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**The Chemistry of naphtho[1,8-*cd*]-1,2-dithiole and its  
related compounds**

By

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A Thesis submitted

In partial fulfilment for the award of

**Doctor of Philosophy of the University of St Andrews**

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## Abstract

This thesis describes the general area of chalcogen metal complexation chemistry and the hard/soft donor mismatch involved in sulfur oxygen containing compounds. Chapter 1 provides a general overview of the class of compounds known as polysulfane compounds and looks at the methods of synthesising such compounds. The latter part of this chapter then concentrates on a particular class of polysulfanes, the cyclic, aromatic disulfanes, looking at a number of relevant examples and how they are synthesised. The oxidised derivatives of a few of these compounds are introduced and the literature of metal complexes of these sulfur and sulfur/oxygen containing compounds is comprehensively reviewed. Chapter 2 details the synthesis and characterisation of a series of group IV complexes of the cyclic, aromatic disulfanes naphtho[1,8-*cd*]-1,2-dithiole and dibenzo[*ce*]-1,2-dithiine and their oxidised derivatives prepared by oxidative addition of the disulfide bridged pro-ligand to a metal pre-cursor and by salt elimination reaction of the di-lithium salts of these pro-ligands with a metal dichloride. Chapter 3 follows this up by describing the platinum chemistry of these sulfur containing compounds, again prepared by both oxidative addition and salt elimination reactions. In Chapter 4 we report a study of these sulfur oxygen compounds as bridging ligands in homo-metallic di-iridium complexes, prepared solely by oxidative addition of the pro-ligand to  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ . Finally, Chapter 5 describes the synthesis of a few new di-chalcogen bridged compounds and deals with some further chemistry of naphtho[1,8-*cd*]-1,2-dithiole, introducing interesting reactions such as exchange reactions of titanocene complexes with platinum dichlorides and also electrocrystallisation of naphtho[1,8-*cd*]-1,2-dithiole with  $[\text{BF}_4]^-$  as the counter ion.

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Firstly, I would like to dedicate this thesis to my Grandad Hodge, who gave me lots of help and encouragement to go to and get through University and unfortunately didn't get to see me finish what he helped me start.

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## Abbreviations

The following abbreviations are used throughout this thesis

Å	Angstrom unit, $10^{-10}$ m
n-Bu	Butyl, <i>n</i> -C <sub>4</sub> H <sub>9</sub>
Ch	Chalcogen
<i>J</i>	Coupling constant
Cp	Cyclopentadienyl, C <sub>5</sub> H <sub>5</sub> <sup>-</sup>
cod	cycloocta-1,5-diene
°	Degree
°C	Degrees Celsius
DMSO	Dimethyl sulfoxide
DPPE	bis(diphenylphosphino)ethane
DPPM	bis(diphenylphosphino)methane
EI	Electron Impact
ES	Electrospray
Et	Ethyl, C <sub>2</sub> H <sub>5</sub>
FAB	Fast Atom Bombardment
Hz	Hertz
HCDTN	Hexachlorodithionaphthalene
IR	Infra-red
i-Pr	Iso-propyl, <i>i</i> -C <sub>3</sub> H <sub>7</sub>
K	Kelvin
MS	Mass Spectroscopy

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<i>m/z</i>	Mass to charge ratio
Me	Methyl, CH <sub>3</sub>
Cp'	Methylcyclopentadienyl, C <sub>5</sub> H <sub>4</sub> Me <sup>-</sup>
MCPBA	Metachloroperoxybenzoic acid
NMR	Nuclear Magnetic Resonance
ppm	parts per million
Cp <sup>*</sup>	Pentamethylcyclopentadienyl, C <sub>5</sub> Me <sub>5</sub> <sup>-</sup>
Ph	Phenyl, C <sub>6</sub> H <sub>5</sub>
<i>t</i> -Bu	Tertiary-butyl, <i>t</i> -C <sub>4</sub> H <sub>9</sub>
TCTTN	Tetrachlorotetrathionaphalene
TCNQ	Tetracyanoquinodimethane
TMEDA	Tetramethylethylenediamine
TTN	Tetrathionaphthalene
TTT	Tetrathiotetracene
cm <sup>-1</sup>	Wavenumber

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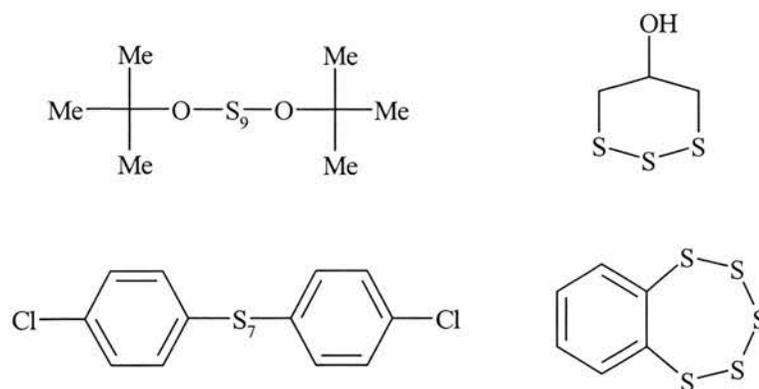
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## CHAPTER 1. INTRODUCTION

### 1.1 POLYSULFANES

Organic sulfanes and polysulfanes can be represented generally by the formula  $R-S_x-R$ , where R is an organic group and  $x = 1, 2, 3, \text{ etc.}$  <sup>(1)</sup> These compounds are covalently bound and the R groups can be linked, giving a cyclic polysulfane, or unlinked, resulting in a chain polysulfane. It is also possible for R to be either aliphatic or aromatic both in the cyclic and the chain form. As a result of this, these compounds are of major interest to both organic and inorganic chemists. This is because they are characterised by organic substituents which terminate the sulfur chain or close this chain to form a ring (giving them their organic “component”) whilst the chain of sulfur atoms make these compounds inorganic enough to captivate the interest of inorganic chemists. Polysulfanes, both cyclic and linear, have been isolated with the value of  $x$  being as high as 16. The reason that so many different compounds containing a long sulfur chain are known is because sulfur atoms have a high propensity to form homoatomic chains and rings as a result of the high S-S bond energy of  $265 \text{ kJ mol}^{-1}$ . <sup>(2)</sup> A selection of examples of chain and cyclic polysulfanes (both aromatic and aliphatic) are shown in figure 1.1.



**Figure 1.1** Examples of aromatic and aliphatic, chain and cyclic polysulfanes.

There are several methods known to synthesise organic polysulfanes and this subject has recently been comprehensively reviewed by Steudel.<sup>(1)</sup> However, this is an appropriate moment to summarise some of the more common methods for synthesis of such compounds.

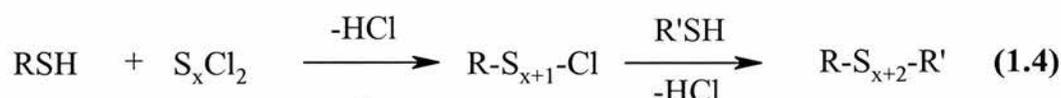
## 1.2 SYNTHESIS OF POLYSULFANES

### 1.2.1 REACTIONS INVOLVING DICHLOROSULFANES

A very simple method for synthesising polysulfane compounds is by the reaction of thiols or thiolates with a dichlorosulfane. This method is effective for the synthesis of both chain and cyclic polysulfanes. The reactions can be summarised generally by equations 1.1 and 1.2 (in the case of chain polysulfanes) and 1.3 (for cyclic polysulfanes).



The method displayed in equations 1.1 and 1.2 are only useful for the preparation of symmetrical polysulfanes. Asymmetric substitution is achieved by a stepwise reaction. This reaction is summarised in equation 1.4.



Since only  $\text{SCl}_2$  and  $\text{S}_2\text{Cl}_2$  are commercially available, this method is only really effective for the synthesis of tri- or tetrasulfanes. More sulfur rich dichlorosulfanes ( $\text{S}_x\text{Cl}_2$ ,  $x = 3-5$ ) can be prepared and used to make longer chain polysulfanes by the analogous reaction of  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{S}_2$  or  $\text{H}_2\text{S}_3$  with an excess of  $\text{SCl}_2$  or  $\text{S}_2\text{Cl}_2$ .<sup>(3)</sup> Longer chain chlorosulfanes ( $x = 6-8$ ) are prepared by a carefully controlled ring opening chlorination of the corresponding cyclo- $\text{S}_x$  molecule with  $\text{Cl}_2$ .<sup>(4-6)</sup>

Polymerisation is a potential problem in the synthesis of cyclic polysulfanes (equation 1.3) but this can be overcome by the simultaneous addition of both reagents to a large volume of solvent to keep the concentrations of the two reactants very low.

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## 1.2.2 REACTION OF THIOLS WITH SULFENYL CHLORIDES

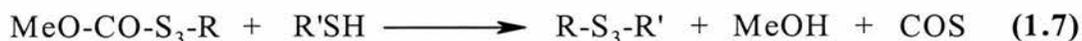
Symmetrical and asymmetrical polysulfanes with various alkyl and aryl substituents can be produced by the reaction of a thiol or organylsulfane with a sulfenyl chloride. This method can be summarised by equation 1.5.



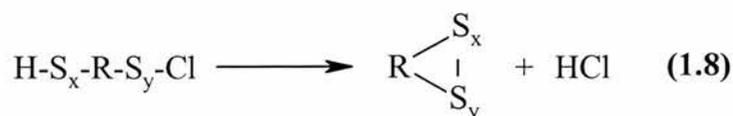
Obviously, if R and R' are the same, then these compounds are symmetrical, otherwise they are asymmetrical. Compounds such as alkoxy carbonyl compounds can be used to produce interesting polysulfane products (equation 1.6).



These products react with thiols and have been previously used to synthesise various asymmetrical trisulfanes in excellent yields (equation 1.7).<sup>(7)</sup>



This method is not suitable for production of cyclic polysulfanes as this would require an intramolecular condensation (equation 1.8).



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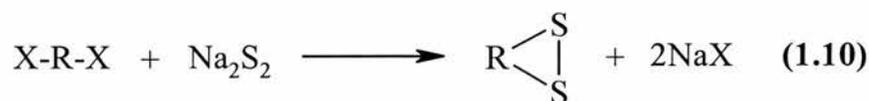
### 1.2.3 REACTION OF SULFENYL HALIDES WITH METAL POLYSULFIDES

Sulfenyl halides can be reacted with  $H_2S$ ,  $H_2S_2$  or their metal salts to produce polysulfanes as demonstrated in equation 1.9. This method is essentially similar to that previously discussed in section 1.2.1.



This method has been shown to be particularly effective in producing chain trisulfanes from  $RSBr$  and  $HgS$ ,  $PbS$ ,  $Ag_2S$  or  $Tl_2S$ .<sup>(8)</sup> The yield is high and the conditions are mild, such reactions being carried out at room temperature and pressure.  $H_2S$  can be used instead of the metal salts but in each case the yield is diminished.

Cyclic polysulfanes can also be synthesised using this method. In these reactions, a sulfenyl halide is not necessarily required but an organic halide can also be used (equation 1.10).

