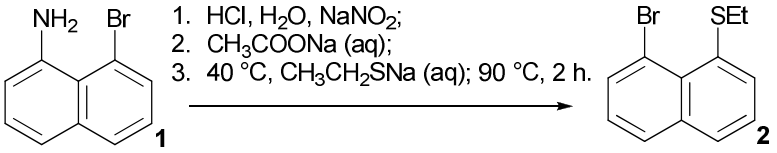
Unlike 1,8-diaminonaphthalene in the previous reaction, 8-bromo-1-naphthoic acid is not commercially available but is accessible from the cheap and available naphthalic anhydride **5**. We tested this method, following the procedure of Bailey *et al.* naphthalic anhydride was reacted with mercuric acetate under acidic conditions to give the colourless anhydro-8-(hydroxymercuri)-1-naphthoic acid **6** in nearly quantitative yield**,** via the release of large amounts of carbon dioxide (Scheme 2.3).[6]

We then reacted anhydro-8-(hydroxymercura)-1-naphthoic acid **6** with sodium bromide and bromine under acidic conditions to give 8-bromo-1-naphthoic acid **7** in 34% yield.[6] **7** was characterised by ^{1}H NMR spectroscopy and melting point analysis (173-175 °C) and gave values which were in accord with the literature.[6] Conversion of **7** to the desired starting material, 8-bromonaphthalen-1-amine **1**, was achieved under acidic conditions via reaction with sodium azide following the procedure from Herbert, Woodgate and Denny (Scheme 2.4).[5] In our hands, the reaction proceeded in 73% yield. The ^{1}H NMR spectrum and melting point (85-87 °C) of **1** were in agreement with the literature and the results from the previous synthesis from **4**.[1,5]



Scheme 2.4 *Synthesis of 8-bromonaphthalen-1-amine* **1** *from 8-bromo-1-naphthoic acid* **7**.[5]

1-bromo-8-(ethylsulfanyl)naphthalene **2** was prepared via a standard diazotisation and substitution reaction of 8-bromonaphthalen-1-amine **1** (Scheme 2.5) following the procedure reported by Oki and Yamada.[7] The diazotised compound reacted with a solution of sodium ethanethiolate to produce the product **2** as yellow crystals in 41% yield.[7] Elemental analysis, mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy and melting point analysis (47-49 °C) values matched those in the literature.[7]



Scheme 2.5 *Synthesis of 1-bromo-8-(ethylsulfanyl)naphthalene* **2**.[7]

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The crystal structure of **2** shows two independent molecules in the asymmetric unit with similar conformations (Figure 2.3).[8]

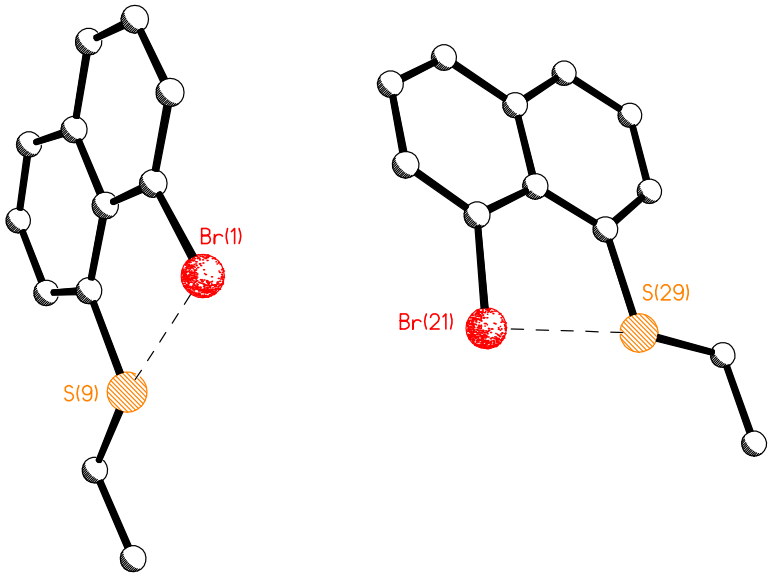

Fig. 2.3 *The crystal structure of 1-bromo-8-(ethylsulfanyl)naphthalene* **2** *showing two independent molecules in the asymmetric unit.*[8]

Intramolecular Br···S(ethyl) distances are 3.056(2) Å and 3.050(2) Å. The bromine and sulfur atoms show minor deviations above/below their attached ring planes; S(9) [0.04(1) Å] and Br(21) [0.01(1) Å] above the plane of the naphthalene ring and Br(1) [-0.14(1) Å] and S(29) [-0.04(1) Å] below the plane. In-plane distortion is observed in both molecules with the three *peri*-region angles (Table 2.2) being greater than those of naphthalene.[4] From the sum of these angles it is observed that the degree of in-plane distortion is similar in both independent molecules and that there is more distortion in **2** compared to in 8-bromonaphthalen-1-amine **1**. The four torsion angles associated with the C10-C5 and C30-C25 bonds show that a limited amount of naphthalene ring buckling has taken place making the two molecules near planar, slightly more so than in **1**.[8]

The molecules pack in a herringbone array with no significant π-π interactions. The shortest intermolecular S···S distance is 4.199(2) Å and there is a weak intermolecular C-H···Br interaction [for C(22)-H(22a)···Br(1): H···Br = 3.025 Å, C-H···Br = 167°]. Bond lengths and angles can be found in Table 2.2 and further details of the crystal structure can be found in Appendix 2.[8]

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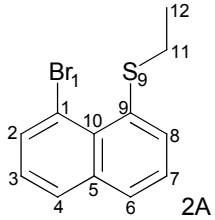
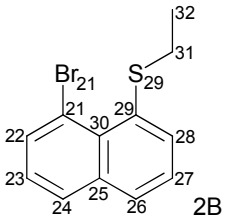
Table 2.2 Selected bond lengths [Å] and angles [°] of 1-bromo-8-(ethylsulfanyl)naphthalene **2**.[8]





Br(1)-S(9)	**3.0561(18)**	**Br(21)-S(29)**	**3.0505(19)**
Br(1)-C(1)	1.901(6)	Br(21)-C(21)	1.897(6)
S(9)-C(9)	1.770(6)	S(29)-C(29)	1.778(6)
Br(1)-C(1)-C(10)	124.5(4)	Br(21)-C(21)-C(30)	124.1(4)
C(1)-C(10)-C(9)	128.8(5)	C(21)-C(30)-C(29)	128.1(5)
S(9)-C(9)-C(10)	121.2(4)	S(29)-C(29)-C(30)	122.9(5)
	Σ = 374.5(9)		**Σ = 375.1(10)**
Distance from naphthalene mean plane			
Br(1)	-0.14(1)	Br(21)	0.01(1)
S(9)	0.04(1)	S(29)	-0.04(1)
Torsion angles			
C(6)-C(5)-C(10)-C(1)	-179.2(5)	C(26)-C(25)-C(30)-C(21)	179.2(5)
C(4)-C(5)-C(10)-C(9)	-178.4(6)	C(24)-C(25)-C(30)-C(29)	179.1(5)

Hydrogen-bond geometry [Å, °]				
***D*-H···A**	***D*-H**	**H···A**	***D*···A**	***D*-H···A**
C(22)-H(22A)···Br(1)	0.95	3.025	3.957(2)	167

We achieved the conversion of 1-bromo-8-(ethylsulfanyl)naphthalene **2** to the desired naphthalene structure **3** substituted with sulfur and phosphorus moieties *peri* to one another by following a similar procedure to that reported by Riihimäki *et al.*.[9] 1-bromo-8-(ethylsulfanyl)naphthalene **2** was reacted with *n*-butyllithium (1 equivalent) and chlorodiphenylphosphine (1 equivalent) to give the novel (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** in 11% yield (Scheme 2.6). **3** was characterised by elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and mass spectrometry.

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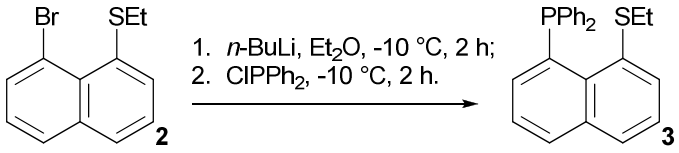
The ^{31}P NMR spectrum for the compound showed a single peak at δ = -5.26 ppm, in the correct region for this type of phosphine.[10]



Scheme 2.6 *Synthesis of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine* **3**.[9]

Analysis of the structure via single crystal X-ray crystallography (Figure 2.4) shows two independent molecules in the asymmetric unit with similar conformations. Intramolecular P···S(ethyl) distances are 2.9737(14) Å and 2.9469(15) Å. Minor relief of steric strain is observed in both independent molecules with the phosphorus and sulfur atoms having undergone out-of-plane distortion. P(1) [-0.11(1) Å] and S(39) [-0.03(1) Å] lie below the mean naphthalene plane and S(9) [0.16(1) Å] and P(31) [0.05(1) Å] lie above the plane. From these values it can be seen that there is more distortion of the *peri*-atoms taking place in **3A** compared to **3B** where the atoms lie close to the naphthalene plane.

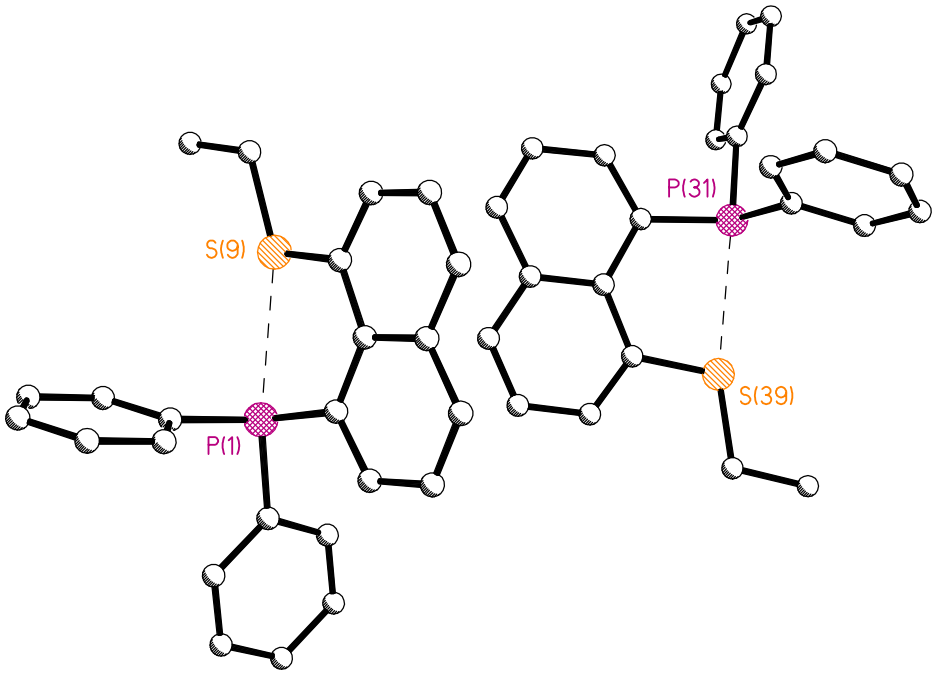


Fig. 2.4 *The crystal structure of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine* **3** *showing two independent molecules in the asymmetric unit.*

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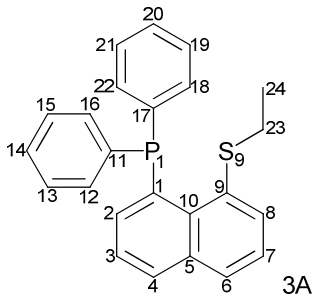
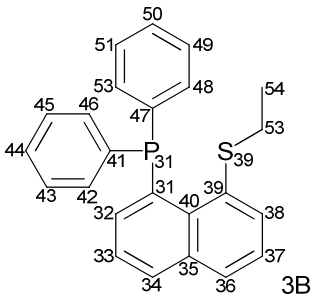
Selected bond lengths and bond angles of the crystal structure are shown in Table 2.3. The size of the *peri*-region angles indicates in-plane distortion has occurred and the sum of these angles shows the distortion is comparable in the two molecules. The torsion angles suggest there is more buckling of the naphthalene ring system in molecule **3A** compared to **3B**. Further details of the crystal structure can be found in Appendix 3.

Table 2.3 Selected bond lengths [Å] and angles [°] of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3**.





P(1)···S(9)	**2.9737(14)**	**P(31)···S(39)**	**2.9469(15)**
P(1)-C(1)	1.838(4)	P(31)-C(31)	1.848(3)
S(9)-C(9)	1.779(4)	S(39)-C(39)	1.776(4)
P(1)-C(1)-C(10)	123.6(3)	P(31)-C(31)-C(40)	122.4(3)
C(1)-C(10)-C(9)	126.9(3)	C(39)-C(40)-C(31)	126.0(3)
S(9)-C(9)-C(10)	121.2(3)	S(39)-C(39)-C(40)	123.0(3)
	Σ = 371.7(6)		**Σ = 371.4(6)**
Distance from naphthalene mean plane			
P(1)	-0.11(1)	P(31)	0.05(1)
S(9)	0.16(1)	S(39)	-0.03(1)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	-177.1(3)	C(36)-C(35)-C(40)-C(31)	179.8(4)
C(4)-C(5)-C(10)-C(9)	-176.5(3)	C(34)-C(35)-C(40)-C(39)	-177.2(4)

Our initial route to (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** although successful was achieved via four intermediates. The yields for the preparation of these intermediates when combined gave concerns over the efficiency of the overall reaction scheme and so a new improved route containing fewer steps to the target molecule was desirable.

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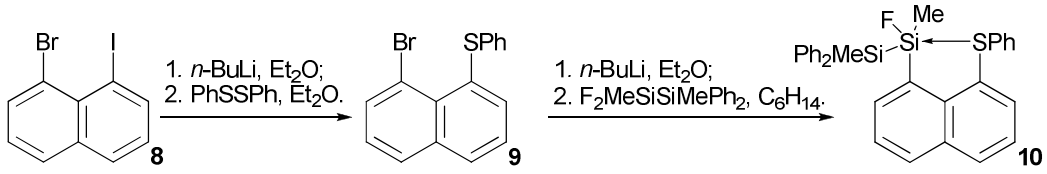
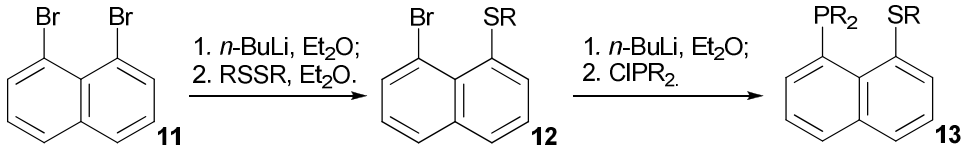


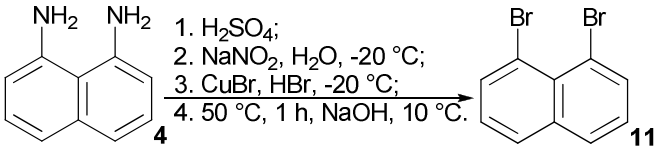
Scheme 2.7 *The general synthesis of pentacoordinate disilanes from the group of Toshimitsu.*[11]

In 2001, Toshimitsu *et al.* reported the synthesis of a series of pentacoordinate disilanes bearing an (8-chalcogeno-1-naphthyl) group synthesised through the stepwise halogen-lithium exchange reactions of 8-bromo-1-iodonaphthalene (Scheme 2.7).[11] The key compound in this synthesis is 1-bromo-8-(phenylsulfanyl)naphthalene **9**. Being able to synthesise compounds of this type in a one step process would give a more efficient route to our desired ligands, (8-alkylsulfanylnaphth-1-yl)dialkylphosphines. Our first experiments using this new method followed a similar procedure, but utilised the more accessible 1,8-dibromonaphthalene **11** as the starting material for these reactions (Scheme 2.8).



Scheme 2.8 *The reaction scheme for the preparation of (8-alkylsulfanylnaphth-1-yl)dialkylphosphines from 1,8-dibromonaphthalene* **11.**

11 was synthesised from 1,8-diaminonaphthalene **4** via a diazotisation followed by reaction with hydrobromic acid (Scheme 2.9)[12] and was characterised by elemental analysis, infra-red spectroscopy, ^{1}H and ^{13}C NMR spectroscopy. The melting point (107-109 °C) was also in accord with the literature (106-108 °C).[12]



Scheme 2.9 *Synthesis of 1,8-dibromonaphthalene* **11** *from 1,8-diaminonaphthalene* **4**.[12]

Reacting 1,8-dibromonaphthalene **11** with *n*-butyllithium (1 equivalent) via the stepwise halogen-lithium exchange reaction, it is possible to replace one of the bromine atoms with a lithium atom.

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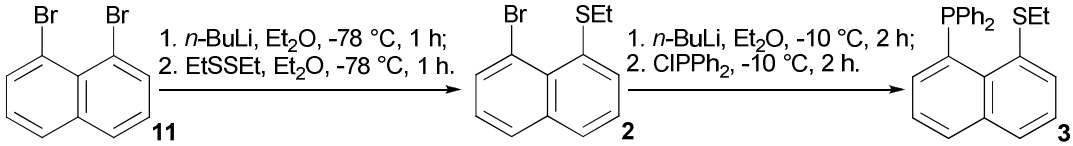
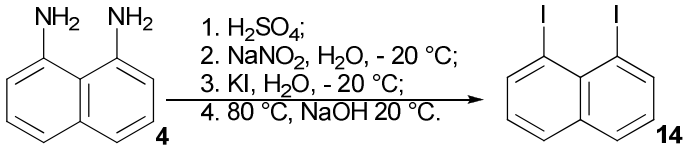
This gives the opportunity for single substitution reactions to take place between the lithium metal and the incoming species. Reaction of **11** with one equivalent of *n*-butyllithium followed by one equivalent of diethyl disulfide gave 1-bromo-8-(ethylsulfanyl)naphthalene **2** in 43% yield (Scheme 2.10).[11]



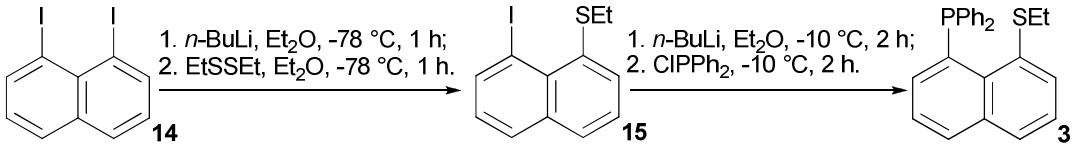
Scheme 2.10 *Synthesis of 1-bromo-8-(ethylsulfanyl)naphthalene* **2** *and (8-ethylsulfanylnaphth-1-yl)diphenylphosphine* **3**.[11]

Characterisation of the product by ^{1}H NMR spectroscopy and mass spectrometry found values in accord with those of the initial reaction which started from **1**. (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** was subsequently synthesised as described above giving an overall higher yielding route (4%) to the desired product. In an analogous series of reactions, (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** was synthesised from 1,8-diiodonaphthalene **14** (Scheme 2.12).[13]



Scheme 2.11 *Synthesis of 1,8-diiodonaphthalene* **14** *from 1,8-diaminonaphthalene* **4**.[13]

14 was synthesised following a similar procedure to 1,8-dibromonaphthalene **11**. Starting from 1,8-diaminonaphthalene **4**, diazotisation was achieved by reaction with aqueous $NaNO_2$ and subsequent reaction with potassium iodide gave the desired compound (Scheme 2.11).[13]



Scheme 2.12 *Synthesis of 1-iodo-8-(ethylsulfanyl)naphthalene* **15** *and (8-ethylsulfanylnaphth-1-yl)diphenylphosphine* **3**.[11]

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The reaction of **14** with *n*-butyllithium (1 equivalent) and diethyl disulfide (1 equivalent) yielded the novel 1-iodo-8-(ethylsulfanyl)naphthalene **15** in 42% yield. Further reaction of **15** with *n*-butyllithium and chlorodiphenylphosphine (as described earlier starting from **2**) afforded compound **3** in 51% yield.

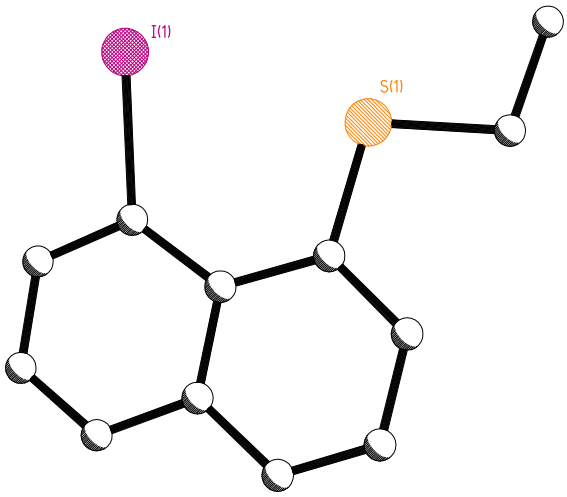

Fig. 2.5 *The crystal structure of 1-iodo-8-(ethylsulfanyl)naphthalene* **15**.

15 was characterised by elemental analysis, infra-red spectroscopy, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The structure of **15** (Figure 2.5) was analysed by single crystal X-ray crystallography and compared to its analogous bromo- counterpart **2**.

With the increase in size of the *peri*-substituent from bromine to iodine it can be seen that **15** exhibits a greater degree of distortion and therefore additional strain. The intramolecular *peri*-distance between the sulfur and iodine atoms of **15** is 3.243(2) Å putting the *peri*-atoms further apart compared to those in **2** [3.0561(18) Å, 3.0505(19) Å]. Out-of-plane distortion is observed to a greater extent in **15** with S(1) [-0.17(1) Å] and I(1) [0.36(1) Å] lying further from the mean naphthalene plane than the S(1) and Br(1) atoms in **2**. Similarly the sum of the *peri*-area angles (Table 2.4) shows a greater in-plane distortion in **15** [376.9°(9)] and a comparison of the torsion angles around the central naphthalene bond shows greater buckling of the naphthalene system for the larger atom. More information regarding the crystal structure can be found in Appendix 4.

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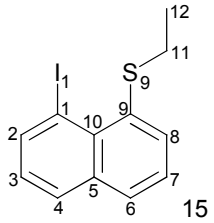
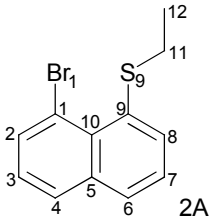
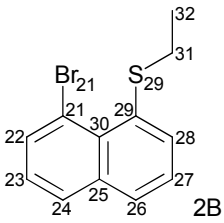
Table 2.4 Selected bond lengths [Å] and angles [°] for 1-iodo-8-(ethylsulfanyl)naphthalene **15** and 1-bromo-8-(ethylsulfanyl)naphthalene **2**.







I(1)···S(1)	**3.2436(17)**	**Br(1)···S(9)**	**3.0561(18)**	**Br(21)···S(29)**	**3.0505(19)**
I(1)-C(1)	2.126(6)	Br(1)-C(1)	1.901(6)	Br(21)-C(21)	1.897(6)
S(1)-C(9)	1.773(6)	S(9)-C(9)	1.770(6)	S(29)-C(29)	1.778(6)
I(1)-C(1)-C(10)	127.1(4)	Br(1)-C(1)-C(10)	124.5(4)	Br(21)-C(21)-C(30)	124.1(4)
C(1)-C(10)-C(9)	128.2(5)	C(1)-C(10)-C(9)	128.8(5)	C(21)-C(30)-C(29)	128.1(5)
S(1)-C(9)-C(10)	121.6(4)	S(9)-C(9)-C(10)	121.2(4)	S(29)-C(29)-C(30)	122.9(5)
	Σ = 376.9(9)		**Σ = 374.5(9)**		**Σ = 375.1(10)**
Distance from naphthalene mean plane					
I(1)	0.36(1)	Br(1)	-0.14(1)	Br(21)	0.01(1)
S(1)	-0.17(1)	S(9)	0.04(1)	S(29)	-0.04(1)
Torsion angle					
C:(6)-(5)-(10)-(1)	-177.0(5)	C:(6)-(5)-(10)-(1)	-179.2(5)	C:(6)-(5)-(10)-(1)	179.2(5)
C:(4)-(5)-(10)-(9)	-177.9(5)	C:(4)-(5)-(10)-(9)	-178.4(6)	C:(4)-(5)-(10)-(9)	179.1(5)

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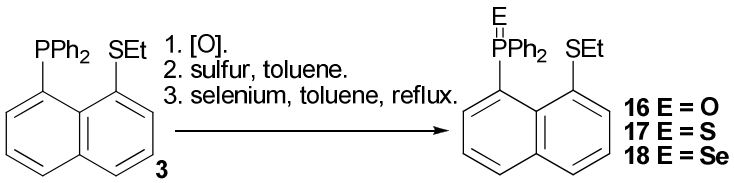
Phosphorus(V) chalcogenides of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine 3



Scheme 2.13 *Synthesis of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine oxide* **16**, *(8-ethylsulfanylnaphth-1-yl)diphenylphosphine sulfide* **17** *and (8-ethylsulfanylnaphth-1-yl)diphenylphosphine selenide* **18**.

Compound **3** reacts to form a series of three phosphorus(V) chalcogenide counterparts. Under atmospheric conditions the phosphorus atom was oxidised and the novel compound (8-ethylsulfanylnaphth-1-yl)diphenylphosphine oxide **16** was obtained (Scheme 2.13, Figure 2.6).

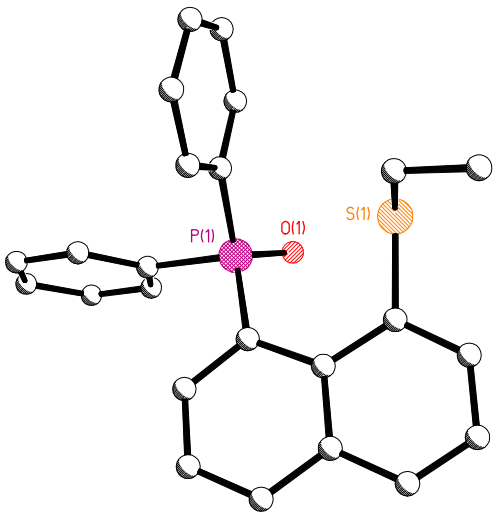


Fig. 2.6 *The crystal structure of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine oxide* **16**.

Reaction of **3** with one equivalent of sulfur in toluene gave the novel (8-ethylsulfanylnaphth-1-yl)diphenylphosphine sulfide **17** and similarly **3** reacted under reflux with one equivalent of selenium in toluene to produce (8-ethylsulfanylnaphth-1-yl)diphenylphosphine selenide **18** (Scheme 2.13).[14] For all three compounds, ^{31}P NMR showed phosphine **3** was converted to the respective phosphorus chalcogenide with a 100% conversion.

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All three compounds were characterised by elemental analysis, infra-red spectroscopy, mass spectrometry and ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The ^{31}P NMR signals show a significant difference between compounds with all three 4-coordinate phosphorus compounds seeing a downfield shift compared to the 3-coordinate ligand **3** [**3** PR_3: δ = -5.3 ppm, **16** $R_3P{=}O$: δ = 36.3 ppm, **17** $R_3P{=}S$: δ = 51.8 ppm, **18** $R_3P{=}Se$: δ = 41.9 ppm]. Additionally the ^{77}Se NMR spectrum of **18** was analysed and shows a doublet at δ = -172.3 ppm. The NMR signals for the three compounds are in accord with values for similar compounds found in the literature.[15]

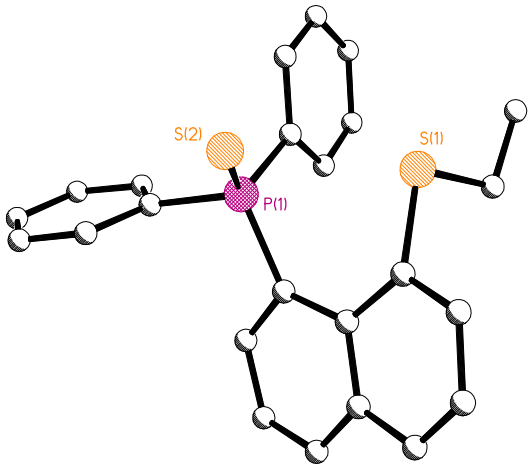

Fig. 2.7 *The crystal structure of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine sulfide* **17**.

The structures of the three chalcogenides were studied and compared by single crystal X-ray crystallography to phosphine **3** (Figure 2.6, 2.7 and 2.8). All three compounds show an increase in intramolecular interaction compared to phosphine **3** as denoted by the degree of distortion in the molecules. In all three cases the *peri*-distance is considerably greater than for **3** and increases with the increasing size of the chalcogen attached to the phosphorus atom P(1) [**3A** 2.9737(14) Å **3B** 2.9469(15) Å, **16** 3.1349(13) Å, **17** 3.2083(14) Å, **18** 3.2283(19) Å]. The length of the phosphorus chalcogen double bond in all three compounds is found to be in accord with average literature values and also increases with the size of the chalcogen [P=O 1.487(2) Å **16**, P=S 1.9550(14) Å **17**, P=Se 2.1103(17) Å **18**].[16]

Comparison of the sums of the *peri*-region angles (Table 2.6) shows similar in-plane distortion has taken place in oxide **16** and selenide **18** with an increase by a couple of degrees compared to **3**. Sulfide **17** shows less in-plane distortion compared to its analogous chalcogenides with *peri*-region angles being comparable to the non-oxidised compound **3**.

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Out-of-plane distortion is observed in all three compounds and is comparable with the *peri*-atoms lying at similar distances from the naphthalene plane. There is a notable increase in distortion compared to **3** with sulfide **17** showing the greatest change. In all three cases the P(1) atom lies below the plane and the S(1) atom lies above the naphthalene plane [**P(1)** -0.5656(41) Å **16**, -0.620(4) Å **17**, -0.5993(65) Å **18**; **S(1)** 0.4038(42) Å **16**, 0.744(4) Å **17**, 0.5272(64) Å **18**].

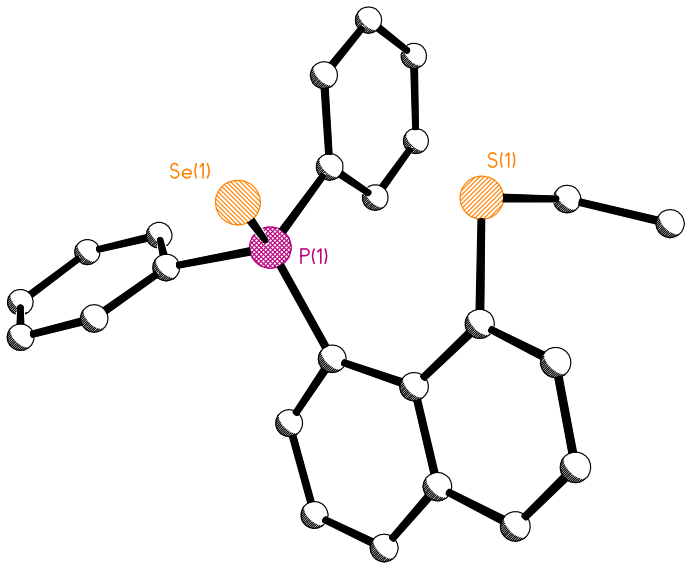

Fig. 2.8 *The crystal structure of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine selenide* **18**.

The chalcogen atoms bonded to P(1) all lie below the plane of the naphthalene with distances from the plane increasing with the increasing size of the atom [**O(1)** -1.7200(51) Å **16**, **S(2)** -2.019(5) Å **17**, **Se(1)** -2.3022(69) Å **18**]. In all cases the chalcogen atom bonded to P(1) is situated above the *peri*-gap in close proximity to S(1) (Figure 2.9) with the non-bonded S(1)···E distance increasing down the series due to sterics [**S(1)···O(1)** 3.033(2) Å **16**, **S(1)···S(2)** 3.2951(15) Å **17**, **S(1)···Se(1)** 3.43(1) Å **18**]. Nevertheless the non-bonded S(1)···E distances are smaller than the sum of the van der Waals radii for the two interacting atoms [**SO** = 3.32 Å, **SS** 3.60 Å, **SSe** 3.70 Å][17] suggesting the non-bonded distance is close enough for possible intramolecular interactions.[18]

The literature contains a large number of organosulfur compounds where conformations are considerably influenced by intramolecular sulfur-nucleophile interactions such as non-bonded S···O, S···N, S···S and S···π interactions. In these molecules the S···nucleophile distance is significantly shorter than the sum of the sulfur and nucleophile van der Waals radii.[17,18]

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While the S(1)···E distances in the phosphorus(V) chalcogenides are in the range for intramolecular interaction, the values are close enough to the van der Waals radii sum of the interacting atoms to suggest very weak interaction.[17,18] A closer look at the structures reveals that rotating around the C(1)-P(1) bond could bring the two interacting moieties closer together and give distances more in line with known non-bonded interaction values in the literature.[18] The fact that this does not occur suggests that if the S(1)···E interaction does take place in the oxides it is very weak and not the fundamental influence on the geometry of the molecules.

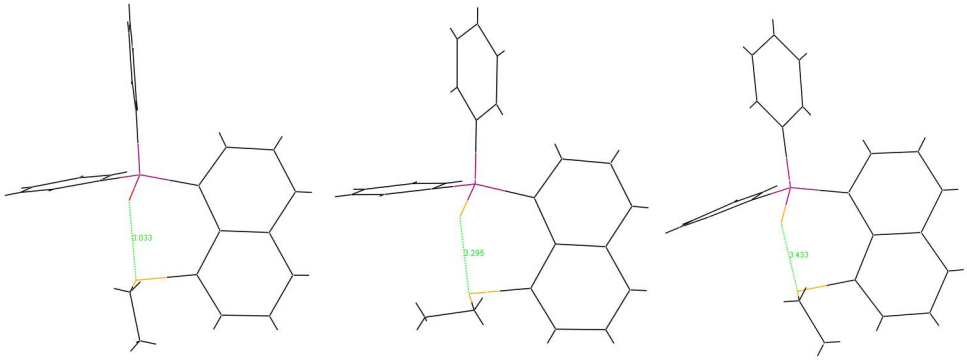

Fig. 2.9 *The crystal structures of the (8-ethylsulfanylnaphth-1-yl)diphenylphosphine chalcogenides* **16**, **17** *and* **18** *showing the non-bonded S(1)···E distance.*

The two torsion angles around the C5-C10 central naphthalene bond in the three compounds shows oxide **16** and selenide **18** have a similar degree of buckling in the naphthalene ring, only slightly greater in the selenide [**16** 175.4(3)°, 175.0(3)°, **18** -173.7(6)°, -175.3(6)°]. Sulfide **17** however is greatly buckled [**17** -168.4(3)°, -171.0(3)°] and the least planar of all our studied compounds (Figure 2.10).

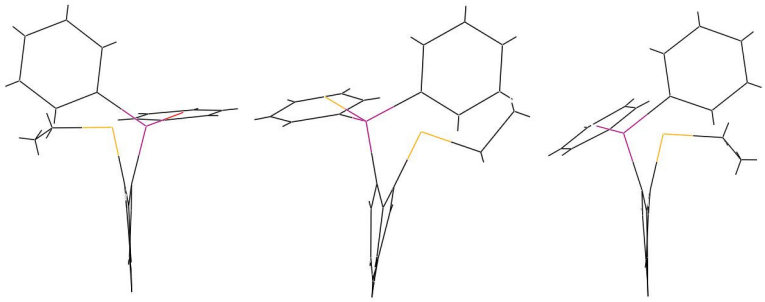

Fig. 2.10 *The crystal structures of the (8-ethylsulfanylnaphth-1-yl)diphenylphosphine chalcogenides* **16**, **17***and* **18** *showing the buckling of the naphthalene planes.*

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The structures of the chalcogenides show distinct differences in the position of the ethyl moiety when compared to that of **3** and also with each other. The repulsive distortion taking place to accommodate the increasingly large chalcogen atoms forces the ethyl group away from the naphthalene plane, adjacent and in close proximity to one of the phenyl π-systems on P(1) in all three cases. The short distance between the ethyl group and the phenyl π-system could suggest CH-π type interactions.[19] These are weak non-covalent attractive 'hydrogen-bond type' interactions between soft acids (CH) and soft bases (π-system) which have previously been shown to be important in self-assembly and molecular recognition processes, in determining conformations, selectivities of reactions and crystal structures.[19]

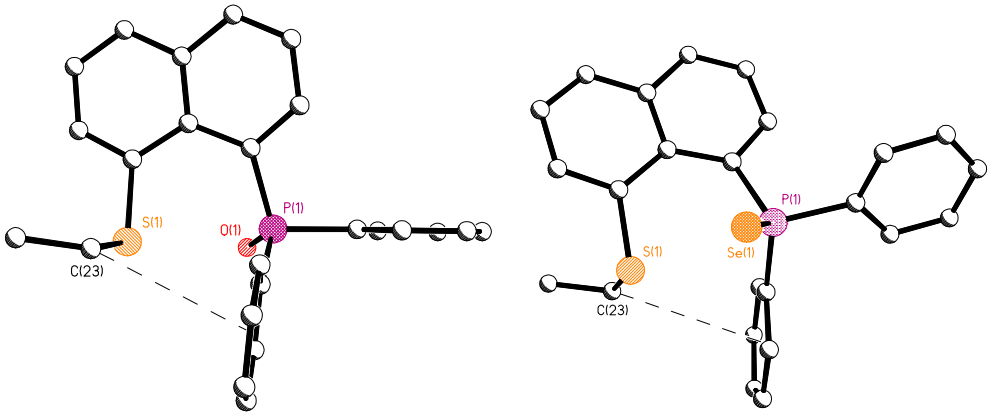

Fig. 2.11 *The crystal structures of the (8-ethylsulfanylnaphth-1-yl)diphenylphosphine chalcogenides* **16** *and* **18** *showing similar alignment of the S(ethyl) groups.*

In oxide **16** and selenide **18** the ethyl groups align so that the C(23)-C(24) bond points directly away from the closest phenyl ring on P(1). In both cases the distance of the C(23) atom from the centre of the phenyl ring [**16** C(23)···centroid 3.644(1) Å, **18** C(23)···centroid 3.578(1) Å], when compared to similar compounds from the literature is small enough to suggest possible CH-π interaction between the two moieties could occur (Figure 2.11).[19]

Conversely the ethyl group in **17** aligns so that the C(23)-C(24) bond lies parallel to the phenyl ring and at a slightly further distance compared to **16** and **18**. The proximity of the two groups is still small enough to envisage CH-π interaction between the π-system and the protons on the ethyl group [**17** C(23)···centroid 4.041(1) Å, C(24)···centroid 3.790(1) Å] (Figure 2.12).[19] CH-π Hydrogen bond distances can be found in Table 2.5.

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Table 2.5 Non-bonded intramolecular ethyl-π interactions [Å] and angles [°] for the (8-ethylsulfanylnaphth-1-yl)diphenylphosphine chalcogenides **16-18**.

Hydrogen bond geometry [Å, °]					
Compound	***D*-H···A**	***D*-H**	**H···A**	***D*···A**	***D*-H···A**
16	C(23)-H(23a)···Cg(17-23)	0.990	3.084	3.644(1)	117.2
	C(23)-H(23b)···Cg(17-23)	0.990	3.588	3.644(1)	85.4
17	C(23)-H(23b)···Cg(17-23)	0.990	3.834	4.041	94.9
	C(24)-H(24b)···Cg(17-23)	0.980	2.900	3.790(1)	151.5
18	C(23)-H(23a)···Cg(17-23)	0.990	3.421	3.578(1)	91.0
	C(23)-H(23b)···Cg(17-23)	0.990	3.164	3.578(1)	106.8

Cg(17-23) is the centroid of atoms C(17)-C(22).

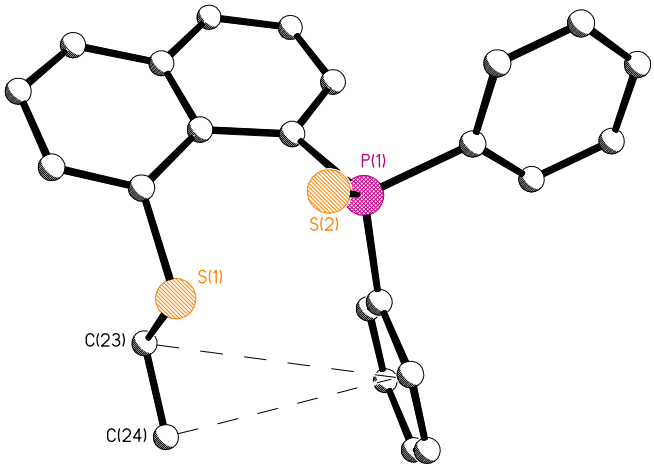

Fig. 2.12 *The crystal structure of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine sulfide* **17** *showing the alignment of the S(ethyl) group.*

In the two independent molecules of **3** there is very little distortion or buckling of the naphthalene ring. This places the ethyl groups coplanar with the naphthalene ring with the C(23)-C(24) and C(53)-C(54) bonds pointing directly up and away from the phenyl rings. The closest phenyl rings on P(1) and P(31) respectively lie at a much greater distance from the plane than for any of the chalcogenide compounds leaving a larger distance between the two moieties and no possible CH-π interaction [**3A** C(23)···centroid 5.561(1) Å, **3B** C(53)···centroid 5.749(1) Å] (Figure 2.13).[19]

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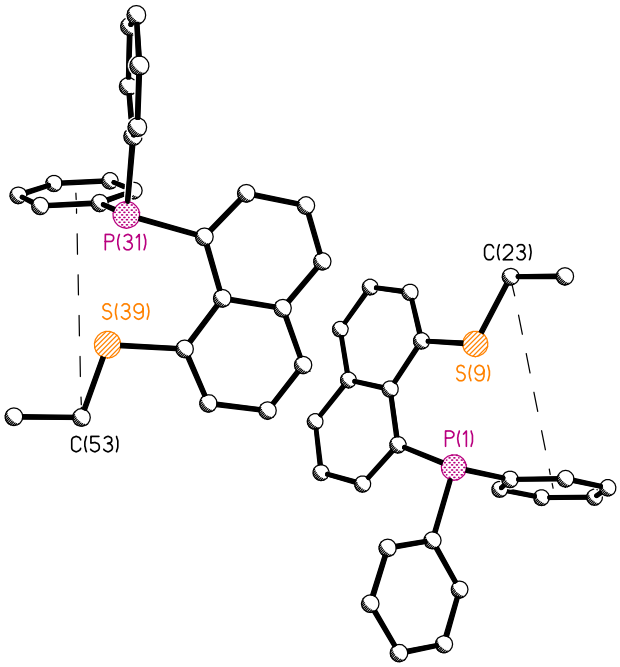

Fig. 2.13 *The crystal structure of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine* **3** *showing the alignment of the S(ethyl) groups in the two independent molecules.*

Selected bond lengths and bond angles of the crystal structures are shown in Table 2.6 and further details can be found in Appendices 5-7.

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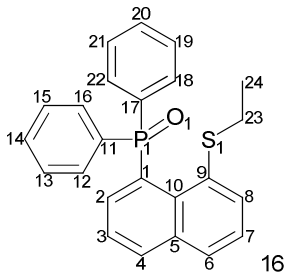
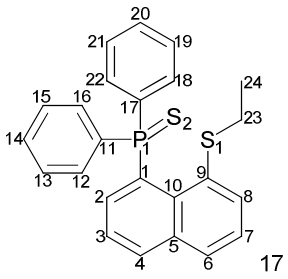
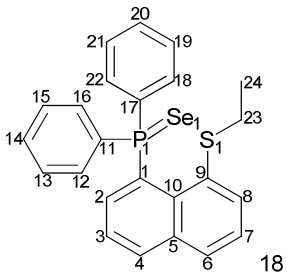
Table 2.6 Selected bond lengths [Å] and angles [°] for (8-ethylsulfanylnaphth-1-yl)diphenylphosphine oxide **16**, (8-ethylsulfanylnaphth-1-yl)diphenylphosphine sulfide **17** and (8-ethylsulfanylnaphth-1-yl)diphenylphosphine selenide **18**.







P(1)···S(1)	**3.1349(13)**	**P(1)···S(1)**	**3.2083(14)**	**P(1)···S(1)**	**3.2283(19)**
P(1)-C(1)	1.832(3)	P(1)-C(1)	1.837(3)	P(1)-C(1)	1.843(5)
S(1)-C(9)	1.772(3)	S(1)-C(9)	1.783(4)	S(1)-C(9)	1.771(6)
S(1)···O(1)	3.033(2)	S(1)···S(2)	3.2951(15)	S(1)···Se(1)	3.43(1)
P(1)=O(1)	1.487(2)	P(1)=S(2)	1.9550(14)	P(1)=Se(1)	2.1103(17)
P(1)-C(1)-(10)	123.9(2)	P(1)-C(1)-(10)	124.5(2)	P(1)-C(1)-C(10)	124.2(3)
C(1)-C(10)-(9)	126.5(3)	C(1)-C(10)-(9)	126.0(3)	C(1)-C(10)-C(9)	127.2(4)
S(1)-C(9)-(10)	122.7(2)	S(1)-C(9)-(10)	121.4(2)	S(1)-C(9)-C(10)	122.4(4)
	Σ = 373.1(5)		**Σ = 371.9(5)**		**Σ = 373.8(8)**
C(9)-S(1)-C(23)	102.1(2)	C(9)-S(1)-C(23)	97.39(19)	C(9)-S(1)-C(23)	99.7(3)
O(1)-P(1)-C(1)	112.50(15)	S(2)-P(1)-C(1)	114.17(12)	Se(1)-P(1)-C(1)	111.67(19)
Distance from naphthalene mean plane					
S(1)	0.404(4)	S(1)	0.744(4)	S(1)	0.527(6)
P(1)	-0.566(4)	P(1)	-0.620(4)	P(1)	-0.599(7)
O(1)	-1.720(5)	S(2)	-2.019(5)	Se(1)	-2.302(7)
Torsion angle					
C:(6)-(5)-(10)-(1)	175.4(3)	C:(6)-(5)-(10)-(1)	-168.4(3)	C:(6)-(5)-(10)-(1)	-173.7(6)
C:(4)-(5)-(10)-(9)	175.0(3)	C:(4)-(5)-(10)-(9)	-171.0(3)	C:(4)-(5)-(10)-(9)	-175.3(6)

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Summary

Repulsive steric strain caused by inserting larger atoms than hydrogen at the 1,8-positions on naphthalene is known to be relieved by in-plane and out-of-plane distortion and buckling of the naphthalene ring. The primary parameter used to quantify the amount of strain relief in non-ideal naphthalenes is the *peri*-distance which encapsulates all molecular deviations in one entity. As the size of the *peri*-atoms increases it could be expected that the repulsion and steric strain increases forcing the atoms further apart, thus increasing the *peri*-distance.

This trend is observed in the Nap[SEt][R] compounds (Figure 2.17); as the *peri*-atom of the R group increases in size (covalent radii) [**3 P**(1.07 Å), **2 Br**(1.20 Å), **15 I**(1.39 Å)][20] the size of the *peri*-distance also increases [**3A**(2.95 Å), **3B**(2.97 Å), **2A**(3.05 Å), **2B**(3.06 Å), **15**(3.24 Å)].

Figure 2.17 shows the comparison of all the *peri*-distances of the compounds in this chapter and show two main anomalies from the trend described above. Compound **1** has a larger than expected *peri*-distance when compared to **2**. By replacing SEt in **2** with NH_2 in **1** the covalent radii of the *peri*-atom decreases from sulfur to nitrogen [S(1.05 Å), N(0.71 Å)].[20] This should mean less steric interaction, less repulsion and a smaller *peri*-distance. The *peri*-distances of the two compounds however are very similar [**1**(3.07 Å), **2A**(3.05 Å), **2B**(3.06 Å)] with a larger than expected distance for **1**.

Hydrogen bonding between the protons on the amine moiety and the Br(1) atom in **1** forces the N(1) and Br(1) atoms to be further apart and less strained than other similar molecules. The chalcogenides **16**, **17** and **18** all have larger *peri*-distances than the non-oxidised phosphine **3** and increase as the size of the chalcogen bonded to P(1) increases (Figure 2.15). This can be accounted for by repulsive forces caused by the presence of the chalcogen atom and shows that not only the size of the *peri*-atoms dictates the size of the *peri*-distance.

The degree of buckling in the naphthalene ring system varies greatly within the series of S(ethyl) substituted naphthalenes. Figure 2.14 shows the two extremities with **2** having the greatest planarity and sulfide **17** the most amount of distortion.

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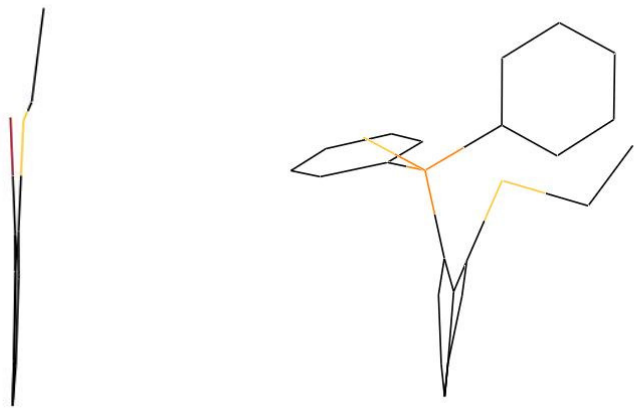

Fig. 2.14 *The greatest and least planar naphthalene ring systems of the Nap[SEt][R] compounds.*

Figure 2.15 quantifies the degree of in-plane distortion found in the compounds of this chapter by comparing the sum of the *peri*-region angles. As *peri*-atom size increases the degree of in-plane distortion increases.

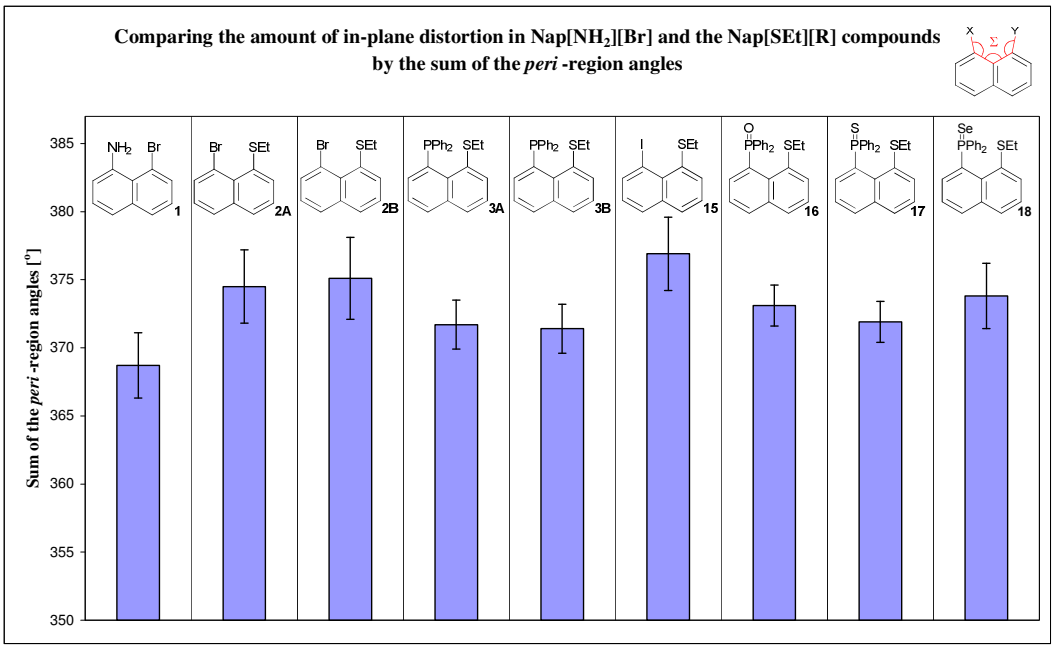

Fig. 2.15 *Comparing the in-plane distortion in Nap[NH_2][Br] and the Nap[SEt][R] compounds.*

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Out-of-plane distortion is compared in Figure 2.16 by looking at the deviation of the *peri*-atoms above and below the mean naphthalene plane. The greatest distortion is found in the chalcogenides **16**-**18** followed by compound **15** containing the large iodine atom.

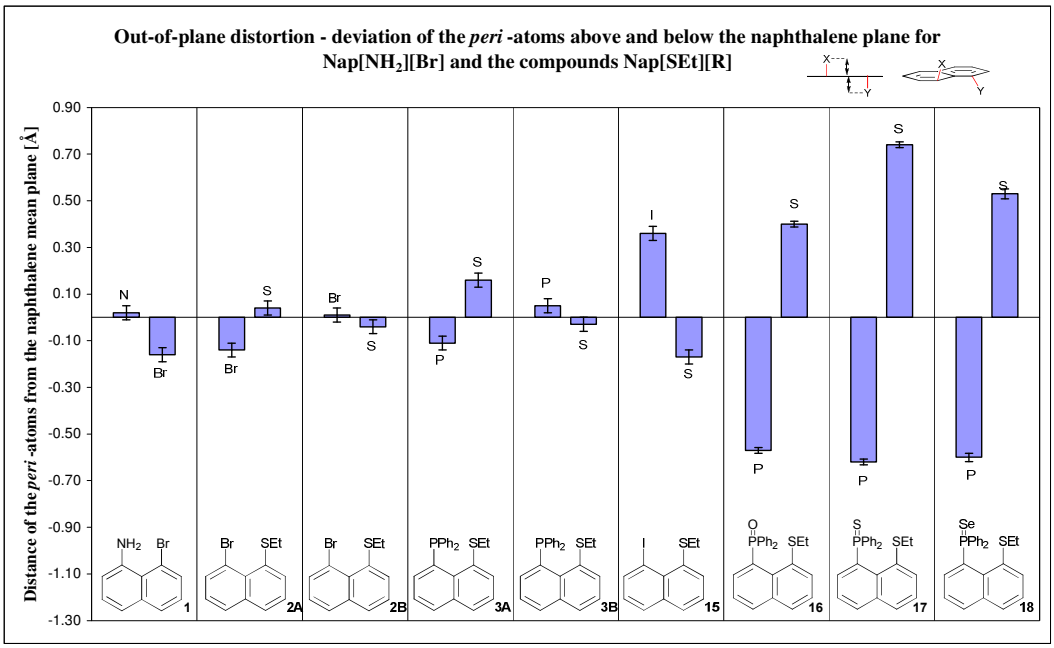

Fig. 2.16 *Comparing the out-of-plane distortion in Nap[NH_2][Br] and the Nap[SEt][R] compounds.*

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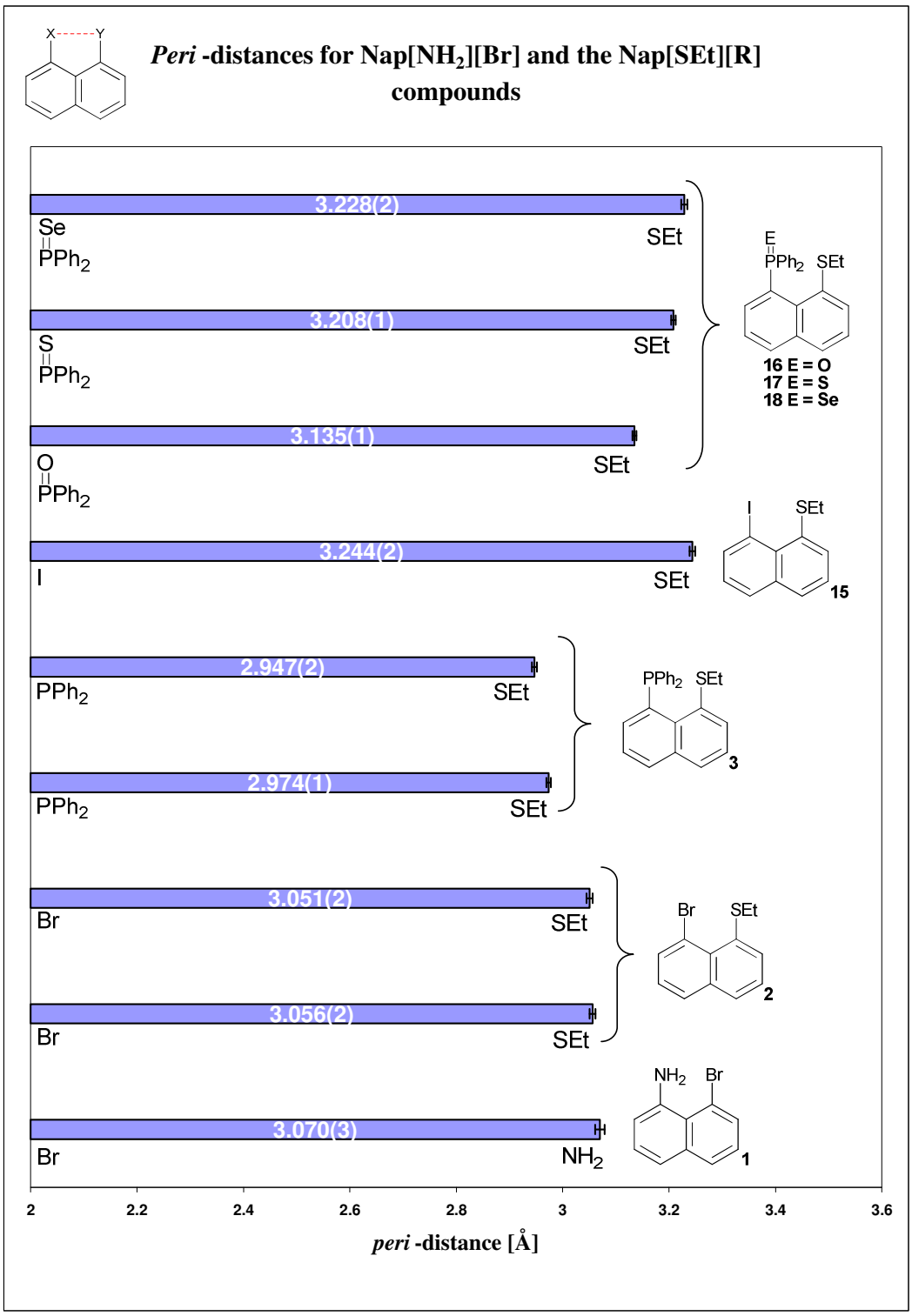

Fig. 2.17 *Comparing the peri-distances for Nap[NH$_2$][Br] and the Nap[SEt][R] compounds.*

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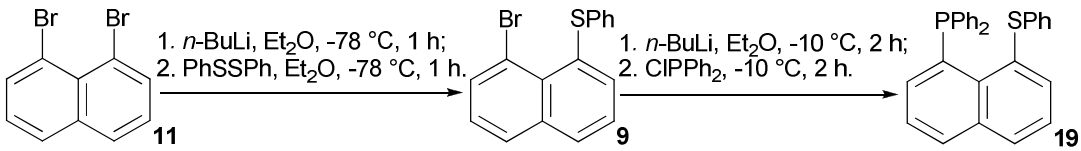
Chapter 3

Preparation and chemistry of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine 19

Following the successful synthesis of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** we envisaged that a halogen-lithium exchange reaction of 8-bromo-1-(phenylsulfanyl)naphthalene **9**, followed by reaction with chlorodiphenylphosphine, would afford the novel S(phenyl) analogue (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** (Scheme 3.1).[1,2]



Scheme 3.1 *The reaction scheme for the preparation of the novel compound (8-phenylsulfanylnaphth-1-yl)diphenylphosphine* **19**.

Our first task was to prepare **9** which we achieved by reaction of **11** with *n*-butyllithium (1 equivalent) and diphenyl disulfide (1 equivalent).[1] The reaction proceeded in 51% yield and characterisation by ^{1}H and ^{13}C NMR spectroscopy found values in accord with those in the literature.[1] The final step in our synthesis converted **9** into the novel phosphine **19** using the Riihimäki *et al.* procedure we implemented when synthesising **3** in the previous chapter.[2] **9** reacted with one equivalent of *n*-butyllithium followed by one equivalent of chlorodiphenylphosphine to give the novel (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** in 64% yield.

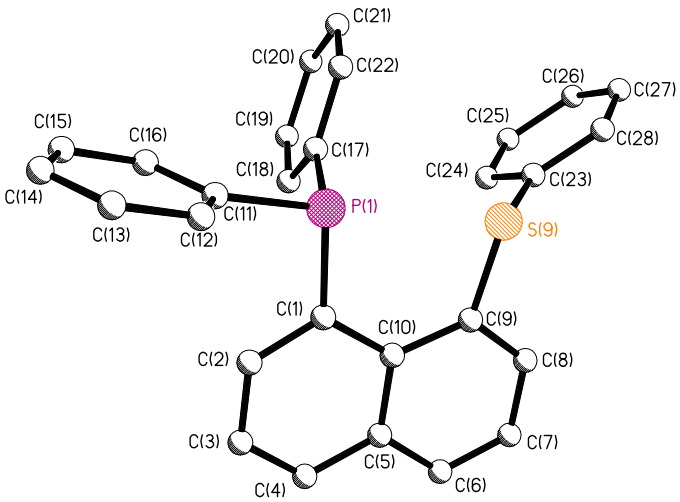


Fig. 3.1 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine* **19**.

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Full characterisation of **19** was accomplished using elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and mass spectrometry. The ^{31}P NMR spectrum shows a single peak at δ = -5.30 ppm which is in the appropriate region for a phosphine of this type and corresponds with the signal found for **3** [δ = -5.26 ppm].[3]

The disparity of electronic and steric affects of phenyl and ethyl groups results in dissimilar intramolecular interactions, naphthalene distortion and structural arrangement of **19** and **3**. Figure 3.1 shows the X-ray crystal structure of **19** and Table 3.1 compares selected bond lengths and angles for the two analogous compounds.

The *peri*-region angles are greater in the S(phenyl) compound **19** showing an increase in in-plane distortion has taken place to accommodate the larger substituent [**19** 374.1(3)°, **3A** 371.7(6)°, **3B** 371.4(6)°]. This forces the *peri*-atoms in **19** further apart giving a slightly larger *peri*-distance of 3.0330(17) Å compared to the S(ethyl) containing compound [**3A** 2.9737(14) Å, **3B** 2.9469(15) Å]. Out-of-plane distortion is comparable in the two compounds with the degree of *peri*-atom deviation in **19**, between that of the two independent molecules of **3**. Deviation of P(1) and S(1) in **19** however, occurs on the same face of the naphthalene plane; P(1) undergoing a very minor deviation [**P(1)** 0.007(1) Å, **S(1)** 0.127(1) Å].

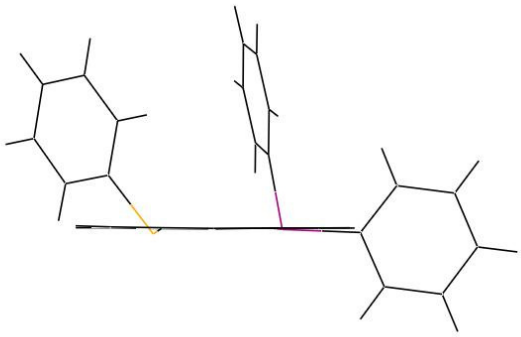

Fig. 3.2 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine* **19** *showing the planarity of the naphthalene backbone.*

In an unusual twist, torsion angles relating to the central C(5)-C(10) naphthalene bond show a greater degree of planarity in the ring system of the S(phenyl) compound (Figure 3.2) compared to **3** whose two independent molecules show varying degrees of buckling in the naphthalene system.

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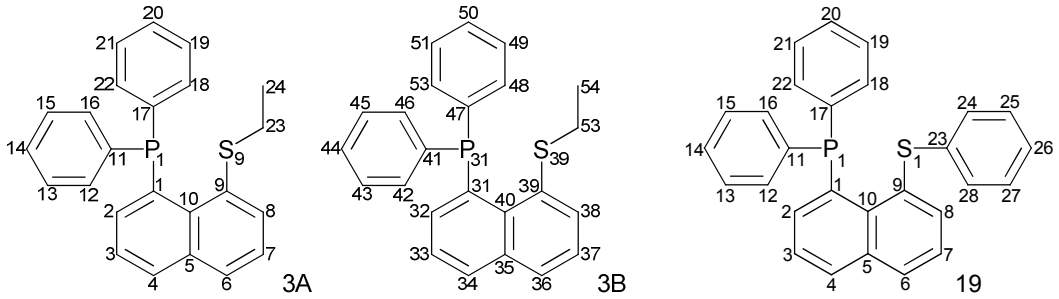
The distortion of the naphthalene geometry and the position of the *peri*-atoms in **19** places the phenyl group attached to S(1) on the same side of the naphthalene plane and in close proximity to one of the phenyl groups on P(1). Although the non-bonded intramolecular C···C distance is only 3.5-3.6 Å, the rings lie at angles to one another with no significant overlap for π···π interaction to occur.[4] The positioning of the phenyl groups must therefore be put down as electronic or steric effects of the system with possible influences coming from the crystal packing. Further information on the crystal structure of **19** can be found in Appendix 8.

Table 3.1 Selected bond lengths [Å] and angles [°] for (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** and (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19**.



P(1)···S(9)	**2.9737(14)**	**P(31)···S(39)**	**2.9469(15)**	**P(1)···S(1)**	**3.0330(7)**
P(1)-C(1)	1.838(4)	P(31)-C(31)	1.848(3)	P(1)-C(1)	1.8548(19)
S(9)-C(9)	1.779(4)	S(39)-C(39)	1.776(4)	C(9)-S(1)	1.785(2)
P(1)-C(1)-C(10)	123.6(3)	P(31)-C(31)-C(40)	122.4(3)	P(1)-C(1)-C(10)	124.1(1)
C(1)-C(10)-C(9)	126.9(3)	C(39)-C(40)-C(31)	126.0(3)	C(1)-C(10)-C(9)	126.9(2)
S(9)-C(9)-C(10)	121.2(3)	S(39)-C(39)-C(40)	123.0(3)	S(1)-C(9)-C(10)	123.1(1)
	Σ = 371.7(6)		**Σ = 371.4(6)**		**Σ = 374.1(3)**
Distance from naphthalene mean plane [Å]					
P(1)	-0.11(1)	P(31)	0.05(1)	P(1)	0.007(1)
S(9)	0.16(1)	S(39)	-0.03(1)	S(1)	0.127(1)
Torsion angle					
C:(6)-(5)-(10)-(1)	-177.1(3)	C:(36)-(35)-(40)-(31)	179.8(4)	C:(6)-(5)-(10)-(1)	178.49(16)
C:(4)-(5)-(10)-(9)	-176.5(3)	C:(34)-(35)-(40)-(39)	-177.2(4)	C:(4)-(5)-(10)-(9)	-179.5(2)

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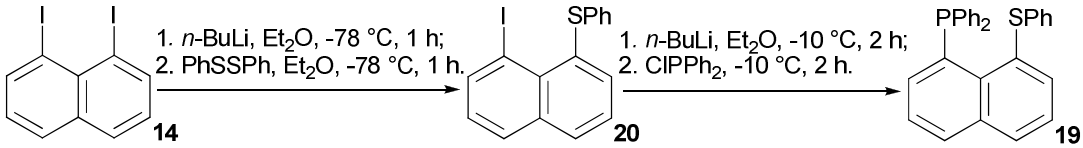
To complete the series of reactions we also synthesised (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** using 1,8-diiodonaphthalene **14** as starting material (Scheme 3.2).[1,2] **14** reacted with *n*-butyllithium (1 equivalent) and diphenyl disulfide (1 equivalent) to afford the novel 1-iodo-8-(phenylsulfanyl)naphthalene **20** in 30% yield.[1] Characterisation was reached by elemental analysis, infra-red spectroscopy, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Subsequent reaction of **20** with a single equivalent each of *n*-butyllithium and chlorodiphenylphosphine afforded compound **19** in 74% yield.[2]



Scheme 3.2 *The reaction scheme for the preparation of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine* **19** *from 1,8-diiodonaphthalene* **14**.

The X-ray structure of **20** is shown in Figure 3.3. The structural dissimilarity between **20** and its S(ethyl) counterpart **15** mirrors that of compounds **3** (SEt) and **19** (SPh) and shows the effect the S(alkyl) group has on the overall structure of the molecule.

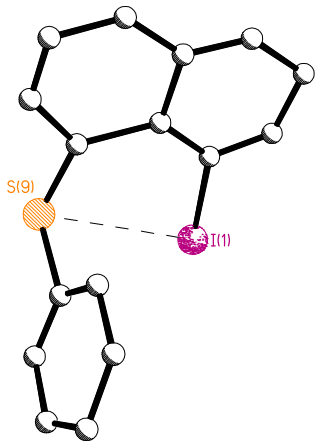


Fig. 3.3 *The crystal structure of 1-iodo-8-(phenylsulfanyl)naphthalene* **20**.

The intramolecular I···S(phenyl) *peri*-distance is again greater than the I···S(ethyl) distance [**20** 3.338(11) Å, **15** 3.2436(17) Å] and the sum of the *peri*-region angles shows in-plane distortion is greater in the S(phenyl) compound compared to its S(ethyl) counterpart [**20** 380.8(17)°, **15** 376.9(9)°].

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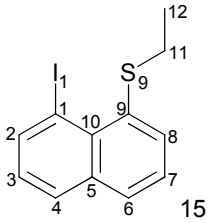
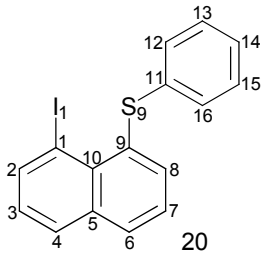
Only minimal deviation of the *peri*-atoms from the naphthalene plane in **20**, results in less out-of-plane distortion compared to **15**. However torsion angles show the planarity of the two compounds is similar. Comparison of selected bond lengths and angles of compounds **15** and **20** can be found in Table 3.2. Further information of the crystal structure of **20** can be seen in Appendix 9.

Table 3.2 Bond lengths [Å] and angles [°] for 1-iodo-8-(ethylsulfanyl)naphthalene **15** and 1-iodo-8-(phenylsulfanyl)naphthalene **20**.

			
I(1)···S(1)	**3.2436(17)**	**I(1)···S(9)**	**3.338(11)**
I(1)-C(1)	2.126(6)	I(1)-C(1)	2.118(11)
S(1)-C(9)	1.773(6)	S(9)-C(9)	1.765(11)
I(1)-C(1)-C(10)	127.1(4)	I(1)-C(1)-C(10)	127.2(8)
C(1)-C(10)-C(9)	128.2(5)	C(1)-C(10)-C(9)	128.4(10)
S(1)-C(9)-C(10)	121.6(4)	S(9)-C(9)-C(10)	125.2(8)
	Σ = 376.9(9)		**Σ = 380.8(17)**
Distance from naphthalene mean plane			
I(1)	0.36(1)	I(1)	-0.072(1)
S(1)	-0.17(1)	S(9)	0.049(1)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	-177.0(5)	C(6)-C(5)-C(10)-C(1)	176.9(10)
C(4)-C(5)-C(10)-C(9)	-177.9(5)	C(4)-C(5)-C(10)-C(9)	-178.3(9)

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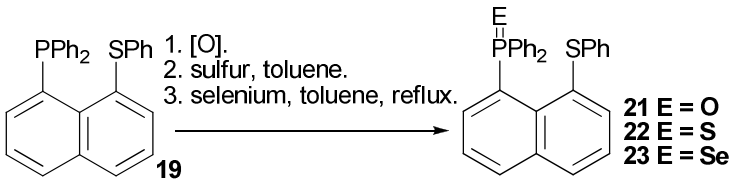
Phosphorus(V) chalcogenides of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine 19



Scheme 3.3 *Synthesis of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine oxide* **21**, *(8-phenylsulfanylnaphth-1-yl)diphenylphosphine sulphide* **22**, *(8-phenylsulfanylnaphth-1-yl)diphenylphosphine selenide* **23**.

In a series of parallel reactions to those observed for compound **3, 19** also reacted to form a series of three phosphorus(V) chalcogenides. Under atmospheric conditions the three-coordinate phosphorus atom of **19** oxidised to form the novel compound (8-phenylsulfanylnaphth-1-yl)diphenylphosphine oxide **21** (Scheme 3.3).

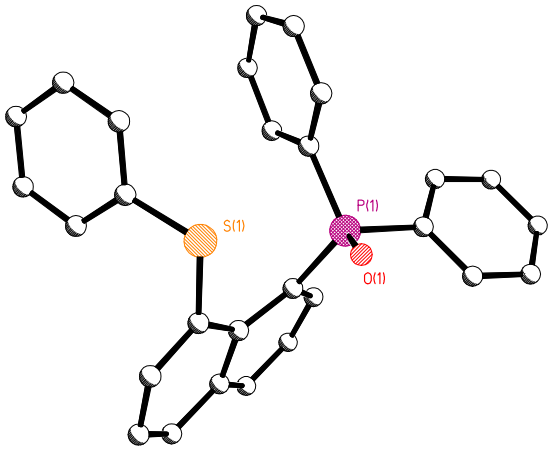


Fig. 3.4 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine oxide* **21**.

Reaction of **19** with one equivalent of sulfur in toluene produced the novel (8-phenylsulfanylnaphth-1-yl)diphenylphosphine sulfide **22**. Similarly **19** reacted under reflux with one equivalent of selenium in toluene to produce the novel (8-phenylsulfanylnaphth-1-yl)diphenylphosphine selenide **23** (Scheme 3.3).[5] For all three compounds, ^{31}P NMR showed phosphine **19** was converted to the respective phosphorus chalcogenide with 100% conversion.

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The ^{31}P NMR signals for the three compounds were found to lie at similar values to the S(ethyl) chalcogenides with all three 4-coordinate phosphorus compounds seeing a downfield shift compared to the 3-coordinate ligand **19** [**19** PR_3: δ = -5.3 ppm, **21** R_3P=O: δ = 37.0 ppm, **22** R_3P=S: δ = 52.5 ppm, **23** R_3P=Se: δ = 42.4 ppm]. The NMR signals for the three compounds are in accord with values for similar compounds found in the literature.[6] The X-ray structures of the three compounds were studied (Figure 3.4, 3.6 and 3.8) and compared to the structures of phosphine **19** and the S(ethyl) chalcogenides (**16**-**18**). All three compounds show a greater degree of steric strain relief than the non-oxidised phosphine **19** as indicated by the extent of molecular distortion in their structures.

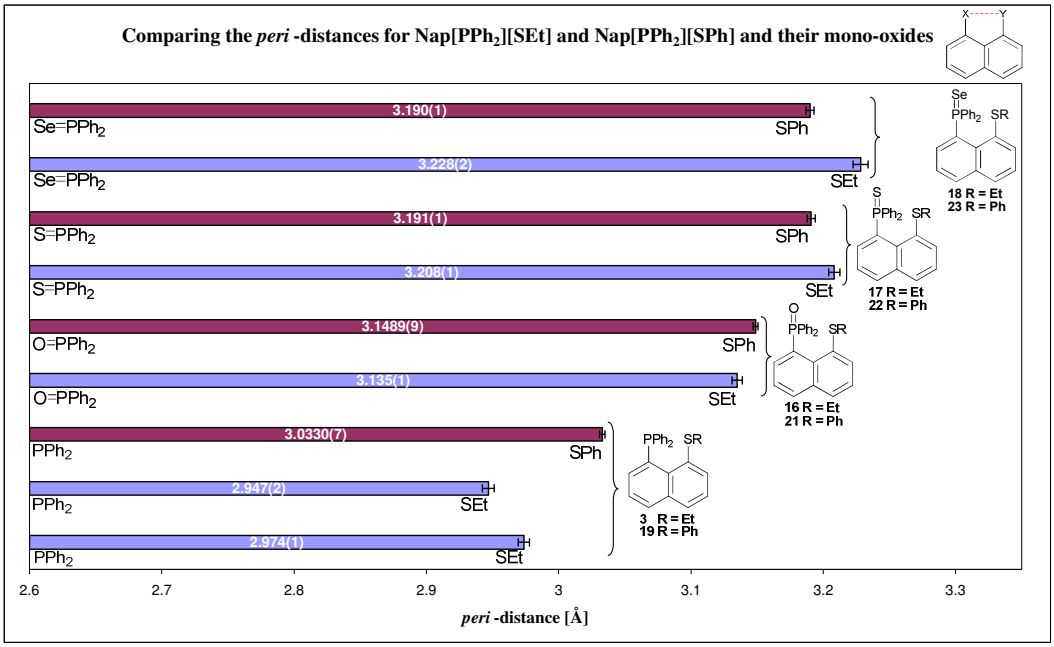

Fig. 3.5 *Comparing the peri-distances for the Nap[PPh$_2$][SR] and Nap[E=PPh$_2$][SR] compounds.*

Intramolecular *peri*-distances (Figure 3.5) are greater in all three compounds compared to **19** with oxide **21** and selenide **22** having lengths comparable to their S(ethyl) counterparts. The *peri*-atoms in selenide **23** lie closer together than expected with the *peri*-distance similar in size to the sulfide compounds [**19** 3.0339(13) Å, **21** 3.1489(9) Å, **22** 3.1909(1) Å, **23** 3.190(1) Å]. The length of the phosphorus chalcogen double bonds in the S(phenyl) oxides are in accord with average literature values and very similar to the values found for the S(ethyl) oxides, increasing in length with the size of the chalcogen atom [P=O 1.492(2) Å **21**, P=S 1.9585(12) Å **22**, P=Se 2.1181(11) Å **23**].[7]

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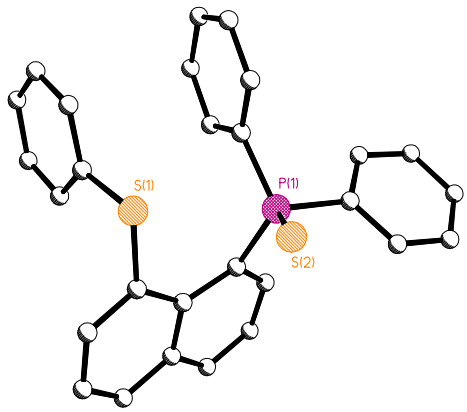

Fig. 3.6 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine sulfide* **22**.

Figure 3.7 shows a comparison of the in-plane distortion occurring in phosphines **3** and **19** and their respective chalcogenides by contrasting the sums of the *peri*-region angles (Table 3.3). The S(ethyl) chalcogenides have all undergone a greater amount of in-plane distortion compared to the free ligand **3**, with sulfide **17** showing a lower than expected value. Conversely the three S(phenyl) chalcogenides all display less distortion than **19** but the degree of distortion increases with increasing size of the chalcogen atom attached to P(1).

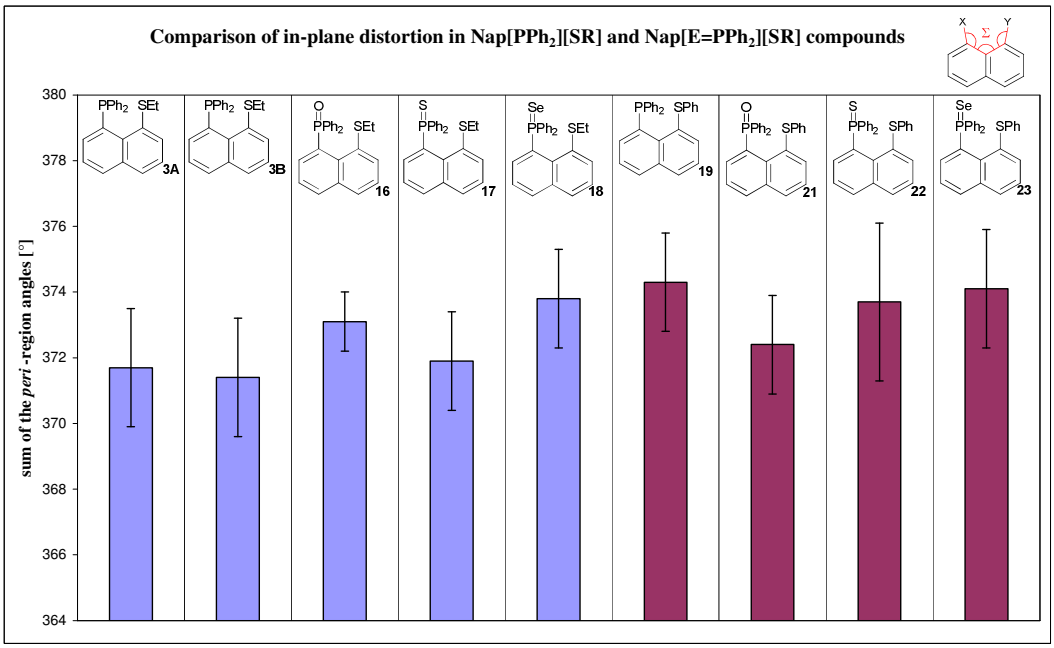

Fig. 3.7 *In-plane distortion in the Nap[PPh$_2$][SR] and Nap[E=PPh$_2$][SR] compounds.*

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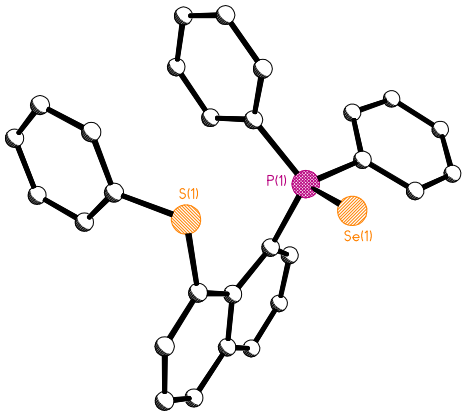

Fig. 3.8 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine selenide* **23**.

Out-of-plane distortion is observed in all three compounds to a similar extent and is considerably greater than in **19** with the *peri*-atoms lying at similar distances from the naphthalene plane (Figure 3.9). The degree of deviation is also similar to the S(ethyl) chalcogenides. In all three cases the P(1) atom lies above the plane and the S(1) atom lies below the naphthalene plane [**P(1)** 0.6312(37) Å **21**, 0.633(4) Å **22**, 0.621(47) Å **23**; **S(1)** -0.582(4) Å **21**, -0.451(4) Å **22**, -0.433(5) Å **23**].

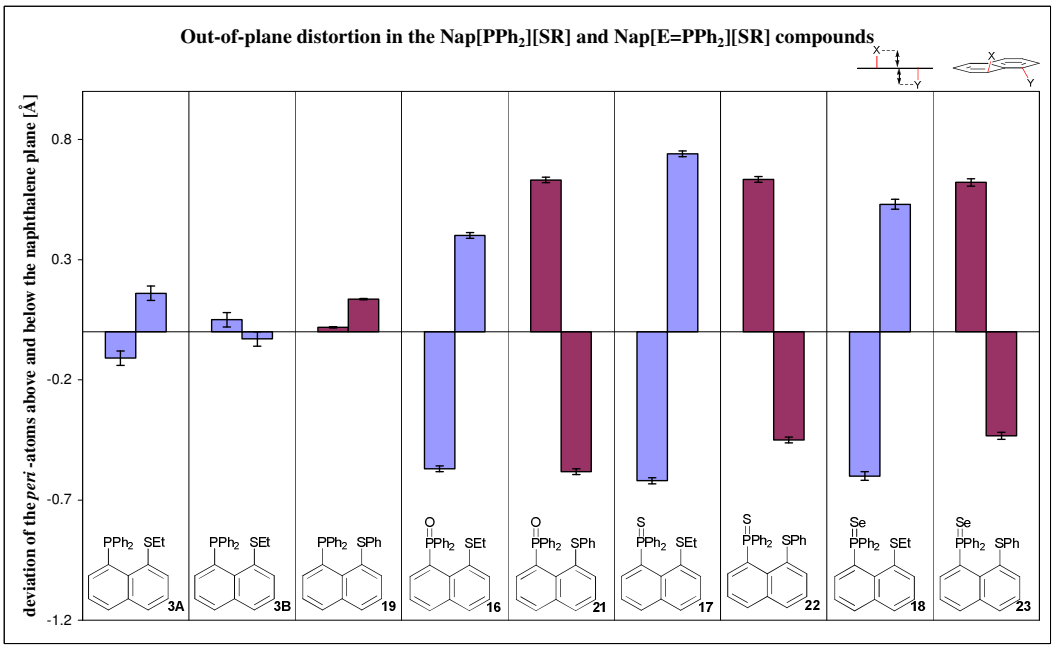

Fig. 3.9 *Out-of-plane distortion in the Nap[PPh$_2$][SR] and Nap[E=PPh$_2$][SR] compounds.*

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The chalcogen atoms bonded to P(1) all lie above the plane of the naphthalene with distances from the plane increasing with the increasing size of the atom [**O(1)** 1.6231(46) Å **21**, **S(2)** 2.1977(43) Å **22**, **Se(1)** 2.3457(51) Å **23**]. Following a similar orientation to the S(ethyl) chalcogenides, the chalcogen atom bonded to P(1) aligns above the *peri*-gap in close proximity to S(1) (Figure 3.10) with the non-bonded S(1)···E distance increasing as the size of the chalcogen atom increases [**S(1)···O(1)** 2.9612(17) Å **21**, **S(1)···S(2)** 3.3142(11) Å **22**, **S(1)···Se(1)** 3.3974(10) Å **23**].

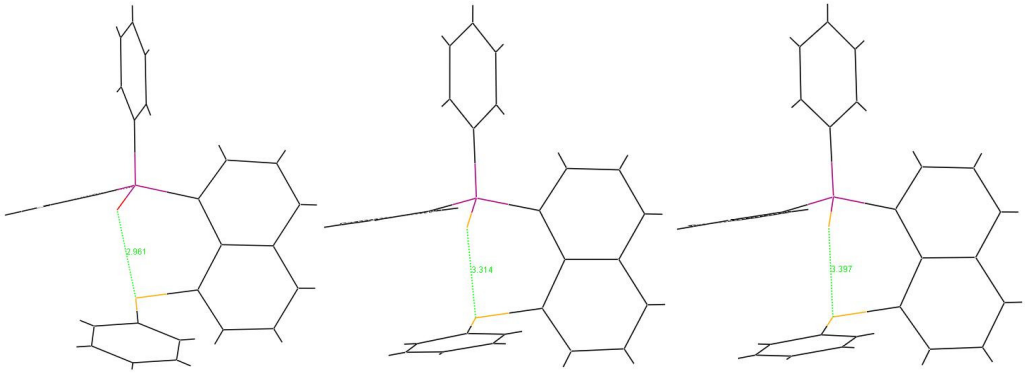

Fig. 3.10 *The crystal structures of the (8-phenylsulfanylnaphth-1-yl)diphenylphosphine chalcogenides* **21**, **22** *and* **23** *showing the non-bonded S(1)···E distance.*

The intramolecular S(1)···E distances are comparable to those found for the S(ethyl) oxides and smaller than the sum of the van der Waals radii for the two interacting atoms [**SO** = 3.32 Å, **SS** 3.60 Å, **SSe** 3.70 Å].[8] This once again suggests the non-bonded distance is close enough for possible weak intramolecular interactions to occur.[9]

The two torsion angles around the C5-C10 central naphthalene bond in the three compounds shows the naphthalene ring systems of the chalcogenides are considerably more buckled than phosphine **19** with an increase in the planarity moving from oxide **21** to selenide **23** (Figure 3.11). The degree of buckling of the naphthalene ring in **21** is greater than in its S(ethyl) counter part **16**. However, sulfide **22** is much more planar than **17**. The two selenide compounds (**18** and **23**) have a similar degree of buckling in the naphthalene ring [**21** 171.7(2)°, 170.3(2)°, **22** 173.7(2)°, 173.4(2)°, **23** 175.4(3)°, 173.1(3)°].

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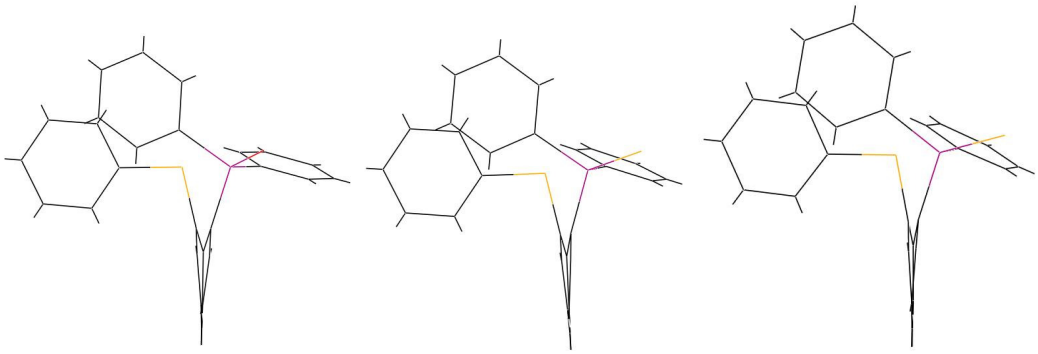

Fig. 3.11 *The crystal structures of the (8-phenylsulfanylnaphth-1-yl)diphenylphosphine chalcogenides* **21**, **22** *and* **23** *showing the buckling of the naphthalene planes.*

Neighbouring aromatic ring systems tend to associate through π-π non-bonded inter- and intramolecular interactions known as π-π stacking.[4] These non-covalent aromatic-aromatic/π-π interactions are important forces similar to hydrogen bonding. They play a key role in self assembly and molecular recognition processes,[10] when extended structures are formed from building blocks with aromatic moieties. Molecular associations utilising π-π stacking have been well documented in organic,[11] biological[12] and polymer chemistry.[13]

Weaker than the hydrogen bonds, calculations give an energy of about 2 kJ mol^{-1} for a typical aromatic-aromatic π-stacking interaction with typical hydrogen bonds between neutral molecules ranging from 15-40 kJ mol^{-1}.[14] Aromatic rings can be arranged and interact either in a stacked arrangement or an edge- or point-to-face arrangement, which is a T-shaped conformation. The stacked arrangement known as face-to-face can be arranged with perfect alignment or slipped packing, known as parallel displacement.[4] The T-shaped conformation is a result of C-H···π interactions.[15] Typical centroid-centroid π-stacking distances range between 3.3-3.8 Å (Figure 3.12).[4]

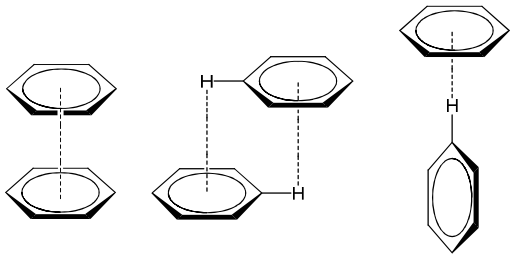

Fig. 3.12 *Schematic illustration of perfect alignment face-to-face, offset or slipped packing (parallel displacement) and point-to-face (T-shaped) arrangements in π-π stacking.*[4]

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The structures of the chalcogenides show distinct differences in the position and orientation of the S(phenyl) moiety when compared to that of **19** and also with one another. The small amount of out-of-plane distortion in **19** aligns the *peri*-atoms with the naphthalene plane so the phenyl rings on S(1) and P(1) point in the same direction and align so they are stacked in a close to perfect alignment. The reason no π-π stacking occurs is the large centroid···centroid distance and the twisting of the phenyl rings and thus no uniform stacked arrangement.