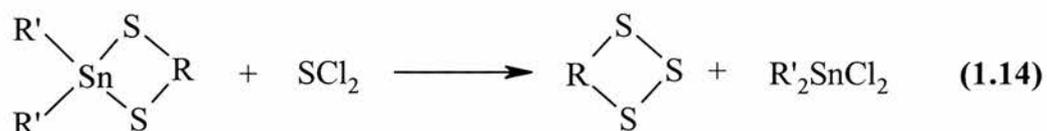
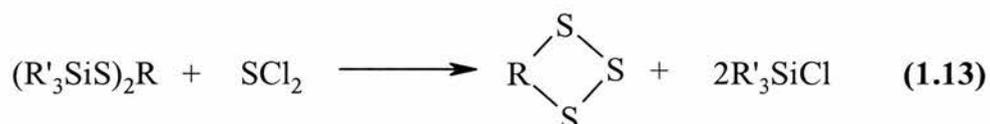
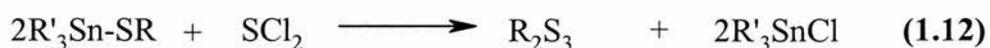


In these reactions, the strongly nucleophilic polysulfide ions substitute the halide ions. Again, since only few  $Na_2S_x$  compounds are known, this method is only really effective in the synthesis of di-, tri- and tetrasulfanes.

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## 1.2.4 ORGANOTIN AND ORGANOSILICON REAGENTS

Silicon and tin are known for their high affinity for chlorine and bromine and this can be exploited to synthesise a variety of polysulfanes. These reactions can be summarised by equations 1.11-1.14 for both chain and cyclic polysulfanes.

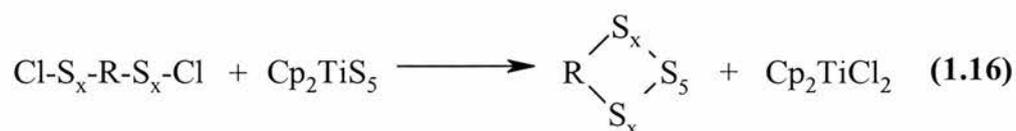


In each case symmetrical polysulfanes are produced. For example, diethyl trisulfane is obtained in high yield from EtS-SiMe<sub>2</sub>Cl and SCl<sub>2</sub>,<sup>(9)</sup> while the best yields for cyclic products are obtained from (Me<sub>3</sub>SiS)<sub>2</sub>R and SCl<sub>2</sub> where R = C<sub>3</sub>H<sub>6</sub> or C<sub>4</sub>H<sub>8</sub>.<sup>(10)</sup>

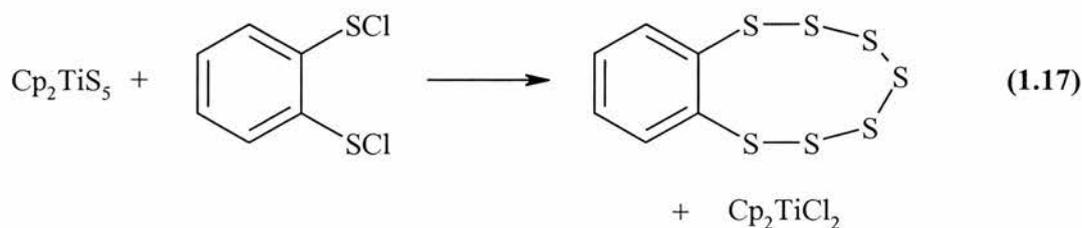
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### 1.2.5 USE OF METAL CENTRES AS LIGAND TRANSFER REAGENTS

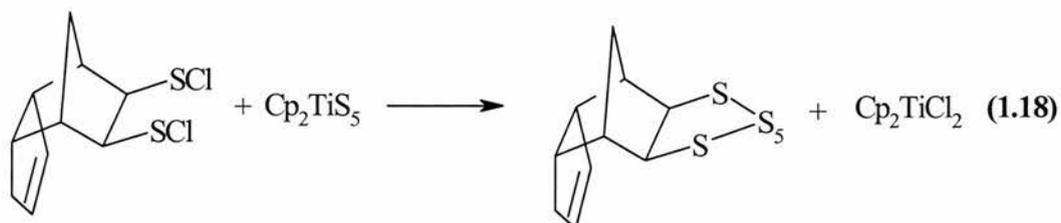
Complexes of titanocene are useful precursors in the synthesis of novel polysulfanes. For example, the synthesis of  $\text{Cp}_2\text{TiS}_5$  from titanocene dichloride and alkali polysulfides is extremely facile.<sup>(11, 12)</sup> This complex is extremely useful as it is air-stable and soluble in organic solvents. The affinity of this complex for chlorine (*ie* to reform titanocene dichloride) can be exploited to produce new polysulfanes as demonstrated by equations 1.15 and 1.16.



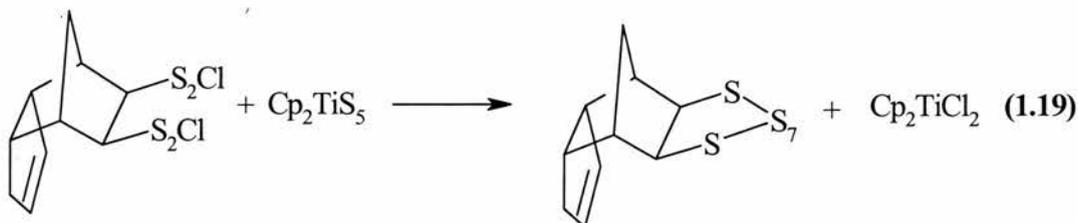
This method is particularly desirable as temperatures of 0-20°C are typically required in solvents such as  $\text{CS}_2$  or  $\text{CH}_2\text{Cl}_2$  and the reactions are regularly quantitative, while this method also gives an easily purifiable product. Further to this,  $\text{Cp}_2\text{TiS}_5$  is desirable as it does not introduce nucleophilic polysulfide anions which can potentially catalyse decomposition and interconversion reactions of meta-stable sulfur rich compounds, a potential problem in other methods of polysulfane synthesis. There are a vast number of examples of titanocene pentasulfide being used to form novel sulfur rich compounds and some of the more interesting examples are shown. For example, equation 1.17 shows a novel sulfur rich ring with an aromatic backbone which was formed from  $\text{Cp}_2\text{TiS}_5$  and 1,2-benzenedithiol.



Other similar complexes have been produced such as the nine-membered aliphatic ring produced by using 1,2-C<sub>2</sub>H<sub>4</sub>(SCl)<sub>2</sub>. More complex heterocycles have also been produced, such as dicyclopentadiene polysulfanes,<sup>(13)</sup> an example of such a reaction is shown in equation 1.18.



When the similar reactant with two S<sub>2</sub>Cl functional groups instead of SCl groups is used then the product contains an eleven-membered ring with nine sulfur atoms (equation 1.19).



While the previous examples have shown the synthesis of novel sulfur rich rings, a number of examples are also known where chain polysulfanes have been produced. For example, titanocene pentasulfide reacts with two equivalents of

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$\text{CCl}_3\text{SCl}$  or  $\text{Pr}^i\text{OSSCl}$  to give chain products with seven and nine sulfur atoms respectively in high yield (equations 1.20 and 1.21).<sup>(14)</sup>



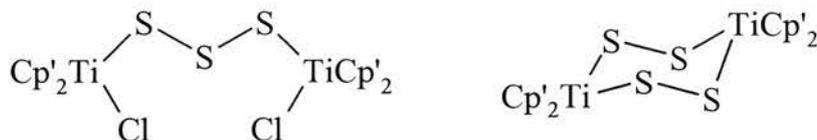
One of the most interesting reactions involving  $\text{Cp}_2\text{TiS}_5$  as a sulfur transfer reagent is the synthesis of new allotropes of sulfur. The most common and stable allotrope of sulfur is cyclo- $\text{S}_8$  but other allotropes can be prepared.<sup>(15)</sup> An example of such a reaction was the preparation of cyclohexasulfur ( $\text{S}_6$ ) and cyclododecasulfur ( $\text{S}_{12}$ ).<sup>(16)</sup> These products were prepared by reaction of  $\text{Cp}_2\text{TiS}_5$  with  $\text{SCl}_2$ . The expected product ( $\text{S}_6$ ) was produced in 87% yield but on analysis, the final product was also found to contain  $\text{S}_{12}$  in 11% yield. Cycloheptasulfur,  $\text{S}_7$ , was also prepared by reaction of titanocene pentasulfide and  $\text{S}_2\text{Cl}_2$  as seen in equation 1.22.<sup>(17)</sup>



This product was the first known allotrope of sulfur to contain an odd number of atoms. Other similar complexes can be used such as  $\text{Cp}_2\text{TiS}_8$  which has been demonstrated to react with  $\text{S}_2\text{Cl}_2$  to give the novel allotrope  $\text{S}_{10}$ .<sup>(18)</sup>

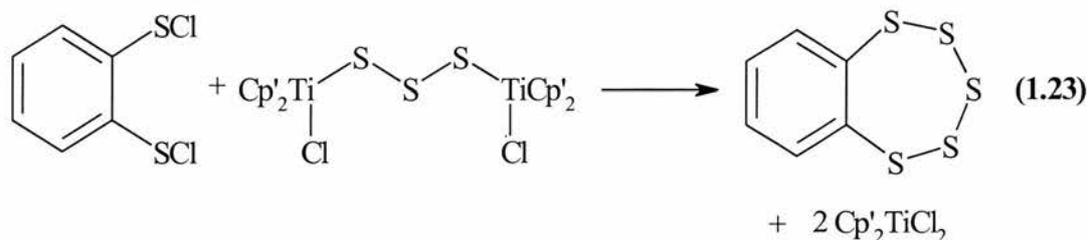
A number of other titanium based sulfur transfer reagents are also known and can be seen in figure 1.2. These reagents work along the same principles as described

for  $\text{Cp}_2\text{TiS}_5$ , reacting with chlorides to form novel sulfur rich compounds and reforming  $\text{Cp}_2\text{TiCl}_2$ .



**Figure 1.2** Examples of titanium based sulfur transfer reagents.

The bimetallic complex  $[(\text{Cp}'_2\text{TiCl})_2\text{S}_3]$  for example, is an  $\text{S}_3$  donor and will react with 1,2-benzenedithiol to give a new cyclic product with five sulfur atoms making up part of a seven-membered ring as shown in equation 1.23.



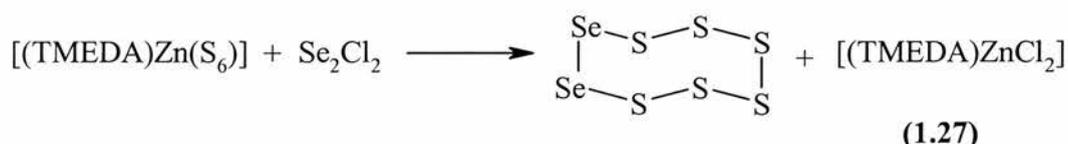
Titanium is not the only metal which is useful for the preparation of novel polysulfanes. Zinc can also be used, in particular the complex  $(\text{TMEDA})\text{ZnS}_6$ ,<sup>(19)</sup> which acts as a sulfur transfer reagent in a similar way to titanocene pentasulfide due to its desire to form  $(\text{TMEDA})\text{ZnCl}_2$ . This method can be summarised by equations 1.24 (chain) and 1.25 (cyclic).



This zinc complex has also been used like  $\text{Cp}_2\text{TiS}_5$  to produce new allotropes of sulfur, in particular cyclo- $\text{S}_{14}$ ,<sup>(20)</sup> which is produced by the reaction with  $\text{S}_8\text{Cl}_2$  as shown in equation 1.26.

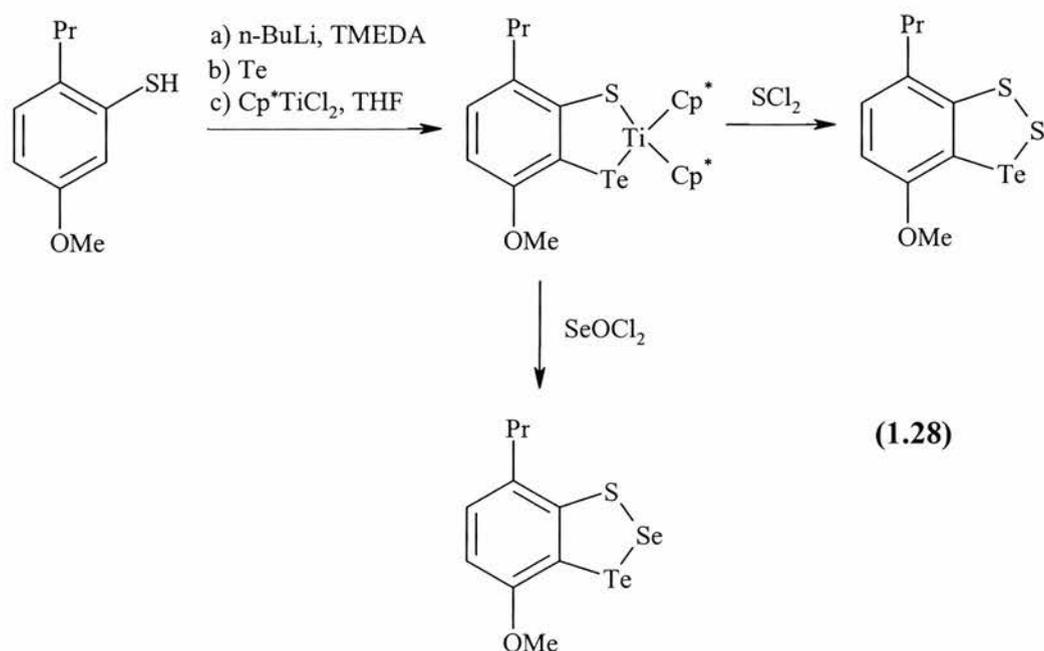


$[(\text{TMEDA})\text{ZnS}_6]$  has also been used to produce the interesting eight-membered ring compound  $\text{Se}_2\text{S}_6$  (equation 1.27).

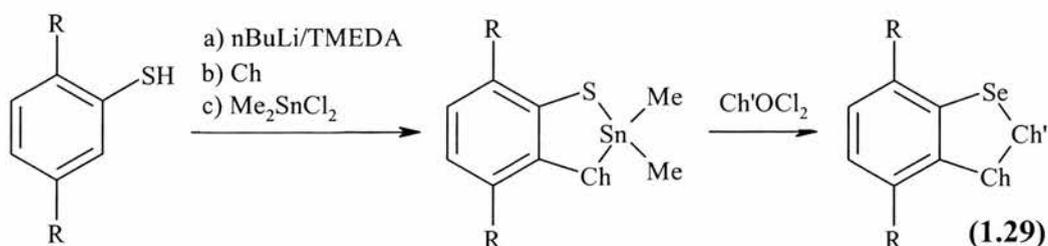


This method of using a metal centre can be expanded to synthesise a number of new polysulfanes. Indeed, it is worth mentioning here that it is not only sulfur containing compounds that can be prepared but also compounds containing the other chalcogens selenium and tellurium, and also compounds with a mixture of these three elements. Titanocene complexes can be reacted in general with chloride compounds, resulting in replacement of the titanium atom with a new atom, normally a chalcogen atom. For example, cyclic, aromatic

trichalcogenanes can be prepared by using decamethyl titanocene dichloride which will form a five-membered ring where the titanium atom is bound to two chalcogen atoms. Replacement of the titanium atom then forms a series of novel compounds containing three chalcogen atoms in a row. <sup>(21, 22)</sup> This is best demonstrated in equation 1.28.

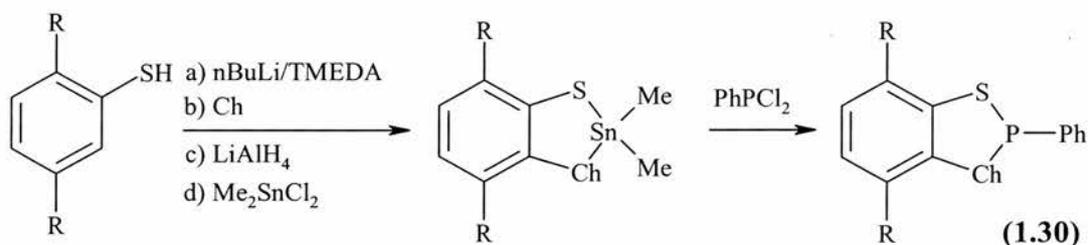


Other metals such as tin can also be used to develop new polychalcogen compounds. Several compounds containing a trichalcogen moiety have been successfully prepared using this metal. <sup>(23)</sup> These reactions proceed in a similar way to that shown in equation 1.28 for a zinc centre, as demonstrated in equation 1.29. The driving force for these reactions is the desire for the tin centre to reform  $\text{Me}_2\text{SnCl}_2$ .



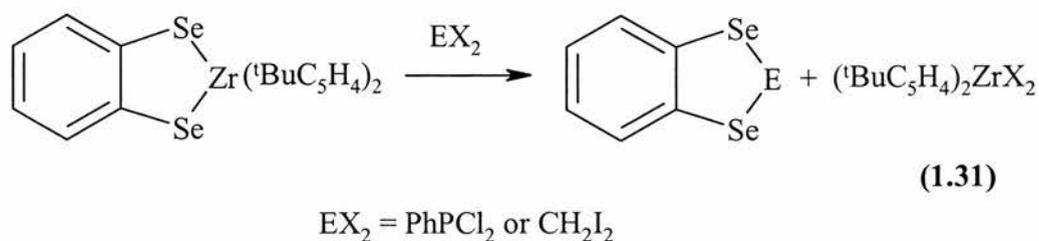
There are several examples of these reactions known where Ch and Ch' are sulfur or selenium and where R is a variety of organic groups.

The reactions discussed up to now have involved the synthesis of a variety of compounds containing a polychalcogenane chain. In particular, the reactions involving a metal centre have involved the replacement of the metal atom with a chalcogen atom and the reformation of a metal dichloride. It is worth acknowledging here that this style of reaction is not limited to the replacement of the metal with a group 16 atom but also works for other groups. For example, a benzene fused five-membered dichalcogenaheterocycle can be synthesised which contains phosphorus between the two chalcogen atoms.<sup>(24)</sup> This reaction, using a tin centre, is similar to that shown in equation 1.29, the difference being that a phosphorus dichloride is used to reform the metal dichloride rather than a group 16 dichloride. This is shown clearly in equation 1.30.



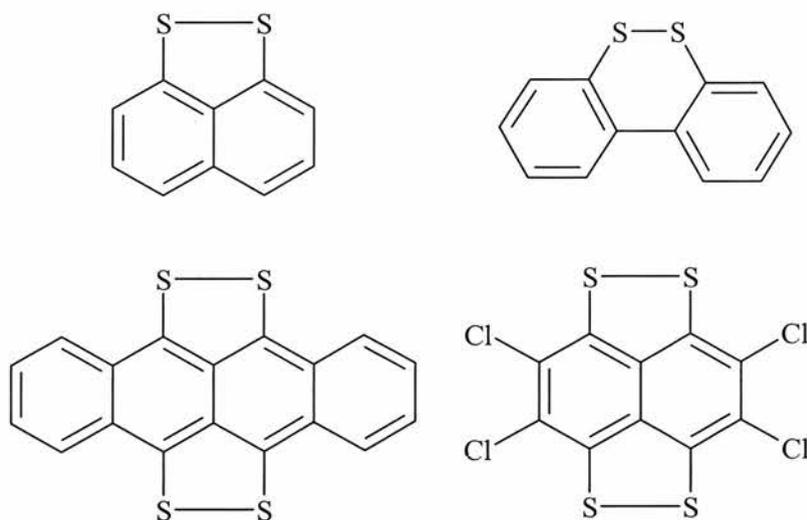
Examples are known for various R groups and also for sulfur sulfur, sulfur selenium and selenium selenium combinations of chalcogens in the five-membered ring.

Zirconium, which is in the same group as titanium, can be used to produce novel heterocyclic compounds where two selenium atoms are bridged by a phosphorus or carbon atom.<sup>(25)</sup> Again, this reaction is driven by the formation of the metal dichloride (equation 1.31).



### 1.3 CYCLIC, AROMATIC DISULFANES

The polysulfane compounds which are of particular interest in this thesis are the cyclic aromatic disulfanes, two of the most important examples being naphtho[1,8-*cd*]-1,2-dithiole and dibenzo[*ce*]-1,2-dithiine (figure 1.3). Other prime examples of this class of compound which have been extensively studied include tetrathiotetracene (TTT) and tetrachlorotetrathionaphthalene (TCTTN).



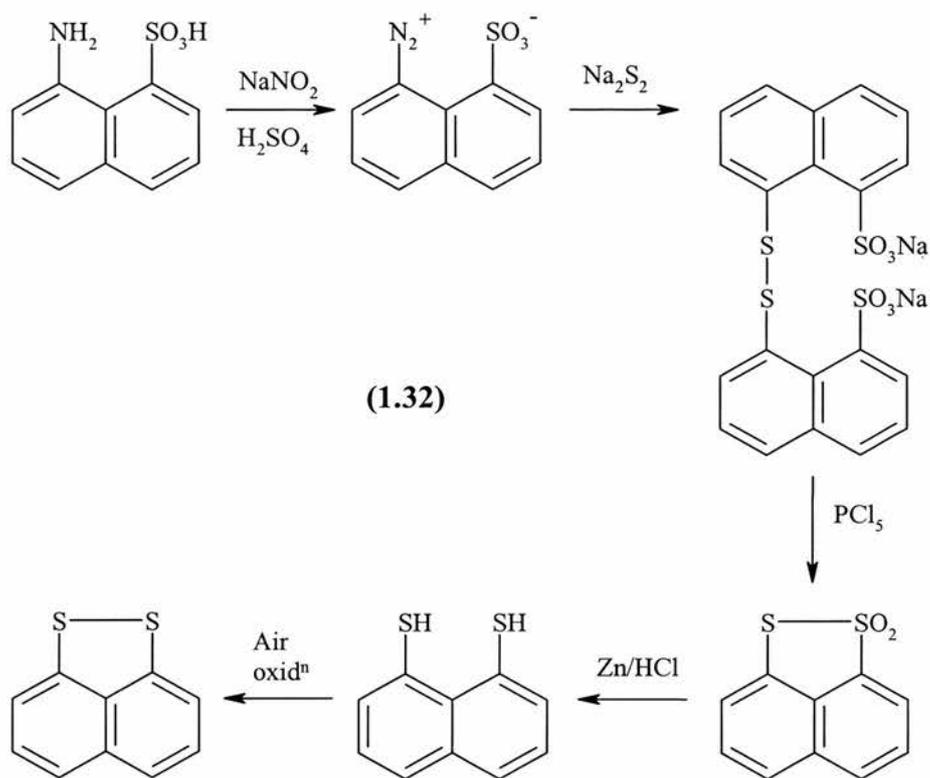
**Figure 1.3** Naphtho[1,8-*cd*]-1,2-dithiole (top left), dibenzo[*ce*]-1,2-dithiine (top right), TTT (bottom left) and TCTTN (bottom right).