Conversely in the chalcogenides, the repulsive distortion taking place to accommodate the increasingly large chalcogen atoms forces the S(1) and P(1) atoms to lie on opposite sides of the naphthalene plane. Again both phenyl rings point in the same direction. However this time they align in a slipped packing arrangement (Figure 3.13) due to the difference in the position of the two *peri*-atoms. This is extenuated in oxide **21** due to the degree of buckling in the naphthalene backbone. The phenyl rings in oxide **21** do not align parallel; both rings twist in towards one another and the distance between the two centroids is much higher than for known π-π stacking (3.3-3.8 Å)[4] resulting in no observed π-π interaction [**Cg(17-22)···Cg(23-28): 21** 4.397(1) Å].

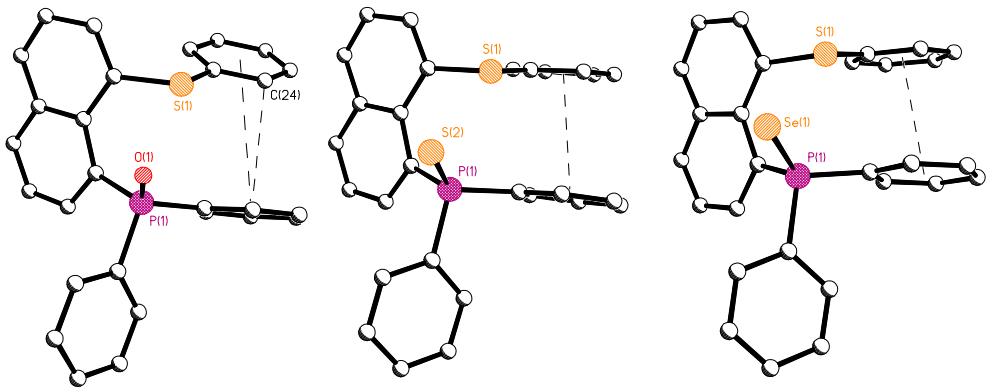

Fig. 3.13 *The crystal structures of the (8-phenylsulfanylnaphth-1-yl)diphenylphosphine chalcogenides* **21**, **22** *and* **23** *showing orientation of phenyl rings and possible π-π stacking.*

The alignment of the rings in **22** and **23** is closer to a parallel alignment and similar to the face-to-face offset arrangement (Figure 3.13).[4] The distances between the two interacting centroids however is slightly longer than the range for typical centroid-centroid π-stacking (3.3-3.8 Å)[4] and so no π-π stacking is envisaged [**Cg(17-22)···Cg(23-28): 22** 3.955(1) Å, **23** 3.995(1) Å].

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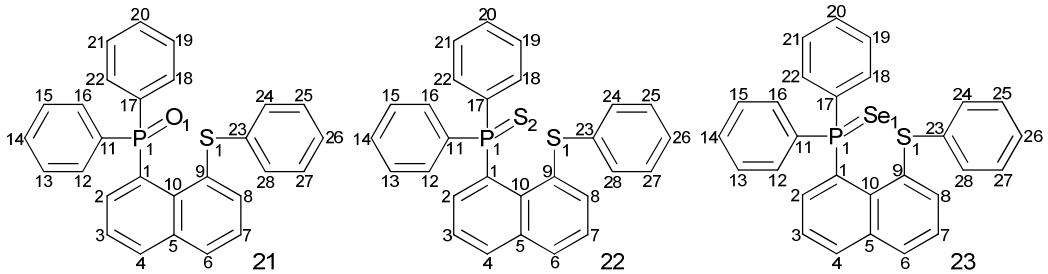
Table 3.3 Bond lengths [Å] and angles [°] for (8-phenylsulfanylnaphth-1-yl)diphenylphosphine chalcogenides **21-23**.



S(1)···P(1)	**3.1489(9)**	**S(1)···P(1)**	**3.191(1)**	**S(1)···P(1)**	**3.190(1)**
P(1)-C(1)	1.835(3)	P(1)-C(1)	1.837(3)	P(1)-C(1)	1.836(4)
S(1)-C(9)	1.777(3)	S(1)-C(9)	1.779(3)	S(1)-C(9)	1.782(4)
P(1)=O(1)	1.492(2)	P(1)=S(2)	1.9585(12)	P(1)=Se(1)	2.1181(11)
S(1)···O(1)	2.9612(17)	S(1)···S(2)	3.3142(11)	S(1)···Se(1)	3.3974(10)
P(1)-C(1)-C(10)	124.6(2)	P(1)-C(1)-C(10)	124.2(2)	P(1)-C(1)-C(10)	125.0(3)
C(1)-C(10)-C(9)	126.2(3)	C(1)-C(10)-C(9)	127.3(3)	C(1)-C(10)-C(9)	126.6(3)
S(1)-C(9)-C(10)	121.6(2)	S(1)-C(9)-C(10)	122.2(2)	S(1)-C(9)-C(10)	122.5(3)
	Σ = 372.4(5)		**Σ = 373.7(5)**		**Σ = 374.1(6)**
C(9)-S(1)-C(23)	102.66(15)	C(9)-S(1)-C(23)	101.96(16)	C(9)-S(1)-C(23)	101.51(19)
O(1)-P(1)-C(1)	114.34(14)	S(2)-P(1)-C(1)	113.09(10)	Se(1)-P(1)-C(1)	112.29(12)
Distance from naphthalene mean plane [Å]					
P(1)	0.6312(37)	P(1)	0.633(4)	P(1)	0.621(5)
S(1)	-0.582(4)	S(1)	-0.451(4)	S(1)	-0.433(5)
O(1)	1.6231(46)	S(2)	2.1977(43)	Se(1)	2.3457(51)
Torsion angle					
C:(6)-(5)-(10)-(1)	171.7(2)	C:(6)-(5)-(10)-(1)	173.7(2)	C:(6)-(5)-(10)-(1)	175.4(3)
C:(4)-(5)-(10)-(9)	170.3(2)	C:(4)-(5)-(10)-(9)	173.4(2)	C:(4)-(5)-(10)-(9)	173.1(3)

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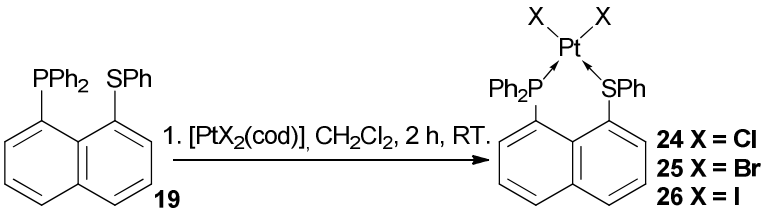
Complexes of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine 19

The theory of hemilability was introduced in the late 1970s[16] and since then there has been great interest in mixed ligands containing different donor atoms[17] and their uses associated with coordination chemistry and homogenous catalysis. The difference in electronic properties of the two donor atoms ensures they have distinctive interactions with the metal center. One site offers a 'soft' donor atom which binds strongly to a 'soft' transition metal atom such as Rh(I), Pt(II) or Ru(II), whilst a 'hard' donor atom is less strongly bound and is thus coordinatively labile. The significance of hemilabile ligands in homogeneous catalysis lies in the susceptibility of the weak donor atom to dissociate from the metal, forming a free coordination site for the incoming substrate, and the increased stability of the catalyst precursor due to the chelating ability of these bidentate ligands.[18]

The ever-increasing demand for novel catalytic systems has focused attention on preparing low-valent transition-metal complexes containing mixed bidentate ligands with a significant contrast between the properties of coordinating groups.[19] Ligands possessing one strong and one weak donor atom such as P,O-[5] and P,N-donor[6] ligands have been extensively applied in catalysis and there is a growing interest with respect to potential applications of P,S-ligands.[22] Additionally, the electronic differences of the P and S donors of the chelate ligand might control reaction selectivities via operation of the *trans* effect. In this context, (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** is a suitable candidate because it is an asymmetric chelating ligand with substantial electronic and steric differences between the two donor atoms. We have prepared a series of platinum(II) dihalides, a series of copper(I) dimers and a ruthenium(I) *p*-cymene complex.

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dihalides 24, 25, 26

Ligand **19** reacts with the well known precursors $[PtX_2(cod)]$ to afford a series of dihaloplatinum(II) complexes, **24**, **25**, **26** (Scheme 3.4).[23]



Scheme 3.4 *The reaction scheme for the preparation of the (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dihalides* **24, 25, 26**.

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19 displaces the cyclooctadiene component, binding via sulfur and phosphorus to form bidentate complexes containing six-membered rings, with platinum adopting a square planar geometry. The phosphorus NMR spectra show single peaks with platinum satellites (Figure 3.14). Chemical shifts move upfield as the electronegativity of the halide decreases from chlorine to iodine and a decrease in the coupling constants of the platinum satellites is observed. [**24 Cl** δ = 1.37 ppm, $^{1}J\{^{31}P\text{-}^{195}Pt\}$ = 3521 Hz, **25 Br** δ = 0.98 ppm, $^{1}J\{^{31}P\text{-}^{195}Pt\}$ = 3408 Hz, **26 I** δ = 0.343 ppm, $^{1}J\{^{31}P\text{-}^{195}Pt\}$ = 3263 Hz]. The values for the chloride coupling constant lie between the values for [Pt(dppe)Cl_2] ($^{1}J\{^{31}P\text{-}^{195}Pt\}$ = 3620 Hz)[24] and [Pt(dppp)Cl_2] ($^{1}J\{^{31}P\text{-}^{195}Pt\}$ = 3406 Hz)[25] and are in the range for similar sulfur/phosphorus platinum dihalide complexes in the literature.[26]

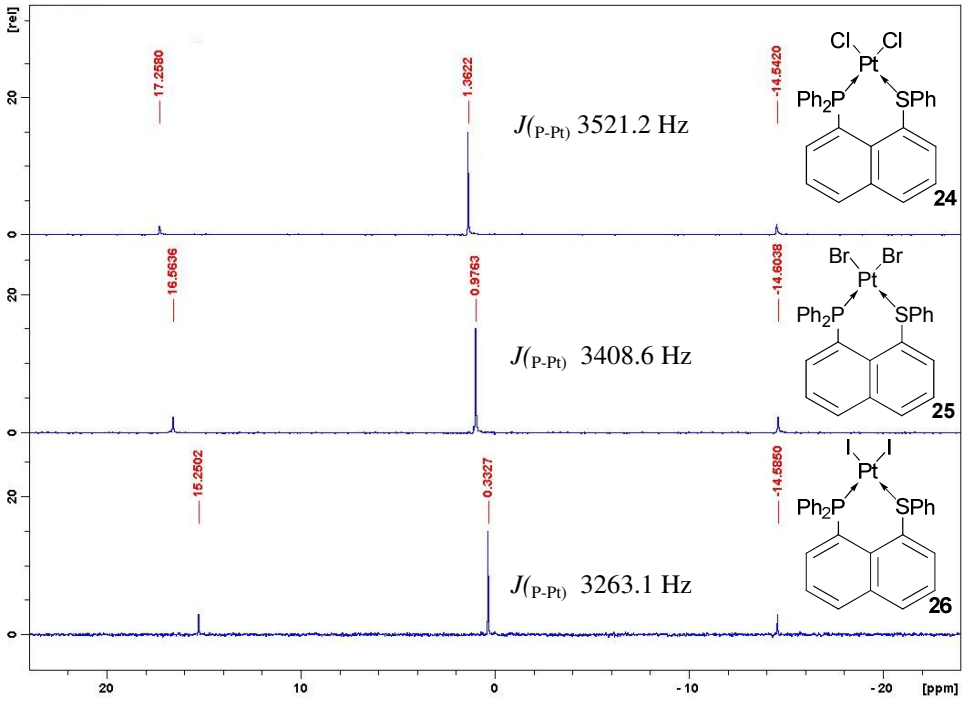

Fig. 3.14 *$^{31}P\text{-}\{^{1}H\}$ NMR spectra for the platinum halide complexes of* **19** *showing the upfield shift with decreasing electronegativity of the halide and decrease in the platinum-phosphorus coupling constant.*

The decrease in the coupling constants from the dichloride complex to the diiodide species is fully consistent with the larger *trans* influence of iodide relative to chloride. The term *trans* influence, also termed the structural *trans* effect,[27] describes the ability of a ligand to selectively weaken the bond between a metal and another ligand trans to itself.[28] In our case the two bonds between the platinum metal and the two *peri*-atoms.

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Although bond weakening is often assumed to be synonymous with bond lengthening, this is not necessarily the case as shown by the P-Pt bond lengths of the three complexes [**24 Cl** 2.22 Å, **25 Br** 2.23 Å, **26 I** 2.23 Å].

Trans influence should not be confused with the 'kinetic trans-effect' (KTE) which is the capacity of a ligand to alter the *lability* of a ligand *trans* to itself. Much of the best evidence for *trans* effects and the majority of work has concentrated on square planar complexes of platinum (II) with many reviews having been written on this subject.[29]

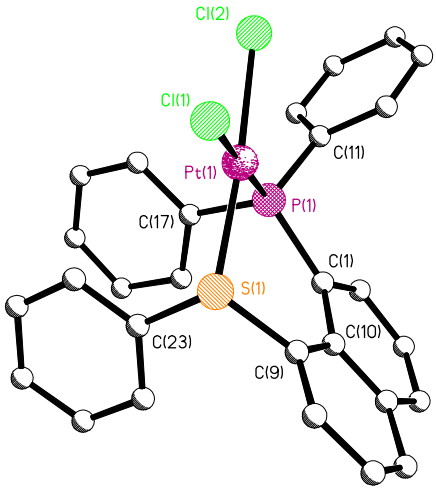

Fig. 3.15 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dichloride* **24**.

The molecular structures of the platinum complexes were determined from single crystal X-ray diffraction studies (Figure 3.15, 3.17 and 3.19). Selected bond lengths and angles are listed in Table 3.4 and further details for the crystal structures can be found in Appendices 13-15. The structures involve monomeric chelated metal complexes with typical square planar metal environments. The unsymmetrical phosphino-sulfanyl ligand **19** acts as a bidentate ligand coordinating via phosphorus(III) and the sulfur atom to form six-membered chelate rings.

The halogen atoms in the three complexes arrange in a *cis*-orientation as required by the structure of the ligand. Square planar geometry around the platinum metal is consistent throughout the series with angles around the platinum metal varying only slightly from 90° (Table 3.4, Figure 3.16).

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The Pt-X(1) bond [**24** 2.38 Å, **25** 2.48 Å, **26** 2.66 Å] *trans* to P(1) is longer in all three species compared to the Pt-X(2) bond [**24** 2.30 Å, **25** 2.42 Å, **26** 2.61 Å] *trans* to S(1), which is consistent with the greater *trans* influence of phosphorus compared to sulfur.[29] With increasing size of the halide the Pt-X bond lengths increase, in the correct range for similar compounds in the literature.[26]

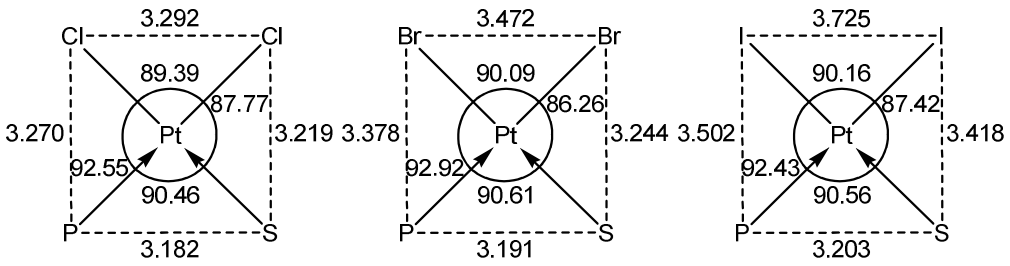

Fig. 3.16 *The angles [°] and distances [Å] associated with the square planar geometry of the platinum metal in the dihalide complexes* **24**, **25** *and* **26**.

Non-bonded intramolecular halide-halide distances increase from the dichloride complex to the diiodide species, accommodating the larger atoms. The remaining non-bonded intramolecular distances around the platinum core (Figure 3.16) subsequently increase to maintain the square planar geometry.

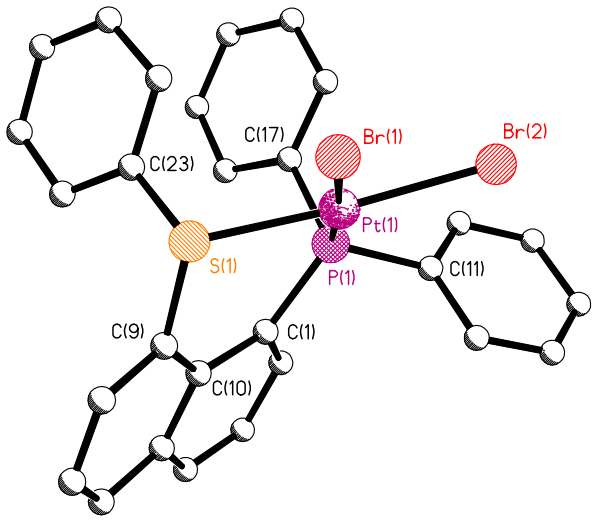

Fig. 3.17 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dibromide* **25**

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The non-bonded *peri*-distance between P(1) and S(1) increases across the series and is much larger than compared to the uncoordinated phosphine [**19** 3.0339(13) Å, **24** 3.182(6) Å, **25** 3.191(3) Å, **26** 3.203(2) Å] (Figure 3.18). These values for the *peri*-distances also give an indication of the greater degree of distortion in the naphthalene structures of the metal complexes compared to the free ligand. The presence of the metal species and the geometry it imposes together with the increasing size of the halides causes enhanced steric interactions and so extra molecular distortion has to occur to relieve this strain.

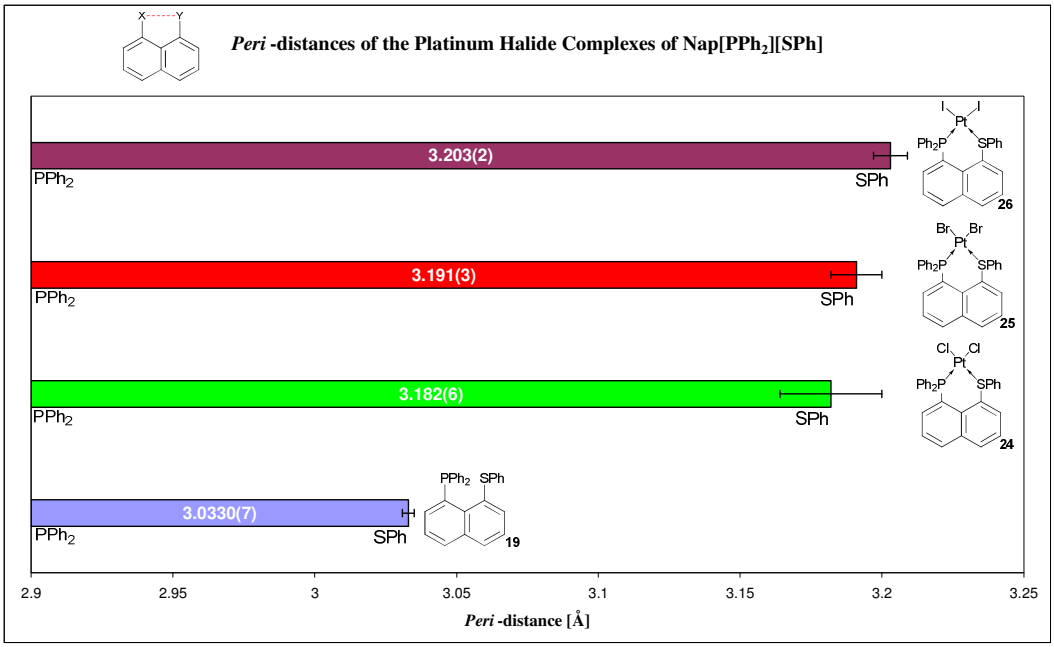

Fig. 3.18 *Comparing the peri-distances in the platinum halide complexes* **24**, **25** *and* **26**.

The widening of the bay in the platinum species depicted by the sum of the angles [**24** 378.1(32)°, **25** 378.3(19)°, **26** 379.9(10)°] shows a greater degree of in-plane distortion is observed in the metal complexes compared to the uncoordinated phosphine **19** [374.3(3)°].

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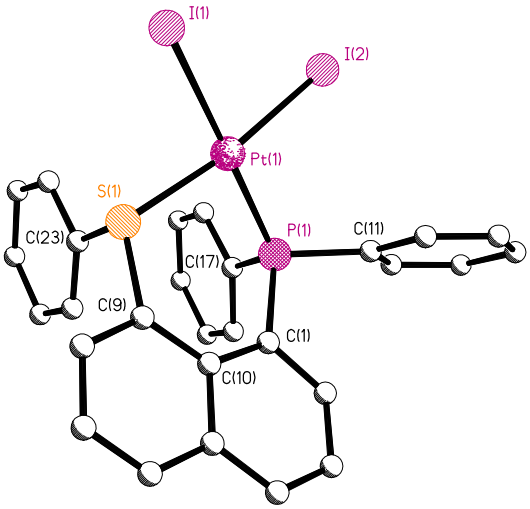

Fig. 3.19 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum diiodide* **26**.

Out-of-plane distortion is similar in the dichloride and dibromide complexes and much greater than for the diiodide complex which shows very little deviation of its *peri*-atoms from the naphthalene plane (Figure 3.20).

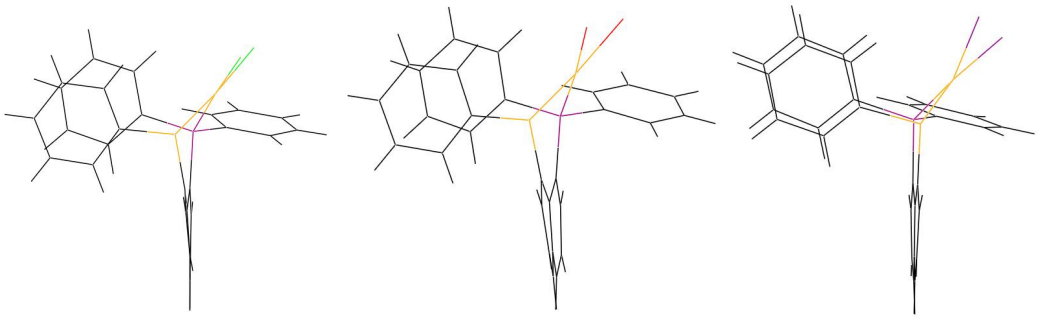

Fig. 3.20 *The crystal structures of the (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dihalides showing the degree of out-of-plane distortion and naphthalene ring planarity*.

The two torsion angles associated with the central naphthalene C5-C10 bond indicates a greater buckling of the naphthalene ring in the dibromide complex compared to the less buckled dichloride shown by slightly larger torsion angles. The angles of the diiodide deviate only slightly from ± 180° resulting in a very planar naphthalene backbone (Table 3.4, Figure 3.20).

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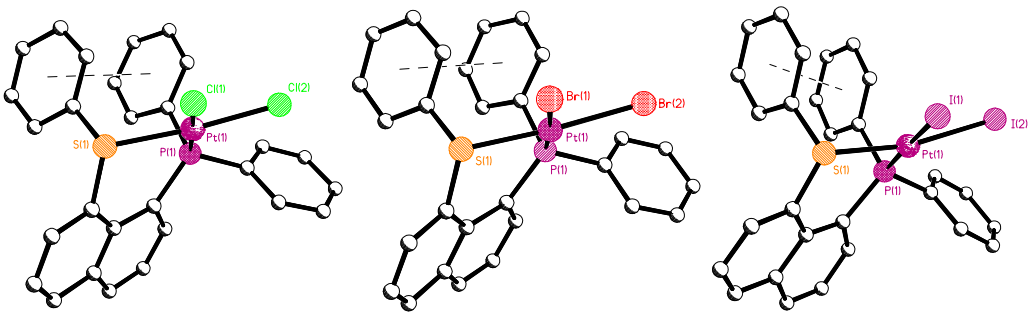

Fig. 3.21 *Crystal structures of the platinum halide complexes* **24**, **25** *and* **26** *illustrating the centroid-centroid distance resulting in π-π stacking.*

The distinct square planar geometry around the central platinum atom together with the affects of steric hindrance from the halide atoms influences the location and arrangement of the aromatic phenyl groups in the three platinum complexes. One phenyl group attached to P(1) and the π-system attached to S(1) lie in close proximity in an offset or slipped packing arrangement of π-π stacking (Figure 3.21).[4] The distance between the two interacting centroids increases with the increasing size of the halogen atoms but in all cases this distance is within the known range for typical centroid-centroid π-stacking distances (3.3-3.8 Å)[4] [**Cg(17-22)···Cg(23-28): 24** 3.536(1) Å, **25** 3.574(1) Å, **26** 3.598(1) Å].

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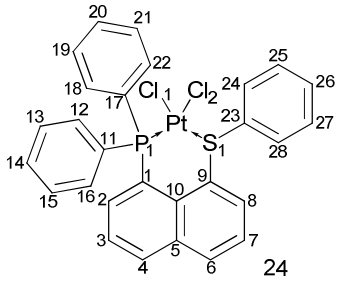
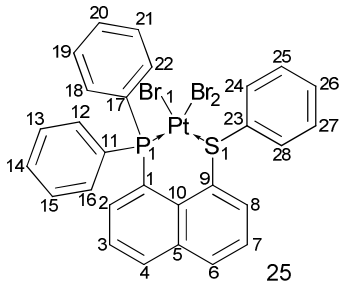
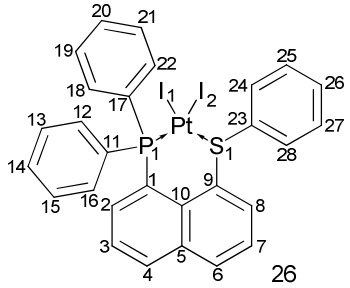
Table 3.4 Selected bond lengths [Å] and angles [°] for (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dihalides **24**-**26**

 24		 25		 26	
S(1)···P(1)	**3.182(6)**	**S(1)···P(1)**	**3.191(3)**	**S(1)···P(1)**	**3.203(2)**
P(1)-C(1)	1.80(2)	P(1)-C(1)	1.807(13)	P(1)-C(1)	1.837(6)
S(1)-C(9)	1.76(2)	S(1)-C(9)	1.763(13)	S(1)-C(9)	1.770(7)
P(1)-Pt(1)	2.221(4)	P(1)-Pt(1)	2.232(3)	P(1)-Pt(1)	2.2326(15)
S(1)-Pt(1)	2.261(4)	S(1)-Pt(1)	2.256(3)	S(1)-Pt(1)	2.2752(16)
Pt(1)-Cl(1)	2.376(4)	Pt(1)-Br(1)	2.4817(14)	Pt(1)-I(1)	2.6553(4)
Pt(1)-Cl(2)	2.300(5)	Pt(1)-Br(2)	2.4244(15)	Pt(1)-I(2)	2.6052(4)
P(1)-C(1)-C(10)	128.7(14)	P(1)-C(1)-C(10)	126.9(8)	P(1)-C(1)-C(10)	125.9(4)
C(1)-C(10)-C(9)	125.0(18)	C(1)-C(10)-C(9)	125.6(11)	C(1)-C(10)-C(9)	127.8(6)
S(1)-C(9)-C(10)	124.4(14)	S(1)-C(9)-C(10)	125.8(8)	S(1)-C(9)-C(10)	126.2(4)
	Σ = 378.1(32)		**Σ = 378.3(19)**		**Σ = 379.9(10)**
P(1)-Pt(1)-S(1)	90.46(17)	P(1)-Pt(1)-S(1)	90.61(11)	P(1)-Pt(1)-S(1)	90.56(5)
P(1)-Pt(1)-Cl(2)	92.55(17)	P(1)-Pt(1)-I(2)	92.92(8)	P(1)-Pt(1)-I(2)	92.43(4)
Cl(1)-Pt(1)-Cl(2)	89.39(17)	I(1)-Pt(1)-I(2)	90.09(4)	I(1)-Pt(1)-I(2)	90.163(15)
S(1)-Pt(1)-Cl(1)	87.77(16)	S(1)-Pt(1)-I(1)	86.26(8)	S(1)-Pt(1)-I(1)	87.42(4)
Distance from naphthalene mean plane					
P(1)	0.212(23)	P(1)	0.303(14)	P(1)	-0.003(8)
S(1)	-0.294(22)	S(1)	-0.299(13)	S(1)	-0.074(9)
Torsion angle					
C:(6)-(5)-(10)-(1)	175.9(16)	C:(6)-(5)-(10)-(1)	170.8(10)	C:(6)-(5)-(10)-(1)	-178.2(7)
C:(4)-(5)-(10)-(9)	176.9(16)	C:(4)-(5)-(10)-(9)	174.7(10)	C:(4)-(5)-(10)-(9)	-177.2(7)

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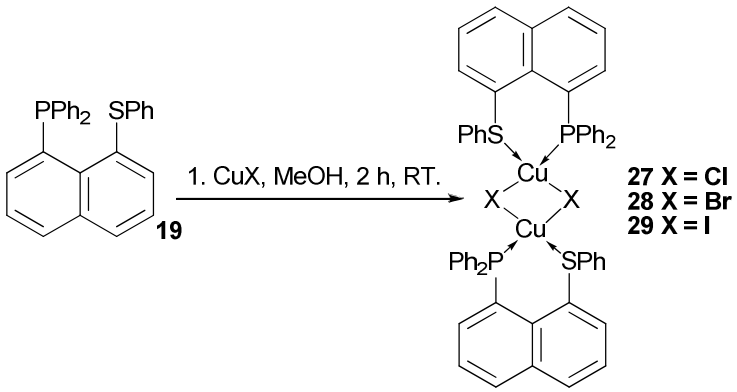
(8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper halide dimers 27, 28, 29

Copper(I) complexes are of special interest in bioinorganic chemistry due to the involvement of Cu(I) in biological redox reactions.[30] The inclination for Cu(I) atoms to adopt a pseudo four-coordinate geometry as a result of dimer formation is of particular importance which is enhanced by the additional possibility of studying metal-metal interactions between the two d^{10} metal centres in these compounds.[31] Subsequently a vast range of dimeric adducts have been studied and structurally characterized.[32]

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** reacts with the copper(I) halides (CuCl, CuBr, CuI) in methanol to afford a series of novel copper(I) dimers, **27**, **28**, **29** (Scheme 3.5).[33]



Scheme 3.5 *The reaction scheme for the preparation of the (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper halide dimers* **27, 28, 29**.

In a similar fashion to the series of platinum complexes (**24**-**26**), **19** binds via phosphorus and sulfur forming a series of bidentate metal complexes containing six-membered rings with copper adopting a tetrahedral-like geometry. The ^{31}P NMR spectra show single peaks with similar chemical shifts for the three compounds with values in the range for similar sulfur/phosphorus copper dihalide complexes in the literature [**27 Cl** δ = 27.78 ppm, **28 Br** δ = 27.73 ppm, **29 I** δ =28.68 ppm].[34]

The molecular structures of the copper dimers were determined from single crystal X-ray diffraction studies (Figure 3.22, 3.24, 3.31). Selected bond lengths and angles are listed in Table 3.5 and further details for the crystal structures can be found in Appendices 16-18.

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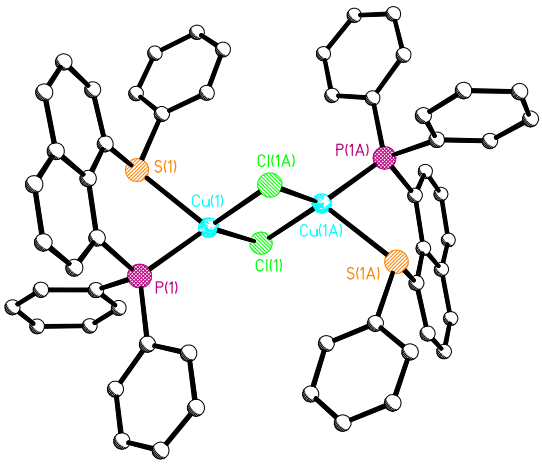

Fig. 3.22 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper chloride dimer* **27**.

The copper atom is coordinated by one halogen atom and by the bidentate ligand **19** via sulfur and phosphorus forming a three coordinated unit containing a six-membered ring [CuX{Nap(PPh_2)(SPh)}]. Two of these units dimerize via halide atoms to form a halide-bridged dimer with ligand **19** terminally bonded [$Cu_2(\mu\text{-}X)_2$\{Nap(PPh_2)(SPh)\}$_2$]. The two copper atoms joined by the two halide bridges form a strictly planar Cu_2X_2 rhombus core in the form of a parallelogram containing two unequal Cu-X bond distances [**27** 2.37 Å, 2.40 Å, **28** 2.43 Å, 2.46 Å, **29** 2.58 Å, 2.61 Å] (Figure 3.23). With increasing size of the halide the Cu-X bond lengths increase, in the correct range for similar bridged compounds in the literature (2.33-2.82 Å).[35]

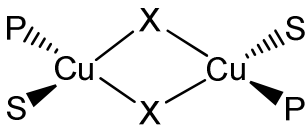

Fig. 3.23 *Two copper atoms are joined by two halide bridges to form a strictly planar Cu_2X_2 rhombus core, in the form of a parallelogram, containing two unequal Cu-X bond distances.*

The unequal Cu-X bond distances gives these binuclear molecules a centre of symmetry and results in both of the copper(I) atoms having identically distorted tetrahedral environments. Copper(I) has a stereochemical preference for tetrahedral coordination with ideal angles around the copper of 109.5°. The copper dimers (**27**-**29**) show a greater distorted tetrahedral geometry compared with other similar compounds containing the Cu_2X_2 rhombus core (Figure 3.23).[35]

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Angles around the copper are similar throughout the range and deviate further from the ideal tetrahedral angle of 109.5° [**27** 81.6-128.4°, **28** 82.9-126.6°, **29** 81.5-125.0°] than similar compounds (95.9-124.9°).[35]

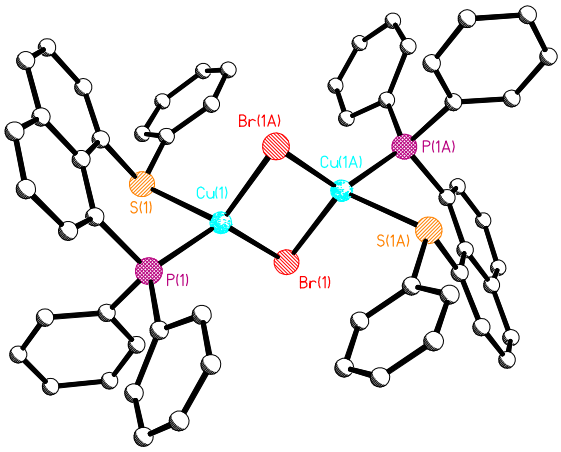

Fig. 3.24 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper bromide dimer* **28**

P-Cu-S bond angles are comparable in the three dimers [**27** 81.55 Å, **28** 82.90 Å, **29** 81.52 Å] but are considerably more acute than similar compounds containing no rigid backbone (109.7-119.8 Å). This suggests the naphthalene backbone plays a role in the geometry around the copper atom and keeps the phosphorus and sulfur atoms from moving further apart and attaining a more ideal tetrahedral. This is seen in similar compounds in the literature containing fixed atoms around the copper.[36] Cu-P bond lengths are as expected [**27** 2.20 Å, **28** 2.22 Å, **29** 2.25 Å] and in the range for similar compounds (2.21-2.26 Å).[35] Cu-S bond lengths although comparable with one another [**27** 2.48 Å, **28** 2.44 Å, **29** 2.44 Å] are longer than in similar compounds from the literature (2.27-2.34 Å) (Figure 3.25).[35]

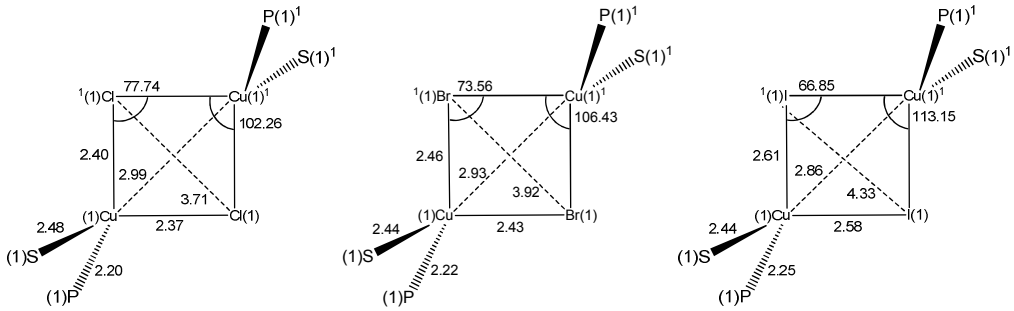

Fig. 3.25 *A schematic illustration of the distances [Å] and angles [°] around the central diamond shaped core of the copper halide dimers.*

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The increase in steric bulk from chloride to iodide causes the halide atoms to move further apart increasing the non-bonded intramolecular X···X distance across the series [**27** 3.710(2) Å, **28** 3.9193(14) Å, **29** 4.3287(8) Å] (Figure 3.25). As a result the two copper atoms are forced closer together with Cu···Cu distances approaching the sum of the van der Waals radii of two interacting copper atoms (2.80 Å)[8] [**27** 2.990(1) Å, **28** 2.9296(14) Å, **29** 2.8568(11) Å]. This increases the X(1)-Cu(1)-X(1)[1] angle and decreases the Cu(1)-X(1)-Cu(1)[1] angle (Table 3.5, Figure 3.25).

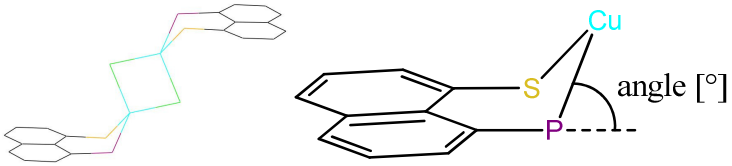

Fig. 3.26 *The positioning of the copper atom in relation to the naphthalene plane.*

The conformation of the central six-membered ring of the copper dimers can be described as an open envelope (Figure 3.26). P(1), S(1), C(1), C(10) and C(9) are approximately co-planar with the copper atom sitting in the *peri*-gap above the level of this plane. The distance of the copper from the P(1)-S(1) plane is comparable in all three compounds as shown by the angle between the Cu(1)-P(1)-S(1) plane and the P(1)-C(1)-C(10)-C(9)-S(1) plane [**27** 60.28°, **28** 59.72°, **29** 59.60°] (Figure 3.26).

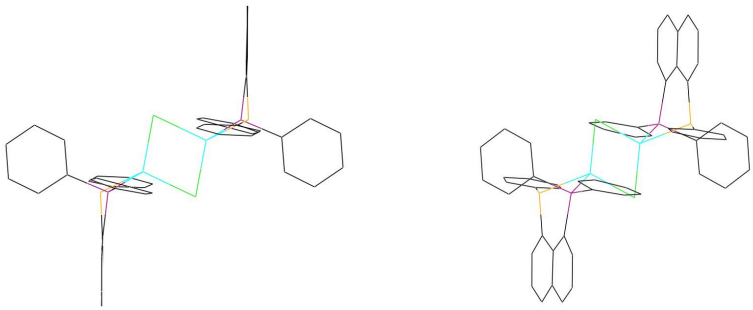

Fig. 3.27 *The crystal structure of* **27** *showing alignment and orientation of the naphthalene rings.*

The angle of the copper atom above the naphthalene plane determines the orientation of the two molecules of ligand **19**; one flipped horizontally and vertically compared to the other. The naphthalene ring systems align parallel with one pointing up and the other pointing downwards (Figure 3.27). The steric bulk of the inner parallelogram core forces the phenyl rings to point away from the centre of the complex avoiding steric interactions with the large copper and halide atoms and no π-π interactions are observed.

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The planar parallelogram comprising two copper atoms and the two halide bridges approaches a perpendicular arrangement with the sulfur/phosphorus plane (Figure 3.28). The copper-halide core is found to be most perpendicular in the chloride complex with angles between the plane and the core decreasing to the iodine complex [**27** 85.16°, **28** 84.41°, **29** 83.44°].

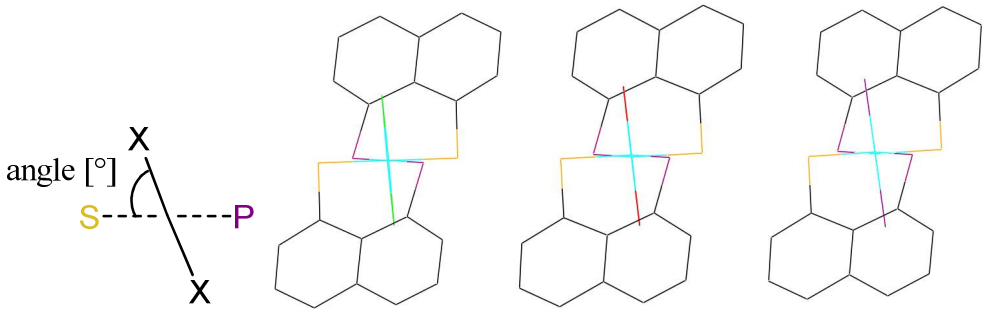

Fig. 3.28 *The crystal structures of the copper halide dimers showing the orientation of the copper-halide parallelogram with the sulfur-phosphorus plane.*

The geometry of the dimers and the unequal bond lengths between the copper atom and P(1) and S(1) forces the two copper atoms of the parallelogram to lie at an angle compared to the two parallel naphthalene planes. The greatest degree of perpendicular alignment with the naphthalene backbone is found in the iodine dimer (Figure 3.29) as shown by the angle between the naphthalene plane and the direction of the planar copper-halide core [**27** 77.06°, **28** 79.02°, **29** 79.81°].

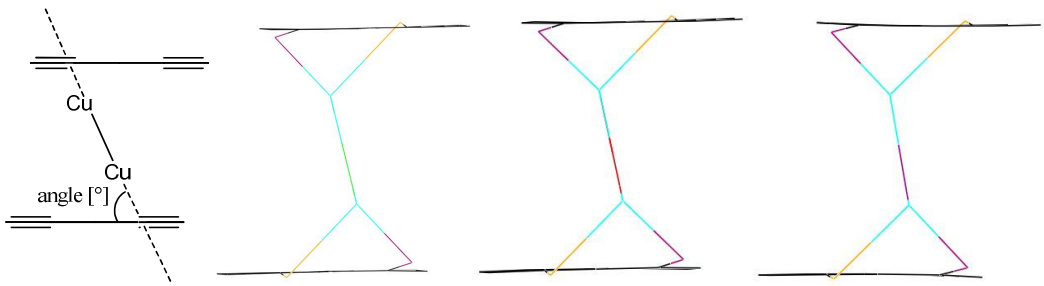

Fig. 3.29 *An illustration showing the orientation of the Cu_2X_2 parallelogram with the naphthalene planes.*

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Unlike the square planar arrangement and influences of platinum on the geometry of the naphthalene in the platinum dihalide complexes, the presence of the copper-halide core in the dimers bares no influence on distortion of the naphthalene ring system and if anything reduces the distortion.

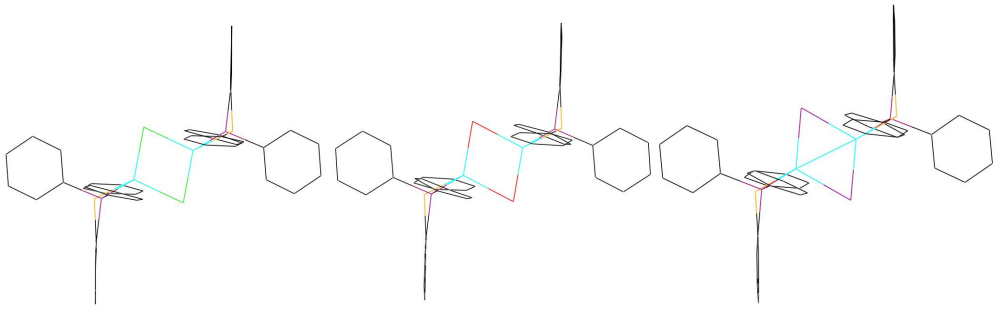

Fig. 3.30 *The crystal structures of the copper halide dimers showing the out-of-plane distortion of the peri-atoms and the planarity in the naphthalene rings.*

Peri-distances in the three dimers are comparable and very similar to the free ligand [**19** 3.0330(7) Å, **27** 3.081(2) Å, **28** 3.089(3) Å, **29** 3.067(2) Å] and in-plane distortion is equivalent with the *peri*-region angles of similar magnitudes. The position of the *peri*-atoms from the mean naphthalene plane are of a similar degree and torsion angles approaching ±180° for the dimers and greater than those in **19** show the copper compounds have more planarity in the naphthalene backbone (Figure 3.30).

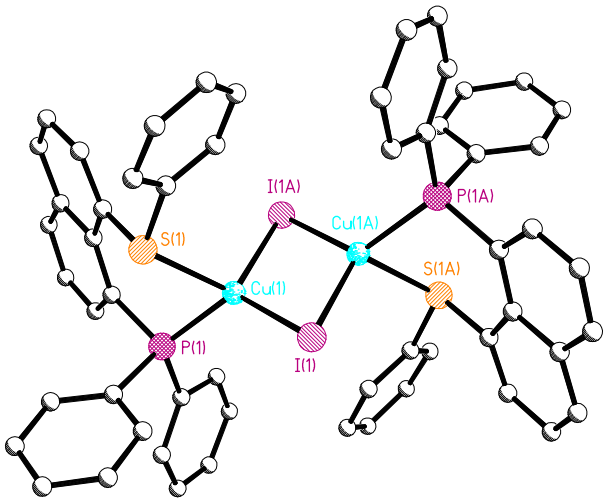

Fig. 3.31 *The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper iodide dimer* **29**.

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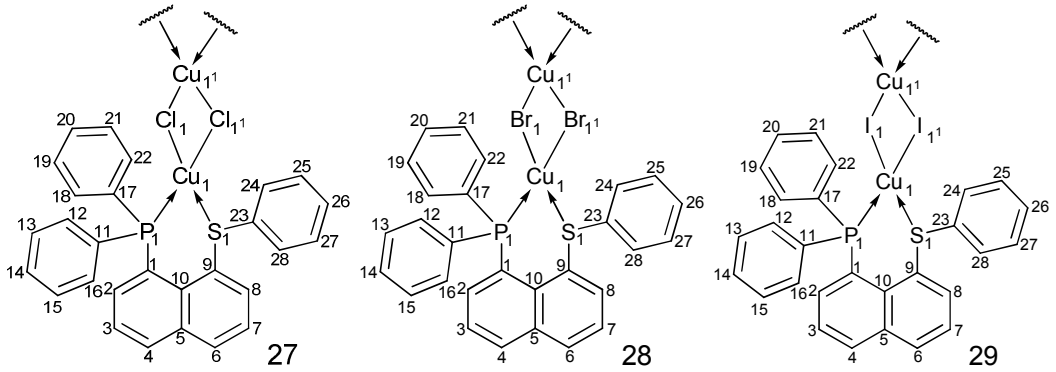
Table 3.5 Selected bond lengths [Å] and angles [°] for (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper halide dimers **27**, **28** and **29**



S(1)-P(1)	**3.081(2)**	**S(1)-P(1)**	**3.089(3)**	**S(1)-P(1)**	**3.067(2)**
P(1)-C(1)	1.833(8)	P(1)-C(1)	1.837(8)	P(1)-C(1)	1.847(8)
S(1)-C(9)	1.806(8)	S(1)-C(9)	1.815(8)	S(1)-C(9)	1.805(8)
Cu(1)-Cu(1)^1	2.990(1)	Cu(1)-Cu(1)^1	2.9296(14)	Cu(1)-Cu(1)^1	2.8568(11)
Cl(1)-Cl(1)^1	3.710(2)	Br(1)-Br(1)^1	3.9193(14)	I(1)-I(1)^1	4.3287(8)
P(1)-Cu(1)	2.201(2)	P(1)-Cu(1)	2.217(2)	P(1)-Cu(1)	2.248(2)
S(1)-Cu(1)	2.475(2)	S(1)-Cu(1)	2.443(2)	S(1)-Cu(1)	2.444(2)
Cu(1)-Cl(1)	2.3706(18)	Cu(1)-Br(1)	2.4303(14)	Cu(1)-I(1)	2.5809(11)
Cu(1)-Cl(1)^1	2.395(2)	Cu(1)-Br(1)^1	2.4634(16)	Cu(1)-I(1)^1	2.6055(12)
P(1)-C(1)-C(10)	124.4(5)	P(1)-C(1)-C(10)	124.1(6)	P(1)-C(1)-C(10)	124.1(6)
C(1)-C(10)-C(9)	127.7(5)	C(1)-C(10)-C(9)	129.0(7)	C(1)-C(10)-C(9)	129.1(7)
S(1)-C(9)-C(10)	122.5(5)	S(1)-C(9)-C(10)	121.4(5)	S(1)-C(9)-C(10)	121.1(5)
	Σ = 374.6(10)		**Σ = 374.5(13)**		**Σ = 374.3(13)**
P(1)-Cu(1)-S(1)	81.55(6)	P(1)-Cu(1)-S(1)	82.90(7)	P(1)-Cu(1)-S(1)	81.52(7)
P(1)-Cu(1)-Cl(1)^1	120.50(8)	P(1)-Cu(1)-Cl(1)^1	116.53(9)	P(1)-Cu(1)-Cl(1)^1	113.00(7)
Cl(1)-Cu(1)-Cl(1)^1	102.26(6)	Cl(1)-Cu(1)-Cl(1)^1	106.43(4)	Cl(1)-Cu(1)-Cl(1)^1	113.15(3)
S(1)-Cu(1)-Cl(1)	108.23(7)	S(1)-Cu(1)-Cl(1)	108.46(7)	S(1)-Cu(1)-Cl(1)	106.70(6)
Distance from naphthalene mean plane					
P(1)	-0.229(8)	P(1)	-0.1958(99)	P(1)	0.1856(92)
S(1)	0.071(8)	S(1)	0.1115(98)	S(1)	-0.090(9)
Torsion angle					
C:(6)-(5)-(10)-(1)	-179.4(11)	C:(6)-(5)-(10)-(1)	179.4(8)	C:(6)-(5)-(10)-(1)	179.0(7)
C:(4)-(5)-(10)-(9)	179.8(6)	C:(4)-(5)-(10)-(9)	179.7(7)	C:(4)-(5)-(10)-(9)	-179.0(7)

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(8-phenylsulfanylnaphth-1-yl)diphenylphosphinechlororuthenium(II)chloride 30

Organometallic complexes containing ruthenium species have been shown to be active as catalysts in a number of important industrial reactions, for example olefin metathesis, hydrogenation and hydrogen generation.[37] Ruthenium arene chemistry was first introduced with the discovery of $[Ru(\eta^6\text{-arene})_2]^{2+}$ complexes in 1957[38] and these compounds have recently been established as mono- and dinuclear tumor inhibitors (Figure 3.32)[39] and show promise as anticancer agents.[40]

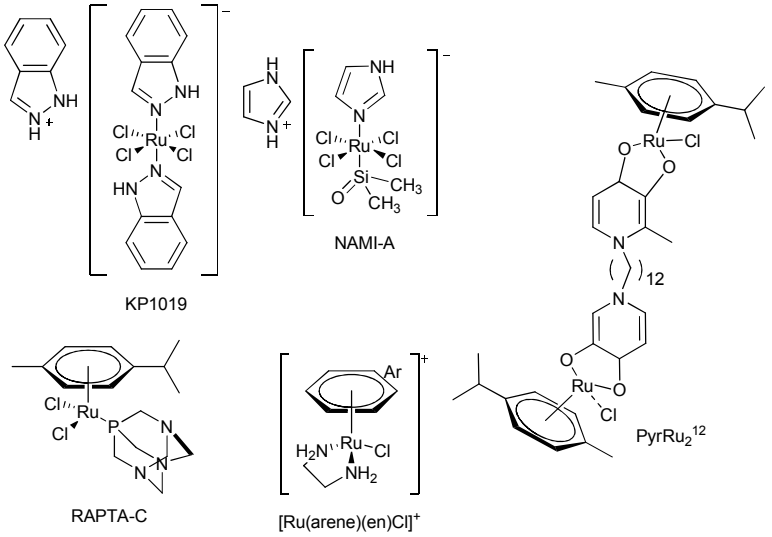
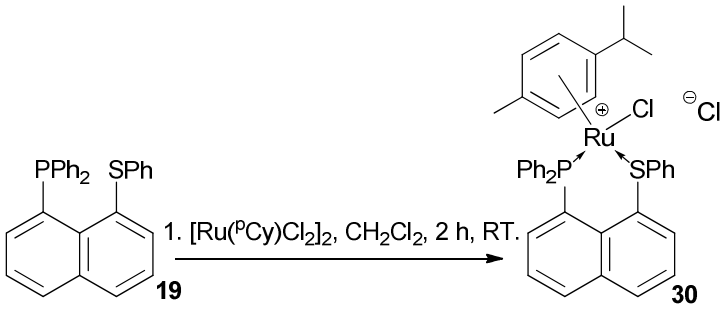


Fig. 3.32 *The structures of ruthenium compounds which have been shown to exhibit anticancer potential.*[39]

Treatment of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** with $[Ru(\eta^6\text{-}MeC_6H_4{}^iPr)Cl_2]_2$ dimer in dichloromethane led to the formation of the air-stable mononuclear ruthenium(II) complex **30** (Scheme 3.6).



Scheme 3.6 *The reaction scheme for the preparation of* $[Nap(PPh_2)(SPh)Ru(Cl)(\eta^6\text{-}MeC_6H_4{}^iPr)]^+Cl^-$ **30**.

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The most common oxidation states for ruthenium are +2 and +3 and although oxidation states lower than +2 are known they are rare and formed mainly with carbonyls, phosphines and derivatives thereof.[41]

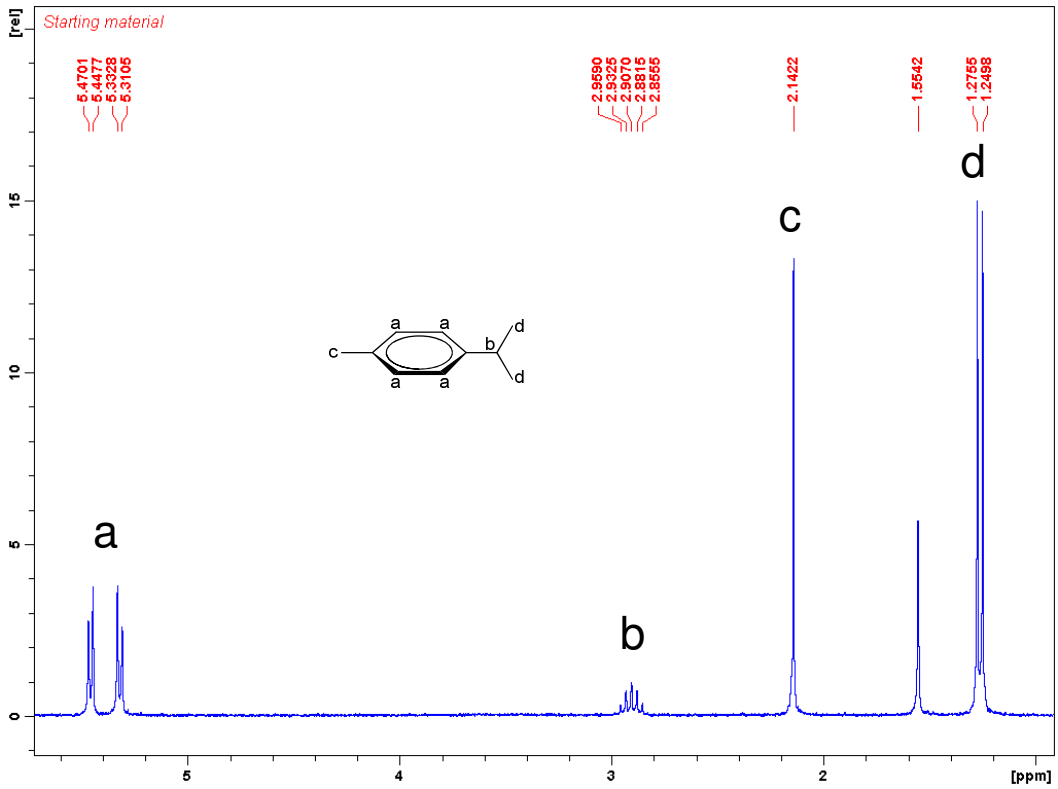

Fig. 3.33 *The ^{1}H NMR spectrum of the $[Ru(\eta^{6}\text{-}C_{10}H_{14})Cl_2]_2$ dimer.*

The ^{1}H NMR spectrum shows a loss of the two-fold symmetry of the *p*-cymene ligand, similar to other reported *p*-cymene complexes.[42] The stereogenic ruthenium atom is due to the coordination of four different ligand atoms which results in the methyl protons of the isopropyl group and the aromatic protons of the *p*-cymene ligand being diastereotopic. This gives rise to the unusual pattern observed in the ^{1}H NMR spectrum (Figure 3.33).[43] The four aromatic hydrogen atoms of the *p*-cymene ligand appear as four sets of doublets at ca. δ = 5.5-4.9 ppm instead of two doublets as in the starting material (a Figure 3.33). The two isopropyl methyls of the *p*-cymene are also inequivalent, appearing as two doublets at δ = 0.93 and 0.69 ppm instead of one doublet as in the starting complex (d Figure 3.33). The ^{31}P NMR spectrum shows a single peak at δ = 37.99 ppm in accordance with compounds of this type.[44]

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The molecular structure of **30** is shown in Figure 3.34, and selected bond lengths and bond angles are listed in Table 3.6. The ruthenium(II) adopts a classical piano-stool geometry with the metal centre being coordinated by the aromatic *p*-cymene ligand, a terminal chloro ligand and the chelating phosphorus/sulfur substituted **19**. The chlorine atom and the *peri*-atoms of **19** act as the legs of the piano stool and point away from the *p*-cymene ligand to avoid steric overcrowding. The six-membered ring formed by the ruthenium and the bidentate **19** adopts an envelope like structure with the ruthenium atom lying above the plane of the atoms in the naphthalene bay region. A chloride counteranion is present in the structure counter balancing the charge of the ruthenium cation complex.

The degree of distortion in the naphthalene geometry is similar to the free ligand. The distance between the *peri*-atoms [3.013(3) Å] is similar to the distance found in **19** [3.0339(16) Å] and the sum of the bay region angles [373.9(16)°] shows similar in-plane distortion has taken place. Out-of-plane distortion is slightly greater in the complex and torsion angles show a greater degree of buckling has taken place in the naphthalene of the ruthenium species. Further information for the crystal structure can be found in Appendix 19.

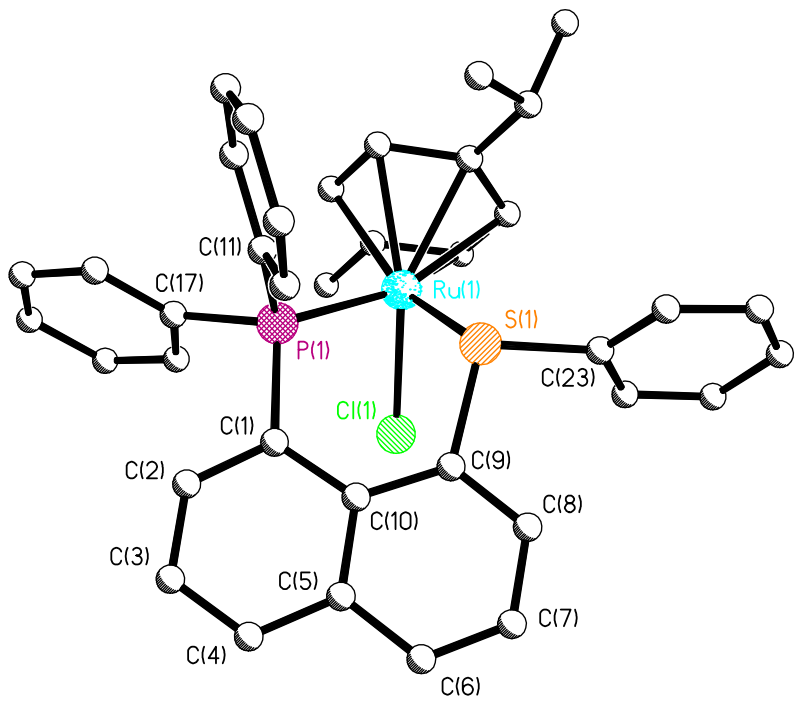

Fig. 3.34 *The crystal structure of [Nap(PPh$_2$)(SPh)Ru(Cl)(η^6-MeC$_6$H$_4$^{i}Pr)]$^+$Cl$^-$* **30**,*(counteranion Cl$^-$ omitted for clarity).*

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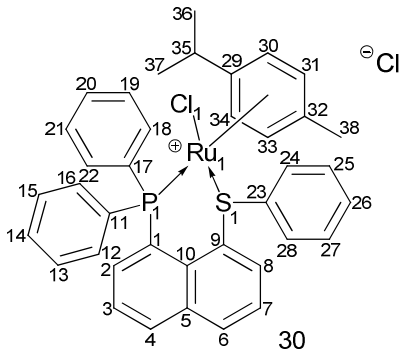
Table 3.6 Selected bond lengths [Å] and angles [°] for (8-phenylsulfanylnaphth-1-yl)diphenylphosphinechlororuthenium(II)chloride **30**.



S(1)-P(1)	**3.013(3)**	P(1)-C(1)-C(10)	124.9(7)
P(1)-C(1)	1.816(10)	C(1)-C(10)-C(9)	127.7(9)
S(1)-C(9)	1.829(10)	S(1)-C(9)-C(10)	121.3(7)
			Σ = 373.9(16)
P(1)-Ru(1)	2.319(2)	P(1)-Ru(1)-S(1)	80.22(8)
S(1)-Ru(1)	2.356(2)	P(1)-Ru(1)-Cl(1)	89.03(9)
Ru(1)-Cl(1)	2.396(2)	S(1)-Ru(1)-Cl(1)	89.61(8)
Ru(1)-centroid	1.744(1)		

Distance from naphthalene mean plane	
P(1)	-0.096(10)
S(1)	0.217(10)

Torsion angle	
C(6)-C(5)-C(10)-C(1)	176.9(7)
C(4)-C(5)-C(10)-C(9)	177.5(7)

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Summary

The Nap[SPh][R] compounds show interesting patterns of molecular deviations associated with the relief of steric strain caused by the presence of large *peri*-atoms and the influence of the metal center. The largest *peri*-distances observed were 3.34 Å for molecule **20**. This could be due to the presence of the larger iodine atom at the second *peri*-position compared to the smaller phosphorus atom of the Nap[SPh][PPh_2] compounds. The preference of platinum to form square planar compounds influences the geometry of the dihalide complexes **24-26** and forces the *peri*-atoms further apart compared to the non-coordinated ligand **19**. The presence of the chalcogen atoms in the chalcogenides **21-23** also increases the steric interactions and results in a greater degree of relief. The *peri*-distances for these six compounds [3.15-3.20 Å] are therefore found to be larger than for the free ligand **19** [3.03 Å]. The copper complexes **27-29** and the ruthenium complex **30** have *peri*-distances equivalent to that of **19** [3.01-3.09 Å] showing the geometry around the metal center is not an overriding factor on the molecular distortion taking place in the compound. The *peri*-distances of the Nap[SPh][R] compounds are compared in Figure 3.37.

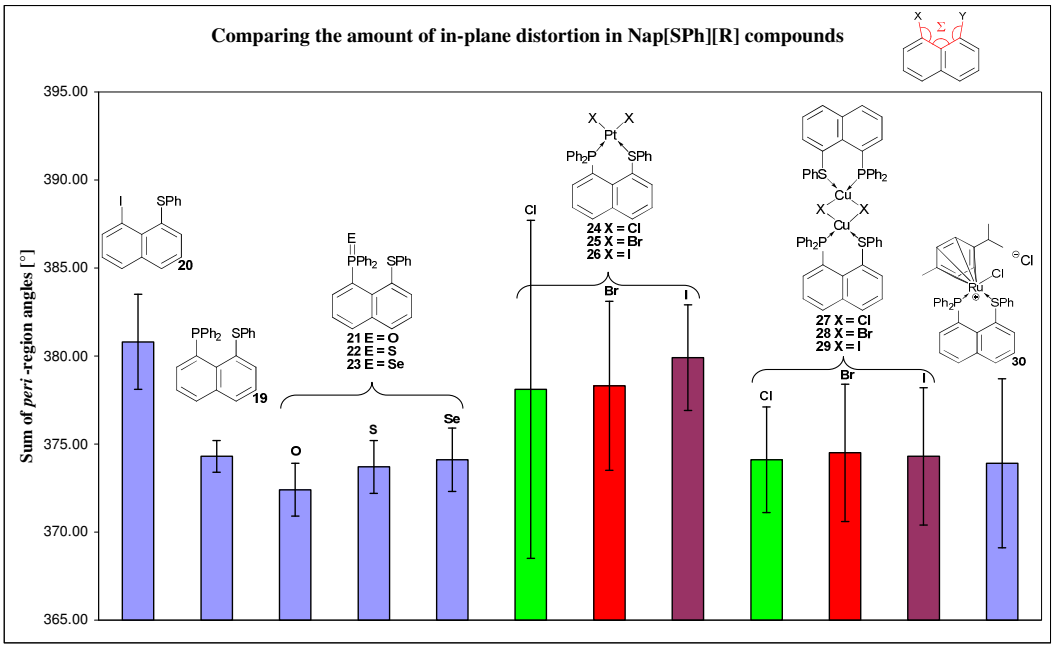

Fig. 3.35 *Comparing the amount of in-plane distortion in the Nap[SPh][R] compounds.*

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Figure 3.35 quantifies the degree of in-plane distortion found in the Nap[SPh][R] compounds of this chapter by comparing the sum of the *peri*-region angles. The greatest degree of in-plane distortion is observed in compound **20** and in the platinum dihalides. This can be attributed to the large size of the iodine atom in **20** and the forced square planar geometry in compounds **24-26**. The degree of in-plane distortion in the copper complexes **27-29**, the ruthenium complex **30** and the chalcogenides **21-23** is similar to that found in the free ligand **19**.

Out-of-plane distortion is compared in Figure 3.36 by looking at the deviation of the *peri*-atoms above and below the mean naphthalene plane. The greatest distortion is found in the chalcogenides **21-23** and the least amount of distortion is found in **19**. The metal complexes undergo a similar degree of deviation to one another, slightly greater than for the free ligand.

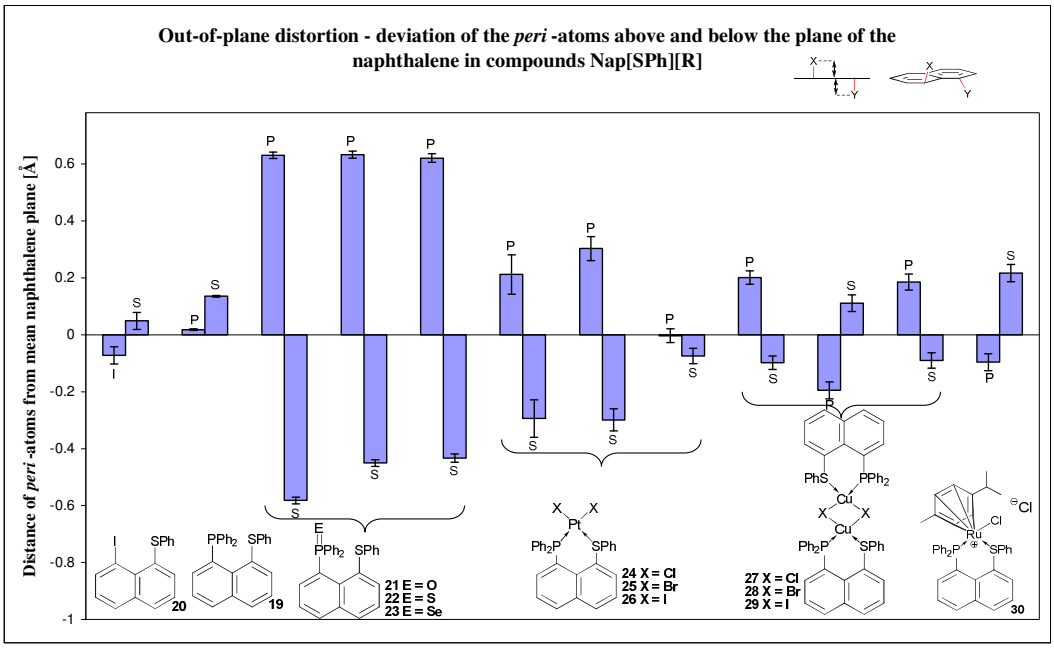

Fig. 3.36 *Comparing the amount of out-of-plane distortion in the Nap[SPh][R] compounds.*

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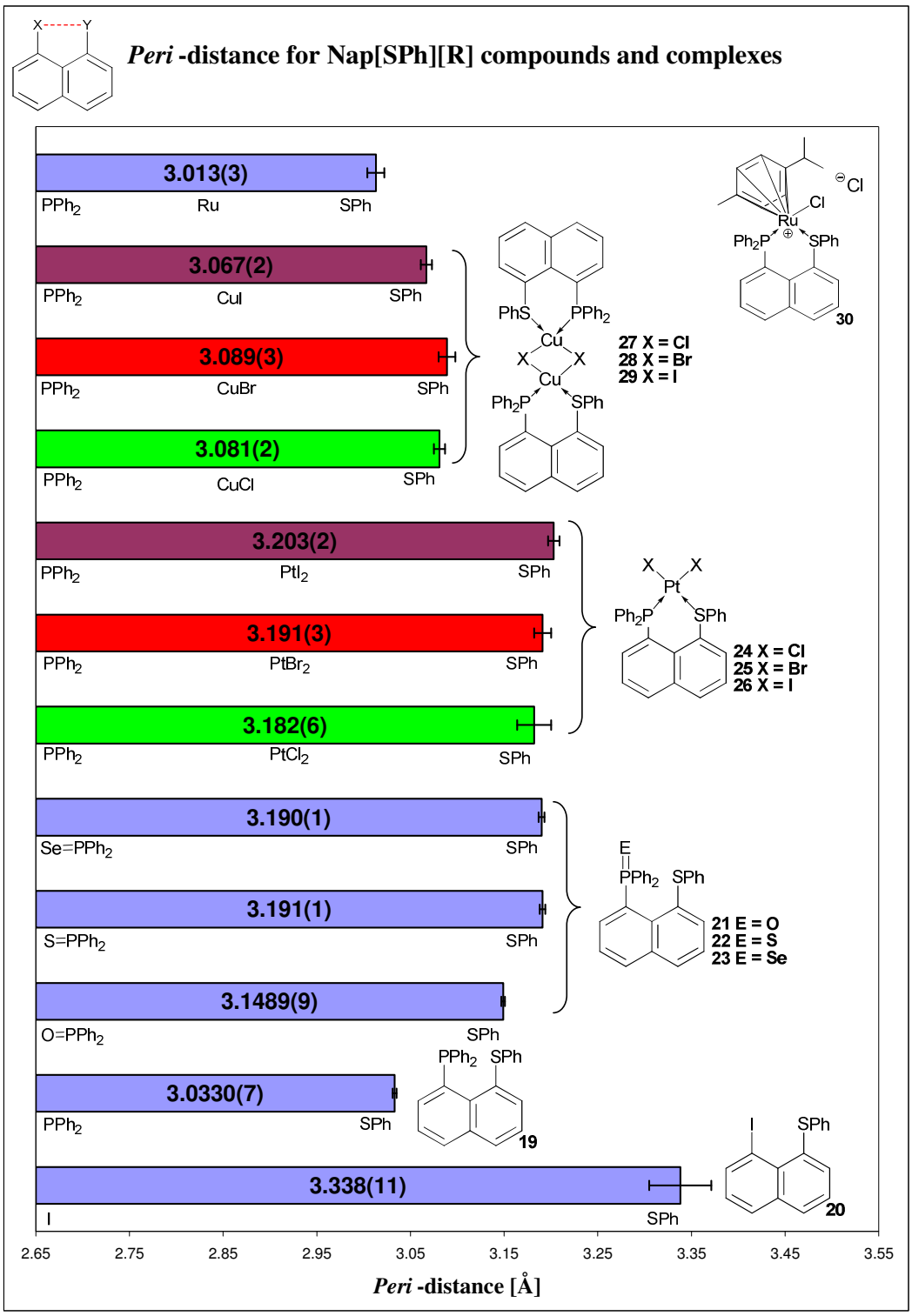

Fig. 3.37 *Comparing the peri-distances in the Nap[SPh][R] compounds.*

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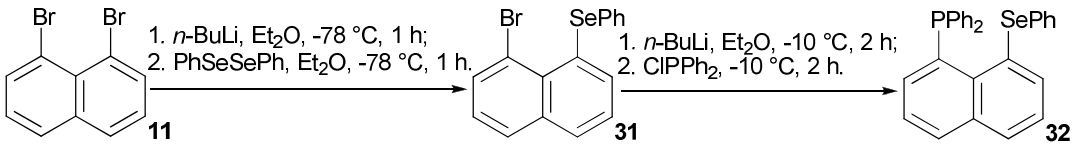
Chapter 4

Preparation and chemistry of (8-phenylselenylnaphth-1-yl)diphenylphosphine 32

In the previous chapters we have shown that mixed donor ligands containing sulfur and phosphorus moieties in the *peri*-positions of naphthalene (**3**, **19**) can be synthesised without difficulty starting from dihalo-naphthalenes. This chapter describes the novel route to the selenium analogue of **19** preparing the known compound (8-phenylselenylnaphth-1-yl)diphenylphosphine **32**,[1] following similar procedures developed for the sulfur species. The preparation of a series of phosphorus(V) chalcogenides is also reported and the molecular structures of the products are compared with those of the analogous sulfur compounds of Chapter 3 (**21**-**23**).

Compound **32** and its mono-oxide **34**, were previously reported by Warô Nakanishi *et al.* whilst investigating non-bonded interactions with the aid of *ab initio* MO calculations. Their main focus was on the possible attractive O···Se-C 3c-4e type interaction in **34** as well as the P···Se interaction in the 1,8-position.[1]



Scheme 4.1 *The reaction scheme for the preparation of (8-phenylselenylnaphth-1-yl)diphenylphosphine* **32** *from 1,8-dibromonaphthalene* **11**.

Following similar methods to those used for the preparation of the sulfur-containing compounds **2** and **9**, 1,8-dibromonaphthalene was reacted with *n*-butyllithium (1 equivalent) and diphenyl diselenide (1 equivalent) to afford the known compound 1-bromo-8-(phenylselenyl)naphthalene **31** in 63% yield (Scheme 4.1).[2,3,4] Characterisation of **31** was achieved by elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy and mass spectrometry and was found to be in accord with the literature.[5]

Conversion of **31** to the target compound was achieved using the procedure adopted in the preparation of the sulfur-phosphorus compounds **3** and **19**.[6] **31** reacted with one equivalent of *n*-butyllithium followed by one equivalent of chlorodiphenylphosphine to give (8-phenylselenylnaphth-1-yl)diphenylphosphine **32** as an oil in 40% yield (Scheme 4.1).[6]

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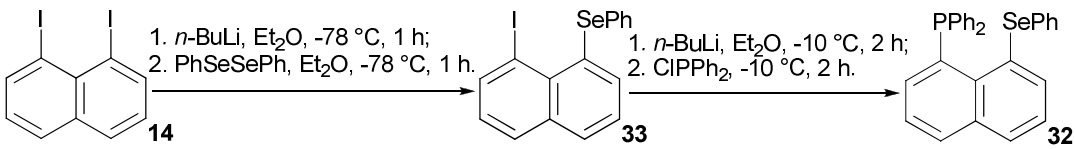
Characterisation of **32** was accomplished by ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectroscopy and mass spectrometry. The phosphorus NMR spectrum shows a signal at δ = -12.94 ppm and the selenium NMR spectrum shows a peak at δ = 439.6 ppm ($^{4}J_{(P,Se)}$ = 391.0 Hz). Both values are in agreement with the literature (^{31}P NMR δ = -12.51 ppm, ^{77}Se NMR δ = 446.2 ppm ($^{4}J_{(P,Se)}$ = 380.9 Hz).[1]



Scheme 4.2 *The reaction scheme for the preparation of (8-phenylselenylnaphth-1-yl)diphenylphosphine* **32** *from 1,8-diiodonaphthalene* **14**.

For completeness, **32** was also synthesised in an analogous reaction starting from 1,8-diiodonaphthalene **14**, via the novel intermediate 1-iodo-8-(phenylselenyl)naphthalene **33**. The reaction of **14** with one equivalent each of *n*-butyllithium and diphenyl diselenide produced the novel compound in 60% yield. Characterisation was accomplished by elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy and mass spectrometry. The selenium NMR spectrum showed a single peak at δ = 430.8 ppm, slightly upfield from the signal for the bromine analogue **31** [δ = 447.8 ppm]. The subsequent reaction of **33** with a single equivalent each of *n*-butyllithium and chlorodiphenylphosphine afforded compound **32** in 60% yield.[6]

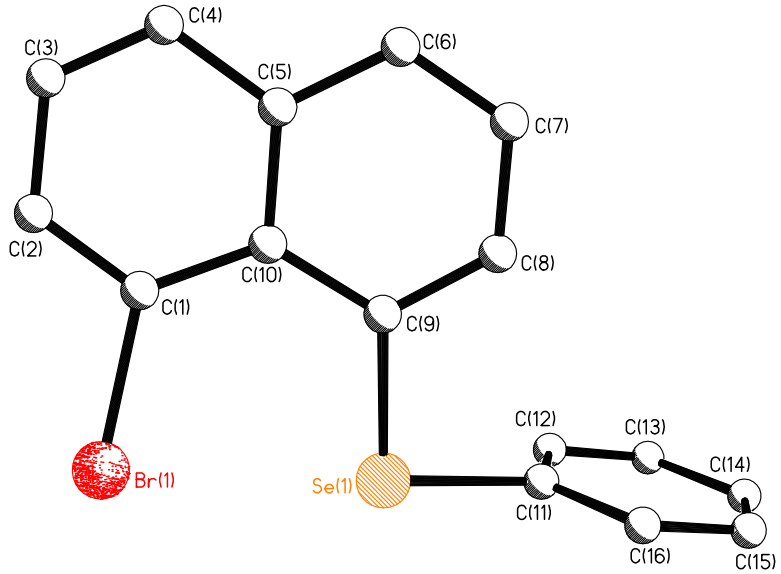


Fig. 4.1 *The molecular structure of 1-bromo-8-(phenylselenyl)naphthalene* **31**.[4]

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The molecular structure of **31** (Figure 4.1)[4] shows an intramolecular bromine-selenium *peri*-distance of 3.1136(5) Å. Out-of-plane distortion is observed with the selenium atom Se(1) -0.42(1) Å and the bromine atom Br(1) 0.40(1) Å lying from the mean plane of the naphthalene backbone. The heavy atoms are further accommodated by in-plane distortions in the C-C-C group between the Br and Se atoms as shown by the sum of the bay region angles [373.0(6)°]. As expected from the heavy atom displacement, the phenylselenyl group lies on one side of the naphthalene plane, the phenyl ring being inclined at 88° to the naphthalene plane. Selected bond lengths and bond angles are shown in Table 4.1; further information can be seen in Appendix 20.

The molecular structure of **33** (Figure 4.2) is similar to its bromine analogue with the phenylselenyl group lying on one side of the naphthalene plane and the phenyl ring inclined by 82° to the naphthalene plane. Compared to **33**, the iodine compound exhibits greater strain relief via naphthalene distortion due to increased steric repulsion between the *peri*-atoms. The larger iodine atom is accommodated by a longer intramolecular non-bonded I···Se(phenyl) distance [3.2524(8) Å] compared to the Br···Se(phenyl) distance of 3.1136(6) Å. An increase in the splay of the bay region is seen by comparison of the sums of the *peri*-region angles [**31** 373.0(6)°, **33** 374.9(8)°] and shows a greater in-plane distortion occurs in the iodine compound. Out-of-plane distortion in the two analogues is observed to a similar degree with the I(1) and Se(1) atoms of **33** lying 0.50(1) Å and -0.42(1) Å from the plane respectively. The degree of planarity in the two naphthalene backbones is also comparable with similar C(5)-C(10) torsion angles in the two compounds. Selected bond lengths and bond angles for **31** and **33** are shown in Table 4.1, further details for the crystal structure of **33** can be found in Appendix 21.

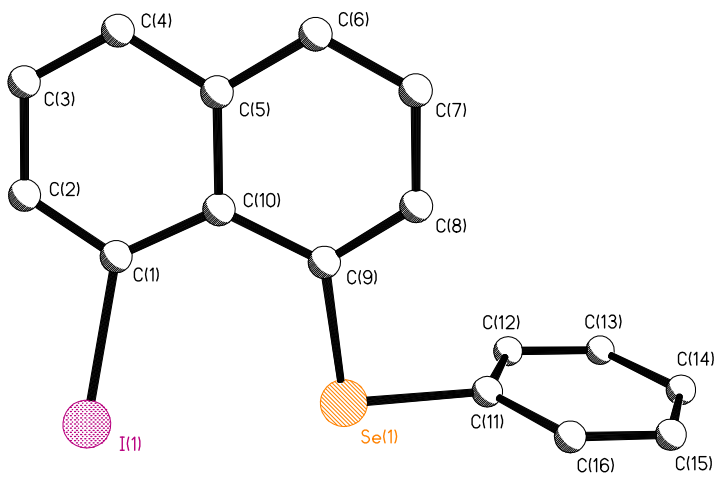

Fig. 4.2 *The molecular structure of 1-iodo-8-(phenylselenyl)naphthalene* **33**.

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In Chapter 1 non-bonded intramolecular interactions occurring between the lone pair orbitals of closely arranged heteroatoms in *peri*-substituted naphthalenes was introduced. Most of the pertinent work in this field has recently been reported by the group of Nakanishi and co-workers. During a wider study of non-bonded intramolecular interactions in sterically crowded naphthalenes of the type 8-G-1-(*p*-$YC_6H_4Se)C_{10}H_6$ (Figure 4.3), Nakanishi *et al.* reported the structure of **31**.[5]

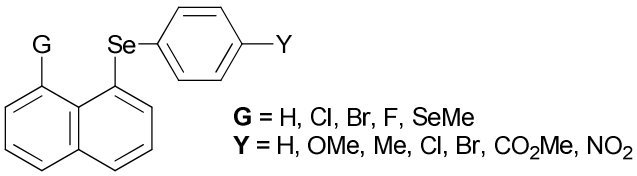

Fig. 4.3 *The series of sterically crowded naphthalenes (8-G-1-(p-$YC_6H_4Se)C_{10}H_6$) investigated by Nakanishi et al. as part of their study of intramolecular interactions.*[5]

Nakanishi *et al.* alleged that systems with Z-R = Se-C at the 1-position and G = (halogens) at the 8-position satisfied the conditions for non-bonded interactions to take place.[5,7] They found that compounds where G = Cl or Br, such as **31**, always adopted the 'type B' structure (see Chapter 1, Figure 1.32) irrelevant of what occupied the Y position and thus formed the linear non-bonded G···Se-C arrangement. From *ab initio* MO calculations Nakanishi *et al.* concluded that *'the linear alignment of the three atoms must be the result of the non-bonded G···Se-C 3c-4e type interaction'*.[5] Additionally, Toshimitsu *et al.* have also reported **31** as an intermediate in the synthesis of a series of pentacoordinate disilanes.[2,3]

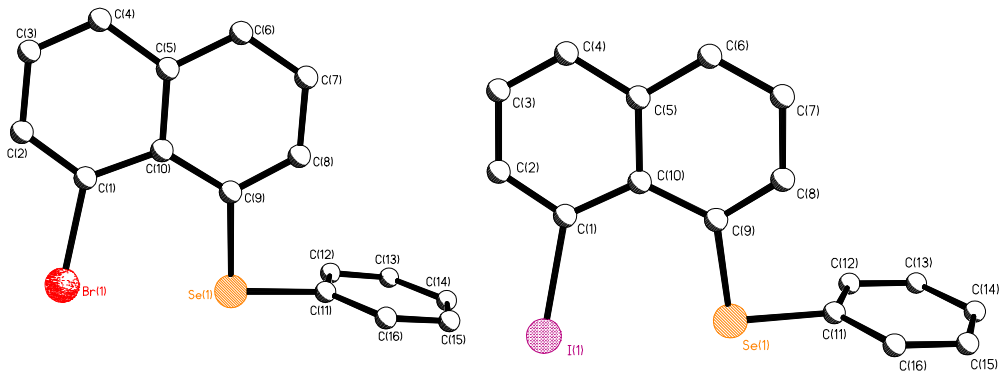

Fig. 4.4 *Comparing the orientation of the phenyl group in the molecular structures of compounds* **31** *and* **33**.

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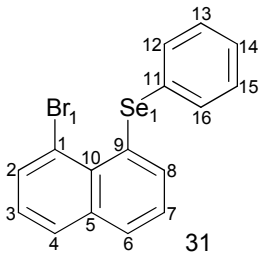
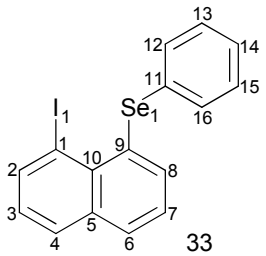
The geometric orientation of the iodine compound **33** mimics that of its bromine analogue **31**. Thus assuming the 'type B' structure described by Nakanishi *et al.*.[5,7] The Se(phenyl) moieties in both compounds sit in a similar location producing a linear arrangement of the type X···Se-C, with angles of **31** 175.7(1)° and **33** 174.3(1)° (Figure 4.4). The observed non-bonded distances between halide X and the selenium atom are shorter than sum of van der Waals radii of the atoms by 0.64 Å for **31** and 0.63 Å for **33** [**31** 3.1136(6) Å, {3.75 Å}; **33** 3.2524(8) Å, {3.88 Å}].[8] The X···Se-C linearity and the close proximity of the *peri*-atoms is conducive to non-bonded interactions.[5,7,9] According to Nakanishi *et al.* the linearity given by the 'type B' structure can be attributed to a 3c-4e type interaction taking place.[5]

Table 4.1 Bond lengths [Å] and angles [°] for 1-bromo-8-(phenylselenyl)naphthalene **31** and 1-iodo-8-(phenylselenyl)naphthalene **33**.





Br(1)···Se(1)	**3.1136(6)**	**I(1)···Se(1)**	**3.2524(8)**
Br(1)-C(1)	1.919(3)	I(1)-C(1)	2.122(4)
Se(1)-C(9)	1.948(3)	Se(1)-C(9)	1.958(4)
Br(1)-C(1)-C(10)	122.1(3)	I(1)-C(1)-C(10)	124.2(3)
C(1)-C(10)-C(9)	128.3(3)	C(1)-C(10)-C(9)	128.3(4)
Se(1)-C(9)-C(10)	122.6(2)	Se(1)-C(9)-C(10)	122.4(4)
	Σ = 373.0(6)		**Σ = 374.9(8)**
Distance from naphthalene mean plane			
Br(1)	0.40(1)	I(1)	0.50(1)
Se(1)	-0.42(1)	Se(1)	-0.42(1)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	175.8(3)	C(6)-C(5)-C(10)-C(1)	174.9(5)
C(4)-C(5)-C(10)-C(9)	173.8(3)	C(4)-C(5)-C(10)-C(9)	174.6(5)

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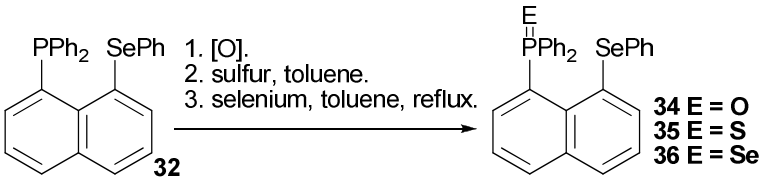
Phosphorus(V) chalcogenides of (8-phenylselenylnaphth-1-yl)diphenylphosphine 32

Phosphine **32** readily oxidises in the atmosphere to afford the known four coordinate (8-phenylselenylnaphth-1-yl)diphenylphosphine oxide **34** with 100% conversion as seen by ^{31}P NMR (Scheme 4.3).



Scheme 4.3 *Synthesis of (8-phenylselenylnaphth-1-yl)diphenylphosphine chalcogenides* **34**, **35**, *and* **36**.

Following similar procedures for the preparation of the phosphorus(V) sulfides (**17** and **22**) and selenides (**18** and **23**), **32** reacted with stoichiometric amounts of sulfur and selenium powder under reflux, selectively affording the novel phosphorus(V) chalcogenides 1-P(:S)Ph$_2$(C$_{10}$H$_6$)-8-SePh **35** and 1-P(:Se)Ph$_2$(C$_{10}$H$_6$)-8-SePh **36** in almost quantitative yields (Scheme 4.3).[10]

The three chalcogenide derivatives were characterised by a combination of elemental analysis, infra-red spectroscopy, mass spectrometry and ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectroscopy. The ^{31}P{^{1}H} NMR spectra showed single peaks at δ = 37.99 ppm **34**, δ = 51.01 ppm **35**, and δ = 40.50 ppm **36**, with expected ^{1}J and ^{4}J values for phosphorus-selenium coupling in **36** [$^{1}J_{P(1)\text{-}Se(2)}$ = 715.3 Hz, $^{4}J_{P(1)\cdots Se(1)}$ = 23.9 Hz]. Phosphorus-selenium coupling was not observed in the spectra for **34** and **35** with the small $^{4}J_{P(1)\cdots Se(1)}$ value within the line-width of the signal (Table 4.2).

Table 4.2 Phosphorus-31 and selenium-77 NMR spectroscopic data for phosphine **32** and its phosphorus V chalcogenides **34**-**36** [δ (ppm), *J* (Hz)]

		chemical shifts			coupling constants	
		δ_P	δ_{Se}	δ_{Se}	$^{4}J_{PSe}$	$^{1}J_{PSe}$
1-PPh$_2$(C$_{10}$H$_6$)-8-SePh	**32**	-12.94	439.6	n/a	391	n/a
1-P(:O)Ph$_2$(C$_{10}$H$_6$)-8-SePh	**34**	37.99	450.4	n/a	-	n/a
1-P(:S)Ph$_2$(C$_{10}$H$_6$)-8-SePh	**35**	51.01	448.5	n/a	19	n/a
1-P(:Se)Ph$_2$(C$_{10}$H$_6$)-8-SePh	**36**	40.50	451.4	-162.8	24	715

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The ^{77}Se NMR spectra for **34** showed a single peak at δ = 450.4 ppm with the expected small $^{4}J_{Se(1)\cdots P(1)}$ value also hidden within the line-width of the signal. The ^{77}Se NMR spectra for **35** showed a doublet at δ = 448.5 ppm with a small value for selenium-phosphorus coupling [$^{4}J_{Se(1)\cdots P(1)}$ 19.1 Hz]. The ^{77}Se NMR spectrum of **36** showed two sharp doublets at δ = 451.4 ppm and δ = -162.8 ppm for the two selenium atoms with ^{1}J and ^{4}J values for selenium-phosphorus coupling [$^{1}J_{Se(2)-P(1)}$ = 715.3 Hz, $^{4}J_{Se(1)\cdots P(1)}$ = 23.9 Hz] (Table 4.2). Data for oxide **34** was found to be in accord with literature values for both ^{31}P [δ = 37.47 ppm][1] and ^{77}Se NMR spectra [δ = 457.9 ppm].[1]

Suitable single crystals for the three compounds were grown by diffusion of pentane into saturated solutions of the chalcogenides in dichloromethane. The molecular structures are shown in Figures 4.5, 4.7 and 4.13. Selected bond distances and angles for the three compounds are compared in Table 4.4 and further crystallographic information on each structure can be found in Appendices 22-24.

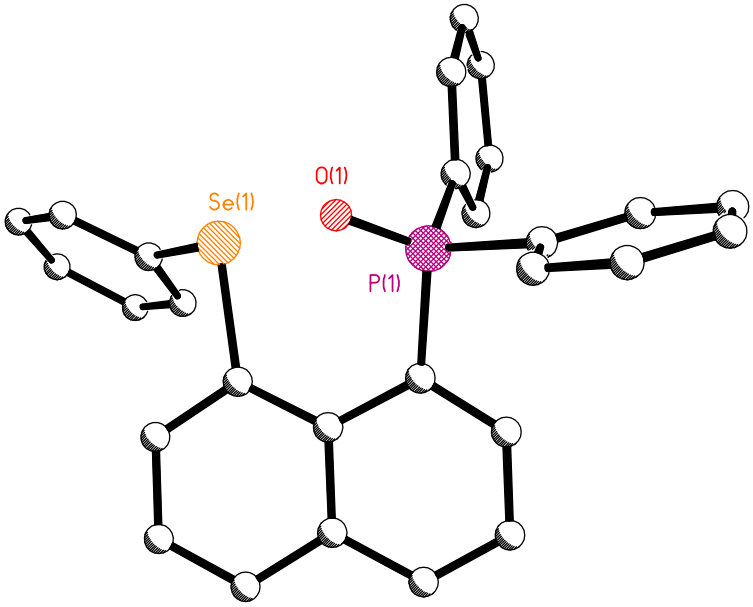

Fig. 4.5 *The crystal structure of (8-phenylselenylnaphth-1-yl)diphenylphosphine oxide* **34**.

In all three compounds the P(:E)Ph$_2$ and SePh groups lie in close proximity to each other, with non-bonded *peri*-distances (P···Se) of 3.215(2) Å **34**, 3.2803(8) Å **35** and 3.278(2) Å **36**, all shorter than the sum of van der Waals radii for phosphorus and selenium [3.70 Å] by 0.42-0.49 Å (Table 4.3).[8]

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Throughout the series, the chalcogen atom resides in the *peri*-gap pointing away from the naphthalene plane (Figure 4.6).[8] E···Se non-bonded distances of 2.770(3) Å **34**, 3.3490(7) Å **35** and 3.4217(8) Å **36**, increase with the size of the chalcogen attached to phosphorus(V) but are considerably shorter than the sum of the van der Waals radii of the atoms in all cases [OSe 3.42 Å, SSe 3.70 Å, SeSe 3.80 Å] (Table 4.3).[8] P=E bond lengths 1.476(4) Å **34**, 1.9567(10) Å **35** and 2.1165(16) Å **36**, are as expected.[11]

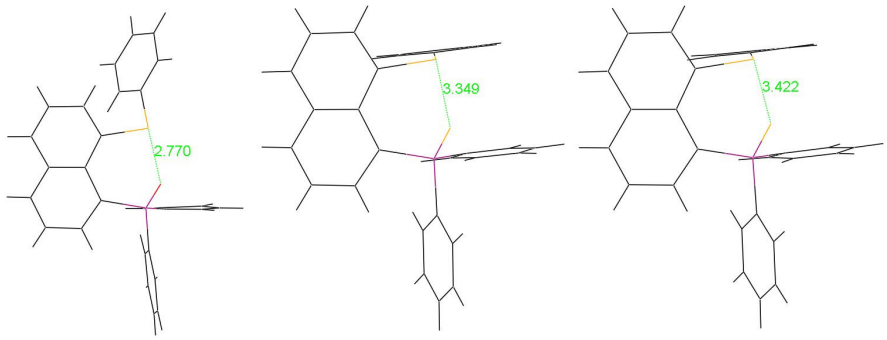

Fig. 4.6 *The crystal structures of the (8-phenylselenylnaphth-1-yl)diphenylphosphine chalcogenides* **34**, **35** *and* **36** *showing the non-bonded Se(1)···E distance.*

The close proximity of the two bulky substituents leads to in-plane and out-of-plane distortion of the *peri*-atoms with respect to the naphthalene ring system. The amount of in-plane distortion of the substituents, indicated by a widening of the bay angles, increases from the oxide to the selenide [375.5(7)° **34**, 376.8(4)° **35**, 377.3(9)° **36**]. The level of displacement of the *peri*-atoms to opposite sides of the best naphthalene plane shows out-of-plane distortion is consistent throughout the series. P(1) lies below the plane in **34** and above the plane in **35** and **36**.

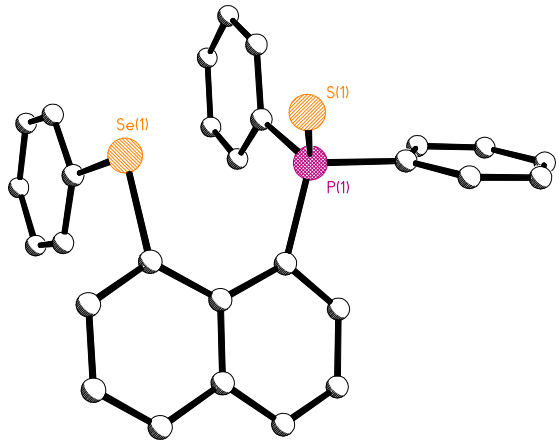

Fig. 4.7 *The crystal structure of (8-phenylselenylnaphth-1-yl)diphenylphosphine sulfide* **35**.

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The displacement of the phosphorus and selenium substituents within and out of the plane is accompanied by a distortion of the usually planar and rigid C_{10}-unit by a twist into a non-planar conformation. This is illustrated by the torsion angles associated with the central C(5)-C(10) bond (Table 4.4). Buckling of the plane is greatest in the oxide species (torsion angles further from the linear 180°) with the selenide compound retaining the most planar naphthalene ring system of the three compounds (Figure 4.8).

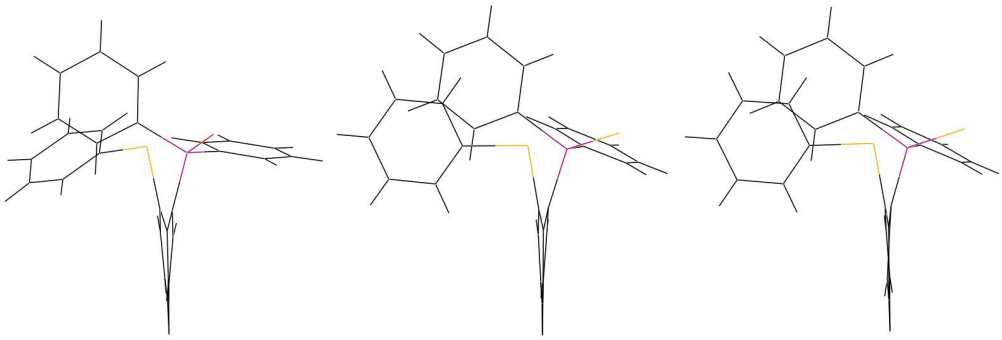

Fig. 4.8 *The crystal structures of the (8-phenylselenyylnaphth-1-yl)diphenylphosphine chalcogenides* **34**, **35** *and* **36** *showing the buckling of the naphthalene planes.*

Oxide **34** assumes a different orientation to that of the sulfide **35** and selenide **36**, which adopt identical structural motifs (Figure 4.9). In all three compounds the orientation of the phenyl groups around the phosphorus align in a similar way placing the chalcogen bonded to phosphorus pointing away from the naphthalene plane in the *peri*-gap. The difference between the two orientations is the positioning of the phenyl group attached to Se(1).

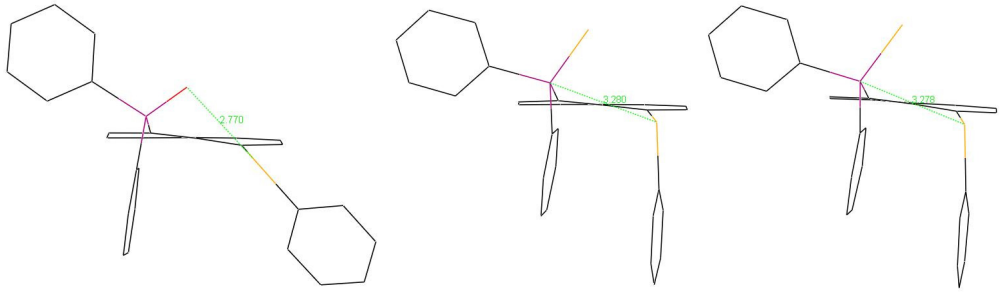

Fig. 4.9 *The crystal structures of the (8-phenylselenylnaphth-1-yl)diphenylphosphine chalcogenides showing the linear arrangement of the type O···Se-C in* **34** *and Se···P-C in* **35** *and* **36**.

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In **35** and **36** the Se(1)phenyl group aligns parallel with one of the phenyl rings on P(1) (Figure 4.9, 4.10). The alignment of the rings is face-to-face offset arrangement with slipped packing, known as parallel displacement (see Chapter 3, Figure 3.12).[12] The distances between the two interacting centroids, however, are longer than the range for typical centroid-centroid π-stacking (3.3-3.8 Å)[12] and so no π-π stacking is envisaged [**Cg(17-22)···Cg(23-28): 41** 4.034(1) Å, **42** 4.075(1) Å] (Figure 4.10).

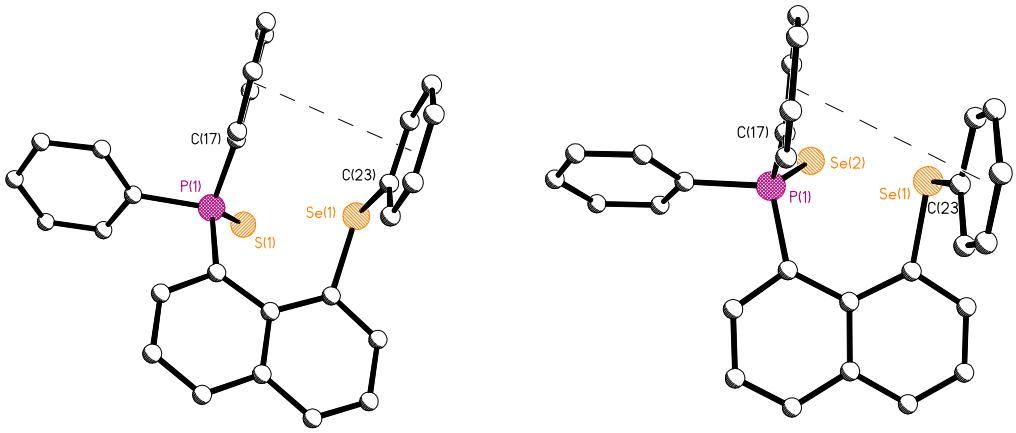

Fig. 4.10 *The crystal structures of (8-phenylselenylnaphth-1-yl)diphenylphosphine sulfide* **35** *and selenide* **36** *showing the phenyl ring orientation.*

The parallel orientation of the phenyl rings produces a linear arrangement of the type Se···P-C with angles of **35** 173.5(1)° and **36** 172.9(1)° (Table 4.3, Figure 4.9). The observed non-bonded distances between P(1) and Se(1) in both compounds [**35** 3.2803(8) Å, **36** 3.278(2) Å] are also shorter than sum of van der Waals radii of the atoms [3.70 Å].[8] These results therefore fit within the parameters set by Nakanishi *et al.* for a 3c-4e bonding interaction to occur.[5,7,9]

Table 4.3 Non-bonded distances [Å] and angles [°] showing the linear arrangement of E···Se(1)-C(23) and Se(1)···P(1)-C(11) for (8-phenylselenylnaphth-1-yl)diphenylphosphine chalcogenides **34**, **35** and **36**.

	34	**35**	**36**
E···Se(1)-C(23)	178.1(1)	145.0(1)	148.4(1)
Se(1)···P(1)-C(11)	167.9(1)	173.5(1)	172.9(1)
E···Se(1)	2.770(3) [3.42 Å]	3.3490(7) [3.70 Å]	3.4217(8) [3.80 Å]
P(1)···Se(1) [3.70 Å]	3.215(2)	3.2803(8)	3.278(2)

[sum of van der Waals radii of interacting atoms]

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The Se(1)phenyl moiety in oxide **34** is twisted and there is no possible parallel overlap with the P(17)phenyl group. This reduces the linearity of the Se···P-C arrangement with an angle of 167.9(1)°, however a linear arrangement of the type E···Se-C with an angle of 178.1(1)° is formed. The observed non-bonded distance between Se(1) and O(1) [2.770(3) Å], shorter than sum of van der Waals radii of the two atoms [3.42 Å],[8] also suggests a 3c-4e interaction could result.

As mentioned, compound **32** and its oxide **34**, were previously reported by Warô Nakanishi *et al.* whilst studying *ab initio* MO calculations of non-bonded interactions.[1] Determining the structure of **34** by x-ray crystallography, they reported that the three O···Se-C atoms align linearly [OSeC = 168.8°]. *Ab initio* calculations were then performed and the conclusion reached based on molecular orbitals was that '*the structure of* **34** *is determined by the predominant 3c-4e type interaction of the linear O···Se-C atoms*'.[1] In order to reach our own conclusions regarding the possibility of 3c-4e non-bonded interactions in **34** and also to look at the potential for non-bonded interactions in the different linear type arrangement observed in **35** and **36,** calculations were performed for us by Prof. M. Bühl in St Andrews (Figure 4.11).

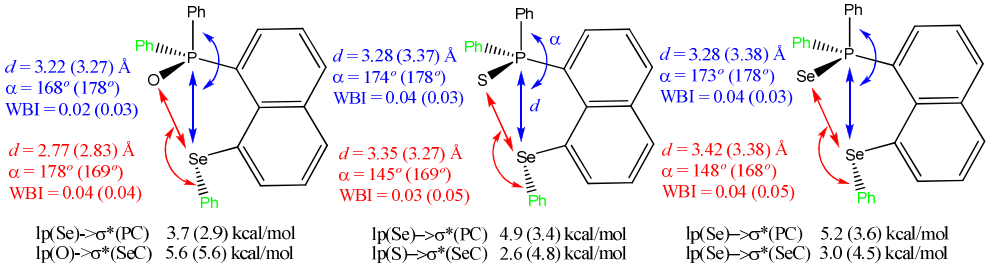

Fig. 4.11 *Results of ab initio MO Calculations performed on (8-phenylselenylnaphth-1-yl)diphenylphosphine chalcogenides* **34-36** *evaluated at the B3LYP/6-31+G* level using H-relaxed X-ray geometries.*

Figure 4.11 shows the results of the *ab initio* MO calculations. For each compound both linear type arrangements [E···Se-C and Se···P-C] were evaluated using B3LYP/6-31+G* level, using H-relaxed X-ray geometries. Experimental data is preceded by fully optimised data in parentheses. The Wiberg bond index (WBI), which measures the covalent bond order, was calculated for both linear arrangements in all three compounds.[13] WBI values of 0.02-0.04 indicate a very minor interaction taking place between non-bonded atoms. For strong interactions these values would be approaching 0.20.[13] We are therefore unable to conclude 3c-4e non-bonded interactions are taking place in these molecules.

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Further calculations were performed on the radical cations of (8-phenylselenylnaphth-1-yl)diphenylphosphine chalcogenides **34-36**. The results are shown in Figure 4.12 with calculated data preceded by the values for the neutral homologue in parentheses.

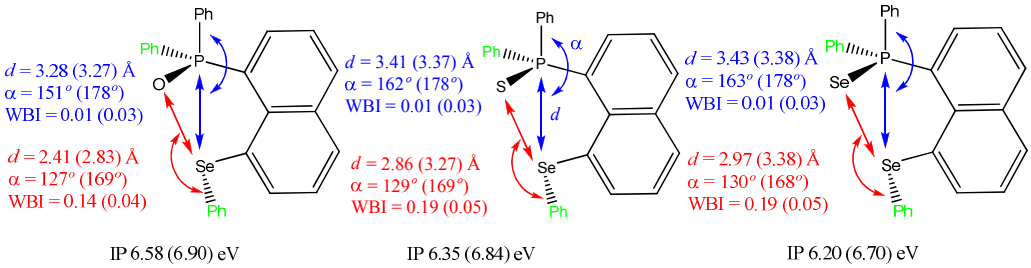

Fig. 4.12 *Results of ab initio MO Calculations performed on radical cations of (8-phenylselenylnaphth-1-yl)diphenylphosphine chalcogenides* **34-36** *evaluated at the B3LYP/6-31+G* level.*

Wiberg bond index values for the E···Se-C linear arrangement in all three radical cation species have increased to 0.14-0.19, showing a greater degree of interaction compared to in the neutral species. The WBI value for the Se···P-C linear arrangement in all three compounds is 0.01 showing no or limited interaction. For each species the adiabatic ionisation potential is shown followed by the vertical ionisation potential in parentheses. The values for the three species 6.58-6.20 (6.90-6.70) eV can be compared to the known compound naphtho[1,8-*cd*]-1,2-dithiole which has an IP value of 7.82(8.03) eV (Figure 4.13). From previous unpublished work from the Woollins group it was shown that naphtho[1,8-*cd*]-1,2-dithiole acts as an inorganic donor and forms crystals of $[C_{10}H_6S_2^+]_3[BF_4^-]_3$ using electrocrystallisation techniques.[14] The IP values for the three chalogenides **34-36** suggests these compounds may have similar electrochemical reactivity to naphtho[1,8-*cd*]-1,2-dithiole and may be able to form charge transfer compounds.

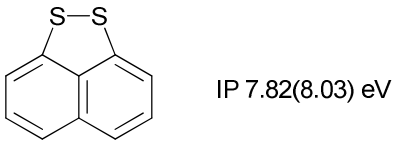

Fig. 4.13 *Electrochemical reactivity of naphtho[1,8-cd]-1,2-dithiole was previously studied within the Woollins Group.*[14]

Figure 4.14 shows the molecular orbitals for both the neutral and radical cation species of (8-phenylselenylnaphth-1-yl)diphenylphosphine selenide **36** at the B3LYP/6-31+G* level.

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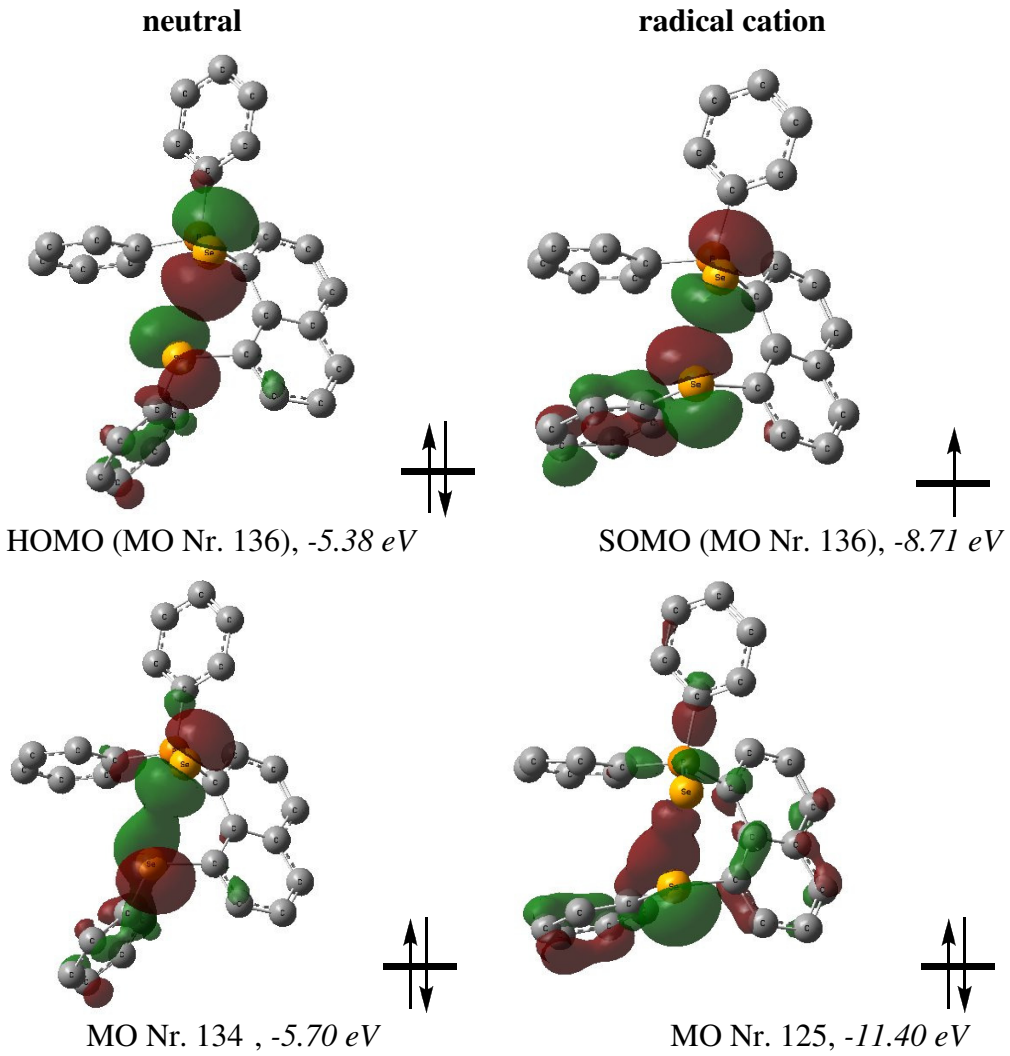

Fig. 4.14 *The molecular orbitals for (8-phenylselenylnaphth-1-yl)diphenylphosphine selenide* **36** *(B3LYP/6-31+G* level).*

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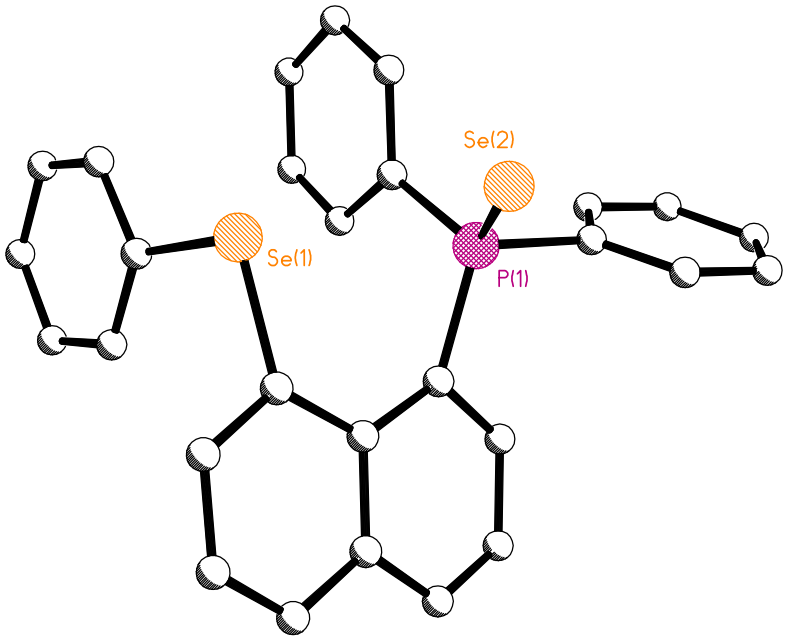

Fig. 4.15 *The crystal structure of (8-phenylselenylnaphth-1-yl)diphenylphosphine selenide* **36**.

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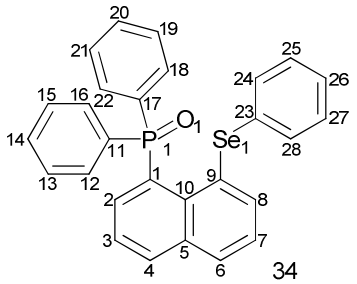
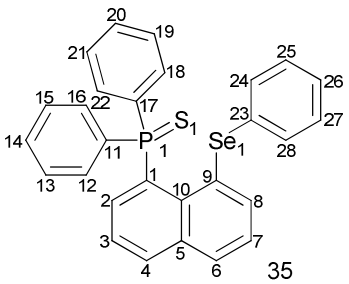
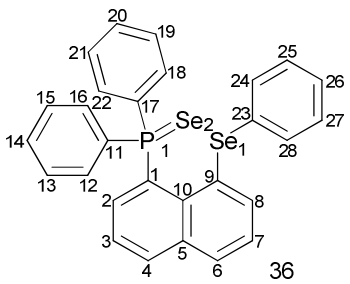
Table 4.4 Bond lengths [Å] and angles [°] for (8-phenylselenylnaphth-1-yl)diphenylphosphine chalcogenides **34**, **35** and **36**.







Se(1)···P(1)	**3.215(2)**	**Se(1)···P(1)**	**3.2803(8)**	**Se(1)···P(1)**	**3.278(2)**
P(1)-C(1)	1.826(5)	P(1)-C(1)	1.837(3)	P(1)-C(1)	1.825(6)
Se(1)-C(9)	1.937(4)	Se(1)-C(9)	1.916(3)	Se(1)-C(9)	1.917(6)
Se(1)···O(1)	2.770(3)	Se(1)···S(1)	3.3490(7)	Se(1)···Se(2)	3.4217(8)
P(1)-O(1)	1.476(4)	P(1)-S(1)	1.9567(10)	P(1)-Se(2)	2.1165(16)
P(1)-C(1)-C(10)	123.6(3)	P(1)-C(1)-C(10)	125.4(2)	P(1)-C(1)-C(10)	126.5(4)
C(1)-C(10)-C(9)	126.8(4)	C(1)-C(10)-C(9)	126.7(2)	C(1)-C(10)-C(9)	126.3(5)
Se(1)-C(9)-C(10)	125.1(3)	Se(1)-C(9)-C(10)	124.7(2)	Se(1)-C(9)-C(10)	124.5(4)
	Σ = 375.5(7)		**Σ = 376.8(4)**		**Σ = 377.3(9)**
Distance from naphthalene mean plane					
P(1)	-0.578(6)	P(1)	0.601(3)	P(1)	0.578(7)
Se(1)	0.450(6)	Se(1)	-0.420(3)	Se(1)	-0.397(7)
O(1)	-1.458(8)	S(1)	2.179(4)	Se(2)	2.314(8)
Torsion angle					
C:(6)-(5)-(10)-(1)	174.4(5)	C:(6)-(5)-(10)-(1)	174.9(2)	C:(6)-(5)-(10)-(1)	175.7(5)
C:(4)-(5)-(10)-(9)	170.5(5)	C:(4)-(5)-(10)-(9)	173.6(2)	C:(4)-(5)-(10)-(9)	175.1(5)

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Summary

Within each series of phosphorus(V) chalcogenides there is a general increase in the *peri*-distance with increasing size of the chalcogen bonded to phosphorus (Figure 4.17). The values for the two series of compounds Nap[PPh_2=E][SPh] **21-23** and Nap[PPh_2=E][SePh] **34-36** also shows the importance of *peri*-atom size on the *peri*-distance (Figure 4.17). As the *peri*-atom size increases from sulfur (**21-23**) to selenium (**34-36**) there is greater steric interaction which forces the *peri*-atoms further apart thus increasing the values for the *peri*-distance. The values for the two series Nap[PPh_2=E][SEt] **16-18** and Nap[PPh_2=E][SPh] **21-23** are similar which implies that the ethyl group (**16-18**) and the phenyl group (**21-23**) attached to S(1) have a similar influence on the overall structure and therefore the *peri*-distance.

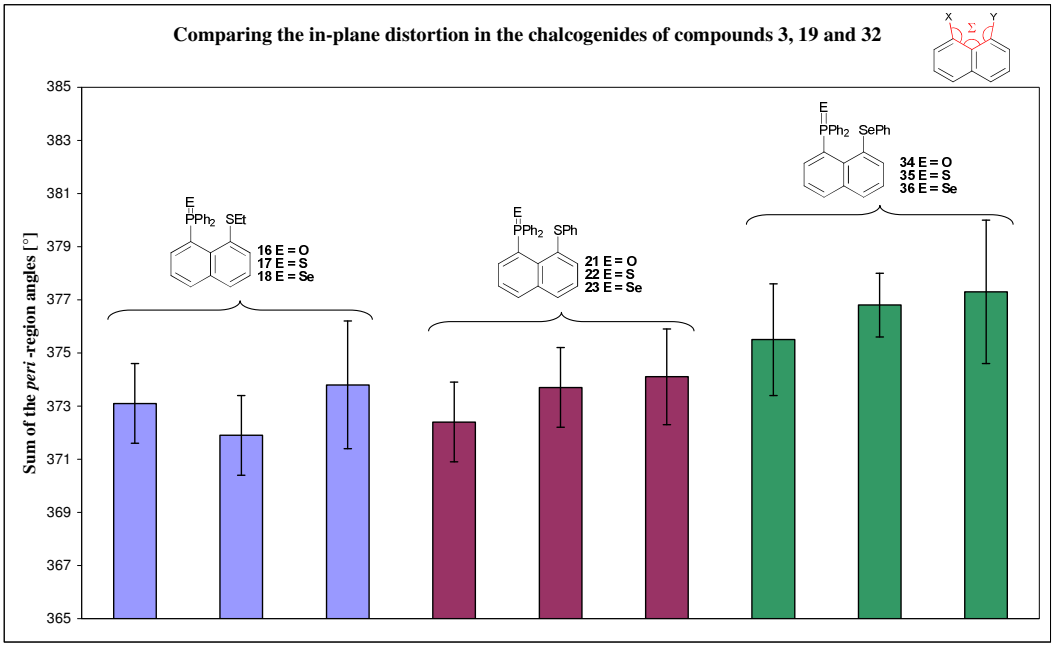

Fig. 4.16 *Comparing the in-plane distortion in the Nap[ER][PPh_2=E^1]compounds* **16-18, 21-23** *and* **34-36**.

Figure 4.16 quantifies the degree of in-plane distortion found in the three series of chalcogenides Nap[PPh_2=E][ER] by comparing the sum of the *peri*-region angles. A general increase in the splay angles is observed in each group due to the increasing size of chalcogen bonded to P(1). The sulfur compounds have similar in-plane distortions but the greatest degree of in-plane distortion is found when selenium occupies one of the *peri*-atom positions and can be attributed to its larger size compared to sulfur.

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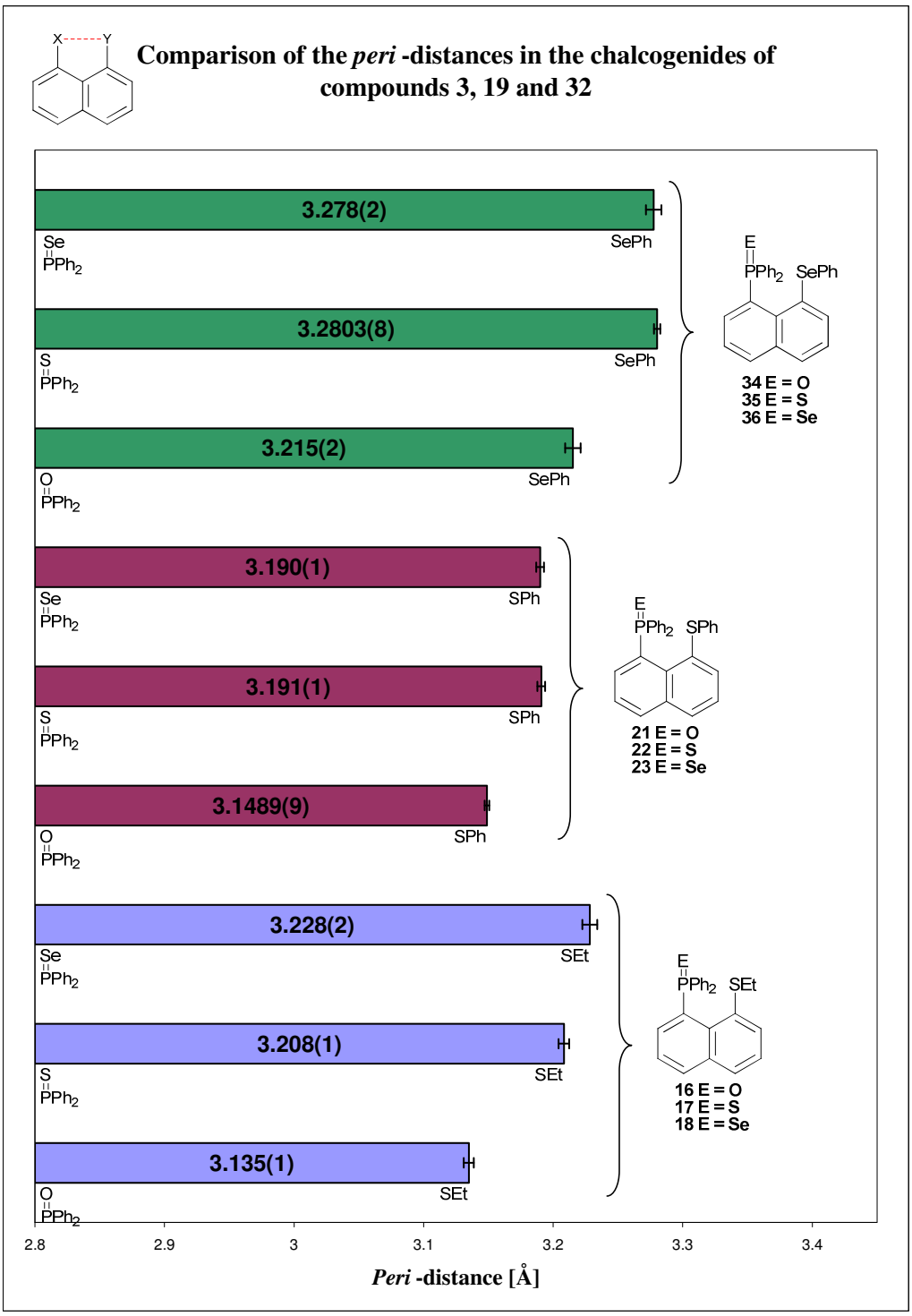

Fig. 4.17 *Comparing the peri-distances in the Nap[ER][PPh$_2$=E^1]compounds* **16-18, 21-23** *and* **34-36**.

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Out-of-plane distortion is compared in Figure 4.18 by looking at the deviation of the *peri*-atoms above and below the mean naphthalene plane. The distortion is found to be not only consistent throughout the three groups of compounds but also between groups. This suggests out-of-plane distortion is not the major factor contributing to the differing *peri*-distances as seen in Figure 4.17. The greatest out-of-plane distortion is observed in Nap[PPh_2=S][SEt] (Figure 4.18).

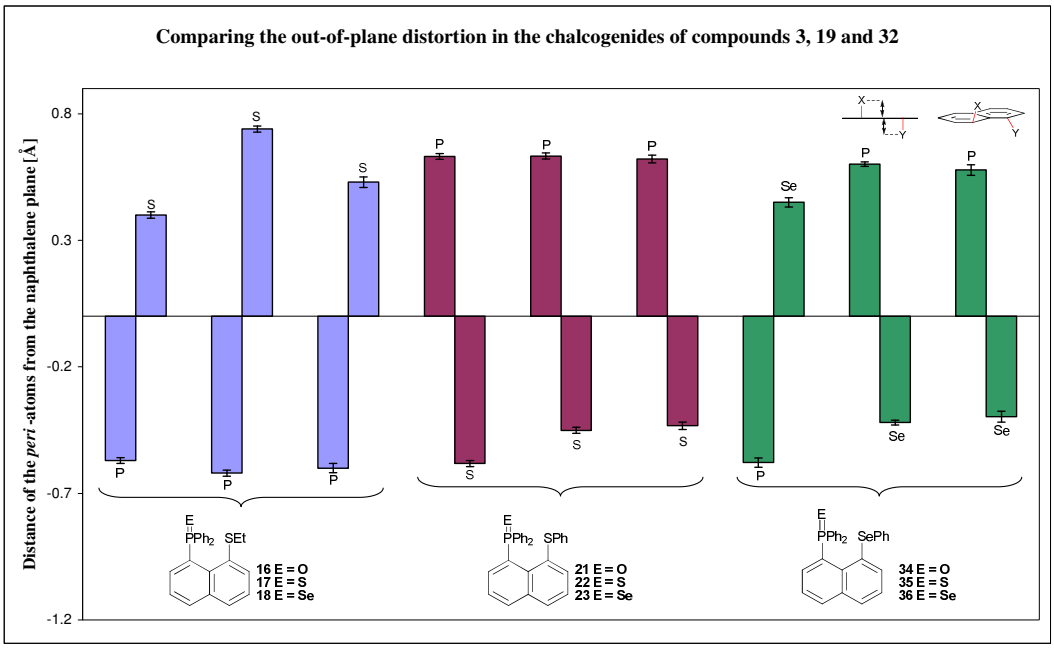

Fig. 4.18 *Comparing out-of-plane distortion in the Nap[ER][PPh_2=E^1]compounds* **16-18, 21-23** *and* **34-36**.

The degree of naphthalene backbone distortion in the chalcogenides is varied with no apparent pattern to indicate the reasons. The S(phenyl) chalcogenides are found to contain naphthalene ring systems with the greatest buckling whilst the least distorted are found overall to be the Se(phenyl) chalcogenides. Figure 4.19 shows the two compounds with the greatest (**17**) and least (**42**) amounts of naphthalene backbone distortion in the nine chalcogenide compounds Nap[ER][PPh_2=E^1] **16-18, 21-23** and **34-36**.

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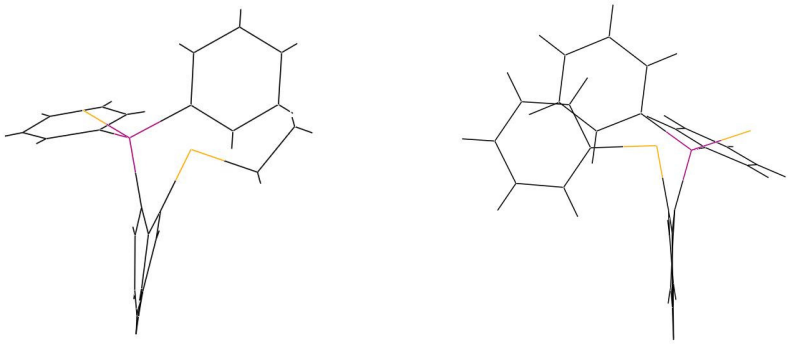

Fig. 4.19 *The greatest* **17** *and least* **42** *amount of naphthalene backbone distortion in the Nap[ER][PPh$_2$=E^1]compounds* **16-18, 21-23** *and* **34-36**.

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Chapter 5

Preparation of 1,8-(arylchalcogeno)naphthalenes

In the first half of this thesis we have shown that mixed donor ligands containing either sulfur or selenium and phosphorus moieties at the *peri*-positions of naphthalene (**3**, **19, 32**) can be synthesised easily starting from dihalo-naphthalenes. In this chapter we build on the reactions already undertaken in Chapters 1-3 to describe novel routes to the known series of 1,8-bis(phenylchalcogeno)naphthalenes **37-39** and the synthesis of the novel 1,8-bis(ethylsulfanyl)naphthalene **40** (Figure 5.1). The routes to three related novel mixed 1,8-(phenylchalcogeno)naphthalenes **41-43** are also described (Figure 5.1). Finally, the oxidation of **37** with different molar equivalents of *meta*-chloroperoxybenzoic acid (mCPBA) to prepare two novel oxides **44** and **45** is discussed.

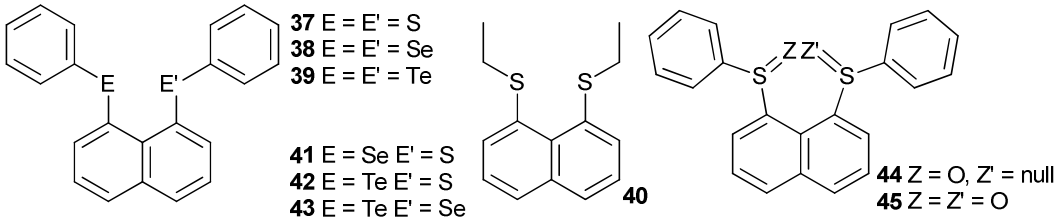

Fig. 5.1 *1,8-bis(phenylchalcogeno)naphthalenes* **37-39***, mixed 1,8-(phenylchalcogeno)naphthalenes* **41-43***, 1,8-(ethylsulfanyl)naphthalene* **40** *and oxides* **44** *and* **45**.

A literature study of 1,8-bis(phenylchalcogeno)naphthalenes 37-39.

The synthesis and molecular structure of 1,8-bis(phenylsulfanyl)naphthalene **37** was first reported in 2002 by Kálmán *et al.* during their investigations into S···S and S···O non-bonded interactions in the series of compounds **46-54** (Figure 5.2).[1] The four compounds contain sulfur *peri*-atoms with different valence states resulting in different S···S close contacts.

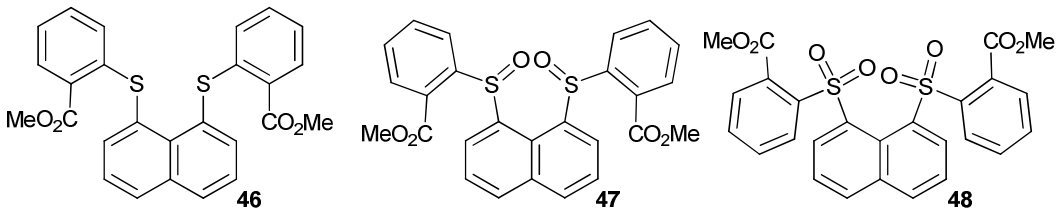

Fig. 5.2 *The three 1,8-disubstituted naphthalene derivatives* **46-48** *reported along with* **43** *by Kálmán et al. during their investigations into S···S and S···O non-bonded interactions.*[1]

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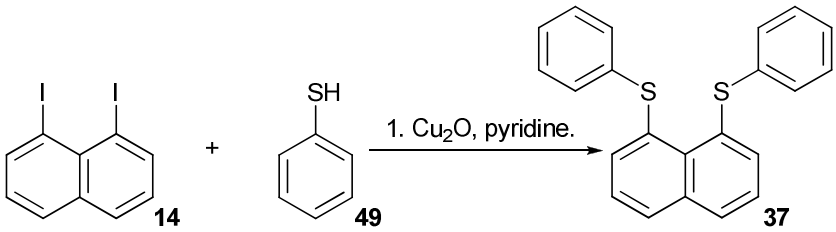
Preparation of **37** was achieved by reacting 1,8-diiodonaphthalene **14** with benzenethiol **49** and copper(I) oxide (Scheme 5.1). The molecular structure of **37** was found to be free from molecular symmetry and *peri*-sulfur atoms were found to lie within the sum of van der Waals radii for the two atoms. Only one favourable quasi-linear arrangement of C(17)-S(2)···S(1) was observed with an angle of 168.5°.[1]



Scheme 5.1 *The reaction scheme for the preparation of 1,8-diphenylsulfanylnaphthalene* **37** *as reported by Kálmán et al..*[1]

Compound **37** was also reported in 2008 by Nakanishi *et al.* as part of a wider study of homonuclear Z···Z (Z = O, S, Se and Te) interactions between *peri*-atoms in 1,8-disubstituted naphthalenes.[2] They synthesised and studied the molecular structures of a series of compounds (Figure 5.3), including **37**, the first reported structure of 1,8-bis(phenylselanyl)naphthalene **38** and the known compound 1,8-bis(phenyltellurenyl)naphthalene **39**. Each structure was classified by the orientation of the Z-C_R bond relative to the naphthalene plane (see Chapter 4).[2,3]

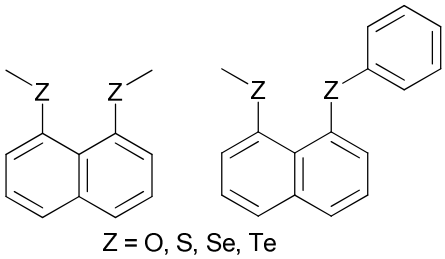


Fig. 5.3 *The 1,8-disubstituted naphthalene derivatives reported by Nakanishi et al. during their investigations into Z···Z homonuclear interactions.*[2]

Compounds **37** and **38** were reported to adopt an 'AB type' orientation with one Z-C_R bond lying on the naphthyl plane and one Z-C_R bond lying perpendicular to the plane (Figure 5.4).[2] **39** adopts a 'CC type' structure with both Z-C_R bonds lying at roughly 135° to the plane and *trans* to one another (Figure 5.4).[2] Based on quantum chemical calculations Nakanishi *et al.* concluded that the 'AB type' structures of **37** and **38** are stabilised by 3c-4e interactions.[2,3]

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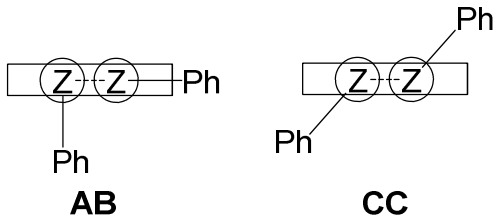
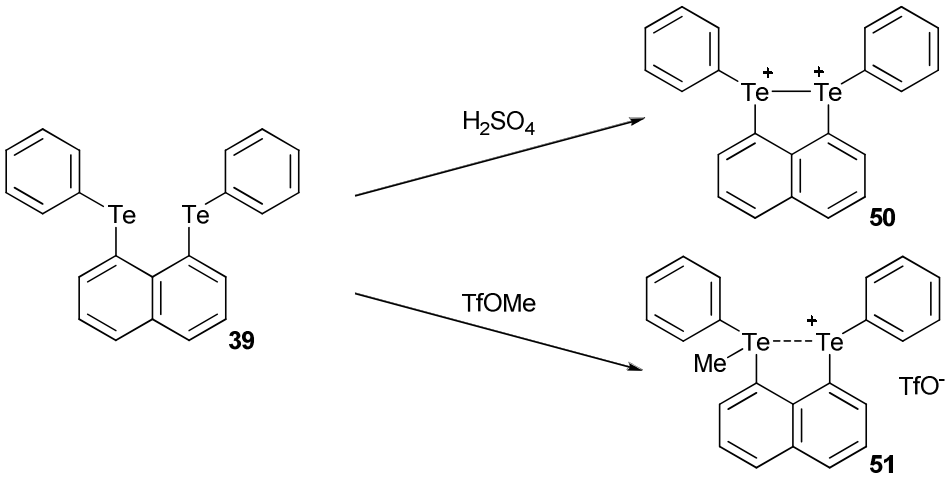


Fig. 5.4 *The orientation of the Z-C_R bond in structure types AB and CC as reported by Nakanishi et al..*[2,3]

1,8-bis(phenyltellurenyl)naphthalene **39** first appeared in the literature in 1995 from the group of Furukawa *et al.* and as such was the first 1,8-ditellurenylnaphthalene to be reported.[4] Electrochemical oxidation of **39** via cyclic voltammetry produced one reversible oxidation peak at a very low oxidation potential of +0.16 V.[4] Furukawa *et al.* attributed this to '*the destabilisation of* **39** *by peri lone pair-lone pair repulsion and the stabilisation of the oxidised species by neighbouring-tellurium participation'*.[4]



Scheme 5.2 *The oxidation reactions of* **39** *as reported by Furukawa et al..*[4]

The ^{125}Te NMR spectrum of **39** in $CDCl_3$ showed a peak at δ = 617 ppm whilst a solution of **39** in D_2SO_4 gave a downfield shift to δ = 964 ppm relating to the dication **50** (Scheme 5.2).[4] Furukawa *et al.* were also able to show the interaction between telluronio-tellurenyl groups at the *peri*-positions of cation **51**.[4] The ^{125}Te NMR spectrum of **51** showed two peaks at δ = 557 ppm (Te) and δ = 656 ppm (Te^+), each peak exhibiting satellites due to ^{125}Te-^{125}Te coupling with coupling constants of $J_{Te\text{-}Te}$ = 1093 Hz.[4]

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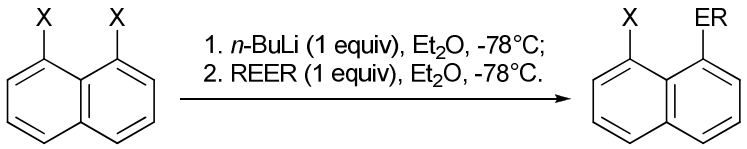
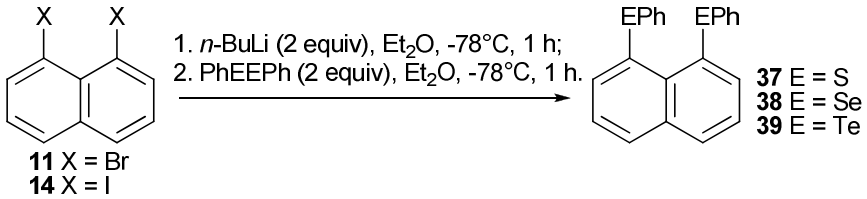
In house preparation of 1,8-bis(phenylchalcogeno)naphthalenes 37-39

In the first three chapters we utilised single substitution reactions of 1,8-dihalonaphthalenes via lithium halogen exchanges followed by addition of a suitable diaryl dichalcogenide to afford compounds of the type Nap[X][ER] (Scheme 5.3).[5]



Scheme 5.3 *The preparation of 1-halo-8-(arylchalcogeno)naphthalenes.*[5]

Treatment of 1,8-dibromonaphthalene **11** with two equivalents of *n*-butyllithium resulted in a double lithium halogen exchange reaction and afforded the doubly substituted 1,8-dilithionaphthalene. Two equivalents of diphenyl disulfide reacted with the lithium species and formed 1,8-bis(phenylsulfanyl)naphthalene **37** in 22% yield (Scheme 5.4). Similar reactions were undertaken with analogous starting materials, diphenyl diselenide and diphenyl ditelluride, to afford 1,8-bis(phenylselanyl)naphthalene **38** (75% yield) and 1,8-bis(phenyltellurenyl)naphthalene **39** (37% yield) respectively (Scheme 5.4).



Scheme 5.4 *The preparation of 1,8-bis(phenylchalocgeno)naphthalenes* **37-39**.[5]

For completeness **37-39** were also synthesised from 1,8-diiodonaphthalene **14** using the same procedure as adopted for 1,8-dibromonaphthalene **11** [Yield: **37** 20%, **38** 82%, **39** 23%]. Due to the low yielding nature of synthesising 1,8-dibromo- and 1,8-diiodonaphthalene a new route to compounds **37-39** was desired starting from a cheaper and more accessible starting material. The key intermediate in the synthesis of the bis-chalcogen compounds is 1,8-dilithionaphthalene. The ability to synthesise this compound without the laborious and time consuming preparation of the dihalide compounds should make the overall reaction more efficient.

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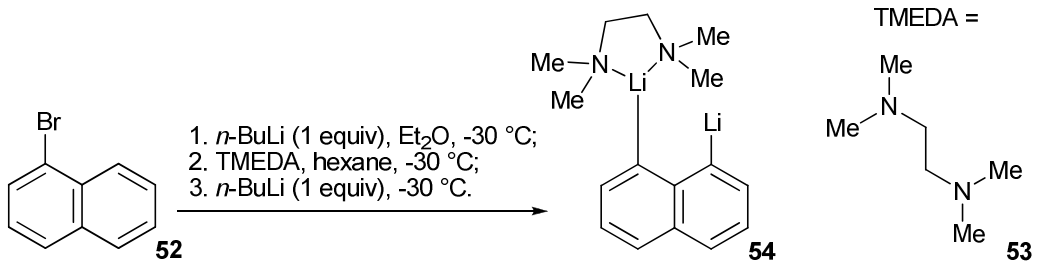
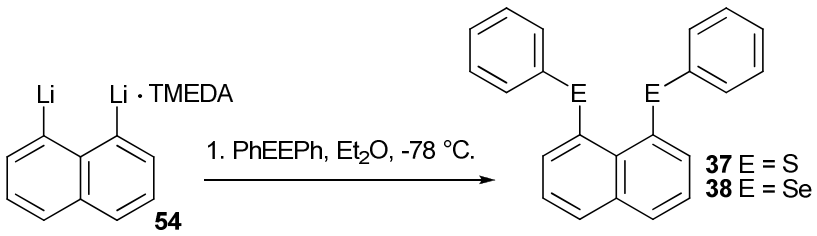
1-bromonaphthalene **52** is cheap and commercially available and reacts with one equivalent of *n*-butyllithium to form the mono-substituted 1-naphthyllithium.[6,7] Further treatment with *n*-butyllithium, as in many cases of 1-substituted naphthalenes, leads to the introduction of the second lithium into the 2-position.[7]

In the presence of tetramethylethylenediamine (TMEDA) **53**, 1-bromonaphthalene **52** undergoes specific metallations through consecutive equivalents of *n*-butyllithium with the second lithium directed to the adjacent *peri*-position. TMEDA has an affinity for lithium and when 1-naphthyllithium and BuLi.TMEDA are refluxed for 3 hours, a bidentate complex dilithionaphthalene·tmeda **54** is formed as the exclusive product in high yield (Scheme 5.5). So far the observed regio-preferences of this reaction have not been adequately determined.[6,7]



Scheme 5.5 *The preparation of 1,8-dilithionaphthalene·tmeda* **54**.[6,7]

The reaction of 1,8-dilithionaphthalene·tmeda **54** with two molar equivalents of diphenyl disulfide affords the corresponding 1,8-bis(phenylsulfanyl)naphthalene **37** in 13% yield (Scheme 5.6). A similar reaction with diphenyl diselenide produced 1,8-bis(phenylselenyl)naphthalene **38** in 14% yield, whilst the preparation of the tellurium analogue **39** from diphenyl ditelluride using the same method was unsuccessful.



Scheme 5.6 *The preparation of* **37** *and* **38** *from 1,8-dilithionaphthalene·tmeda* **54**.

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This route to **37** provides a higher yielding pathway (13% yield) compared to the combined yields of synthesising 1,8-dibromonaphthalene (26 + 22 = 6%) or 1,8-diiodonaphthalene (10 + 20 = 2%) followed by the subsequent lithium halogen exchange reaction to form the product. Preparing **38** by this method affords a higher yielding route (14%) compared to going via 1,8-diiodonaphthalene (10 + 82 = 8%), but the route via 1,8-dibromonaphthalene as an intermediate is higher yielding (26 + 75 = 20%).

The three 1,8-bis(phenylchalcogeno)naphthalenes **37-39** were fully characterised by elemental analysis, infra-red spectroscopy, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. **38** was also analysed by ^{77}Se NMR spectroscopy [δ = 428.6 ppm (lit.,[2] δ = 435.4 ppm)] and similarly **39** was analysed by ^{125}Te NMR spectroscopy [δ = 619.7 ppm, $J_{(Te---Te)}$ 52.7 Hz (lit.,[4] δ = 617 ppm)]. ^{1}H and ^{13}C NMR spectroscopy values for **37**-**39** were in accord with literature values.[2,4]

Crystal structure data was obtained for compounds **37** and **38**. The data for **39**, used throughout this thesis for comparison, is taken from the literature[4] (Table 5.1). Molecular structures of **37**-**39** are shown in Figures 5.5-5.7.[4] The structures and data obtained for **37** and **38** were in close agreement to those reported in the literature.[1,2] Further crystallographic information for **37** and **38** can be found in Appendices 25 and 26.

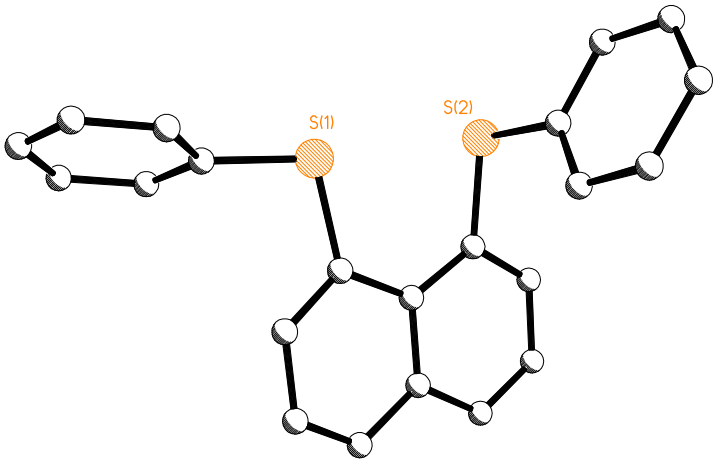

Fig. 5.5 *The crystal structure of 1,8-bis(phenylsulfanyl)naphthalene* **37**.

In all three compounds the E(phenyl) groups lie in close proximity to each other, with non-bonded *peri*-distances (E···E) of 3.0036(13) **37**, 3.1332(9) **38** and 3.287(1) **39**,[4] shorter than the sum of van der Waals radii of the atoms [3.60 Å, 3.80 Å, 4.12 Å] by 0.60-0.83 Å (Table 5.1) suggesting the possible existence of intramolecular interactions.[8]

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The close proximity of the two bulky substituents leads to in-plane and out-of-plane distortion of the *peri*-atoms with respect to the naphthalene ring system. The amount of in-plane distortion of the substituents, indicated by a widening of the bay angles, increases from the bis-sulfide to the bis-telluride compound [373.1(5)° **37**, 373.9(11)° **38**, 375.0(2)° **39**[4]]. The level of displacement of the *peri*-atoms to opposite sides of the best naphthalene plane shows out-of-plane distortion is also enhanced with the increasing size of the *peri*-atoms (Table 5.1).

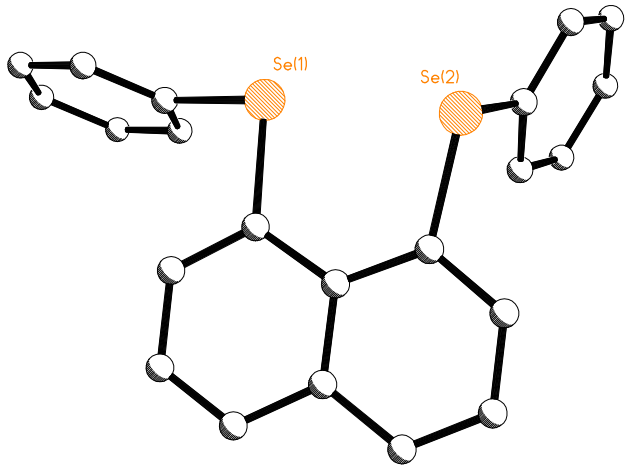

Fig. 5.6 *The crystal structure of 1,8-bis(phenylselenyl)naphthalene* **38**.

The displacement of the *peri*-atoms within and out of the plane is accompanied by a distortion of the usually planar and rigid C_{10}-unit by a twist into a non-planar conformation. This is illustrated by the torsion angles associated with the central C(5)-C(10) bond (Table 5.1). Buckling of the plane is greatest in **38** and **39** (torsion angles further from the linear 180°) with **37** retaining the most planar naphthalene ring system of the three compounds (Figure 5.8).

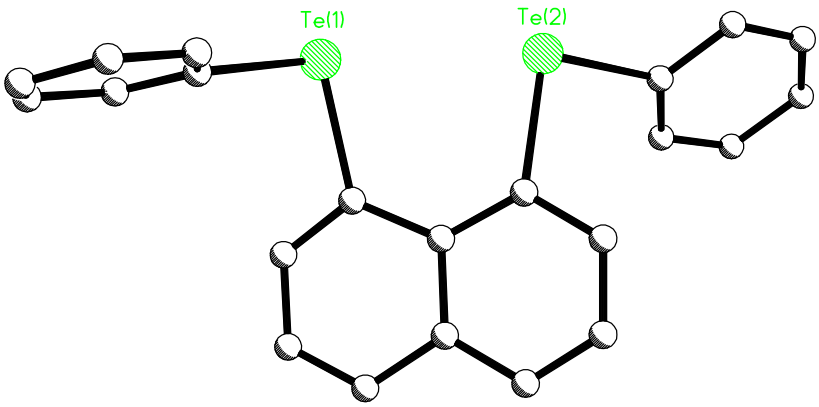

Fig. 5.7 *The crystal structure of 1,8-bis(phenyltellurenyl)naphthalene* **39**.[4]

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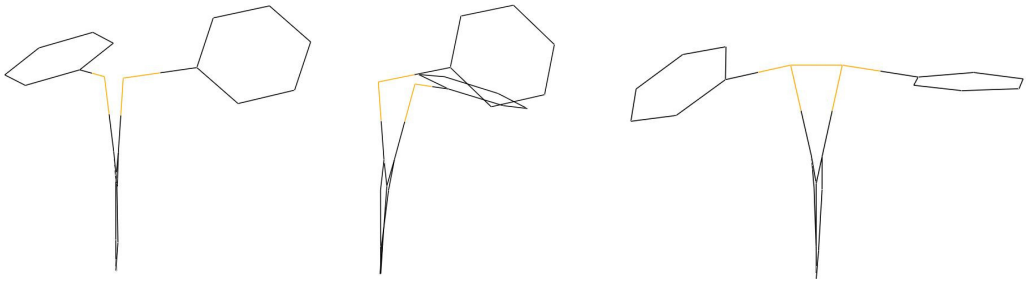

Fig. 5.8 *The structures of 1,8-bis(phenylsulfanyl)naphthalene* **37**, *1,8-bis(phenylselenyl)naphthalene* **38** *and 1,8-bis(phenyltellurenyl)naphthalene* **39**,[4] *showing the planarity of the naphthalene backbone.*

Molecular structures **37** and **38**, as reported by Nakanishi *et al.*,[2] adopt similar orientations of the 'type AB' with one E-C_{Ph} bond aligning close to the naphthyl plane and one roughly perpendicular to it. The tellurium analogue **39** adopts the 'CC-*t* type' structure with both E-C_{Ph} bonds lying at roughly 135° to the naphthyl plane (Figure 5.9).[2,4] Although **37** and **38** both adopt the 'AB type' arrangement the phenyl rings in **37** lie across the naphthalene plane (*trans*) and in **38** lie on the same side of the naphthalene plane (*cis*) (Figure 5.9). The 'CC-*t* type' orientation in **39** sees the phenyl rings *trans* to one another.[2,4]

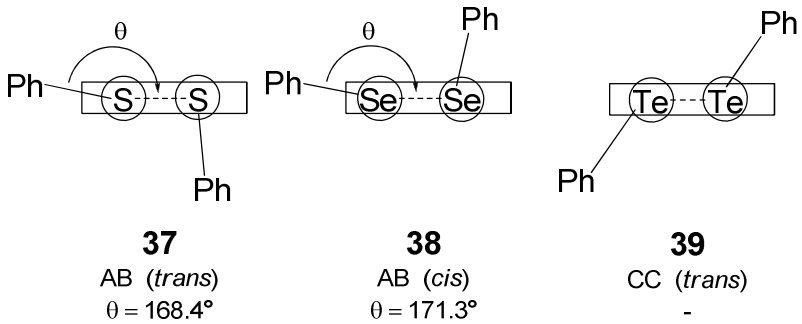

Fig. 5.9 *The structures of* **37-39** *showing the orientation of the E(phenyl) groups, the type of structure and the linear arrangement* C_{Ph}*-E···E'* (**37**,**38**).[2,4]

Only one attractive quasi-linear arrangement [C(11)-S(1)···S(2)] is observed in **37** with an angle of 168.4(1)° and again only one [C(11)-Se(1)···Se(2)] appears in **38** with an angle of 171.3(1)°. There are no similar linear arrangements found in **39** with angles of 145.7(1)° [C(11)-Te(1)···Te(2)] and 154.2(1)° [C(17)-Te(2)···Te(1)].[4]

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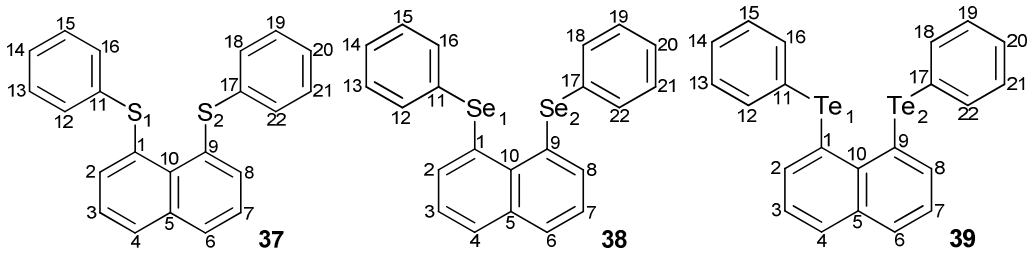
Table 5.1 Selected bond lengths [Å] and angles [°] for 1,8-bis(phenylsulfanyl)naphthalene **37,** 1,8-bis(phenylselenyl)naphthalene **38** and 1,8-bis(phenyltellurenyl)naphthalene **39**.[4]



S(1)-S(2)	**3.0036(13)**	**Se(1)-Se(2)**	**3.1332(9)**	**Te(1)-Te(2)**	**3.287(1)**
S(1)-C(1)	1.794(3)	Se(1)-C(1)	1.922(7)	Te(1)-C(4)	2.14(1)
S(2)-C(9)	1.783(4)	Se(2)-C(9)	1.930(7)	Te(2)-C(6)	2.14(2)
S(1)-C(1)-C(10)	121.8(2)	Se(1)-C(1)-C(10)	123.5(5)	Te(1)-C(1)-C(10)	123(1)
C(1)-C(10)-C(9)	126.8(3)	C(1)-C(10)-C(9)	126.6(6)	C(1)-C(10)-C(9)	128(1)
S(2)-C(9)-C(10)	124.5(2)	Se(2)-C(9)-C(10)	123.8(5)	Te(2)-C(9)-C(10)	124(1)
	Σ = 373.1(5)		**Σ = 373.9(11)**		**Σ = 375.0(2)**
Distance from naphthalene mean plane					
S(1)	0.270(4)	Se(1)	0.468(9)	Te(1)	-0.506(1)
S(2)	-0.163(4)	Se(2)	-0.327(9)	Te(2)	0.565(1)
Torsion angle					
C:(6)-(5)-(10)-(1)	178.6(3)	C:(6)-(5)-(10)-(1)	173.5(6)	C:(9)-(10)-(5)-(4)	174.2(1)
C:(4)-(5)-(10)-(9)	177.2(3)	C:(4)-(5)-(10)-(9)	174.6(6)	C:(1)-(10)-(5)-(6)	175.1(1)

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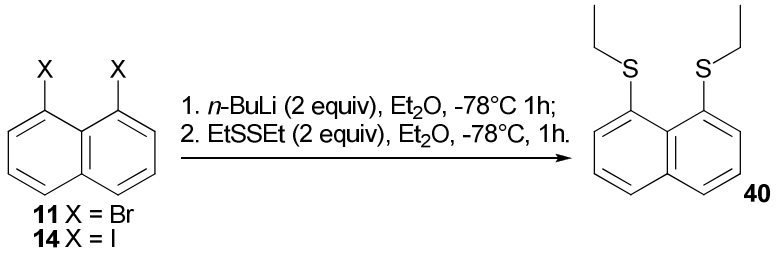
Preparation of the novel compound 1,8-bis(ethylsulfanyl)naphthalene 40

The novel compound 1,8-bis(ethylsulfanyl)naphthalene **40** was synthesised following similar procedures to those used for the preparation of the 1,8-bis(phenylchalcogeno)naphthalenes **37-39**. 1,8-dibromonaphthalene **11** reacted with two molar equivalences of *n*-butyllithium followed by two equivalences of diethyl disulfide to give **40** in 27% yield (Scheme 5.7). The analogous reaction employing 1,8-diiodonaphthalene **14** as the starting point afforded the product in 80% yield (Scheme 28). **40** was fully characterised by elemental analysis, infra-red spectroscopy, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.



Scheme 5.7 *The preparation of 1,8-bis(ethylsulfanyl)naphthalene* **40**.

The molecular structure of **40** is shown in Figure 5.10 and selected bond lengths and bond angles are listed in Table 5.2. Compared to its S(phenyl) analogue **37**, the degree of distortion in the naphthalene geometry of **40** is notably reduced.

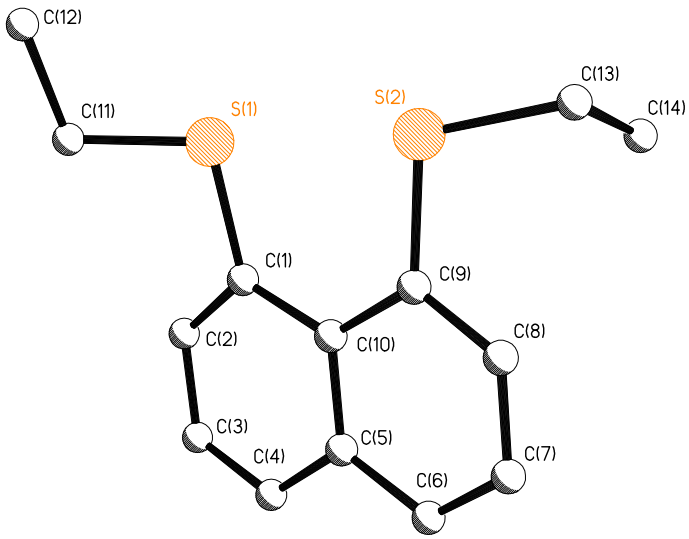


Fig. 5.10 *The crystal structure of 1,8-bis(ethylsulfanyl)naphthalene* **40**.

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The distance between the *peri*-atoms [2.9323(13) Å] is smaller than the distance found in **37** [3.0336(13) Å] and much shorter than the sum of the van der Waals radii of two sulfur atoms [3.60 Å].[8] The sum of the bay region angles shows there is also a reduction in the in-plane distortion going from the S(phenyl) compound **37** [373.1(5)°] to the S(ethyl) compound **40** [370.8(5)°]. Displacement of the two sulfur atoms from the naphthalene plane is seen to be larger in the S(phenyl) compound with the *peri*-atoms of **40** lying 0.182(4) Å and -0.176(5) Å from the naphthalene plane respectively. In both **37** and **40** (Figure 5.11) the naphthalene backbones are relatively planar. Torsion angles for the C(10)-C(5) bond for both compounds also indicates a greater distortion in the S(phenyl) analogue. Selected bond angles and distances for **37** and **40** are compared in Table 5.2, further information for the crystal structure of **40** can be found in Appendix 27.

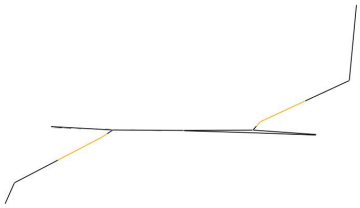

Fig. 5.11 *The molecular orientation of 1,8-bis(ethylsulfanyl)naphthalene* **40**.

Figure 5.11 shows the orientation of 1,8-bis(ethylsulfanyl)naphthalene **40** which adopts the 'BB type' arrangement with the two ethyl moieties lying *trans* to one another.[2] This is different from that observed for the S(phenyl) analogue **37** which adopts the 'type AB'.[2] There is no observed linear arrangement of atoms with angles C(11)-S(1)···S(2) 157.3(1)° and C(13)-S(2)···S(1) 159.6(1)°. Figure 5.12 illustrates the ethyl moieties in **40** adopting different orientations, the C(11)-C(12) bond points up in line with the naphthalene plane and the C(13)-C(14) bond lies roughly perpendicular to the plane.

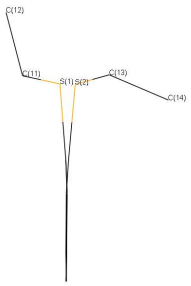

Fig. 5.12 *The molecular orientation of 1,8-bis(ethylsulfanyl)naphthalene* **40** *showing out-of-plane distortion and naphthalene planarity.*

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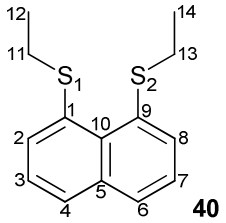
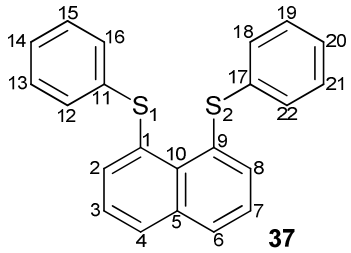
Table 5.2 Selected bond lengths [Å] and angles [°] for 1,8-bis(ethylsulfanyl)naphthalene **40** and 1,8-bis(phenylsulfanyl)naphthalene **37**.





S(1)-S(2)	**2.9323(13)**	**S(1)-S(2)**	**3.0036(13)**
S(1)-C(1)	1.776(4)	S(1)-C(1)	1.794(3)
S(2)-C(9)	1.778(4)	S(2)-C(9)	1.783(4)
S(1)-C(1)-C(10)	122.6(2)	S(1)-C(1)-C(10)	121.8(2)
C(1)-C(10)-C(9)	126.1(3)	C(1)-C(10)-C(9)	126.8(3)
S(2)-C(9)-C(10)	122.1(2)	S(2)-C(9)-C(10)	124.5(2)
	Σ = 370.8(5)		**Σ = 373.1(5)**
Distance from naphthalene mean plane			
S(1)	0.182(4)	S(1)	0.270(4)
S(2)	-0.176(5)	S(2)	-0.163(4)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	-178.7(3)	C(6)-C(5)-C(10)-C(1)	178.6(3)
C(4)-C(5)-C(10)-C(9)	-178.9(3)	C(4)-C(5)-C(10)-C(9)	177.2(3)

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Preparation of 1-halo-8-(phenyltellurenyl)naphthalenes 53,54

In Chapters 2 and 3 we described the single substitution reactions of 1,8-dibromo- **11** and 1,8-diiodonaphthalene **14** in the synthesis of compounds **9**, **20**, **31** and **33** (Figure 5.13). To complete the series the tellurium analogues **55** and **56** were prepared following the same procedure.

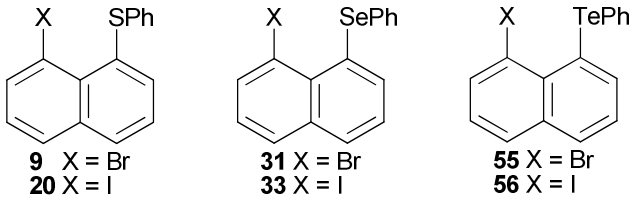

Fig. 5.13 *The products of single substitution reactions of 1,8-dibromo and 1,8-diiodonaphthalene with diphenyl dichalcogenides.*

1,8-dibromonaphthalene **11** and 1,8-diiodonaphthalene **14** both reacted with one equivalent each of *n*-butyllithium and diphenyl ditelluride to give the novel compounds 1-bromo-8-(phenyltellurenyl)naphthalene **55** (32% yield) and 1-iodo-8-(phenyltellurenyl)naphthalene **56** (18% yield) respectively. Both compounds were characterised by elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C and ^{125}Te NMR spectroscopy and mass spectrometry. The ^{125}Te NMR spectra gave signals at δ = 731.23 ppm for **55** and δ = 698.26 ppm for **56**.

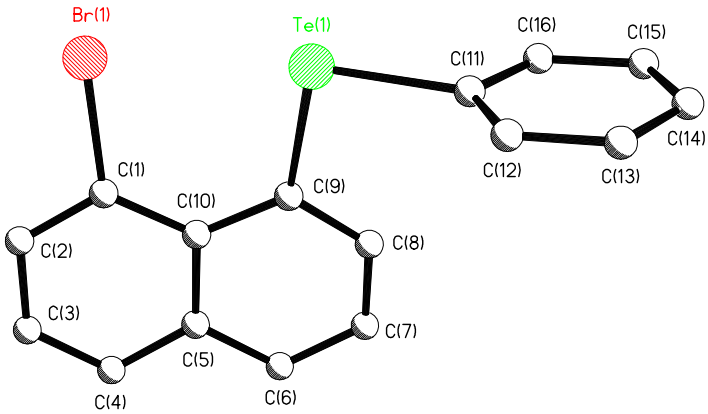

Fig. 5.14 *The molecular structure of 1-bromo-8-(phenyltellurenyl)naphthalene* **55**.

The molecular structure of **55** (Figure 5.14) shows an intramolecular bromine-tellurium *peri*-distance of 3.1909(10) Å, much shorter than the sum of the van der Waals radii for the two *peri*-atoms [3.91 Å].[8]

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Out-of-plane distortion is observed with the tellurium atom Te(1) -0.53(9) Å and the bromine atom Br(1) 0.406(8) Å lying from the mean plane of the naphthalene backbone (Table 5.3). The heavy atoms are further accommodated by in-plane distortions in the C-C-C group between the Br and Se atoms as shown by the sum of the bay region angles [373.6(11)°]. As expected from the heavy atom displacement, the phenyltellurenyl group lies on one side of the naphthalene plane, the phenyl ring being inclined at 87° to the naphthalene plane.

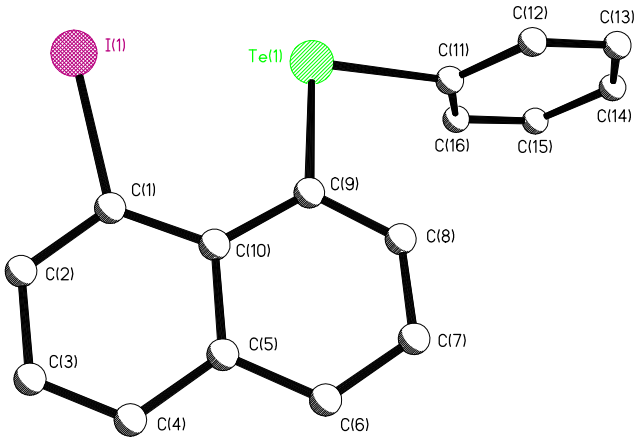

Fig. 5.15 *The molecular structure of 1-iodo-8-(phenyltellurenyl)naphthalene* **56**.

The molecular structure of **56** (Figure 5.15) is similar to its bromine analogue with the phenyltellurenyl group lying on one side of the naphthalene plane and the phenyl ring inclined by 88° to the naphthalene plane. Compared to **55**, the iodine compound exhibits greater strain relief via naphthalene distortion due to increased steric repulsion between the *peri*-atoms. The larger iodine atom is accommodated by a longer intramolecular non-bonded I···Te(phenyl) distance [3.3146(6) Å] compared to the Br···Te(phenyl) distance of 3.1909(10) Å, but this distance is still considerably shorter than the sum of the van der Waals radii of the interacting atoms [4.04 Å].[8]

An increase in the splay of the bay region is seen by comparison of the sums of the *peri*-region angles [**55** 373.6(11)°, **56** 376.2(10)°] and shows a greater in-plane distortion occurs in the iodine compound. Out-of-plane distortion in the two analogues is observed to a similar degree with the I(1) and Te(1) atoms of **56** lying -0.415(9) Å and 0.536(9) Å from the plane respectively. The degree of planarity in the two naphthalene backbones is also comparable with similar C(5)-C(10) torsion angles in the two compounds. Selected bond lengths and angles for **55** and **56** are compared in Table 5.3, further information on the molecular structures can be found in Appendices 28 and 29.

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The difference in the naphthalene distortion when replacing bromine for iodine in compounds **55** and **56** matches the pattern found in the selenium analogues (**31** and **33**) as discussed in Chapter 3. In both cases replacing bromine for iodine increases the amount of steric interaction and therefore naphthalene distortion, best observed by comparing their *peri*-distances [**31** 3.1136(6) Å (BrSe), **33** 3.2524(8) Å (ISe), **55** 3.1909(10) Å (BrTe), **56** 3.3146(6) Å (ITe)]. These values also illustrate that replacing the selenium *peri*-atom for tellurium also increases the degree of steric interaction between the heavy atoms and therefore the amount of strain relief.

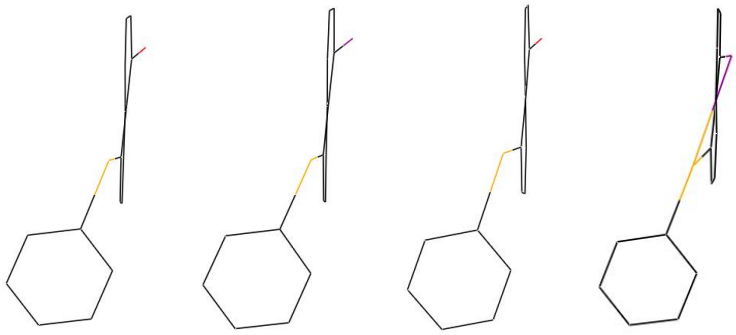

Fig. 5.16 *The orientation of compounds* **31**, **33**, **55** *and* **56** *showing the 'type B structure'.*

All four compounds adopt the same orientation, described by Nakanishi *et al.* as 'type B' structure with E-C bonds lying close to the naphthalene plane (Figure 5.16).[2,3] The E(phenyl) moieties sit in a similar location and produce a linear arrangement of the type X···E-C with similar angles approaching 180° throughout [**31** Br···Se-C 175.7(1)°, **33** I···Se-C 174.3(1)°, **55** Br···Te-C 173.1(1)°, **56** I···Te-C 175.1(1)°] (Figure 5.16). The observed non-bonded distances between X and E in all compounds are shorter than sum of van der Waals radii of the atoms by 0.64 Å for **31**, 0.63 Å for **33**, 0.72 Å for **55,** 0.73 Å for **56**.[8] As described in Chapter 3, according to Nakanishi *et al.*, the linearity of the three atoms X···E-C and the close proximity of the *peri*-atoms is conducive to non-bonded interactions and can be attributed to a 3c-4e type interaction taking place.[2,3]

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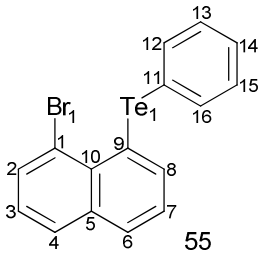
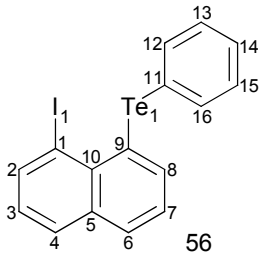
Table 5.3 Selected bond lengths [Å] and angles [°] for 1-bromo-8-(phenyltellurenyl)naphthalene **55** and 1-iodo-8-(phenyltellurenyl)naphthalene **56**.





Br(1)···Te(1)	**3.1909(10)**	**I(1)···Te(1)**	**3.3146(6)**
Br(1)-C(1)	1.917(6)	I(1)-C(1)	2.108(6)
Te(1)-C(9)	2.153(6)	Te(1)-C(9)	2.151(6)
Br(1)-C(1)-C(10)	121.7(6)	I(1)-C(1)-C(10)	123.4(5)
C(1)-C(10)-C(9)	128.6(6)	C(1)-C(10)-C(9)	129.2(5)
Te(1)-C(9)-C(10)	123.3(4)	Te(1)-C(9)-C(10)	123.6(4)
	Σ = 373.6(11)		**Σ = 376.2(10)**
Distance from naphthalene mean plane			
Br(1)	0.4058(84)	I(1)	-0.4152(86)
Te(1)	-0.529(88)	Te(1)	0.5355(86)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	174.8(6)	C(6)-C(5)-C(10)-C(1)	-174.5(6)
C(4)-C(5)-C(10)-C(9)	173.4(6)	C(4)-C(5)-C(10)-C(9)	-175.1(6)

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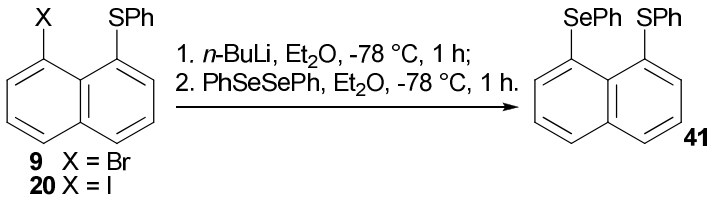
Preparation of mixed chalcogen ligands: 1,8-(chalcogeno)naphthalenes 41-43

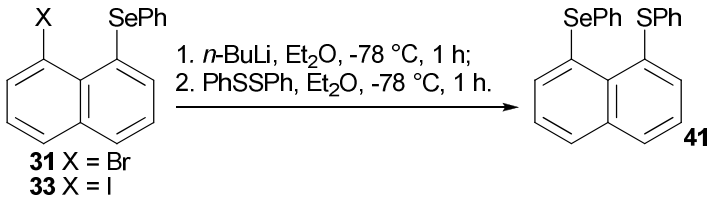
On completing the synthesis of the series of compounds Nap[X][EPh] (X = Br, I; E = S, Se, Te) **9**, **20**, **31**, **33**, **55** and **56**, further substitution reactions were carried out to afford three novel mixed chalcogen ligands. Following the same procedure used in their own preparation, the mono-substituted compounds were reacted via a second substitution reaction involving a lithium halogen exchange and treatment with a suitable dichalcogenide.

Preparation of 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene 41.
1-bromo-8-(phenylsulfanyl)naphthalene **9** and 1-iodo-8-(phenylsulfanyl)naphthalene **20** reacted with *n*-butyllithium and diphenyl diselenide to afford the novel compound 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene **41** in 75% and 63% yield respectively (Scheme 5.8).



Scheme 5.8 *The reaction scheme for the preparation of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene* **41** *from 1-halo-8-(phenylsulfanyl)naphthalenes* **9** *and* **20**.

Analogous reactions starting from 1-bromo-8-(phenylselenyl)naphthalene **31** and 1-iodo-8-(phenylselenyl)naphthalene **33** afforded the desired product **41**, upon treatment with diphenyl disulfide, in lower yields of 34% and 15% respectively (Scheme 5.9). The clear crystals of **41** obtained were characterised by elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy and mass spectrometry. The ^{77}Se NMR spectrum showed a single peak at δ = 455.3 ppm.



Scheme 5.9 *The reaction scheme for the preparation of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene* **41** *from 1-halo-8-(phenylselenyl)naphthalenes* **31** *and* **33**.

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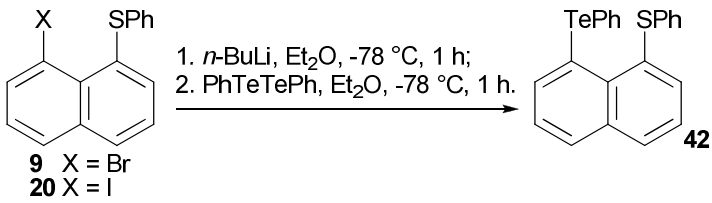
Preparation of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene 42.

The novel compound 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene **42** was synthesised from 1-bromo-8-(phenylsulfanyl)naphthalene **9** and 1-iodo-8-(phenylsulfanyl)naphthalene **20** upon treatment with diphenyl ditelluride in 51% and 88% yield respectively (Scheme 5.10).

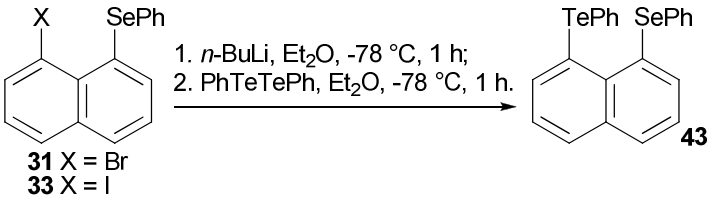


Scheme 5.10 *The reaction scheme for the preparation of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene* **42**.

The preparation of **42** starting from 1-bromo-8-(phenyltellurenyl)naphthalene **55** followed by the addition of diphenyl disulfide was unsuccessful and gave 1-bromo-8-(phenylsulfanyl)naphthalene **9** as the major product. This may indicate the facile cleavage of the Te-C_{Nap} bond is more susceptible to attack by *n*-butyllithium. For this reason the reaction of the iodide analogue **56** was not undertaken. Characterisation of **42** was accomplished by elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy and mass spectrometry. The ^{125}Te NMR spectrum showed a single peak at δ = 715.2 ppm.

Preparation of 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene 43.

Comparable to the synthesis of **42**, 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene **43** could only be prepared upon reaction of either 1-bromo-8-(phenylselenyl)naphthalene **31** or 1-iodo-8-(phenylselenyl)naphthalene **33** with diphenyl ditelluride [81%, 18% yield] (Scheme 5.11).