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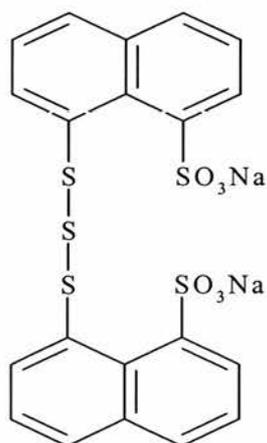
These compounds are interesting due to the extensive  $\pi$  delocalisation of the aromatic electrons. The introduction of the dichalcogenide bridge lowers the first ionisation potential, resulting in materials whose cation-radical salts are stable at room temperature and which crystallise in linear chain arrays. <sup>(26)</sup> The result is that they can then be used as donor molecules with acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) to give highly conducting ion-radical solids with a uniform segregated stack crystal structure <sup>(27)</sup> with potentially useful electrical, magnetic and optical properties. <sup>(28, 29)</sup>

The resulting complexes between most donor and acceptor molecules are usually in the ratio 1:1 although it is known that TCNQ complexes favour a composition rich in acceptors while the 2,5-dimethyl and 2,5-dimethoxy derivatives of TCNQ favour a composition rich in donor molecules. <sup>(30)</sup> This then affects their electrical conductivities, which can range from 8 to  $10^{-9}$  S cm<sup>-1</sup> depending on the combination of donor and acceptor molecules.

Naphtho[1,8-*cd*]-1,2-dithiole, one of the most important compounds in this thesis, was originally prepared by Price and Smiles. <sup>(31)</sup> This method was later improved upon by Zweig and Hoffman <sup>(32)</sup> and is shown in equation 1.32.



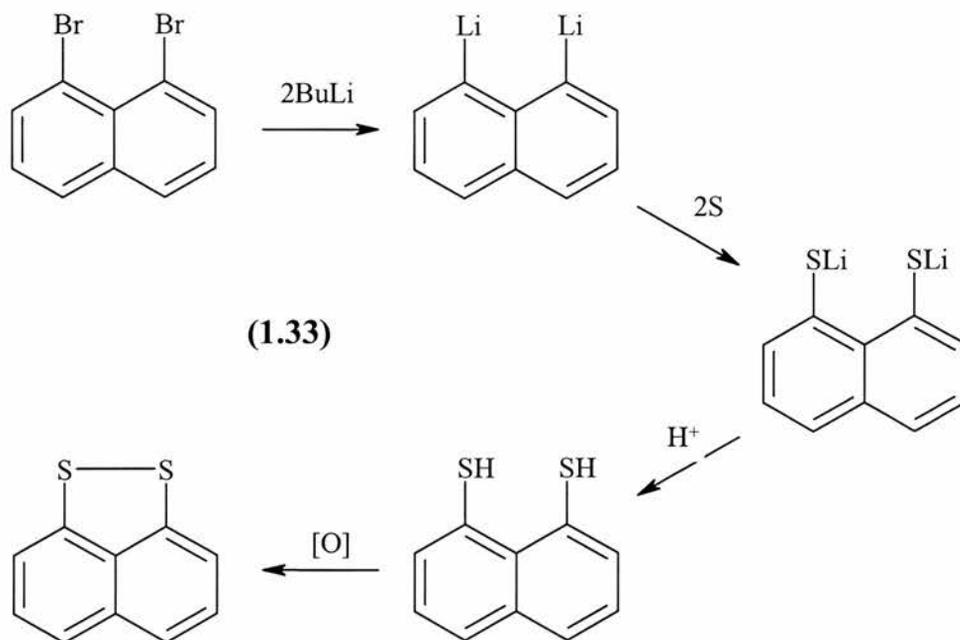
Since this synthesis was first reported, the yield has been greatly increased by a modification<sup>(33)</sup> whereby the diazonium salt was reacted with  $\text{Na}_2\text{S}_3$  rather than  $\text{Na}_2\text{S}_2$ . This leads to the formation of a trisulfide disulfonic acid (figure 1.4) rather than the disulfide disulfonic acid. Refluxing the disodium salt of the trisulfide disulfonic acid in thionyl chloride then yields the naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide.



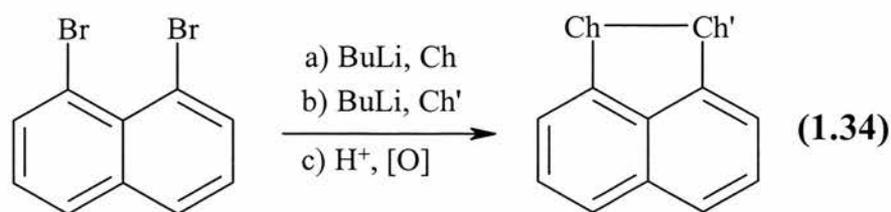
**Figure 1.4**

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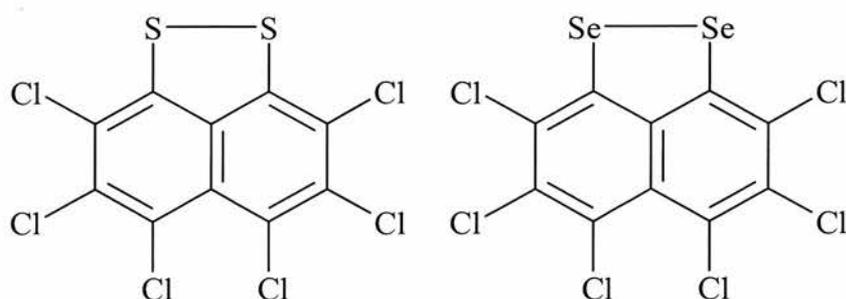
A much simpler method for synthesis of naphtho[1,8-*cd*]-1,2-dithiole was later developed by Meinwald *et al.* <sup>(34)</sup> This method (equation 1.33) involves less steps and milder conditions.



This method also yielded the selenium and tellurium analogues (by addition of the corresponding elemental chalcogen to the 1,8-dilithio species), although these were formed in lesser yield. It later emerged <sup>(35)</sup> that a mixed chalcogen product could be obtained by addition of 1 equivalent of BuLi and 1 equivalent of the first chalcogen, followed by another equivalent of BuLi and 1 equivalent of the second chalcogen. Work up was the same, acidification followed by air oxidation to form the dichalcogen bridge (equation 1.34). In each case, the yield, plus the identity of any by-products, was dependent on the order in which the two chalcogens were added.

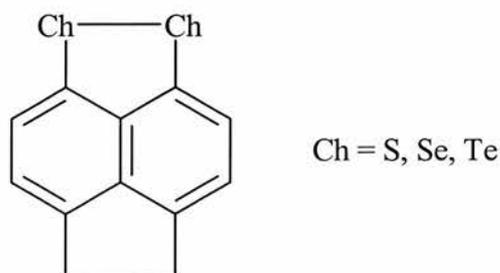


The per-chlorinated equivalents of naphtho[1,8-*cd*]-1,2-dithiole and naphtho[1,8-*cd*]-1,2-diselenole are also known (figure 1.5).<sup>(36)</sup> These are prepared by reacting octachloronaphthalene with a solution of  $\text{Na}_2\text{S}_2$  or elemental selenium respectively, although the conditions required to produce the selenium analogue are particularly harsh. However, in each case the yield was good.



**Figure 1.5**

Another naphthalene based example where the sulfur, selenium and tellurium derivatives are all known is 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenole (figure 1.6).<sup>(37)</sup>

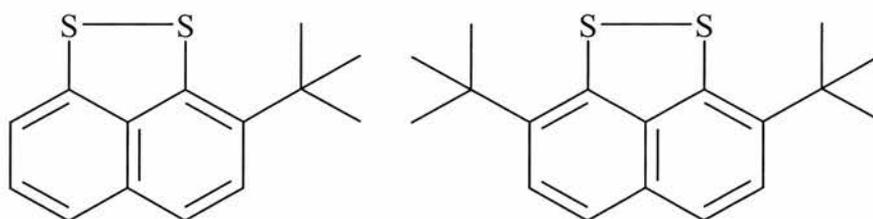


**Figure 1.6**

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The dithiole is prepared along similar methods to that described for naphtho[1,8-*cd*]-1,2-dithiole (equation 1.33). Acenaphthene is brominated and then lithiated at the 5 and 6 positions with butyl lithium. Elemental sulfur is added and work up is achieved by acidification followed by air oxidation to yield the final product. The same procedure with the addition of elemental selenium yields the diselenole but the di-tellurole cannot be obtained by adding elemental tellurium to the di-lithiated species. Instead, acenaphthene must be chlorinated with sulfuryl chloride in the presence of aluminium chloride and the resulting product reacted with  $\text{Na}_2\text{Te}_2$  in HMPA. In each of the three cases, the yield never exceeds 17%. However, these compounds were found to be useful as they can act as electron donors for low dimensional molecular complexes as their donor characteristics are markedly enhanced compared with the dichalcogen bridged naphthalenes mentioned earlier.

Other derivatives with a naphthalene based backbone are also of great interest to this thesis, two good examples being the sterically hindered compounds 2-(tert-butyl)naphtho[1,8-*cd*]-1,2-dithiole and 2,7-di(tert-butyl)naphtho[1,8-*cd*]-1,2-dithiole which can be seen in figure 1.7.

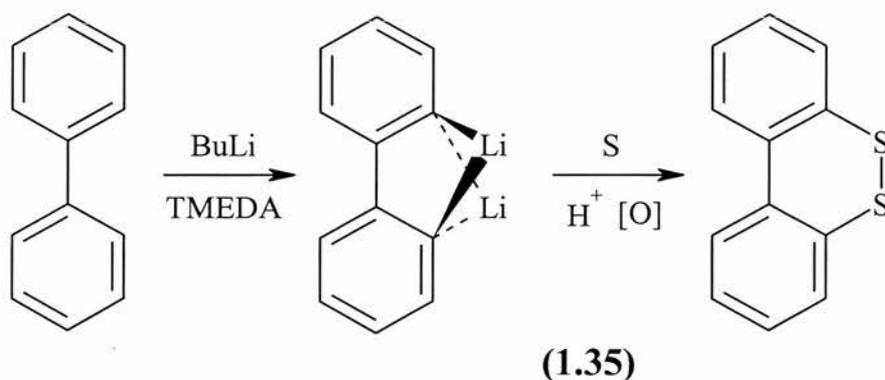


**Figure 1.7**

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These are actually prepared from naphtho[1,8-*cd*]-1,2-dithiole, which is reacted with tert-butyl chloride in the presence of aluminium chloride. <sup>(38)</sup> Both products are formed and can easily be separated by size-exclusion chromatography.

As mentioned previously the other class of compounds which are of interest are the biphenyl backboned disulfides, for example dibenzo[*ce*]-1,2-dithiine. This was originally prepared by Barber and Smiles in 1928 <sup>(39)</sup> but this method was very complicated and involved a number of steps including a coupling reaction of 2-iodobenzenesulfonate. This method was later refined by Atkinson *et al.*, <sup>(40)</sup> Armarego and Turner <sup>(41)</sup> and finally Chau and Kice <sup>(42)</sup> but in each case the general idea was the same. Cossu *et al.* <sup>(43)</sup> later demonstrated a new method which involved less steps and a greater yield. This method, as seen in equation 1.35, involves the di-lithiation of biphenyl (stabilised by chelation with TMEDA) followed by addition of elemental sulfur and work up and is actually similar to the method described earlier for synthesis of naphtho[1,8-*cd*]-1,2-dithiole.