Scheme 5.11 *The reaction scheme for the preparation of 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene* **43**.

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Characterisation was carried out by elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C, ^{77}Se and ^{125}Te NMR spectroscopy and mass spectrometry. ^{77}Se NMR and ^{125}Te NMR spectra showed single peaks at δ = 362.8 ppm and δ = 687.6 ppm respectively which were in similar ranges compared to compounds **41** [^{77}Se NMR δ = 455.3 ppm] and **42** [^{125}Te NMR δ = 715.2 ppm].

Reaction of 1-bromo-8-(phenyltellurenyl)naphthalene **55** with *n*-butyllithium and diphenyl diselenide gave 1,8-bis(phenylselenyl)naphthalene as the major product, again suggesting the Te-C_{Nap} bond is susceptible to attack and cleavage.

Crystal structure analysis of compounds 41-43

The molecular structures of the mixed chalcogen ligands **41**-**43** are shown in Figures 5.17-5.19 and a comparison of selected bond lengths and angles can be found in Tables 5.4 and 5.5. Both compounds **42** and **43** crystallise with two independent molecules in the asymmetric unit showing similar conformations and distortions. Further information for the three crystal structures can be found in Appendices 30-32.

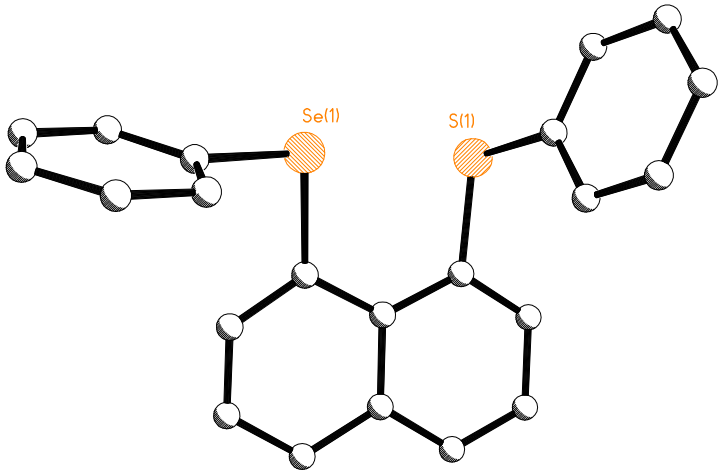

Fig. 5.17 *The crystal structure of 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene* **41**.

Throughout the series there is a general trend for increasing naphthalene distortion with increasing *peri*-atom size. This is best observed by looking at the change in *peri*-distance for the three compounds [**41** 3.063(2) Å, **42A** 3.0684(13) Å, **42B** 3.0984(11) Å, **43A** 3.1919(11) Å, **43B** 3.1580(12) Å]. This finding is supported by comparing the *peri*-distances of the series of bis-chalcogenides **37**-**39** [**37** 3.004(1) Å, **38** 3.1332(9) Å, **39** 3.287(1) Å].

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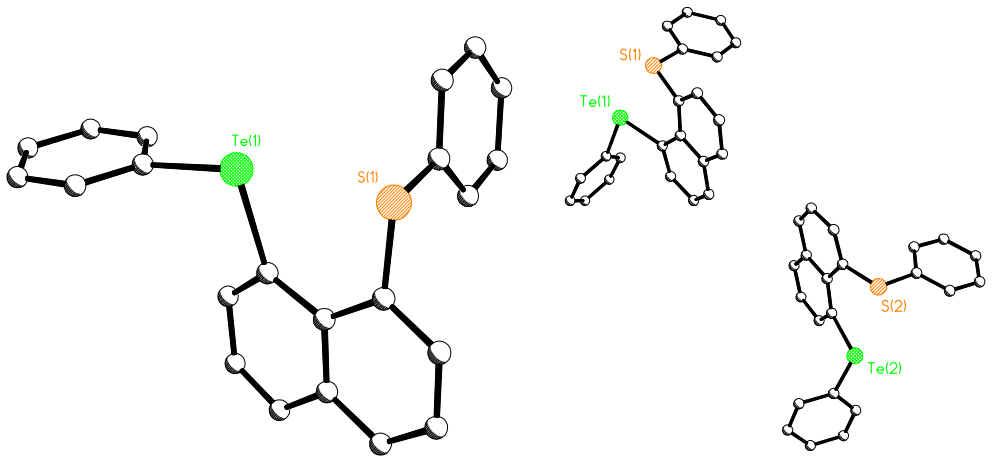

Fig. 5.18 *The crystal structure of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene* **42** *showing two independent molecules in the unit cell.*

The degree of in-plane distortion is comparable for **41** [372.4(13)°] and the two independent molecules of **42** [**A** 371.8(7)°, **B** 372.2(9)°]. A slight increase is observed for the independent molecules of **43** which exhibit a greater widening of their splay angles [**A** 374.3(18)°, **B** 374.7(17)°]. The displacement of the *peri*-atoms above and below the naphthalene plane is found to occur in all five structures for the three compounds with out-of-plane distortion comparable throughout (Tables 5.4 and 5.5).

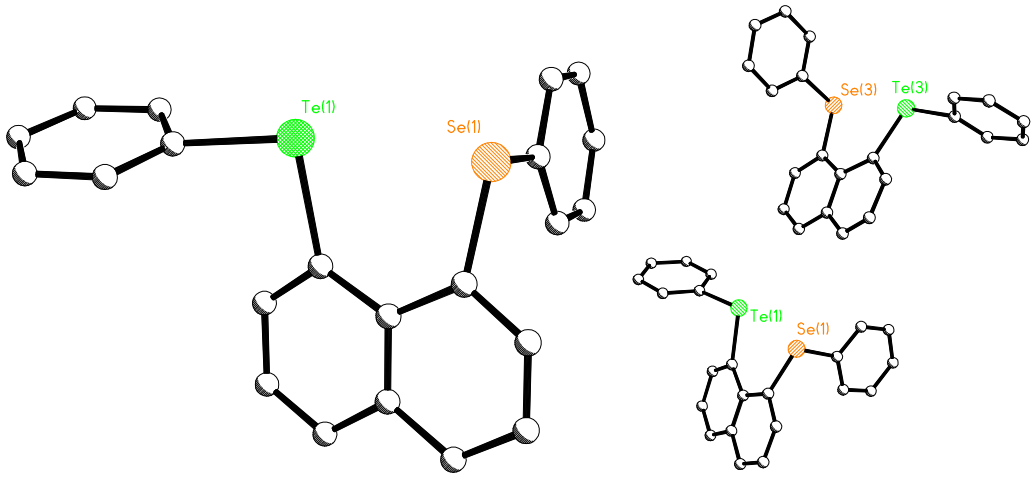

Fig. 5.19 *The crystal structure of 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene* **43**.

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With increasing size of the *peri*-atom across the series there is an unusual increase in the planarity of the naphthalene backbone with the sulfur-selenium containing **41** having the most buckled frame and the selenium-tellurium analogue **43A** having the most planar (see torsion angles, Tables 5.4 and 5.5).

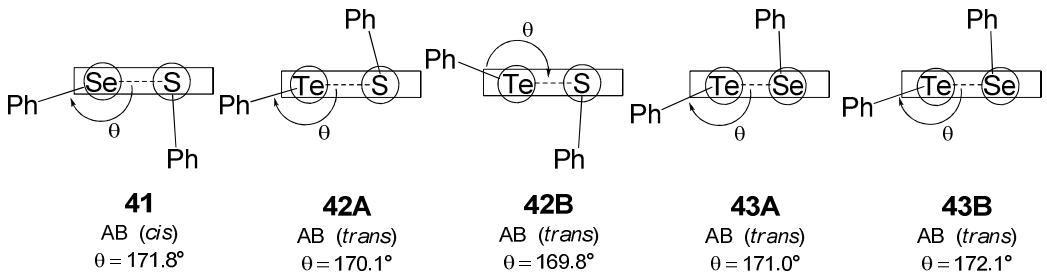

Fig. 5.20 *The orientation of the E(phenyl) groups and type of structure of the mixed compounds* **41**-**43** *and the* C_{Ph}*-E···E' angle.*[2]

All five structures adopt the 'AB type' arrangement[2] with one E-C_{Ph} bond lying close to the naphthyl plane and one approaching perpendicular to the plane (Figure 5.20). The E(Phenyl) groups in **41** adopt a similar (*cis*) arrangement to that of the bis-selenide **38** whilst the independent molecules of **42** and **43** all adopt a *trans* orientation similar to the bis-sulfide analogue **37**. Only one quasi-linear arrangement of the type C-E···E' is observed for each structure, similar to **37** and **38**, with angles in the range of 169-172° (Figure 5.20).

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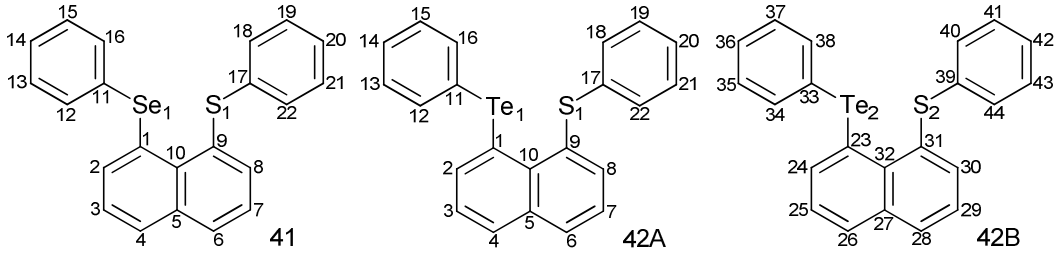
Table 5.4 Selected bond lengths [Å] and angles [°] for **41**, and the two independent molecules **42 A** & **B**.



Se(1)-S(2)	**3.063(2)**	**Te(1)-S(1)**	**3.0684(13)**	**S(2)-Te(2)**	**3.0984(11)**
Se(1)-C(1)	1.907(9)	Te(1)-C(1)	2.141(5)	Te(1)-C(23)	2.100(5)
S(2)-C(9)	1.813(8)	S(1)-C(9)	1.770(5)	S(2)-C(31)	1.771(5)
Se(1)-C(1)-C(10)	122.3(6)	Te(1)-C(1)-C(10)	122.9(3)	Te(2)-C(23)-C(32)	123.2(4)
C(1)-C(10)-C(9)	127.8(7)	C(1)-C(10)-C(9)	126.1(4)	C(23)-C(32)-C(31)	126.1(5)
S(1)-C(9)-C(10)	122.3(6)	S(1)-C(9)-C(10)	122.8(4)	S(2)-C(31)-C(32)	122.9(3)
	Σ = 372.4(13)		**Σ = 371.8(7)**		**Σ = 372.2(9)**
Distance from naphthalene mean plane					
Se(1)	0.432(11)	S(1)	0.1460(67)	S(1)	0.4491(67)
S(2)	-0.320(11)	Te(1)	-0.565(7)	Te(1)	-0.406(7)
Torsion angle					
C:(6)-(5)-(10)-(1)	-175.2(8)	C:(6)-(5)-(10)-(1)	-176.9(6)	C:(28)-(27)-(32)-(23)	176.7(6)
C:(4)-(5)-(10)-(9)	-174.5(8)	C:(4)-(5)-(10)-(9)	-174.6(6)	C:(26)-(27)-(32)-(31)	173.8(5)

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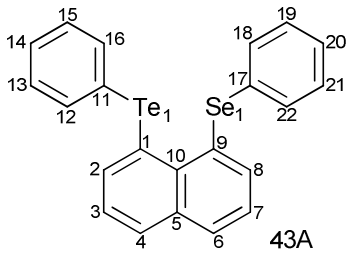
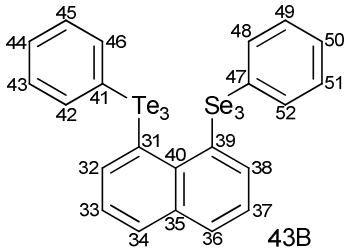
Table 5.5 Selected bond lengths [Å] and angles [°] for the two independent molecules **43 A** & **B**.





Te(1)-Se(1)	**3.1919(11)**	**Te(3)-Se(3)**	**3.1580(12)**
Te(1)-C(1)	2.137(11)	Te(3)-C(31)	2.124(10)
Se(1)-C(9)	1.920(12)	Se(3)-C(39)	1.925(10)
Te(1)-C(1)-C(10)	125.2(9)	Te(3)-C(31)-C(40)	126.4(6)
C(1)-C(10)-C(9)	125.5(10)	C(31)-C(40)-C(39)	124.9(9)
Se(1)-C(9)-C(10)	123.6(7)	Se(3)-C(39)-C(40)	123.4(9)
	Σ = 374.3(18)		**Σ = 374.7(17)**
Distance from naphthalene mean plane			
Te(1)	0.372(15)	Te(3)	-0.500(14)
Se(1)	-0.425(15)	Se(3)	0.170(14)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	-177.4(12)	C(36)-C(35)-C(40)-C(31)	-174.8(13)
C(4)-C(5)-C(10)-C(9)	-175.0(12)	C(34)-C(35)-C(40)-C(39)	-176.9(13)

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Oxidation reactions of 1,8-bis(phenylsulfanyl)naphthalene 37

Compounds **47** and **48** (Figure 5.21), as revealed earlier in the chapter, were reported in 2002 by Kálmán *et al.* during investigations into non-bonded S···S and S···O interactions.[1]

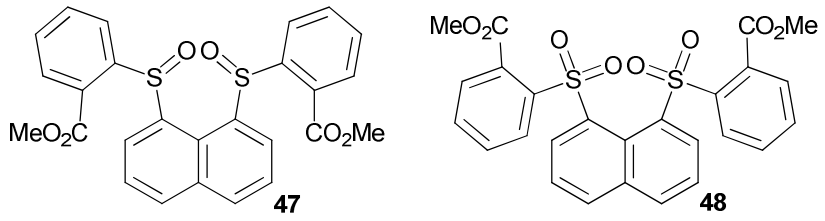
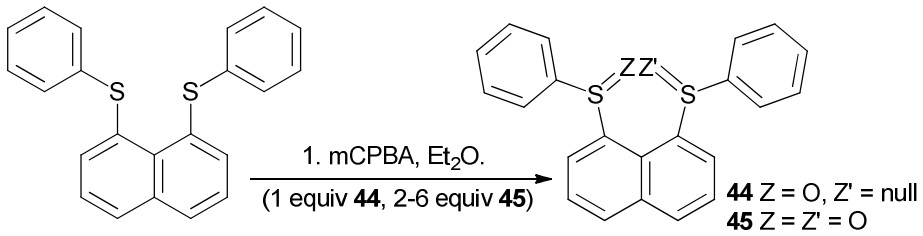


Fig. 5.21 *The 1,8-disubstituted naphthalene derivatives* **47** *and* **48** *reported by Kálmán et al. during investigations into S···S and S···O non-bonded interactions.*[1]

We envisaged that reacting 1,8-bis(phenylsulfanyl)naphthalene **37** with different molar equivalents of mCPBA would afford a series of mono, di, tri and tetra-oxides similar in design to **47** and **48**. Reaction of **37** with a single equivalence of mCPBA in diethyl ether afforded the novel mono-substituted oxide **44** (Scheme 5.12). Two equivalents of mCPBA reacting with **37** produced the di-oxide **45** with both sulfur atoms mono-oxidised (Scheme 5.12). The reaction of further equivalents (3-6) of mCPBA with **37** gave compound **45** exclusively and no higher oxidation to form the tri- or tetra-oxide was observed.



Scheme 5.12 *The reaction scheme for the preparation of the oxidised compounds* **44** *and* **45**.

44 and **45** were fully characterised by elemental analysis, infra-red spectroscopy, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.

Notable differences are observed in the ^{1}H NMR spectra for the two oxides with peaks for non-equivalent phenyl rings easily distinguished for **44** as well as individual naphthyl proton peaks.

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The data for **45** is consistent for an NMR symmetrical compound and shows half the number of signals than the spectra of **44**. Suitable single crystals for the two compounds were grown by diffusion of pentane into saturated solutions of the oxides in dichloromethane. The molecular structures are shown in Figures 5.22 and 5.23. Selected bond distances and angles are listed in Table 5.6 and further crystallographic information can be found in Appendices 33 and 34.

Although these two oxides contain sulfur atoms of different valence states positioned at the *peri*-positions, the close proximity of these atoms is comparable[1] between the two compounds [**44** 3.0460(11) Å, **45** 3.0757(13) Å]. These non-bonded *peri*-distances are found to be slightly higher than the non-oxidised ligand **37** [3.0036(13) Å], but still within the sum of van der Waals radii for two interacting sulfur atoms [3.60 Å].[8]

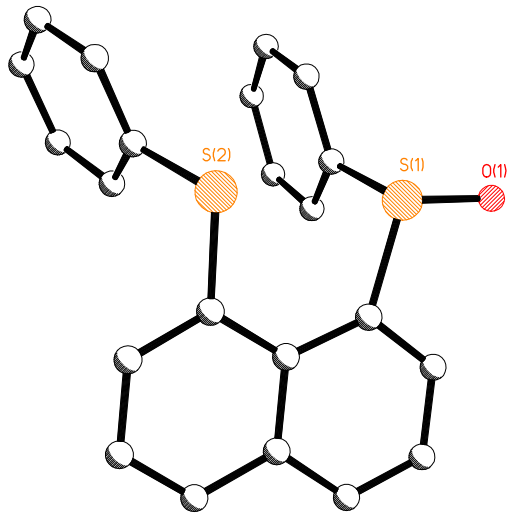

Fig. 5.22 *The molecular structure of 1-(phenylsulfinyl)-8-(phenylsulfanyl)naphthalene* **44**.

The close proximity of the two bulky substituents leads to in-plane and out-of-plane distortion of the *peri*-atoms with respect to the naphthalene ring system. The amount of in-plane distortion of the sulfur atoms, indicated by a widening of the bay angles, is virtually the same in both oxides [375.3(5)° **44**, 375.2(6)° **45**] and greater than the distortion taking place in the non-oxidised **37** [373.1(5)°]. The level and orientation of *peri*-atom displacement above and below the naphthalene plane occurs differently in the two oxides. Out-of-plane distortion in **44** is observed with S(1), S(2) and O(1) all lying above the naphthalene plane whilst in **45** S(1), S(2) and O(1) lie below the plane and O(2) lies above the plane (Table 5.6). The degree to which these atoms are displaced is also different with greater distortion found in di-oxide **45** (Table 5.6).

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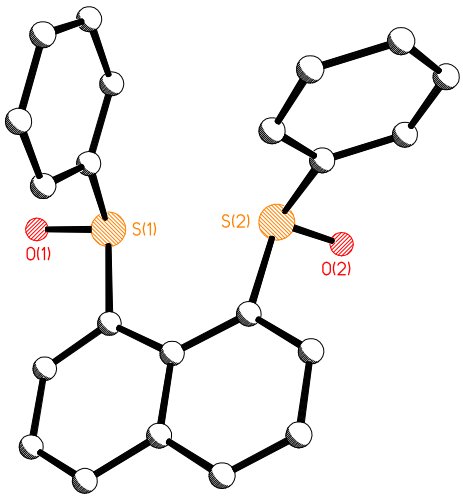

Fig. 5.23 *The molecular structure of 1,8-bis(phenylsulfinyl)naphthalene* **45**.

Torsion angles associated with the central C(5)-C(10) naphthalene bond (Table 5.6) show both oxides contain relatively planar backbones with the mono-oxide **44** containing the most distortion (Figure 5.26). Both compounds have naphthalene structures which are more planar than the non-oxidised compound **37**.

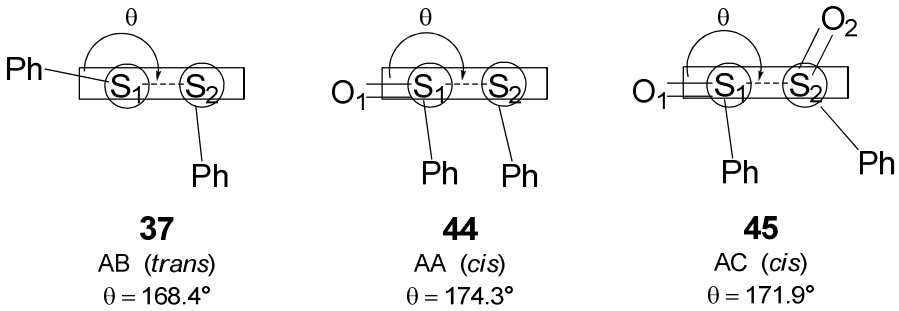

Fig. 5.24 *Comparing the orientation of 1,8-bis(phenylsulfanyl)naphthalene* **37** *and oxides* **44** *and* **45**.[2]

Oxides **44** and **45** adopt different structural arrangements compared to the 'AB-*t* type' arrangement[2] of the non-oxidised **37** (Figure 5.24).[2] In **44**, both S-C_{Ph} bonds lie roughly perpendicular to and on the same side of the naphthyl plane ('AA-*cis* type')[2] with the linear arrangement O(1)=S(1)···S(2) lying along the naphthyl plane [174.3(1)°] (Figure 5.24/5.25). **45** adopts a similar structure but one of the S-C_{Ph} bonds lies closer to 135° and so is thus classified as adopting the 'AC-*cis* type' arrangement[2] (Figure 5.24/5.25).[2]

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The same linear arrangement of the type O(1)=S(1)···S(2) [171.9°] is observed and the second oxygen atom taking up position on the opposite side of the naphthalene plane gives an S(1)···S(2)=O(2) angle of 120.8(1)°. Again the linearity of the three atoms O(1)=S(1)···S(2) and the close proximity of the sulfur atoms is conducive to non-bonded interactions and could be attributed to a 3c-4e type interaction taking place.[5]

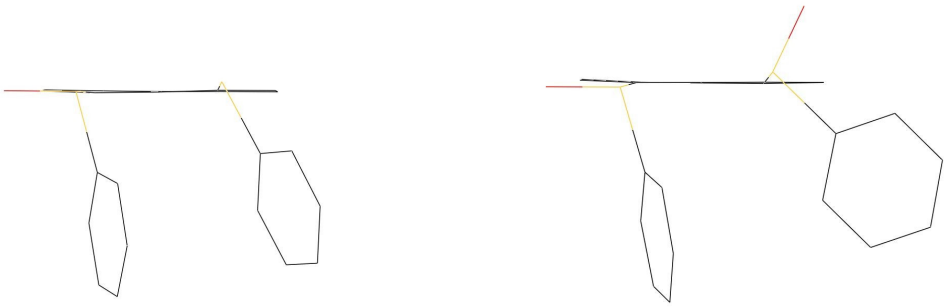

Fig. 5.25 *The crystal structures of* **44** *and* **45** *showing the orientation of the phenyl substituents.*

The arrangement of the 'type AA-*cis*'[2] in compound **44** allows for the close configuration and overlap of the two phenyl rings.[9] The alignment of the rings is face-to-face offset arrangement with slipped packing, known as parallel displacement (see Chapter 3, Figure 5.26/5.27).[9] The distance between the two interacting centroids [3.821(1) Å] is at the top end of the range for typical centroid-centroid π-stacking [3.3-3.8 Å][9] so possible π-π stacking could be envisaged (Figure 5.27).[9]

Fig. 5.26 *The crystal structures of* **44** *and* **45** *showing the planarity of the naphthalene backbones and the overlap of the phenyl rings.*

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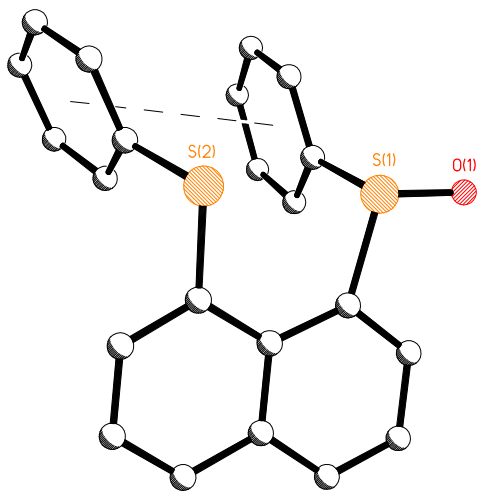

Fig. 5.27 *The crystal structure of* **44** *showing the overlap of the phenyl rings.*

The 'AC type' arrangement[2] in **45** inhibits phenyl ring overlap with the S-C_{Ph} moiety of the 'C type' arrangement being inclined at a greater angle from the naphthalene plane compared to the moiety adopting the 'A type' arrangement[2] (phenyl ring on S(1)). The phenyl ring bonded to S(2) is also twisted upwards impeding phenyl ring interaction resulting in no π-π stacking taking place (Figure 5.25/5.26).

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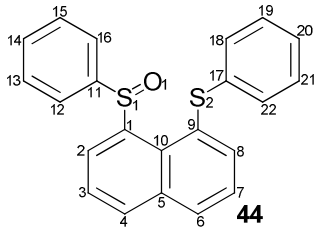
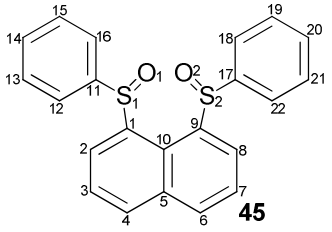
Table 5.6 Selected bond lengths [Å] and angles [°] for the oxides of 1,8-bis(phenylsulfanyl) naphthalene **37**, **44** and **45**.





S(1)-S(2)	**3.0460(11)**	**S(1)-S(2)**	**3.0757(13)**
S(1)-C(1)	1.830(3)	S(1)-C(1)	1.814(3)
S(2)-C(9)	1.774(3)	S(2)-C(9)	1.804(3)
S(1)-O(1)	1.500(2)	S(1)-O(1)	1.497(3)
		S(2)-O(2)	1.486(3)
S(1)-C(1)-C(10)	126.8(2)	S(1)-C(1)-C(10)	125.7(2)
C(1)-C(10)-C(9)	126.4(3)	C(1)-C(10)-C(9)	128.0(3)
S(2)-C(9)-C(10)	122.1(2)	S(2)-C(9)-C(10)	121.5(3)
	Σ = 375.3(5)		**Σ = 375.2(6)**
Distance from naphthalene mean plane			
S(1)	0.0095(39)	S(1)	0.1206(45)
S(2)	0.2103(39)	S(2)	-0.2127(44)
O(1)	0.0203(51)	O(1)	0.1291(58)
		O(2)	-0.15452(56)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	-179.4(3)	C(6)-C(5)-C(10)-C(1)	-179.5(3)
C(4)-C(5)-C(10)-C(9)	-177.7(3)	C(4)-C(5)-C(10)-C(9)	179.0(3)

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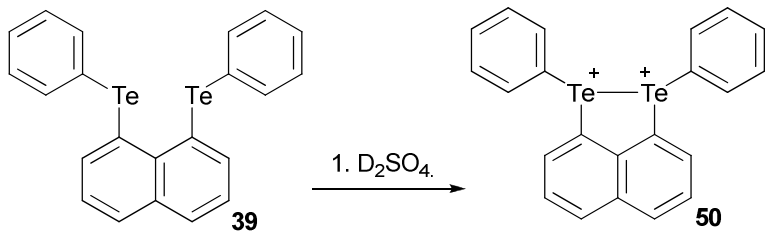
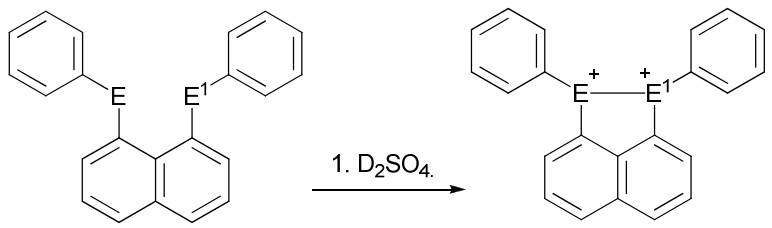
^{77}Se and ^{125}Te NMR Studies

As previously mentioned, with the help of ^{125}Te NMR spectroscopy studies, Furukawa *et al.* reported the oxidation of 1,8-bis(phenyltellurenyl)naphthalene **39** and proposed the formation of the dication species **50** (Scheme 5.13).[4] The ^{125}Te NMR signal of a solution of **39** in D_2SO_4 [δ = 964 ppm] showed a significant downfield shift compared to the signal for a solution of **39** in $CDCl_3$ [δ = 617 ppm].[4] The large shift was proposed to be due to the formation of the dication.[4]



Scheme 5.13 *The oxidation reaction of* **39** *with D_2SO_4 as reported by Furukawa et al..*[4]

Following the synthesis of 1,8-bis(phenylselenyl)naphthalene **38** and the three mixed chalcogen compounds **41-43**, ^{77}Se and ^{125}Te NMR spectra were run in D_2SO_4 to try and elucidate if similar cationic species could be created from these compounds (Scheme 5.14).



Scheme 5.14 *The oxidation reaction of chalcogen compounds with D_2SO_4.*[4]

The results of the ^{77}Se and ^{125}Te NMR studies are shown in Table 5.7. For each NMR experiment there is a significant downfield shift in the signal for spectra run in D_2SO_4 compared to the signal for the spectra run in $CDCl_3$. These results are in agreement with the work undertaken by Furukawa *et al.* and the downfield shift could be due to the formation of the cationic species depicted in Scheme 5.14.[4]

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Table 5.7 ^{77}Se and ^{125}Te NMR spectroscopy data [δ (ppm)] run in $CDCl_3$ and D_2SO_4 for **38** and **41-43**

	38	**41**	**42**	**43**
***peri*-atoms**	**SeSe**	**SeS**	**TeS**	**TeSe**
^{77}Se NMR ($CDCl_3$)	428.6	455.3	-	362.8
^{77}Se NMR (D_2SO_4)	828.0	927.3	-	554.7
^{125}Te NMR ($CDCl_3$)	-	-	715.2	687.6
^{125}Te NMR (D_2SO_4)	-	-	1018.3	1279.6

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Summary

Repulsive steric strain caused by inserting increasingly larger atoms at the 1,8-positions in the six chalcogen analogues **37**-**39** and **41**-**43** is shown to be relieved to a greater extent as the overall combined size of the *peri*-atoms increases. The primary parameter used to quantify the amount of strain relief in non-ideal naphthalenes is the *peri*-distance which encapsulates all molecular deviations in one entity. Table 5.8 lists the six chalcogen containing compounds in order of *peri*-atom combined size and compares the change in *peri*-distance as the combined atom size increases.[8] The values suggest that increasing degrees of steric strain occurring in the molecule due to enhanced *peri*-atom size are relieved by greater naphthalene distortions, observed by a general increase in the *peri*-distance.

Table 5.8 Comparison of the *peri*-distance [Å] and the sum of van der Waals radii of *peri*-atoms [Å] for the chalcogen containing compounds **37-39** and **41-43**[8]

compound	*peri*-atoms	VDWs[8]	*peri*-distance
37	S···S	3.60	3.00
41	S···Se	3.70	3.06
38	Se···Se	3.80	3.13
42A	S···Te	3.86	3.07
42B	S···Te	3.86	3.10
43A	Se···Te	3.96	3.19
43B	Se···Te	3.96	3.16
39	Te···Te	4.12	3.29

The chalcogenides generally adopt a similar structure with one phenyl moiety aligning with the naphthyl plane and one perpendicular to it ('AB type').[2] The bis-telluride **39** with the largest steric interaction between its *peri*-atoms adopts a different arrangement and places its two phenyl rings at angles close to 135° to the plane ('CC type').[2]

Upon oxidation, the structure of bis-sulfide **37** is dramatically changed and adopts either an 'AA type' arrangement **44** or 'AC type' arrangement **45**.[2] The overriding factor in these two structures is the linear arrangement of the type O(1)=S(1)···S(2) which forces the two phenyl rings in both cases to align on the same side of the naphthalene plane. In compound **44** this overlap is close enough for possible π-π stacking to occur.[9]

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In all compounds in this chapter (excluding bis-telluride **39**) there is one quasi-linear arrangement of three atoms, two of which are the *peri*-atoms. In each case the non-bonded distance is well within the sum of van der Waals radii of the two interacting atoms. The linearity and close proximity of non-bonded atoms could suggest that possible 3c-4e bonding as reported by Nakanishi *et al.* could occur.[2,10]

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Chapter 6

Hypervalent adducts of chalcogen substituted naphthalenes

Reactions of sulfur, selenium and tellurium with dihalogens

Organic molecules containing the Group 16 donor atoms sulfur, selenium and tellurium react with dihalogens (Br_2, I_2) and inter-halogens (IBr, ICl) to form a variety of addition complexes with wide structural diversity. Although well-known, reactions of this type have received renewed attention over the last few years due to both the structural interest in the addition products as well as perceived applications in a wide array of research fields including synthetic, biological, material and industrial chemistry.[1,2]

Experimental conditions control the pathway these reactions take and subsequently the structural motifs and geometry around the Group 16 atoms in the addition products. Factors such as the type of chalcogen donor atom, the form of the dihalogen or inter-halogen, the stoichiometry of the reactants and the nature of the donor atoms R group(s) all play a role in determining the structure of these compounds.[1,2]

To date these reactions have produced products exhibiting charge-transfer (C.-T.) 'spoke' and 'extended spoke' adducts, polyiodide, see-saw, ionic, 'T-shaped', bent, mixed-valence, dication-bridged and dimeric structural motifs. Three classical ionic structures are also known for products having chalcogen–halogen terminal bonds ($[RE–X]^+$),[1-4] two chalcogen-halogen coordinated complexes ($[RE–X–ER]^+$),[1,2,5–7] and dications incorporating a chalcogen–chalcogen single bond ($[RE–ER]^{2+}$).[1-3,8] These ionic compounds are often accompanied by counteranions of polyhalides which adopt unusual and sometimes complex structures.[1,2,4,5]

Husebye proposed that the final structure from reactions between chalcogen-donors [RE] and di- and inter-halogens could be predicted because the end products were derived from a common intermediate species $[RE–X]^+$ and followed a general reactive pathway.[1,2,9] In this way the dication species $[RE–ER]^{2+}$ along with the C.-T. 'spoke' and 'T-shaped' hypervalent adducts could be prepared; nucleophilic attack occurring at the chalcogen or the halogen site of the $[RE–X]^+$ cation.[1,2]

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The neutral charge-transfer (C.-T.) 'spoke' adduct featuring a quasi-linear E–X–Y alignment (X = Y = I, Br; X = I, Y = Br, Cl)[1,2,10,11] and the 'T-shaped' X–E–Y fragment of the insertion adduct (X = Y = I, Br, Cl; X = I, Y = Br)[1,8,12,13] are the two most common structural motifs generated from the reaction of chalcogen-donors [RE] with inter- or di-halogens. Both linear arrangements are similar to the linear trihalide anions (I_3^-, Br_3^-, IBr_2^-, and ICl_2^-) with the chalcogen atom having the ability to acquire more than the required octet of electrons in the valence shell. These types of compounds are termed hypervalent.[14,15]

Hypervalency of the 'higher' main group elements continues to intrigue chemists and the reasons behind its existence are still under debate. For a considerable period, the availability of low-lying unfilled *d*-orbitals which could accommodate the additional electrons was thought to occur. This is known as valence shell or octet expansion.[14] The rarity of hypervalency in Period 2 was therefore attributed to the lack of 2d orbitals. This however, could just as easily be due to the difficulty of packing more than four atoms around a small central atom.[14]

Another explanation is aptly demonstrated by the molecular orbital energy diagram for the octahedral and hypervalent SF_6 molecule, containing a hexacoordinate sulfur atom (Figure 6.1). A simple basis set consisting of ten atomic orbitals (the valence shell s and p orbitals of sulfur and one p orbital from each of the six fluorine atoms) can be used to create ten molecular orbitals. Calculations by Reed and Weinhold indicate that four of these orbitals are bonding, two are non-bonding and four are antibonding.[16] As illustrated by Figure 6.1, four bonding orbitals and two non-bonding orbitals are occupied by the twelve electrons without the use of the antibonding orbitals. This theory therefore accounts for hypervalency and the formation of SF_6 without the use of low lying 3d orbitals on sulfur.[14]

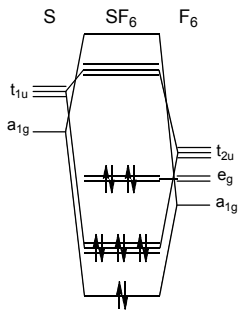

Fig. 6.1 *The molecular orbital energy diagram for the hypervalent SF_6 molecule.*[14]

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Recently, based on quantum chemical calculations, the concept of a three centre four-electron bond (3c-4e) has become a favoured concept for explaining the existence of hypervalency. The 3c-4e bond was first proposed by Rundle during structural studies of XeF_4 and XeF_2.[17]

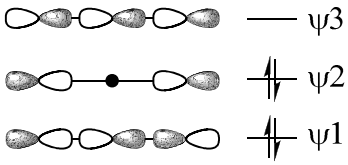

Fig. 6.2 *An approximate representation of a molecular orbital model for hypervalent X-E-X 3c–4e bonds.*[17,18]

Figure 6.2 is an approximate representation of the molecular orbitals for a hypervalent X-E-X three centre-four electron bond as proposed by Rundle and shows bonding (ψ1), non-bonding (ψ2) and anti-bonding (ψ3) orbitals.[17] The four electrons occupy the bonding (ψ1) and the non-bonding (ψ2) molecular orbitals. Electrons in (ψ2) localise on X of X-E-X so terminal atoms are required to be more electronegative than the central atom. Consequently hypervalent X-E-X bonds are weaker than electron pair bonds between the same elements as only one bonding pair is available for the two bonds. The bond orders of apical E-X bonds in hypervalent 3c-4e are normally less than one (~0.5) with bond distances for bond orders of 0.5 predicted to be 0.18 Å longer than bond orders of 1.0.[17-19]

In 2001 du Mont *et al.* used structural analysis to review selenium-iodine interactions ranging from weak van der Waals contacts to strong covalent bonds (3.8-2.4 Å).[15] They proposed that distances below 2.60 Å were predominantly covalent in nature, 2.60-3.00 Å are typical of 3c-4e bonding with 3.00-3.90 Å represented by weak van der Waals interactions (3.90 Å being the sum of I and Se van der Waals radii).[15,18] Consequently the region for 3c-4e bonding was proposed to be roughly the sum of the van der Waals radii for the interacting species minus ~1.0 Å.[18]

In solution, the C.-T. 'spoke' adduct and the 'T-shaped' adduct of $RR^1E{\cdot}X_2$ type compounds are in equilibrium as illustrated in Scheme 6.1.[15,18,20] Structural determination of the final product can be achieved with a generalisation based on the degree of charge-transfer between the non-bonding orbitals of the chalcogen donor n(E) to the LUMO of the di- or inter-halogen acceptor σ^*(X-X). This can be estimated from the electronegativity (χ) of the elements. Most of the observed structures for R of standard organic groups follows the loose rule that the 'T-shaped' (TBP) adduct will be formed if halide X is more electronegative than chalcogen E [$RE^{\delta+}$-$X^{\delta-}$] whilst if the

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converse is true then the C.-T. 'spoke' adducts will predominate.[18,20,21] This is exemplified by the fact that no C.-T. adducts are known for Te-donors [χ(Te) 2.08][22] with any di- or inter-halogen [χ(F) 3.94- χ(I) 2.36].[1,2,22]

Scheme 6.1 *The equilibrium between $RR^1E{\cdot}X_2$ (C.-T. 'spoke') and $RR^1E{\cdot}X_2$ ('T-shaped') in solution.*[15,18,20]

It must be recognised however, that the electronegativity of the chalcogen atom and the electronic property of RR^1E can be affected by the R groups which can influence the outcome of the reaction. Compounds with bulky groups around E will favour the 3 coordinate chalcogen of C.-T. 'spoke' adducts over the 4 coordinate chalcogen of 'T-shaped' adducts.[18,20] It is therefore possible to prepare compounds that do not conform to the general rule based on χ values by modifying the electronic and steric properties of the surrounding R groups.[18]

Charge-transfer (C.-T.) 'spoke' adducts and 'T-shaped' insertion adducts.

The 'spoke' adducts form a quasi-linear E-X-Y fragment via the transfer of electron density from non-bonding orbitals of the chalcogen donor atom into the LUMO of the di- or inter-halogen acceptor molecule (hence termed charge-transfer adducts). As mentioned above, the C.-T. 'spoke' adducts generally form when χ(E) > χ(X), *i.e.* there is more electron density available on E to promote into the empty orbitals on X. This has the effect of lowering the X-Y bond order and consequently increasing the X-Y bond length.[1,2]

The majority of neutral C.-T. 'spoke' adducts reported in the literature are formed by reaction of organosulfur [χ(S) 2.58][22] donors with di-iodine [χ(I) 2.36],[1,2,7,11,22,23] for example benzyl sulfide diiodine (Figure 6.3).[24] Organoselenium diiodine C.-T. adducts are less common but those reported in the literature exhibit a considerable increase in the iodine-iodine bond length from free iodine (2.66 Å)[26] compared to similar sulfur compounds.[25] This increase is found to be on average nearly double that for organosulfur adducts showing organoselenides are better donor molecules than organosulfides [χ(Se) 2.35, χ(S) 2.58].[1,2,22]

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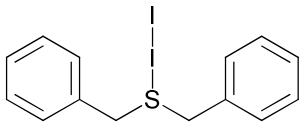

Fig. 6.3 *The C.-T. 'spoke' structure of benzyl sulfide diiodine showing a linear S-I-I arrangement.*[24]

Whilst few adducts resulting from reactions of sulfur- and selenium-donors with the inter-halogens (IBr, ICl)[1,2,23,27] have been reported, all those structurally characterised in the literature exclusively adopt the C.-T. 'spoke' design. The greater acceptor capacity of IBr over I_2 is illustrated by comparing the inter-halogen compound 1,4-dithiane·2IBr with its isostructural diiodine analogue (Figure 6.4).[28,29] The sulfur-iodine distance in the IBr adduct [2.687(2) Å] is significantly shorter compared to the I_2 adduct [2.867(6) Å] and shows there is a stronger sulfur–acceptor interaction taking place in the inter-halogen adduct.[28,29]

Fig. 6.4 *The C.-T. 'spoke' structures of isostructural compounds 1,4-dithiane (bis) diiodine and 1,4-dithiane·2IBr.*[28,29]

Reaction of dibromine with S- and Se-donors produces adducts of different geometries. Following the general rule based on electronegativity values, reaction of S- [χ(S) 2.58] and Se- [χ(Se) 2.48] donors with dibromine [χ(Br) 2.68] should produce 'T-shaped' compounds [χ(X) > χ (E)].[18,20,21,22] Interestingly all known organosulfur dibromine compounds adopt the C.-T. 'spoke' structure with an Se-Br-Br linear arrangement whilst all structurally reported selenium compounds exclusively adopt the 'T-shaped' structure with a Br-Se-Br linear arrangement (Figure 6.5).[25,30-32]

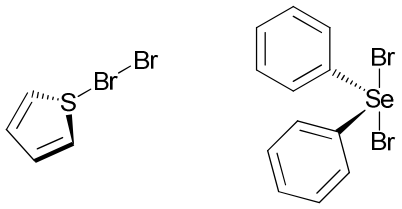

Fig. 6.5 *The C.-T. 'spoke' structure of thiophane·Br_2 and the 'T-shaped' structure of diphenylselenium·Br_2.*[31,32]

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The difference in the two structures can be attributed to the greater electron donor ability of selenium over sulfur. Dibromine is a strong acceptor and reacts with selenium to form a strong donor-strong acceptor system sufficient enough to be able to cleave the Br-Br bond and oxidation of the selenium atom occurs.[1,2]

The greater oxidising power (or acceptor ability) of dichlorine over dibromine enables bis(4-chlorophenyl) sulfide chloride to form the expected 'T-shaped' geometry [χ(X) > χ (E)].[18,20,21] Greater charge is donated from sulfur [χ(S) 2.58][22] into the anti-bonding orbital of the dichlorine molecule [χ(Cl) 3.00][22] enabling cleavage of the Cl-Cl bond. Subsequently the sulfur atom is oxidised and the 'T-shaped' adduct is formed (Figure 6.6).[21]

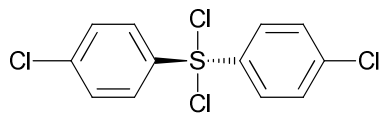

Fig. 6.6 *The 'T-shaped' structure of bis(4-chlorophenyl) sulfide dichloride.*[21]

Structural parameters of charge-transfer (C.-T.) 'spoke' adducts.

Figure 6.7 illustrates the directional parameters used to calculate the structural geometry of C.-T. 'spoke' adducts; primarily the positioning of the di-/inter-halogen species with respect to the plane containing both electron-pairs of the tetrahedral sp^3 chalcogen atom.[2] θ represents the dihedral angle between the E-X vector and this plane and φ measures the rotational angle between the bisection of the R_2E angle and where the E-X vector is projected onto the plane.[2]

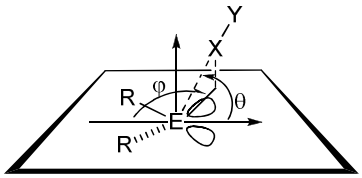

Fig. 6.7 *The directional parameters for the geometry of C.-T. 'spoke' adducts formed from di-/inter-halogens binding to sp^3 hybridised chalcogen donor atoms.*[2]

In most C.-T. 'spoke' adducts of thioethers, selenoethers, and of most thiocarbonyl and selenocarbonyl compounds di-/inter-halogens are found to lie on the plane of the chalcogen lone pairs with angles (θ) approaching 0°.[10,11] Thiocarbonyl and selenocarbonyl donors are also known to form C.-T. 'perpendicular-spoke' adducts with angles (θ) around 80° and the di-/inter-halogen molecule lying quasi-perpendicular to the electron pair plane. This is due to sterically crowded lone-pairs on the chalcogen atom.[10,11]

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Charge-transfer (C.-T.) 'extended spoke' adducts.

The bonding in RE–X–Y type systems results in a partial negative charge on the terminal Y atom allowing it to act as a donor towards other acceptors (A). This produces adducts which are structurally more complex, known as C.-T. 'extended spoke' adducts [RE–X–Y···A] (where A is normally another XY molecule and XY···A angles are typically close to 90°).[1,2] The terminal Y atom-acceptor (A) interaction delocalises negative charge onto Y which in turn strengthens the E-X bond. With an extremely strong Y···A interaction systems of the type $[RE\text{-}X]^{+}[Y\text{-}A]^{-}$ can be envisaged.[2]

An example of this is the adduct formed by reaction of N-methylbenzothiazole-2(*3H*)-selone with IBr (Figure 6.8).[2,33] The Se atom forms a strong bond with the first molecule of IBr simultaneously weakening the I-Br bond which extends to 3.129(1) Å. The terminal Br atom then interacts with the second molecule of IBr forming an IBr_2^- fragment [d(Br–I) = 2.803(1) and 2.645(1) Å]. The ionic system created can be depicted by the formula $[RE–I]^{+} \cdots [Br–IBr]^{-}$.[2,33]

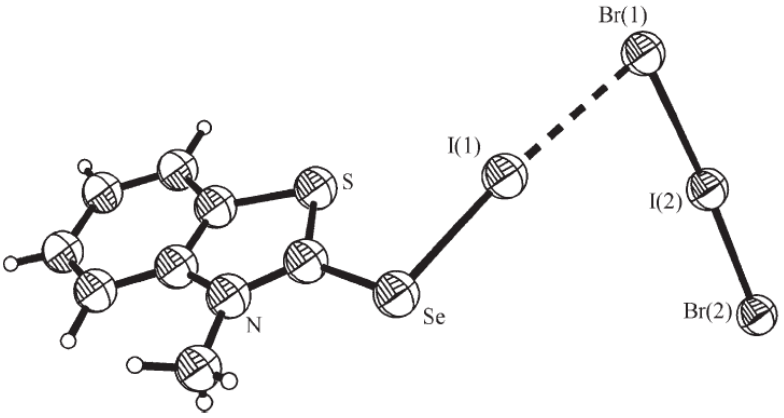

Fig. 6.8 *C.-T. 'extended spoke' adduct of N-methylbenzothiazole-2(3H)-selone and IBr forming an ionic species depicted by the formula* $[RE–I]^{+} \cdots [Br–IBr]^{-}$.[2,33]

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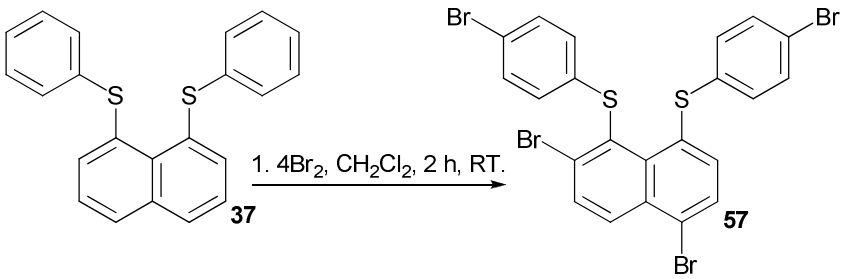
Hypervalent adducts of chalcogen substituted naphthalenes

In Chapter 4, 1,8-bis(phenylsulfanyl)naphthalene **37** and 1,8-bis(phenylselenyl)naphthalene **38** were introduced along with three novel mixed chalcogen naphthalene systems **41**-**43**. These five chalcogen donor compounds, along with the tellurium compounds **55** and **56**, have been treated with dibromine and diiodine and produce a range of different adducts; C.-T. 'spoke', C.-T. 'extended spoke', 'T-shaped' (or TBP) adducts and an ionic form of C.-T. 'extended spoke' with formula $[RE\text{-}X]^{+}\cdots[X\text{-}X_2]^{-}$. In all these compounds the steric effect of the phenyl groups and the naphthalene backbone as well as their influence on the effective electronegativity of the reacting chalcogen species played an important role on the geometry of the final structure.

Charge-transfer 'spoke' and 'extended spoke' adducts

Reaction of 1,8-bis(phenylsulfanyl)naphthalene 37 with dibromine.

The structural geometry of the product of the reaction of 1,8-bis(phenylsulfanyl)naphthalene **37** and dibromine is hard to predict. The general rule based on electronegativity of the interacting species suggests a 'T-shaped' moiety will be produced [χ(S) 2.58 < χ(Br) 2.68] but as mentioned above products of known reactions between S- donors and dibromine adopt C.-T. 'spoke' geometries.[30] Upon reaction of 1,8-bis(phenylsulfanyl)naphthalene with dibromine, no adduct is isolated. Instead electrophilic aromatic substitution dominates to produce 1,8-bis(4-bromophenylsulfanyl)-2,5-dibromonaphthalene **57** (Scheme 6.2). Varying the loading of dibromine (1-6 equiv), produced **57** exclusively each time.



Scheme 6.2 *The reaction scheme for the preparation of 1,8-bis(4-bromophenylsulfanyl)-2,5-dibromonaphthalene* **57**.[34]

Aromatic groups bearing -OR and $-NR_2$ groups are strongly activated by delocalisation of resonance lone-pairs into the aromatic π-system and are therefore highly reactive towards electrophilic substitution.[35] Sulfur is less electronegative than oxygen and nitrogen thus its electron

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pair is higher in energy and more available to interact with the aromatic π-system.[22,35] With the sulfur lone pair delocalised into the aromatic system it is unavailable for donation into the empty orbitals in dibromine; no adduct is formed and electrophilic aromatic substitution dominates.[35]

The regioselectivity of the bromination which occurs during the preparation of **57** (Scheme 6.2) can be explained by the relative reactivity of the naphthalene and the S(phenyl) rings and by the directing ability of the sulfur activators. Naphthalene is less aromatic and thus more susceptible towards electrophilic substitution compared with the two phenyl groups so the initial bromination reactions take place around the naphthalene ring.[35]

In substituted naphthalenes the ring carrying the substituent is the most reactive during electrophilic attack. Activating groups such as S(phenyl) donate electrons into the π-system and direct incoming electrophiles to the *ortho* or *para* positions within the same ring. Figure 6.9 shows two resonance structures for the first bromination attack towards the *ortho* (C2) and *para* (C4) positions. From the two structures it can be seen that attack at the *para* position would be sterically more favourable with the large bromine atom further from the bulky phenyl groups.[35]

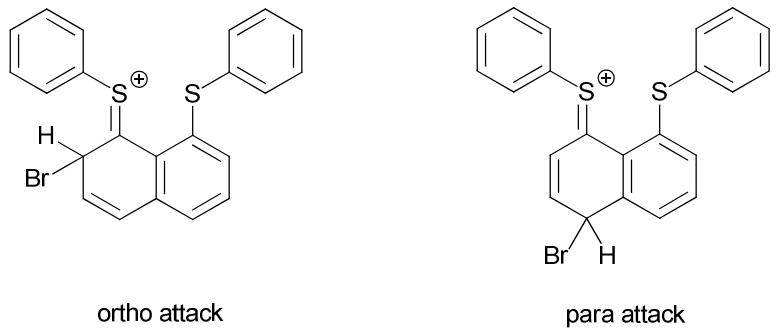

Fig. 6.9 *Two resonance structures for the electrophilic attack para and ortho to the first S(phenyl) moiety for the first bromination in the preparation of* **57**.[35]

The second bromination is directed by the second S(phenyl) moiety to the *ortho* (C7) and *para* (C5) positions. Again two resonance structures can be drawn (Figure 6.10). Bromination occurs this time at the *ortho* position due to the steric crowding two close bromine atoms would produce upon *para* substitution. The final bromination step takes place in the phenyl rings with the sulfur atoms directing the substitution to the two *para* positions, furthest away from the steric bulk of the molecule.[35]

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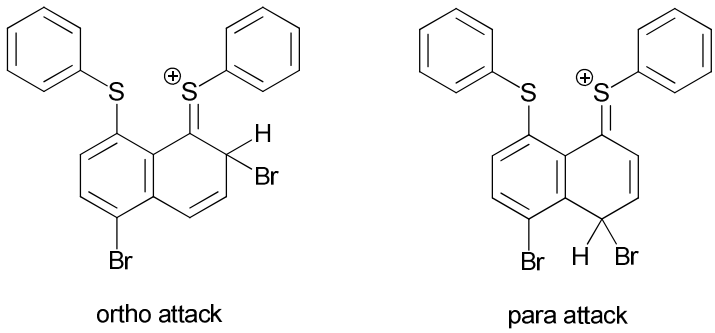

Fig. 6.10 *Two resonance structures for the second electrophilic attack para and ortho to the second S(phenyl) moiety in the preparation of* **57**.[35]

The molecular structure of **57** (Figure 6.11) shows an intramolecular sulfur-sulfur *peri*-distance of 2.935(4) Å, much shorter than the sum of the van der Waals radii for two sulfur atoms [3.60 Å][36] and marginally shorter than for the non-brominated analogue **37** [3.0036(13) Å].

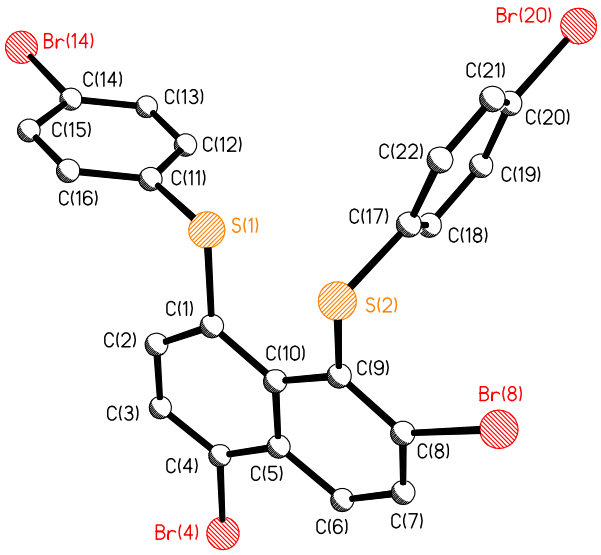

Fig. 6.11 *The molecular structure of 1,8-bis(4-bromophenylsulfanyl)-2,5-dibromonaphthalene* **57**.

Out-of-plane distortion is observed with the two sulfur atoms lying at equal distances from the naphthalene plane, S(1) -0.343(13) Å and S(2) 0.343(13) Å (Table 6.1). The sulfur atoms are further accommodated by in-plane distortions in the C-C-C group between the *peri*-atoms as shown by the sum of the bay region angles [369.9(18)°]. Torsion angles about the C5-C10 bond also indicate there is a reduction in the planarity of the naphthalene backbone compared to **37**. Selected bond lengths and angles for **37** and **57** are compared in Table 6.1, more information on the structure of **57** can be found in Appendix 35.

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Molecular structures **37** and **57**, adopt similar orientations of the 'type AB' with one E-C_{Ph} bond aligning close to the naphthyl plane and one roughly perpendicular to it.[2,4,37] The phenyl rings in **37** lie across the naphthalene plane (*trans*) and in **57** lie on the same side of the naphthalene plane (*cis*) (Figure 6.12).[37] Although the orientation of the phenyl groups in the two compounds is marginally different the linearity of the C_{Ph}-S_1···S_2 fragment in both compounds is very similar (Figure 6.12).

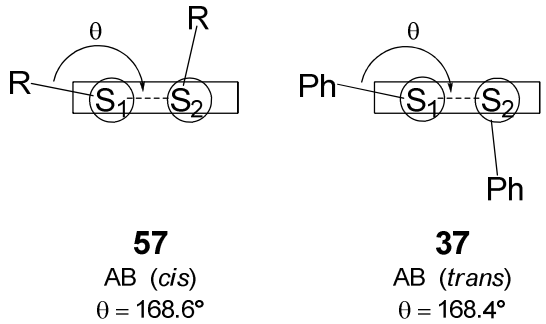

Fig. 6.12 *The structures of* **57** *and* **37** *showing the orientation of the E(aryl) groups, the type of structure and the linear arrangement C_{Ph}-S_1···S_2 [angle θ].*[37]

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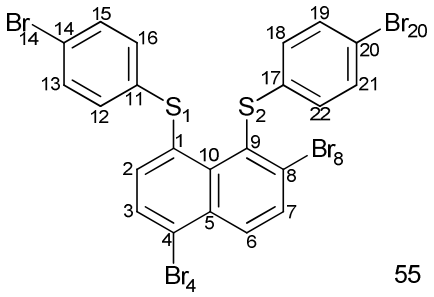
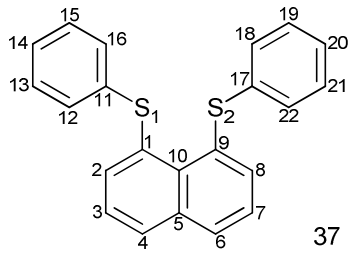
Table 6.1 Selected bond lengths [Å] and angles [°] for 1,8-bis(4-bromophenylsulfanyl)-2,5-dibromonaphthalene **57** and 1,8-bis(phenylsulfanyl) naphthalene **37**.



55



37

S(1)···S(2)	**2.935(4)**	**S(1)···S(2)**	**3.0036(13)**
S(1)-C(1)	1.787(11)	S(1)-C(1)	1.794(3)
S(2)-C(9)	1.780(11)	S(2)-C(9)	1.783(4)
S(1)-C(1)-C(10)	122.3(8)	S(1)-C(1)-C(10)	121.8(2)
C(1)-C(10)-C(9)	126.0(10)	C(1)-C(10)-C(9)	126.8(3)
S(2)-C(9)-C(10)	121.6(8)	S(2)-C(9)-C(10)	124.5(2)
	Σ = 369.9(18)		**Σ = 373.1(5)**
Distance from naphthalene mean plane			
S(1)	-0.343(13)	S(1)	0.270(4)
S(2)	0.343(13)	S(2)	-0.163(4)
Br(4)	0.025(13)		
Br(8)	0.103(11)		
Torsion angle			
C(6)-C(5)-C(10)-C(1)	176.1(10)	C(6)-C(5)-C(10)-C(1)	178.6(3)
C(4)-C(5)-C(10)-C(9)	176.2(9)	C(4)-C(5)-C(10)-C(9)	177.2(3)

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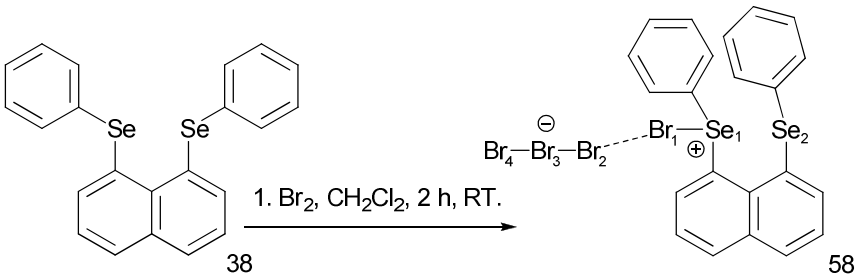
Reaction of 1,8-bis(phenylselenyl)naphthalene 38 with dibromine.

Upon reaction with dibromine, 1,8-bis(phenylselenyl)naphthalene **38** forms an ionic C.-T. 'extended spoke' adduct which can be represented by the formula $[RSe–Br]^{+}\cdots[Br–Br_2]^{-}$ (Scheme 6.3).[2,34]



Scheme 6.3 *The reaction scheme for the preparation of the C.-T. 'extended spoke' adduct* **58**.[34]

The Se atom forms a strong bond with the first molecule of Br_2 simultaneously weakening the Br(1)-Br(2) bond which extends from 2.28 Å (free bromine) to 3.172(1) Å.[26] This places a partial negative charge on the terminal Br(2) atom which acts as a donor towards a second (acceptor) molecule of Br_2. The new interaction between the terminal Br(2) atom and the second Br_2 molecule delocalises negative charge onto the original terminal Br(2) in turn strengthening the Se(1)-Br(1) bond [2.4878(8) Å].[2] The formation of a hypervalent 3c-4e Br_3^- fragment [Br(2)-Br(3) 2.5170(8) Å, Br(3)-Br(4) 2.5668(8) Å] results (Figure 6.14).[15,17-19] An increase in these Br-Br distances compared to free bromine [2.28 Å][26] is an indication of the weaker 3c-4e bond (only one bonding pair of electrons between three atoms lowers the bond order).[15,17-19]

The molecular structure of the 'extended spoke' adduct **58** is shown in Figure 6.13 and a comparison of selected bond lengths and angles with 1,8-bis(phenylselenyl)naphthalene **38** can be found in Table 6.2. The crystallographic data shows an intramolecular *peri*-distance between the two selenium atoms for **58** of 2.7619(7) Å much less than for **38** [3.1332(9) Å] and over 1.0 Å shorter than the sum of van der Waals radii for two selenium atoms [3.80 Å].[36] This indicates that the Br(1)-Se(1)···Se(2) quasi-linear arrangement [172.1(1)°] (Figure 6.14) could be described as a hypervalent 3c-4e bond.[15,17-19]

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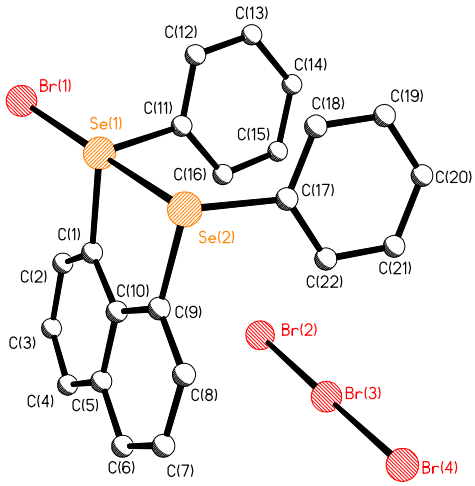

Fig. 6.13 *The molecular structure of the C.-T. 'extended spoke' adduct* **58** *formed from the reaction of 1,8-bis(phenylselenyl)naphthalene* **38** *with dibromine.*

The magnitude of the *peri*-distance in **58** is an indication of the overall reduction in naphthalene deformation compared to **38**. In-plane distortion is reduced with the sum for the bay region angles lower in **58** [366.1(9)°] by ~8° compared to **38** [373.9(11)°]. The displacement of the selenium atoms above and below the plane is also reduced and torsion angles for the C5-C10 bond in both compounds suggest the naphthalene backbone in **58** is more planar than in **38** (Table 6.2). The reduction in naphthalene distortion could be a result of the different structural geometries the two compounds adopt. We have shown that the E-C_{Ph} bonds in **38** align along the naphthyl plane and perpendicular to it in an 'AB-*cis*' arrangement.[37] The linearity of the Br(1)-Se(1)···Se(2) fragment in **58** ensures the two E-C_{Ph} bonds lie perpendicular to the plane assuming the 'AA-*cis*' arrangement (Figure 6.14).[37]

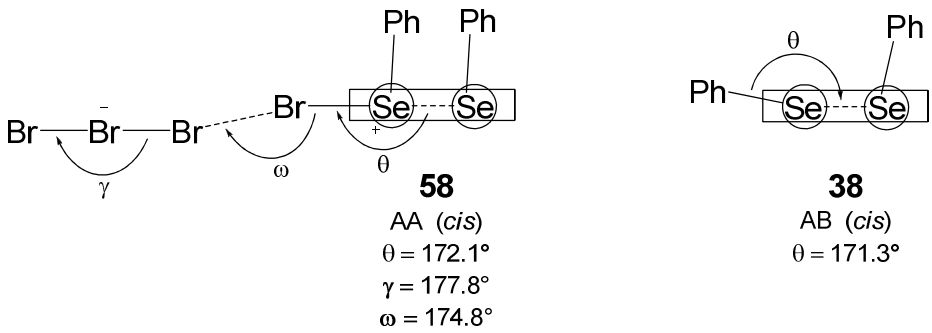

Fig. 6.14 *The structures of* **58** *and* **38** *showing the orientation of the Se(phenyl) groups, the type of structure and the linear arrangements in the two compounds.*[37]

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Subsequently the phenyl rings are forced to lie in close proximity and adopt a face-to-face offset arrangement with slipped packing (see Chapter 3).[38] The distance between the two interacting centroids [Cg(11-16)···Cg(17-22) 3.691(1) Å] is within the range for typical centroid-centroid π-stacking (3.3-3.8 Å).[38]

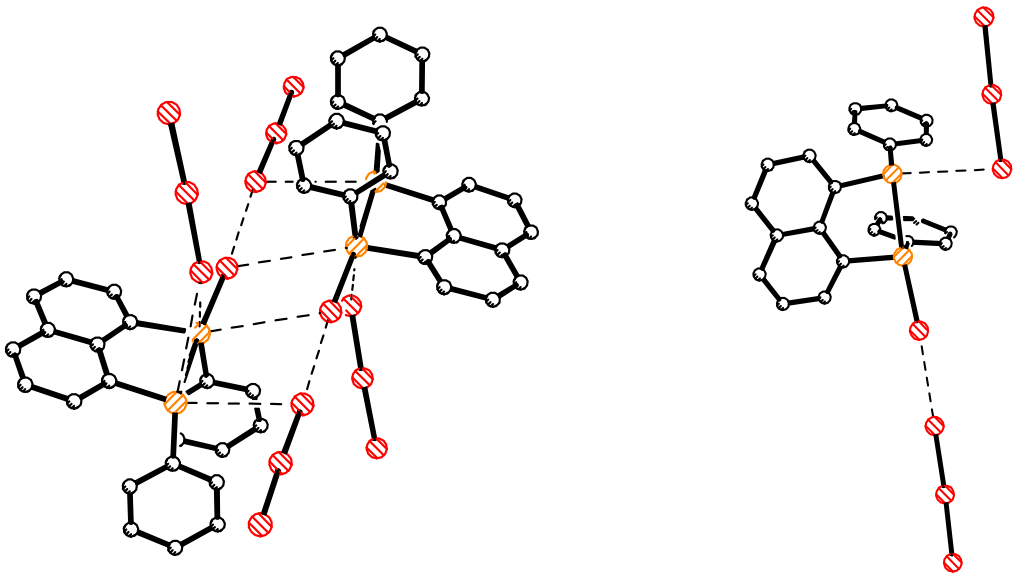

Fig. 6.15 *The molecular structure of the C.-T. 'extended spoke' adduct* **58** *showing short contact packing interactions.*

Figures 6.15-6.17 show the close contact interactions within the molecular structure of **58**. The packing within the crystal structure occurs with a number of close intermolecular and intramolecular non-bonded interactions.

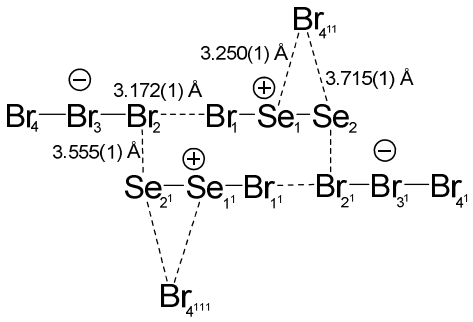

Fig. 6.16 *An illustration of the quasi-planar rectangular arrangement of atoms formed in adduct* **58** *from non-bonded inter- and intramolecular interactions.*

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A quasi-planar rectangular arrangement of eight atoms is formed between two neighbouring molecules from non-bonded interactions between Br(1)···Br(2) 3.172(1) Å and Se(2^1)···Br(2) 3.555(1) Å, depicted in Figures 6.16 and 6.17. Two further non-bonded intermolecular interactions are seen between a terminal Br(4^{11}) atom of a neighbouring Br_3^- fragment and the two selenium atoms [Se(1)···Br(4^{11}) 3.250(1) Å and Se(2)···Br(4^{11}) 3.715(1) Å]. Further information on the molecular structure of **56** can be found in Appendix 36.

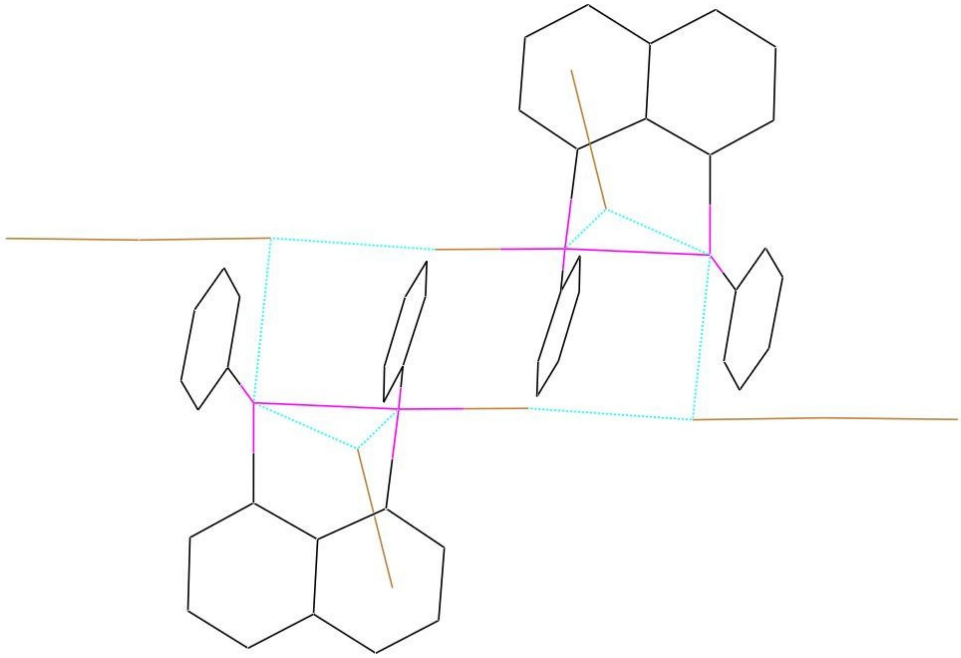

Fig. 6.17 *The molecular structure of* **58** *showing the quasi-planar rectangular arrangement of atoms formed between two molecules from non-bonded inter- and intramolecular interactions.*

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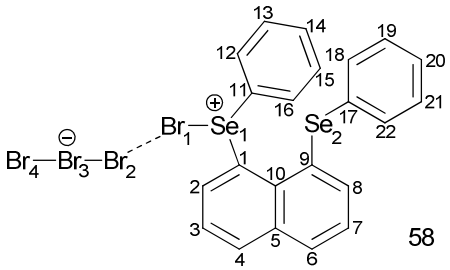
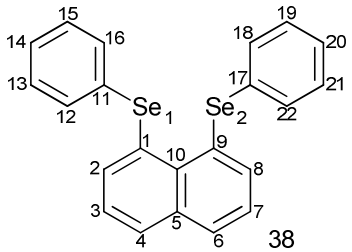
Table 6.2 Selected bond lengths [Å] and angles [°] for the C.-T. 'extended spoke' adduct **58** and 1,8-bis(phenylselenyl)naphthalene **38**.





Se(1)···Se(2)	**2.7619(7)**	**Se(1)-Se(2)**	**3.1332(9)**
Se(1)-C(1)	1.957(6)	Se(1)-C(1)	1.922(7)
Se(2)-C(9)	1.918(5)	Se(2)-C(9)	1.930(7)
Br(1)-Se(1)	2.4878(8)		
Br(2)-Br(3)	2.5170(8)		
Br(3)-Br(4)	2.5668(8)		
Se(1)-C(1)-C(10)	119.8(4)	Se(1)-C(1)-C(10)	123.5(5)
C(1)-C(10)-C(9)	126.2(5)	C(1)-C(10)-C(9)	126.6(6)
Se(2)-C(9)-C(10)	120.1(4)	Se(2)-C(9)-C(10)	123.8(5)
	Σ = 366.1(9)		**Σ = 373.9(11)**
Br(2)-Br(3)-Br(4)	177.78(3)		
Br(1)-Se(1)-Se(2)	172.10(3)		
Se(2)-Se(1)-C(11)	92.15(15)		
Se(2)-Se(1)-C(1)	85.58(16)		
C(1)-Se(1)-C(11)	100.6(2)		
Br(1)-Se(1)-C(1)	98.97(16)		
Br(1)-Se(1)-C(11)	93.33(15)		
Distance from naphthalene mean plane			
Se(1)	0.2887(66)	Se(1)	0.468(9)
Se(2)	-0.0101(66)	Se(2)	-0.327(9)
Br(1)	0.8521(81)		
Torsion angle			
C(6)-C(5)-C(10)-C(1)	-177.4(12)	C(6)-C(5)-C(10)-C(1)	173.5(6)
C(4)-C(5)-C(10)-C(9)	-175.0(12)	C(4)-C(5)-C(10)-C(9)	174.6(6)

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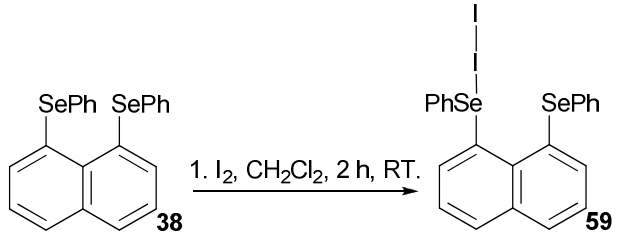
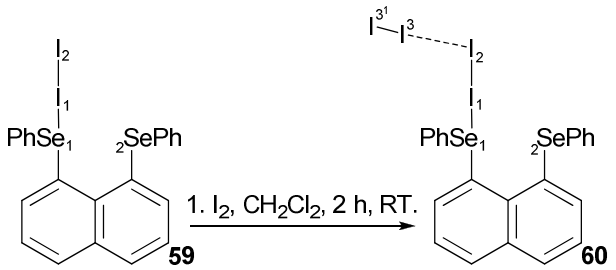
Reaction of 1,8-bis(phenylselenyl)naphthalene 38 with diiodine.

1,8-Bis(phenylselenyl)naphthalene **38** reacts with one molar equivalence of diiodine to form the neutral C.-T. ''spoke'' adduct **59** containing a quasi-linear Se-I-I fragment [177.6°] (Scheme 6.4). Iodine [χ(I) 2.36][21], unlike bromine [χ(Br) 2.68][22], has a similar electronegativity to selenium [χ(Se) 2.35][22] and accepts electron density from non-bonding orbitals of the selenium donor to form the charge-transfer adduct. This has the effect of lowering the bond order and consequently weakening the I-I bond which extends from 2.66 Å (free iodine) to 2.7987(6) Å.[1,2,26]



Scheme 6.4 *The reaction scheme for the preparation of the neutral C.-T. 'spoke' compound* **59** *formed from the reaction of* **38** *with diiodine.*[34]

The subsequent partial negative charge formed on the terminal I(2) atom in the hypervalent 3c-4e Se(1)–I(1)–I(2) bond means I(2) can act as a donor towards a second molecule of diiodine. This affords the C.-T. 'extended spoke' adduct **60** (Scheme 6.5)[2] containing two quasi-linear arrangements Se(1)-I(1)-I(2) [178.1(1)°] and I(2)···I(3)-I(3)[1] [177.5(1)°] (Figure 6.20). The I(1)-I(2)-A angle (A = the second molecule of I_2) between the two linear fragments is 107.9(1)° which is slightly larger than average [90°] for known 'extended spoke' compounds.[1,2] The interaction between the terminal I(2) atom of the 'spoke' adduct and the second I_2 molecule weakens the I(1)-I(2) bond further, extending the distance to 2.8672(8) Å. This strengthens the Se(1)-I(1) bond which shortens from 2.9795(8) Å in **59** to 2.8497(9) Å **60**.[1,2]



Scheme 6.5 *The reaction scheme for the preparation of the C.-T. 'extended spoke' compound* **60**.[34]

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59 was fully characterised by elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy and mass spectrometry. The ^{77}Se NMR spectrum shows a downfield shift compared to **38** [δ = 428.6 ppm] with two peaks at δ = 436.9 ppm and δ = 436.7 ppm corresponding to the two different selenium environments. **60** was characterised by ^{1}H and ^{77}Se NMR spectroscopy. The ^{1}H NMR spectrum displays similar shifts to **59** however, there is a slight upfield shift of roughly 0.1 ppm. The ^{77}Se NMR spectrum shows two peaks at δ = 445.1 ppm and δ = 444.3 ppm corresponding to the two different selenium environments.

The molecular structures of the C.-T. spoke adducts **59** and **60** are shown in Figures 6.18 and 6.19 and a comparison of selected bond lengths and angles can be found in Table 6.3. Further information for the two crystal structures can be found in Appendices 37 and 38.

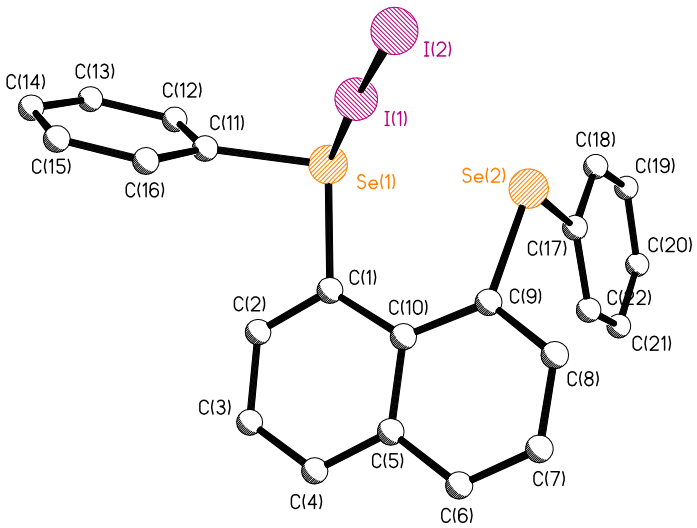

Fig. 6.18 *The molecular structure of the neutral C.-T. 'spoke' adduct* **59**.

Naphthalene distortion occurring in the two 'spoke' adducts **59** and **60** is comparable to the un-reacted selenium starting material **38**. This is best illustrated by the similarity of the intramolecular selenium-selenium *peri*-distances [3.1339(6) Å **59**, 3.0756(14) Å **60**, 3.1332(9) Å **38**]. In-plane distortion in the three structures is almost identical with the sum of the bay region angles differing by less than 1° [**59** 373.3(7)°, **60** 373.6(14)°, **38** 373.9(11)°]. Out-of-plane distortion is greatest in 'spoke' adduct **59** with Se(1) -0.329(7) Å below the plane and Se(2) 0.536(7) Å above the plane. Torsion angles for the central C5-C10 naphthalene bond suggest that the 'extended spoke' **60** has the greatest degree of planarity in the naphthyl backbone (Table 6.3).

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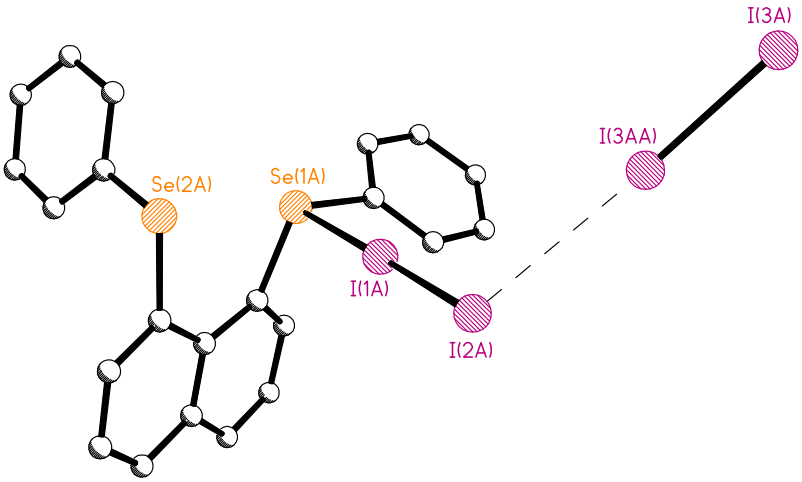

Fig. 6.19 *The molecular structure of the C.-T. 'extended spoke' adduct* **60** *showing the intramolecular I(2)···I(3) non-bonded interaction.*

The two C.-T. adducts adopt the 'AB-*trans* type' arrangement with one E-C_{Ph} bond lying close to the naphthyl plane and the other approaching perpendicular to it (Figure 6.20).[37] The linear arrangements involving iodine atoms have been discussed above. Both adducts also exhibit a possible weak 3c-4e C_{Ph}-Se(1)···Se(2) quasi-linear arrangement as depicted by angle θ in Figure 6.20 [171.0(1)° **59** and 177.6(1)° **60**].

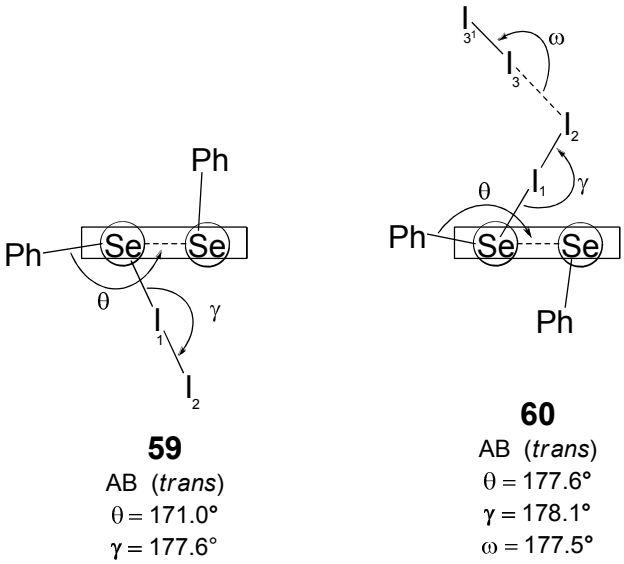

Fig. 6.20 *The structures of* **59** *and* **60** *showing the orientation of the Se(phenyl) groups, the type of structure and the linear arrangements within the compounds.*[37]

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From Figure 6.20 it can be seen that I(1) sits in the *peri*-gap in close contact with Se(2) for both compounds. Se(2)···I(1) non-bonded distances are 3.6956(7) Å **59** and 3.8730(9) Å **60** just within the sum of van der Waals radii for interacting selenium and iodine atoms [3.88 Å].[36] Adduct **59** also exhibits an intermolecular non-bonded interaction between the I(2) and Se(2) atoms of neighbouring molecules (A and B) with an I(2A)···Se(2B) distance of 3.663(1) Å (Figure 6.21).

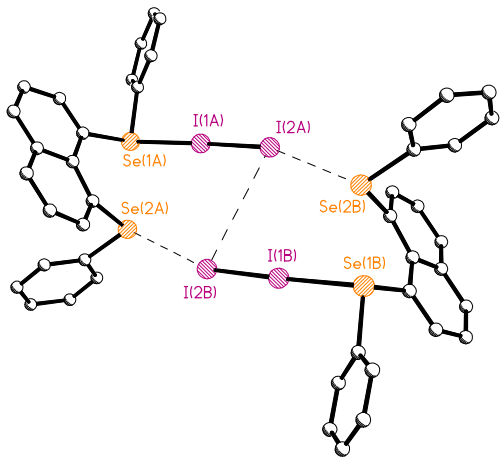

Fig. 6.21 *The molecular structures of* **59** *showing the intermolecular non-bonded interactions between iodine and selenium atoms in two neighbouring molecules (A and B).*

The positioning of the diiodine species I(1)-I(2) with respect to the plane containing both electron-pairs of the tetrahedral sp^3 selenium donor atom in adducts **59** and **60** is illustrated by Figure 6.22.[2] θ represents the dihedral angle between the Se(1)-I(1) vector and this plane.[2] Both compounds adopt a quasi-perpendicular arrangement with angle θ ≈ 80° caused by steric crowding around the lone-pairs on selenium.[10,11]

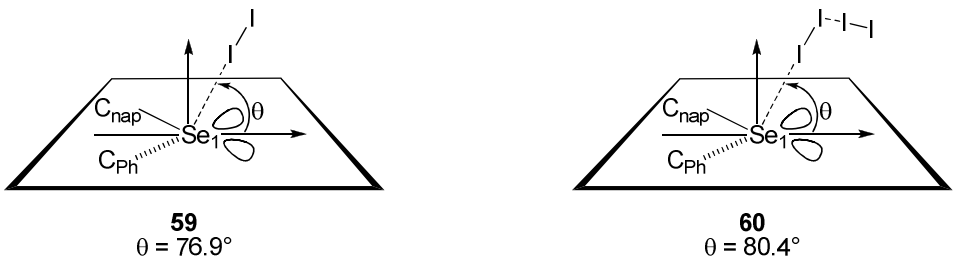

Fig. 6.22 *The positioning of the diiodine species in the C.-T. 'spoke' adducts* **59** *and* **60**.[2]

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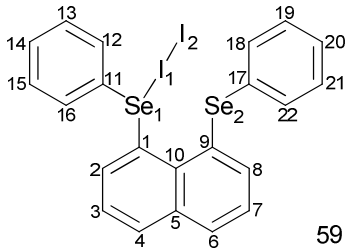
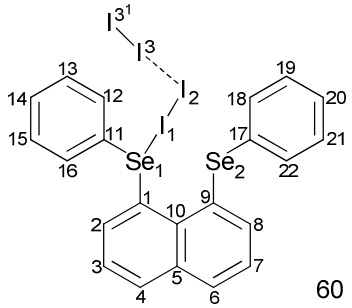
Table 6.3 Selected bond lengths [Å] and angles [°] for the C.-T. 'spoke' adduct **59** and the C.-T. 'extended spoke' adduct **60**.



59



60

Se(1)···Se(2)	**3.1339(6)**	**Se(1)···Se(2)**	**3.0756(14)**
Se(1)-C(1)	1.953(5)	Se(1)-C(1)	1.948(8)
Se(2)-C(9)	1.933(5)	Se(2)-C(9)	1.929(7)
		I(3)-I(3)[1]	2.7402(11)
I(1)···Se(2)	3.6956(7)	I(1)···Se(2)	3.8730(9)
I(1)-Se(1)	2.9795(8)	I(1)-Se(1)	2.8497(9)
I(1)-I(2)	2.7987(6)	I(1)-I(2)	2.8672(8)
		I(2)···I(3)	3.543(1)
Se(1)-C(1)-C(10)	121.9(3)	Se(1)-C(1)-C(10)	122.5(7)
C(1)-C(10)-C(9)	128.4(4)	C(1)-C(10)-C(9)	126.9(7)
Se(2)-C(9)-C(10)	123.0(4)	Se(2)-C(9)-C(10)	124.2(6)
	Σ = 373.3(7)		**Σ = 373.6(14)**
I(2)-I(1)-Se(1)	177.637(15)	I(2)-I(1)-Se(1)	178.09(3)
I(1)-Se(1)-C(11)	97.0(2)	I(1)-Se(1)-C(11)	99.4(2)
I(1)Se(1)-C(1)	100.2(2)	I(1)Se(1)-C(1)	98.7(2)
C(1)-Se(1)-C(11)	98.4(2)	C(1)-Se(1)-C(11)	100.3(3)
I(1)-Se(1)-Se(2)	74.33(1)	I(1)-Se(1)-Se(2)	81.54(1)
Distance from naphthalene mean plane			
Se(1)	-0.3290(74)	Se(1)	0.415(11)
Se(2)	0.5359(73)	Se(2)	-0.246(11)
I(1)	-2.8382(78)	I(1)	3.076(11)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	-172.7(7)	C(6)-C(5)-C(10)-C(1)	176.7(6)
C(4)-C(5)-C(10)-C(9)	-176.2(7)	C(4)-C(5)-C(10)-C(9)	174.8(7)

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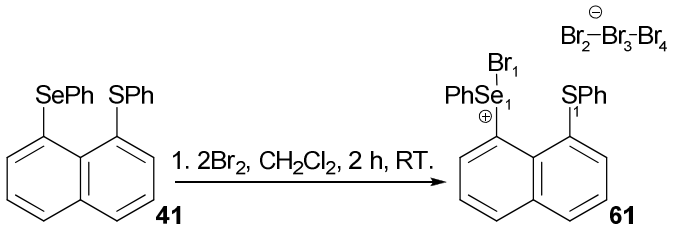
Reaction of 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene 41 with bromine.

1-(Phenylselenyl)-8-(phenylsulfanyl)naphthalene **41** reacts with dibromine to form a similar ionic C.-T. 'extended spoke' adduct as **58** and can be represented by the formula $[RSe–Br]^{+}\cdots[Br_3]^{-}$ (Scheme 6.6).[2,34]



Scheme 6.6 *The reaction scheme for the preparation of the ionic adduct* **61** *from the reaction of* **41** *with dibromine.*

The selective reactivity of dibromine towards selenium can be attributed to its greater electronegativity and hence greater electron donor ability over sulfur.[1,2,22] The strong donor-strong acceptor system prepared upon the formation of the Se-Br bond is sufficient enough to be able to cleave the Br(1)-Br(2) bond and subsequently oxidise the selenium atom.[1,2] This affords the quasi-linear 3c-4e hypervalent Br_3^- fragment Br(2)-Br(3)-Br(4) [178.6(1)°] exhibiting increased Br-Br distances compared to free bromine [Br(2)-Br(3) 2.551(2) Å, Br(3)-Br(4) 2.542(2) Å, Br_2 2.28 Å].[15,17-19,26] The cleavage of the Br(1)-Br(2) bond also increases the strength of the Se(1)-Br(1) bond which shortens to 2.4232(15) Å compared to adduct **58** 2.4878(8) Å.

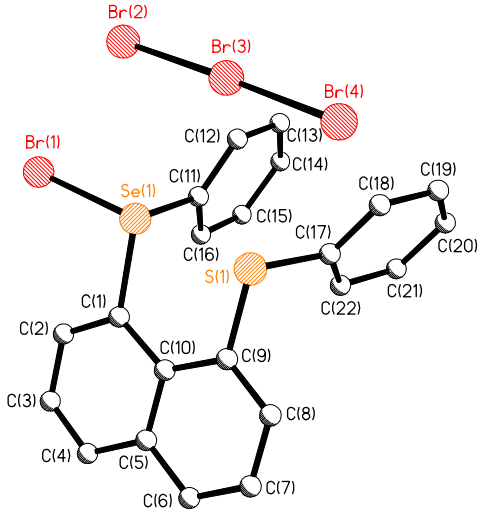


Fig. 6.23 *The molecular structure of the ionic compound* **61** *formed from the reaction of* **41** *with dibromine.*

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The molecular structure of adduct **61** (Figure 6.23) shows an intramolecular non-bonded Se(1)···S(1) *peri*-distance of 2.721(2) Å. The size of the *peri*-atoms is unusually similar in size to the Se(1)···Se(2) distance in **58** [2.7619(7) Å]. The corresponding angles of the bay region in the two adducts are comparable showing in-plane distortion occurs to the same degree. Out-of-plane distortion occurs in **61**, with both *peri*-atoms being displaced to the same side of the naphthalene plane [Se(1) 0.112(11) Å, S(1) 0.139(11) Å]. In adduct **58** Se(1) [0.289(7) Å] lies above the plane and Se(2) lies just below the plane [-0.101(66) Å]. The naphthalene backbone of **61** exhibits a greater degree of planarity than that of **58** with torsion angles deviating little from 180° (Table 6.4).

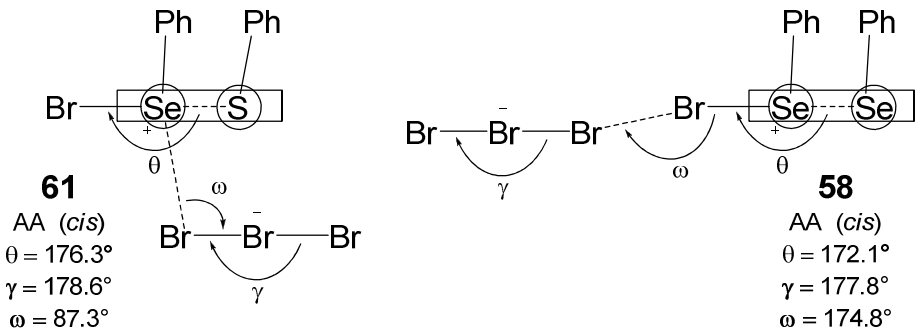

Fig. 6.24 *The structures of* **61** *and* **58** *showing the orientation of the E(phenyl) groups, the type of structure and the linear arrangements in the two compounds.*[37]

Adduct **61** adopts the same 'AA-*cis* type' arrangement as **58** with both the E-C_{Ph} bonds aligning perpendicular and to the same side of naphthyl plane (Figure 6.24).[37]

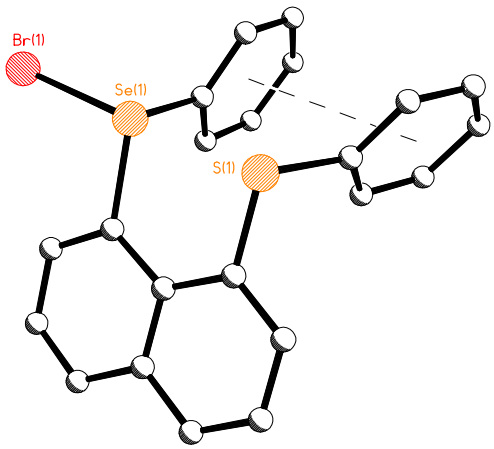

Fig. 6.25 *The molecular structure of the ionic compound* **61** *showing the alignment of the phenyl rings and subsequent π-stacking.*

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The phenyl rings align, adopting a face-to-face offset arrangement with a centroid-centroid distance of Cg(11-16)···Cg(17-22) 3.79(1) Å: within the range for typical π-stacking [3.3-3.8 Å] (Figure 6.25).[38] The Br(1)-Se(1)···S(1) fragment in **61** depicted by angle θ in Figure 6.24 aligns with greater linearity than the Br(1)-Se(1)···Se(2) arrangement in **58**.

The main difference between the structures of **61** and **58** is the intra- and intermolecular interactions and subsequent molecular packing. Adduct **58** has been shown to form a quasi-planar rectangular arrangement of eight atoms formed from two molecules by non-bonded interactions, including an intramolecular non-bonded interaction between Br(1) and the Br_3^- counter ion. No such arrangement occurs in **61** and no interaction is seen between Br(1) and the Br_3^- counter ion (Figure 6.26). The three linear bromine atoms adopt a position above the *peri*-atoms with a non-bonded intramolecular interaction between Se(1)···Br(2) [3.562(1) Å] and an Se(1)···Br(2)-Br(3) angle of 87.3(1)° (Figure 6.24). More information regarding the molecular structure of **61** can be found in Appendix 39.

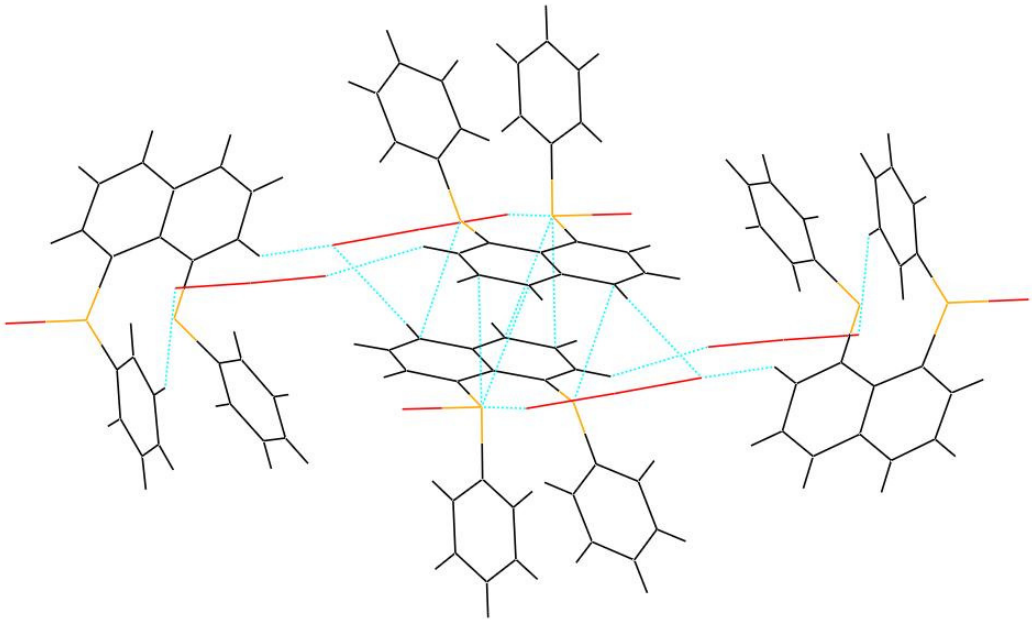

Fig. 6.26 *The molecular structure of the ionic compound* **61** *showing the packing arrangement of molecules and the close contact intermolecular interactions.*

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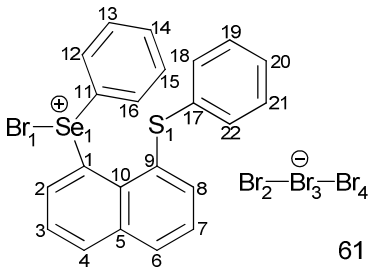
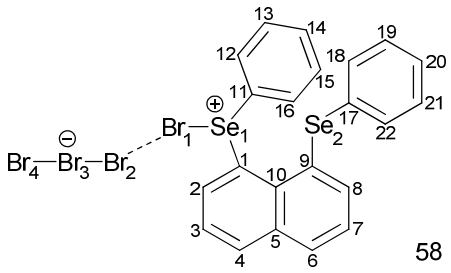
Table 6.4 Selected bond lengths [Å] and angles [°] for the ionic compounds **61** and **58**.



61



58

Se(1)···S(1)	**2.721(2)**	**Se(1)···Se(2)**	**2.7619(7)**
Se(1)-C(1)	1.955(8)	Se(1)-C(1)	1.957(6)
S(1)-C(9)	1.796(9)	Se(2)-C(9)	1.918(5)
Br(1)-Se(1)	2.4232(15)	Br(1)-Se(1)	2.4878(8)
Br(2)-Br(3)	2.5514(17)	Br(2)-Br(3)	2.5170(8)
Br(3)-Br(4)	2.5433(17)	Br(3)-Br(4)	2.5668(8)
Se(1)-C(1)-C(10)	119.5(6)	Se(1)-C(1)-C(10)	119.8(4)
C(1)-C(10)-C(9)	126.0(8)	C(1)-C(10)-C(9)	126.2(5)
S(1)-C(9)-C(10)	119.8(7)	Se(2)-C(9)-C(10)	120.1(4)
	Σ = 365.3(15)		**Σ = 366.1(9)**
Br(2)-Br(3)-Br(4)	178.57(5)	Br(2)-Br(3)-Br(4)	177.78(3)
Br(1)-Se(1)-S(1)	176.34(1)	Br(1)-Se(1)-Se(2)	172.10(3)
S(1)-Se(1)-C(11)	87.80(1)	Se(2)-Se(1)-C(11)	92.15(15)
S(1)-Se(1)-C(1)	83.52(1)	Se(2)-Se(1)-C(1)	85.58(16)
C(1)-Se(1)-C(11)	101.9(3)	C(1)-Se(1)-C(11)	100.6(2)
Br(1)-Se(1)-C(1)	99.2(3)	Br(1)-Se(1)-C(1)	98.97(16)
Br(1)-Se(1)-C(11)	94.0(2)	Br(1)-Se(1)-C(11)	93.33(15)
Distance from naphthalene mean plane			
Se(1)	0.112(11)	Se(1)	0.2887(66)
S(1)	0.139(11)	Se(2)	-0.0101(66)
Br(1)	0.195(14)	Br(1)	0.8521(81)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	179.3(8)	C(6)-C(5)-C(10)-C(1)	-177.4(12)
C(4)-C(5)-C(10)-C(9)	-179.2(8)	C(4)-C(5)-C(10)-C(9)	-175.0(12)

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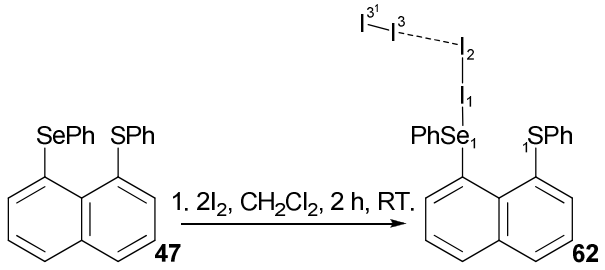
Reaction of 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene 41 with diiodine.

The reaction of 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene **41** with diiodine is comparable to the reaction of 1,8-bis(phenylselenyl)naphthalene **38** with diiodine and affords a similar C.-T. 'extended spoke' adduct to compound **60** (Scheme 6.7).



Scheme 6.7 *The reaction scheme for the preparation of the C.-T. 'extended spoke' adduct* **62**.

Reaction with diiodine occurs at selenium which has a greater donor ability compared to sulfur.[1,2,22] Iodine [χ(I) 2.36][22] having a similar electronegativity to selenium [χ(Se) 2.35][22] accepts electron density from non-bonding orbitals of selenium forming a charge-transfer adduct. A second molecule of diiodine then interacts with the partial negative charge on the terminal I(2) atom to form the 'extended spoke' adduct **62** (Scheme 6.7).[2]

62 was fully characterised by elemental analysis, infra-red spectroscopy, ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy and mass spectrometry. The ^{77}Se NMR spectrum shows a downfield shift compared to **41** [δ = 455.3 ppm] with a single peak at δ = 476.9 ppm.

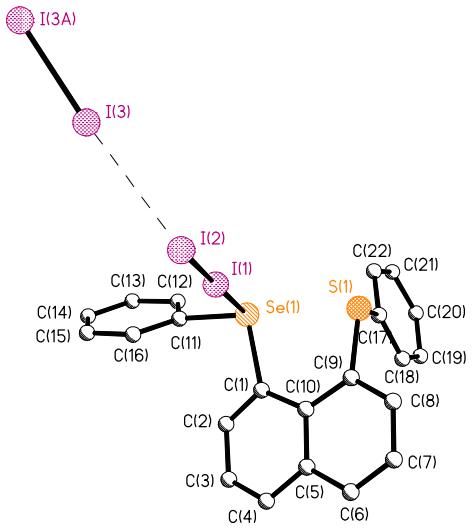


Fig. 6.27 *The molecular structure of the C.-T. 'extended spoke' adduct* **62**.

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The molecular structure of adduct **62** (Figure 6.27) is very similar to that of the selenium analogue **58** and exhibits an intramolecular non-bonded Se(1)···S(1) *peri*-distance of 2.9798(13) Å, slightly shorter than the Se(1)···Se(2) distance in **60** [3.0756(14) Å]. In-plane distortion is observed to be reduced in **62** [370.9(9)°] with smaller angles found in the bay region compared to **60** [373.6(14)°]. The displacement of the *peri*-atoms above and below the naphthyl plane is comparable in the two adducts and torsion angles suggest both compounds display the same degree of planarity in their naphthalene backbones. Selected bond lengths and angles for the two adducts are compared in Table 6.5 and further information on the crystal structure analysis for **62** can be found in Appendix 40.

The two quasi-linear arrangements Se(1)-I(1)-I(2) [179.0(1)°] and I(2)···I(3)-I(3)^1 [176.3(1)°] (angles γ, ω; Figure 6.28) in **62** are separated by an I(1)-I(2)-A angle (A = the second molecule of I_2) of 108.0(1)°. This angle, as for **60**, is slightly larger than average [90°] for known 'extended spoke' compounds.[1,2] The interaction between the terminal I(2) atom and the second molecule of I_2 is observed by the weakening of the I(1)-I(2) bond which lengthens to 2.8706(5) Å, similar in size to the I(1)-I(2) bond in **60** [2.8672(8) Å]. This strengthens and shortens the Se(1)-I(1) bond to 2.8436(6) Å [**60** 2.8497(9) Å].[1,2] The interaction between the terminal I(2) atom and the second molecule of I_2 also has the effect of increasing the I_3-I_3^1 bond length from 2.66 Å for free iodine to 2.7418(7) Å.[26]

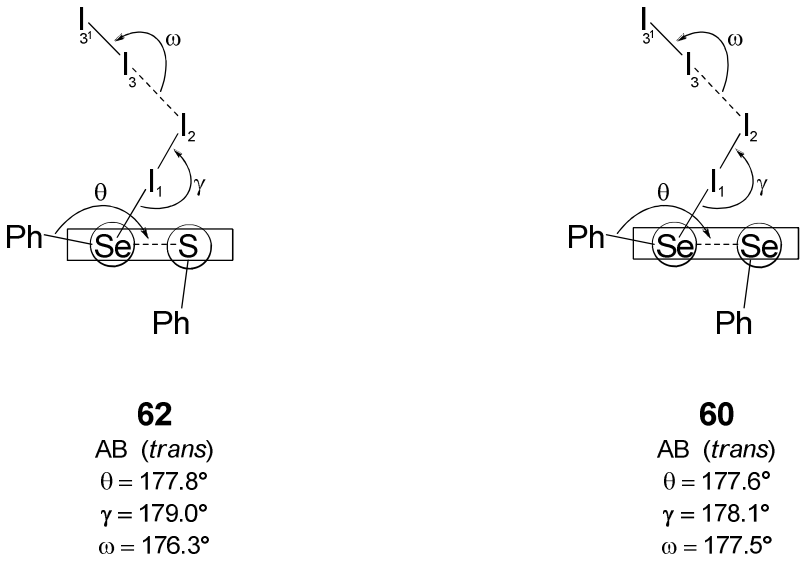

Fig. 6.28 *The structures of* **62** *and* **60** *showing the orientation of the E(phenyl) groups, the type of structure and the linear arrangements within the compounds.*[37]

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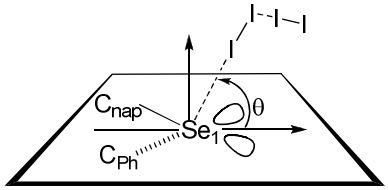
Figure 6.29 illustrates the 'AB-*trans* type' arrangement adducts **62** and **60** adopt; one E-C_{Ph} bond lying close to the naphthyl plane and one approaching perpendicular to it.[37] The result is the linear alignment of three atoms, C_{Ph}-Se(1)···S(1) in **62** and C_{Ph}-Se(1)···Se(2) in **60**, which can be thought of as weak 3c-4e interactions.[15,17-19] The positioning of I(1) in the *peri*-gap in close proximity to the S(1) atom in **62** suggests a similar interaction to I(1)···Se(2) in **60** [3.8730(9) Å] could take place. The I(1)···S(1) non-bonded distance of [3.8527(13) Å] however, is longer than the sum of the van der Waals radii for interacting S and I atoms [3.78 Å] so no non-bonded intramolecular interaction is envisaged.[36]



62 θ = 76.9°
60 θ = 80.4°

Fig. 6.29 *The directional parameters for the geometry of C.-T. 'spoke' adducts formed from di-/inter-halogens binding to sp^3 hybridised chalcogen donor atoms.*[2]

Due to steric crowding around the lone-pairs on selenium, **62** and **60** adopt a quasi-perpendicular arrangement. Angle θ between the diiodine species I(1)-I(2) and the plane containing both electron-pairs of the tetrahedral sp^3 selenium donor atom approaches 80° in both cases (Figure 6.29).[2,10,11] The intermolecular interactions occurring in **62** involving molecules of I_2 are illustrated by Figure 6.30.

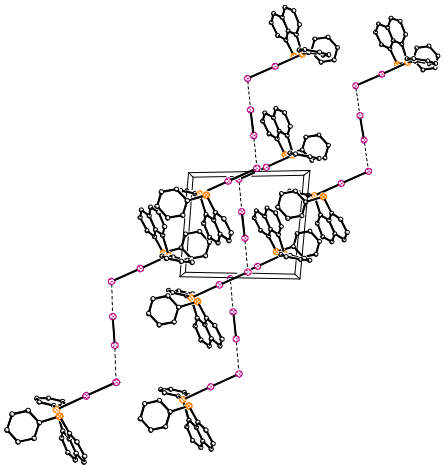


Fig. 6.30 *The molecular structure of the C.-T. 'extended spoke' adduct* **62** *showing the molecular packing viewed along the b-axis.*

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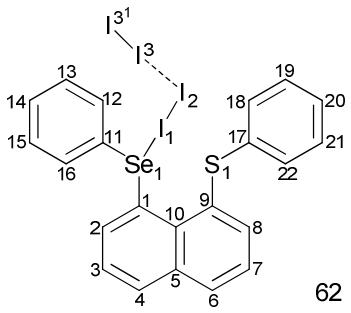
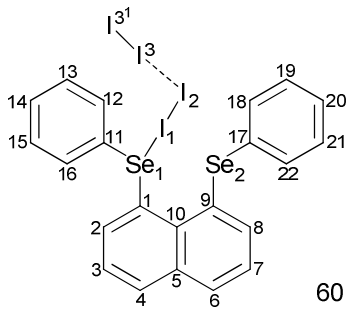
Table 6.5 Selected bond lengths [Å] and angles [°] for the two C.-T. 'extended spoke' adducts **62** and **60**.



62



60

Se(1)···S(1)	**2.9798(18)**	**Se(1)···Se(2)**	**3.0756(14)**
Se(1)-C(1)	1.958(5)	Se(1)-C(1)	1.948(8)
S(1)-C(9)	1.773(5)	Se(2)-C(9)	1.929(7)
I(3)-I(3)^{1}	2.7418(7)	I(3)-I(3)^{1}	2.7402(11)
I(1)···S(1)	3.8527(13)	I(1)···Se(2)	3.8730(9)
I(1)-Se(1)	2.8436(6)	I(1)-Se(1)	2.8497(9)
I(1)-I(2)	2.8706(5)	I(1)-I(2)	2.8672(8)
I(2)···I(3)	3.526(1)	I(2)···I(3)	3.543(1)
Se(1)-C(1)-C(10)	121.7(4)	Se(1)-C(1)-C(10)	122.5(7)
C(1)-C(10)-C(9)	126.8(5)	C(1)-C(10)-C(9)	126.9(7)
S(1)-C(9)-C(10)	122.4(4)	Se(2)-C(9)-C(10)	124.2(6)
	Σ = 370.9(9)		**Σ = 373.6(14)**
I(2)-I(1)-Se(1)	179.04(2)	I(2)-I(1)-Se(1)	178.09(3)
I(1)-Se(1)-C(11)	99.31(16)	I(1)-Se(1)-C(11)	99.4(2)
I(1)-Se(1)-C(1)	98.08(16)	I(1)-Se(1)-C(1)	98.7(2)
C(1)-Se(1)-C(11)	100.7(2)	C(1)-Se(1)-C(11)	100.3(3)
I(1)-Se(1)-S(1)	82.81(1)	I(1)-Se(1)-Se(2)	81.54(1)
Distance from naphthalene mean plane			
Se(1)	0.438(11)	Se(1)	0.415(11)
S(1)	-0.233(11)	Se(2)	-0.246(11)
I(1)	3.106(11)	I(1)	3.076(11)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	176.8(4)	C(6)-C(5)-C(10)-C(1)	176.7(6)
C(4)-C(5)-C(10)-C(9)	174.9(4)	C(4)-C(5)-C(10)-C(9)	174.8(7)

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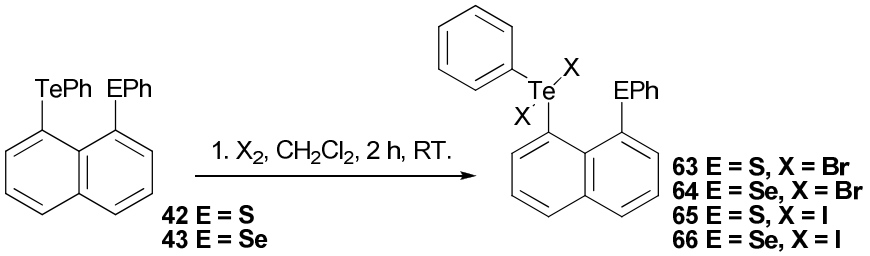
Hypervalent 'T-shaped' adducts of tellurium compounds

Generally, when the halide species (X) is more electronegative than the chalcogen atom (E), 'T-shaped' or trigonal bipyramidal (TBP) adducts are formed.[18,20,21] Consequently, all the known reactions between tellurium-donors [χ(Te) 2.08][22] and di- or inter-halogens [χ(F) 3.94- χ(I) 2.36] form 'T-shaped' adducts with no tellurium C.-T. adducts known.[1,2,22] Tellurium forms a strong donor-strong acceptor system with the di-halogen molecule sufficient enough to cleave the X-X bond and oxidise tellurium.[1,2] Subsequent nucleophilic attack occurring at the tellurium site of the $[RTe–X]^+$ cation affords the 'T-shaped' hypervalent adduct containing the quasi linear X-Te-X alignment.[1,2]

Dihalogen reactions of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene 42 and 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene 43.

The tellurium-donor compounds 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene **42** and 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene **43** react with dibromine and diiodine, to produce a series of four 'T-shaped' insertion adducts (Scheme 6.8). In all four reactions the dihalogen reacts at the larger, less electronegative tellurium atom due to its greater electron donor ability over sulfur or selenium.



Scheme 6.8 *The reaction scheme for the preparation of the series of T-shaped adducts* **63-66** *from the reaction of compounds* **42** *and* **43** *with di-halogens Br_2 and I_2.*

The ^{125}Te NMR and ^{77}Se NMR spectroscopy data for adducts **64** and **66** and the ^{125}Te NMR spectroscopy data for adducts **63** and **65** are summarised in Table 6.6 and compared with starting compounds **42** and **43**.

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Table 6.6 ^{77}Se and ^{125}Te NMR spectroscopy data [δ (ppm)] for the 'T-shaped' insertion adducts **63-66**

	63	**64**	**65**	**66**	**42**	**43**
peri-atoms	TeS	TeSe	TeS	TeSe	TeS	TeSe
X-Te-X	Br-Te-Br	Br-Te-Br	I-Te-I	I-Te-I	-	-
^{77}Se NMR	-	500.0	-	428.8	-	362.8
^{125}Te NMR	958.9	941.4	790.9	747.0	715.18	687.6

In the ^{125}Te NMR spectra, the expected downfield shifts due to the presence of the more electronegative halogen atoms are seen in **63** and **65** compared to **42** and likewise in the spectra for **64** and **66** compared to **43**. The greater electronegativity of Br over I is also observed with an up-field shift observed when Br-Te-Br in **63** and **64** is replaced by I-Te-I in **65** and **66** respectively. The ^{77}Se NMR spectra of **64** and **66** also show a downfield shift compared to **43** [δ = 362.8 ppm] with a peaks at δ = 500.0 ppm and δ = 428.8 respectively.

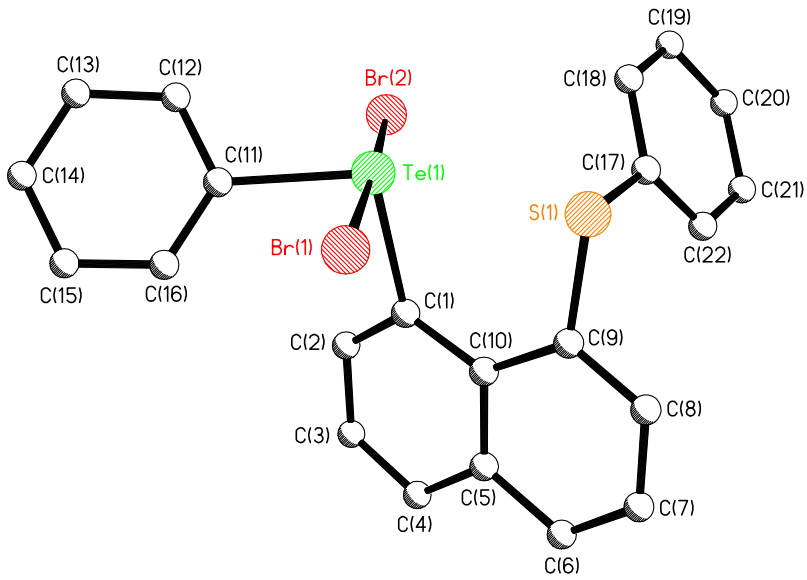

Fig. 6.31 *The molecular structure of the 'T-shaped' adduct* **63**.

The molecular structures of the four 'T-shaped' adducts **63-66** (Figures 6.31-6.34) show similar structural geometries with minor deviations observed which can be attributed to steric crowding and naphthalene distortion. Selected bond lengths and angles for the bromine adducts (**63** and **64)** are compared in Table 6.7 and for the iodine adducts (**65** and **66**) in Table 6.8. Further information for the crystal structures can be found in Appendices 41-44.

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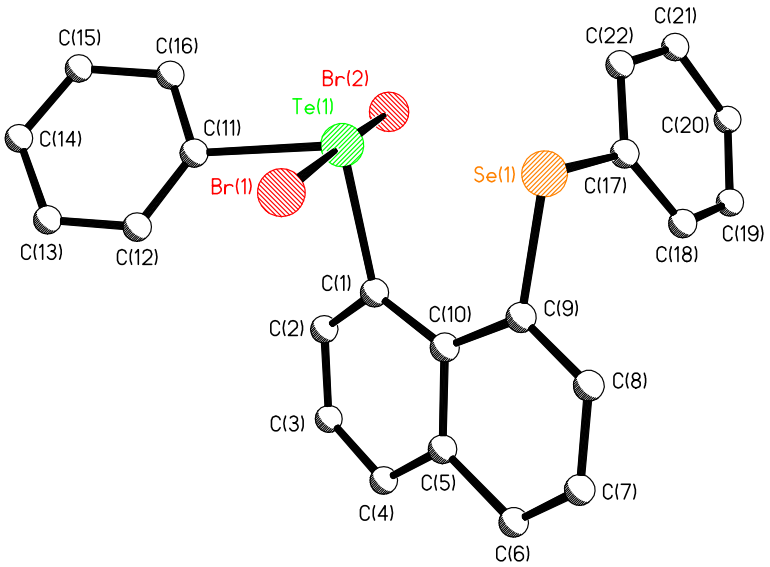

Fig. 6.32 *The molecular structure of the 'T-shaped' adduct* **64**.

Intramolecular non-bonded Te(1)···S(1) *peri*-distances for **63** [3.075(2) Å] and **65** [3.0767(17) Å] are comparable to the distances found in the two independent molecules of **42** [**A** 3.0684(13) Å, **A** 3.0984(11) Å]. The larger selenium atom in adducts **64** and **66** causes an expected increase in the Te(1)···Se(1) *peri*-distances for these adducts [**64** 3.141(2) Å, **66** 3.137(2) Å] which exhibit distances comparable to the independent molecules of **43** [**A** 3.1919(11) Å, **B** 3.1580(12) Å].

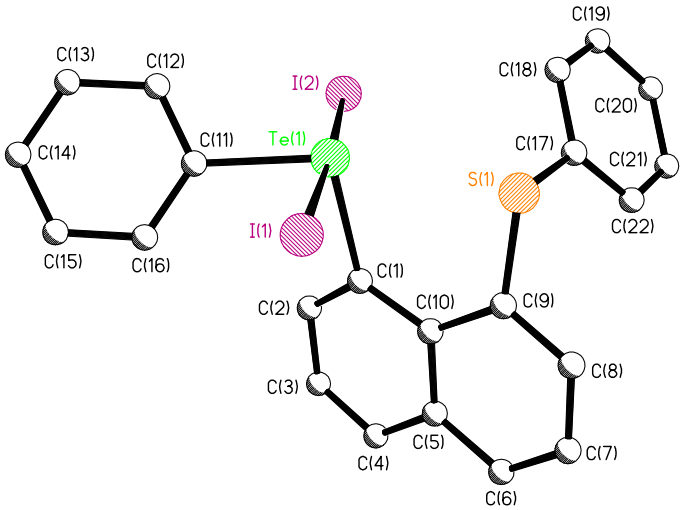

Fig. 6.33 *The molecular structure of the 'T-shaped' adduct* **65**.

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In-plane distortion in the C-C-C group between the *peri*-atoms is shown to be similar in all four adducts with the sums of the bay region angles between 372.0° and 373.5°. The degree of displacement of the *peri*-atoms above and below the naphthalene plane is also found to be consistent throughout the series. However, tellurium sits further from the naphthyl plane than the sulfur atom in **63** and **65** but in adducts **64** and **66** the *peri*-atoms sit at roughly equal distances from the plane.

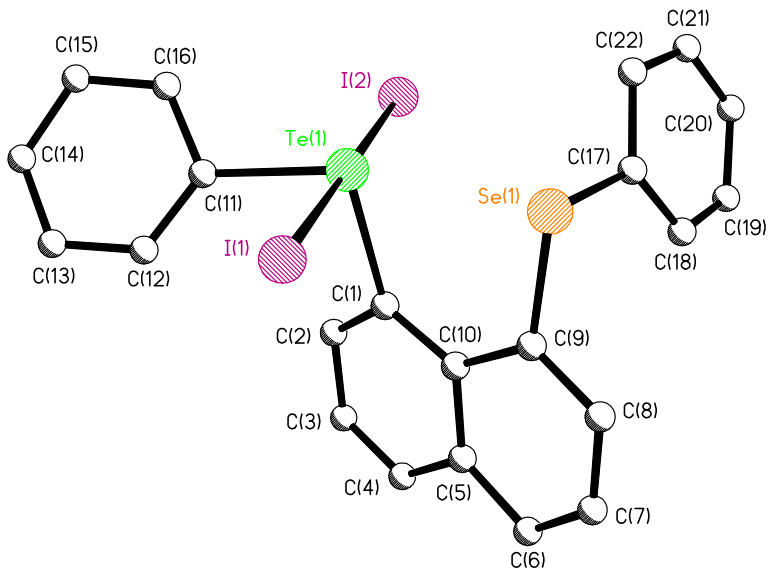

Fig. 6.34 *The molecular structure of the 'T-shaped' adduct* **66**.

Torsion angles associated with the C5-C10 bond give evidence for greatest naphthalene planarity in **66** with the most buckling occurring in adduct **64** (Figure 6.35).

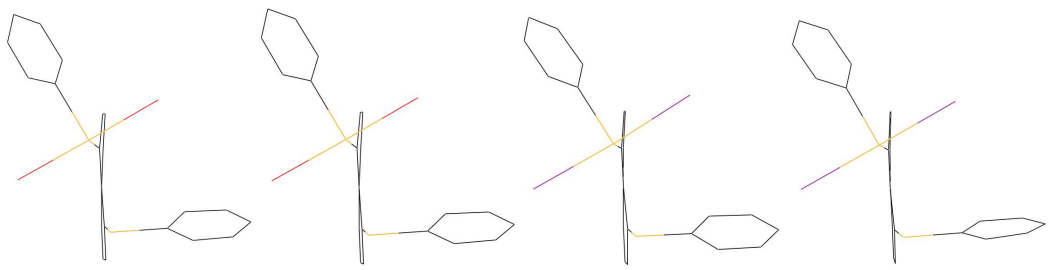

Fig. 6.35 *The molecular structures of adducts* **63-66** *showing the planarity of the naphthalene backbone and orientation of the X-Te-X moiety.*

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Figure 6.36 illustrates the 'AB-*trans* type' arrangement all four adducts adopt with Te-C_{Ph} bonds approaching the naphthyl plane and Se-C_{Ph} bonds lying perpendicular to the plane.[37] Two quasi-linear arrangements of the type Se(1)···Te(1)-C_{Ph} and X-Te-X are observed in each adduct with angles θ and γ in the range 159.8(1)-163.1(1)° and 176.7(1)-179.6(1)° respectively. Additionally, X-Te bond lengths in the X-Te-X moiety (Tables 6.7, 6.8) of the four adducts are over 1.0 Å shorter than the sum of the respective van der Waals radii [BrTe 3.91, ITe 4.04][36] in the known region for 3c-4e bonding.[15,17-19]

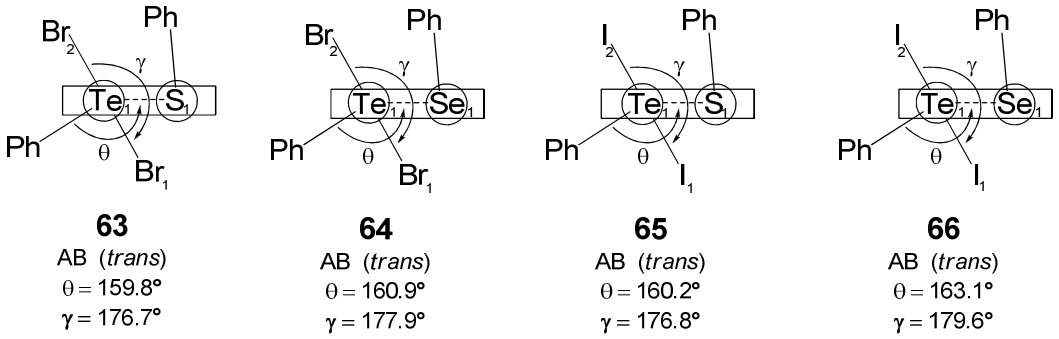

Fig. 6.36 *The structures of* **63-66** *showing the orientation of the Te(phenyl) groups, the type of structure and the linear arrangements within the compounds.*[37]

The 'T-shaped' geometry in the four adducts places one X atoms of the X-Te-X alignment in the *peri*-gap in close proximity to the second *peri*-atom [**63/65** S, **64/66** Se] (Figure 6.36). In each case the distance between the interacting X and S/Se atoms is shorter than the respective sum of van der Waals radii indicating the possibility an intramolecular interaction is taking place [BrS 3.65 Å, **63** Br(1)···S(1) 3.486(2) Å; BrSe 3.75 Å, **64** Br(1)···Se(1) 3.542(2) Å; IS 3.78 Å, **65** I(1)···S(1) 3.6136(16) Å; ISe 3.88 Å, **66** I(1)···Se(1) 3.696(2) Å]. All four adducts adopt the same packing geometry with intermolecular interactions occurring between X-Te-X moieties of two molecules as depicted in Figure 6.37.

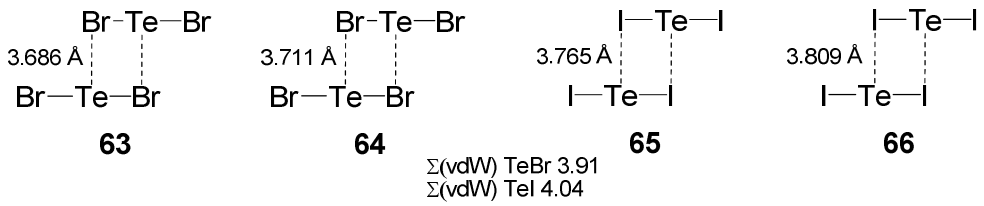

Fig. 6.37 *The molecular structures of the 'T-shape adducts* **63-66** *showing intermolecular packing interactions.*

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In all cases the Te···X distance is shorter than the sum of van der Waals radii for the two interacting atoms. Figure 6.38 shows the molecular structures of **63** and **65** illustrating the intermolecular interactions taking place in the four adducts (**64** and **66** adopt the same arrangement and so pictures of their intermolecular interactions are not illustrated).

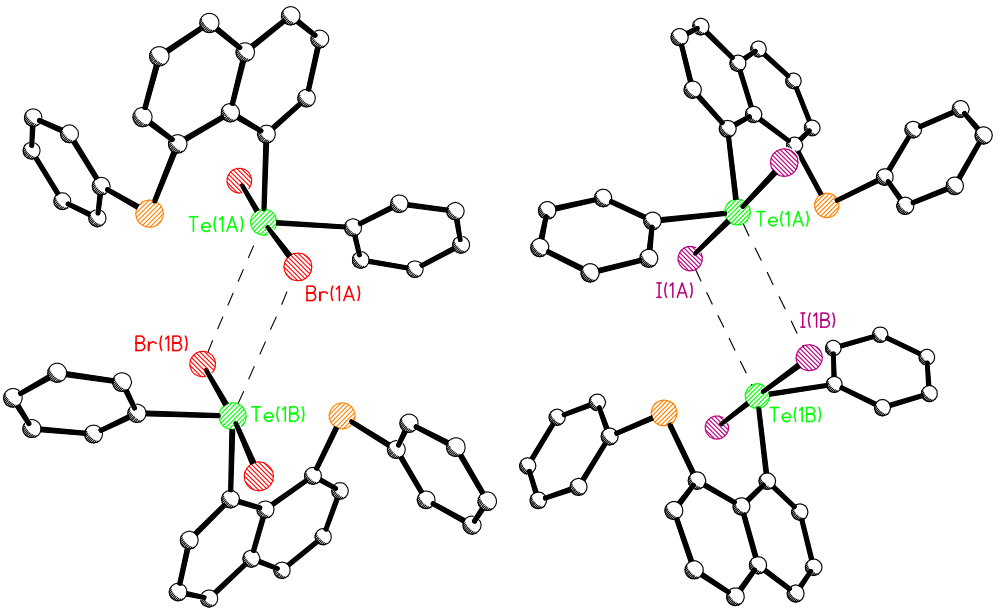

Fig. 6.38 *The molecular structures of the 'T-shape adducts* **63** *and* **65** *showing intermolecular packing interactions.*

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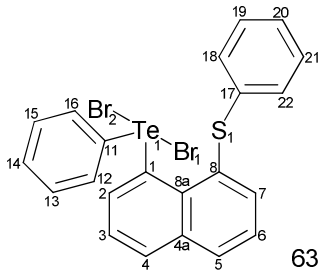
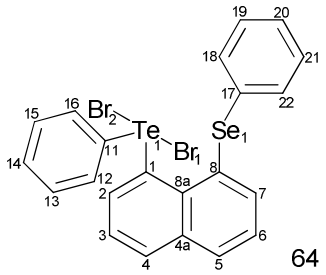
Table 6.7 Selected bond lengths [Å] and angles [°] for the 'T-shaped' insertion adducts **63** and **64**.





Te(1)···S(1)	**3.075(2)**	**Te(1)···Se(1)**	**3.141(2)**
Te(1)-C(1)	2.124(10)	Te(1)-C(1)	2.148(15)
S(1)-C(9)	1.782(11)	Se(1)-C(9)	1.933(14)
S(1)···Br(1)	3.486(2)	Se(1)···Br(1)	3.542(2)
Te(1)-Br(1)	2.7072(11)	Te(1)-Br(1)	2.719(2)
Te(1)-Br(2)	2.6688(12)	Te(1)-Br(2)	2.671(2)
Te(1)-C(1)-C(10)	123.1(7)	Te(1)-C(1)-C(10)	122.2(10)
C(1)-C(10)-C(9)	127.6(9)	C(1)-C(10)-C(9)	130.4(15)
S(1)-C(9)-C(10)	121.3(7)	Se(1)-C(9)-C(10)	120.9(13)
	Σ = 372.0(16)		**Σ = 373.5(27)**
Br(1)-Te(1)-Br(2)	176.67(4)	Br(1)-Te(1)-Br(2)	177.94(6)
Br(1)-Te(1)-C(1)	89.1(2)	Br(1)-Te(1)-C(1)	88.9(4)
Br(1)-Te(1)-C(11)	87.4(2)	Br(1)-Te(1)-C(11)	87.9(4)
Br(2)-Te(1)-C(1)	90.0(2)	Br(2)-Te(1)-C(1)	89.4(4)
Br(2)-Te(1)-C(11)	89.5(2)	Br(2)-Te(1)-C(11)	91.0(4)
Br(1)-Te(1)-S(1)	73.85(2)	Br(1)-Te(1)-Se(1)	73.98(2)
Br(2)-Te(1)-S(1)	109.0(2)	Br(2)-Te(1)-Se(1)	106.9(2)
Distance from naphthalene mean plane			
Te(1)	-0.401(12)	Te(1)	-0.444(1)
S(1)	0.250(12)	Se(1)	0.259(1)
Br(1)	-2.780(11)	Br(1)	-2.816(1)
Br(2)	1.881(14)	Br(2)	1.871(1)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	-179.1(8)	C(6)-C(5)-C(10)-C(1)	-177.0(12)
C(4)-C(5)-C(10)-C(9)	-174.3(8)	C(4)-C(5)-C(10)-C(9)	-173.5(13)

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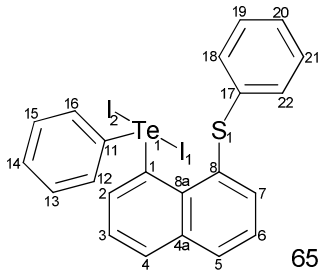
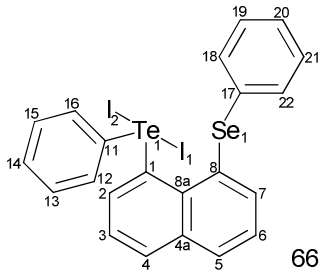
Table 6.8 Selected bond lengths [Å] and angles [°] for the 'T-shaped' insertion adducts **65** and **66**.





Te(1)···S(1)	**3.0767(17)**	**Te(1)···S(1)**	**3.137(2)**
Te(1)-C(1)	2.138(6)	Te(1)-C(1)	2.14(2)
S(1)-C(9)	1.784(6)	Se(1)-C(9)	1.915(19)
S(1)···I(1)	3.6136(16)	Se(1)···I(1)	3.696(2)
Te(1)-I(1)	2.9457(6)	Te(1)-I(1)	2.9538(17)
Te(1)-I(2)	2.9073(6)	Te(1)-I(2)	2.8943(17)
Te(1)-C(1)-C(10)	122.5(4)	Te(1)-C(1)-C(10)	122.6(14)
C(1)-C(10)-C(9)	127.1(6)	C(1)-C(10)-C(9)	129.4(17)
S(1)-C(9)-C(10)	122.7(5)	Se(1)-C(9)-C(10)	120.4(14)
	Σ = 372.3(11)		**Σ = 372.4(31)**
I(1)-Te(1)-I(2)	176.81(2)	I(1)-Te(1)-I(2)	179.59(6)
I(1)-Te(1)-C(1)	89.66(18)	I(1)-Te(1)-C(1)	90.0(4)
I(1)-Te(1)-C(11)	87.38(18)	I(1)-Te(1)-C(11)	89.5(4)
I(2)-Te(1)-C(1)	91.53(18)	I(2)-Te(1)-C(1)	90.2(4)
I(2)-Te(1)-C(11)	89.51(18)	I(2)-Te(1)-C(11)	90.2(4)
I(1)-Te(1)-S(1)	73.71(18)	I(1)-Te(1)-Se(1)	74.66(4)
I(2)-Te(1)-S(1)	109.46(18)	I(2)-Te(1)-Se(1)	105.71(4)
Distance from naphthalene mean plane			
Te(1)	-0.3690(82)	Te(1)	-0.372(8)
S(1)	0.3007(77)	Se(1)	0.317(8)
I(1)	-2.9482(75)	I(1)	-2.977(8)
I(2)	2.0949(94)	I(2)	2.172(9)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	-177.3(6)	C(6)-C(5)-C(10)-C(1)	179.7(14)
C(4)-C(5)-C(10)-C(9)	-174.1(5)	C(4)-C(5)-C(10)-C(9)	-174.7(13)

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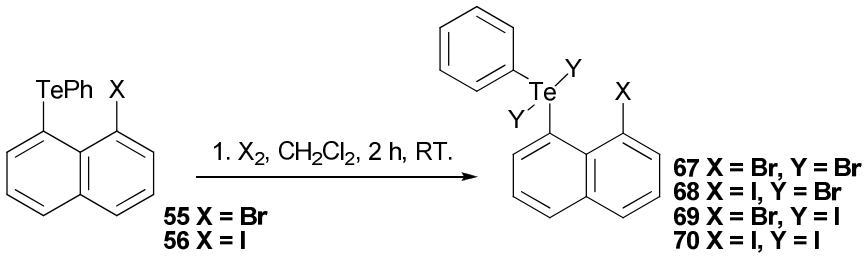
Dihalogen reactions of 1-bromo-8-(phenyltellurenyl)naphthalene 55 and 1-iodo-8-(phenyltellurenyl)naphthalene 56.

1-Bromo-8-(phenyltellurenyl)naphthalene **55** and 1-iodo-8-(phenyltellurenyl)naphthalene **56** react with dihalogens (Br_2, I_2) at the tellurium-donor atom, to afford the four analogous 'T-shaped' insertion adducts **67-70** (Scheme 6.9).



Scheme 6.9 *The reaction scheme for the preparation of the series of 'T-shaped' insertion adducts* **67-70**.

The ^{125}Te NMR spectroscopy data for the three 'T-shaped' adducts **67-70** is compared in Table 6.9 with the two starting compounds **55** and **56**. As expected all four adducts see a downfield shift compared to the starting materials **55** and **56**. This can be explained by the presence of the electronegative Br and I atoms forming the X-Te-X arrangement. The greater electronegativity of Br over I is also observed with an upfield shift seen when Br-Te-Br in **67** and **68** is replaced by I-Te-I in **69** and **70** respectively.

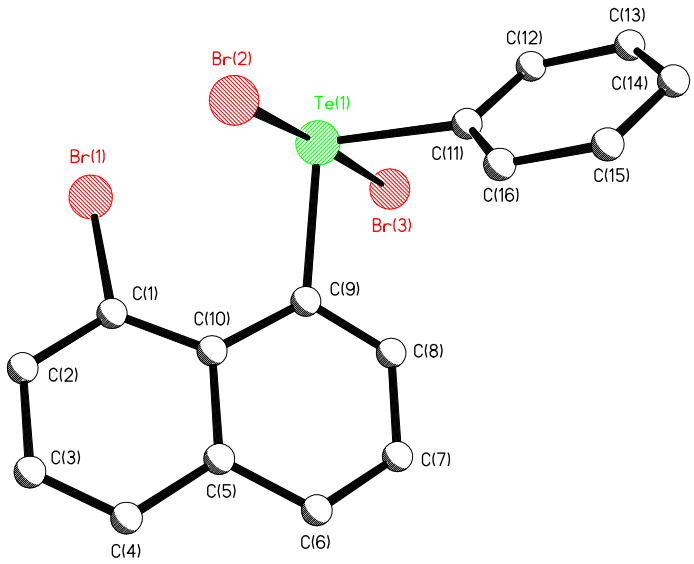


Fig. 6.39 *The molecular structure of the 'T-shaped' insertion adduct* **67**.

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Table 6.9 ^{77}Se and ^{125}Te NMR spectroscopy data [δ (ppm)] for the 'T-shaped' insertion adducts **67-70**.

	67	**68**	**69**	**70**	**55**	**56**
peri-atoms	TeBr	TeI	TeBr	TeI	TeBr	TeI
X-Te-X	Br-Te-Br	Br-Te-Br	I-Te-I	I-Te-I	-	-
^{125}Te NMR	942.8	903.0	887.5	848.0	731.2	698.3

The molecular structures (Figures 6.39-6.42) show the four 'T-shaped' adducts **67-70** arrange with similar structural geometries with minor deviations through steric crowding and naphthalene distortion. Bond lengths and angles of the bromine adducts **67** and **68** are compared in Table 6.10 while those of the iodine adducts **69** and **70** are compared in Table 6.11. Further information on all the crystal structures can be found in Appendices 45-48.

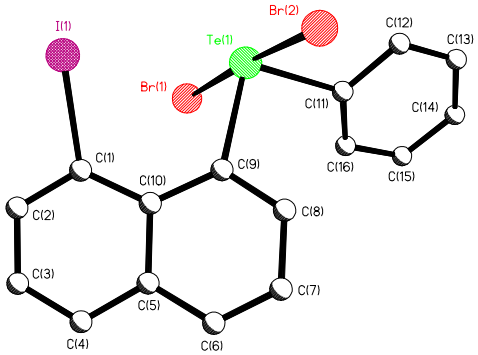

Fig. 6.40 *The molecular structure of the 'T-shaped' insertion adduct* **66**.

Intramolecular non-bonded Br(1)···Te(1) *peri*-distances for **67** [3.2397(15) Å] and **69** [3.1563(6) Å] are comparable to the donor compound **55** [3.1909(10) Å] and likewise expected larger values for the I(1)···Te(1) interaction in **68** [3.3810(7) Å] and **70** [3.3608(11) Å] match the distance in **56** [3.3146(6) Å].

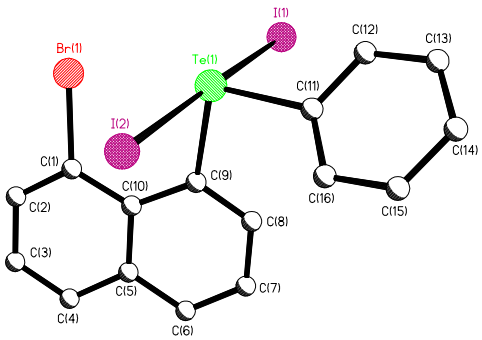

Fig. 6.41 *The molecular structure of the 'T-shaped' insertion adduct* **69**.

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In-plane distortions in the C-C-C group between the *peri*-atoms is shown by the sum of the bay region angles to be similar in **67** [373.1(18)°] and **69** [372.4(9)°] and comparable to **55** [373.6(11)°]. The *peri*-iodine atom in **68** and **70** is accommodated by greater in-plane distortion with values for the bay region angles [375.9(14)°, 378.7(15)°] comparable to **56** [376.2(10)°].

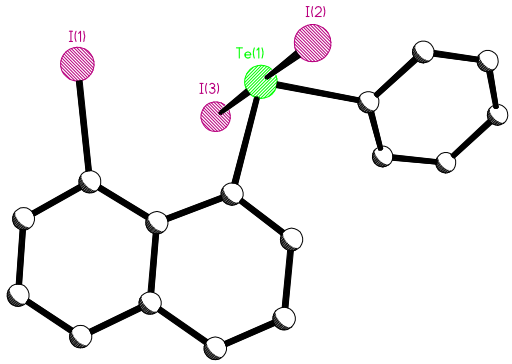

Fig. 6.42 *The molecular structure of the 'T-shaped' insertion adduct* **70**.

Compounds **67** and **68**, containing the Br-Te-Br linear fragment, exhibit a greater degree of out-of-plane distortion compared with **69** and **70**. Torsion angles associated with the C5-C10 bond also suggest these compounds display less planarity in their naphthalene backbones (Figure 6.43).

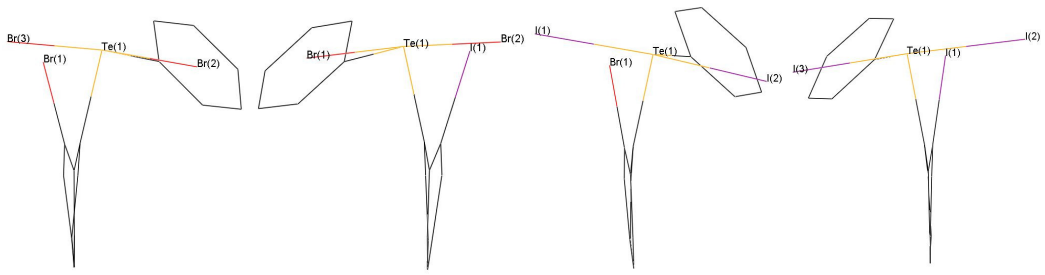

Fig. 6.43 *The molecular structures of the 'T-shaped' insertion adducts* **67-70** *showing the planarity of the naphthalene backbones.*

Figure 6.44 illustrates the 'B-type' arrangement all four adducts adopt for the Te(phenyl) group with angles for the Te-C_{Ph} bond approaching the naphthyl plane between 144-159°.[37] Two quasi-linear arrangements of the type X···Te-C_{Ph} and X-Te-X are observed in each adduct with angles θ and γ in the range 162.5(1)-173.2(1)° and 175.8-177.3(1)° respectively. Additionally, X-Te bond lengths in the X-Te-X fragment of the four adducts are over 1.0 Å shorter than the sum of the respective van der Waals radii in the known region for 3c-4e bonding to take place.[15,17-19]

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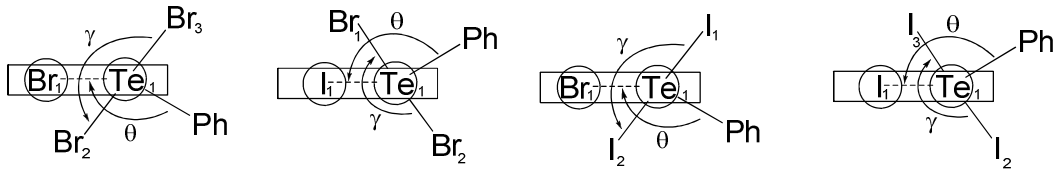

67	**68**	**69**	**70**
'type B'	'type B'	'type B'	'type B'
θ = 162.5°	θ = 163.9°	θ = 172.0°	θ = 173.2°
γ = 175.8°	γ = 176.6°	γ = 176.4°	γ = 177.3°

Fig. 6.44 *The structures of* **67-70** *showing the orientation of the Te(phenyl) groups, the type of structure and the linear arrangements within the compounds.*[37]

The 'T-shaped' geometry in the four adducts results in one of the X atoms of the X-Te-X alignment sitting in the *peri*-gap in close proximity to the *peri*-halide atom (Figure 6.44). In each case the distance between these two halogen atoms is greater than the sum of their van der Waals radii so no interaction is envisaged.

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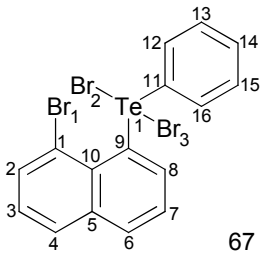
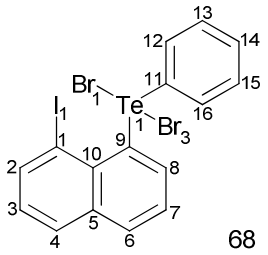
Table 6.10 Selected bond lengths [Å] and angles [°] for the 'T-shaped' insertion adducts **67** and **68**.



67



68

Te(1)···Br(1)	**3.2397(15)**	**Te(1)···I(1)**	**3.3810(7)**
Br(1)-C(1)	1.900(11)	Te(1)-C(9)	2.150(8)
Te(1)-C(9)	2.153(10)	I(1)-C(1)	2.117(9)
Br(1)···Br(2)	3.7079(17)	I(1)···Br(1)	3.8497(11)
Te(1)-Br(2)	2.6664(13)	Te(1)-Br(1)	2.6578(10)
Te(1)-Br(3)	2.6686(13)	Te(1)-Br(2)	2.6779(11)
Br(1)-C(1)-C(10)	121.3(8)	Te(1)-C(9)-C(10)	124.6(6)
C(1)-C(10)-C(9)	129.3(10)	C(1)-C(10)-C(9)	129.3(8)
Te(1)-C(9)-C(10)	122.5(8)	I(1)-C(1)-C(10)	122.0(6)
	Σ = 373.1(18)		**Σ = 375.9(14)**
Br(2)-Te(1)-Br(3)	175.80(4)	Br(1)-Te(1)-Br(2)	176.55(3)
Br(2)-Te(1)-C(9)	88.8(2)	Br(1)-Te(1)-C(9)	89.2(2)
Br(2)-Te(1)-C(11)	88.4(3)	Br(1)-Te(1)-C(11)	88.6(2)
Br(3)-Te(1)-C(9)	87.4(2)	Br(2)-Te(1)-C(9)	87.7(2)
Br(3)-Te(1)-C(11)	90.2(3)	Br(2)-Te(1)-C(11)	90.2(2)
Br(2)-Te(1)-Br(1)	77.10(2)	Br(1)-Te(1)-I(1)	78.20(2)
Br(3)-Te(1)-Br(1)	103.53(2)	Br(2)-Te(1)-I(1)	102.34(2)
Distance from naphthalene mean plane			
Te(1)	0.641(15)	Te(1)	0.646(15)
Br(1)	-0.550(14)	I(1)	-0.644(14)
Br(2)	2.825(13)	Br(1)	2.825(13)
Br(3)	-1.541(17)	Br(2)	-1.549(17)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	174.0(10)	C(6)-C(5)-C(10)-C(1)	-168.7(8)
C(4)-C(5)-C(10)-C(9)	170.2(10)	C(4)-C(5)-C(10)-C(9)	-175.5(8)

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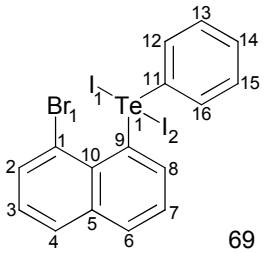
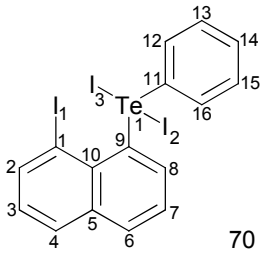
Table 6.11 Selected bond lengths [Å] and angles [°] for the 'T-shaped' insertion adducts **69** and **70**.



69



70

Te(1)···Br(1)	**3.1563(6)**	**Te(1)···I(1)**	**3.3608(11)**
Br(1)-C(1)	1.911(6)	I(1)-C(1)	2.097(11)
Te(1)-C(9)	2.150(6)	Te(1)-C(9)	2.159(9)
Br(1)···I(2)	4.0089(6)	I(1)···I(3)	2.9042(7)
Te(1)-I(1)	2.9343(5)	Te(1)-I(2)	2.9480(7)
Te(1)-I(2)	2.8952(4)	Te(1)-I(3)	2.9042(7)
Br(1)-C(1)-C(10)	121.5(4)	I(1)-C(1)-C(10)	126.3(7)
C(1)-C(10)-C(9)	128.1(5)	C(1)-C(10)-C(9)	128.2(8)
Te(1)-C(9)-C(10)	122.8(3)	Te(1)-C(9)-C(10)	124.2(7)
	Σ = 372.4(9)		**Σ = 378.7(15)**
I(1)-Te(1)-I(2)	176.405(19)	I(2)-Te(1)-I(3)	177.27(3)
I(1)-Te(1)-C(9)	90.47(14)	I(2)-Te(1)-C(9)	89.3(2)
I(1)-Te(1)-C(11)	91.21(15)	I(2)-Te(1)-C(11)	90.5(2)
I(2)-Te(1)-C(9)	86.18(14)	I(3)-Te(1)-C(9)	88.4(2)
I(2)-Te(1)-C(11)	90.63(15)	I(3)-Te(1)-C(11)	91.2(2)
I(1)-Te(1)-Br(1)	95.06(15)	I(2)-Te(1)-I(1)	95.2(2)
I(2)-Te(1)-Br(1)	82.85(14)	I(3)-Te(1)-I(1)	82.9(2)
Distance from naphthalene mean plane			
Br(1)	0.312(14)	I(1)	-0.410(14)
Te(1)	-0.614(14)	Te(1)	0.436(14)
I(1)	2.063(14)	I(2)	-2.305(14)
I(2)	-3.187(14)	I(3)	3.130(14)
Torsion angle			
C(6)-C(5)-C(10)-C(1)	174.4(5)	C(6)-C(5)-C(10)-C(1)	-175.2(9)
C(4)-C(5)-C(10)-C(9)	176.5(5)	C(4)-C(5)-C(10)-C(9)	-176.8(9)

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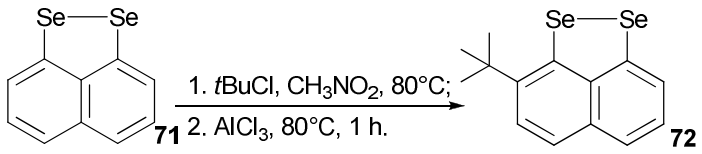
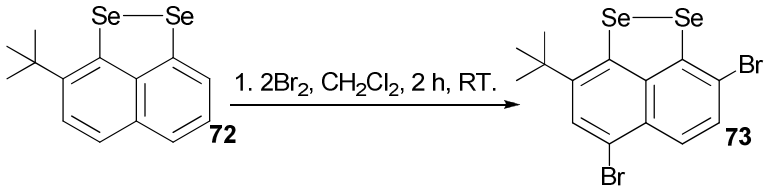
Reaction of 2-mono-*tert*-butylnaphtho[1,8-*c,d*][1,2]diselenole 72 with dibromine.

2-Mono-*tert*-butylnaphtho[1,8-*c,d*][1,2]diselenole **72** was prepared in house in the Woollins Group by Amy Fuller following methods reported for the preparation of the thiol analogue (Scheme 6.10).[39,40]



Scheme 6.10 *The reaction scheme for the preparation of* **72**.[39,40]

Upon reaction of 2-mono-*tert*-butylnaphtho[1,8-*c,d*][1,2]diselenole **72** with dibromine no interaction between selenium and bromine is observed. Instead electrophilic aromatic substitution dominates to produce the doubly substituted compound 4,7-dibromo-2-mono-*tert*-butylnaphtho[1,8-*c,d*][1,2]diselenole **73** (Scheme 6.11).



Scheme 6.11 *The reaction scheme for the preparation of 4,7-dibromo-2-mono-tert-butylnaphtho[1,8-c,d][1,2]diselenole* **73**.

In substituted naphthalenes the ring carrying the substituent is the one most affected during electrophilic attack. Selectivity of the two electrophilic aromatic substitution reactions can therefore be explained by the directing influence of selenium and the steric bulk of the *t*-butyl group. Both selenium and *t*-butyl groups donate electrons into the π-system, activating the naphthalene ring and directing incoming electrophiles to the *ortho* or *para* positions. Attack at the position *para* to selenium would be sterically more favourable, keeping the two large bromine and *t*-butyl groups further apart. The second substitution reaction is directed to the *ortho* position on the second ring to avoid the steric interaction with the first bromine atom.[35]

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The ^{77}Se NMR spectrum of **73** shows a downfield shift compared to **72** [δ = 413.61 ppm and δ = 360.07 ppm][40] with two shifts at δ = 453.77 ppm and δ = 374.37 ppm for the two different selenium environments.

The molecular structure of **73** is shown in Figure 6.45. Selected bond lengths and angles are listed in Table 6.12 and further information on the crystal structure can be found in Appendix 49. The molecular structure of **73** shows a selenium-selenium bonding *peri*-distance of 2.3388(14) Å which is shorter than the known *peri*-distance calculated for naphthalene [2.44 Å].[41] Evidence for a negative in-plane distortion and conformation of a *peri*-bond is observed from the sum of the splay angles [355.2(15)°], which being lower than 357.2(2)° for naphthalene, show the *peri*-atoms have come closer as a result of a favourable interaction. As there is no steric hindrance between the *peri*-atoms, no distortion of the naphthalene geometry is required. The two bonding *peri*-selenium atoms lie on the naphthyl plane with no observed out-of-plane distortion and a strictly planar naphthalene backbone (Figure 6.46).

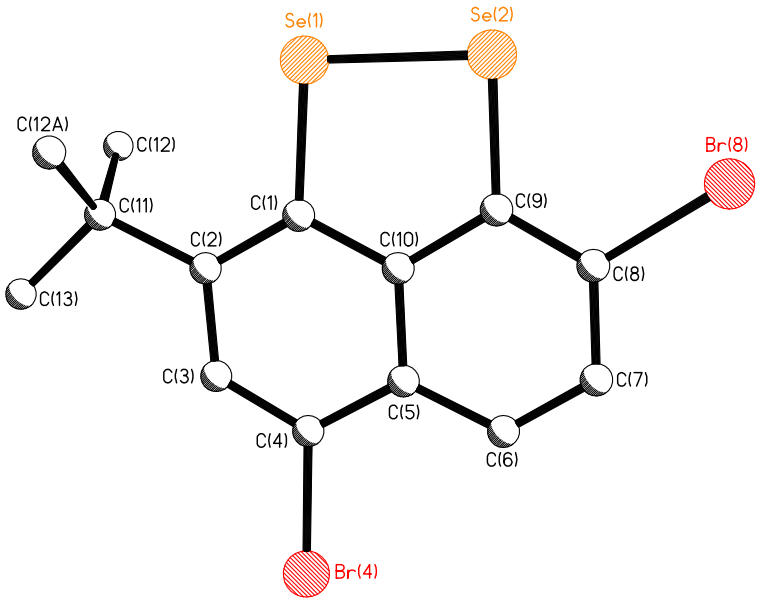

Fig. 6.45 *The crystal structure of 4,7-dibromo-2-mono-tert-butylnaphtho[1,8-c,d][1,2]diselenole* **73**.

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The two bromine atoms, the quaternary carbon [C11] of the *t*-butyl group and one of carbons of the methyl groups [C13] also lie on the naphthalene plane. The two remaining methyl carbons are found at equal distances above and below the plane [**C12** 1.26(1) Å, **C12A** -1.26(1) Å] (Figure 6.46).

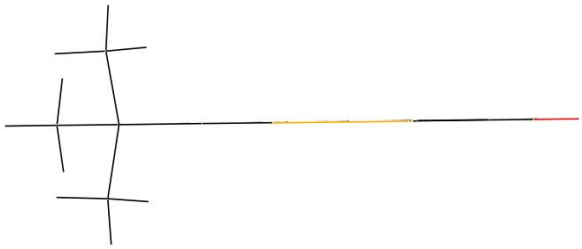

Fig. 6.46 *The molecular structure of 4,7-dibromo-2-mono-tert-butylnaphtho[1,8-c,d][1,2]diselenole* **73** *showing the strictly planar geometry and the alignment of the t-butyl group.*

Figure 6.47 illustrates the intermolecular non-bonded interactions observed between two molecules of **73**, with Br(8)···Br(4') distances [3.479(1) Å] shorter than the sum of van der Waals radii for two interacting bromine atoms [3.70 Å].[36]

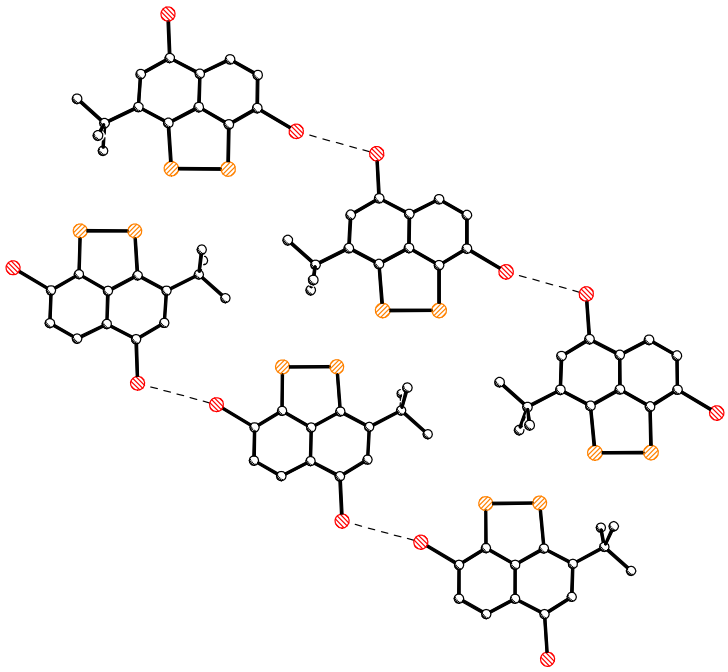

Fig. 6.47 *The crystal structure of* **73** *showing intermolecular packing between bromine atoms of two interacting molecules.*

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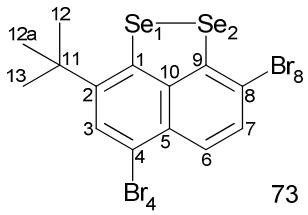
Table 6.12 Selected bond lengths [Å] and angles [°] for 4,7-dibromo-2-mono-*tert*-butylnaphtho[1,8-*c,d*][1,2]diselenole **73**.



73

Se(1)-Se(2)	**2.3388(14)**
Se(1)-C(1)	1.935(9)
Se(2)-C(9)	1.888(9)
Se(2)···Br(8)	3.2567(15)
Br(8)···Br(4')	3.479(1)
Se(1)-C(1)-C(10)	114.4(6)
C(1)-C(10)-C(9)	121.7(8)
Se(2)-C(9)-C(10)	119.1(7)
	Σ = 355.2(15)

Distance from naphthalene mean plane	
Se(1)	0.000(1)
Se(2)	0.000(1)

Torsion angle	
C(6)-C(5)-C(10)-C(1)	180.0(1)
C(4)-C(5)-C(10)-C(9)	180.0(1)

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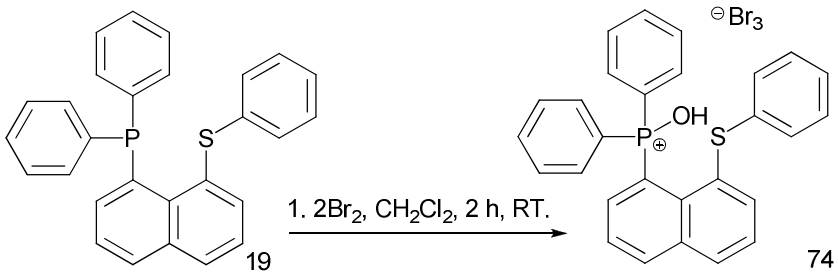
Reaction of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine 19 with dibromine.

Treatment of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** with excess dibromine in dichloromethane led to the formation of the air-stable phosphonium salt **74**. Phosphorus forms a 4 co-ordinate cationic fragment via the addition of a hydroxyl group which is balanced by a linear Br_3^- counteranion (Scheme 6.12). The ^{31}P NMR spectrum shows a single peak at δ = 52.48 ppm.



Scheme 6.12 *The reaction scheme for the preparation of hydroxydiphenyl[(8-phenylsulfanyl)naphthalene-1-yl]phosphonium tribromide* **74**.

The molecular structure of **74** is shown in Figure 6.48. Selected bond lengths and angles are listed in Table 6.13 and compared with those for phosphine **19**. Further information on the crystal structure can be found in Appendix 50.

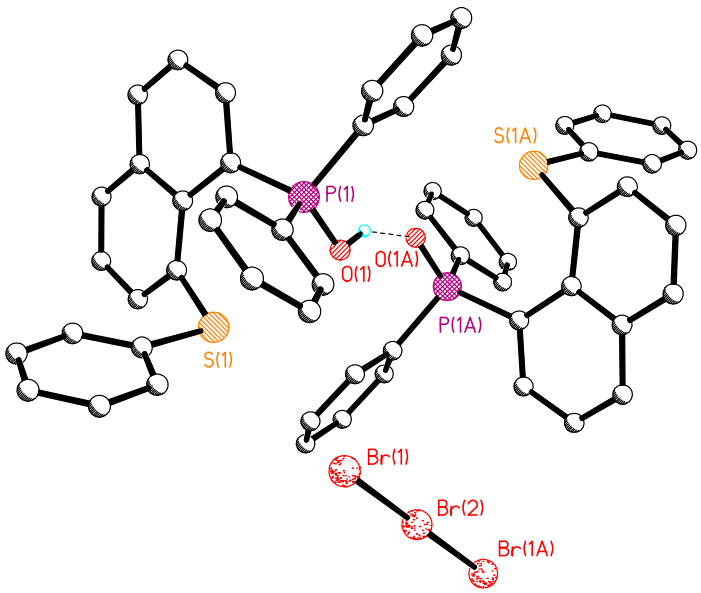


Fig. 6.48 *The molecular structure of hydroxydiphenyl[(8-phenylsulfanyl)naphthalene-1-yl]phosphonium tribromide* **74**.

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In the crystal structure, two molecules of **74** share a proton between the two oxygen atoms forming a P-O-H-O-P bridge. All five atoms lie on the same plane with P-O-H angles of 131.2(1)° and the O-H-O angle of 180.0(1)°. P-O bond lengths are the same in both molecules [1.527(6) Å] and are in between values for the phosphine oxide **21** [1.492(2) Å] and a standard single P-OH bond [1.56 Å].[42] This value can be explained by the equilibrium taking place between a phosphine oxide and a phosphonium cation with an averaged structure as depicted by Figure 6.49.

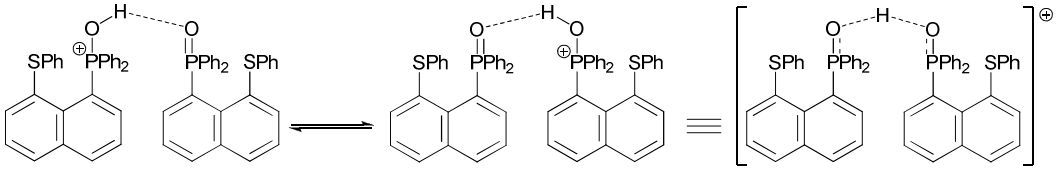

Fig. 6.49 *In the crystal structure of* **74***, two molecules share a proton to form a P-O-H-O-P bridge; explained by the equilibrium between a phosphine oxide and a phosphonium cation.*

Compared to **19**, the phosphonium salt **74** exhibits greater strain relief via naphthalene distortion due to increased steric repulsion occurring in the compound. The *peri*-atoms are accommodated by a longer intramolecular non-bonded P···S distance [3.165(2) Å] compared to the same distance in **19** [3.0330(7) Å]. An increase in the splay of the bay region in **74** is seen by comparison of the sums of the *peri*-region angles [**72** 375.5(17)°, **19** 374.1(3)°] and shows a greater in-plane distortion occurs in the phosphonium salt. The displacement of the phosphorus [0.436(11) Å] and sulfur [-0.466(11) Å] atoms above and below the naphthalene plane is also much greater in **74**. Torsion angles (Table 6.13) also indicate that the naphthalene backbone displays a greater buckling compared with **19** (Figure 6.50).

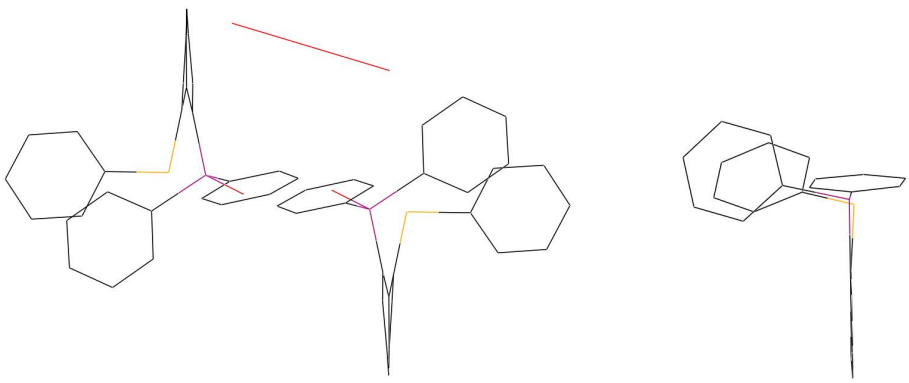

Fig. 6.50 *The crystal structures of* **74** *and* **19** *showing the difference in out-of-plane distortion and planarity of the naphthalene backbones.*

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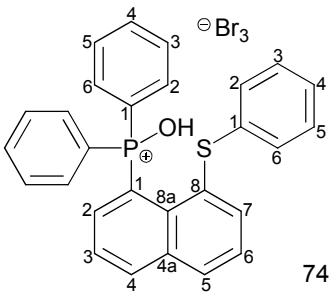
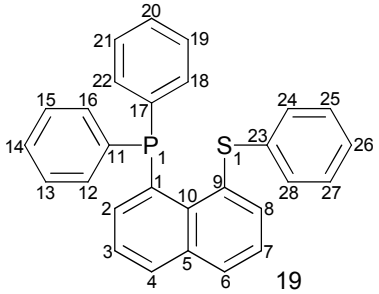
Table 6.13 Selected bond lengths [Å] and angles [°] for **74** and **19**.





S(1)···P(1)	**3.165(2)**	**S(1)···P(1)**	**3.0330(7)**
P(1)-C(1)	1.796(11)	P(1)-C(1)	1.8548(19)
S(1)-C(9)	1.789(12)	S(1)-C(9)	1.785(2)
P(1)-O(1)	1.527(6)		
O(1)···S(1)	2.951(4)		
Br(1)-Br(2)	2.5984(12)		
Br(2)-Br(1A)	2.5984(12)		
P(1)-C(1)-(10)	126.2(7)	P(1)-C(1)-(10)	124.07(13)
C(1)-C(10)-C(9)	126.4(10)	C(1)-C(10)-C(9)	126.90(17)
S(1)-C(9)-(10)	122.9(7)	S(1)-C(9)-(10)	123.11(13)
	Σ = 375.5(17)		**Σ = 374.1(3)**
Br(1)-Br(2)-Br(1A)	180.00(6)		
O(1)-P(1)-C(1)	113.1(4)		
P(1)-O(1)-H(1o)	131.2(1)		
Distance from naphthalene mean plane [Å]			
P(1)	0.436(11)	P(1)	0.007(1)
S(1)	-0.466(11)	S(9)	0.127(1)
O(1)	1.518(13)		
Torsion angles			
C(6)-C(5)-C(10)-C(1)	171.9(7)	C(6)-C(5)-C(10)-C(1)	178.49(16)
C(4)-C(5)-C(10)-C(9)	174.9(7)	C(4)-C(5)-C(10)-C(9)	-179.51(16)

Hydrogen bond geometry for 72

***D*-H···A**	***D*-H**	**H···A**	***D*···A**	***D*-H···A**
O(1)-H(1o)···O(1A)	1.218(1)	1.218(1)	2.435(1)	180.0(1)

Summary

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1,8-Bis(phenylsulfanyl)naphthalene **37**, 1,8-bis(phenylselenyl)naphthalene **38**, the three novel mixed chalcogen naphthalene systems **41**-**43** along with the tellurium compounds **55** and **56** reacted with dibromine and diiodine to produce a range of different adducts; C.-T. 'spoke', C.-T. 'extended spoke', 'T-shaped' (or TBP) adducts and an ionic form of C.-T. 'extended spoke' with formula $[RE\text{-}X]^{+}\cdots[X\text{-}X_2]^{-}$.

For each adduct the structure of the final product can be explained by the amount of charge-transfer occurring between the chalcogen donor atom and the di-halogen acceptor. This is estimated based on the electronegativity (χ) of the elements involved. 'T-shaped' (TBP) adducts will form if the halogen X is more electronegative than chalcogen E $[RE^{\delta+}\text{-}X^{\delta-}]$ whilst if the converse is true then the C.-T. 'spoke' adducts will predominate.[18,20,21]

1,8-Bis(phenylsulfanyl)naphthalene proved to be an exception and upon reaction with bromine no adduct was formed. The unavailability of the lone-pair on sulfur for donation into the empty orbitals of dibromine meant electrophilic aromatic substitution dominated and compound **57** was formed.

The selenium compound 1,8-bis(phenylselenyl)naphthalene **38** and the mixed selenium-sulfur compound 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene **41** both react in a similar way to the dihalogens. In the mixed compound, the selective reactivity towards selenium can be attributed to its lower electronegativity and hence greater donor ability over sulfur.[1,2,22]

Upon reaction with dibromine, both selenium compounds **38** and **41** form an ionic C.-T. 'extended spoke' adduct represented by the formula $[RSe\text{–}Br]^{+}\cdots[Br\text{–}Br_2]^{-}$.[2,34] Reaction of the compounds with diiodine leads to the formation of C.-T. 'spokes' and C.-T. 'extended spokes'.

Generally, when the halogen (X) is more electronegative than the chalcogen atom (E), 'T-shaped' or trigonal bipyramidal (TBP) adducts are formed.[18,20,21] Consequently, all the known reactions between tellurium-donors [χ(Te) 2.08][22] and di- or inter-halogens [χ(F) 3.94- χ(I) 2.36] form 'T-shaped' adducts.

Reaction of the four tellurium compounds (**42**, **43**, **55**, **56**) with the dihalogens is no exception. In each case, tellurium forms a strong donor-strong acceptor system with the dihalogen molecule sufficient enough to cleave the X-X bond and oxidise tellurium.[1,2] Subsequent nucleophilic attack

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occurring at the tellurium site of the $[RTe–X]^+$ cation affords the 'T-shaped' hypervalent adduct containing the quasi linear X-Te-X alignment.[1,2] In the mixed tellurium-sulfur **42** and tellurium-selenium **43** compounds, reaction with the dihalogen occurs at the larger, less electronegative tellurium atom due to its greater donor ability over sulfur or selenium.

2-Mono-*tert*-butylnaphtho[1,8-*c,d*][1,2]diselenole **72** favours aromatic electrophilic substitution over the formation of adducts by dibromine reacting at selenium. From molecular structure of the disubstituted compound produced **73**, the selenium-selenium *peri*-bond reflects the lack of steric strain within the molecule and therefore the lack of structural distortion required for its relief. This compound is strictly planar with no out-of-plane distortion and a negative in-plane distortion showing the approach of the *peri*-atoms.

Reaction of phosphine **19** with dibromine produced the tetravalent phosphonium salt **74** which packs via a P-O-H-O-P bridge showing intermediate bond lengths and properties between a phosphine oxide and phosphonium cation.

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Chapter 7 - Conclusion

Atomic interactions are a fundamental aspect of chemistry, biology and materials science.[1] Great advances have been made in the knowledge of strong covalent and ionic bonding yet, a major challenge for chemists is to develop a full understanding of weak intra- and intermolecular forces. *Peri*-substituted naphthalenes are able to constrain heavy polarisable elements in close proximity using a rigid C_3-backbone and are therefore ideal models for studying such interactions.

The *peri*-carbon atoms of naphthalene itself are separated by a distance of 2.44 Å,[2] sufficient for accommodating two hydrogen atoms, but it is reasonable to expect larger substituents at the *peri*-positions will experience considerable steric hindrance.[3] While this is true, intramolecular interactions between *peri*-substituents can also be attractive due to the presence of weak or strong bonding.[4]

The ease of forming sterically crowded *peri*-substituted naphthalenes is the result of relieving steric strain via naphthalene distortions which effectively changes the geometry away from that of 'ideal' naphthalene. The most common forms of naphthalene distortion are in-plane and out-of-plane deviations of the exocyclic bonds and buckling of the naphthalene ring system.[3]

X-ray structural data is central for assessing the repulsive steric effects between heavy *peri*-substituents and therefore quantifying naphthalene distortion. Molecular structures also help to elucidate attractive effects between *peri*-atoms and verify the existence of weak intra- and intermolecular interactions.

In efforts to understand the factors which influence naphthalene distortion and study possible weak interactions between heavy heteroatoms, a mixture of 1,8-disubstituted naphthalenes have been prepared containing a variety of *peri*-substituents.

Initial investigations focussed on mixed 1,8-disubstituted naphthalene systems and the synthesis and structural study of a series of mixed phosphorus-chalcogenide species has been described. The study of interactions between mixed heavy atoms progressed towards a series of mixed chalcogenide compounds of the type Nap[Eph][E'Ph] (E = S, Se, Te) (Figure 7.1).

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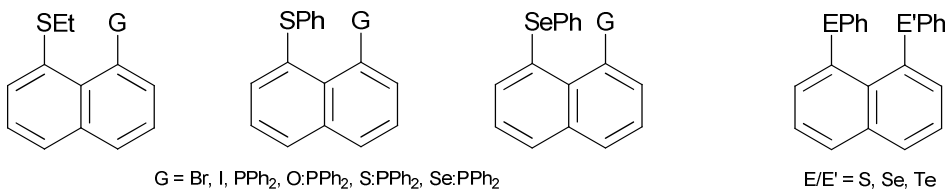

Fig. 7.1 *The structural motifs for the series of phosphorus-chalcogenide and mixed chalcogenide compounds synthesised.*

The compounds synthesised exhibit intramolecular *peri*-interactions extending from no interaction due to repulsive effects, weak attractive 3c-4e type interactions and one example containing a strong covalent *peri*-bond.

Peri-distances [3.38-2.34 Å] give an indication of the size of the interacting *peri*-atoms [1.55(N) - 2.06(Te) Å] and are influenced by the degree of exocyclic bond distortion. In-plane distortion [sum of *peri*-angles = 380.8-365.3°] occurs in all compounds with a positive splay angle where the sum of the bay region angles is greater than that for naphthalene [357.2°][2] (apart from in **73** containing the covalent *peri*-bond [355.2°]) (Figure 7.2).

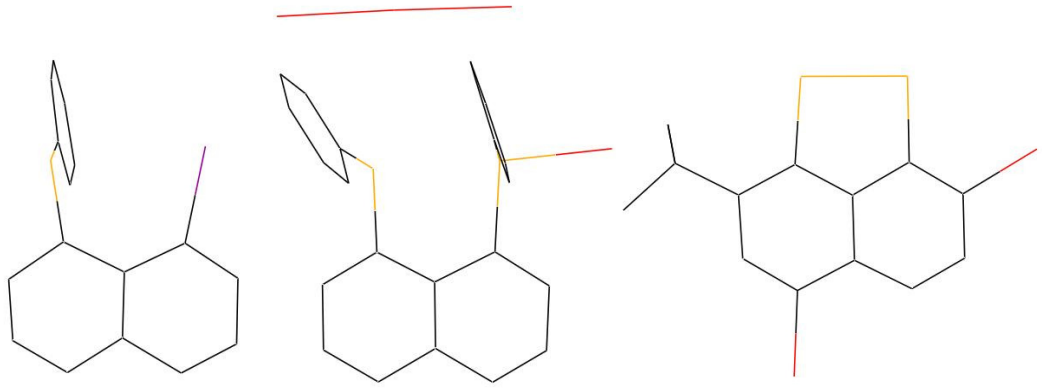

Fig. 7.2 *Comparing the positive splay angles in the crystal structures of compounds* **20** *and* **61** *with the negative splay angle caused by the covalent bond in* **73**.

Displacement of the *peri*-atoms above and below the naphthalene ranges from no distortion, atoms lying on the naphthyl plane, to 0.744 Å away from the plane. The least planar naphthalene backbone observed in the series of compounds, **17**, displays a torsion angle of 168.4°, 11.6° from the 'ideal' planar geometry as found in compound **73** [180°] (Figure 7.3).[2]

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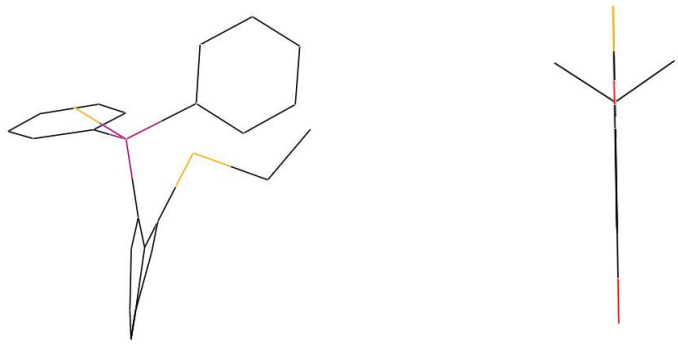
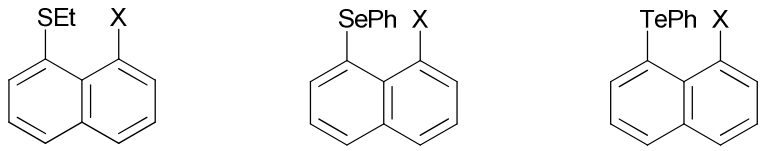


Fig. 7.3 *Comparing the planarity of the naphthalene backbones in the crystal structures of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine sulfide* **17** *and 4,7-dibromo-2-mono-tert-butylnaphtho[1,8-c,d][1,2]diselenole* **73**.