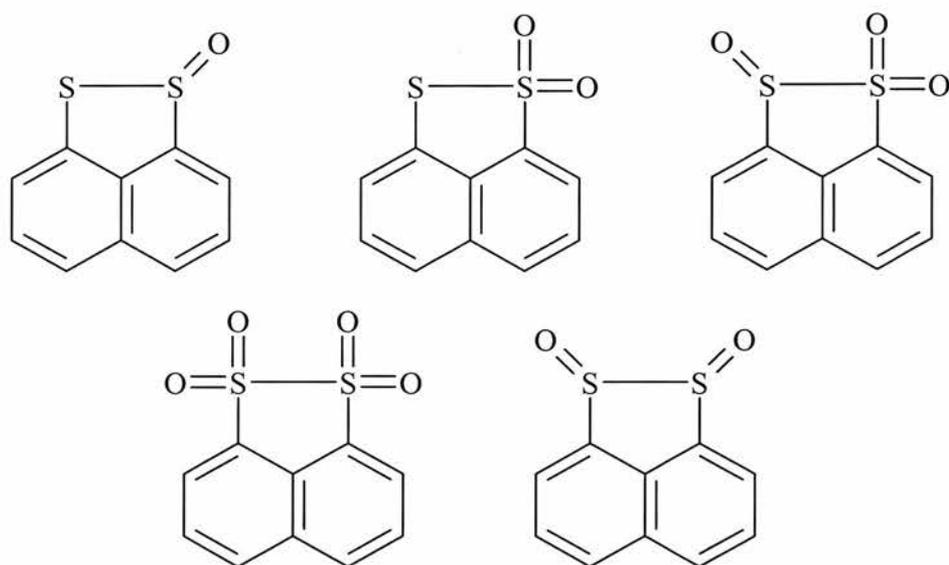


The di-selenium analogue dibenzo[*ce*]-1,2-diselenin is also known <sup>(44-47)</sup> but so far there is no evidence of the di-tellurium analogue or of any mixed examples.

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## 1.4 OXIDISED DERIVATIVES

So far we have only discussed examples where the chalcogen atom, predominantly sulfur, is not oxidised and only has a co-ordination number of 2. However, examples of polysulfane compounds are known where the sulfur atoms are bonded to one or two oxygen atoms. Some of the most well known examples, which are of high importance to this thesis, are the oxides of naphtho[1,8-*cd*]-1,2-dithiole (figure 1.8). Indeed, this compound is also known with one, two, three and four oxygen atoms bound to the two sulfur atoms. Naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide is the easiest of the four compounds to synthesise and is actually a pre-cursor in the synthesis of naphtho[1,8-*cd*]-1,2-dithiole as shown in equation 1.32 and is easily isolated.<sup>(32)</sup>



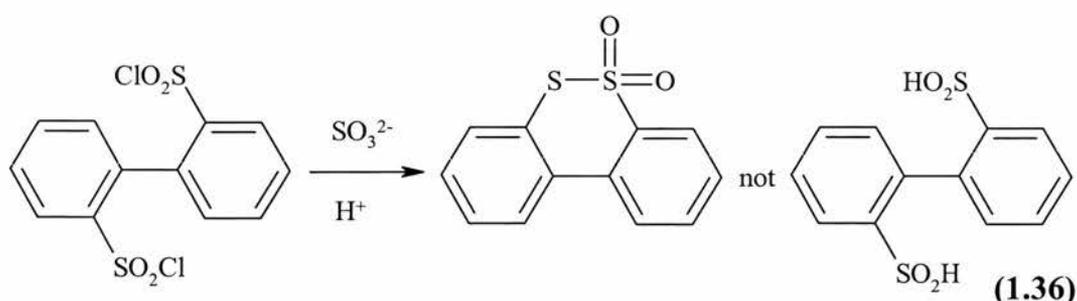
**Figure 1.8** Possible oxides of naphtho[1,8-*cd*]-1,2-dithiole.

Naphtho[1,8-*cd*]-1,2-dithiole 1-oxide is readily prepared by oxidising naphtho[1,8-*cd*]-1,2-dithiole with *m*-chloroperoxybenzoic acid (MCPBA) followed by purification by column chromatography.<sup>(48)</sup> Naphtho[1,8-*cd*]-1,2-

dithiole 1,1,2-trioxide is prepared by converting the previously mentioned dioxide to a sodium salt and then acidifying to yield the trioxide <sup>(42)</sup> while the tetroxide is prepared by treating the dioxide with MCPBA. <sup>(49)</sup>

Although it is possible for one of the sulfur atoms to be bonded to only one oxygen atom (*ie* with a co-ordination number of 4), for example naphtho[1,8-*cd*]-1,2-dithiole 1-oxide or 1,1,2-trioxide, nobody has ever been able to synthesise a sample of the 1,2-dioxide (the final structure of figure 1.8).

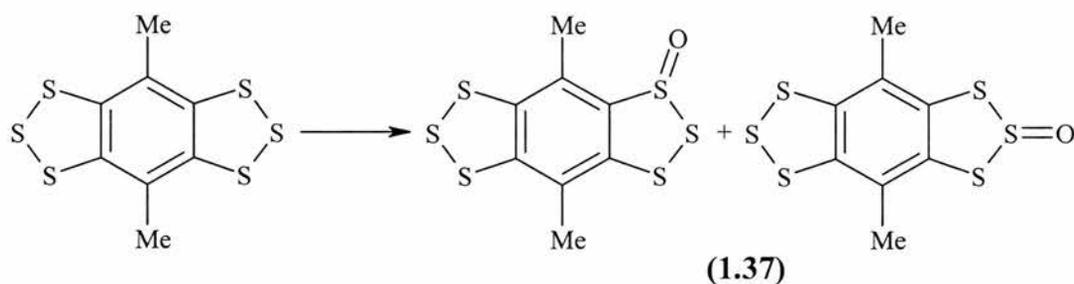
Oxides of dibenzo[*ce*]-1,2-dithiine are also known. Like naphtho[1,8-*cd*]-1,2-dithiole, the mono-, di-, tri- and tetroxide are known but the example where both sulfur atoms have only one oxygen atom bound to them is not known. Dibenzo[*ce*]-1,2-dithiine 1-oxide, 1,1,2-trioxide and 1,1,2,2-tetroxide are prepared by analogous reactions to their naphthalene backboned counterparts, but dibenzo[*ce*]-1,2-dithiine 1,1-dioxide is not a precursor of dibenzo[*ce*]-1,2-dithiine and was actually discovered by accident when diphenyl 2,2'-disulfonyl chloride was reduced with sulfite and then acidified in an attempt to synthesise diphenyl-2,2'-disulfonic acid as shown in equation 1.36. <sup>(39)</sup>



Other examples of oxidation of the sulfur atoms in a polysulfane bridge are also known. For example, the tri-sulfane bridge of 4,8-dimethylbenzobistrithiole can

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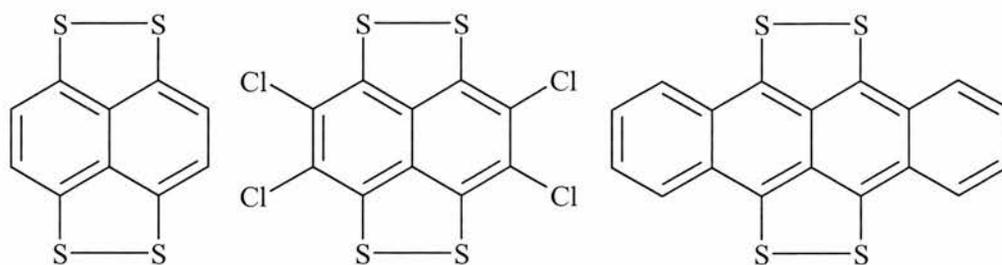
be oxidised with MCPBA to yield two products, the 1-oxide and the 2-oxide (equation 1.37).<sup>(50)</sup>



These two products are also obtained when N-bromosuccinimide and N-iodosuccinimide were used as the oxidising agent but in each case the ratio of the two products were greatly different.

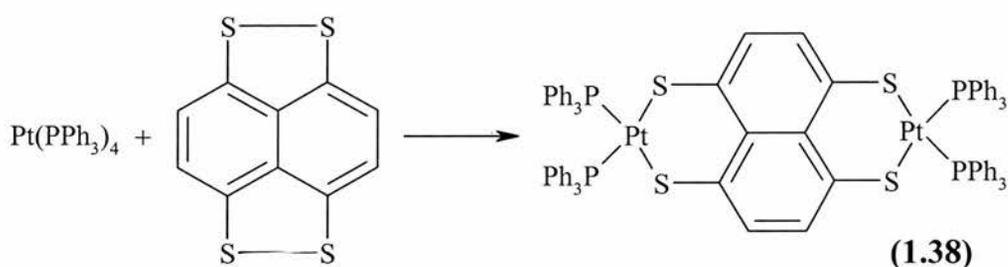
### 1.5 TRANSITION METAL COMPLEXES OF AROMATIC DISULFANES

Our interest in the naphthalene and biphenyl backboned disulfides and their oxidised derivatives lies in their co-ordination chemistry, the oxides being particularly interesting as they offer two different possible points of co-ordination, namely the hard oxygen atoms or the soft sulfur atoms. This co-ordination chemistry has been largely overlooked with a few notable exceptions on the co-ordination chemistry of naphtho[1,8-*cd*]-1,2-dithiole and its structurally similar compounds tetrathionaphthalene (TTN), tetrachlorotetrathionaphthalene (TCTTN) and tetrathiotetracene (TTT) to a variety of low-valent metal substrates (figure 1.9).



**Figure 1.9** Structures of TTN, TCTTN and TTT.

Most of this work on TTN, TCTTN and TTT has been carried out by Teo and co-workers. For example, all three of these compounds have been bound to platinum in an oxidative addition reaction with  $\text{Pt}(\text{PPh}_3)_4$  to give a dimeric complex with a bridging tetrathiolene ligand (equation 1.38) <sup>(51, 52)</sup> and the X-ray crystal structures of these complexes have been determined. <sup>(53)</sup>

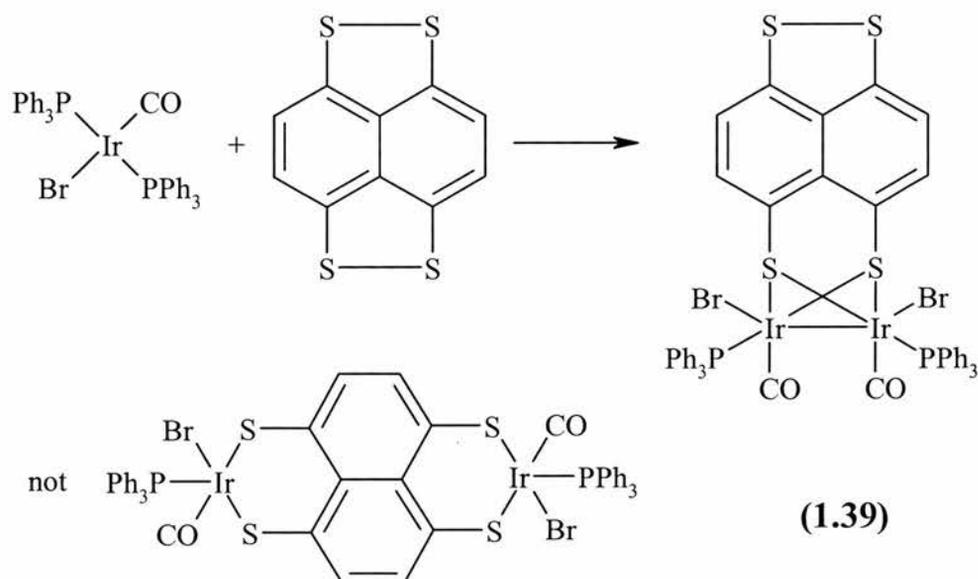


This oxidative addition chemistry to  $\text{Pt}(0)$  has been exploited by us and is covered in great detail in chapter 3.