Dependence of the *peri*-distance on *peri*-atom size.

The primary parameter used to quantify the amount of strain in non-ideal naphthalenes is the *peri*-distance which encapsulates all molecular deviations in one parameter. As the size of the *peri*-atoms increase it could be expected that repulsion and steric strain increases forcing the atoms further apart, thus increasing the *peri*-distance.[3]



Compound	2	15	31	33	55	56
X	Br	I	Br	I	Br	I
sum vdW[5]	(BrS) 3.65	(IS) 3.78	(BrSe) 3.75	(ISe) 3.88	(BrTe) 3.91	(ITe) 4.04
PD	3.05/3.06	3.24	3.11	3.25	3.19	4.04
splay angles	374.5/375.1	376.9	373	374.9	373.6	376.2

Fig. 7.4 *The dependence of peri-distance (PD) on in-plane distortion and the peri-atom size for compounds* **2**, **15**, **31**, **33**, **55** *and* **56**.

For the Nap[SEt][X], Nap[SePh][X] and Nap[TePh][X] (X = Br, I) compounds, the increased size of iodine compared to bromine causes greater steric interaction. Naphthalene in-plane distortion, taking place to relieve the steric strain, increases in each case to accommodate the larger iodine atom. This forces the *peri*-atoms further apart resulting in a longer non-bonded *peri*-distance, *i.e.* dependence on the size of the *peri*-atoms (Figure 7.4).

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Repulsive steric strain caused by inserting increasingly larger atoms at the 1,8-positions in the six chalcogen analogues **37**-**39** and **41**-**43** is also shown to occur to a greater extent as the overall combined size of the *peri*-atoms increases. Figure 7.5 shows the general relationship between *peri*-atom size and its effect on increasing the *peri*-distance in the chalcogenide series.

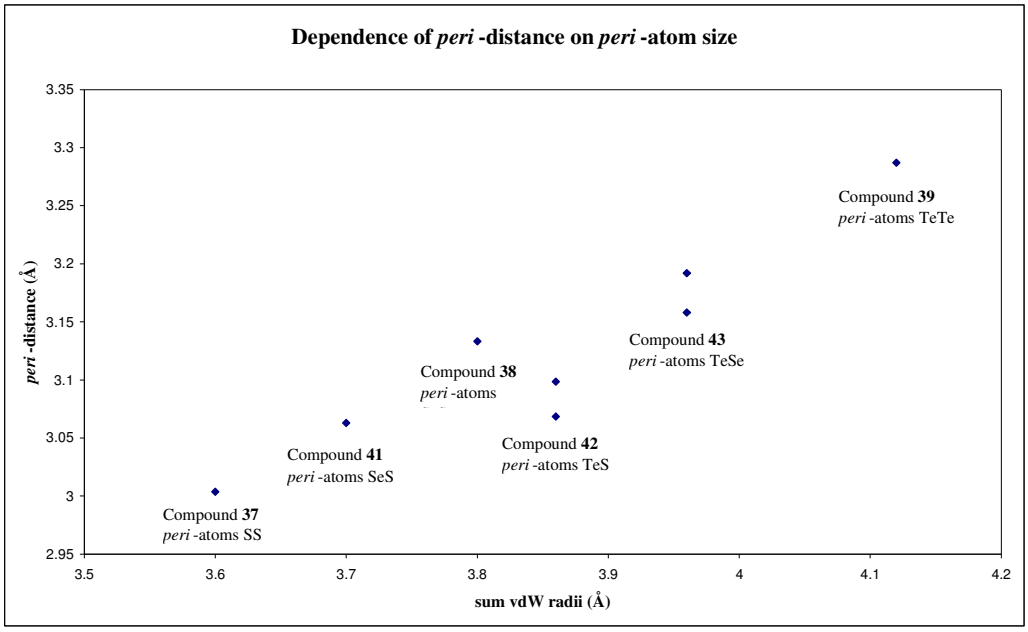

Fig. 7.5 *The dependence of peri-distance on the peri-atom size for Nap[EPh][E'Ph] compounds* **37-39** *and* **41-43**.

Substituent effects on molecular distortions.

Peri-atom size is therefore crucial in determining the overall geometry of the molecule but not necessarily an overriding factor. Inter- and intramolecular interactions can also have an impact and give *peri*-distances which are unforeseen. The *peri*-distance of 8-bromonaphthalen-1-amine **1** [3.07 Å] is larger than expected based on the size of its *peri*-atoms; the value is comparable to those of the molecules of **2** Nap[Br][SEt] [**A** 3.05 Å, **B** 3.06 Å]. Hydrogen bonding between the protons on the amine moiety and the Br(1) atom in **1** forces the N(1) and Br(1) atoms to be further apart and less strained than other similar molecules.

The number, size and electronic properties of substituents attached to the *peri*-atoms can also affect the geometry of substituted naphthalenes and influence the extent of steric interactions.

The variation in the electronic and steric effects of phenyl and ethyl substituents, is the reason why analogous compounds **19** and **3** (Figure 7.6) exhibit dissimilar intramolecular interactions,

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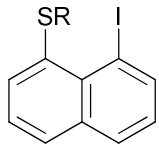
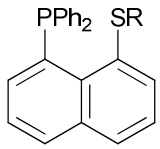
naphthalene distortion and structural arrangements. Greater in-plane distortion occurring in **19** compared to **3** to accommodate the larger phenyl substituent [**19** 374.1°, **3A** 371.7°, **3B** 371.4°], forces the *peri*-atoms in further apart [3.0330(17) Å] compared to the S(ethyl) compound [**3A** 2.9737(14) Å, **3B** 2.9469(15) Å].





Compound	15	20	3A	3B	19
R	Et	Ph	Et	Et	Ph
sum vdW[5]	(IS) 3.78	(IS) 3.78	(PS) 3.6	(PS) 3.6	(PS) 3.6
PD	3.24	3.34	2.97	2.94	3.03
splay angles	376.9	380.8	371.7	371.4	374.1

Fig. 7.6 *The dependence of peri-distance (PD) on peri-atom substituent number, size and electronic properties in compounds* **15**, **20**, **3** *and* **19**.

The structural dissimilarity between **20** and its S(ethyl) counterpart **15** mirrors that of compounds **3** (SEt) and **19** (SPh) and shows the effect the S(alkyl) group has on the overall structure of the molecule. The intramolecular I···S(phenyl) *peri*-distance is again greater than the I···S(ethyl) distance [**20** 3.338(11) Å, **15** 3.2436(17) Å] (Figure 7.6).

The influence of metal coordination on molecular distortion.

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** is a suitable candidate as an asymmetric chelating ligand with substantial electronic and steric differences between the two donor atoms.[6] The bidenticity and rigid C_3 backbone makes it a suitable candidate for metal coordination and the design of ligands for catalysis.[7] A series of platinum(II) dihalides **24**-**26**, a series of copper(I) dimers **27**-**29** and a ruthenium(II) *p*-cymene complex **30** have all been prepared. The metal complexes **24**-**30** display different patterns of molecular deviations with a variation in the magnitude of steric strain occurring in the naphthalene moiety. The size of the central metal, its coordination and electronic interactions with the ligands around it has an overall influence on the geometry of the complex.[8]

The strong preference for the formation of platinum square planar complexes governs the naphthalene structure in the dihalide complexes **24-26** and instigates a greater amount of molecular

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distortion.[8] The *peri*-atoms are forced further apart to coincide with the 'ideal' square planar geometry around the platinum, subsequently increasing the splay angles compared to the non-coordinated ligand **19** (Figure 7.7).

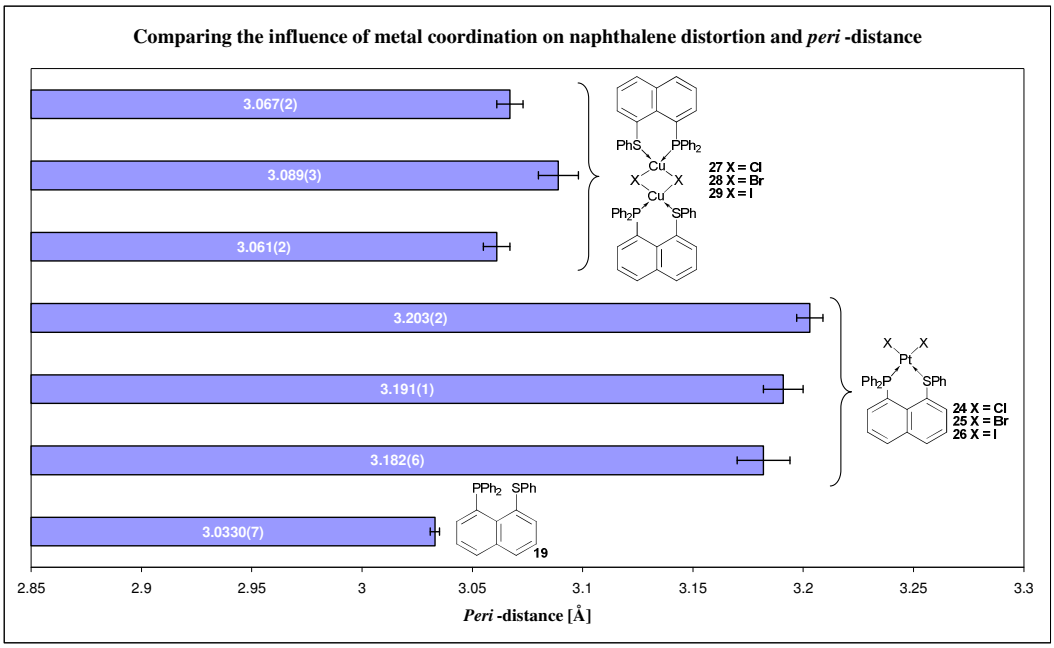

Fig. 7.7 *The influence of metal coordination on naphthalene molecular distortion and peri-distance in compounds* **24-29**.

The metal centre in the copper dimers **27-29** has less impact on the naphthalene geometry (Figure 7.8). Copper has a stereochemical preference for tetrahedral coordination with 'ideal' angles around the copper of 109.5°.[8] The copper dimers (**27-29**) show a greater distorted tetrahedral geometry compared with other similar compounds containing the Cu_2X_2 rhombus core with angles around the copper varying between 81.5° and 128.4° (Figure 3.23).[9]

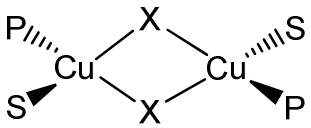

Fig. 7.8 *Two copper atoms are joined by two halide bridges to form a strictly planar Cu_2X_2 rhombus core, in the form of a parallelogram, containing two unequal Cu-X bond distances.*

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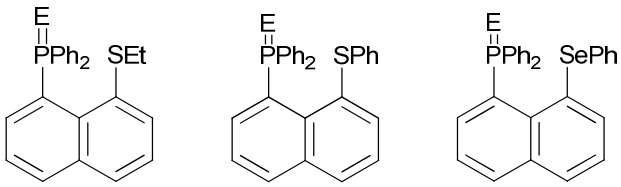
Molecular distortion comparable to the non-coordinated ligand **19** implies the metal center has little influence on the geometry of the complex [*peri*-distances: **19** 3.03 Å, **27** 3.06 Å, **28** 3.09 Å, **29** 3.07 Å] (Figure 7.8). Instead it is the rigid nature of the naphthalene which distorts the copper geometry away from its preferred 'ideal' tetrahedral environment.[8]

Weak intramolecular interactions.

The three mixed phosphorus-chalcogenide species **3**, **19** and **32** react to form three analogous series of phosphorus(V) chalcogenides (Figure 7.9).



16 E = O
17 E = S
18 E = Se

21 E = O
22 E = S
23 E = Se

34 E = O
35 E = S
36 E = Se

Fig. 7.9 *The phosphorus(V) chalcogenides which exhibit weak intramolecular E···E' type interactions.*[10]

Consistent throughout the compounds is the positioning of the chalcogen atom bonded to the phosphorus atom which resides in the *peri*-gap pointing away from the naphthalene plane. The close proximity to the *peri*-chalcogen atom allows for a weak E···E' type non-bonded interaction to take place (Figure 7.10).[10]

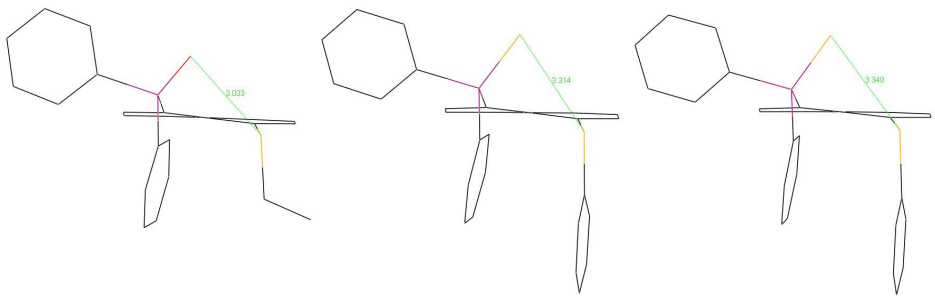


Fig. 7.10 *Examples of the weak E···E' type non-bonded interactions taking place in the phosphorus(V) chalcogenides.*[10]

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In all three series the non-bonded E···S/E···Se distance increases with the size of the chalcogen atom bonded to P(1) due to steric hindrance. Nevertheless the non-bonded distances are all smaller than the sum of the van der Waals radii for the two interacting atoms, suggesting the non-bonded distance is close enough for possible intramolecular interactions to occur.[5,10]

Table 7.1 Non-bonded intramolecular E···E' distances [Å] between interacting chalcogen atoms in the phosphorus(V) chalcogenides **16-18, 21-23** and **34-36**.

	16	**17**	**18**	**21**	**22**	**23**	**34**	**35**	**36**
E···E'	3.03	3.30	3.43	2.96	3.31	3.40	2.77	3.35	3.42
Σ vdW[5]	(OS) 3.32	(SS) 3.60	(SeS) 3.70	(OS) 3.32	(SS) 3.60	(SeS) 3.70	(OSe) 3.42	(SSe) 3.70	(SeSe) 3.80

The repulsive distortion taking place in the Nap[SEt][PPh_2] chalcogenides **16-18**, to accommodate the increasingly large chalcogen atoms, forces the ethyl group away from the naphthalene plane, adjacent and in close proximity to one of the phenyl π-systems on P(1). The short distance between the ethyl group and the phenyl π-system allows for another type of intramolecular interaction to occur; CH-π type interactions (Figure 7.11).[11]

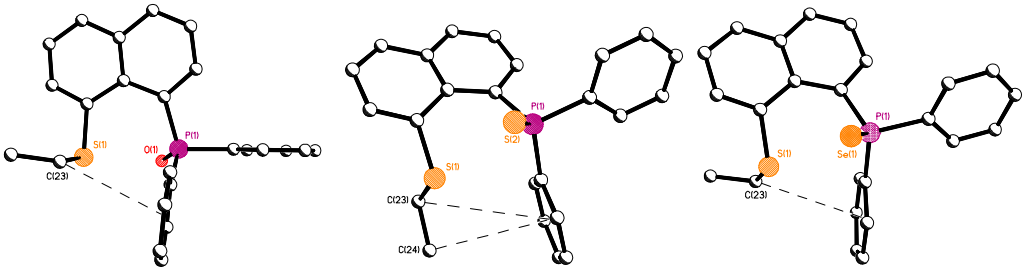

Fig. 7.11 *The crystal structures of the (8-ethylsulfanylnaphth-1-yl)diphenylphosphine chalcogenides* **16-18** *showing the possible non-bonded CH-π interactions between the S(ethyl) and P(phenyl) groups.*[11]

The ethyl carbon-centroid distances found for the three chalcogenides are within the range for known CH-π interactions and small enough to envisage interaction between the π-system and the protons on the ethyl group [**16** C(23)···centroid 3.644(1) Å, **17** C(23)···centroid 4.041(1) Å, C(24)···centroid 3.790(1) Å, **18** C(23)···centroid 3.578(1) Å] (Figure 7.11).[11]

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Linear arrangements and 3c-4e interactions.

Structures containing linear arrangements of heteroatoms in close proximity to one another are of particular interest because they satisfy the conditions required for the occurrence of non-bonded interactions.[12,13] Much of the pertinent work in this field has been reported by the group of Nakanishi *et al.*[13,14] During a study of non-bonded intramolecular interactions in sterically crowded naphthalenes [8-G-1-(*p*-$YC_6H_4Se)C_{10}H_6$] (Figure 7.12),[13,14] Nakanishi *et al* found that these systems formed linear non-bonded G···Se-C arrangements.[13,14] From *ab initio* MO calculations they concluded that *'the linear alignment of the three atoms must be the result of the non-bonded G···Se-C 3c-4e type interaction'*.[13,14]

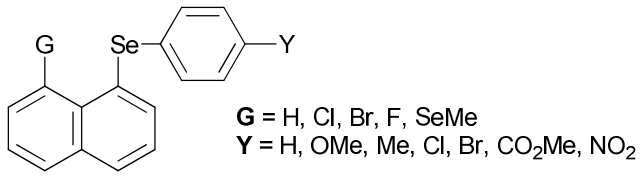

Fig. 7.12 *The series of sterically crowded naphthalenes (8-G-1-(p-$YC_6H_4Se)C_{10}H_6$) investigated by Nakanishi et al as part of their study of intramolecular interactions.*[13,14]

During the synthesis of the phosphorus-chalcogenide species and mixed chalcogenide systems in this thesis, a number of compounds exhibiting a three atom linear arrangement have been prepared. Compound **31**, previously reported by Nakanishi *et al* to contain a 3c-4e interaction,[13,14] was synthesised along with analogous compounds **33**, **55** and **56** (Figure 7.13).

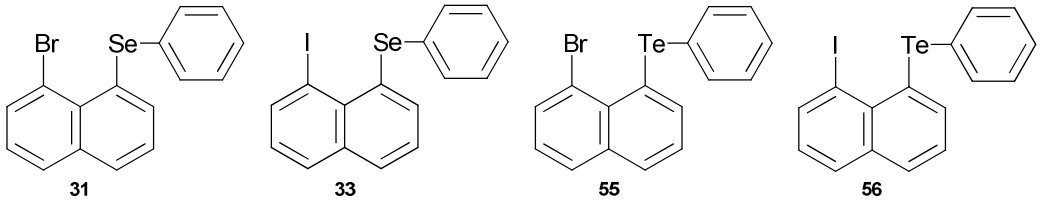

Fig. 7.14 *Compounds* **31**, **33**, **55** *and* **56** *all exhibit a X···E-C type linear alignment.*

All four compounds adopt the same orientation, with E-C bonds lying close to the naphthalene plane (Figure 7.13).[13,14] This produces a linear arrangement of the type X···E-C with angles approaching 180° throughout [**31** Br···Se-C 175.7°, **33** I···Se-C 174.3°, **55** Br···Te-C 173.1°, **56** I···Te-C 175.1°] (Figure 7.14).

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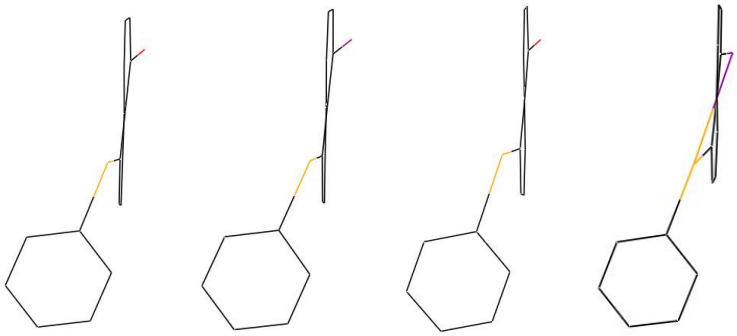

Fig. 7.14 *The orientation of compounds* **31**, **33**, **55** *and* **56** *showing the 'type B structure' and linear X···E-C type alignment.*

The observed non-bonded *peri*-distances are shorter than sum of van der Waals radii of the interacting atoms by 0.64 Å for **31**, 0.63 Å for **33**, 0.72 Å for **55,** 0.73 Å for **56**.[5] According to Nakanishi *et al*, the X···E-C linearity and the close proximity of the *peri*-atoms is conducive to non-bonded interactions and can be attributed to a 3c-4e type interaction taking place.[13,14]

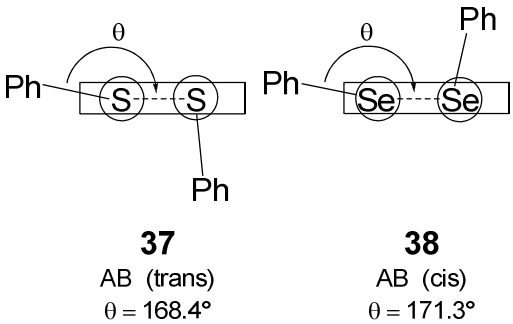

Fig. 7.15 *The orientation of the E(phenyl) groups and type of structure of the chalcogen compounds* **37** *and* **38** *and the* C_{Ph}*-E···E' linear arrangement.*

A similar linear arrangement is found in compounds **37**, **38**, **41**-**43**, when both *peri*-positions of the naphthalene are occupied by elements of Group 16. Described by Nakanishi *et al* as 'type AB',[13,14] one E-C bond aligns with the naphthalene plane and the other aligns perpendicular to it. This produces one quasi-linear fragment of the type C-E···E' with angles 168.4-171.8° and non-bonded *peri*-distances shorter than the sum of van der Waals radii for the interacting atoms (Figure 7.15, 7.16).

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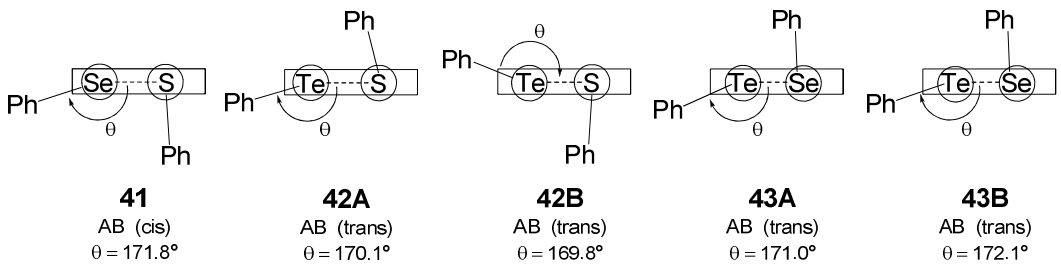

Fig. 7.16 *The C_{Ph}-E···E' linear arrangement of the chalcogen compounds* **41**-**43**.[2]

Upon oxidation, the structure of bis-sulfide **37** is dramatically changed and adopts either an 'AA type' arrangement **44** or 'AC type' arrangement **45**.[13,14] The overriding factor in these two structures is the linear arrangement of the type O(1)=S(1)···S(2); again angles approach 180° [174.3°, 171.9°] and non-bonded S(1)···S(2) distances [3.05 Å, 3.08 Å] are shorter than the sum of van der Waals radii for two sulfur atoms [3.60 Å].[5] This arrangement forces the two phenyl rings in both cases to align on the same side of the naphthalene plane. In compound **44** this overlap is in the range for a typical centroid-centroid interaction [3.3-3.8 Å],[15] so possible π-π stacking could be envisaged (Figure 7.17).[15]

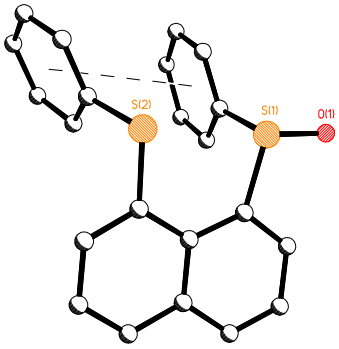

Fig. 7.17 *The crystal structure of* **44** *illustrating the overlap of the phenyl rings and possible π-π stacking interaction.*

The phosphorus(V) chalcogenides **34**-**36** each exhibit one quasi-linear arrangement of atoms. Oxide **34** comprises an O···Se-C linear interaction [168.8°] whilst sulfide **35** and selenide **36** both form linear arrangements of the type Se···P-C [**35** 173.5° and **36** 172.9°] (Figure 7.18). The observed non-bonded O(1)···Se(1) and P(1)···Se(1) distances [**34** 2.770(3) Å, **35** 3.2803(8) Å, **36** 3.278(2) Å] are also shorter than sum of van der Waals radii of the interacting atoms [3.42 Å, 3.70 Å].[8] Based on *ab initio* MO calculations, Nakanishi *et al* recently reported the formation of the linear O···Se-C arrangement in **34** was due to an energy lowering 3c-4e interaction.[13,14]

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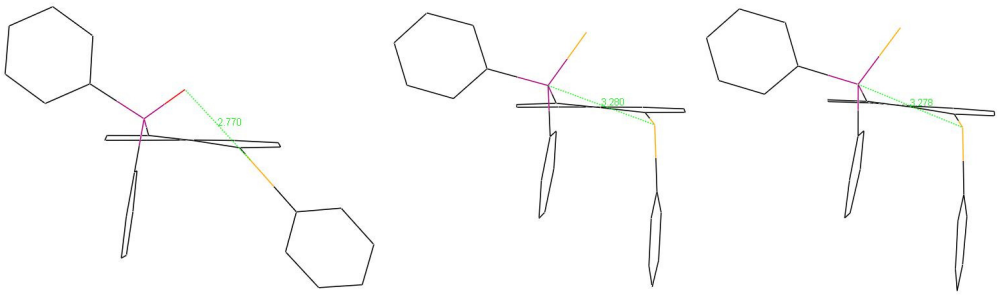

Fig. 7.18 *The crystal structures of the (8-phenylselanylnaphth-1-yl)diphenylphosphine chalcogenides showing the linear arrangement of the type O···Se-C in* **34** *and Se···P-C in* **35** *and* **36**.

Calculations performed for us by Prof. M. Bühl in St Andrews however, were contrary to these earlier reported results. For each of the three chalcogenide compounds **34**-**36**, both linear type arrangements [E···Se-C and Se···P-C] were evaluated using B3LYP/6-31+G* level, using H-relaxed X-ray geometries and the Wiberg bond index (WBI), which measures the covalent bond order, was calculated for both linear arrangements.[16] WBI values of 0.02-0.04 indicate a very minor interaction taking place between non-bonded atoms. For strong interactions these values would be approaching 0.20.[16] We are therefore unable to conclude 3c-4e non-bonded interactions are taking place in these molecules. Additional calculations performed on the radical cations of **34-36** revealed an increase in Wiberg bond index values for the E···Se-C linear arrangement [0.14-0.19] and an enhanced interaction compared to the neutral species.[16]

Reactions of chalcogen compounds with di-halogens.

Organic molecules containing Group 16 donor atoms sulfur, selenium and tellurium react with di-halogens (Br_2, I_2) and inter-halogens (IBr, ICl) to form a variety of addition complexes with a wide structural diversity. Experimental conditions have a vital control over the pathway these reactions take and subsequently on the structural motifs and geometry around the Group 16 atoms in the addition products. Factors such as the type of chalcogen donor atom, the form of the di-halogen or inter-halogen, the stoichiometry of the reactants and the nature of the donor atoms R group(s) all play a part in determining the structure of these compounds.[17,18]

1,8-bis(phenylsulfanyl)naphthalene **37**, 1,8-bis(phenylselanyl)naphthalene **38**, the three novel mixed chalcogen naphthalene systems **41**-**43** along with the tellurium compounds **55** and **56** all react differently with the di-halogens affording a collection of different charge transfer and

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insertion adducts; C.-T. 'spoke', C.-T. 'extended spoke', 'T-shaped' (or TBP) adducts and an ionic form of C.-T. 'extended spoke' with formula $[RE\text{-}X]^{+}\cdots[X\text{-}X_2]^{-}$.

1,8-bis(phenylsulfanyl)naphthalene proved to be an exception and reacted with di-bromine via electrophilic aromatic substitution; no adduct was isolated and the substitution compound **57** was afforded. Aromatic groups bearing –SR groups are strongly activated by resonance through donation of electron pairs into the aromatic π-system and are therefore highly reactive towards electrophilic substitution.[19,20]

The selenium compound 1,8-bis(phenylselanyl)naphthalene **38** and the mixed selenium-sulfur compound 1-(phenylselanyl)-8-(phenylsulfanyl)naphthalene **41** both reacted with the di-halogens to form structurally similar adducts **58, 61** (Figure 7.19, 7.20). The selective reactivity towards selenium in the mixed compound can be attributed to the larger electronegativity and hence greater donor ability of selenium over sulfur.[17-19] Upon reaction with dibromine, both selenium compounds form an ionic C.-T. 'extended spoke' adduct represented by the formula $[RSe\text{–}Br]^{+}\cdots[Br\text{–}Br_2]^{-}$ (Figure 7.19).[18,21]

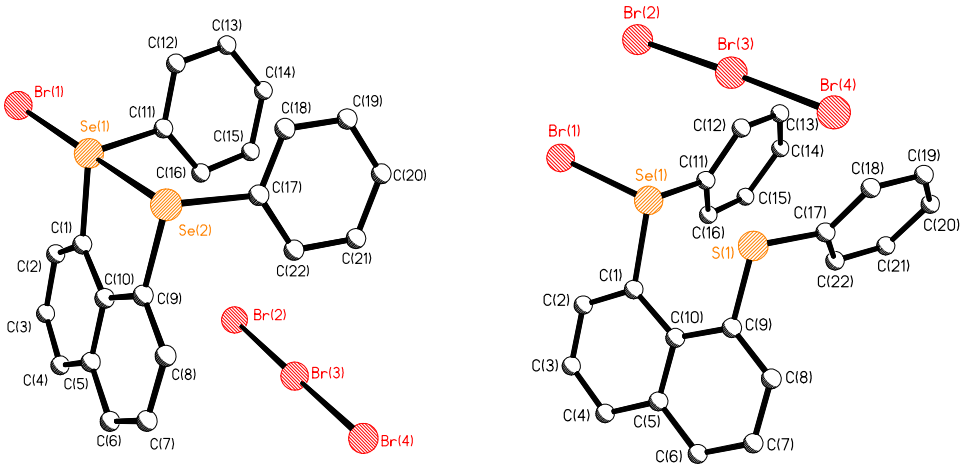

Fig. 7.19 *The selenium compounds* **37** *and* **41** *react with di-bromine to form similar ionic C.-T. 'extended spoke' adducts* **58** *and* **61** *represented by the formula* $[RSe\text{–}Br]^{+}\cdots[Br\text{–}Br_2]^{-}$.

The interacting Se atom reacts with the first molecule of Br_2 forming a strong donor-strong acceptor system upon the creation of the Se-Br bond. This simultaneously weakens the Br(1)-Br(2) bond which extends from 2.28 Å (free bromine)[22] and places a partial negative charge on the terminal Br(2) atom which can act as a donor towards a second (acceptor) molecule of Br_2.

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Cleavage of the Br(1)-Br(2) bond, delocalises negative charge onto the original terminal Br(2) strengthening the Se(1)-Br(1) bond which noticeably shortens.[18] This affords the quasi-linear 3c-4e hypervalent Br_3^- counteranion Br(2)-Br(3)-Br(4) exhibiting increased Br-Br distances compared to free bromine [2.28 Å].[22-24] The cleavage of the Br(1)-Br(2) also results in the formation of a linear Br-Se···E arrangement which can also be described by the hypervalent 3c-4e interaction model.[22-24]

Reaction of **37** and **41** with diiodine leads to the formation of C.-T. 'spokes' and C.-T. 'extended spokes' **59, 60** and **62** (Figure 7.20). Iodine [χ(I) 2.21][25], unlike bromine [χ(Br) 2.75][19], is less electronegative than selenium [χ(Se) 2.48][19] and accepts electron density from non-bonding orbitals of the selenium donor to form charge-transfer adducts [$\chi(E) > \chi(X)$].[17,18]

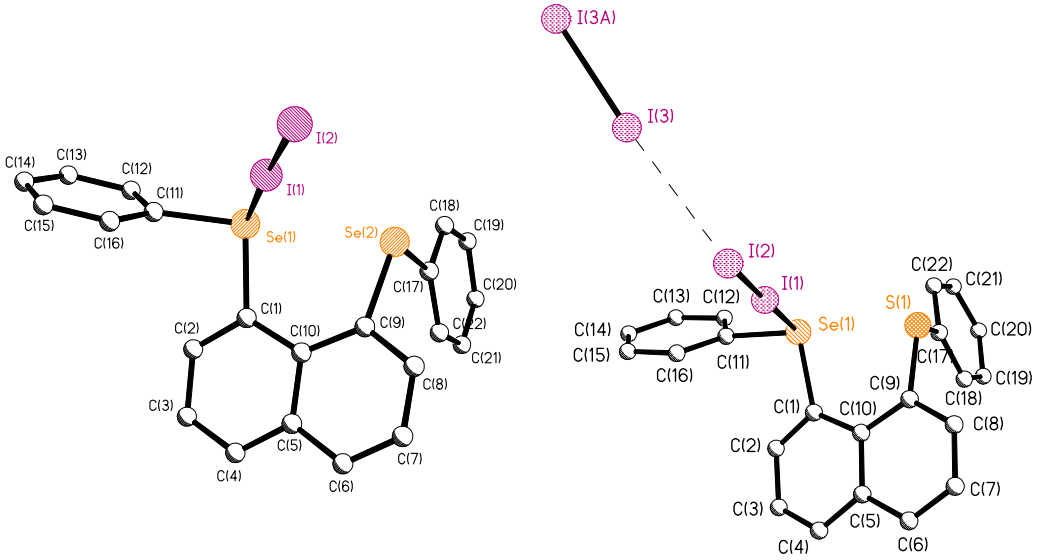

Fig. 7.20 *The selenium compounds* **37** *and* **41** *react with di-iodine to form similar C.-T. 'spoke' and 'extended spoke' adducts* **59, 60** *and* **62**.

The selenium atom reacts with one molar equivalence of diiodine to form a quasi-linear hypervalent Se-I-I fragment (C.-T. 'spoke').[23,24] This has the effect of lowering the bond order and consequently weakening the I-I bond which extends from 2.66 Å (free iodine).[17,18,22] The subsequent partial negative charge formed on the terminal I(2) atom in the hypervalent 3c-4e Se(1)–I(1)–I(2) bond means I(2) can act as a donor towards a second molecule of diiodine. This affords the C.-T. 'extended spoke' adduct containing two quasi-linear arrangements Se(1)-I(1)-I(2) and I(2)···I(3)-I(3).[17] Both linear arrangements are classified as 3c-4e interactions.[23,24] The elongation of bond lengths in these fragments gives evidence for the bond weakening due to the reduction in bond order.[17,18]

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The reaction of the organo-tellurium compounds (**42**, **43**, **55**, **56**) with the dihalogens strictly affords 'T-shaped' (TBP) adducts (Figure 7.21).[24-26] Tellurium forms a strong donor-strong acceptor system with the di-halogen molecule sufficient enough to cleave the X-X bond and oxidise tellurium.[17,18] Tellurium [χ(Te) 2.01][19] is less electronegative than the halogens [χ(F) 4.10-χ(I) 2.21].[19] Subsequent nucleophilic attack occurring at the tellurium site of the $[RTe–X]^+$ cation affords the 'T-shaped' hypervalent adduct containing the quasi linear X-Te-X alignment.[17,18] In the mixed tellurium-sulfur **42** and tellurium-selenium **43** compounds, reaction with the di-halogen occurs at the larger, less electronegative tellurium atom due to its greater donor ability over sulfur or selenium.

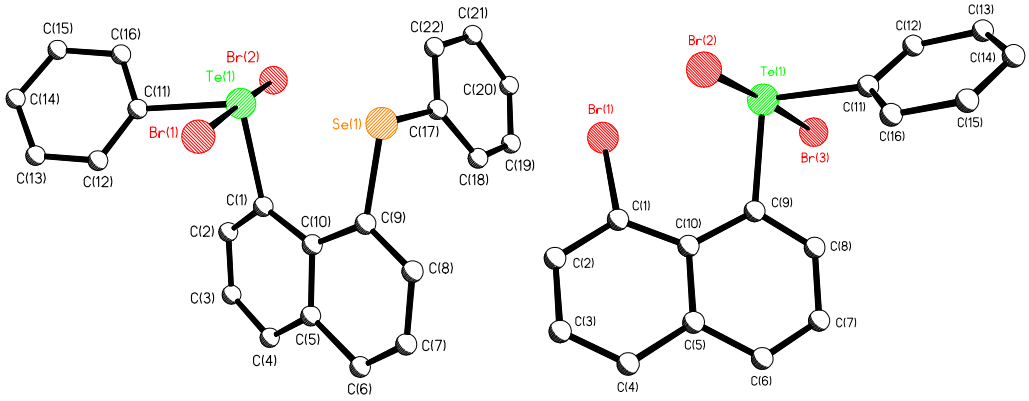

Fig. 7.21 *The organo-tellurium compounds* **42, 43, 55** *and* **56** *all react with the di-halogens to form 'T-shaped' adducts similar to those depicted here for* **64** *and* **67**.

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Experimental

General experimental

Unless otherwise stated all the procedures were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques and glassware. Reagents were obtained from commercial sources and used as received. Dry solvents were collected from a MBraun solvent system.

Elemental analysis.

Elemental analyses were performed by the University of St. Andrews School of Chemistry Microanalysis Service.

Infra-red spectroscopy.

Infra-red spectra were recorded as KBr discs in the range 4000-300 cm^{-1} on a Perkin-Elmer System 2000 Fourier transform spectrometer.

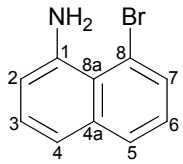
NMR spectroscopy.

^{1}H and ^{13}C NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(H) and δ(C) referenced to external tetramethylsilane. ^{31}P, ^{77}Se and ^{125}Te NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(P), δ(Se) and δ(Te) referenced to external phosphoric acid, dimethylselenide and diphenyl ditelluride respectively. COSY, HSQC and PENDANT NMR spectra were recorded on a Brucker Advance 300 MHz spectrometer and a Brucker Advance II 400 MHz spectrometer. All measurements were performed at 25 °C. All values reported for NMR spectroscopy in this report unless otherwise stated are in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz).

Mass spectrometry.

Mass spectrometry was performed by the University of St. Andrews Mass Spectrometry Service. Electron impact mass spectrometry (EIMS) and Chemical Ionisation Mass Spectrometry (CIMS) was carried out on a Micromass GCT orthogonal acceleration time of flight mass spectrometer. Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer.

Compound 1 - 8-bromonaphthalen-1-amine 1 (from 4)



A solution of sodium nitrite (6.7 g, 97.1 mmol) in water (150 mL) was added to a solution of 1,8-diaminonaphthalene (15.0 g, 94.8 mmol) in hydrochloric acid (0.4 M, 1.0 L) at -5 °C. The mixture was then stirred at -5 °C for 2 h and at 18 °C for 18 h. The black precipitate was filtered off, washed with water, dried at room temperature for 1 h and then dissolved in aqueous hydrobromic acid (48 %, 100 mL). Copper bronze (4.0 g, 63 mmol), first activated by heating with a flame for 10 min under nitrogen, was added to the resulting solution at 60 °C. The mixture was stirred for 18 h, water (220 mL) was then added, and the mixture was heated to boiling point. The precipitate was filtered off with suction and boiled with additional water. The combined filtrate was neutralised with ammonium carbonate and extracted with dichloromethane (3 x 40 mL); the extract was dried with magnesium sulfate and evaporated. The black crude product was recrystallised from petroleum ether to give pink crystals (4.3 g, 21 %); mp 85-87 °C (lit.,[4] 87-88 °C); (Found: C, 54.7; H, 3.2; N, 6.25. Calc. for $C_{10}H_8BrN$: C, 54.1; H, 3.6; N, 6.3 %); ν_{max}(KBr disc)/cm^{-1}: 3442s, 3303s, 3199s, 3053w, 1907w, 1781w, 1628vs, 1561vs, 1453s, 1433s, 1376s, 1339s, 1287s, 1171s, 1138w, 1012s, 960w, 909s, 865w, 805vs, 749vs, 626w, 585w, 492w, 446w; δ_H(270 MHz, $CDCl_3$) 7.71-7.58 (2 H, m, nap 4,5-H), 7.27-7.24 (2 H, m, nap 6,7-H), 7.17-7.09 (1 H, m, nap 3-H), 6.78-6.69 (1 H, m, nap 2-H), 5.09 (2 H, br s, NH_2); δ_C(67.9 MHz, $CDCl_3$) 143.7(q), 137.5(q), 131.8(s), 129.2(s), 127.2(s), 125.8(s), 121.0(q), 119.3(s), 117.5(q), 112.5(s); *m/z* (ES$^+$) 222.0 ([M]$^+$, 100 %).

Compound 1 - (from 7)

Sodium azide (3.1 g, 0.048 mol) was added over a 10 min period to a stirred suspension of 8-bromo-1-naphthoic acid (2.0 g, 0.008 mol) in concentrated sulfuric acid (7 mL) and chloroform (7 mL) at 45 °C; each successive portion of sodium azide being added after the effervescence resulting from the previous addition had subsided. The mixture was stirred for 90 min at 45 °C and added to water (140 mL). The mixture was made alkaline with aqueous ammonia and extracted with chloroform (3 x 140 mL). The combined extracts were dried with magnesium sulfate and evaporated to give the product (1.3 g, 73 %). The product was identified by ^{1}H NMR spectroscopy and melting point analysis comparing the results to those previously characterised from the preparation starting with 1,8-diaminonaphthalene.

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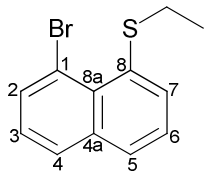
Compound 2 - 1-bromo-8-(ethylsulfanyl)naphthalene (from 1)



8-bromonaphthalen-1-amine (5.0 g, 22.5 mmol) was dissolved in water (50 mL) and concentrated hydrochloric acid (6 mL) by heating. To the cooled mixture, was added a solution of sodium nitrite (1.6 g, 23 mmol) in water (10 mL) with shaking. The diazotized solution was neutralised by adding aqueous sodium acetate whilst cooling and the solution was filtered. The solution was added at 40 °C to an aqueous solution of ethanethiolate prepared from sodium hydroxide (1.0 g, 25 mmol), ethanethiol (1.6 mL, 22 mmol) and water (50 mL). The mixture was heated to 90 °C and stirred at that temperature for 2 h. The cooled mixture was extracted with benzene, and the extract was washed with water. After drying over magnesium sulfate, the solvent was evaporated and the residue was submitted to chromatography on silica gel with hexane as an eluent. The desired product was obtained after recrystallisation from hexane (2.5 g, 41 %); mp 47-49 °C (lit.,[7] 47-48 °C); (Found: C, 54.1; H, 4.3. Calc. for $C_{12}H_{11}BrS$: C, 54.0; H, 4.2 %); ν_{max}(KBr disc)/cm^{-1}: 3056w, 2971w, 2925w, 2851w, 1923w, 1544vs, 1511w, 1493w, 1461w, 1434w, 1416w, 1356s, 1308s, 1256w, 1191vs, 1148s, 1057w, 967s, 857s, 801vs, 702s, 545w, 439w; δ_H(270 MHz, $CDCl_3$) 7.75 (1 H, dd, *J* 1.2 and 7.4 Hz, nap 4-H), 7.68 (1 H, dd, *J* 1.1 and 8.1 Hz, nap 2-H), 7.55 (1 H, dd, *J* 1.1 and 8.0 Hz, nap 5-H), 7.42 (1 H, dd, *J* 1.0 and 7.5 Hz, nap 7-H), 7.28 (1 H, t, *J* 7.8 Hz, nap 6-H), 7.14 (1 H, t, *J* 7.8 Hz, nap 3-H), 2.92 (2 H, q, *J* 7.3 Hz, -C*H*$_2$-), 1.28 (3 H, t, *J* 7.4 Hz, -C*H*$_3$); δ_C(67.9 MHz, $CDCl_3$) 136.9(q), 136.1(q), 134.2(s), 130.8(q), 129.5(s), 127.8(s), 127.1(s), 126.2(s), 125.9(s), 119.4(q), 30.0(-*C*H$_2$-), 13.4(-*C*H$_3$); *m/z* (CI$^+$) 265.98 ([M+H]$^+$, 100 %).

Compound 2 - (from 11)

To a solution of 1,8-dibromonaphthalene (0.6 g, 2.2 mmol) in diethyl ether (10 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.9 mL, 2.2 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diethyl disulfide (0.3 g, 0.3 mL, 2.2 mmol,) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (20 mL x 2). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give the product (0.3 g, 43%). The product was identified by ^{1}H NMR spectroscopy and mass spectrometry.

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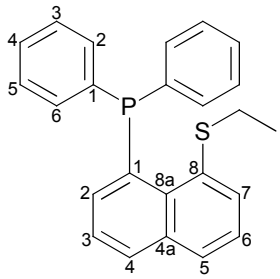
Compound 3 – (8-ethylsulfanylnaphth-1-yl)diphenylphosphine (from 2)



A solution of 2.5 M *n*-butyllithium in hexane (0.5 mL, 1.1 mmol) was transferred dropwise to a freshly prepared solution of 1-bromo-8-(ethylsulfanyl)naphthalene (0.3 g, 1.1 mmol) in diethyl ether (10 mL) at -10-0 °C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.24 g, 0.2 mL, 1.1 mmol) was added slowly. The addition coloured the reaction mixture first bright yellow and finally a pale yellow. Stirring was continued for a further 2 h at -10-0 °C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo*. The crude yellow oil obtained was recrystallised from toluene (0.2 g, 40 %); (Found: C, 74.5; H, 6.1. Calc. for $C_{24}H_{21}PS$: C, 74.2; H, 5.5 %); ν_{max}(KBr disc)/cm^{-1}: 3430br, 3054s, 2919s, 2227s, 1587s, 1480s, 1434vs, 1308s, 1261s, 1185s, 1096vs, 1021s, 997s, 910s, 820s, 725vs, 690vs, 528vs, 321s, 294s; δ_H(270 MHz, $CDCl_3$) 7.82-7.63 (5 H, m, nap 4,5,7-H, 2 x P*Ph*$_2$ 4-H), 7.39-7.30 (2 H, m, nap 3,6-H), 7.28-7.10 (9 H, m, nap 2-H, 2 x P*Ph*$_2$ 2,3,5,6-H), 2.64 (2 H, q, *J* 7.42 Hz, -SC*H*$_2$-), 0.91 (3 H, t, *J* 7.42 Hz, -SCH$_2$C*H*$_3$); δ_C(67.9 MHz, $CDCl_3$) 137.0(s), 136.0(s), 134.1(d, *J* 19.7 Hz), 130.8 (s), 130.0(s), 128.6(s), 128.4(d, *J* 7.2 Hz), 125.6(d, *J* 5.8 Hz), 125.5(s), 35.2 (-*C*H$_2$-), 13.3 (-*C*H$_3$); δ_P (109.4 MHz, $CDCl_3$) -5.26; *m/z* (ES$^+$) 411.18 ([M+K]$^+$, 100 %).

Compound 3 - (from 15)

A solution of 2.5 M *n*-butyllithium in hexane (0.4 mL, 1.0 mmol) was transferred dropwise to a freshly prepared solution of 1-iodo-8-ethylsulfanylnaphthalene (0.3 g, 1.0 mmol) in diethyl ether (10 mL) at -10-0 °C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.23 g, 0.2 mL, 1.0 mmol) was added slowly. The addition coloured the reaction mixture first bright yellow and finally a pale yellow. Stirring was continued for a further 2 h at -10-0 °C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo* (0.2 g, 52 %). The product was identified by ^{1}H and ^{31}P NMR spectroscopy.

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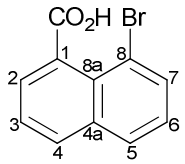
Compound 7 - 8-bromo-1-naphthoic acid 7 (via 6)



This procedure was carried out under atmospheric conditions. 1,8-naphthalic anhydride (49.6 g, 0.3 mol) was suspended in aqueous sodium hydroxide (35.1 g, 0.88 mol, in 1500 mL of water) and refluxed until the solid material had dissolved. The excess base was neutralised with glacial acetic acid (25 mL) and a solution of mercuric acetate (81.3 g, 0.26 mol) in water (250 mL) added in one portion. After the mixture was refluxed for 30 min, additional glacial acetic acid (45 mL) was added to the white slurry, resulting in slow evolution of carbon dioxide. The slurry was refluxed for 1 week or until no further gas was expelled, cooled and filtered. The highly insoluble solid was washed with water and then dried under vacuum at 105 °C overnight to give a tan storable powder. Anhydro-8-(hydroxymercuri)-1-naphthoic acid (19.0 g, 0.05 mol) suspended in glacial acetic acid (75 mL) and water (12 mL) was stirred vigorously at 0 °C. Sodium bromide (34.1 g, 0.17 mol) in water (60 mL) and bromine (8.5 g, 2.9 mL, 0.05 mol) were added slowly while the reaction temperature was maintained at 0-5 °C. The resulting slurry was then slowly heated to 100 °C and poured onto ice (150 g). The precipitate was washed with water, dissolved in hot aqueous sodium hydroxide (12 g, 0.3 mL in 25 mL of water) and filtered through Celite. The filtrate was acidified with concentrated hydrochloric acid (25 mL), cooled and filtered to give the product as a white solid (4.3 g, 34 %); mp 173-175 °C (lit.,[5] 174-175 °C); δ_H(270 MHz, $CDCl_3$) 9.07 (1 H, br s, -CO_2*H*), 8.20 (1 H, d, *J* 8.0 Hz, nap 2-H), 7.94 (2 H, td, *J* 1.1 and 8.4 Hz, nap 4,5-H), 7.87 (1 H, dd, *J* 1.1 and 7.7 Hz, nap 7-H), 7.56-7.50 (1 H, m, nap 3-H), 7.41-7.35 (1 H, m, nap 6-H).

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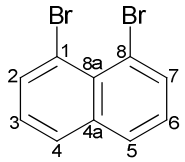
Compound 11 - 1,8-dibromonaphthalene



1,8-diaminonaphthalene (29.8 g, 189 mmol) was suspended in sulfuric acid (500 mL, 6.9 M). The suspension was cooled to -20 °C in a dry ice/acetone bath, and a solution of sodium nitrite (40 g, 0.58 mol) in water (250 mL) was added slowly. The temperature was maintained at -20 °C throughout the addition. Immediately after the sodium nitrite solution was added, cuprous bromide (107.6 g, 0.75 mol) in concentrated hydrobromic acid (250 mL) was added. The black solution was warmed carefully to 50 °C. During the warming, a great deal of gas evolution was observed, causing a large quantity of foam to be produced. The addition of small quantities of diethyl ether was required to break up the foam. After 1 h, the solution was cooled to 10 °C with the aid of an ice bath, and made alkaline to litmus paper by slow, careful addition of solid sodium hydroxide. The black residue was filtered and extracted with boiling tetrahydrofuran until the extract was colourless. The tetrahydrofuran was removed from the filtrate by rotary evaporation to leave a red-black residue. This residue was then extracted with boiling diethyl ether until the extract was colourless. The diethyl ether was removed from the filtrate by rotary evaporation to leave a dark red residue which was purified by column chromatography on silica gel (hexane/toluene 80:20) (15.0 g, 26 %); mp 106-108 °C (lit.,[11] 106 °C); (Found: C, 43.0; H, 1.7. Calc. for $C_{10}H_6Br_2$: C, 42.3; H, 2.1 %); δ_H(270 MHz, $CDCl_3$) 7.93 (2 H, dd, *J* 1.2 and 7.4 Hz, nap 4,5-H), 7.80 (2 H, dd, *J* 1.2 and 8.4 Hz, nap 2,7-H), 7.25 (2 H, t, *J* 7.8 Hz, nap 3,6-H); δ_C(67.9 MHz, $CDCl_3$) 135.5(s), 129.8(s), 126.6(s), 119.7(q).

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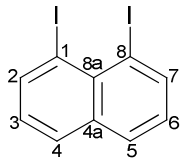
Compound 14 - 1,8-diiodonaphthalene



1,8-diaminonaphthalene (15.1 g, 0.095 mol) was suspended in sulfuric acid (175 mL, 6.9 M). The suspension was cooled to -20 °C in a dry ice/acetone bath, and a solution of sodium nitrite (19 g, 0.28 mol) in water (70 mL) was added slowly with stirring. The temperature was maintained at -20 °C throughout the addition. Immediately after the sodium nitrite solution was added, potassium iodide (96.4 g, 0.58 mol) in water (80 mL) was added dropwise with stirring. Additional portions of concentrated sulfuric acid were added as needed to keep the reaction mixture from freezing. The resulting mixture was warmed rapidly to 80 °C with stirring, then cooled to 20 °C and made alkaline to litmus paper by slow, careful addition of solid sodium hydroxide. The mixture was filtered and the black solid residue was collected, pulverised and extracted with boiling diethyl ether until the extract was colourless. The ethereal solution was washed successively with aqueous 10 % hydrochloric acid, saturated aqueous sodium thiosulfate and dilute aqueous sodium hydroxide then dried and concentrated. The residual brown solid was recrystallised from hexane to separate the pure diiodide as tan prisms (3.7 g, 10 %); δ_H(270 MHz, $CDCl_3$) 8.41 (2 H, dd, *J* 1.4 and 7.5 Hz, nap 4,5-H), 7.84 (2 H, dd, *J* 1.4 and 8.0 Hz, nap 2,7-H), 7.06 (2 H, t, *J* 7.7 Hz, nap 3,6-H).

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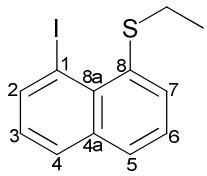
Compound 15 - 1-iodo-8-(ethylsulfanyl)naphthalene



To a solution of 1,8-diiodonaphthalene (0.88 g, 2.3 mmol) in diethyl ether (10 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.9 mL, 2.3 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diethyl disulfide (0.28 g, 0.3 mL, 2.3 mmol) was added dropwise. The resulting solution was stirred at -78 °C for a further h and then was washed with 0.1 M sodium hydroxide (20 mL x 2). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give the product (0.3 g, 42 %); (Found: C, 46.7; H, 3.1. Calc. for $C_{10}H_6I_2$: C, 45.9; H, 3.5 %); ν_{max}(KBr disc)/cm^{-1}: 3412br, 3051w, 2965w, 2924s, 1539s, 1500w, 1440w, 1372w, 1354w, 1308w, 1259s, 1190s, 1142w, 1096w, 1049w, 1020w, 963w, 942w, 898w, 849w, 790vs, 762vs, 689w, 642w, 561w, 538w, 401w; δ_H(270 MHz, $CDCl_3$) 8.26 (1 H, dd, *J* 1.3 and 7.4 Hz, nap 4-H), 7.74 (1 H, dd, *J* 1.2 and 8.1 Hz, nap 2-H), 7.67-7.58 (2 H, m, nap 5,7-H), 7.31 (1 H, t, *J* 7.7 Hz, nap 6-H), 7.02-6.95 (1 H, m, nap 3-H), 2.89 (2 H, q, *J* 7.4 Hz, -SC*H*$_2$-), 1.22 (3 H, t, *J* 7.4 Hz, -SCH$_2$C*H*$_3$); δ_C(67.9 MHz, $CDCl_3$) 143.3(s), 131.3(s), 130.4(s), 128.7(s), 126.8(s), 125.6(s) 31.9(-*C*H$_2$-), 13.6(-*C*H$_3$); *m/z* (EI$^+$) 313.97 (M$^+$, 22 %), 253.96 ([M-SEt]$^+$, 72%).

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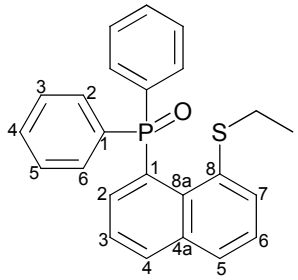
Compound 16 - (8-ethylsulfanylnaphth-1-yl)diphenylphosphine oxide



(8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** readily oxidised in contact with the atmosphere to produce (8-ethylsulfanylnaphth-1-yl)diphenylphosphine oxide **16** with 100 % conversion as seen by ^{31}P NMR spectroscopy (Found: C, 74.5; H, 6.1. Calc. for $C_{24}H_{21}POS$: C, 74.2; H, 5.5 %); ν_{max}(KBr disc)/cm^{-1}: 3406w, 3050w, 2924w, 2360vs, 2341vs, 1815w, 1765w, 1726w, 1710w, 1961w, 1658s, 1641s, 1592vs, 1548s, 1536s, 1482s, 1438vs, 1316s, 1187vs, 1112s, 1096s, 994s, 885s, 818vs, 761vs, 730s, 715w, 690s, 562vs, 539vs, 524s, 507vs, 434s, 403w, 389w, 363w; δ_H(270 MHz, $CDCl_3$) 7.92 (1 H, d, *J* 8.2 Hz, nap 4-H), 7.82-7.76 (2 H, m, nap 5,7-H), 7.59-7.51 (4 H, m, 2 x P*Ph*$_2$ 2,6-H), 7.51-7.44 (1 H, m, nap 2-H), 7.44-7.30 (7 H, m, nap 6-H, 2 x P*Ph*$_2$ 3-5-H), 7.28-7.22 (1 H, m, nap 3-H), 2.32 (2 H, q, *J* 7.4 Hz, -SC*H*$_2$-), 0.65 (3 H, t, *J* 7.4 Hz, -SCH$_2$C*H*$_3$); δ_C(67.9 MHz, $CDCl_3$) 138.7(d, *J* 12.5 Hz), 137.7(s), 134.4(d, *J* 3.1 Hz), 131.3(d, *J* 9.3 Hz), 130.7(d, *J* 2.1 Hz), 128.4(d, *J* 12.4 Hz), 126.5(s), 124.1(d, *J* 14.6 Hz), 33.9(-*C*H$_2$-), 13.5(-*C*H$_3$); δ_P(109.4 MHz, $CDCl_3$) 36.34; *m/z* (ES$^+$) 411.00 ([M+Na]$^+$, 100 %).

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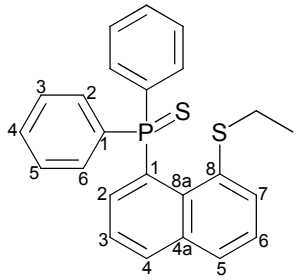
Compound 17 - (8-ethylsulfanylnaphth-1-yl)diphenylphosphine sulfide



To a solution of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** (0.10 g, 0.27 mmol) in toluene (10 mL) powdered sulfur (9 mg, 0.27 mmol) was added in small batches at 0 °C. The mixture was stirred for ½ h at 0 °C and another 2 h at ambient temperature. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The solid product was collected by filtration and recrystallised from dichloromethane/hexane (0.02 g, 72 %); (Found: C, 70.1; H, 5.7. Calc. for $C_{24}H_{21}PS_2$: C, 71.3; H, 5.2 %); ν_{max}(KBr disc)/cm^{-1}: 3048w, 2957s, 2923vs, 2851s, 1987w, 1962w, 1896w, 1820w, 1737w, 1666w, 1585w, 1476w, 1433s, 1370w, 1320w, 1260s, 1183w, 1092s, 1019w, 991w, 968w, 920w, 880w, 849w, 820vs, 801vs, 765s, 746s, 718s, 690s, 645s, 609w, 576w, 546w, 512w, 490w, 442w, 407s ; δ_H(270 MHz, $CDCl_3$) 7.98-7.89 (2 H, m, nap 4,5-H), 7.89-7.65 (5 H, m, nap 7-H, 2 x P*Ph*$_2$ 2,6-H), 7.54-7.33 (8 H, m, nap 3,6-H, 2 x P*Ph*$_2$ 3-5-H), 7.32-7.21 (1 H, m, nap 2-H), 2.18-2.04 (2 H, m, -SC*H*$_2$-), 0.54 (3 H, t, *J* 7.4 Hz, - SCH$_2$C*H*$_3$); δ_C(67.9 MHz, $CDCl_3$) 138.1(s), 137.8(d, *J* 10.4 Hz), 134.0(d, *J* 3.1 Hz), 131.5(d, *J* 2.1 Hz), 131.2(d, *J* 10.4 Hz), 130.5(d, *J* 2.1 Hz), 130.3(s), 128.7(d, *J* 12.4 Hz), 128.4(d, *J* 12.4 Hz), 126.7(s), 124.0(d, *J* 14.5 Hz), 35.2(*C*H$_2$), 13.2(*C*H$_3$); δ_P(109.4 MHz, $CDCl_3$) 51.84; *m/z* (EI$^+$) 374.98 ([M-Et]$^+$, 28 %), 342.99 ([M-SEt]$^+$, 100 %), 188.96 ([M-SPPh$_2$]$^+$, 63 %).

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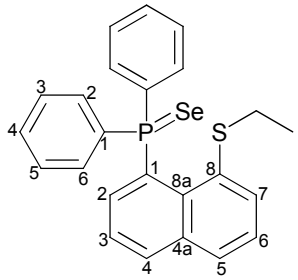
Compound 18 - (8-ethylsulfanylnaphth-1-yl)diphenylphosphine selenide



(8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** (0.62 g, 1.5 mmol) and Se (0.12 g, 1.5 mmol) were heated under reflux in toluene (10 mL) for 2 h. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The solid product was collected by filtration and recrystallised from dichloromethane/hexane (0.18 g, 65 %); (Found: C, 63.4; H, 4.7. Calc. for $C_{24}H_{21}PSSe$: C, 63.9; H, 4.7 %); ν_{max}(KBr disc)/cm^{-1}: 3047w, 2952w, 2922s, 2851w, 2360vs, 2336vs, 1475w, 1435s, 1318w, 1247w, 1180w, 1096s, 1088s, 1023w, 994w, 973w, 917w, 880w, 820s, 764s, 746s, 690vs, 615w, 587s, 565s, 533s, 508s, 489w, 442w, 409w; δ_H(270 MHz, $CDCl_3$) 7.84-7.82 (2 H, m, nap 4,5-H), 7.81-7.60 (5 H, m, nap 7-H, 2 x P*Ph*$_2$ 2,6-H), 7.42-7.40 (1 H, m, nap 6-H), 7.40-7.19 (8 H, m, nap 2,3-H, 2 x P*Ph*$_2$ 3-5-H), 2.09-1.92(2 H, m, -SC*H*$_2$-), 0.48 (3 H, t, *J* 7.4 Hz, -SCH$_2$C*H*$_3$); δ_C(67.9 MHz, $CDCl_3$) 138.3(s), 137.5(dd, *J* 10.4 Hz), 134.1(d, *J* 3.1 Hz), 133.4-131.4(br m), 130.6(d, *J* 2.0 Hz), 130.4(s), 128.4(d, *J* 12.4 Hz), 126.8(s), 124.0(d, *J* 13.5 Hz), 35.9(*C*H$_2$), 13.8(*C*H$_3$); δ_P(109.4 MHz, $CDCl_3$) 41.92; δ_{Se}(51.5 MHz, $CDCl_3$) -172.3; *m/z* (EI$^+$) 343.07 ([M-Se]$^+$, 100 %), 188.99 ([M-SePPh$_2$]$^+$, 15%).

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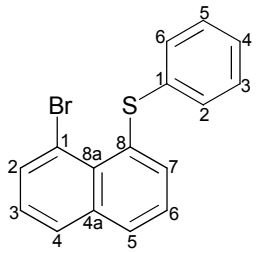
Compound 9 - 1-bromo-8-(phenylsulfanyl)naphthalene



To a solution of 1,8-dibromonaphthalene (0.67 g, 2.3 mmol) in diethyl ether (15 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.9 mL, 2.3 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl disulfide (0.51 g, 2.3 mmol) in diethyl ether (15 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane/ethyl acetate 20:1) to give a yellow oil (0.7 g, 51 %); δ_H(270 MHz, $CDCl_3$) 7.80 (1 H, dd, *J* 1.3 and 7.4 Hz, nap 4-H), 7.73 (1 H, dd, *J* 1.1 and 8.2 Hz, nap 2-H), 7.65 (1 H, dd, *J* 1.2 and 8.1 Hz, nap 5-H), 7.55 (1 H, dd, *J* 1.3 and 7.5 Hz, nap 7-H), 7.28-7.14 (7 H, m, nap 3,6-H, S*Ph* 2-6-H); δ_C(67.9 MHz, $CDCl_3$) 137.6(s), 133.2(s), 131.9(s), 129.53(s), 129.49(s), 128.9(s), 127.4(s), 126.4(s), 126.1(s).

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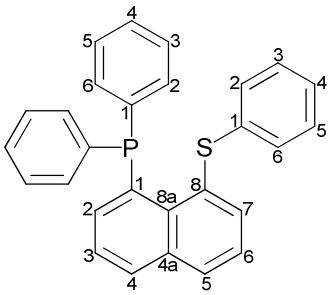
Compound 19 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (from 9)



A solution of 2.5 M *n*-butyllithium in hexane (1.3 mL, 3.2 mmol) was transferred dropwise to a freshly prepared solution of 1-bromo-8-(phenylsulfanyl)naphthalene (1.02 g, 3.2 mmol) in diethyl ether (30 mL) at -10-0 °C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.71 g, 0.6 mL, 3.2 mmol) was added slowly. Stirring was continued for a further 2 h at -10-0 °C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo*. The crude yellow oil obtained was recrystallised from hexane (0.9 g, 64 %); (Found: C, 79.7; H, 5.0. Calc. for $C_{28}H_{21}PS$: C, 79.9; H, 5.0 %); ν_{max}(KBr disc)/cm^{-1}: 3050s, 2963s, 1949w, 1884w, 1828w, 1579s, 1544s, 1472s, 1432vs, 1352w, 1308w, 1261vs, 1197s, 1092vs, 1021vs, 864w, 817vs, 801vs, 767vs, 740vs, 691vs, 592w, 539w, 499s, 474s, 424w, 387s; δ_H(270 MHz, $CDCl_3$) 7.93-7.81 (2 H, m, nap 4,5-H), 7.71 (1 H, d, *J* 1.5 Hz, nap 2-H), 7.45-7.36 (1 H, m, nap 3-H), 7.36-7.28 (1 H, m, nap 6-H), 7.26-7.13 (11 H, m, nap 2-H, 2 x P*Ph*$_2$ 2-6-H), 7.09-6.97 (3 H, m, S*Ph* 3-5-H), 6.77-6.70 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 140.0(q), 139.8(q), 137.6(s), 137.0(s), 135.6(q), 134.1(d, *J* 19.8 Hz), 132.2(q), 131.3(d, *J* 9.4 Hz), 130.9(s), 130.6(s), 128.6(s), 128.4(d, *J* 7.3 Hz), 128.1(d, *J* 3.1 Hz), 126.4(q), 125.9(s), 125.8(s), 125.4(s); δ_P(109.4 MHz, $CDCl_3$) -5.30; *m/z* (ES$^-$) 459.20 ([M+K]$^+$, 100 %).

Compound 19 - (from 20)

A solution of 1.6 M *n*-butyllithium in hexane (1.9 mL, 3.0 mmol) was transferred dropwise to a freshly prepared solution of 1-iodo-8-(phenylsulfanyl)naphthalene (1.10 g, 3.0 mmol) in diethyl ether (30 mL) at -10-0 °C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.67 g, 0.5 mL, 3.0 mmol) was added slowly. Stirring was continued for a further 2 h at -10-0 °C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo*. The crude yellow oil obtained was recrystallised from hexane (0.9 g, 74 %). The product was identified by ^{1}H and ^{31}P NMR spectroscopy.

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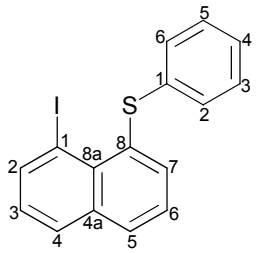
Compound 20 - 1-iodo-8-(phenylsulfanyl)naphthalene



To a solution of 1,8-diiodonaphthalene (0.47 g, 1.2 mmol) in diethyl ether (15 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.5 mL, 1.2 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl disulfide (0.27 g, 1.2 mmol) in diethyl ether (15 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane) and recrystallised from dichloromethane/pentane (0.1 g, 26 %); (Found: C, 53.0; H, 3.4. Calc. for $C_{16}H_{11}IS$: C, 53.0; H, 3.1 %); ν_{max}(KBr disc)/cm^{-1}: 3442br, 3056w, 2955s, 2924s, 2848w, 1937w, 1790w, 1719w, 1654w, 1578s, 1535s, 1474s, 1432s, 1346w, 1314w, 1261s, 1187s, 1080vs, 1022vs, 959w, 891w, 850w, 815vs, 755vs, 733vs, 688s, 613w, 566w, 516w, 462w, 400w; δ_H(270 MHz, $CDCl_3$) 8.27 (1 H, dd, *J* 1.3 and 7.4 Hz, nap 4-H), 7.79 (1 H, dd, *J* 1.2 and 8.1 Hz, nap 2-H), 7.75 (1 H, dd, *J* 1.3 and 8.2 Hz, nap 5-H), 7.64 (1 H, dd, *J* 1.4 and 7.3 Hz, nap 7-H), 7.33-7.26 (1 H, m, nap 6-H), 7.21-6.97 (6 H, m, nap 3-H, S*Ph* 2-6-H); δ_C(67.9 MHz, $CDCl_3$) 143.9(s), 136.4(s), 130.7(s), 130.5(s), 129.7(s), 129.3(s), 127.1(s), 126.3(s), 126.0(s); *m/z* (ES$^+$) 384.80 ([M+Na]$^+$, 100 %).

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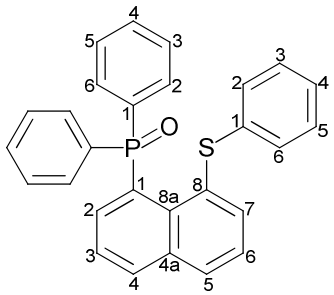
Compound 21 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine oxide



(8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** oxidised in contact with the atmosphere to produce (8-phenylsulfanylnaphth-1-yl)diphenylphosphine oxide **21** with 100 % conversion as seen by ^{31}P NMR spectroscopy (Found: C, 77.7; H, 5.0. Calc. for $C_{28}H_{21}PSO$: C, 77.0; H, 4.9 %); ν_{max}(KBr disc)/cm^{-1}: 3393w, 3051w, 2360vs, 2339vs, 1954w, 1868w, 1843w, 1769w, 1716w, 1699w, 1651w, 1581w, 1557w, 1539w, 1519w, 1507w, 1475s, 1435vs, 1357w, 1321w, 1259w, 1211w, 1181vs, 1153s, 1111s, 1097s, 1067s, 1024w, 993s, 930w, 886s, 827vs, 770s, 734vs, 715s, 689vs, 632w, 614w, 587w, 563vs, 540vs, 507s, 455s, 419w; δ_H(270 MHz, $CDCl_3$) 7.97 (1 H, d, *J* 8.2 Hz, nap 4-H), 7.90 (1 H, d, *J* 8.1 Hz, nap 5-H), 7.83 (1 H, dd, *J* 1.3 and 7.2 Hz, nap 7-H), 7.52-7.40 (6 H, m, nap 2,6-H, 2 x P*Ph*$_2$ 2,6-H), 7.32-7.23 (3 H, m, nap 3-H, 2 x P*Ph*$_2$ 4-H), 7.23-7.15 (4 H, m, 2 x P*Ph*$_2$ 3,5-H), 6.84-6.72 (3 H, m, S*Ph* 3-5-H), 6.18-6.12 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.8(s) 138.4(d, *J* 12.4 Hz), 134.2(d, *J* 4.1 Hz), 131.2(d, *J* 9.3 Hz), 130.6(d, *J* 2.1 Hz), 128.2(s), 128.1(d, *J* 3.8 Hz), 127.1(s), 126.3(s), 124.6(s), 124.3(d, *J* 14.5 Hz); δ_P(109 MHZ, $CDCl_3$) 37.01; *m/z* (CI$^+$) 437.12 ([M+H]$^+$, 100 %), 327.09 ([M-SPh]$^+$, 32 %).

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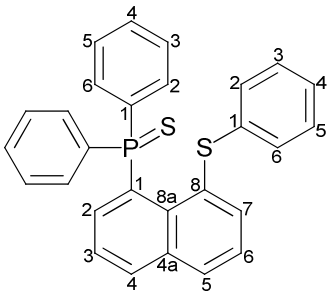
Compound 22 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine sulfide



To a solution of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** (0.239 g, 0.569 mmol) in toluene (10 mL) powdered sulfur (18.2 mg, 0.569 mmol) was added in small batches at 0 °C. The mixture was stirred for ½ h at 0 °C and another 2 h at ambient temperature. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The solid product was collected by filtration and recrystallised from dichloromethane/hexane (0.1 g, 44 %); (Found: C, 73.3; H, 4.7. Calc. for $C_{28}H_{21}PS_2$: C, 74.3; H, 4.7 %); ν_{max}(KBr disc)/cm^{-1}: 3446br, 3062w, 1966w, 1847w, 1579s, 1543w, 1473s, 1430s, 1381w, 1357w, 1321s, 1302s, 1272w, 1199w, 1177s, 1150s, 1089s, 1022w, 989s, 916w, 882w, 824s, 766vs, 736vs, 687s, 642vs, 611s, 547s, 578w, 547s, 523s, 511vs, 492s, 468s, 447w, 407s; δ_H(270 MHz, $CDCl_3$) 7.99-7.88 (3 H, m, nap 4,5,7-H), 7.54-7.48 (1 H, m, nap 6-H), 7.32-7.10 (12 H, m, nap 2,3-H, 2 x P*Ph*$_2$ 2-6-H), 6.81-6.69 (3 H, m, S*Ph* 3-5-H), 5.93-5.87 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 140.7(s), 137.7(d, *J* 11.4 Hz), 134.2(d, *J* 3.1 Hz), 131.8(s), 130.5(s), 128.3(d, *J* 12.5 Hz), 128.1(s), 127.4(s),125.3(s), 124.4(s), 124.2(s); δ_P(109.4 MHz, $CDCl_3$) 52.52; *m/z* (ES$^+$) 474.97 ([M+Na]$^+$, 100 %).

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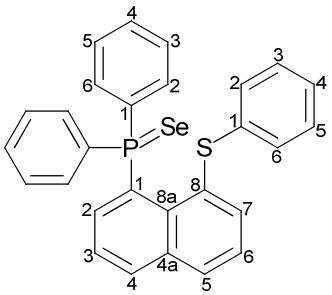
Compound 23 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine selenide



(8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** (0.23 g, 0.55 mmol) and Se (0.047 g, 0.55 mmol) were heated under reflux in toluene (10 mL) for 2 h. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The solid product was collected by filtration and recrystallised from dichloromethane/hexane (0.2 g, 85 %); (Found: C, 65.9; H, 4.4. Calc. for $C_{28}H_{21}PSSe$: C, 67.3; H, 4.2 %); ν_{max}(KBr disc)/cm^{-1}: 2856vs, 2395w, 1718w, 1646s, 1542w, 1461vs, 1378vs, 1308w, 1181w, 1120w, 973w, 886w, 809s, 722s, 691w, 616w, 562w, 539w, 506w; δ_H(270 MHz, $CDCl_3$) 8.00-7.91 (3 H, m, nap 4,5,7-H), 7.56-7.49 (1 H, m, nap 6-H), 7.30-7.10 (12 H, m, nap 2,3-H, 2 x P*Ph*$_2$ 2-6-H), 6.77-6.67 (3 H, m, S*Ph* 3-5-H), 5.86-5.81 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 140.7(s), 137.3(d, *J* 10.4 Hz), 134.2(d, *J* 3.2 Hz), 131.9(s), 130.6(d, *J* 3.1 Hz), 128.3(d, *J* 12.4 Hz), 128.1(s), 127.6(s), 125.0(s), 124.3(s), 124.2(s); δ_P(109.4 MHz, $CDCl_3$) 42.46 ($J_{P(1)-Se(1)}$ 722.4 Hz); δ_{Se}(51.5 MHz, $CDCl_3$) -341.0 ($J_{Se(1)-P(1)}$ 722.4 Hz); *m/z* (Cl^+) 501.04 ($[M+H]^+$, 4 %), 421.12 ($[M-Se]^+$, 75 %), 391.02 ($[M-SPh]^+$, 12 %), 343.08 ($[M-SePh]^+$, 100%).

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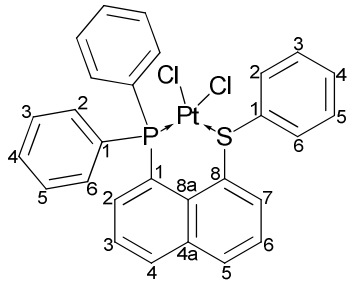
Compound 24 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dichloride



To a schlenk tube containing ligand (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (0.05 g, 0.12 mmol) and Pt(COD)Cl_2 (0.044 g, 0.12 mmol) was added dichloromethane (5 mL). The reaction was stirred for 1 h. Removal of solvent to near dryness and recrystallising from dichloromethane/pentane gave green crystalline needles in near quantitative yield (0.08 g, 98 %); (Found: C, 48.6; H, 3.4. Calc. for $C_{28}H_{21}PSPtCl_2$: C, 49.1; H, 3.1 %); ν_{max}(KBr disc)/cm^{-1}: 3430br, 3054s, 2919s, 1964w, 1577s, 1478s, 1434s, 1321s, 1258w, 1154s, 1096vs, 1204s, 994s, 941s, 885s, 830vs, 765vs, 736vs, 687vs, 584vs, 526vs, 505vs, 418vs, 330vs, 294s; δ_H(270 MHz, $CDCl_3$) 8.31-8.26 (1 H, m, nap 5-H), 8.26-8.21 (2 H, m, nap 4,7-H), 7.70-7.64 (1 H, m, nap 6-H), 7.53-7.42 (3 H, m, nap 3-H, 2 x P*Ph*$_2$ 4-H), 7.42-6.94 (12 H, m, nap 2-H, 2 x P*Ph*$_2$ 2,3,5,6-H), 6.85-6.76 (1 H, m, S*Ph* 4-H), 6.73-6.63 (4 H, m, S*Ph* 2,3,5,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.3(d, *J* 4.2 Hz), 137.6(s), 135.2(s), 134.8(s), 133.7(s), 131.2(s), 128.8(d, *J* 6.2 Hz), 128.3(s), 128.1(d, *J* 5.1 Hz), 127.7(s), 126.6(s), 126.3(d, *J* 10.4 Hz); δ_P(109 MHZ, $CDCl_3$) 1.37 ($J_{P\text{-}Pt}$ 3521.2 Hz); *m/z* (ES^+) 651.10, ($[M\text{-}Cl]^+$, 60 %), 614.13 ($[M\text{-}Cl_2]^+$, 100 %).

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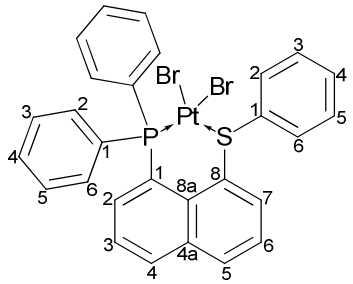
Compound 25 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dibromide



To a schlenk tube containing ligand (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (0.13 g, 0.30 mmol) and $Pt(COD)Br_2$ (0.14 g, 0.30 mmol) was added dichloromethane (5 mL). The reaction was stirred for 1 h. Removal of solvent to near dryness and recrystallising from dichloromethane/pentane gave clear crystalline needles in near quantitative yield (0.2 g, 98 %); (Found: C, 43.0; H, 2.6. Calc. for $C_{28}H_{21}PSPtBr_2$: C, 43.5; H, 2.7 %); ν_{max}(KBr disc)/cm^{-1}: 3047s, 1578w, 1477s, 1434vs, 1339s, 1269s, 1181s, 1154s, 1095vs, 996s, 887s, 827s, 766vs, 735vs, 585s, 569s, 525vs, 503vs; δ_H(270 MHz, $CDCl_3$) 8.30-8.26 (2 H, m, nap 5,7-H), 8.26-8.22 (1 H, m, nap 4-H), 7.69-7.64 (1 H, m, nap 6-H), 7.53-7.46 (2 H, m, nap 2,3-H), 7.46-6.96 (10 H, m, 2 x P*Ph*$_2$ 2-6-H), 6.84-6.78 (1 H, m, S*Ph* 4-H), 6.74-6.62 (4 H, m, S*Ph* 2,3,5,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.6(d, *J* 4.2 Hz), 137.5(s), 135.2(s), 134.7(s), 133.8(br s), 131.1(s), 128.8(s), 128.6(s), 128.2(br s), 127.7(s), 126.6(s), 126.2(d, *J* 9.3 Hz); δ_P(109 MHZ, $CDCl_3$) 0.98 ($J_{P\text{-}Pt}$ 3408.6 Hz); *m/z* (ES$^+$) 695.05 ([M-Br]$^+$, 100 %), 614.13 ([M-Br$_2$]$^+$, 22 %).

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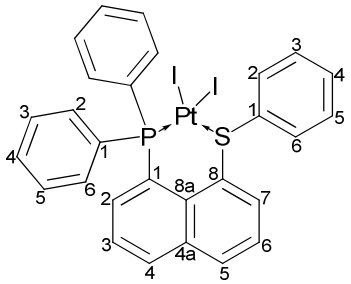
Compound 26 – (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum diiodide



To a schlenk tube containing ligand (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (0.062 g, 0.15 mmol) and Pt(COD)I_2 (0.082 g, 0.15 mmol) was added dichloromethane (5 mL). The reaction was stirred for 1 h. Removal of solvent to near dryness and recrystallising from dichloromethane/pentane gave clear crystalline needles in near quantitative yield (0.1 g, 99 %); (Found: C, 36.1; H, 2.2. Calc. for $C_{28}H_{21}PSPtI_2$: C, 36.5; H, 2.4 %); ν_{max}(KBr disc)/cm^{-1}: 3050w, 2962w, 2221w, 1573w, 1476s, 1434s, 1335w, 1260s, 1151w, 1095vs, 1021vs, 907s, 882s, 800vs, 764s, 727vs, 690vs, 581s, 564s, 522s, 502s, 476w, 450w; δ_H(270 MHz, $CDCl_3$) 8.33-8.27 (2 H, m, nap 5,7-H), 8.27-8.20 (1 H, m, nap 4-H), 7.70-7.62 (1 H, m, nap 6-H), 7.57-7.43 (2 H, m, nap 2,3-H), 7.43-6.95 (10 H, m, 2 x P*Ph*$_2$ 2-6-H), 6.83-6.75 (1 H, m, S*Ph* 4-H), 6.75-6.68 (2 H, m, S*Ph* 2,6-H), 6.68-6.59 (2 H, m, S*Ph* 3,5-H); δ_C(67.9 MHz, $CDCl_3$) 139.7(d, *J* 3.4 Hz), 137.3(s), 134.9(s), 134.4(d, *J* 2.9 Hz), 130.9(s), 128.7(s), 128.3(s), 127.7(s), 126.5(s), 126.1(d, *J* 10.5 Hz); δ_P(109 MHZ, $CDCl_3$) 0.34 ($J_{P\text{-}Pt}$ 3263.1 Hz); *m/z* (ES$^+$) 742.06 ([M-I]$^+$, 100 %).

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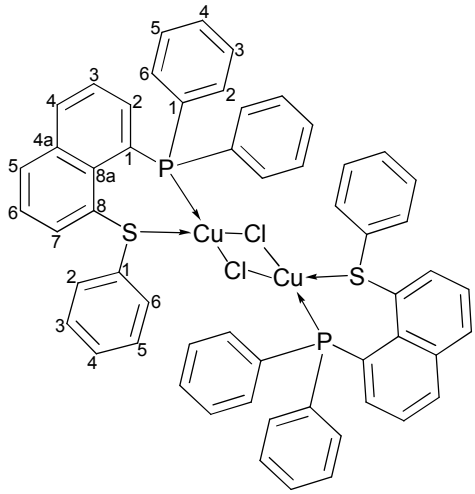
Compound 27 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper chloride dimer



To a schlenk tube containing ligand (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (0.68 g, 1.6 mmol) and copper (I) chloride (0.16 g, 1.6 mmol) was added dichloromethane (5 mL) and methanol (5 mL). The reaction was stirred for 2 h. Removal of the solvent and addition of hexane caused precipitation of excess copper (I) chloride. The excess salt was removed by filtration and the solvent was concentrated under reduced pressure. The oil was recrystallised from dichloromethane/pentane to give green crystalline needles (1.3 g, 76 %); (Found: C, 50.7; H, 3.2. Calc. for $(C_{56}H_{42}P_2S_2Cu_2Cl_2)(CH_2Cl_2)_5$: C, 50.1; H, 3.6 %); ν_{max}(KBr disc)/cm^{-1}: 2957w, 2914w, 2859w, 2360vs, 2340vs, 2117w, 1771w, 1733w, 1715w, 1699w, 1651w, 1581w, 1476w, 1455w, 1435s, 1392w, 1360w, 1317w, 1261w, 1227w, 1185s, 1113s, 1066w, 1023w, 994w, 924w, 883w, 822s, 800w, 769w, 731s, 716s, 689s, 668s, 587w, 563s, 539s, 506w, 472w, 454w, 420w; δ_H(270 MHz, $CDCl_3$) 7.97 (1 H, d, *J* 8.2 Hz, nap 4-H), 7.90 (1 H, d, *J* 8.1 Hz, nap 5-H), 7.83 (1 H, dd, *J* 1.3 and 7.2 Hz, nap 7-H), 7.52-7.40 (6 H, m, nap 2,6-H, 2 x P*Ph*$_2$ 2,6-H), 7.32-7.23 (3 H, m, nap 3-H, 2 x P*Ph*$_2$ 4-H), 7.23-7.15 (4 H, m, 2 x P*Ph*$_2$ 3,5-H), 6.84-6.72 (3 H, m, S*Ph* 3,4,5-H), 6.18-6.12 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.8(s) 138.4(d, *J* 12.4 Hz), 134.2(d, *J* 4.1 Hz), 131.2(d, *J* 9.3 Hz), 130.6(d, *J* 2.1 Hz), 128.2(s), 128.1(d, *J* 3.8 Hz), 127.1(s), 126.3(s), 124.6(s), 124.3(d, *J* 14.5 Hz); δ_P(109 MHZ, $CDCl_3$) 27.78; *m/z* (ES$^+$) 903.10 ([M-CuCl$_2$]$^+$, 100 %).

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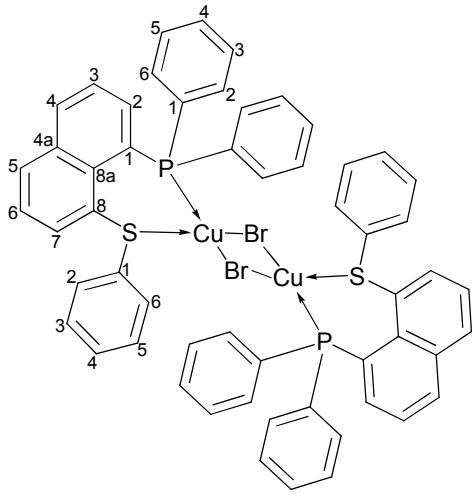
Compound 28 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper bromide dimer



To a schlenk tube containing ligand (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (0.57 g, 1.4 mmol) and copper (I) bromide (0.39 g, 1.4 mmol) was added dichloromethane (5 mL) and methanol (5 mL). The reaction was stirred for 2 h. Removal of the solvent and addition of hexane caused precipitation of excess copper (I) bromide. The excess salt was removed by filtration and the solvent was concentrated under reduced pressure. The oil was recrystallised from dichloromethane/pentane to give green crystalline needles (0.9 g, 61 %); (Found: C, 57.5; H, 4.4. Calc. for $(C_{56}H_{42}P_2S_2Cu_2Br_2)_2CH_2Cl_2$: C, 58.0; H, 3.7 %); ν_{max}(KBr disc)/cm^{-1}: 2963w, 2853w, 2361vs, 2340vs, 2215w, 1944w, 1699w, 1651w, 1580w, 1558w, 1541w, 1475w, 1435s, 1318w, 1261s, 1184w, 1098s, 1023w, 993w, 925w, 883w, 821s, 802s, 768w, 731s, 689s, 587w, 563s, 540s, 506w, 419w; δ_H(270 MHz, $CDCl_3$) 7.98 (1 H, d, *J* 8.1 Hz, nap 4-H), 7.91 (1 H, d, *J* 8.1 Hz, nap 5-H), 7.84 (1 H, dd, *J* 1.2 and 7.2 Hz, nap 7-H), 7.56-7.39 (6 H, m, nap 2,6-H, 2 x P*Ph*$_2$ 2,6-H), 7.34-7.26 (3 H, m, nap 3-H, 2 x P*Ph*$_2$ 4-H), 7.26-7.15 (4 H, m, 2 x P*Ph*$_2$ 3,5-H), 6.86-6.74 (3 H, m, S*Ph* 3,4,5-H), 6.20-6.12 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.8(s), 138.4(d, *J* 12.1 Hz), 134.2 (d, *J* 4.0 Hz), 131.2(s), 131.2(d, *J* 8.7 Hz), 130.6(d, *J* 2.9 Hz), 128.2(d, *J* 8.1 Hz), 128.1(s), 127.1(s), 126.3(s), 124.6(s), 124.3(d, *J* 14.4 Hz); δ_P(109 MHZ, $CDCl_3$) 27.73; *m/z* (ES$^+$) 903.23 ([M-$CuBr_2$]$^+$, 3%), 299.18 ([$C_{10}H_6SPhCu$]$^+$, 100 %).