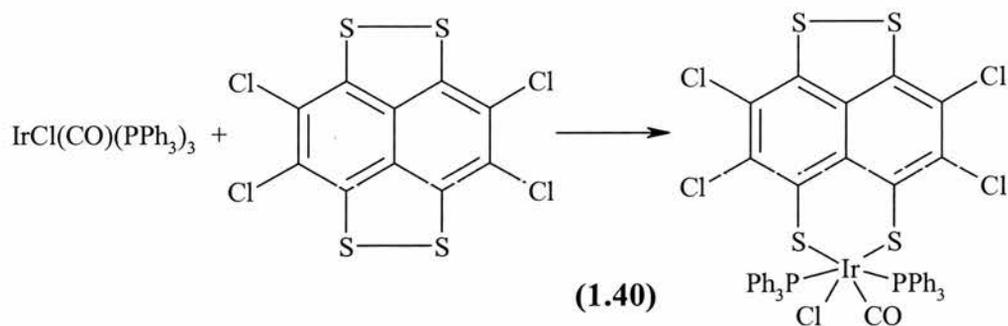
Another metal whose co-ordination chemistry to these compounds has been extensively studied is iridium. Initially the reaction of two equivalents of *trans*- $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Br}$  to TTN was studied <sup>(54)</sup> in attempt to synthesise a similar planar dimeric complex using the molecule of TTN as a bridging ligand. However, this was found to give a complex where one of the dithiolato groups was bound to both iridium atoms (which also contained an iridium-iridium bond) by an

oxidative addition reaction while the other dithiolato group remained unchanged.

This chemistry can be seen more clearly in equation 1.39.



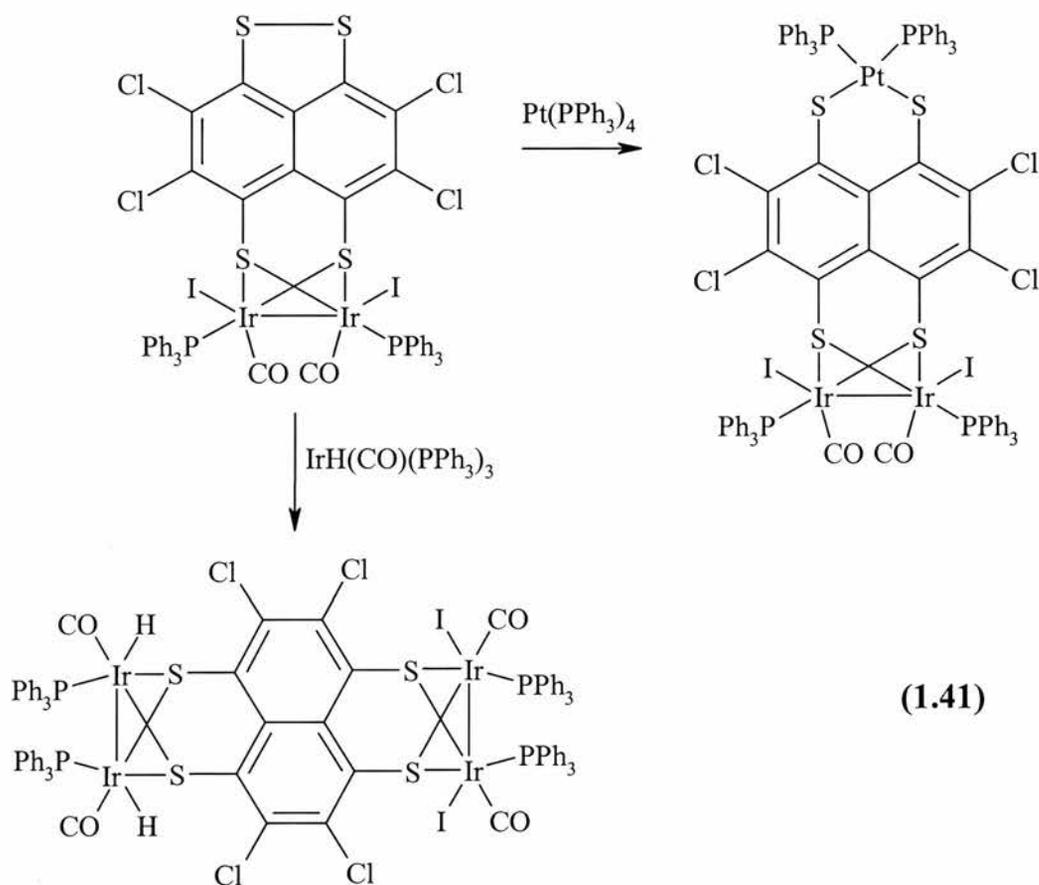
A monomeric iridium complex was also produced by the reaction of TCTTN with one equivalent of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_3$  (equation 1.40)<sup>(55)</sup> and its X-ray crystal structure was determined.<sup>(56)</sup> This reaction was carried out in the presence of a small amount of  $\text{PPh}_3$  to prevent dimerisation as described in equation 1.39.



The dimeric iridium complex shown in equation 1.39 was also used to give a tetrameric iridium complex by reaction with a further two equivalents of  $\text{IrH}(\text{CO})(\text{PPh}_3)_3$  and also a novel complex where the previously untouched

dithiolato moiety undergoes oxidative addition to platinum(0) to give a hetero tri-metallic complex (equation 1.41).

Again, we have taken this iridium chemistry further and the results are comprehensively presented in chapter 4.



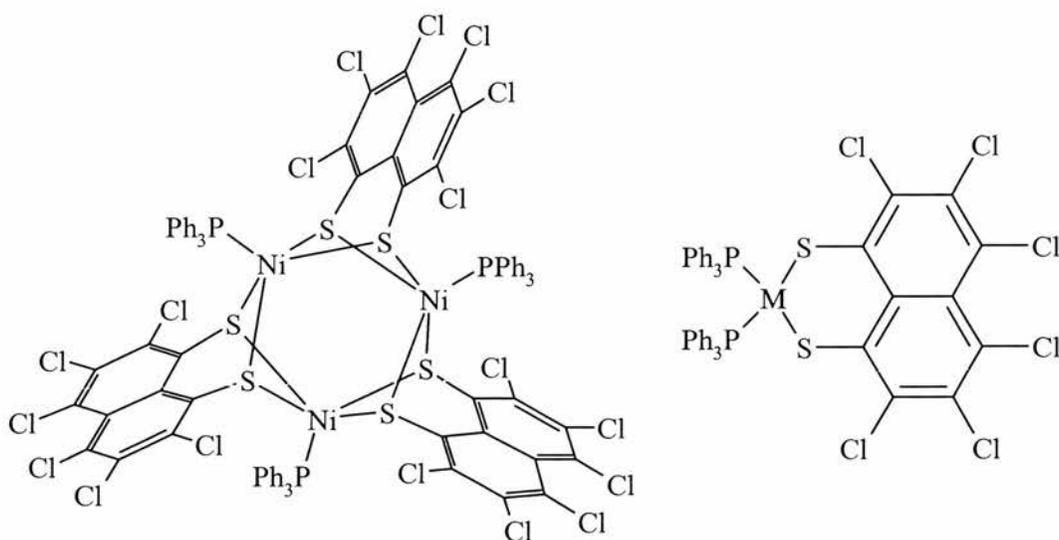
Other important co-ordination studies include that of TTN with  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}_2(\text{CO})_8$  and  $\text{Fe}_2(\text{CO})_9$ <sup>(57)</sup> to give a pair of inorganic semiconductors in the case of nickel and cobalt and an interesting homo tetra-metallic iron complex respectively (figure 1.10). The inorganic semiconductors were found to be linear polymeric structures of general formula  $\dots\text{Ni TTN Ni TTN}\dots$  and  $\dots\text{Co}_2(\text{CO})_2 \text{TTN Co}_2(\text{CO})_2 \text{TTN}\dots$



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reaction under very mild conditions leaving one of the two ligands bound to the Fe centre by a carbon atom rather than a sulfur atom, which is the case for all the other metal ligand bonds. Also, this complex is found to contain only an iron iron single bond rather than the expected double bond. The nickel and cobalt containing complexes are more conventional and contain the expected metal metal single bond and no metal metal bond respectively.

Other reported examples of complexes containing the type of ligand system with only one dithiolato group include an unusual homometallic trinuclear nickel(II) complex obtained by oxidative addition of hexachlorodithionaphthalene (HCDTN) to  $\text{Ni}(\text{cod})_2$  in the presence of triphenylphosphine (figure 1.11).<sup>(59)</sup> The trimeric nature of this nickel species is in contrast to the mononuclear square planar complexes  $[\text{M}(\text{PPh}_3)_2(\text{HCDTN})]$  ( $\text{M} = \text{Pt}$  or  $\text{Pd}$ ) which were obtained by reaction of  $\text{M}(\text{PPh}_3)_4$  with the same ligand and are much more closely related to those di-platinum complexes shown in equation 1.38.

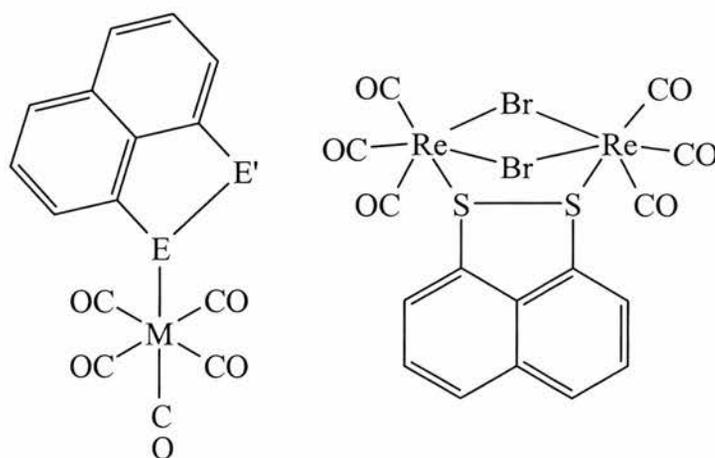


**Figure 1.11**

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Oligomeric, dimeric and monomeric zinc complexes with no co-ligands, or with pyridine or neocuprin as co-ligands, have recently been reported using sterically crowded and electron poor naphthalene-1,8-dithiolate ligands. <sup>(38)</sup>

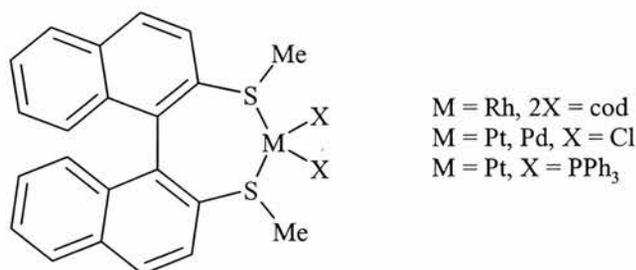
Other complexes where the chalcogen chalcogen bond remains unbroken have recently been described. For example, a series of group 6 pentacarbonyl systems bearing monodentate naphtho[1,8-*cd*]-1,2-dichalcogenole ligands (M = Cr or Mo, E and E' = S or Se) <sup>(60)</sup> are known as is a binuclear Re(I) carbonyl complex with bridging bromides and a naphtho[1,8-*cd*]-1,2-dithiole ligand (figure 1.12).



**Figure 1.12**

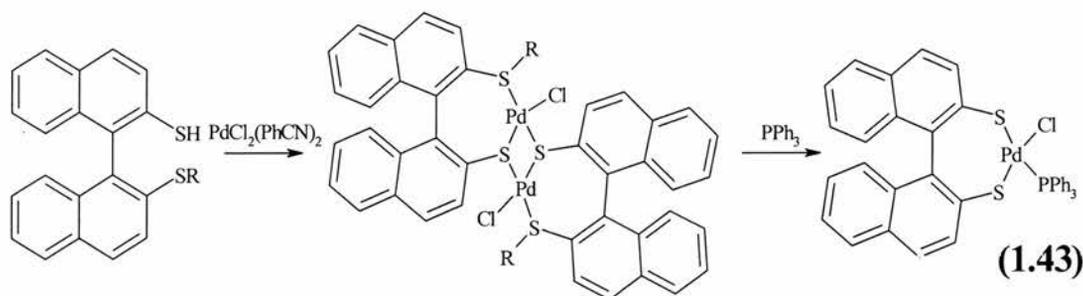
The co-ordination chemistry of dibenzo[*ce*]-1,2-dithiine and its structurally related compounds has also been largely overlooked. A number of complexes have been prepared containing the structurally related ligand 1,1'-binaphthalene-2,2'-dithiol but in each case these have been formed in straight forward metathesis reactions. In many of these reactions the purpose has been to develop complexes for catalytic reactions such as the regioselective hydroformylation of styrene <sup>(61)</sup> *eg.* by reaction of the dithiol with  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2$  to give a rhodium dimer with a bridging disulfide ligand. Complexes containing the ligand

4,4-biphenanthrene-3,3'-dithiol have also been shown to react with carbon monoxide <sup>(62, 63)</sup> to give interesting dinuclear tetracarbonyl complexes and react with  $PR_3$  ( $R = Ph, C_6H_{11}, OC_6H_4Bu^t-o$ ) to give mixed ligand di- and tetra-nuclear complexes. Monomeric complexes <sup>(64, 65)</sup> which are formed from the related thioether ligand are known, as seen in figure 1.13.



**Figure 1.13**

Ruiz has also produced an interesting palladium dimer complex using the mixed thiol-thioether derivative <sup>(66)</sup> which was shown to convert to a monomer on addition of triphenylphosphine (equation 1.43).



While these examples contain structurally similar ligands, a limited number of complexes containing the biphenyl dithiolate ligand are known. A derivatised version of dibenzo[*ce*]-1,2-dithiine has been used as a tetravalent ligand bound to

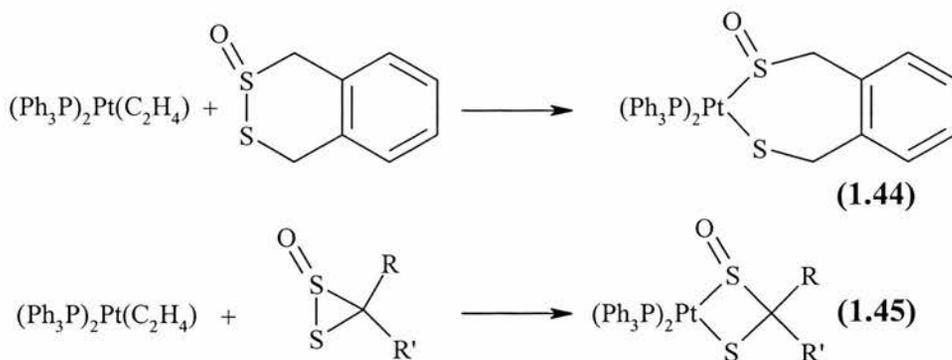
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copper <sup>(67)</sup> and a molybdenum complex <sup>(68)</sup> containing two biphenyl dithiolate ligands in a distorted square planar like complex with a molybdenum oxygen triple bond are also known. Mono- and di-nuclear nickel complexes have also been reported. <sup>(69)</sup>

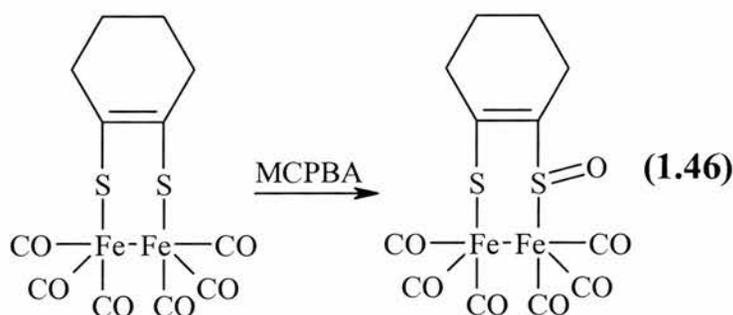
Rauchfuss <sup>(70)</sup> reported the synthesis of titanocene 2,2'-dithiolato biphenyl by ring opening of dibenzothiophene with lithium metal followed by addition of sulfur and titanocene dichloride giving the final product from a salt elimination reaction.

## 1.6 METAL COMPLEXES WITH SULFENATO/SULFINATO LIGANDS

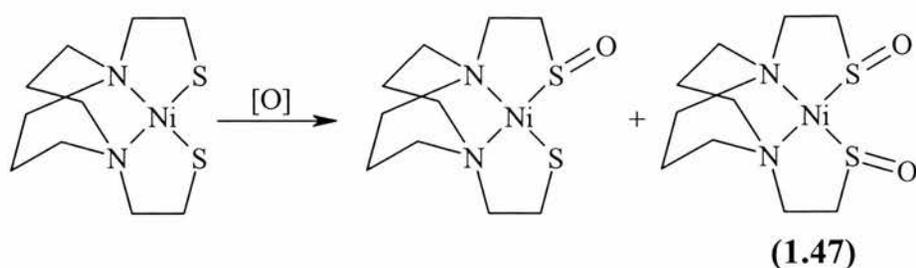
The previously discussed metal complexes (section 1.5) have all involved naphtho[1,8-*cd*]-1,2-dichalcogenoles and their structurally similar compounds as ligands. However, there are no examples in the literature of naphthalene-1,8 mixed thiolato-sulfenato (-S-M-S(=O)-), thiolato-sulfinato (-S-M-S(=O)<sub>2</sub>-), sulfenato-sulfinato (-(O=)S-M-S(=O)<sub>2</sub>-) or disulfinato (-(O=)<sub>2</sub>S-M-S(=O)<sub>2</sub>-) metal complexes, *ie* with the various oxides described in figure 1.8. In fact, transition metal complexes of sulfenato (-S(=O)R) or sulfinato (-S(=O)<sub>2</sub>R) are extremely rare in comparison to the vast number of known thiolate complexes. Of those that are known only the mixed thiolato-sulfenato have been obtained by oxidative addition reactions and examples of this seem to be limited to reactions of Pt(0) precursors with cyclic thiosulfinates prepared by Weigand and co-workers <sup>(71-77)</sup> and dithiirane 1-oxides (equations 1.44 and 1.45 respectively). <sup>(78)</sup>



Thiolato-sulfenato (-S-M-S(=O)-) complexes have also been prepared through the mono-oxidation of dithiolate complexes. One of the best examples of such reaction is the oxidation of a series of di-iron carbonyl compounds containing bridging 1,2-ethanesulfenatothiolato and 1,2-cyclohexylsulfenatothiolato ligands (equation 1.46).<sup>(79, 80)</sup>

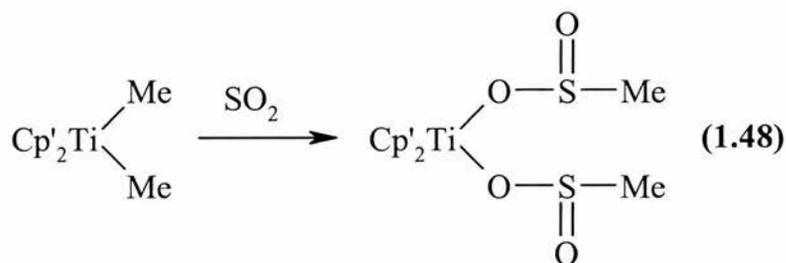


This preparative method has also been utilised by Darensbourg and co-workers who have prepared a series of thiolato-sulfenato, disulfenato, thiolato-sulfinato, sulfenato-sulfinato and disulfinato complexes of nickel(II) and palladium(II) from bis(2-mercaptoethyl)-1,5-diazacyclooctane-M(II) (M = Ni, Pd), equation 1.47, and N,N'-bis(2-methyl-2-mercaptoethyl)-1,5-diazacyclooctane-Ni(II) by oxidation with MCPBA or H<sub>2</sub>O<sub>2</sub>.<sup>(81-85)</sup>



There are several more examples of thiolato-sulfenato, thiolato-sulfinato and disulfinato complexes of nickel, <sup>(86)</sup> rhodium, <sup>(87)</sup> platinum <sup>(88, 89)</sup> and palladium <sup>(90, 91)</sup> prepared from oxidation of the parent thiolato complex.

An interesting disulfinato complex which is bound to the metal by oxygen rather than sulfur has also been reported where the metal is titanium. <sup>(92)</sup> In this case, a titanocene complex with two organic ligands is reacted with sulfur dioxide, the result being SO<sub>2</sub> insertion into the titanium carbon bond, as shown in equation 1.48. The final complex is unsurprisingly O bound to the metal since titanium is a hard metal and will preferentially bind to oxygen rather than sulfur when given the choice.



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## 1.7 AIMS

The aims of this thesis are to study the co-ordination chemistry of a series of aromatic backboned disulfide compounds. The principal ligands of choice are naphthalene and biphenyl backboned as these have differing properties in terms of rigidity of the backbone and how rigidly the two sulfur atoms are held in place. Further to this, they have a variable in terms of the ring size, the two sulfur atoms of naphtho[1,8-*cd*]-1,2-dithiole being in a five membered ring and those of dibenzo[*ce*]-1,2-dithiine being part of a six membered ring.

The hard soft mismatch between sulfur and oxygen is a very interesting and important consideration and this thesis aims to investigate this, by studying the co-ordination chemistry of a number of oxides of the previously mentioned ligands. These ligands are ambidentate and therefore hard (titanium) and soft (platinum and iridium) metals are chosen. These metals are also chosen as they will provide us with a chance to study a variety of different geometries around the metal centre, since these titanium complexes ( $d^4$ ) are expected to adopt a tetrahedral geometry while the platinum ( $d^8$ ) and iridium ( $d^7$ ) complexes should adopt square planar and octahedral geometries respectively.

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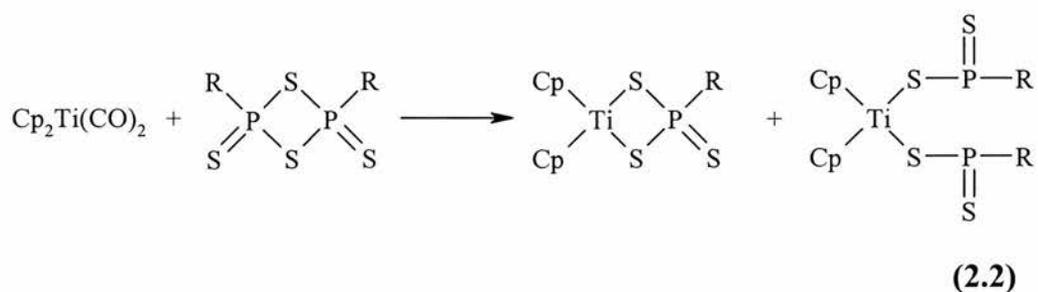
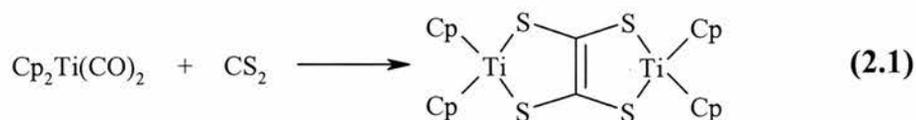
## CHAPTER 2. THE GROUP IV CHEMISTRY OF NAPHTHO[1,8-*cd*]-1,2-DITHIOLE, DIBENZO[*ce*]-1,2- DITHIINE AND THEIR OXIDISED DERIVATIVES