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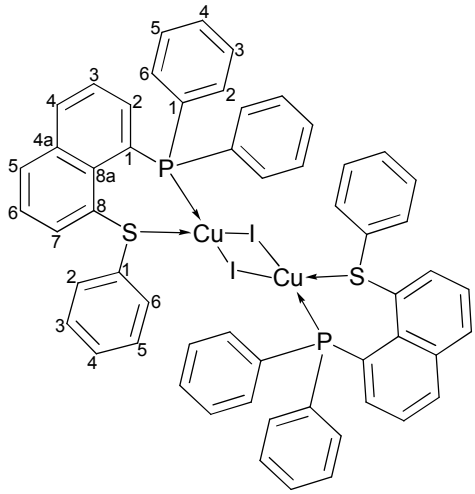
Compound 29 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper iodide dimer



To a schlenk tube containing ligand (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (0.52 g, 1.3 mmol) and copper (I) iodide (0.24 g, 1.3 mmol) was added dichloromethane (5 mL) and methanol (5 mL). The reaction was stirred for 2 h. Removal of the solvent and addition of hexane caused precipitation of excess copper (I) iodide. The excess salt was removed by filtration and the solvent was concentrated under reduced pressure. The oil was recrystallised from dichloromethane/pentane to give green crystalline needles (0.5 g, 31 %); (Found: C, 53.9; H, 3.5. Calc. for $(C_{56}H_{42}P_2S_2Cu_2I_2)_2CH_2Cl_2$: C, 53.7; H, 3.4 %); ν_{max}(KBr disc)/cm^{-1}: 3417w, 3050w, 2346w, 1956w, 1881w, 1806w, 1656w, 1548s, 1477s, 1433vs, 1358s, 1308s, 1196w, 1142w, 1095s, 1060w, 1023s, 998w, 980w, 912w, 816vs, 764s, 748vs, 689vs, 613w, 561w, 529s, 512vs, 490s, 440w; δ_H(270 MHz, $CDCl_3$) 7.98 (1 H, d, *J* 8.1 Hz, nap 4-H), 7.91 (1 H, d, *J* 8.1 Hz, nap 5-H), 7.84 (1 H, dd, *J* 1.3 and 7.2 Hz, 7-H), 7.55-7.42 (6 H, m, nap 2,6-H, 2 x P*Ph*$_2$ 2,6-H), 7.35-7.25 (3 H, m, nap 3-H, 2 x P*Ph*$_2$ 4-H), 7.25-7.16 (4 H, m, 2 x P*Ph*$_2$ 3,5-H), 6.86-6.74 (3 H, m, S*Ph* 3,4,5-H), 6.20-6.13 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.9(s), 138.3(d, *J* 19.8 Hz), 134.6 (d, *J* 3.1 Hz), 131.4(s), 131.2(s), 130.6(d, *J* 3.1 Hz), 128.3(s), 128.12(d, *J* 4.1 Hz), 127.1(s), 126.4(s), 124.7(s), 124.4(d, *J* 17.7 Hz); δ_P(109 MHZ, $CDCl_3$) 28.68; *m/z* (ES$^-$) 903.20 ([M-CuI_2]$^-$, 1%), 299.19 ([$C_{10}H_6$SphCu]$^+$, 100 %).

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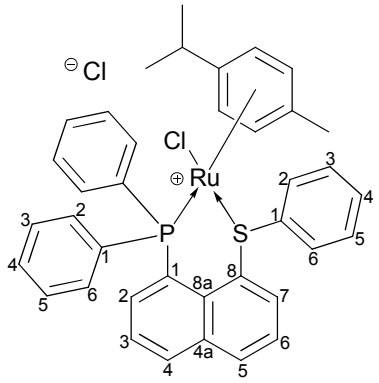
Compound 30 - (8-phenylsulfanylnaphth-1-yl)diphenylphosphinechlororuthenium(II)chloride



To a schlenk tube containing ligand (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (0.12 g, 0.29 mmol) and $[Ru(^{p}Cy)Cl_2]_2$ (0.18 g, 0.29 mmol) was added dichloromethane (5 mL). The reaction was stirred for 2 h and the filtered. Removal of the solvent and recrystallisation of the red oil from dichloromethane/pentane gave orange crystals (0.1 g, 92 %); ν_{max}(KBr disc)/cm^{-1}: 3397br, 3053vs, 2961vs, 2272w, 1656vs, 1467s, 1436vs, 1387vs, 1319s, 1278w, 1198w, 1157w, 1113s, 1093s, 1055s, 1030s, 997w, 875s, 821w, 758s, 693vs, 560s, 519s, 498s, 448vs, 294s; δ_H(270 MHz, $CDCl_3$) 8.03 (1 H, d, *J* 7.2 Hz, S*Ph* 4-H), 7.99-7.87 (3 H, m, nap 4-H, S*Ph* 2,6-H), 7.83 (1 H, d, *J* 8.0 Hz, nap 5-H), 7.65-7.35 (12 H, m, S*Ph* 3,5-H, 2 x PPh_2 2-6-H), 7.35-7.16 (3 H, m, nap 2,3,6-H), 7.03 (1 H, d, *J* 6.9 Hz, nap 7-H), 5.47 (1 H, d, *J* 6.4 Hz, Ar-*H*), 5.40 (1 H, d, *J* 5.9 Hz, Ar-*H*), 5.27 (1 H, d, *J* 5.9 Hz, Ar-*H*), 4.98 (1 H, d, *J* 6.4 Hz, Ar-*H*), 2.30-2.10 (1 H, m, Ar-C*H*$(CH_3)_2$), 1.89 (3 H, s, Ar-CH_3), 0.93 (3 H, d, *J* 6.9 Hz, Ar-CH(CH_3)$_2$), 0.69 (3 H, d, *J* 6.9 Hz, Ar-CH(CH_3)$_2$); δ_C(67.9 MHz, $CDCl_3$) 134.6(d, *J* 2.1 Hz), 134.0(d, *J* 4.1 Hz), 133.9(d, *J* 3.1 Hz), 133.3(s), 132.5(s), 132.4(s), 131.8(d, *J* 2.0 Hz), 131.7(s), 131.5(s), 130.8(s), 129.8(d, *J* 10.4 Hz), 129.4(d, *J* 10.4 Hz), 125.7(s), 125.5(d, *J* 9.4 Hz), 96.0(s), 95.9(s), 81.3(s), 80.6(s), 30.7(s), 22.8(s), 20.6(s), 18.4(s); δ_P(109 MHZ, $CDCl_3$) 37.99; *m/z* (ES$^+$) 691.12 ([M-Cl]$^+$, 100 %).

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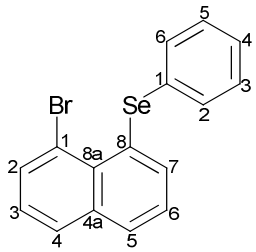
Compound 31 - 1-bromo-8-(phenylselenyl)naphthalene



To a solution of 1,8-dibromonaphthalene (5.0 g, 0.018 mol) in diethyl ether (35 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (7 mL, 0.018 mol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl diselenide (5.45 g, 0.018 mol) in diethyl ether (10 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane/dichloromethane 20:1). The brown oil obtained was recrystallised from dichloromethane/pentane (4.0 g, 63 %); (Found: C, 52.6; H, 3.6. Calc. for $C_{16}H_{11}BrSe$: C, 53.0; H, 3.1 %); ν_{max}(KBr disc)/cm^{-1}: 3058w, 2955w, 2925w, 1787w, 1573w, 1541s, 1473w, 1462w, 1434s, 1353w, 1299w, 1269w, 1187s, 1139s, 1089w, 1061w, 1020w, 997w, 953w, 903w, 841w, 806vs, 746vs, 691vs, 557w, 533w, 476w, 436w, 315w; δ_H(270 MHz, $CDCl_3$) 7.88 (1 H, dd, *J* 1.2 and 7.4 Hz, nap 4-H), 7.81 (1 H, d, *J* 8.1 Hz, nap 2-H), 7.74-7.59 (3 H, m, nap 5-H, S*Ph* 2,6-H), 7.49-7.36 (3 H, m, S*Ph* 3-5-H), 7.34-7.22 (2 H, m, nap 3,7-H), 7.19-7.09 (1 H, m, nap 6-H); δ_C(67.9 MHz, $CDCl_3$) 137.1(q), 136.8(s), 133.5(q), 133.4(s), 132.1(q), 131.7(q), 130.9(s), 130.0(s), 129.4(s), 128.9(s), 127.6(s), 126.4(s), 126.2(s), 120.6(q); δ_{Se}(51.5 MHz, $CDCl_3$) 447.8; *m/z* (EI$^+$) 361.92 ([M]$^+$, 100 %).

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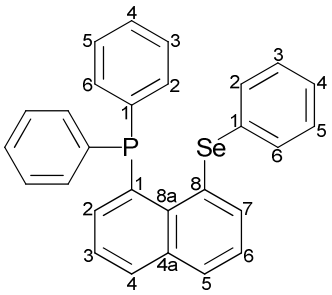
Compound 32 - (8-phenylselenylnaphth-1-yl)diphenylphosphine 32 (from 31)



A solution of 2.5 M *n*-butyllithium in hexane (1.1 mL, 2.8 mmol) was transferred dropwise to a freshly prepared solution of 1-bromo-8-(phenylselenyl)naphthalene (1.02 g, 2.8 mmol) in diethyl ether (30 mL) at -10-0 °C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.62 g, 0.5 mL, 2.8 mmol) was added slowly. Stirring was continued for a further 2 h at -10-0 °C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo* (0.5 g, 40 %); (Found: C, 68.4; H, 4.6. Calc. for $(C_{28}H_{21}PSe)_4CDCl_3$: C, 68.2; H, 4.4 %); ν_{max}(KBr disc)/cm^{-1}: 3853w, 3735w, 3673w, 3649w, 3628w, 3049w, 2911w, 2851w, 2360vs, 2340vs, 1734w, 1699w, 1651w, 1558w, 1541w, 1474w, 1433s, 1310w, 1259w, 1193w, 1153w, 1088w, 1021w, 996w, 971w, 911w, 815s, 765s, 739s, 690s, 669s, 538w, 504w, 420w, 397w, 352w; δ_H(270 MHz, $CDCl_3$) 7.76 (1 H, dd, *J* 1.5 and 7.9 Hz, nap 4-H), 7.66 (1 H, d, *J* 8.1 Hz, nap 5-H), 7.52 (1 H, dd, *J* 1.2 and 7.4 Hz, nap 7-H), 7.35-7.30 (1 H, m, nap 2-H), 7.30-7.05 (17 H, m, nap 2,3-H, S*Ph* 2-6-H, 2 x PPh_2 2-6-H); δ_C(67.9 MHz, $CDCl_3$) 137.7(s), 135.0(s), 133.9(d, *J* 5.2 Hz), 133.7(s), 131.2(s), 129.2(s), 128.9(s), 128.5(d, *J* 6.2 Hz), 128.3(s), 127.4(s), 126.1(s), 125.6(s); δ_P(109.4 MHz, $CDCl_3$) -12.94 ($J_{P(1)-Se(1)}$ 386.2.0 Hz); δ_{Se}(51.5 MHz, $CDCl_3$) 439.6 ($J_{Se(1)-P(1)}$ 386.2.0 Hz); *m/z* (CI$^+$) 469.06 ([M+H]$^+$, 65 %), 391.02 ([M+H-Ph]$^+$, 98 %).

Compound 32 – (from 33)

A solution of 2.5 M *n*-butyllithium in hexane (0.5 mL, 1.2 mmol) was transferred dropwise to a freshly prepared solution of 1-iodo-8-(phenylselenyl)naphthalene (0.50 g, 1.2 mmol) in diethyl ether (30 mL) at -10-0 °C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.27 g, 0.2 mL, 1.2 mmol) was added slowly. Stirring was continued for a further 2 h at -10-0 °C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo* (0.5 g, 89 %); The product was identified by ^{1}H and ^{31}P NMR spectroscopy.

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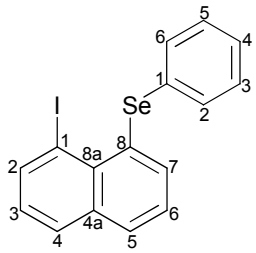
Compound 33 - 1-iodo-8-(phenylselenyl)naphthalene



To a solution of 1,8-diiodonaphthalene (0.49 g, 1.3 mmol) in diethyl ether (15 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.5 mL, 1.3 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl diselenide (0.40 g, 1.3 mmol) in diethyl ether (15 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane) and recrystallised from dichloromethane/pentane (0.3 g, 60 %); (Found: C, 47.0; H, 2.5. Calc. for $C_{16}H_{11}ISe$: C, 47.0; H, 2.7 %); ν_{max}(KBr disc)/cm^{-1}: 3442br, 3051s, 1961w, 1911w, 1887w, 1778w, 1633w, 1571s, 1537vs, 1488w, 1473s, 1434s, 1349s, 1311s, 1299s, 1272w, 1185s, 1133s, 1089w, 1062s, 1018s, 997w, 947w, 897w, 829w, 804vs, 742vs, 691vs, 607w, 551w, 524w, 474s, 427w, 306w; δ_H(270 MHz, $CDCl_3$) 8.22 (1 H, dd, *J* 1.3 and 7.4 Hz, nap 4-H), 7.74 (1 H, dd, *J* 1.0 and 8.1 Hz, nap 2-H), 7.57 (1 H, dd, *J* 1.1 and 8.0 Hz, nap 5-H), 7.49-7.43 (2 H, m, S*Ph* 2,6-H), 7.35 (1 H, dd, *J* 1.2 and 7.5 Hz, nap 7-H), 7.32-7.24 (3 H, m, S*Ph* 3-5-H), 7.12-6.99 (2 H, m, nap 3,6-H); δ_C(67.9 MHz, $CDCl_3$) 142.2(s), 135.6(s), 133.1(s), 130.2(s), 129.8(s), 128.6(s), 128.4(s), 126.8(s), 126.3(s); δ_{Se}(51.5 MHz, $CDCl_3$) 430.8; *m/z* (EI$^+$) 409.9 ([M]$^+$, 51 %).

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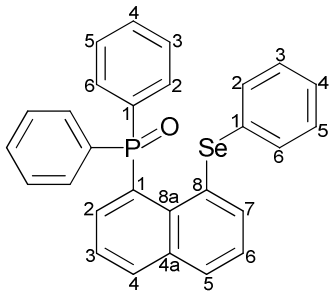
Compound 34 - (8-phenylselenylnaphth-1-yl)diphenylphosphine oxide



(8-phenylselenylnaphth-1-yl)diphenylphosphine **32** readily oxidised in contact with the atmosphere to produce (8-phenylselenylnaphth-1-yl)diphenylphosphine oxide **35** with 100 % conversion as seen by ^{31}P NMR spectroscopy (Found C, 68.5; H, 4.6. Calc. for $C_{28}H_{21}PSeO$: C, 69.4; H, 4.4 %); ν_{max}(KBr disc)/cm^{-1}: 3423br, 3053s, 2924w, 1960w, 1893w, 1809w, 1589w, 1472s, 1436vs, 1314s, 1176vs, 1115vs, 1068w, 1022w, 997w, 981w, 923w, 866w, 821s, 763vs, 744vs, 721vs, 693vs, 541vs, 505s, 469w, 447w, 426w; δ_H(270 MHz, $CDCl_3$) 7.92 (1 H, d, *J* 8.2 Hz, nap 4-H), 7.88 (1 H, d, *J* 6.4 Hz, nap 5-H), 7.79 (1 H, d, *J* 8.1 Hz, nap 7-H), 7.57-7.48 (4 H, m, 2 x P*Ph*$_2$ 2,6-H), 7.40-7.32 (3 H, m, nap 2-H, 2 x P*Ph*$_2$ 4-H), 7.30-7.21 (6 H, m, nap 3,6-H, 2 x P*Ph*$_2$ 3,5-H), 6.97-6.90 (1 H, m, S*Ph* 4-H), 6.90-6.81 (2 H, m, S*Ph* 3,5-H), 6.59 (2 H, d, *J* 7.2 Hz, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 140.3(s), 137.6(q), 137.3(q), 135.6(q), 134.3(s), 131.8(d, *J* 9.4 Hz), 131.1(s), 130.3(s), 128.6(s), 128.4(s), 128.2(s), 127.1(s), 126.1(s), 123.8(d, *J* 15.5 Hz); δ_P(109 MHZ, $CDCl_3$) 37.99; δ_{Se}(51.5 MHz, $CDCl_3$) 450.4; *m/z* (ES$^+$) 507.02 ([M+Na]$^+$, 100 %).

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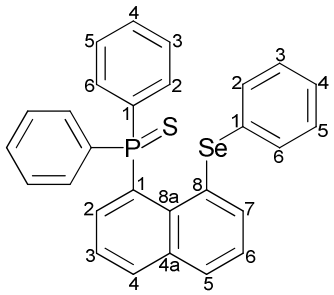
Compound 35 - (8-phenylselenylnaphth-1-yl)diphenylphosphine sulfide



To a solution of (8-phenylselenylnaphth-1-yl)diphenylphosphine **32** (0.086 g, 0.21 mmol) in toluene (10 mL) powdered sulfur (0.065 g, 0.21 mmol) was added in small batches at 0 °C. The mixture was stirred for ½ h at 0 °C and another 2 h at ambient temperature. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The solid product was collected by filtration and recrystallised from dichloromethane/hexane (0.05 g, 54 %); (Found C, 66.7; H, 3.9. Calc. for $C_{28}H_{21}PSSe$: C, 67.2; H, 4.2 %); ν_{max}(KBr disc)/cm^{-1}: 2925vs, 1871vs, 1574w, 1474s, 1434vs, 1375w, 1317w, 1260s, 1192w, 1177w, 1095s, 1064w, 1021s, 994w, 936s, 863w, 797vs, 769s, 732vs, 718vs, 690vs, 639s, 539s, 509s, 454w, 414w; δ_H(270 MHz, $CDCl_3$) 8.12 (1 H, dd, *J* 1.4 and 7.1 Hz, nap 5-H), 8.00-7.88 (2 H, m, nap 4,7-H), 7.76-7.62 (4 H, m, 2 x P*Ph*$_2$ 2,6-H), 7.48-7.22 (9 H, m, nap 2,3,6-H, 2 x P*Ph*$_2$ 3-5-H), 6.97-6.81 (3 H, m, S*Ph* 3-5-H), 6.43-6.35 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$)141.2(s), 137.9(s), 134.3(d, *J* 3.1 Hz), 132.0(d, *J* 10.4 Hz), 131.1(s), 130.8(d, *J* 2.0 Hz), 129.4(s), 128.5(d, *J* 4.2 Hz), 128.3(s), 127.3(s), 125.6(s), 123.9(s); δ_P(109 MHZ, $CDCl_3$) 51.01; δ_{Se}(51.5 MHz, $CDCl_3$) 448.5(d, $J_{Se\text{-}P}$ 19.1 Hz); *m/z* (CI$^+$) 501.04 ([M+H]$^+$, 3 %), 419.10 ([M-Ph]$^+$, 11 %), 345.08 ([M-Ph$_2$]$^+$, 100 %).

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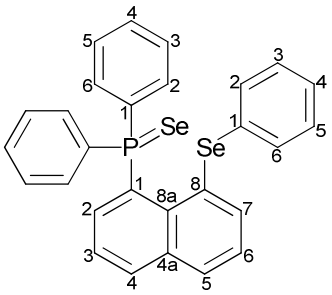
Compound 36 - (8-phenylselenylnaphth-1-yl)diphenylphosphine selenide 36



(8-phenylselenylnaphth-1-yl)diphenylphosphine **32** (1.09 g, 2.3 mmol) and Se (0.18 g, 2.3 mmol) were heated under reflux in toluene (20 mL) for 2 h. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The solid product was collected by filtration and recrystallised from dichloromethane/hexane (0.8 g, 60 %); (Found C, 61.4; H, 3.3. Calc. for $C_{28}H_{21}PSe_2$: C, 61.6; H, 3.9 %); ν_{max}(KBr disc)/cm^{-1}: 2018vs, 1954vs, 1918vs, 1732w, 1651s, 1574w, 1473s, 1433s, 1316w, 1261s, 1197w, 1178w, 1156w, 1096s, 1019w, 995w, 978w, 905w, 862w, 824s, 800s, 774w, 765s, 748s, 735s, 686s, 662w, 615w, 583s, 557s, 524s, 505s, 486s, 458s, 443s, 413s; δ_H(270 MHz, $CDCl_3$) 8.11 (1 H, dd, *J* 1.3 and 7.2 Hz, nap 5-H), 7.94-7.83 (2 H, m, nap 4,7-H), 7.43-7.14 (13 H, m, nap 2,3,6-H, 2 x P*Ph*$_2$ 2-6-H), 6.88-6.74 (3 H, m, S*Ph* 3-5-H), 6.27-6.19 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 141.4(s), 137.4(d, *J* 9.4 Hz), 134.4(d, *J* 3.1 Hz), 131.2(s), 130.8(d, *J* 3.1 Hz), 128.8(s), 128.6(s), 128.5(s), 128.4(s), 128.3(s), 127.4(s), 125.5(s), 123.9(d, *J* 13.5 Hz); δ_P(109 MHZ, $CDCl_3$) 40.50 ($J_{P\text{-}Se(2)}$ 715.3 Hz)($J_{P\text{---}Se(1)}$ 23.9 Hz); δ_{Se}(51.5 MHz, $CDCl_3$) 451.4(d, $J_{Se(1)\text{---}P}$ 23.9 Hz), -162.8(d, $J_{Se(2)\text{-}P}$ 715.3 Hz); *m/z* (EI$^+$) 390.01 ([M-SePh]$^+$, 5 %), 311.10 ([M-Se_2Ph]$^+$, 18 %), 236.94 ([M-Ph_3Se]$^+$, 12 %), 233.04 ([M-Se_2Ph_2]$^+$, 100 %).

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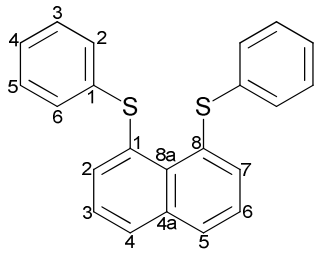
Compound 37 - 1,8-bis(phenylsulfanyl)naphthalene (from 11)



To a solution of 1,8-dibromonaphthalene (0.096 g, 0.34 mmol) in diethyl ether (10 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.27 mL, 0.68 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl disulfide (0.30 g, 0.68 mmol) in diethyl ether (10 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.03 g, 22 %); (Found: C, 76.4; H, 4.6. Calc. for $C_{22}H_{16}S_2$: C, 76.7; H, 4.7 %); ν_{max}(KBr disc)/cm^{-1}: 3442br, 3054s, 1937w, 1719w, 1578s, 1544s, 1473vs, 1435s, 1352s, 1322s, 1260w, 1197s, 1145w, 1079s, 1021s, 977w, 844w, 812vs, 740vs, 688vs, 557w, 486w, 409w; δ_H(270 MHz, $CDCl_3$) 7.75 (2 H, dd, *J* 1.4 and 8.2 Hz, nap 4,5-H), 7.45 (2 H, dd, *J* 1.4 and 7.2 Hz, nap 2,7-H), 7.35-7.28 (2 H, m, nap 3,6-H), 7.28-7.02 (10 H, m, 2 x S*Ph* 2-6-H); δ_C(67.9 MHz, $CDCl_3$) 134.0(s), 131.1(s), 129.3(s), 129.2(s), 126.8(s), 125.9(s); *m/z* (ES$^+$) 344.09 ([M]$^+$, 100 %).

Compound 37 - (from 14)

To a solution of 1,8-diiodonaphthalene (0.15 g, 0.40 mmol) in diethyl ether (10 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.3 mL, 0.80 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl disulfide (0.17 g, 0.80 mmol) in diethyl ether (10 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.03 g, 20 %).

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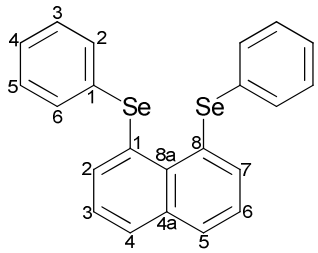
Compound 37 - (from 52)

To a solution of 1-bromonaphthalene (5 mL, 7.43 g, 35.9 mmol) in diethyl ether (30 mL) at -30 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (14.4 mL, 35.9 mmol). The mixture was warmed to room temperature and stirred for 15 min after which the solvent was evaporated *in vacuum*. The white solid was dissolved in hexane (35 mL) and the mixture cooled to -30 °C. A 2.5 M solution of *n*-butyllithium in hexane (14.4 mL, 35.9 mmol) was added followed by TMEDA (7.5 mL, 50.2 mmol). The mixture was refluxed for 3 h and then the solvent was removed *in vacuum*. The solid was dissolved in diethyl ether (50 mL) cooled to -78 °C and a solution of diphenyl disulfide (7.9 g, 36.0 mmol) in diethyl ether (50 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (1.6 g, 13 %).

Compound 38 - 1,8-bis(phenylselenyl)naphthalene (from 14)



To a solution of 1,8-dibromonaphthalene (0.11 g, 0.40 mmol) in diethyl ether (10 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.3 mL, 0.80 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl diselenide (0.25 g, 0.80 mmol) in diethyl ether (10 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a yellow solid (0.1 g, 75 %); (Found: C, 60.2; H, 3.3. Calc. for $C_{22}H_{16}Se_2$: C, 60.0; H, 3.7 %); ν_{max}(KBr disc)/cm^{-1}: 3047w, 1944w, 1804w, 1641w, 1572s, 1538s, 1473s, 1432s, 1381w, 1351w, 1325w, 1244w, 1188s, 1141w, 1088w, 1062s, 1018s, 995w, 956w, 914w, 841w, 810vs, 735vs, 690vs, 662w, 615w, 562w, 472s, 455s; δ_H(270 MHz, $CDCl_3$) 7.74 (2 H, dd, *J* 1.4 and 8.2 Hz, nap 4,5-H), 7.65 (2 H, dd, *J* 1.4 and 7.2 Hz, nap 2,7-H), 7.47-7.37 (4 H, m, 2 x Se*Ph* 2,6-H), 7.29-7.20 (8 H, m, nap 3,6-H, 2 x Se*Ph* 3-5-H); δ_C(67.9 MHz, $CDCl_3$) 135.6(s), 133.5(s), 129.4(s), 129.3(s), 127.5(s), 126.1(s); δ_{Se}(51.5 MHz, $CDCl_3$) 428.6; δ_{Se}(51.5 MHz, D_2SO_4) 828.0; *m/z* (ES$^+$) 439.98 ([M]$^+$, 100 %).

Compound 38 - (from 14)

To a solution of 1,8-diiodonaphthalene (0.20 g, 0.52 mmol) in diethyl ether (5 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.42 mL, 1.1 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl diselenide (0.33 g, 1.1 mmol) in diethyl ether (10 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a yellow solid (0.2 g, 82 %).

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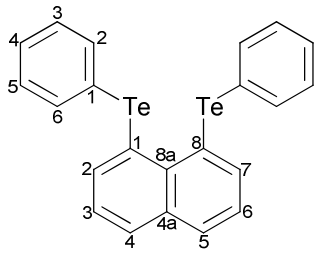
Compound 38 – (from 52)

To a solution of 1-bromonaphthalene (5 mL, 7.43 g, 35.9 mmol) in diethyl ether (30 mL) at -30 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (14.4 mL, 35.9 mmol). The mixture was warmed to room temperature and stirred for 15 min after which the solvent was evaporated *in vacuum*. The white solid was dissolved in hexane (35 mL) and the mixture cooled to -30 °C. A 2.5 M solution of *n*-butyllithium in hexane (14.4 mL, 35.9 mmol) was added followed by TMEDA (7.5 mL, 50.2 mmol). The mixture was refluxed for 3 h and then the solvent was removed *in vacuum*. The solid was dissolved in diethyl ether (50 mL) cooled to -78 °C and a solution of diphenyl diselenide (11.2 g, 36.0 mmol) in diethyl ether (50 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a yellow solid (2.3 g, 14 %).

Compound 39 - 1,8-bis(phenyltellurenyl)naphthalene 39 (from 11)



To a solution of 1,8-dibromonaphthalene (0.09 g, 0.32 mmol) in diethyl ether (10 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.3 mL, 0.64 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl ditelluride (0.26 g, 0.64 mmol) in diethyl ether (10 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a yellow solid (0.04 g, 33 %); (Found: C, 49.6; H, 2.7. Calc. for $C_{22}H_{16}Te_2$: C, 48.9; H, 3.0 %); ν_{max}(KBr disc)/cm^{-1}: 3424br, 3047w, 2918w, 2369w, 1932w, 1871w, 1806w, 1653w, 1567w, 1529w, 1468s, 1430s, 1345w, 1325w, 1295w, 1258w, 1190w, 1132w, 1058w, 1013w, 994s, 903w, 839w, 808vs, 757vs, 729vs, 689vs, 457w; δ_H(270 MHz, $CDCl_3$) 8.01 (2 H, dd, *J* 1.2 and 7.2 Hz, nap 4,5-H), 7.67 (2 H, dd, *J* 1.0 and 8.1 Hz, nap 2,7-H), 7.57-7.48 (4 H, m, 2 x Te*Ph* 2,6-H), 7.23-7.15 (2 H, m, 2 x Te*Ph* 4-H), 7.15-7.07 (6 H, m, nap 3,6-H, 2 x Te*Ph* 3-5-H); δ_C(67.9 MHz, $CDCl_3$) 141.7(s), 137.4(s), 130.4(s), 129.6(s), 127.9(s), 126.6(s); δ_{Te}(85 MHz, $CDCl_3$) 619.7 ($J_{(Te---Te)}$ 52.7 Hz); *m/z* (ES$^+$) 458.97 ([M-Ph]$^+$, 100 %).

Compound 39 – (from 14)

To a solution of 1,8-diiodonaphthalene (0.11 g, 0.28 mmol) in diethyl ether (10 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.2 mL, 0.56 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl ditelluride (0.23 g, 0.56 mmol) in diethyl ether (10 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a yellow solid (0.04 g, 23 %).

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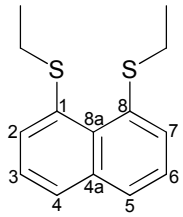
Compound 40 - 1,8-bis(ethylsulfanyl)naphthalene (from 11)



To a solution of 1,8-dibromonaphthalene (0.34 g, 1.2 mmol) in diethyl ether (15 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (1.0 mL, 2.4 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diethyl disulfide (0.29 g, 2.4 mmol, 0.3 mL) in diethyl ether (15 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.08 g, 27 %); (Found: C, 66.8; H, 6.5. Calc. for $C_{14}H_{16}S_2$: C, 67.7; H, 6.5 %); ν_{max}(KBr disc)/cm^{-1}: 3047w, 2965s, 2924s, 2851s, 1932w, 1868w, 1784w, 1720w, 1597w, 1546s, 1490w, 1446s, 1420s, 1370w, 1313s, 1259vs, 1193s, 1093s, 1046s, 1022s, 985w, 900w, 874s, 811vs, 759vs, 713w, 579w; δ_H(270 MHz, $CDCl_3$) 7.65 (2 H, dd, *J* 1.2 and 8.1 Hz, 4,5-H), 7.55 (2 H, dd, *J* 1.3 and 7.5 Hz, 2,7-H), 7.39-7.30 (2 H, m, 3,6-H), 2.96 (2 H, q, *J* 7.4 Hz, -C*H*$_2$-), 1.30 (3 H, t, *J* 7.4 Hz, -C*H*$_3$); δ_C(67.9 MHz, $CDCl_3$) 130.1(s), 127.9(s), 125.4(s), 31.6(-*C*H$_2$-), 13.4(-*C*H$_3$); *m/z* (EI$^+$) 248.07 ([M]$^+$, 2 %), 219.03 ([M-Et]$^+$, 4 %), 189.99 (]M-Et$_2$]$^+$, 100 %).

Compound 40 – (from 14)

To a solution of 1,8-diiodonaphthalene (0.54 g, 1.4 mmol) in diethyl ether (10 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (1.2 mL, 2.9 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diethyl disulfide (0.4 mL, 0.35 g, 2.9 mmol) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.3 g, 80 %).

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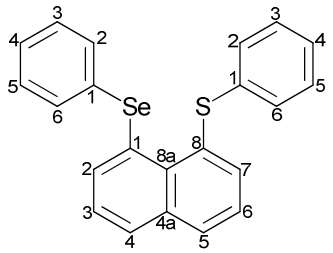
Compound 41 - 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene (from 31)



To a solution of 1-bromo-8-(phenylselenyl)naphthalene (0.40 g, 1.1 mmol) in diethyl ether (20 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.5 mL, 1.1 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl disulfide (0.24 g, 1.1 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.2 g, 34 %); (Found: C, 66.7; H, 4.2. Calc. for $C_{22}H_{16}SSe$: C, 67.3; H, 4.1 %); ν_{max}(KBr disc)/cm^{-1}: 3249s, 3053vs, 2957w, 2862w, 2638w, 2583w, 2386w, 2336w, 2168w, 1944s, 1876w, 1818w, 1773w, 1720w, 1644w, 1574vs, 1544vs, 1474vs, 1434vs, 1381w, 1353s, 1323s, 1261s, 1194s, 1152w, 1076s, 1618vs, 998w, 911w, 861w, 811vs, 755vs, 735vs, 688vs, 620w, 573w, 542w, 472s; δ_H(270 MHz, $CDCl_3$) 7.90-7.82 (2 H, m, nap 5,7-H), 7.65 (1 H, dd, *J* 1.4 and 7.7 Hz, nap 4-H), 7.62-7.54 (2 H, m, Se*Ph* 2,6-H), 7.42 (1 H, t, *J* 7.6 Hz, nap 6-H), 7.38-7.28 (3 H, m, Se*Ph* 3-5-H), 7.24-7.05 (7 H, m, nap 2,3-H, S*Ph* 2-6-H); δ_C(67.9 MHz, $CDCl_3$) 138.2(s), 136.6(s), 131.2(s), 130.8(s), 129.7(s), 129.0(s), 128.5(s), 127.9(s), 127.4(s), 126.3(s), 125.9(s), 125.8(s); δ_{Se}(51.5 MHz, $CDCl_3$) 455.3; δ_{Se}(51.5 MHz, D_2SO_4) 927.3; *m/z* (CI^+) 392.01 ($[M]^+$, 33 %), 314.97 ($[M-Ph]^+$, 35 %), 236.07 ($[M-Ph_2]^+$, 100 %).

Compound 41 – (from 9)

To a solution of 1-bromo-8-(phenylsulfanyl)naphthalene (0.23 g, 0.72 mmol) in diethyl ether (20 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.3 mL, 0.72 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl diselenide (0.23 g, 0.72 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.2 g, 75 %).

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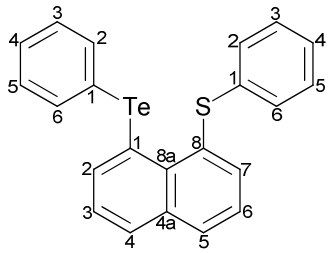
Compound 41 – (from 33)

To a solution of 1-iodo-8-(phenylselenyl)naphthalene (0.12 g, 0.3 mmol) in diethyl ether (15 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.1 mL, 0.3 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl disulfide (0.07 g, 0.3 mmol) in diethyl ether (15 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.02 g, 15 %).

Compound 41 – (from 20)

To a solution of 1-iodo-8-(phenylsulfanyl)naphthalene (0.17 g, 0.47 mmol) in diethyl ether (20 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.2 mL, 0.47 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl diselenide (0.15 g, 0.47 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.1 g, 63 %).

Compound 42 - 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene (from 9)



To a solution of 1-bromo-8-(phenylsulfanyl)naphthalene (0.32 g, 1.0 mmol) in diethyl ether (20 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.4 mL, 1.0 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl ditelluride (0.41 g, 1.0 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.2 g, 51 %); (Found: C, 60.1; H, 3.2. Calc. for $C_{22}H_{16}STe$: C, 60.1; H, 3.7 %); ν_{max}(KBr disc)/cm^{-1}: 3436br, 3051s, 2924w, 1931w, 1878w, 1812w, 1725w, 1578s, 1475s, 1433s, 1348w, 1325w, 1262w, 1193s, 1101w, 1074w, 1022s, 995w, 969w, 898w, 864w, 811vs, 758s, 735vs, 689vs, 621w, 539s, 455s, 405w; δ_H(270 MHz, $CDCl_3$) 7.96-7.85 (4 H, m, nap 5,7-H, Te*Ph* 2,6-H), 7.67 (1 H, dd, *J* 1.1 and 8.0 Hz, nap 4-H), 7.50-7.37 (3 H, m, nap 2,6-H, Te*Ph* 4-H), 7.36-7.27 (2 H, m, Te*Ph* 3,5-H), 7.26-7.16 (2 H, m, S*Ph* 3,5-H), 7.16-7.02 (4 H, m, nap 3-H, S*Ph* 2,4,6-H); δ_C(67.9 MHz, $CDCl_3$) 141.0(s), 139.6(q), 138.3(s), 137.0(s), 136.3(s), 134.9(s), 132.1(s), 130.4(q), 129.8(s), 129.1(s), 128.7(s), 127.9(s), 127.4(s), 127.0(s), 126.1(s), 125.8(s), 123.4(q), 118.3(s); δ_{Te}(81.2 MHz, $CDCl_3$) 715.2; δ_{Te}(85.2 MHz, D_2SO_4) 1018.3; *m/z* (ES$^+$) 472.84 [M + OMe]$^+$.

Compound 42 – (from 20)

To a solution of 1-iodo-8-(phenylsulfanyl)naphthalene (0.16 g, 0.45 mmol) in diethyl ether (20 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.2 mL, 0.45 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl ditelluride (0.18 g, 0.45 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.2 g, 88 %).

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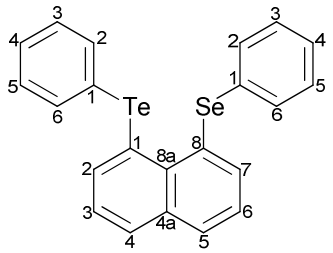
Compound 43 - 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene (from 31)



To a solution of 1-bromo-8-(phenylselenyl)naphthalene (0.11 g, 0.31 mmol) in diethyl ether (20 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.1 mL, 0.31 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl ditelluride (0.13 g, 0.31 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.1 g, 81 %); (Found: C, 54.6; H, 3.5. Calc. for $C_{22}H_{16}SeTe$: C, 53.9; H, 3.3 %); ν_{max}(KBr disc)/cm^{-1}: 3428br, 3042w, 2957w, 1969w, 1879w, 1809w, 1720w, 1655w, 1573s, 1535w, 1474s, 1431s, 1328w, 1261w, 1189w, 1138w, 1062s, 1019s, 995s, 953w, 897w, 839w, 809vs, 758vs, 733vs, 690s, 665w, 612w, 456s; δ_H(270 MHz, $CDCl_3$) 7.99 (1 H, dd, *J* 1.3 and 7.1 Hz, nap 4-H), 7.84-7.77 (3 H, m, nap 2-H, Se*Ph* 2,6-H), 7.60 (1 H, d, *J* 7.6 Hz, nap 5-H), 7.45 (1 H, dd, *J* 1.0 and 7.4 Hz, nap 7-H), 7.36-7.28 (2 H, m, nap 3-H, Se*Ph* 4-H), 7.26-7.20 (2 H, m, Se*Ph* 3,5-H), 7.20-7.14 (2 H, m, Te*Ph* 2,6-H), 7.14-7.06 (3 H, m, Te*Ph* 3-5-H), 7.01 (1 H, t, *J* 7.7 Hz, nap 6-H); δ_C(67.9 MHz, $CDCl_3$) 140.4(s), 139.7(s), 136.0(s), 131.8(s), 130.2(s), 129.7(s), 129.3(s), 128.5(s), 128.2(s), 126.8(s), 126.7(s), 125.9(s); δ_{Se}(51.5 MHz, $CDCl_3$) 362.8; δ_{Te}(81.2 MHz, $CDCl_3$) 687.6 ($J_{(Te\text{-}Se)}$ 834.0 Hz); *m/z* (ES$^+$) 410.99 ([M-Ph]$^+$, 100 %).

Compound 43 – (from 33)

To a solution of 1-iodo-8-(phenylselenyl)naphthalene (0.16 g, 0.40 mmol) in diethyl ether (20 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.2 mL, 0.40 mmol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl ditelluride (0.16 g, 0.40 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (hexane) to give a brown solid (0.03 g, 18 %).

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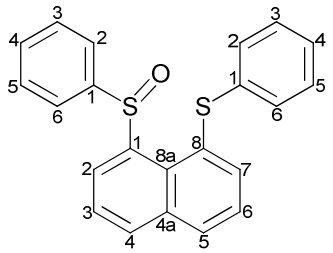
Compound 44 - 1-(phenylsulfinyl)-8-(phenylsulfanyl)naphthalene



To a solution of 1,8-(diphenylsulfanyl)naphthalene (0.12 g, 0.34 mmol) in ether (5 mL) was added mCPBA (0.06 g, 0.34 mmol). The reaction mixture was stirred for 2 h, concentrated under vacuum and recrystallised from dichloromethane/pentane (0.05 g, 41 %); (Found: C, 72.2; H, 5.2. Calc. for $C_{22}H_{16}S_2O$: C, 73.3; H, 4.5 %); ν_{max}(KBr disc)/cm^{-1}: 3432br s, 3057w, 1576s, 1546w, 1492w, 1475s, 1439s, 1353w, 1336w, 1202w, 1173w, 1156w, 1079s, 1036vs, 971w, 928w, 902w, 848w, 820vs, 763vs, 736vs, 682vs, 595w, 558w, 518s, 501w, 471s, 433s; δ_H(270 MHz, $CDCl_3$) 8.75 (1 H, d, *J* 7.0 Hz, nap 4-H), 8.08 (1 H, d, *J* 8.0 Hz, nap 2-H), 8.03 (1 H, dd, *J* 1.2 and 8.2 Hz, nap 5-H), 7.82 (1 H, dd, *J* 1.3 and 7.2 Hz nap 7-H), 7.80-7.72 (1 H, m, nap 3-H), 7.56-7.48 (1 H, m, nap 6-H), 7.48-7.40 (2 H, m, SO*Ph* 2,6-H), 7.30-7.20 (3 H, m, SO*Ph* 3-5-H), 7.16-7.06 (3 H, m, S*Ph* 3-5-H), 6.84-6.74 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.0(s), 132.9(s), 131.4(s), 130.3(s), 129.2(s), 129.1(s), 127.2(s), 127.1(s), 126.7(s), 126.3(s), 126.1(s); *m/z* (ES$^+$) 382.89 ([M+Na]$^+$,100 %).

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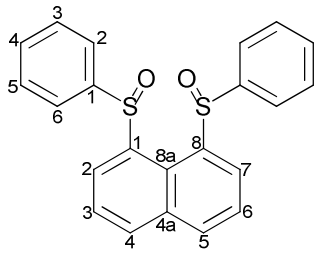
Compound 45 - 1,8-bis(phenylsulfinyl)naphthalene



To a solution of 1,8-(diphenylsulfanyl)naphthalene (0.12 g, 0.35 mmol) in ether (5 mL) was added mCPBA (0.18 g, 1.1 mmol). The reaction mixture was stirred for 2 h, after which a white precipitate was formed. The mixture was filtered and the filtrate reduced under vacuum to give a cream solid. The crude product was recrystallised from dichloromethane/pentane (0.06 g, 44 %); (Found: C, 69.3; H, 4.4. Calc. for $C_{22}H_{16}S_2O_2$: C, 70.2; H, 4.3 %); ν_{max}(KBr disc)/cm^{-1}: 3445br s, 3052w, 1578w, 1490w, 1471s, 1438s, 1338w, 1210w, 1177w, 1147w, 1075vs, 1045vs, 996w, 965w, 911w, 845w,823vs, 753vs, 690vs, 621s, 578s, 503s, 461w, 438s, 408w; δ_H(270 MHz, $CDCl_3$) 8.58 (2 H, dd, *J* 1.4 and 7.4 Hz, nap 4,5-H), 8.13 (2 H, dd, *J* 1.4 and 8.3 Hz, nap 2,7-H), 7.83-7.74 (2 H, m, nap 3,6-H), 7.64-7.53 (4 H, m, 2 x SO*Ph* 2,6-H), 7.42-7.34 (6 H, m, 2 x SO*Ph* 3-5-H); δ_C(67.9 MHz, $CDCl_3$) 133.5(s), 131.2(s), 129.6(s), 127.4(s), 126.7(s), 126.2(s); *m/z* (ES$^+$) 398.84 ([M+Na]$^+$, 100 %).

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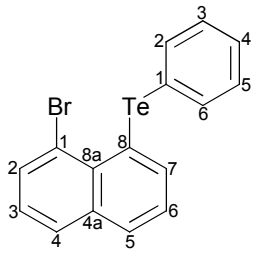
Compound 55 - 1-bromo-8-(phenyltellurenyl)naphthalene (from 11)



To a solution of 1,8-dibromonaphthalene (0.55 g, 1.9 mol) in diethyl ether (35 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.5 mL, 1.9 mol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl ditelurride (0.79 g, 1.9 mol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (ethyl acetate/hexane 1:20). The brown oil obtained was recrystallised from dichloromethane/pentane (0.3 g, 32 %); (Found: C, 46.8; H, 2.7. Calc. for $C_{16}H_{11}BrTe$: C, 46.8; H, 2.7 %); ν_{max}(KBr disc)/cm^{-1}: 3409w, 3056w, 2921w, 2584w, 2365w, 2343w, 1723w, 1659w, 1640w, 1568w, 1535s, 1469s, 1431s, 1385w, 1350s, 1329w, 1299w, 1262w, 1185s, 1133s, 1059s, 1015s, 996s, 946w, 908w, 834s, 804vs, 739vs, 692s, 602w, 553w, 527w, 459s; δ_H(270 MHz, $CDCl_3$) 8.02-7.92 (2 H, m, Te*Ph* 2,6-H), 7.80 (1 H, dd, *J* 1.3 and 7.5 Hz, nap 5-H), 7.76 (1 H, dd, *J* 1.1 and 8.3 Hz, nap 7-H), 7.63-7.55 (1 H, m, nap 4-H), 7.52-7.41 (2 H, m, nap 2-H, Te*Ph* 4-H), 7.41-7.31 (2 H, m, Te*Ph* 3,5-H), 7.28-7.20 (1 H, m, nap 6-H), 7.02 (1 H, t, *J* 7.7 Hz, nap 3-H); δ_C(67.9 MHz, $CDCl_3$) 141.3(s), 137.3(q), 135.4(s), 134.0(q), 132.5(s), 130.2(s), 129.8(s), 129.2(s), 128.2(s), 126.9(s), 126.1(s), 122.5(q), 121.2(q), 117.6(q); δ_{Te}(81.2 MHz, $CDCl_3$) 731.2; *m/z* (CI^+) 411.91 ($[M]^+$, 85 %), 334.87 ($[M-Ph]^+$, 45 %).

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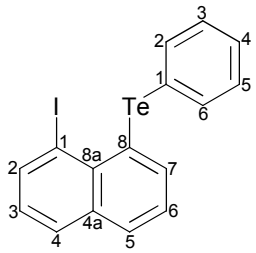
Compound 56 - 1-iodo-8-(phenyltellurenyl)naphthalene (from 14)



To a solution of 1,8-diiodonaphthalene (0.43 g, 1.1 mol) in diethyl ether (35 mL) at -78 °C was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.5 mL, 1.1 mol). The mixture was stirred at this temperature for 1 h after which a solution of diphenyl ditelluride (0.46 g, 1.1 mol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at -78 °C for a further h. The reaction mixture was washed with 0.1 M sodium hydroxide (2 x 45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (ethyl acetate/hexane 1:20). The brown oil obtained was recrystallised from dichloromethane/pentane (0.09 g, 18 %); (Found: C, 42.6; H, 2.6. Calc. for $C_{16}H_{11}ITe$: C, 42.0; H, 2.4 %); ν_{max}(KBr disc)/cm^{-1}: 3422br, 3051w, 2923s, 2851w, 1566w, 1529s, 1467w, 1430s, 1381w, 1344w, 1296w, 1256w, 1182w, 1130s, 1056w, 1013w, 996w, 942w, 905w, 823w, 802vs, 739vs, 691s, 663w, 546w, 520w, 457s; δ_H(270 MHz, $CDCl_3$) 8.11 (1 H, dd, *J* 1.2 and 7.4 Hz, nap 4-H), 7.79-7.73 (2 H, m, Te*Ph* 2,6-H), 7.68 (1 H, dd, *J* 1.0 and 8.1 Hz, nap 2-H), 7.53-7.46 (2 H, m, nap 5,7-H), 7.34-7.27 (1 H, m, Te*Ph* 4-H), 7.25-7.18 (2 H, m, Te*Ph* 3-5-H), 7.02-6.95 (1 H, m, nap 3-H), 6.93 (1 H, m, nap 6-H); δ_C(67.9 MHz, $CDCl_3$) 141.0(s), 140.5(s), 137.0(s), 130.5(s), 130.0(s), 128.8(s), 128.8(s), 126.7(s), 126.6(s); δ_{Te}(81.2 MHz, $CDCl_3$) 698.3; *m/z* (ES$^+$) 490.78 ([M+OMe]$^+$, 100 %).

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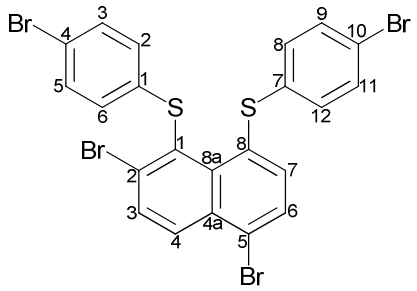
Compound 57 - 1,8-bis(4-bromophenylsulfanyl)-2,5-dibromonaphthalene



A solution of 1,8-diphenylsulfanylnaphthalene (0.22 g, 0.63 mmol) in dichloromethane (20 mL) was cooled to 0 °C and slowly treated with bromine (0.2 g, 0.06 mL, 1.3 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.3 g, 75 %); (Found: C, 41.2; H, 1.8. Calc. for $C_{22}H_{12}S_2Br_4$: C, 40.3; H, 1.8 %); ν_{max}(KBr disc)/cm^{-1}: 3401w, 3075w, 2920w, 2848w, 2362w, 1881w, 1570s, 1558s, 1470vs, 1400w, 1382s, 1320w, 1282s, 1268s, 1185s, 1083s, 1065s, 1018w, 1006vs, 805vs, 765w, 745s, 688w, 641w, 608w, 561w, 517w, 497w, 471s, 417w, 396w, 373w, 352w; δ_H(270 MHz, $CDCl_3$) 8.19 (1 H, d, *J* 9.1 Hz, nap 4-H), 7.80 (1 H, d, *J* 9.1 Hz, nap 3-H), 7.46 (1 H, d, *J* 8.2 Hz, nap 6-H), 7.33 (2 H, d, *J* 8.4 Hz, S*Ph*Br 3,5-H), 7.21 (2 H, d, *J* 8.6 Hz, S*Ph*Br 9,11-H), 7.05 (2 H, d, *J* 8.4 Hz, S*Ph*Br 2,6-H), 6.95 (1 H, d, *J* 8.2 Hz, nap 2-H), 6.74 (2 H, d, *J* 8.6 Hz, S*Ph*Br 8,12-H); δ_C(67.9 MHz, $CDCl_3$) 135.4(s), 132.9(s), 132.5(s), 132.1(s), 131.8(s), 130.7(s), 128.3(s); *m/z* (EI$^+$) 659.69 ([M]$^+$, 100 %, 347.80 ([M-2(ArBr)]$^+$, 98 %).

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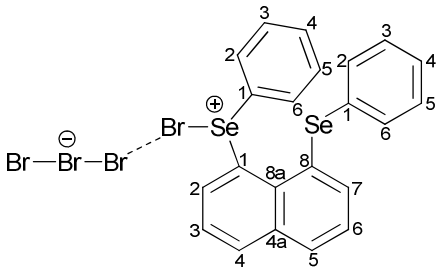
Compound 58



A solution of 1,8-bis(phenylselenyl)naphthalene (0.21 g, 0.47 mmol) in dichloromethane (20 mL) was cooled to 0 °C and slowly treated with bromine (0.15 g, 0.05 mL, 0.93 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.2 g, 57 %); (Found: C, 39.6; H, 1.3. Calc. for $C_{22}H_{16}Se_2Br_4$: C, 40.3; H, 2.5 %); ν_{max}(KBr disc)/cm^{-1}: 3396w, 3050w, 2920w, 2848w, 2356w, 2325w, 1589w, 1566w, 1486s, 1470s, 1438s, 1346s, 1261w, 1212w, 1194w, 1176w, 1083w, 1047s, 1016w, 992s, 825s, 812vs, 757w, 744vs, 730vs, 679vs, 659w, 533w, 484w, 463s, 457s, 442w, 378w; *m/z* (ES$^+$) 539.11 ([M-Br_3+Na]$^+$, 100 %).

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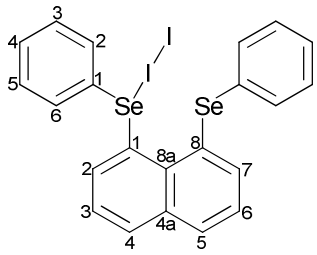
Compound 59



A solution of 1,8-bis(phenylselenyl)naphthalene (0.23 g, 0.53 mmol) in dichloromethane (20 mL) was cooled to 0 °C and slowly treated with iodine (0.13 g, 0.53 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.2 g, 66 %); (Found: C, 39.5; H, 2.2. Calc. for $C_{22}H_{16}Se_2I_2$: C, 38.2; H, 2.3 %); ν_{max}(KBr disc)/cm^{-1}: 3406w, 3050w, 2920w, 2848w, 2382w, 1690w, 1659w, 1573s, 1550w, 1473s, 1435s, 1331w, 1191w, 1137w, 1088w, 1060s, 1018s, 995w, 956w, 912w, 838w, 811vs, 750s, 737vs, 687vs, 662s, 613w, 471w, 453w; δ_H(270 MHz, $CDCl_3$) 7.82 (2 H, dd, *J* 1.0 and 8.2 Hz, nap 4,5-H), 7.72 (2 H, dd, *J* 1.2 and 7.4 Hz, nap 2,7-H), 7.47-7.37 (4 H, m, Se*Ph* 2,6-H), 7.36-7.20 (8 H, m, nap 3,6-H, Se*Ph* 3-5-H); δ_C(67.9 MHz, $CDCl_3$) 136.2(s), 133.1(s), 130.1(s), 129.7(s), 128.0(s), 126.4(s); δ_{Se}(51.5 MHz, $CDCl_3$) 436.9, 436.7; *m/z* (EI$^+$) 565.99 ([M-I]$^+$, 5 %), 440.12 ([M-I_2]$^+$, 100 %).

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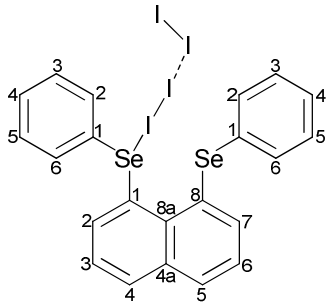
Compound 60



A solution of compound **57** (0.24 g, 0.35 mmol) in dichloromethane (20 mL) was cooled to 0 °C and slowly treated with iodine (0.09 g, 0.35 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product; δ_H(270 MHz, $CDCl_3$) 7.74 (2 H, dd, *J* 1.0 and 8.2 Hz, nap 4,5-H), 7.63 (2 H, dd, *J* 1.2 and 7.4 Hz, nap 2,7-H), 7.44-7.37 (4 H, m, Se*Ph* 2,6-H), 7.28-7.20 (8 H, m, nap 3,6-H, Se*Ph* 3-5-H); δ_{Se}(51.5 MHz, $CDCl_3$) 445.1, 444.3.

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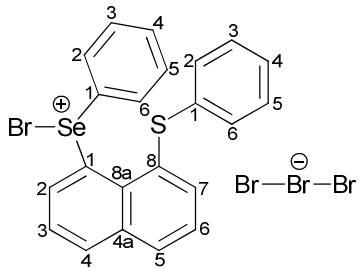
Compound 61



A solution of 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene (0.02 g, 0.051 mmol) in dichloromethane (5 mL) was cooled to 0 °C and slowly treated with bromine (0.02 g, 0.005 mL, 0.10 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.01 g, 33 %); ν_{max}(KBr disc)/cm^{-1}: 3447vs, 3418vs, 2924vs, 2848s, 2372w, 1985w, 1918w, 1773w, 1735s, 1718s, 1703s, 1686s, 1654s, 1636s, 1578s, 1543s, 1523w, 1459s, 1436s, 1383w, 1343w, 1261w, 1203w, 1177w, 1148w, 1087s, 1020w, 913w, 814vs, 751vs, 735vs, 692w, 602w, 541w, 456s, 398w; *m/z* (ES$^+$) 422.83 ([M-Br$_4$+OMe]$^+$, 97 %), 391.83 ([M-Br$_4$]$^+$, 100 %).

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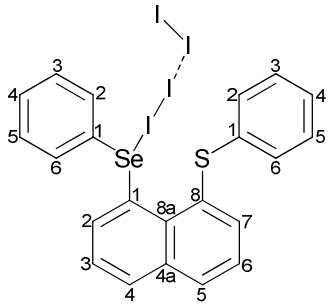
Compound 62



A solution of 1-(phenylselenyl)-8-(phenylsulfanyl)-naphthalene (0.066 g, 0.17 mmol) in dichloromethane (5 mL) was treated with iodine (0.043 g, 0.17 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.07 g, 46 %); (Found: C, 34.6; H, 2.1. Calc. for $(C_{22}H_{11}SSeI_2)I_2$: C, 34.2; H, 2.1 %); ν_{max}(KBr disc)/cm^{-1}: 3434brs, 3040w, 1940w, 1880w, 1803w, 1720w, 1655w, 1575s, 1541w, 1473s, 1435s, 1350w, 1324s, 1301w, 1196s, 1139w, 1059w, 1019s, 996s, 968w, 900w, 815vs, 783s, 754s, 737vs, 687vs, 615w, 540w, 520w, 483w, 455s; δ_H(270 MHz, $CDCl_3$) 7.98-7.89 (2 H, m, nap 2,4-H), 7.76 (1 H, dd, *J* 1.9 and 7.2 Hz, nap 5-H), 7.68-7.60 (2 H, m, Se*Ph* 2,6-H), 7.50 (1 H, t, *J* 7.7 Hz, nap 3-H), 7.43-7.33 (3 H, m, Se*Ph* 3-5-H), 7.28-7.15 (4 H, m, nap 6-H, S*Ph* 3-5-H), 7.15-7.06 (1 H, m, nap 7-H), 7.06-6.97 (2 H, m, S*Ph* 2,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.2(s), 135.9(s), 132.3(s), 131.7(s), 131.6(s), 130.1(s), 129.6(s), 129.2(s), 127.4(s), 126.5(s), 126.4(s), 126.0(s); δ_{Se}(51.5 MHz, $CDCl_3$) 476.9; *m/z* (ES$^+$) 391.89 ([M-I_2]$^+$, 100 %).

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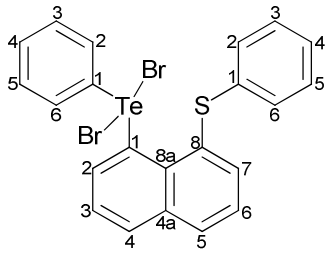
Compound 63



A solution of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene (0.032 g, 0.073 mmol) in dichloromethane (5 mL) was treated with bromine (0.023 g, 0.007 mL, 0.15 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.04 g, 80 %); (Found: C, 42.6; H, 2.7. Calc. for $C_{22}H_{16}TeSBr_2$: C, 44.0; H, 2.7 %); ν_{max}(KBr disc)/cm^{-1}: 3441br s, 3052w, 2953w, 1944w, 1869w, 1578s, 1475s, 1437s, 1325w, 1261w, 1200w, 1180w, 1072w, 1049w, 1046w, 1023w, 991s, 907w, 814vs, 757vs, 738s, 726vs, 680vs, 619w, 564w, 538w, 480w, 448s; δ_H(270 MHz, $CDCl_3$) 8.26-7.96 (6 H, m, nap 2,4,5,7-H, Te*Ph* 2,6-H), 7.70-7.40 (5 H, m, nap 3,6-H, Te*Ph* 3-5-H), 7.32-7.00 (5 H, m, S*Ph* 2-6-H); δ_C(67.9 MHz, $CDCl_3$) 139.7(s), 138.1(s), 134.3(s), 133.5(s), 132.5(s), 131.5(s), 130.3(s), 130.1(s), 129.6(s), 128.8(s), 127.4(s), 127.3(s); δ_{Te}(81.2 MHz, $CDCl_3$) 958.9; *m/z* (ES$^+$) 472.79 ([M-Br_2+OMe]$^+$, 100 %).

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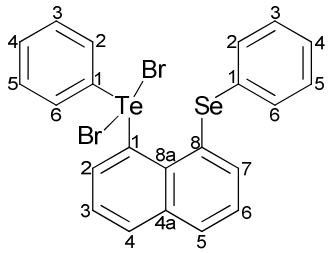
Compound 64



A solution of 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene (0.12 g, 0.24 mmol) in dichloromethane (5 mL) was treated with bromine (0.038 g, 0.01 mL, 0.24 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.1 g, 75 %); (Found: C, 40.7; H, 2.0 Calc. for $C_{22}H_{16}TeSeBr_2$: C, 40.9; H, 2.5 %); ν_{max}(KBr disc)/cm^{-1}: 3441brs, 3052s, 1944w, 1869w, 1738w, 1721w, 1651w, 1604w, 1572s, 1535w, 1475s, 1436s, 1378w, 1331s, 1209w, 1195w, 1177w, 1136w, 1081w, 1064w, 1049s, 1020w, 994s, 907w, 813vs, 755vs, 727vs, 680s, 613w, 555w, 526w, 446s, 314w δ_H(270 MHz, $CDCl_3$) 8.32 (2 H, d, *J* 7.0 Hz, Te*Ph* 2,6-H), 8.28 (1 H, d, *J* 7.2 Hz, nap 4-H), 8.21 (1 H, d, *J* 7.3 Hz, nap 5-H), 8.09 (1 H, d, *J* 7.6 Hz, nap 7-H), 8.05 (1 H, d, *J* 7.7 Hz, nap 2-H), 7.64-7.44 (5 H, m, nap 3,6-H, Te*Ph* 3-5-H), 7.36-7.29 (2 H, m, Se*Ph* 2,6-H), 7.24-7.17 (3 H, m, Se*Ph* 3-5-H); δ_C(67.9 MHz, $CDCl_3$) 141.1(s), 138.8(s), 136.7(s), 133.6(s), 132.3(s), 131.3(s), 130.7(s), 129.9(s), 129.6(s), 127.7(s), 127.2(s), 126.9(s); δ_{Se}(51.5 MHz, $CDCl_3$) 500.0; δ_{Te}(81.2 MHz, $CDCl_3$) 941.4; *m/z* (ES$^+$) 518.69 ([M-Br_2+OMe]$^+$, 100 %).

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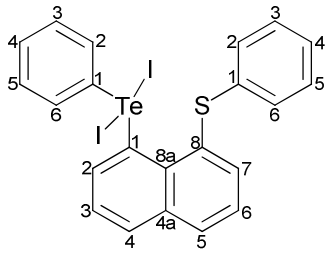
Compound 65



A solution of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene (0.032 g, 0.073 mmol) in dichloromethane (5 mL) was treated with iodine (0.018 g, 0.073 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.04 g, 80 %); ν_{max} (KBr disc)/cm^{-1}: 3448br s, 3045w, 2920w, 2371w, 2342w, 1720w, 1686w, 1652w, 1635w, 1578w, 1541w, 1524w, 1509w, 1475s, 1432s, 1381w, 1324s, 1261w, 1196w, 1156w, 1136w, 1073w, 1045w, 1022w, 991w, 928w, 905w, 813vs, 755vs, 734s, 723vs, 681vs, 617w, 563w, 535w, 478w, 446s, 350w; δ_H (270 MHz, $CDCl_3$) 8.37 (1 H, dd, *J* 0.6 and 7.5 Hz, nap 4-H), 8.22 (2 H, d, *J* 7.5 Hz, Te*Ph* 2,6-H), 8.17 (1 H, d, *J* 7.2 Hz, nap 2-H), 8.13-8.04 (2 H, m, nap 5,7-H), 7.66 (1 H, t, *J* 7.8 Hz, nap 6-H), 7.59-7.48 (2 H, m, nap 3-H, Te*Ph* 4-H), 7.43-7.34 (2 H, m, Te*Ph* 3,5-H), 7.23-7.15 (3 H, m, S*Ph* 3-5-H), 7.05-6.97 (2 H, m, S*Ph* 2,6-H); δ_C (67.9 MHz, $CDCl_3$) 140.1(s), 139.3(s), 138.2(s), 133.5(s), 132.6(s), 131.4(s), 130.1(s), 129.7(s), 128.1(s), 127.8(s), 127.6(s), 127.5(s); δ_{Te} (81.2 MHz, $CDCl_3$) 790.9; *m/z* (ES$^+$) 470.86 ([M-I_2+OMe]$^+$, 100 %).

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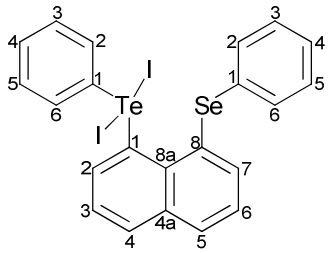
Compound 66



A solution of 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene (0.13 g, 0.26 mmol) in dichloromethane (5 mL) was treated with iodine (0.065 g, 0.26 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.2 g, 85 %); (Found: C, 36.0; H, 1.7. Calc. for $C_{22}H_{16}TeSeI_2$: C, 35.7; H, 2.2 %); ν_{max}(KBr disc)/cm^{-1}: 3441br s, 3046w, 2273w, 1572w, 1474s, 1434s, 1328s, 1189w, 1064w, 1046w, 1017w, 991w, 834w, 810vs, 752vs, 722vs, 680vs, 610w, 523w, 438s, 314w; δ_H(270 MHz, $CDCl_3$) 8.12 (1 H, d, *J* 7.0 Hz, nap 4-H), 8.04 (1 H, d, *J* 8.1 Hz, nap 2-H), 8.00 (2 H, d, *J* 7.5 Hz, Te*Ph* 2,6-H), 7.68 (1 H, d, *J* 7.3 Hz, nap 5-H), 7.58 (2 H, d, *J* 7.4 Hz, nap 3,7-H), 7.49-43 (1 H, m, Te*Ph* 4-H), 7.42-7.32 (4 H, m, Te*Ph* 3,5-H, Se*Ph* 2,6-H), 7.22-7.16 (4 H, m, nap 6-H, Se*Ph* 3-5-H); δ_C(67.9 MHz, $CDCl_3$) 139.2(s), 135.7(s), 135.6(s), 133.4(s), 132.5(s), 131.6(s), 130.5(s), 129.5(s), 129.3(s), 127.7(s), 127.5(s), 126.1(s); δ_{Se}(51.5 MHz, $CDCl_3$) 428.8; δ_{Te}(81.2 MHz, $CDCl_3$) 747.0; *m/z* (ES$^+$) 518.66 ([M-I_2+OMe]$^+$, 100 %).

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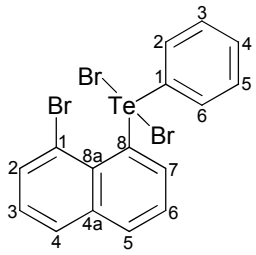
Compound 67



A solution of 1-bromo-8-(phenyltellurenyl)naphthalene (0.10 g, 0.25 mmol) in dichloromethane (5 mL) was treated with a 0.1 M solution of bromine in dichloromethane (0.25 mmol, 2.5 mL). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.1 g, 91 %); (Found: C, 33.9; H, 2.2. Calc. for $C_{16}H_{11}TeBr_3$: C, 33.7; H, 2.0 %); ν_{max}(KBr disc)/cm^{-1}: 3424brs, 3051w, 2920w, 1655w, 1589w, 1569w, 1535w, 1470s, 1432s, 1330s, 1260s, 1186s, 1133w, 1048s, 993w, 945w, 917w, 897w, 806vs, 735vs, 681s, 453s; δ_H(270 MHz, $CDCl_3$) 8.45 (2 H, d, *J* 6.6 Hz, Te*Ph* 2,6-H), 8.08 (1 H, d, *J* 6.7 Hz, nap 5-H), 8.01 (2 H, d, *J* 7.5 Hz, nap 4,7-H), 7.91 (1 H, d, *J* 7.9 Hz, nap 2-H), 7.70-7.51 (3 H, m, Te*Ph* 3-5-H), 7.51-7.36 (2 H, m, nap 3,6-H); δ_C(67.9 MHz, $CDCl_3$) 137.2(s), 134.3(s), 133.5(s), 132.0(s), 130.2(s), 127.4(s), 126.9(s); δ_{Te}(81.2 MHz, $CDCl_3$) 942.8; *m/z* (ES$^+$) 442.76 ([M-Br_2+OMe]$^+$, 100 %).

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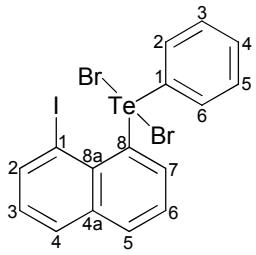
Compound 68



A solution of 1-iodo-8-(phenyltellurenyl)naphthalene (0.09 g, 0.20 mmol) in dichloromethane (5 mL) was cooled to 0 °C and slowly treated with a 0.1 M solution of bromine in dichloromethane (2.0 mL, 0.20 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.1 g, 86 %); ν_{max}(KBr disc)/cm^{-1}: 3449br s, 3045w, 2954s, 2924s, 2851w, 1561w, 1532w, 1467w, 1432s, 1324w, 1260s, 1182w, 1094w, 1019w, 991w, 937w, 902w, 871w, 805vs, 766w, 746w, 731vs, 697w, 680s, 643w, 560w, 520w, 501w, 452s, 387w; δ_H(270 MHz, $CDCl_3$) 8.41-8.29 (3 H, m, nap 4-H, Te*Ph* 2,6-H), 8.12 (1 H, d, *J* 7.2 Hz, nap 5-H), 7.96 (1 H, d, *J* 8.0 Hz, nap 7-H), 7.92 (1 H, d, *J* 7.4 Hz, nap 2-H), 7.63-7.46 (3 H, m, Te*Ph* 3-5-H), 7.38 (1 H, t, *J* 7.7 Hz, nap 6-H), 7.28 (1 H, t, *J* 7.7 Hz, nap 3-H); δ_C(67.9 MHz, $CDCl_3$) 142.2(s), 138.6(s), 137.2(s), 133.9(s), 131.8(s), 130.9(s), 130.1(s), 127.9(s), 126.6(s); δ_{Te}(81.2 MHz, $CDCl_3$) 903.0; *m/z* (ES$^+$) 488.71 ([M-Br_2+OMe]$^+$, 100 %).

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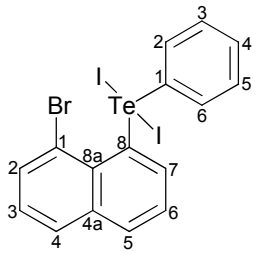
Compound 69



A solution of 1-bromo-8-(phenyltellurenyl)naphthalene (0.039 g, 0.095 mmol) in dichloromethane (5 mL) was treated with iodine (0.0024 g, 0.095 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.03 g, 54 %); ν_{max}(KBr disc)/cm^{-1}: 3433br s, 3040w, 2925w, 2371w, 1652w, 1638w, 1561w, 1532w, 1467s, 1432s, 1381w, 1327w, 1259w, 1207w, 1184w, 1130w, 1045s, 991w, 942w, 911w, 825w, 805vs, 746s, 729s, 680s, 603w, 526w, 446s, 432w; δ_H(270 MHz, $CDCl_3$) 8.48 (2 H, dd, *J* 1.1 and 8.5 Hz, Te*Ph* 2,6-H), 8.15 (1 H, dd, *J* 1.1 and 7.7 Hz, nap 4-H), 8.07 (2 H, m, nap 2,5-H), 7.92 (1 H, dd, *J* 0.8 and 8.3 Hz, nap 7-H), 7.67-7.59 (1 H, m, Te*Ph* 4-H), 7.53-7.42 (3 H, m, nap 6-H, Te*Ph* 3,5-H), 7.40 (1 H, t, *J* 7.8 Hz, nap 3-H); δ_C(67.9 MHz, $CDCl_3$) 139.7(s), 138.5(s), 134.2(s), 133.3(s), 131.8(s), 130.3(s), 130.1(s), 127.5(s), 127.1(s); δ_{Te}(81.2 MHz, $CDCl_3$) 887.5; *m/z* (ES$^+$) 442.76 ([M-I_2+OMe]$^+$, 100 %).

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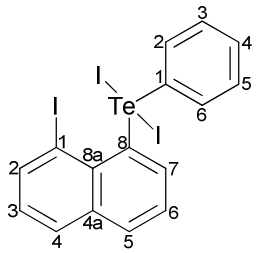
Compound 70



A solution of 1-iodo-8-(phenyltellurenyl)naphthalene (0.11 g, 0.25 mmol) in dichloromethane (5 mL) was treated with iodine (0.063 g, 0.25 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.1 g, 81 %); (Found: C, 27.5; H, 1.3. Calc. for $C_{16}H_{11}TeI_3$: C, 26.9; H, 1.6 %); ν_{max}(KBr disc)/cm^{-1}: 3430br s, 2959s, 2924vs, 2853s, 1735w, 1654w, 1529w, 1465w, 1430w, 1375w, 1363w, 1317w, 1261vs, 1177w, 1090vs, 1020vs, 866w, 802vs, 747w, 727w, 680w, 663w, 587w, 561w, 535w, 520w, 448w, 389w; δ_H(270 MHz, $CDCl_3$) 8.38-8.29 (2 H, m, Te*Ph* 2,6-H), 8.27 (1 H, dd, *J* 1.1 and 7.4 Hz, nap 4-H), 8.15 (1 H, dd, *J* 1.0 and 7.6 Hz, nap 5-H), 7.93 (1 H, d, *J* 8.1 Hz, nap 7-H), 7.86 (1 H, dd, *J* 1.0 and 8.2 Hz, nap 2-H), 7.57-7.49 (1 H, m, Te*Ph* 4-H), 7.44-7.34 (2 H, m, Te*Ph* 3,5-H), 7.30 (1 H, t, *J* 7.8 Hz, nap 6-H), 7.23 (1 H, t, *J* 7.8 Hz, nap 3-H); δ_C(67.9 MHz, $CDCl_3$) 142.1(s), 140.0(s), 139.4(s), 133.7(s), 131.6(s), 130.7(s), 130.2(s), 128.1(s), 126.9(s); δ_{Te}(81.2 MHz, $CDCl_3$) 848.0; *m/z* (ES$^+$) 490.68 ([M-I_2+OMe]$^+$, 100 %).

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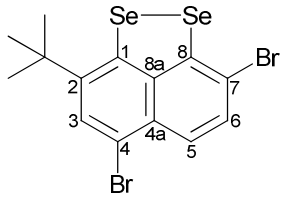
Compound 73 - 4,7-dibromo-2-mono-*tert*-butylnaphtho[1,8-*c,d*][1,2]diselenole



A solution of 2-mono-*tert*-butylnaphtho[1,8-*c,d*][1,2]diselenole (0.11 g, 0.33 mmol) in dichloromethane (10 mL) was cooled to 0 °C and slowly treated with bromine (0.11 g, 0.034 mL, 0.66 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.1 g, 74 %); ν_{max}(KBr disc)/cm^{-1}: 3424br s, 3069w, 2955s, 2854w, 1584w, 1568w, 1514w, 1482s, 1466vs, 1392s, 1361s, 1282s, 1218s, 1186w, 1147s, 1116vs, 996vs, 913s, 881s, 860w, 820s, 799s, 741s, 663w, 558w, 509w, 485w, 468w, 381w; δ_H(270 MHz, $CDCl_3$) 7.77-7.64 (2 H, m, 3,5-H), 7.53-7.40 (1 H, m, 6-H), 1.52 (9 H, s, -C(C*H*$_3$)$_3$; δ_C(67.9 MHz, $CDCl_3$) 130.6(s), 130.1(s), 124.9(s), 28.7(s); δ_{Se}(51.5 MHz, $CDCl_3$) 453.8, 374.4; *m/z* (EI$^+$) 497.98 (M$^+$, 100 %).

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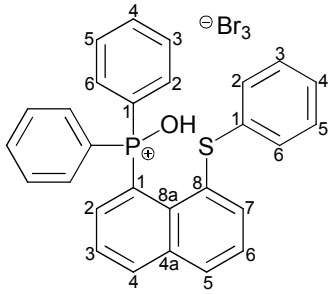
Compound 74 – Hydroxydiphenyl[(8-phenylsulfanyl)naphthalene-1-yl]phosphonium tribromide



A solution of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (0.30 g, 0.71 mmol) in dichloromethane (15 mL) was treated with bromine (0.45 g, 0.15 mL, 2.8 mmol). An analytically pure sample was obtained by crystallisation from diffusion of dichloromethane into a pentane solution of the product (0.2 g, 32 %); ν_{max}(KBr disc)/cm^{-1}: 3430brs, 3069w, 3052w, 2691w, 2197w, 1968w, 1898w, 1814w, 1738w, 1636w, 1578s, 1543w, 1477vs, 1435vs, 1320s, 1264w, 1197s, 1151s, 1115vs, 1064w, 1023w, 988w, 921w, 887s, 825s, 765vs, 738vs, 718vs, 687vs, 625w, 613w, 581w, 561vs, 535vs, 503s, 468s, 413s, 346vs; δ_H(270 MHz, $CDCl_3$) 8.41 (1 H, d, *J* 8.0 Hz, nap 4-H), 8.25 (1 H, d, *J* 8.0 Hz, nap 5-H), 7.87 (2 H, d, *J* 6.8 Hz, nap 2,7-H), 7.69 (1 H, t, *J* 7.7 Hz, nap 6-H), 7.66-7.59 (1 H, m, nap 3-H), 7.57-7.42 (6 H, m, 2 x P*Ph*$_2$ 3-5-H), 7.41-7.30 (4 H, m, 2 x P*Ph*$_2$ 2,6-H), 6.96 (1 H, t, *J* 7.3 Hz, S*Ph* 4-H), 6.92-6.83 (2 H, m, S*Ph* 3,5-H), 6.15 (2 H, d, *J* 7.5 Hz, S*Ph* 2,6-H), 2.99 (1 H, br s, -O*H*); δ_C(67.9 MHz, $CDCl_3$) 140.6(s), 137.3(s), 132.8(s), 132.6(s), 131.5(d, *J* 10.4 Hz), 129.2(d, *J* 13.5 Hz), 128.7(s), 128.2(s), 128.1(s), 126.2(s), 125.7(s), 125.5(s); δ_P(109 MHZ, $CDCl_3$) 52.48; *m/z* (ES$^+$) 458.85 ([M-Br$_3$+Na]$^+$, 100 %).

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Appendix

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II. **Crystal structure experimental**

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IV. **Crystal structure and experimental codes for all compounds**

I - Crystal data and structure refinement

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Appendix 1 – FKDW15e – FRKI9

Compound **1** - 8-bromonaphthalen-1-amine

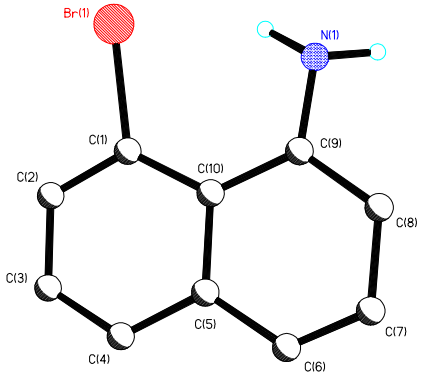

Table 1 Crystal data and structure refinement

Empirical Formula	$C_{10}H_8NBr$
Formula Weight	222.08
Temperature (°C)	-148(1)
Crystal Colour, Habit	red, prism
Crystal Dimensions (mm^3)	0.35 X 0.13 X 0.09
Crystal System	monoclinic
Lattice Parameters	a = 13.6692(14) Å
	b = 4.1579(4) Å
	c = 15.8256(16) Å
	β = 109.941(3)°
Volume ($Å^3$)	V = 845.52(15)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	1.744
F000	440
μ(MoKα) (cm^{-1})	48.111
No. of Reflections Measured	6823
Rint	0.061
Min and Max Transmissions	0.381 - 0.649
Independent Reflections	1527
Observed Reflection (No. Variables)	1281(110)
Reflection/Parameter Ratio	13.88
Residuals: R_1 (I>2.00σ(I))	0.0512
Residuals: R (All reflections)	0.0644
Residuals: wR_2 (All reflections)	0.1164
Goodness of Fit Indicator	1.104
Flack Parameter	-
Maximum peak in Final Diff. Map	1.76 e-/$Å^3$
Minimum peak in Final Diff. Map	-0.39 e-/$Å^3$

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Appendix 2 – FKDW2 – FRKI5

Compound **2** - 1-bromo-8-(ethylsulfanyl)naphthalene

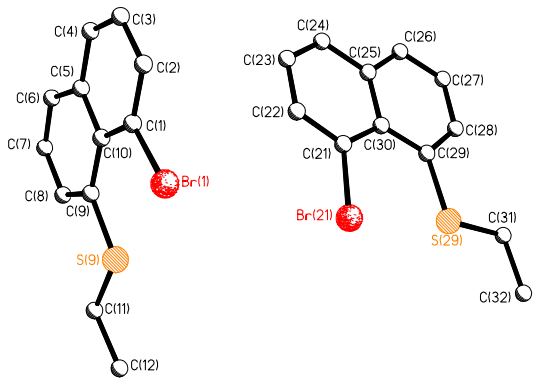

Table 2 Crystal data and structure refinement

Empirical Formula	$C_{12}H_{11}BrS$
Formula Weight	267.18
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, block
Crystal Dimensions (mm^3)	0.25 X 0.20 X 0.20
Crystal System	monoclinic
Lattice Parameters	a = 11.632(4) Å
	b = 12.260(4) Å
	c = 14.748(4) Å
	β = 91.692(9)°
Volume ($Å^3$)	V = 2102.2(11)
Space Group	$P2_1/c$
Z value	8
Dcalc (g/cm^3)	1.688
F000	1072
μ(MoKα) (mm^{-1})	4.063
No. of Reflections Measured	6713
Rint	0.0793
Min and Max Transmissions	0.9305 - 1.000
Independent Reflections	3543
Observed Reflection (No. Variables)	2316(254)
Reflection/Parameter Ratio	13.95
Residuals: R_1 (I>2.00σ(I))	0.0532
Residuals: R (All reflections)	0.1023
Residuals: wR_2 (All reflections)	0.1057
Goodness of Fit Indicator	0.992
Flack Parameter	-
Maximum peak in Final Diff. Map	0.462 e-/$Å^3$
Minimum peak in Final Diff. Map	-0.472 e-/$Å^3$

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Appendix 3 – FKDW3 – FRKI15

Compound **3** - (8-ethylsulfanylnaphth-1-yl)diphenylphosphine

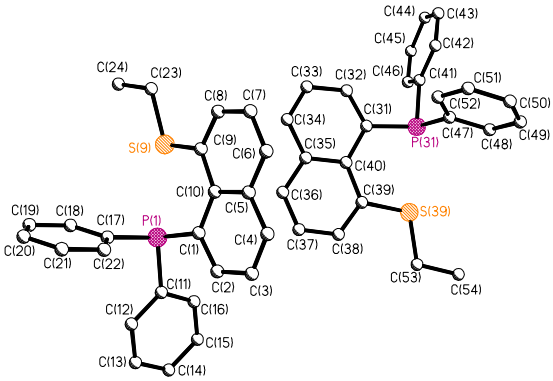

Table 3 Crystal data and structure refinement

Empirical Formula		$C_{24}H_{21}PS$
Formula Weight		372.44
Temperature (°C)		-180(1)
Crystal Colour, Habit		colourless, prism
Crystal Dimensions (mm^3)		0.06 X 0.06 X 0.03
Crystal System		triclinic
Lattice Parameters		a = 8.6734(17) Å
		b = 13.165(3) Å
	α = 102.307(6)°	c = 17.525(4) Å
	γ = 93.395(4)°	β = 96.444(6)°
Volume (Å^3)		V = 1935.7(7)
Space Group		P-1
Z value		4
Dcalc (g/cm^3)		1.278
F000		784
μ(MoKα) (mm^{-1})		0.254
No. of Reflections Measured		12531
Rint		0.0595
Min and Max Transmissions		0.5879 – 1.000
Independent Reflections		6626
Observed Reflection (No. Variables)		3809(470)
Reflection/Parameter Ratio		14.10
Residuals: R_1 (I>2.00σ(I))		0.0614
Residuals: R (All reflections)		0.1131
Residuals: wR_2 (All reflections)		0.1245
Goodness of Fit Indicator		0.952
Flack Parameter		-
Maximum peak in Final Diff. Map		0.382 e-/Å^3
Minimum peak in Final Diff. Map		-0.332 e-/Å^3

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Appendix 4 – FKDW123-1 – FRKII123

Compound **15** - 1-iodo-8-(ethylsulfanyl)naphthalene

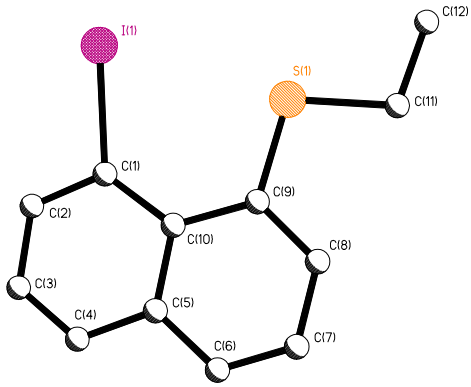

Table 4 Crystal data and structure refinement

Empirical Formula	$C_{12}H_{11}IS$
Formula Weight	314.18
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.21 X 0.09 X 0.06
Crystal System	orthorhombic
Lattice Parameters	a = 7.768(2) Å
	b = 20.971(6) Å
	c = 13.735(4) Å
	–
Volume ($Å^3$)	V = 2237.5(12)
Space Group	Pbca
Z value	8
Dcalc (g/cm^3)	1.865
F000	1216
μ(MoKα) (cm^{-1})	30.068
No. of Reflections Measured	6575
Rint	0.033
Min and Max Transmissions	0.504 - 0.835
Independent Reflections	1953
Observed Reflection (No. Variables)	1824(128)
Reflection/Parameter Ratio	15.26
Residuals: R_1 (I>2.00σ(I))	0.0435
Residuals: R (All reflections)	0.0560
Residuals: wR_2 (All reflections)	0.2054
Goodness of Fit Indicator	1.285
Flack Parameter	-
Maximum peak in Final Diff. Map	2.18 e-/$Å^3$
Minimum peak in Final Diff. Map	-2.50 e-/$Å^3$

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Appendix 5 – FKDW15(ox)-8 – FRKI15ox

Compound **16** - (8-ethylsulfanylnaphth-1-yl)diphenylphosphine oxide

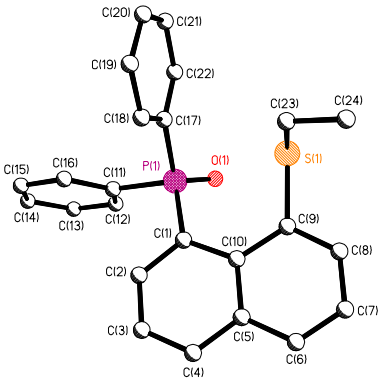

Table 5 Crystal data and structure refinement

Empirical Formula	$C_{24}H_{21}OPS$
Formula Weight	388.46
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.21 X 0.21 X 0.03
Crystal System	monoclinic
Lattice Parameters	a = 12.851(3) Å
	b = 10.384(3) Å
	c = 29.473(8) Å
	β = 91.689(8)°
Volume ($Å^3$)	3931.5(18)
Space Group	C2/c
Z value	8
Dcalc (g/cm^3)	1.312
F000	1632
μ(MoKα) (cm^{-1})	2.57
No. of Reflections Measured	10443
Rint	0.044
Min and Max Transmissions	0.946 - 0.992
Independent Reflections	3418
Observed Reflection (No. Variables)	3044 (246)
Reflection/Parameter Ratio	13.89
Residuals: R_1 (I>2.00σ(I))	0.0677
Residuals: R (All reflections)	0.0844
Residuals: wR_2 (All reflections)	0.2324
Goodness of Fit Indicator	1.183
Flack Parameter	-
Maximum peak in Final Diff. Map	0.75 e /$Å^3$
Minimum peak in Final Diff. Map	-0.84 e /$Å^3$

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Appendix 6 – FKDW147A-1 – FRKII147A

Compound **17** - (8-ethylsulfanylnaphth-1-yl)diphenylphosphine sulfide

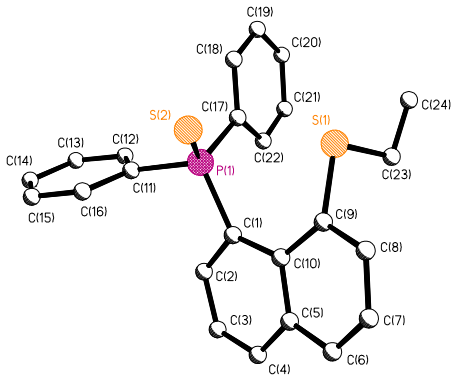

Table 6 Crystal data and structure refinement

Empirical Formula	$C_{24}H_{21}PS_2$
Formula Weight	404.52
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.21 X 0.18 X 0.15
Crystal System	monoclinic
Lattice Parameters	a = 11.652(2) Å
	b = 9.6047(18) Å
	c = 18.293(3) Å
	β = 92.268(5)°
Volume ($Å^3$)	V = 2045.6(6)
Space Group	$P2_1/c$
Z value	4
Dcalc (g/cm^3)	1.313
F000	848
μ(MoKα) (cm^{-1})	3.446
No. of Reflections Measured	12018
Rint	0.06
Min and Max Transmissions	0.928 - 0.950
Independent Reflections	3571
Observed Reflection (No. Variables)	3334 (246)
Reflection/Parameter Ratio	14.52
Residuals: R_1 (I>2.00σ(I))	0.0658
Residuals: R (All reflections)	0.0735
Residuals: wR_2 (All reflections)	0.1767
Goodness of Fit Indicator	1.274
Flack Parameter	-
Maximum peak in Final Diff. Map	0.46 e /$Å^3$
Minimum peak in Final Diff. Map	-0.42 e /$Å^3$

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Appendix 7 – FKDW150B-6 – FRKII150B

Compound **18** - (8-ethylsulfanylnaphth-1-yl)diphenylphosphine selenide

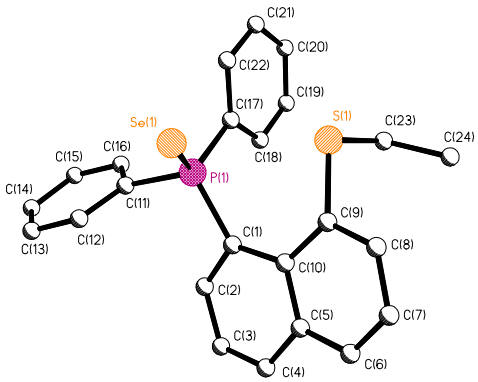

Table 7 Crystal data and structure refinement

Empirical Formula	$C_{24}H_{21}PSSe$
Formula Weight	451.42
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.12 X 0.09 X 0.06
Crystal System	monoclinic
Lattice Parameters	a = 13.622(3) Å
	b = 9.3562(18) Å
	c = 17.224(4) Å
	β = 112.028(4)°
Volume ($Å^3$)	V = 2034.9(8)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	1.473
F000	920
μ(MoKα) (cm^{-1})	20.33
No. of Reflections Measured	11654
Rint	0.075
Min and Max Transmissions	0.779 - 0.885
Independent Reflections	3570
Observed Reflection (No. Variables)	3162 (246)
Reflection/Parameter Ratio	14.51
Residuals: R_1 (I>2.00σ(I))	0.069
Residuals: R (All reflections)	0.0808
Residuals: wR_2 (All reflections)	0.1172
Goodness of Fit Indicator	1.209
Flack Parameter	-
Maximum peak in Final Diff. Map	0.49 e /$Å^3$
Minimum peak in Final Diff. Map	-0.51 e /$Å^3$

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Appendix 8 – FKDW4MER – FRKI20

Compound **19** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine

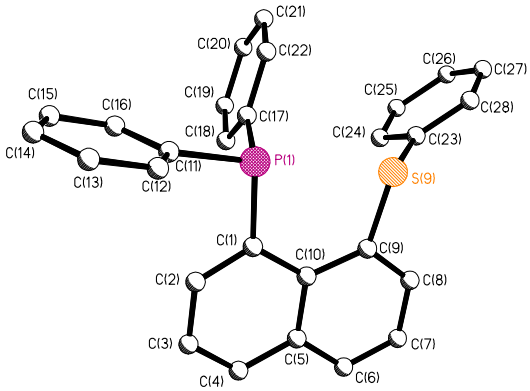

Table 8 Crystal data and structure refinement

Empirical Formula	$C_{28}H_{21}PS$
Formula Weight	420.48
Temperature (°C)	-180(1)
Crystal Colour, Habit	colourless, platelet
Crystal Dimensions (mm^3)	0.10 X 0.10 X 0.10
Crystal System	monoclinic
Lattice Parameters	a = 11.1461(12) Å
	b = 8.8914(10) Å
	c = 21.587(2) Å
	β = 90.837(4)°
Volume ($Å^3$)	V = 2139.1(4)
Space Group	$P2_1/c$
Z value	4
Dcalc (g/cm^3)	1.306
F000	880
μ(MoKα) (mm^{-1})	0.239
No. of Reflections Measured	13424
Rint	0.0325
Min and Max Transmissions	0.8678 – 1.000
Independent Reflections	3774
Observed Reflection (No. Variables)	3348(272)
Reflection/Parameter Ratio	13.88
Residuals: R_1 (I>2.00σ(I))	0.0408
Residuals: R (All reflections)	0.0462
Residuals: wR_2 (All reflections)	0.1049
Goodness of Fit Indicator	1.042
Flack Parameter	-
Maximum peak in Final Diff. Map	0.906 e-/$Å^3$
Minimum peak in Final Diff. Map	-0.314 e-/$Å^3$

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Appendix 9 – FERG56 – FRKI45

Compound **20** - 1-iodo-8-(phenylsulfanyl)naphthalene

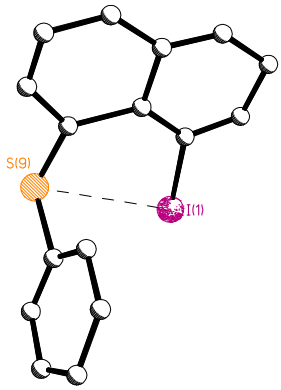

Table 9 Crystal data and structure refinement

Empirical Formula	$C_{16}H_{11}IS$
Formula Weight	362.21
Temperature (°C)	20(1)
Crystal Colour, Habit	colourless, platelet
Crystal Dimensions (mm^3)	0.10 X 0.10 X 0.10
Crystal System	orthorhombic
Lattice Parameters	a = 10.204(4) Å b = 7.992(3) Å c = 32.888(10) Å –
Volume ($Å^3$)	V = 2682.0(17)
Space Group	Pbca
Z value	8
Dcalc (g/cm^3)	1.794
F000	1408
μ(MoKα) (mm^{-1})	2.521
No. of Reflections Measured	14054
Rint	0.2862
Min and Max Transmissions	0.7461 – 1.000
Independent Reflections	2440
Observed Reflection (No. Variables)	1526(165)
Reflection/Parameter Ratio	14.79
Residuals: R_1 (I>2.00σ(I))	0.0999
Residuals: R (All reflections)	0.1347
Residuals: wR_2 (All reflections)	0.2692
Goodness of Fit Indicator	0.975
Flack Parameter	-
Maximum peak in Final Diff. Map	2.198 e-/$Å^3$
Minimum peak in Final Diff. Map	-1.651 e-/$Å^3$

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Appendix 10 – FKDW20(ox)-1 – FRKI20ox

Compound **21** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine oxide

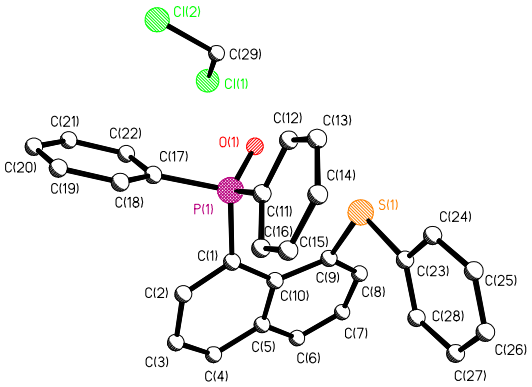

Table 10 Crystal data and structure refinement

Empirical Formula		$C_{29}H_{23}OPSCl_2$
Formula Weight		521.44
Temperature (°C)		-148(1)
Crystal Colour, Habit		colourless, prism
Crystal Dimensions (mm^3)		0.09 X 0.09 X 0.09
Crystal System		triclinic
Lattice Parameters		a = 9.2265(17) Å
		b = 11.6406(16) Å
	α = 102.74(2)°	c = 13.239(3) Å
	γ = 112.23(2)°	β = 98.54(2)°
Volume ($Å^3$)		V = 1240.7(5)
Space Group		P-1
Z value		2
Dcalc (g/cm^3)		1.396
F000		540
μ(MoKα) (cm^{-1})		4.313
No. of Reflections Measured		12814
Rint		0.041
Min and Max Transmissions		0.961 - 0.962
Independent Reflections		4275
Observed Reflection (No. Variables)		3896 (308)
Reflection/Parameter Ratio		13.88
Residuals: R_1 (I>2.00σ(I))		0.0508
Residuals: R (All reflections)		0.061
Residuals: wR_2 (All reflections)		0.1469
Goodness of Fit Indicator		1.203
Flack Parameter		-
Maximum peak in Final Diff. Map		0.51 e-/$Å^3$
Minimum peak in Final Diff. Map		-0.51 e-/$Å^3$

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Appendix 11 – FKDWI22-1-9 – FRKII111C

Compound **22** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine sulfide

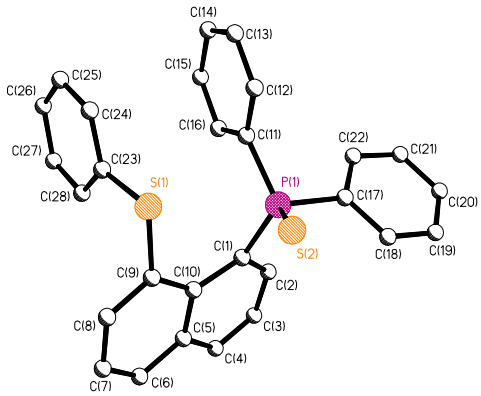

Table 11 Crystal data and structure

Empirical Formula	$C_{28}H_{21}S_2P$
Formula Weight	452.57
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, platelet
Crystal Dimensions (mm^3)	0.18 X 0.12 X 0.06
Crystal System	monoclinic
Lattice Parameters	a = 9.3241(13) Å
	b = 17.769(2) Å
	c = 13.7930(19) Å
	β = 97.328(3)°
Volume ($Å^3$)	V = 2266.6(5)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	1.326
F000	944
μ(MoKα) (cm^{-1})	3.191
No. of Reflections Measured	12358
Rint	0.054
Min and Max Transmissions	0.943 - 0.981
Independent Reflections	3948
Observed Reflection (No. Variables)	3521(281)
Reflection/Parameter Ratio	14.05
Residuals: R_1 (I>2.00σ(I))	0.0582
Residuals: R (All reflections)	0.0694
Residuals: wR_2 (All reflections)	0.123
Goodness of Fit Indicator	1.201
Flack Parameter	-
Maximum peak in Final Diff. Map	0.29 e /$Å^3$
Minimum peak in Final Diff. Map	-0.36 e /$Å^3$

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Appendix 12 – FKDW111D-2 – FRKII111D

Compound **23** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine selenide

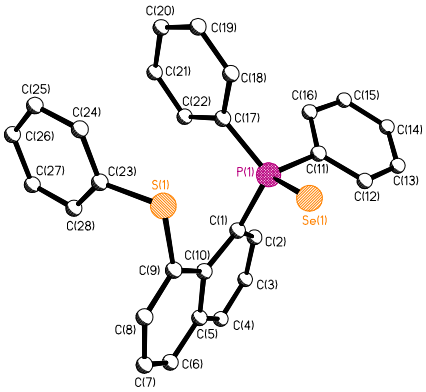

Table 12 Crystal data and structure refinement

Empirical Formula	$C_{28}H_{21}PSSe$
Formula Weight	499.47
Temperature (°C)	-148(1)
Crystal Colour, Habit	yellow, block
Crystal Dimensions (mm^3)	0.15 X 0.12 X 0.12
Crystal System	monoclinic
Lattice Parameters	a = 9.432(4) Å
	b = 17.849(6) Å
	c = 13.701(4) Å
	β = 96.511(7)°
Volume ($Å^3$)	V = 2291.8(13)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	1.447
F000	1016
μ(MoKα) (cm^{-1})	18.131
No. of Reflections Measured	12375
Rint	0.04
Min and Max Transmissions	0.757 - 0.804
Independent Reflections	4012
Observed Reflection (No. Variables)	3694(281)
Reflection/Parameter Ratio	14.28
Residuals: R_1 (I>2.00σ(I))	0.0427
Residuals: R (All reflections)	0.0504
Residuals: wR_2 (All reflections)	0.1537
Goodness of Fit Indicator	1.231
Flack Parameter	-
Maximum peak in Final Diff. Map	0.56 e /$Å^3$
Minimum peak in Final Diff. Map	-0.53 e /$Å^3$

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Appendix 13 – FKDW54-1 – FRKI54

Compound **24** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dichloride

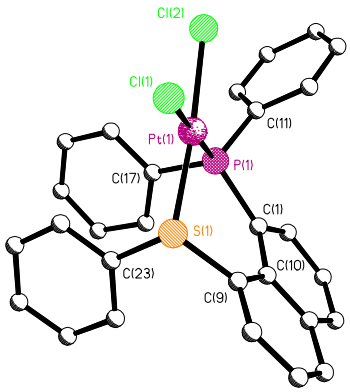

Table 13 Crystal data and structure refinement

Empirical Formula	$C_{29}H_{22}Cl_5PPtS$
Formula Weight	805.88
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.10 X 0.05 X 0.03
Crystal System	monoclinic
Lattice Parameters	a = 13.524(6) Å
	b = 15.311(7) Å
	c = 14.029(6) Å
	β = 102.103(9)°
Volume ($Å^3$)	V = 2840(2)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	1.884
F000	1560
μ(MoKα) (cm^{-1})	55.392
No. of Reflections Measured	22810
Rint	0.087
Min and Max Transmissions	0.570 - 0.847
Independent Reflections	4928
Observed Reflection (No. Variables)	4650(335)
Reflection/Parameter Ratio	14.71
Residuals: R_1 (I>2.00σ(I))	0.0987
Residuals: R (All reflections)	0.1044
Residuals: wR_2 (All reflections)	0.2505
Goodness of Fit Indicator	1.169
Flack Parameter	-
Maximum peak in Final Diff. Map	5.58 e /$Å^3$
Minimum peak in Final Diff. Map	-2.23 e /$Å^3$

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Appendix 14 – FKDW20-10-8a – FRKI20-10

Compound **25** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dibromide

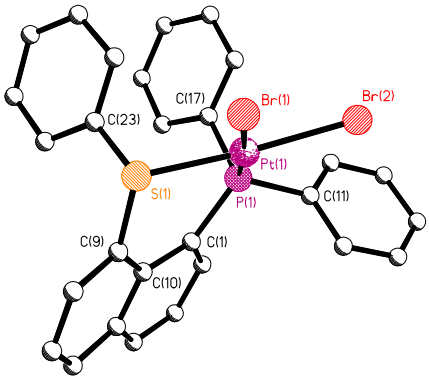

Table 14 Crystal data and structure refinement

Empirical Formula	$C_{29}H_{23}Br_2PPtSCl_2$
Formula Weight	860.34
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, platelet
Crystal Dimensions (mm^3)	0.12 X 0.12 X 0.03
Crystal System	monoclinic
Lattice Parameters	a = 12.8977(13) Å
	b = 15.5520(14) Å
	c = 14.5122(15) Å
	β = 103.571(3)°
Volume ($Å^3$)	V = 2829.7(5)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	2.019
F000	1640
μ(MoKα) (cm^{-1})	81.09
No. of Reflections Measured	15702
Rint	0.069
Min and Max Transmissions	0.493 - 0.784
Independent Reflections	5127
Observed Reflection (No. Variables)	4639(326)
Reflection/Parameter Ratio	15.73
Residuals: R_1 (I>2.00σ(I))	0.0677
Residuals: R (All reflections)	0.0774
Residuals: wR_2 (All reflections)	0.1637
Goodness of Fit Indicator	1.255
Flack Parameter	-
Maximum peak in Final Diff. Map	1.10 e /$Å^3$
Minimum peak in Final Diff. Map	-1.61 e /$Å^3$

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Appendix 15 – FKDW20-7-2 – FRKI20-7

Compound **26** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum diiodide

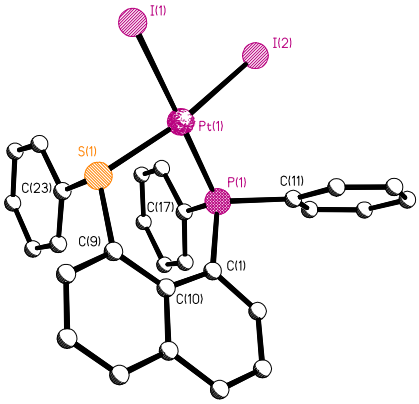

Table 15 Crystal data and structure refinement

Empirical Formula	$C_{29}H_{23}I_2PPtSCl_2$
Formula Weight	954.34
Temperature (°C)	-148(1)
Crystal Colour, Habit	yellow, prism
Crystal Dimensions (mm^3)	0.21 X 0.21 X 0.03
Crystal System	monoclinic
Lattice Parameters	a = 15.053(4) Å
	b = 11.559(3) Å
	c = 17.567(4) Å
	β = 108.385(5)°
Volume ($Å^3$)	V = 2900.7(12)
Space Group	$P2_1/c$
Z value	4
Dcalc (g/cm^3)	2.185
F000	1784
μ(MoKα) (cm^{-1})	72.769
No. of Reflections Measured	18781
Rint	0.042
Min and Max Transmissions	0.475 - 0.804
Independent Reflections	5877
Observed Reflection (No. Variables)	5732(326)
Reflection/Parameter Ratio	18.03
Residuals: R_1 (I>2.00σ(I))	0.0394
Residuals: R (All reflections)	0.041
Residuals: wR_2 (All reflections)	0.1146
Goodness of Fit Indicator	1.223
Flack Parameter	-
Maximum peak in Final Diff. Map	2.32 e /$Å^3$
Minimum peak in Final Diff. Map	-2.25 e /$Å^3$

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Appendix 16 – FKDW26off – FRKII99Cu

Compound **27** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper chloride dimer

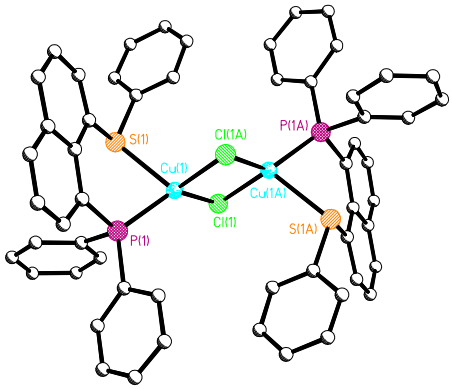

Table 16 Crystal data and structure refinement

Empirical Formula		$C_{56}H_{42}Cl_2Cu_2P_2S_2$
Formula Weight		1039.01
Temperature (°C)		-148(1)
Crystal Colour, Habit		yellow, block
Crystal Dimensions (mm^3)		0.24 X 0.14 X 0.11
Crystal System		triclinic
Lattice Parameters		a = 10.184(8) Å
		b = 10.366(8) Å
	α = 77.52(2)°	c = 11.668(9) Å
	γ = 75.24(2)°	β = 81.46(3)
Volume ($Å^3$)		V = 1157.2(15)
Space Group		P-1
Z value		1
Dcalc (g/cm^3)		1.491
F000		532
μ(MoKα) (cm^{-1})		12.33
No. of Reflections Measured		10019
Rint		0.078
Min and Max Transmissions		0.709 - 0.873
Independent Reflections		4062
Observed Reflection (No. Variables)		2819(290)
Reflection/Parameter Ratio		14.01
Residuals: R_1 (I>2.00σ(I))		0.0857
Residuals: R (All reflections)		0.1176
Residuals: wR_2 (All reflections)		0.259
Goodness of Fit Indicator		1.067
Flack Parameter		-
Maximum peak in Final Diff. Map		2.17 e /$Å^3$
Minimum peak in Final Diff. Map		-0.73 e /$Å^3$

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Appendix 17 – FKDW107A-1 – FRKII107A

Compound **28** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper bromide dimer

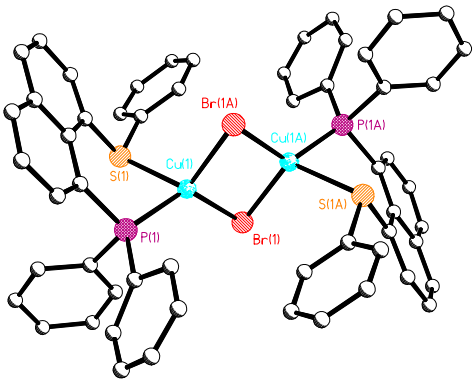

Table 17 Crystal data and structure refinement

Empirical Formula		$C_{56}H_{42}Br_2Cu_2P_2S_2$
Formula Weight		1127.92
Temperature (°C)		-148(1)
Crystal Colour, Habit		yellow, platelet
Crystal Dimensions (mm^3)		0.09 X 0.09 X 0.03
Crystal System		triclinic
Lattice Parameters		a = 10.218(2) Å
		b = 10.400(3) Å
	α = 80.20(2)°	c = 11.690(3) Å
	γ = 74.909(18)°	β = 80.20(2)°
Volume ($Å^3$)		V = 1156.9(5)
Space Group		P-1
Z value		1
Dcalc (g/cm^3)		1.619
F000		568
μ(MoKα) (cm^{-1})		28.502
No. of Reflections Measured		12396
Rint		0.068
Min and Max Transmissions		0.768 - 0.918
Independent Reflections		3998
Observed Reflection (No. Variables)		3527(290)
Reflection/Parameter Ratio		13.79
Residuals: R_1 (I>2.00σ(I))		0.0858
Residuals: R (All reflections)		0.0985
Residuals: wR_2 (All reflections)		0.149
Goodness of Fit Indicator		1.212
Flack Parameter		-
Maximum peak in Final Diff. Map		1.44 e /$Å^3$
Minimum peak in Final Diff. Map		-0.81 e /$Å^3$

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Appendix 18 – FKDW107B-1 – FRKII107B

Compound **29** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine copper iodide dimer

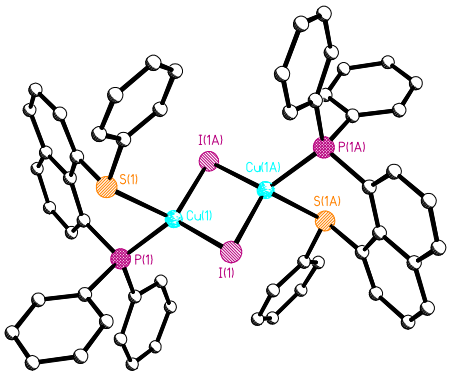

Table 18 Crystal data and structure refinement

Empirical Formula		$C_{56}H_{42}Cu_2I_2P_2S_2$
Formula Weight		1221.92
Temperature (°C)		-148(1)
Crystal Colour, Habit		yellow, block
Crystal Dimensions (mm^3)		0.12 X 0.12 X 0.09
Crystal System		triclinic
Lattice Parameters		a = 10.3416(17) Å
		b = 10.6256(13) Å
	α = 73.87(2)°	c = 11.988(2) Å
	γ = 73.326(18)°	β = 77.76(2)°
Volume ($Å^3$)		V = 1199.6(3)
Space Group		P-1
Z value		1
Dcalc (g/cm^3)		1.691
F000		604
μ(MoKα) (cm^{-1})		23.658
No. of Reflections Measured		13313
Rint		0.052
Min and Max Transmissions		0.578 - 0.808
Independent Reflections		4756
Observed Reflection (No. Variables)		4431(290)
Reflection/Parameter Ratio		16.4
Residuals: R_1 (I>2.00σ(I))		0.0684
Residuals: R (All reflections)		0.0741
Residuals: wR_2 (All reflections)		0.1592
Goodness of Fit Indicator		1.257
Flack Parameter		-
Maximum peak in Final Diff. Map		1.12 e /$Å^3$
Minimum peak in Final Diff. Map		-1.38 e /$Å^3$

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Appendix 19 – FKDW20-1-8TAKE2 – FRKI20-1

Compound **30** - (8-phenylsulfanylnaphth-1-yl)diphenylphosphine ruthenium(II) complex

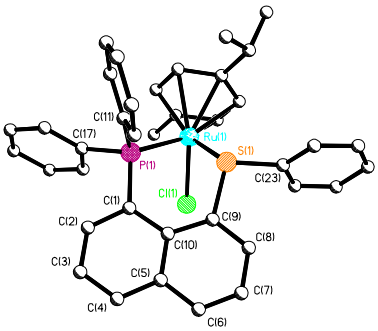

Table 19 Crystal data and structure refinement

Empirical Formula	$C_{41}H_{41}Cl_2OPRuS$
Formula Weight	784.78
Temperature (°C)	-148(1)
Crystal Colour, Habit	orange, block
Crystal Dimensions (mm^3)	0.21 X 0.09 X 0.03
Crystal System	monoclinic
Lattice Parameters	a = 9.829(3) Å
	b = 22.199(6) Å
	c = 17.506(5) Å
	β = 106.021(6)°
Volume ($Å^3$)	V = 3671.4(18)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	1.42
F000	1616
μ(MoKα) (cm^{-1})	7.045
No. of Reflections Measured	16039
Rint	0.083
Min and Max Transmissions	0.861 - 0.979
Independent Reflections	6381
Observed Reflection (No. Variables)	5505(430)
Reflection/Parameter Ratio	14.84
Residuals: R_1 (I>2.00σ(I))	0.1126
Residuals: R (All reflections)	0.1311
Residuals: wR_2 (All reflections)	0.1848
Goodness of Fit Indicator	1.3
Flack Parameter	-
Maximum peak in Final Diff. Map	0.93 e /$Å^3$
Minimum peak in Final Diff. Map	-0.57 e /$Å^3$

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Appendix 20 – FKDW8 – FRKI49

Compound **31** - 1-bromo-8-(phenylselenyl)naphthalene

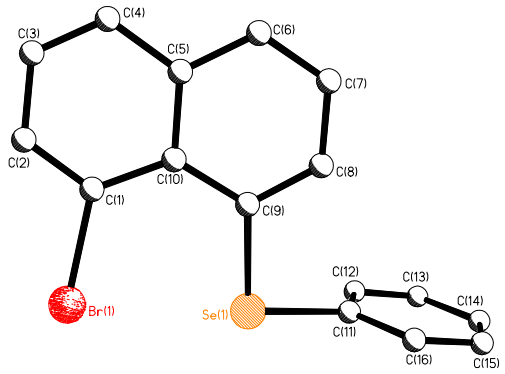

Table 20 Crystal data and structure refinement

Empirical Formula	$C_{16}H_{11}BrSe$
Formula Weight	362.13
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, platelet
Crystal Dimensions (mm^3)	0.40 X 0.16 X 0.13
Crystal System	monoclinic
Lattice Parameters	a = 12.2378(6) Å
	b = 7.8921(4) Å
	c = 14.7367(8) Å
	β = 110.9800(13)o
Volume ($Å^3$)	V = 1328.94(12)
Space Group	$P2_1/c$
Z value	4
Dcalc (g/cm^3)	1.810
F000	704
μ(MoKα) (cm^{-1})	58.19
No. of Reflections Measured	13396
Rint	0.059
Min and Max Transmissions	0.220 - 0.469
Independent Reflections	3044
Observed Reflection (No. Variables)	2482(164)
Reflection/Parameter Ratio	18.56
Residuals: R_1 (I>2.00σ(I))	0.0393
Residuals: R (All reflections)	0.0556
Residuals: wR_2 (All reflections)	0.0937
Goodness of Fit Indicator	0.879
Flack Parameter	-
Maximum peak in Final Diff. Map	0.52 e-/$Å^3$
Minimum peak in Final Diff. Map	-0.43 e-/$Å^3$

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Appendix 21 – FKDW7 – FRKI46

Compound **33** - 1-iodo-8-(phenylselenyl)naphthalene

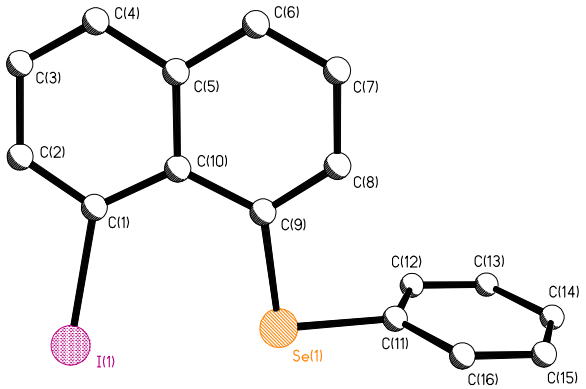

Table 21 Crystal data and structure refinement

Empirical Formula		$C_{16}H_{11}ISe$
Formula Weight		409.13
Temperature (°C)		-148(1)
Crystal Colour, Habit		colourless, prism
Crystal Dimensions (mm^3)		0.30 X 0.24 X 0.12
Crystal System		triclinic
Lattice Parameters		a = 7.8388(7) Å
		b = 8.1008(7) Å
	α = 98.5504(19)°	c = 11.9491(10) Å
	γ = 98.007(2)°	β = 108.8828(18)°
Volume ($Å^3$)		V = 695.57(10)
Space Group		P-1
Z value		2
Dcalc (g/cm^3)		1.953
F000		388
μ(MoKα) (cm^{-1})		48.984
No. of Reflections Measured		6026
Rint		0.072
Min and Max Transmissions		0.257 - 0.556
Independent Reflections		2455
Observed Reflection (No. Variables)		2138(164)
Reflection/Parameter Ratio		14.97
Residuals: R_1 (I>2.00σ(I))		0.0445
Residuals: R (All reflections)		0.0522
Residuals: wR_2 (All reflections)		0.1063
Goodness of Fit Indicator		1.094
Flack Parameter		-
Maximum peak in Final Diff. Map		0.77 e-/$Å^3$
Minimum peak in Final Diff. Map		-0.86 e-/$Å^3$

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Appendix 22 – FKDW53-2 – FRKI53

Compound **34** - (8-phenylselenylnaphth-1-yl)diphenylphosphine oxide

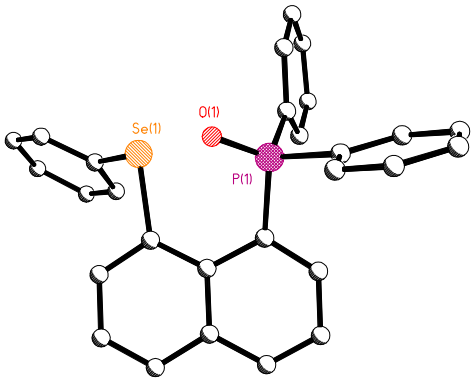

Table 22 Crystal data and structure refinement

Empirical Formula	$C_{28}H_{21}PSeO$
Formula Weight	483.41
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, chunk
Crystal Dimensions (mm^3)	0.30 X 0.15 X 0.12
Crystal System	monoclinic
Lattice Parameters	a = 10.1430(16) Å
	b = 10.6578(17) Å
	c = 10.6907(19) Å
	β = 100.935(4)°
Volume ($Å^3$)	V = 1134.7(3)
Space Group	$P2_1$
Z value	2
Dcalc (g/cm^3)	1.415
F000	492
μ(MoKα) (cm^{-1})	17.43
No. of Reflections Measured	6648
Rint	0.029
Min and Max Transmissions	0.588 - 0.811
Independent Reflections	3674
Observed Reflection (No. Variables)	3611(281)
Reflection/Parameter Ratio	13.07
Residuals: R_1 (I>2.00σ(I))	0.0374
Residuals: R (All reflections)	0.0406
Residuals: wR_2 (All reflections)	0.1131
Goodness of Fit Indicator	1.203
Flack Parameter	0.022(13)
Maximum peak in Final Diff. Map	0.69 e /$Å^3$
Minimum peak in Final Diff. Map	-0.67 e /$Å^3$

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Appendix 23 – FKDW119-1-3 – FRKII119

Compound **35** - (8-phenylselenylnaphth-1-yl)diphenylphosphine sulfide

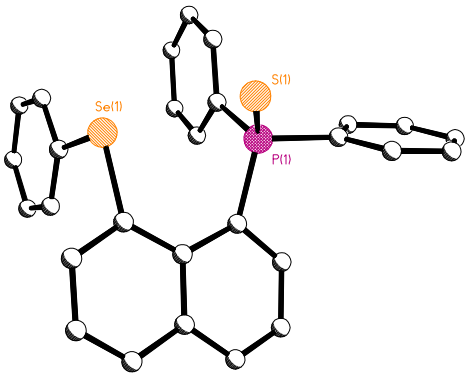

Table 23 Crystal data and structure refinement

Empirical Formula	$C_{28}H_{21}PSeS$
Formula Weight	499.47
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, block
Crystal Dimensions (mm^3)	0.15 X 0.15 X 0.15
Crystal System	monoclinic
Lattice Parameters	a = 9.3748(15) Å
	b = 17.820(3) Å
	c = 13.847(2) Å
	β = 97.820(5)°
Volume ($Å^3$)	V = 2291.7(6)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	1.448
F000	1016
μ(MoKα) (cm^{-1})	18.132
No. of Reflections Measured	13337
Rint	0.034
Min and Max Transmissions	0.756 - 0.762
Independent Reflections	4607
Observed Reflection (No. Variables)	4279(281)
Reflection/Parameter Ratio	16.4
Residuals: R_1 (I>2.00σ(I))	0.0431
Residuals: R (All reflections)	0.0486
Residuals: wR_2 (All reflections)	0.087
Goodness of Fit Indicator	1.14
Flack Parameter	-
Maximum peak in Final Diff. Map	0.41 e /$Å^3$
Minimum peak in Final Diff. Map	-0.45 e /$Å^3$

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Appendix 24 – FKDW146A-2 – FRKII146A

Compound **36** - (8-phenylselenylnaphth-1-yl)diphenylphosphine selenide

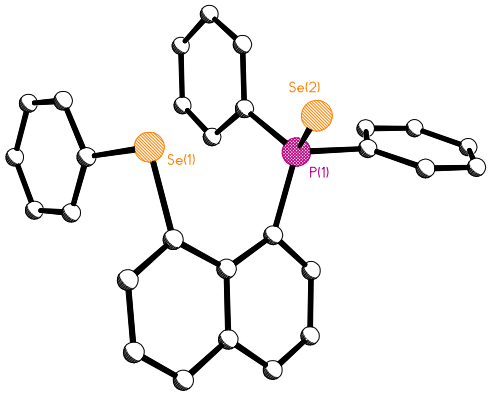

Table 24 Crystal data and structure refinement

Empirical Formula	$C_{28}H_{21}PSe_2$
Formula Weight	546.37
Temperature (°C)	-148(1)
Crystal Colour, Habit	yellow, prism
Crystal Dimensions (mm^3)	0.18 X 0.15 X 0.09
Crystal System	monoclinic
Lattice Parameters	a = 9.4797(12) Å
	b = 17.844(2) Å
	c = 13.7175(16) Å
	β = 96.789(3)°
Volume ($Å^3$)	V = 2304.1(5)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	1.575
F000	1088
μ(MoKα) (cm^{-1})	32.93
No. of Reflections Measured	12528
Rint	0.051
Min and Max Transmissions	0.543 - 0.744
Independent Reflections	4046
Observed Reflection (No. Variables)	3691(281)
Reflection/Parameter Ratio	14.4
Residuals: R_1 (I>2.00σ(I))	0.0553
Residuals: R (All reflections)	0.065
Residuals: wR_2 (All reflections)	0.1585
Goodness of Fit Indicator	1.291
Flack Parameter	-
Maximum peak in Final Diff. Map	0.71 e /$Å^3$
Minimum peak in Final Diff. Map	-0.67 e /$Å^3$

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Appendix 25 – FKDW95-2 – FRKII95

Compound **37** - 1,8-bis(phenylsulfanyl)naphthalene

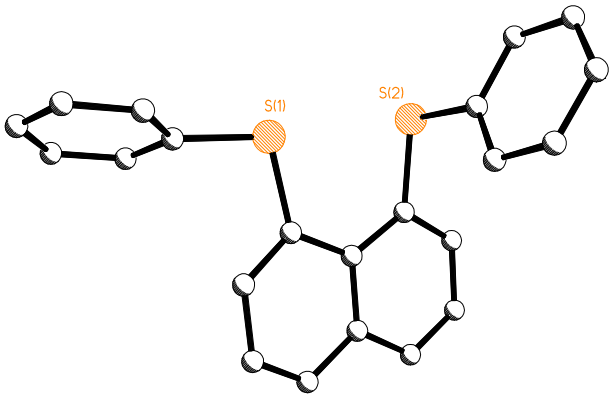

Table 25 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}S_2$
Formula Weight	344.49
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, chunk
Crystal Dimensions (mm^3)	0.15 X 0.15 X 0.09
Crystal System	monoclinic
Lattice Parameters	a = 8.330(3) Å
	b = 19.401(7) Å
	c = 10.544(4) Å
	β = 90.910(8)°
Volume ($Å^3$)	V = 1703.9(10)
Space Group	$P2_1/c$
Z value	4
Dcalc (g/cm^3)	1.343
F000	720
μ(MoKα) (cm^{-1})	3.114
No. of Reflections Measured	9305
Rint	0.058
Min and Max Transmissions	0.953 - 0.972
Independent Reflections	2979
Observed Reflection (No. Variables)	2662(218)
Reflection/Parameter Ratio	13.67
Residuals: R_1 (I>2.00σ(I))	0.0658
Residuals: R (All reflections)	0.0794
Residuals: wR_2 (All reflections)	0.1856
Goodness of Fit Indicator	1.25
Flack Parameter	-
Maximum peak in Final Diff. Map	0.40 e /$Å^3$
Minimum peak in Final Diff. Map	-0.41 e /$Å^3$

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Appendix 26 – FKDW92-0-2 – FRKII92

Compound **38** - 1,8-bis(phenylselenyl)naphthalene

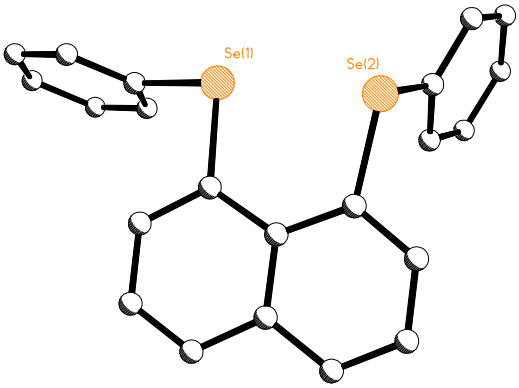

Table 26 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}Se_2$
Formula Weight	438.29
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.15 X 0.09 X 0.09
Crystal System	orthorhombic
Lattice Parameters	a = 21.353(5) Å
	b = 5.6814(12) Å
	c = 14.424(4) Å
	-
Volume ($Å^3$)	V = 1749.9(7)
Space Group	$Pca2_1$
Z value	4
Dcalc (g/cm^3)	1.663
F000	864
μ(MoKα) (cm^{-1})	42.257
No. of Reflections Measured	5919
Rint	0.048
Min and Max Transmissions	0.525 – 0.684
Independent Reflections	2890
Observed Reflection (No. Variables)	2735(218)
Reflection/Parameter Ratio	13.26
Residuals: R_1 (I>2.00σ(I))	0.0473
Residuals: R (All reflections)	0.0514
Residuals: wR_2 (All reflections)	0.0947
Goodness of Fit Indicator	1.116
Flack Parameter	0.04(2)
Maximum peak in Final Diff. Map	0.53 e /Å3
Minimum peak in Final Diff. Map	-0.76 e /Å3

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Appendix 27 – FKDW126-3 – FRKII126

Compound **40** - 1,8-bis(ethylsulfanyl)naphthalene

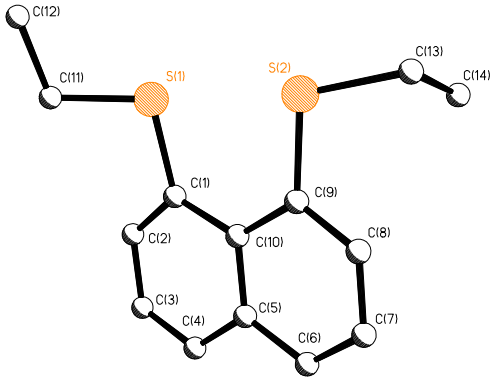

Table 27 Crystal data and structure refinement

Empirical Formula	$C_{14}H_{16}S_2$
Formula Weight	248.40
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.15 X 0.09 X 0.09
Crystal System	orthorhombic
Lattice Parameters	a = 9.0074(15) Å
	b = 16.221(3) Å
	c = 17.386(3) Å
	-
Volume ($Å^3$)	V = 2540.2(8)
Space Group	Pbca
Z value	8
Dcalc (g/cm^3)	1.299
F000	1056
μ(MoKα) (cm^{-1})	3.888
No. of Reflections Measured	7639
Rint	0.076
Min and Max Transmissions	0.942 - 0.966
Independent Reflections	2216
Observed Reflection (No. Variables)	1963(148)
Reflection/Parameter Ratio	14.97
Residuals: R_1 (I>2.00σ(I))	0.0764
Residuals: R (All reflections)	0.0894
Residuals: wR_2 (All reflections)	0.1333
Goodness of Fit Indicator	1.245
Flack Parameter	-
Maximum peak in Final Diff. Map	0.24 e-/$Å^3$
Minimum peak in Final Diff. Map	-0.27 e-/$Å^3$

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Appendix 28 – FKDW182-1 – FRKII182

Compound **55** - 1-bromo-8-(phenyltellurenyl)naphthalene

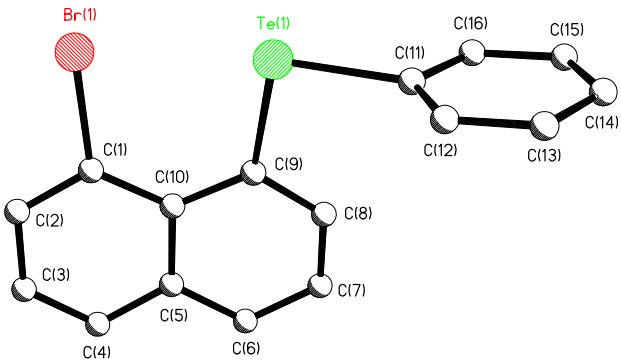

Table 28 Crystal data and structure refinement

Empirical Formula	$C_{16}H_{11}BrTe$
Formula Weight	410.77
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.09 X 0.06 X 0.06
Crystal System	monoclinic
Lattice Parameters	a = 12.556(3) Å
	b = 8.0136(16) Å
	c = 14.803(4) Å
	β = 111.945(4)°
Volume ($Å^3$)	V = 1381.5(6)
Space Group	$P2_1/c$
Z value	4
Dcalc (g/cm^3)	1.975
F000	776
μ(MoKα) (cm^{-1})	50.327
No. of Reflections Measured	8205
Rint	0.039
Min and Max Transmissions	0.611 - 0.739
Independent Reflections	2759
Observed Reflection (No. Variables)	2579(164)
Reflection/Parameter Ratio	16.82
Residuals: R_1 (I>2.00σ(I))	0.0483
Residuals: R (All reflections)	0.0572
Residuals: wR_2 (All reflections)	0.1490
Goodness of Fit Indicator	1.212
Flack Parameter	-
Maximum peak in Final Diff. Map	1.50 e-/$Å^3$
Minimum peak in Final Diff. Map	-1.69 e-/$Å^3$

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Appendix 29 – FKDW205-2 – FRKIII205

Compound **56** - 1-iodo-8-(phenyltellurenyl)naphthalene

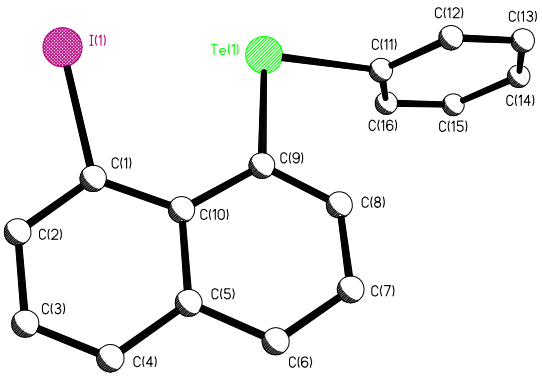

Table 29 Crystal data and structure refinement

Empirical Formula	$C_{16}H_{11}ITe$
Formula Weight	457.77
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.15 X 0.09 X 0.09
Crystal System	monoclinic
Lattice Parameters	a = 12.437(8) Å
	b = 8.174(4) Å
	c = 14.694(10) Å
	β = 110.305(14)°
Volume ($Å^3$)	V = 1400.9(15)
Space Group	$P2_1/c$
Z value	4
Dcalc (g/cm^3)	2.170
F000	848
μ(MoKα) (cm^{-1})	43.072
No. of Reflections Measured	9065
Rint	0.032
Min and Max Transmissions	0.470 - 0.679
Independent Reflections	2814
Observed Reflection (No. Variables)	2695(164)
Reflection/Parameter Ratio	17.16
Residuals: R_1 (I>2.00σ(I))	0.0356
Residuals: R (All reflections)	0.0408
Residuals: wR_2 (All reflections)	0.1465
Goodness of Fit Indicator	1.263
Flack Parameter	-
Maximum peak in Final Diff. Map	1.41 e-/$Å^3$
Minimum peak in Final Diff. Map	-1.72 e-/$Å^3$

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Appendix 30 – FKDW112-1 – FRKII112

Compound **41** - 1-(phenylselenyl)-8-(phenylsulfanyl)naphthalene

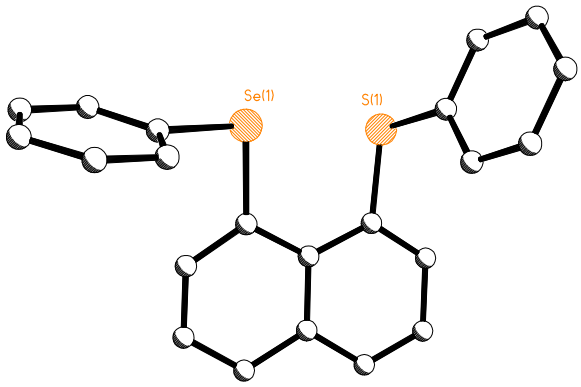

Table 30 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}SSe$
Formula Weight	391.39
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, block
Crystal Dimensions (mm^3)	0.27 X 0.09 X 0.09
Crystal System	orthorhombic
Lattice Parameters	a = 21.150(5) Å
	b = 5.7154(12) Å
	c = 14.421(3) Å
	-
Volume ($Å^3$)	V = 1743.3(7)
Space Group	$Pca2_1$
Z value	4
Dcalc (g/cm^3)	1.491
F000	792
μ(MoKα) (cm^{-1})	22.731
No. of Reflections Measured	6528
Rint	0.063
Min and Max Transmissions	0.397 - 0.815
Independent Reflections	2368
Observed Reflection (No. Variables)	2217(218)
Reflection/Parameter Ratio	10.86
Residuals: R_1 (I>2.00σ(I))	0.0593
Residuals: R (All reflections)	0.0655
Residuals: wR_2 (All reflections)	0.1574
Goodness of Fit Indicator	1.140
Flack Parameter	0.07(2)
Maximum peak in Final Diff. Map	0.67 e /$Å^3$
Minimum peak in Final Diff. Map	-0.68 e /$Å^3$

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Appendix 31 – FKDW98-0-8 – FRKII98

Compound **42** - 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene

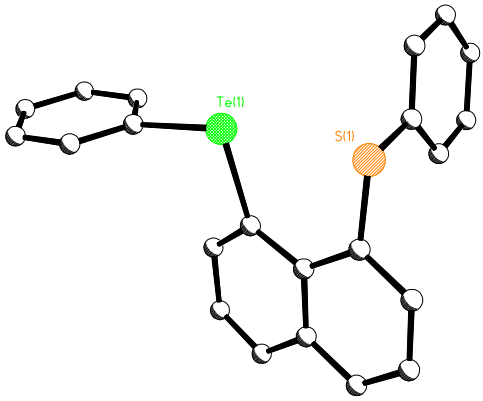

Table 31 Crystal data and structure refinement

Empirical Formula		$C_{22}H_{16}STe$
Formula Weight		440.03
Temperature (°C)		-148(1)
Crystal Colour, Habit		yellow, prism
Crystal Dimensions (mm^3)		0.18 X 0.15 X 0.12
Crystal System		triclinic
Lattice Parameters		a = 9.997(2) Å
		b = 11.2364(18) Å
	α = 74.309(18)°	c = 17.928(3) Å
	γ = 66.344(13)°	β = 87.24(2)°
Volume ($Å^3$)		V = 1771.7(6)
Space Group		P-1
Z value		4
Dcalc (g/cm^3)		1.65
F000		864
μ(MoKα) (cm^{-1})		17.962
No. of Reflections Measured		19899
Rint		0.032
Min and Max Transmissions		0.718 - 0.806
Independent Reflections		7014
Observed Reflection (No. Variables)		6663(434)
Reflection/Parameter Ratio		16.16
Residuals: R_1 (I>2.00σ(I))		0.0566
Residuals: R (All reflections)		0.0599
Residuals: wR_2 (All reflections)		0.1714
Goodness of Fit Indicator		1.099
Flack Parameter		-
Maximum peak in Final Diff. Map		1.64 e /$Å^3$
Minimum peak in Final Diff. Map		-1.86 e /$Å^3$

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Appendix 32 – FKDW73-2 – FRKI73

Compound **43** - 1-(phenyltellurenyl)-8-(phenylselenyl)naphthalene

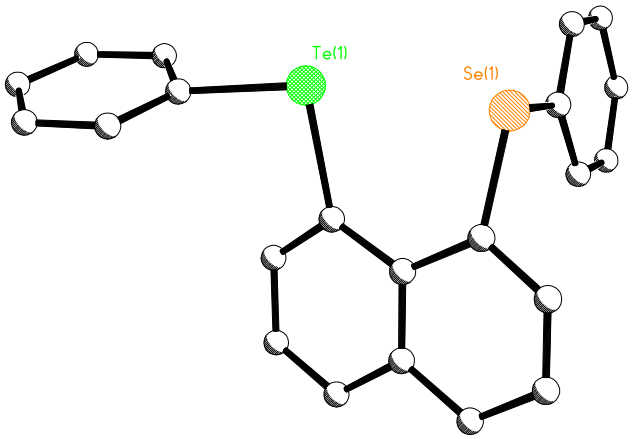

Table 32 Crystal data and structure refinement

Empirical Formula		$C_{22}H_{16}SeTe$
Formula Weight		486.93
Temperature (°C)		-148(1)
Crystal Colour, Habit		yellow, prism
Crystal Dimensions (mm^3)		0.21 X 0.09 X 0.09
Crystal System		triclinic
Lattice Parameters		a = 10.094(4) Å
		b = 11.2590(19) Å
	α = 73.66(4)°	c = 18.122(8) Å
	γ = 67.06(3)°	β = 87.13(4)°
Volume ($Å^3$)		V = 1815.9(13)
Space Group		P-1
Z value		4
Dcalc (g/cm^3)		1.781
F000		936
μ(MoKα) (cm^{-1})		36.424
No. of Reflections Measured		18410
Rint		0.050
Min and Max Transmissions		0.461 - 0.720
Independent Reflections		6253
Observed Reflection (No. Variables)		5691(434)
Reflection/Parameter Ratio		14.41
Residuals: R_1 (I>2.00σ(I))		0.0646
Residuals: R (All reflections)		0.0848
Residuals: wR_2 (All reflections)		0.2886
Goodness of Fit Indicator		1.211
Flack Parameter		-
Maximum peak in Final Diff. Map		2.10 e-/$Å^3$
Minimum peak in Final Diff. Map		-2.27 e-/$Å^3$

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Appendix 33 – FKDW211A-2 – FRKIII211A

Compound **44** - 1-(phenylsulfinyl)-8-(phenylsulfanyl)naphthalene

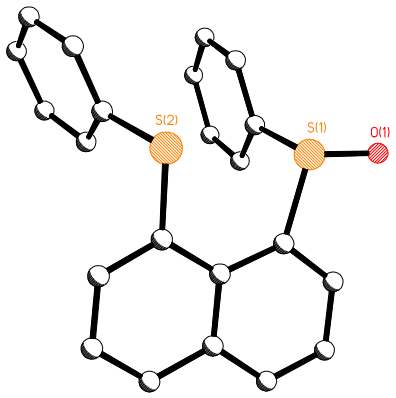

Table 33 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}OS_2$
Formula Weight	360.49
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.18 X 0.09 X 0.09
Crystal System	monoclinic
Lattice Parameters	a = 10.139(5) Å
	b = 15.379(6) Å
	c = 11.575(6) Å
	β = 111.083(15)°
Volume ($Å^3$)	V = 1684.0(14)
Space Group	$P2_1/c$
Z value	4
Dcalc (g/cm^3)	1.422
F000	752
μ(MoKα) (cm^{-1})	3.227
No. of Reflections Measured	9709
Rint	0.054
Min and Max Transmissions	0.943 - 0.971
Independent Reflections	3400
Observed Reflection (No. Variables)	3089(227)
Reflection/Parameter Ratio	14.98
Residuals: R_1 (I>2.00σ(I))	0.0693
Residuals: R (All reflections)	0.0789
Residuals: wR_2 (All reflections)	0.1670
Goodness of Fit Indicator	1.169
Flack Parameter	-
Maximum peak in Final Diff. Map	0.34 e-/$Å^3$
Minimum peak in Final Diff. Map	-0.60 e-/$Å^3$

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Appendix 34 – FKDW211C-1 – FRKIII211C

Compound **45** - 1,8-bis(phenylsulfinyl)naphthalene

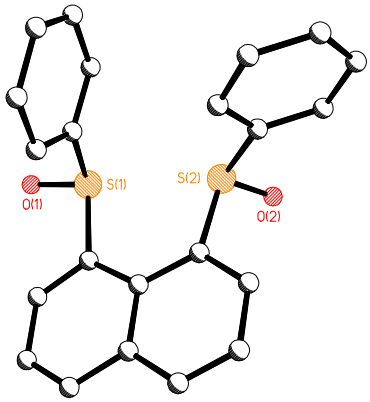

Table 34 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}O_2S_2$
Formula Weight	376.49
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, prism
Crystal Dimensions (mm^3)	0.18 X 0.09 X 0.09
Crystal System	monoclinic
Lattice Parameters	a = 17.275(9) Å
	b = 15.216(7) Å
	c = 13.591(7) Å
	β = 105.593(11)°
Volume ($Å^3$)	V = 3441(3)
Space Group	C2/c
Z value	8
Dcalc (g/cm^3)	1.453
F000	1568
μ(MoKα) (cm^{-1})	3.234
No. of Reflections Measured	10825
Rint	0.059
Min and Max Transmissions	0.961 - 0.981
Independent Reflections	3459
Observed Reflection (No. Variables)	3114(236)
Reflection/Parameter Ratio	14.66
Residuals: R_1 (I>2.00σ(I))	0.0675
Residuals: R (All reflections)	0.0808
Residuals: wR_2 (All reflections)	0.1995
Goodness of Fit Indicator	1.312
Flack Parameter	-
Maximum peak in Final Diff. Map	0.57 e-/$Å^3$
Minimum peak in Final Diff. Map	-0.55 e-/$Å^3$

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Appendix 35 – FKDW164-3 – FRKII164

Compound **57** - 1,8-bis(4-bromophenylsulfanyl)-2,5-dibromonaphthalene

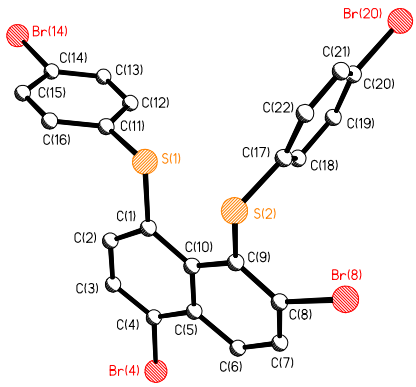

Table 35 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{12}Br_4S_2$
Formula Weight	660.07
Temperature (°C)	-148(1)
Crystal Colour, Habit	yellow, prism
Crystal Dimensions (mm^3)	0.12 X 0.06 X 0.06
Crystal System	monoclinic
Lattice Parameters	a = 32.535(13) Å
	b = 5.4833(18) Å
	c = 27.215(9) Å
	β = 92.729(11)°
Volume ($Å^3$)	V = 4850(3)
Space Group	C2/c
Z value	8
Dcalc (g/cm^3)	1.808
F000	2528
μ(MoKα) (cm^{-1})	68.368
No. of Reflections Measured	13347
Rint	0.068
Min and Max Transmissions	0.406 - 0.664
Independent Reflections	4268
Observed Reflection (No. Variables)	3398(254)
Reflection/Parameter Ratio	16.8
Residuals: R_1 (I>2.00σ(I))	0.0866
Residuals: R (All reflections)	0.1144
Residuals: wR_2 (All reflections)	0.2732
Goodness of Fit Indicator	1.206
Flack Parameter	-
Maximum peak in Final Diff. Map	2.78 e /$Å^3$
Minimum peak in Final Diff. Map	-1.00 e /$Å^3$

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Appendix 36 – FKDW157A-2 – FRKII157A

Compound **58**

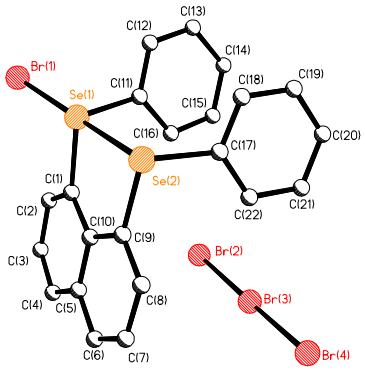

Table 36 Crystal data and structure refinement

Empirical Formula	$C_{16}H_{11}Br_4Se_2$
Formula Weight	757.90
Temperature (°C)	-148(1)
Crystal Colour, Habit	orange, block
Crystal Dimensions (mm^3)	0.12 X 0.12 X 0.12
Crystal System	monoclinic
Lattice Parameters	a = 9.293(3) Å
	b = 14.082(5) Å
	c = 17.212(6) Å
	β = 97.177(9)°
Volume ($Å^3$)	V = 2234.8(13)
Space Group	$P2_1/n$
Z value	4
Dcalc (g/cm^3)	2.252
F000	1424
μ(MoKα) (cm^{-1})	104.897
No. of Reflections Measured	13998
Rint	0.042
Min and Max Transmissions	0.268 - 0.284
Independent Reflections	4524
Observed Reflection (No. Variables)	3974(254)
Reflection/Parameter Ratio	17.81
Residuals: R_1 (I>2.00σ(I))	0.0435
Residuals: R (All reflections)	0.0540
Residuals: wR_2 (All reflections)	0.1236
Goodness of Fit Indicator	1.175
Flack Parameter	-
Maximum peak in Final Diff. Map	1.32 e-/$Å^3$
Minimum peak in Final Diff. Map	-1.17 e-/$Å^3$

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Appendix 37 – FKDW157B-3 – FRKII157B

Compound **59**

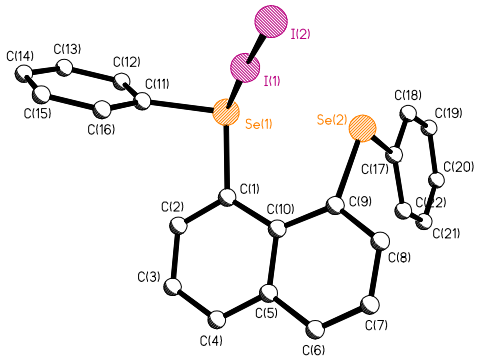

Table 37 Crystal data and structure refinement

Empirical Formula		$C_{22}H_{16}I_2Se_2$
Formula Weight		692.1
Temperature (°C)		-148(1)
Crystal Colour, Habit		orange, prism
Crystal Dimensions (mm^3)		0.12 X 0.12 X 0.06
Crystal System		triclinic
Lattice Parameters		a = 10.003(3) Å
		b = 10.453(2) Å
	α = 102.307(6)°	c = 11.749(3) Å
	γ = 93.395(4)°	β = 84.68(3)°
Volume ($Å^3$)		V = 1089.3(5)
Space Group		P-1
Z value		2
Dcalc (g/cm^3)		2.11
F000		644
μ(MoKα) (cm^{-1})		62.337
No. of Reflections Measured		11727
Rint		0.036
Min and Max Transmissions		0.486 - 0.688
Independent Reflections		3715
Observed Reflection (No. Variables)		3557(236)
Reflection/Parameter Ratio		15.74
Residuals: R_1 (I>2.00σ(I))		0.0302
Residuals: R (All reflections)		0.0359
Residuals: wR_2 (All reflections)		0.1262
Goodness of Fit Indicator		1.28
Flack Parameter		-
Maximum peak in Final Diff. Map		1.44 e /$Å^3$
Minimum peak in Final Diff. Map		-1.77 e /$Å^3$

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Appendix 38 – FKDW157BI-3 – FRKII157BI$_2$

Compound **60**

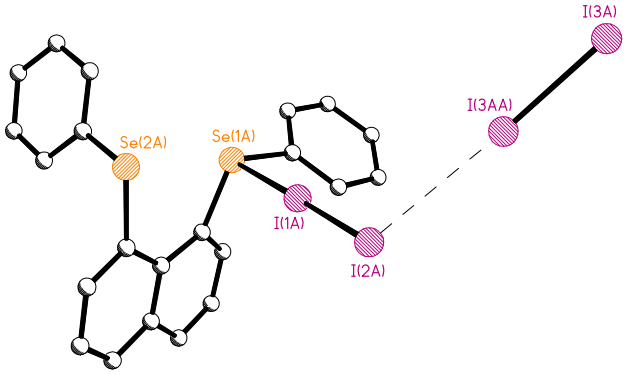

Table 38 Crystal data and structure refinement

Empirical Formula		$C_{44}H_{32}I_6Se_4$
Formula Weight		1638.00
Temperature (°C)		-148(1)
Crystal Colour, Habit		red, prism
Crystal Dimensions (mm^3)		0.15 X 0.09 X 0.09
Crystal System		triclinic
Lattice Parameters		a = 9.6503(18) Å
		b = 11.3357(16) Å
	α = 65.996(10)°	c = 11.8269(16) Å
	γ = 83.206(14)°	β = 82.763(14)°
Volume (Å^3)		V = 1169.3(3)
Space Group		P-1
Z value		1
Dcalc (g/cm^3)		2.326
F000		750
μ(MoKα) (cm^{-1})		71.303
No. of Reflections Measured		13845
Rint		0.043
Min and Max Transmissions		0.336 - 0.526
Independent Reflections		4628
Observed Reflection (No. Variables)		4222(245)
Reflection/Parameter Ratio		18.89
Residuals: R_1 (I>2.00σ(I))		0.0483
Residuals: R (All reflections)		0.0569
Residuals: wR_2 (All reflections)		0.1746
Goodness of Fit Indicator		1.185
Flack Parameter		-
Maximum peak in Final Diff. Map		1.32 e-/Å^3
Minimum peak in Final Diff. Map		-1.56 e-/Å^3

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Appendix 39 – FKDW173-1 – FRKII173

Compound **61**

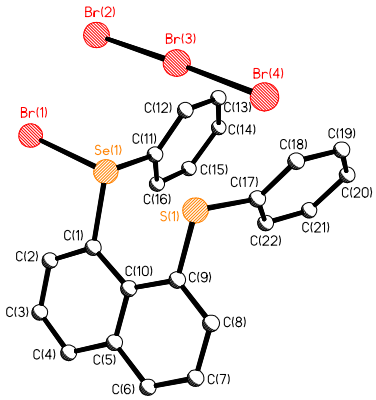

Table 39 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}Br_4SSe$
Formula Weight	711
Temperature (°C)	-148(1)
Crystal Colour, Habit	orange, platelet
Crystal Dimensions (mm^3)	0.18 X 0.12 X 0.06
Crystal System	monoclinic
Lattice Parameters	a = 13.555(2) Å
	b = 9.2381(13) Å
	c = 18.663(3) Å
	β = 103.009(3)°
Volume ($Å^3$)	V = 2277.0(6)
Space Group	$P2_1/c$
Z value	4
Dcalc (g/cm^3)	2.074
F000	1352
μ(MoKα) (cm^{-1})	87.882
No. of Reflections Measured	12771
Rint	0.064
Min and Max Transmissions	0.294 - 0.590
Independent Reflections	3971
Observed Reflection (No. Variables)	3489(254)
Reflection/Parameter Ratio	15.63
Residuals: R_1 (I>2.00σ(I))	0.0699
Residuals: R (All reflections)	0.0813
Residuals: wR_2 (All reflections)	0.1938
Goodness of Fit Indicator	1.15
Flack Parameter	-
Maximum peak in Final Diff. Map	2.33 e /$Å^3$
Minimum peak in Final Diff. Map	-1.18 e /$Å^3$

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Appendix 40 – FKDW217A-1 – FRKIII217A

Compound **62**

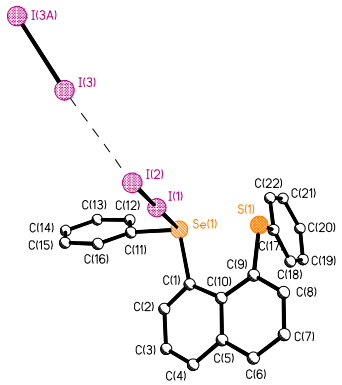

Table 40 Crystal data and structure refinement

Empirical Formula		$C_{44}H_{32}I_6S_2Se_2$
Formula Weight		1544.20
Temperature (°C)		-148(1)
Crystal Colour, Habit		red, prism
Crystal Dimensions (mm^3)		0.21 X 0.15 X 0.09
Crystal System		triclinic
Lattice Parameters		a = 9.6066(17) Å
		b = 11.2528(14) Å
	α = 65.855(9)°	c = 11.8080(14) Å
	γ = 83.443(14)°	β = 82.839(14)°
Volume ($Å^3$)		V = 1152.9(3)
Space Group		P-1
Z value		1
Dcalc (g/cm^3)		2.224
F000		714
μ(MoKα) (cm^{-1})		57.432
No. of Reflections Measured		13510
Rint		0.038
Min and Max Transmissions		0.403 - 0.596
Independent Reflections		4542
Observed Reflection (No. Variables)		4336(245)
Reflection/Parameter Ratio		18.54
Residuals: R_1 (I>2.00σ(I))		0.0429
Residuals: R (All reflections)		0.0479
Residuals: wR_2 (All reflections)		0.1587
Goodness of Fit Indicator		1.148
Flack Parameter		-
Maximum peak in Final Diff. Map		2.46 e-/$Å^3$
Minimum peak in Final Diff. Map		-1.98 e-/$Å^3$

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Appendix 41 – FKDW195A-1 – FRKII195A

Compound **63**

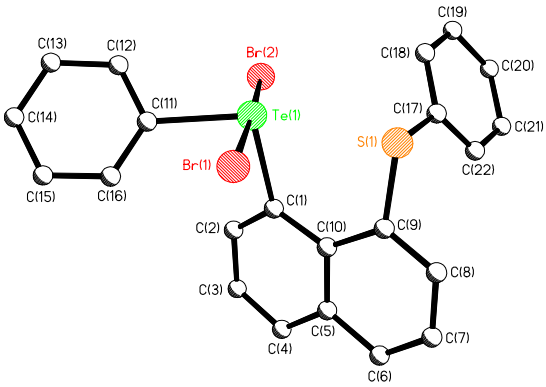

Table 41 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}Br_2STe$
Formula Weight	599.84
Temperature (°C)	-148(1)
Crystal Colour, Habit	yellow, prism
Crystal Dimensions (mm^3)	0.21 X 0.03 X 0.03
Crystal System	monoclinic
Lattice Parameters	a = 18.873(10) Å
	b = 15.452(7) Å
	c = 13.922(6) Å
	β = 100.423(11)°
Volume ($Å^3$)	V = 3993(3)
Space Group	C2/c
Z value	8
Dcalc (g/cm^3)	1.995
F000	2288
μ(MoKα) (cm^{-1})	56.13
No. of Reflections Measured	10797
Rint	0.082
Min and Max Transmissions	0.542 - 0.845
Independent Reflections	3510
Observed Reflection (No. Variables)	2992(236)
Reflection/Parameter Ratio	14.87
Residuals: R_1 (I>2.00σ(I))	0.0696
Residuals: R (All reflections)	0.0876
Residuals: wR_2 (All reflections)	0.1808
Goodness of Fit Indicator	1.261
Flack Parameter	-
Maximum peak in Final Diff. Map	1.50 e /$Å^3$
Minimum peak in Final Diff. Map	-1.67 e /$Å^3$

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Appendix 42 – FERG58 – FRKIII244

Compound **64**

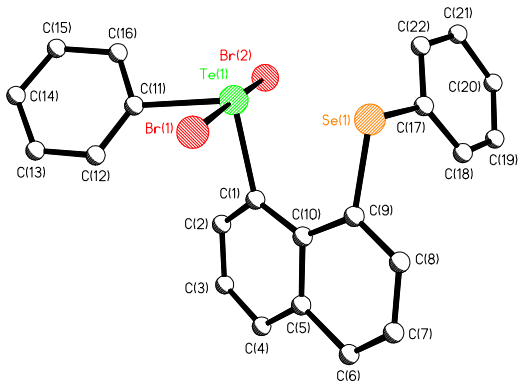

Table 42 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}Br_2SeTe$
Formula Weight	646.73
Temperature (°C)	-180(1)
Crystal Colour, Habit	colourless, platelet
Crystal Dimensions (mm^3)	0.06 X 0.06 X 0.03
Crystal System	monoclinic
Lattice Parameters	a = 19.172(8) Å
	b = 15.285(6) Å
	c = 14.070(7) Å
	β = 100.442(13)°
Volume ($Å^3$)	V = 4055(3)
Space Group	C2/c
Z value	8
Dcalc (g/cm^3)	2.119
F000	2432
μ(MoKα) (mm^{-1})	7.207
No. of Reflections Measured	12736
Rint	0.1295
Min and Max Transmissions	0.652 - 1.000
Independent Reflections	3669
Observed Reflection (No. Variables)	2284(236)
Reflection/Parameter Ratio	15.55
Residuals: R_1 (I>2.00σ(I))	0.0947
Residuals: R (All reflections)	0.1436
Residuals: wR_2 (All reflections)	0.2625
Goodness of Fit Indicator	1.077
Flack Parameter	-
Maximum peak in Final Diff. Map	2.515 e-/$Å^3$
Minimum peak in Final Diff. Map	-1.557 e-/$Å^3$

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Appendix 43 – FKDW195B-1 – FRKII195B

Compound **65**

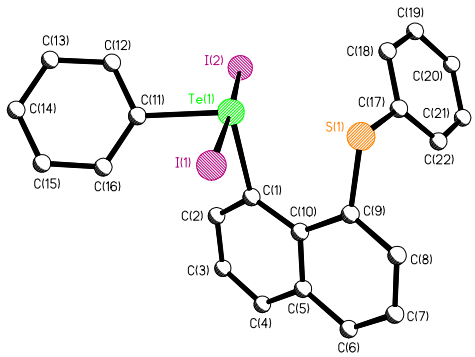

Table 43 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}I_2STe$
Formula Weight	693.84
Temperature (°C)	-148(1)
Crystal Colour, Habit	orange, prism
Crystal Dimensions (mm^3)	0.15 X 0.09 X 0.09
Crystal System	monoclinic
Lattice Parameters	a = 18.909(4) Å
	b = 15.954(3) Å
	c = 14.282(3) Å
	β = 99.994(5)°
Volume ($Å^3$)	V = 4243.1(15)
Space Group	P2/c
Z value	8
Dcalc (g/cm^3)	2.172
F000	2576
μ(MoKα) (cm^{-1})	44.16
No. of Reflections Measured	12261
Rint	0.033
Min and Max Transmissions	0.487 - 0.672
Independent Reflections	4204
Observed Reflection (No. Variables)	3961(236)
Reflection/Parameter Ratio	17.81
Residuals: R_1 (I>2.00σ(I))	0.0361
Residuals: R (All reflections)	0.0429
Residuals: wR_2 (All reflections)	0.1341
Goodness of Fit Indicator	1.244
Flack Parameter	-
Maximum peak in Final Diff. Map	1.65 e-/$Å^3$
Minimum peak in Final Diff. Map	-1.63 e-/$Å^3$

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Appendix 44 – FERG57 – FRKIII245

Compound **66**

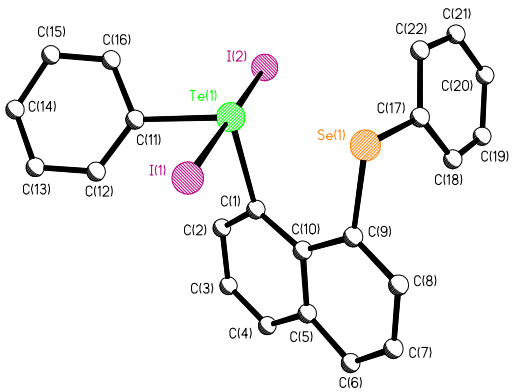

Table 44 Crystal data and structure refinement

Empirical Formula	$C_{22}H_{16}I_2SeTe$
Formula Weight	740.71
Temperature (°C)	-180(1)
Crystal Colour, Habit	colourless, platelet
Crystal Dimensions (mm^3)	0.05 X 0.05 X 0.05
Crystal System	monoclinic
Lattice Parameters	a = 19.723(9) Å
	b = 15.191(6) Å
	c = 14.463(6) Å
	β = 100.692(12)°
Volume ($Å^3$)	V = 4258(3)
Space Group	C2/c
Z value	8
Dcalc (g/cm^3)	2.311
F000	2720
μ(MoKα) (mm^{-1})	6.011
No. of Reflections Measured	13494
Rint	0.1378
Min and Max Transmissions	0.797 - 1.000
Independent Reflections	3836
Observed Reflection (No. Variables)	2117(236)
Reflection/Parameter Ratio	16.25
Residuals: R_1 (I>2.00σ(I))	0.0823
Residuals: R (All reflections)	0.1495
Residuals: wR_2 (All reflections)	0.2132
Goodness of Fit Indicator	0.992
Flack Parameter	-
Maximum peak in Final Diff. Map	3.359 e-/$Å^3$
Minimum peak in Final Diff. Map	-1.375 e-/$Å^3$

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Appendix 45 – FKDW161-2 – FRKIII219A

Compound **67**

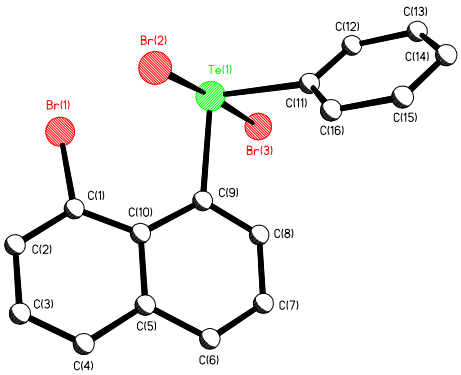

Table 45 Crystal data and structure refinement

Empirical Formula	$C_{16}H_{11}Br_3Te$
Formula Weight	570.57
Temperature (°C)	-148(1)
Crystal Colour, Habit	colourless, platelet
Crystal Dimensions (mm^3)	0.12 X 0.12 X 0.01
Crystal System	orthorhombic
Lattice Parameters	a = 8.4839(18) Å
	b = 12.041(2) Å
	c = 15.592(3) Å
	–
Volume ($Å^3$)	V = 1592.8(6)
Space Group	$Pca2_1$
Z value	4
Dcalc (g/cm^3)	2.379
F000	1056
μ(MoKα) (cm^{-1})	94.028
No. of Reflections Measured	4898
Rint	0.057
Min and Max Transmissions	0.409 - 0.910
Independent Reflections	2459
Observed Reflection (No. Variables)	2353(182)
Reflection/Parameter Ratio	13.51
Residuals: R_1 (I>2.00σ(I))	0.0461
Residuals: R (All reflections)	0.0503
Residuals: wR_2 (All reflections)	0.0996
Goodness of Fit Indicator	1.089
Flack Parameter	-
Maximum peak in Final Diff. Map	0.77 e-/$Å^3$
Minimum peak in Final Diff. Map	-1.09 e-/$Å^3$

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Appendix 46 – FKDW223A-1 – FRKIII223A

Compound **68**

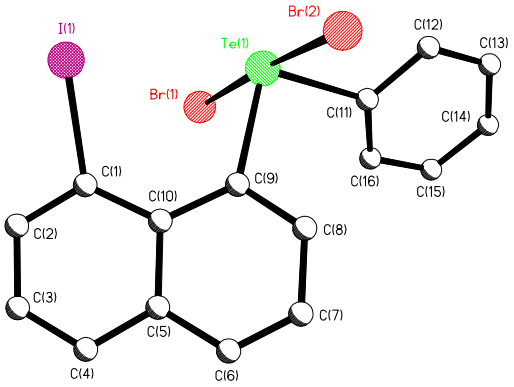

Table 46 Crystal data and structure refinement

Empirical Formula	$C_{16}H_{11}Br_2ITe$
Formula Weight	617.58
Temperature (°C)	-148(1)
Crystal Colour, Habit	yellow, prism
Crystal Dimensions (mm^3)	0.15 X 0.09 X 0.09
Crystal System	orthorhombic
Lattice Parameters	a = 8.5238(18) Å
	b = 12.165(3) Å
	c = 15.780(3) Å
	–
Volume ($Å^3$)	V = 1636.3(6)
Space Group	$Pca2_1$
Z value	4
Dcalc (g/cm^3)	2.507
F000	1128
μ(MoKα) (cm^{-1})	85.916
No. of Reflections Measured	4932
Rint	0.040
Min and Max Transmissions	0.290 - 0.462
Independent Reflections	2609
Observed Reflection (No. Variables)	2579(182)
Reflection/Parameter Ratio	14.34
Residuals: R_1 (I>2.00σ(I))	0.0313
Residuals: R (All reflections)	0.0332
Residuals: wR_2 (All reflections)	0.0967
Goodness of Fit Indicator	1.206
Flack Parameter	-
Maximum peak in Final Diff. Map	1.41 e-/$Å^3$
Minimum peak in Final Diff. Map	-1.50 e-/$Å^3$

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Appendix 47 – FKDW219B-1 – FRKIII219B

Compound **69**

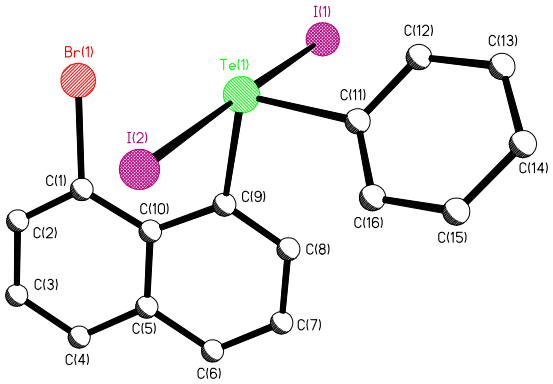

Table 47 Crystal data and structure refinement

Empirical Formula		$C_{16}H_{11}BrI_2Te$
Formula Weight		664.58
Temperature (°C)		-148(1)
Crystal Colour, Habit		red, platelet
Crystal Dimensions (mm^3)		0.15 X 0.15 X 0.03
Crystal System		triclinic
Lattice Parameters		a = 8.221(2) Å
		b = 9.639(3) Å
	α = 105.274(8)°	c = 11.613(3) Å
	γ = 102.945(9)°	β = 90.454(4)°
Volume ($Å^3$)		V = 863.0(4)
Space Group		P-1
Z value		2
Dcalc (g/cm^3)		2.557
F000		600
μ(MoKα) (cm^{-1})		76.13
No. of Reflections Measured		9862
Rint		0.044
Min and Max Transmissions		0.335 - 0.796
Independent Reflections		3384
Observed Reflection (No. Variables)		3262(182)
Reflection/Parameter Ratio		18.59
Residuals: R_1 (I>2.00σ(I))		0.0373
Residuals: R (All reflections)		0.0391
Residuals: wR_2 (All reflections)		0.1186
Goodness of Fit Indicator		1.144
Flack Parameter		-
Maximum peak in Final Diff. Map		1.43 e-/$Å^3$
Minimum peak in Final Diff. Map		-1.29 e-/$Å^3$

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Appendix 48 – FKDW236-1 – FRKIII223B

Compound **70**

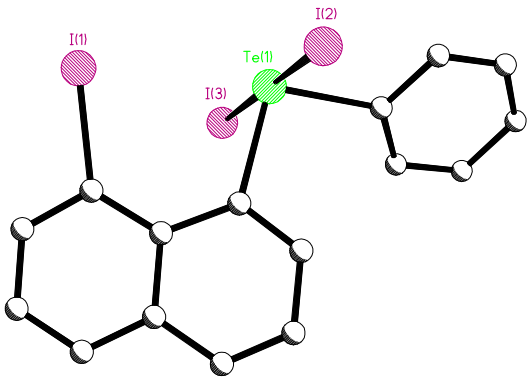

Table 48 Crystal data and structure refinement

Empirical Formula		$C_{16}H_{11}I_3Te$
Formula Weight		711.58
Temperature (°C)		-148(1)
Crystal Colour, Habit		orange, prism
Crystal Dimensions (mm^3)		0.12 X 0.03 X 0.03
Crystal System		triclinic
Lattice Parameters		a = 7.290(4) Å
		b = 9.642(6) Å
	α = 104.034(9)°	c = 13.294(7) Å
	γ = 103.475(12)°	β = 92.232(12)°
Volume ($Å^3$)		V = 877.0(9)
Space Group		P-1
Z value		2
Dcalc (g/cm^3)		2.695
F000		636
μ(MoKα) (cm^{-1})		69.675
No. of Reflections Measured		9605
Rint		0.071
Min and Max Transmissions		0.632 - 0.811
Independent Reflections		3429
Observed Reflection (No. Variables)		3196(182)
Reflection/Parameter Ratio		18.84
Residuals: R_1 (I>2.00σ(I))		0.0589
Residuals: R (All reflections)		0.0675
Residuals: wR_2 (All reflections)		0.1966
Goodness of Fit Indicator		1.134
Flack Parameter		-
Maximum peak in Final Diff. Map		2.28 e-/$Å^3$
Minimum peak in Final Diff. Map		-2.40 e-/$Å^3$

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Appendix 49 – FKDW168A-2 – FRKII168A

Compound **73** - 4,7-dibromo-2-mono-*tert*-butylnaphtho[1,8-*c,d*][1,2]diselenole

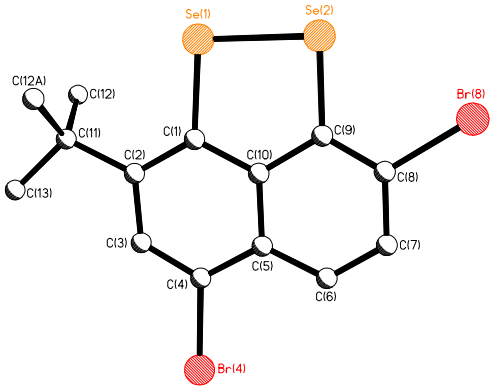

Table 49 Crystal data and structure refinement

Empirical Formula	$C_{14}H_{14}Br_2Se_2$
Formula Weight	499.99
Temperature (°C)	-148(1)
Crystal Colour, Habit	red, prism
Crystal Dimensions (mm^3)	0.09 X 0.06 X 0.06
Crystal System	monoclinic
Lattice Parameters	a = 9.638(7) Å
	b = 7.112(5) Å
	c = 10.499(8) Å
	β = 94.263(15)°
Volume ($Å^3$)	V = 717.6(8)
Space Group	$P2_1/m$
Z value	2
Dcalc (g/cm^3)	2.314
F000	472
μ(MoKα) (cm^{-1})	107.166
No. of Reflections Measured	4132
Rint	0.039
Min and Max Transmissions	0.373 - 0.526
Independent Reflections	1362
Observed Reflection (No. Variables)	1267 (115)
Reflection/Parameter Ratio	11.84
Residuals: R_1 (I>2.00σ(I))	0.0452
Residuals: R (All reflections)	0.0499
Residuals: wR_2 (All reflections)	0.1072
Goodness of Fit Indicator	1.181
Flack Parameter	-
Maximum peak in Final Diff. Map	0.66 e /$Å^3$
Minimum peak in Final Diff. Map	-0.99 e /$Å^3$

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Appendix 50 – FKDW237A-1 – FRKIII237A

Compound **74 -** Hydroxydiphenyl[(8-phenylsulfanyl)naphthalene-1-yl]phosphonium tribromide

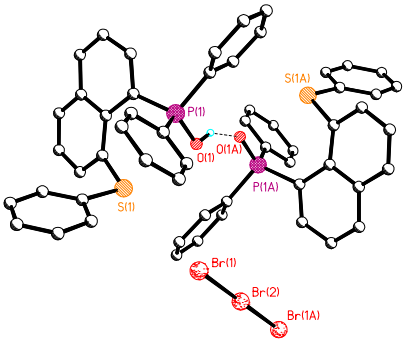

Table 50 Crystal data and structure refinement

Empirical Formula		$C_{56}H_{43}O_2P_2S_2Br_3$
Formula Weight		1113.73
Temperature (°C)		-148(1)
Crystal Colour, Habit		colourless, prism
Crystal Dimensions (mm^3)		0.12 X 0.09 X 0.09
Crystal System		triclinic
Lattice Parameters		a = 9.1606(13) Å
		b = 11.537(3) Å
	α = 83.21(5)°	c = 12.606(4) Å
	γ = 66.89(4)°	β = 71.33(4)°
Volume ($Å^3$)		V = 1160.8(7)
Space Group		P-1
Z value		1
Dcalc (g/cm^3)		1.593
F000		562
μ(MoKα) (cm^{-1})		28.176
No. of Reflections Measured		11962
Rint		0.105
Min and Max Transmissions		0.511 - 0.776
Independent Reflections		4041
Observed Reflection (No. Variables)		3185(296)
Reflection/Parameter Ratio		13.65
Residuals: R_1 (I>2.00σ(I))		0.1109
Residuals: R (All reflections)		0.1398
Residuals: wR_2 (All reflections)		0.1854
Goodness of Fit Indicator		1.241
Flack Parameter		-
Maximum peak in Final Diff. Map		0.93 e-/$Å^3$
Minimum peak in Final Diff. Map		-0.79 e-/$Å^3$

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II - Crystal structure experimental

X-ray crystal structures were determined by Prof. A. M. Z. Slawin and Amy Fuller. Data for compounds **1**, **2**, **27**, **31** and **33** (Appendix 1, 2, 16, 20 & 21) were collected at -148(1) °C on a Rigaku SCXmini CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data was corrected for Lorentz, polarisation and absorption. Data for compounds **3**, **19**, **20**, **62** and **64**, (Appendix 3, 8, 9, 42 & 44) were collected at -180(1) °C by using a Rigaku MM007 High brilliance RA generator (Mo Kα radiation, confocal optic) and Mercury CCD system. At least a full hemisphere of data was collected using ω scans. Intensities were corrected for Lorentz, polarisation and absorption. Data for all other compounds was collected at -148(1) °C on a Rigaku ACTOR-SM, Saturn 724 CCD area detector with confocal optic Mo-Kα radiation (λ = 0.71073 Å). The data was corrected for Lorentz, polarisation and absorption.

The data for the complexes analysed was collected and processed using CrystalClear (Rigaku).[1] The structure was solved by direct methods[2] and expanded using Fourier techniques.[3] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[4] crystallographic software package except for refinement, which was performed using SHELXL-97.[5]

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III - Publications to date

Fergus R. Knight, Amy L. Fuller, Michael Bühl, Alexandra M. Z. Slawin and J. Derek Woollins, "Synthetic and structural studies of 1-halo-8-(alkylchalcogeno)naphthalene derivatives", *Chem. Eur. J.*, submitted.

Amy L. Fuller, **Fergus R. Knight**, Alexandra M. Z. Slawin and J. Derek Woollins, "Platinum Complexes of Aromatic Selenides", *Eur. J. Inorg. Chem.*, submitted.

Fergus R. Knight, Amy L. Fuller, Michael Bühl, Alexandra M. Z. Slawin and J. Derek Woollins, "Synthetic and structural studies of 1,8-chalcogen naphthalene derivatives", *Chem. Eur. J.*, submitted.

Fergus R. Knight, Amy L. Fuller, Alexandra M. Z. Slawin and J. Derek Woollins, "Preparation and compounds of (8-methoxynaphth-1-yl)diphenylphosphine", *Inorg. Chem. Commun.,* submitted.

Fergus R. Knight, Amy L. Fuller, Alexandra M. Z. Slawin and J. Derek Woollins, "Controlling Cu···Cu distances using halides: (8-phenylthionaphth-1-yl)diphenylphosphine copper halide dimers", *Dalton Trans.*, 2009, 8476-8478.

Amy L. Fuller, **Fergus R. Knight**, Alexandra M. Z. Slawin and J. Derek Woollins, "8-Bromonaphthalen-1-amine", *Acta Cryst.*, 2008, **E64**, o977.

Amy L. Fuller, **Fergus R. Knight**, Alexandra M. Z. Slawin and J. Derek Woollins, "1-Bromo-8-(ethylsulfanyl)naphthalene", *Acta Cryst.*, 2007, **E63**, o3957.

Amy L. Fuller, **Fergus R. Knight**, Alexandra M. Z. Slawin and J. Derek Woollins, "1-Bromo-8-(phenylselenyl)naphthalene", *Acta Cryst.*, 2007, **E63**, o3855.

Matthew L. Clarke, Marcia B. France, **Fergus R. Knight**, Jamie J. R. Frew and Geoffrey J. Roff, "Enantio- and Diastereoselective Hydrogenation of a Fluorinated Diketone", *Synlett.*, 2007, **11**, 1739-1741.

IV - Crystal structure and experimental codes for all compounds

Compound	Crystal Structure Code	Experiment Code
1	FKDW15e	FRKI9
2	FKDW2	FRKI5
3	FKDW3	FRKI15
15	FKDW123-1	FRKII123
16	FKDW15(ox)-8	FRKI15ox
17	FKDW147A-1	FRKII147A
18	FKDW150B-6	FRKII150B
19	FKDW4MER	FRKI20
20	FERG56	FRKI45
21	FKDW20(ox)-1	FRKI20ox
22	FKDW122-1-9	FRKII111C
23	FKDW111D-2	FRKII111D
24	FKDW54-1	FRKI54
25	FKDW20-10-8a	FRKI20-10
26	FKDW20-7-2	FRKI20-7
27	FKDW26off	FRKII99Cu
28	FKDW107A-1	FRKII107A
29	FKDW107B-1	FRKII107B
30	FKDW20-1-8TAKE2	FRKI20-1
31	FKDW8	FRKI49
33	FKDW7	FRKI46
34	FKDW53-2	FRKI53
35	FKDW119-1-3	FRKII119
36	FKDW146A-2	FRKII146A
37	FKDW95-2	FRKII95
38	FKDW92-0-2	FRKII92
40	FKDW126-3	FRKII126
41	FKDW112-1	FRKII112
42	FKDW98-0-8	FRKII98
43	FKDW73-2	FRKI73
44	FKDW211A-2	FRKIII211A
45	FKDW211C-1	FRKIII211C
55	FKDW182-1	FRKII182
56	FKDW205-2	FRKIII205
57	FKDW164-3	FRKII164
58	FKDW157A-2	FRKII157A
59	FKDW157B-3	FRKII157B
60	FKDW157BI-3	FRKII157BI2
61	FKDW173-1	FRKII173
62	FKDW217A-1	FRKIII217A
63	FKDW195A-1	FRKII195A
64	FERG58	FRKIII244
65	FKDW195B-1	FRKII195B
66	FERG57	FRKIII245
67	FKDW161-2	FRKIII219A
68	FKDW223A-1	FRKIII223A
69	FKDW219B-1	FRKIII219B
70	FKDW223B-5	FRKIII223B
73	FKDW168A-2	FRKII168A
74	FKDW237A-1	FRKIII237A