### 2.1 Introduction

Thiolato complexes containing the  $\text{Cp}_2\text{Ti}$  group ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) have long been known and are of considerable interest to synthetic inorganic chemists. These complexes can take a number of different forms where the two sulfur bearing groups can be unconnected ( $\text{Cp}_2\text{Ti}(\text{SR})_2$ ), attached to each other by an organic group ( $\text{Cp}_2\text{TiS}_2\text{X}$ , X = bridging group) or attached to each other by a chain of x sulfur atoms ( $\text{Cp}_2\text{TiS}_{2+x}$ ). Examples of these complexes include  $\text{Cp}_2\text{Ti}(\text{SMe})_2$ ,<sup>(93)</sup>  $\text{Cp}_2\text{TiS}_2\text{C}_6\text{H}_4$ <sup>(94)</sup> and  $\text{Cp}_2\text{TiS}_5$ .<sup>(95)</sup>

There are a variety of different ways in which these complexes can be prepared. The early methods involved the substitution reaction of a thiolate anion with titanocene dichloride ( $\text{Cp}_2\text{TiCl}_2$ , Ti(IV)) in which the chloride ligands are removed by nucleophilic displacement. An example of this is the reaction of titanocene dichloride with two molar equivalents of NaSMe which yields  $\text{Cp}_2\text{Ti}(\text{SMe})_2$  in excellent yield.<sup>(93)</sup> More recently, the air sensitive complex titanocene dicarbonyl [ $\text{Cp}_2\text{Ti}(\text{CO})_2$ , Ti(II)] has been used. In this case, the reaction involves an oxidative addition reaction with a disulfide (RSSR) where the sulfur sulfur bond is cleaved and the  $\text{Cp}_2\text{Ti}$  unit is inserted between the two sulfur atoms to yield a new complex,  $\text{Cp}_2\text{Ti}(\text{SR})_2$ , accompanied by the evolution of two equivalents of carbon monoxide.<sup>(96)</sup> This is a very effective method for

producing compounds such as these and even carbon disulfide<sup>(97)</sup> and Lawesson's reagent<sup>(98)</sup> can be reduced by titanocene dicarbonyl to give the following products (equations 2.1 and 2.2 respectively).



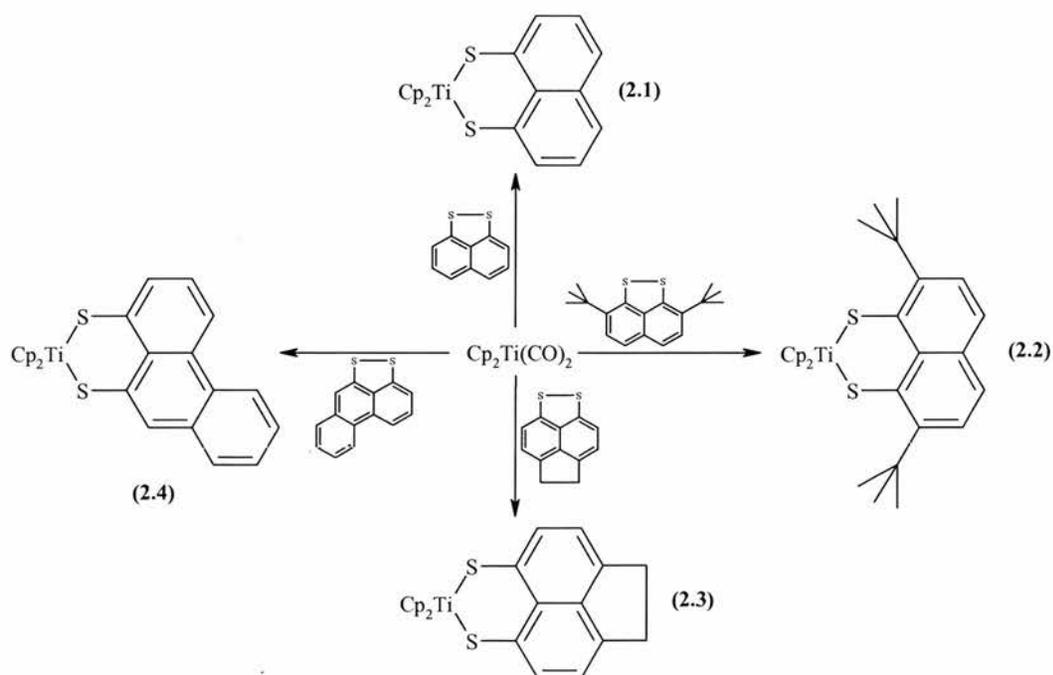
These titanocene complexes are useful in further reactions as they can be used as ligand transfer reagents with chlorine containing compounds. These reactions proceed as the thermodynamically favourable complex  $\text{Cp}_2\text{TiCl}_2$  is formed along with a new compound. For example a novel allotrope of sulfur, cycloheptasulfur, was developed by reaction of  $\text{Cp}_2\text{TiS}_5$  with disulfur dichloride.<sup>(15)</sup> Other examples are also known, such as exchange with a platinum dichloride complex to yield novel platinum dithiolato complexes.<sup>(99)</sup>

In this chapter, we have studied the insertion of the  $\text{Cp}_2\text{Ti}$  group into the sulfur-sulfur bond of a variety of disulfide compounds whose two sulfur atoms are members of a ring, the ring being completed by members of an aromatic backbone. As previously mentioned in chapter 1, the backbones of primary interest are naphthalene (a very rigid backbone which can rock backwards and forwards in an envelope conformation along the S-S axis) and biphenyl (which is

twisted along the C2-C2' axis and has no opportunity to move further). We have also used a variety of similar compounds whose sulfur atoms have been mono- and di-oxidised in an attempt to find out what this effect has on the final complex. Complexes such as these have been reported but they have never before been prepared by the insertion of the Cp<sub>2</sub>Ti unit into the sulfur-sulfur bond but rather by the insertion of SO<sub>2</sub> into the titanium-carbon bond of Cp<sub>2</sub>TiR<sub>2</sub>.  
(92)

## 2.2 Results and discussion

The titanium (IV) complexes **2.1-2.4** were prepared by the oxidative addition reaction of titanocene dicarbonyl [Ti(II)] with one molar equivalent of the corresponding disulfide pro-ligand in toluene at room temperature (Scheme 2.1).



**Scheme 2.1** Oxidative addition reactions of disulfide pro-ligands to titanium species.

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In each case, the pro-ligand was prepared by literature methods. Two equivalents of carbon monoxide were evolved resulting in the oxidative addition of the Cp<sub>2</sub>Ti unit into the sulfur sulfur bond, resulting in a new complex with a greater ring size being formed. These complexes were formed in varying yields (19-80%) and were found to be air stable in both the solid state and in solution.

The <sup>1</sup>H NMR spectrum of **2.1** displays a multiplet in the aromatic region and a broad singlet at 6.31 ppm in the intensity ratio 6:10. These peaks can be assigned to the 6 aromatic naphthalene protons and the 10 cyclopentadienyl protons respectively. This shows that the two cyclopentadienyl groups are in identical environments. The <sup>13</sup>C NMR spectrum was as expected with the three non-quaternary aromatic carbons of the naphthalene group being obvious along with two of the three quaternary carbons. Further to this, the peak representing the carbons of the cyclopentadienyl groups was noticed at 114.9 ppm. Microanalysis was satisfactory and the mass spectrum displayed the parent ion as expected at *m/z* 368 ([M]<sup>+</sup>).

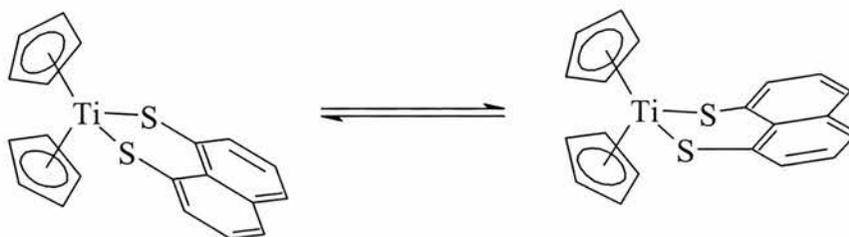
Complexes **2.2-2.4** have similar <sup>1</sup>H and <sup>13</sup>C NMR spectra to that of **2.1**. They all display the expected peaks for the aromatic backbone. However, while **2.2** and **2.4** showed the expected singlet for the two equivalent cyclopentadienyl groups in the <sup>1</sup>H NMR at 6.28 and 6.31 ppm respectively, **2.3** displays a broad doublet in the range 6.8-6.0 ppm which has the correct intensity to be attributed to these groups. This suggests that while the other three complexes have the cyclopentadienyl groups in equal environments, complex **2.3** has its two cyclopentadienyl groups in unequivalent environments. In each case the

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microanalysis suggests that these complexes are pure and the parent ion is seen in the mass spectra at  $m/z$  480, 394 and 418 respectively.

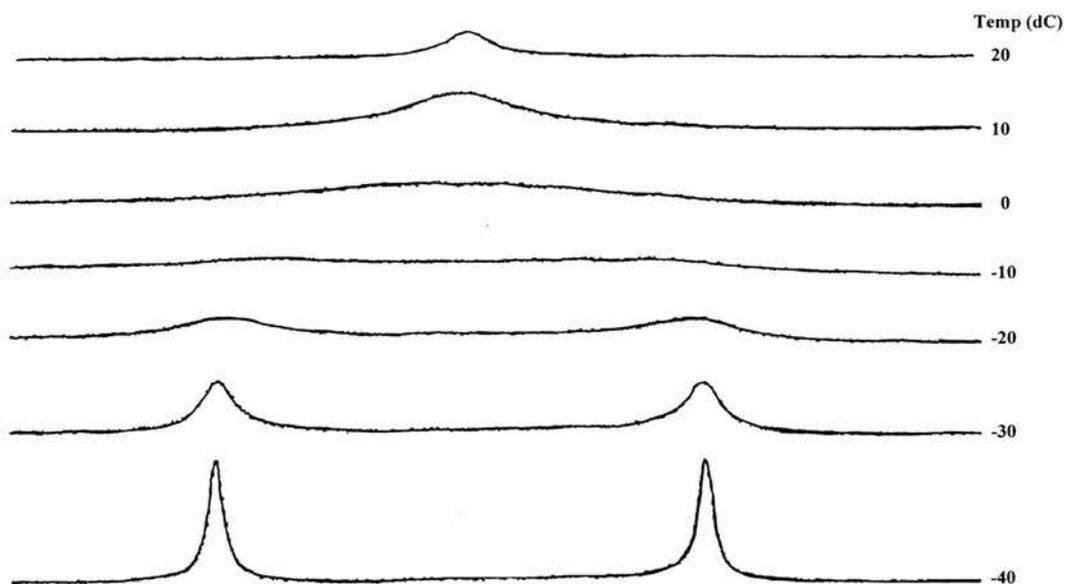
Similar titanocene complexes containing a disulfide ligand where the two sulfur atoms are connected by a rigid aromatic backbone have previously been shown to exhibit interesting temperature dependant  $^1\text{H}$  NMR spectra due to the fluxionality of the aromatic backbone. <sup>(100, 101)</sup> In these particular cases it was discovered that inversion of the chelate ring along the S-S axis occurs.

In the dynamic  $^1\text{H}$  NMR spectrum of **2.1**, the singlet due to the ten equivalent cyclopentadienyl protons at room temperature was subject to a coalescence phenomenon at a lower temperature and was split into two sharp singlets of equal intensity below room temperature which is compatible with ring inversion (scheme 2.2).



**Scheme 2.2** Ring inversion of titanium complex **2.1**.

This was also noticed in the dynamic  $^1\text{H}$  NMR spectra of **2.2-2.4** (the NMR spectra of complex **2.4** is shown in graph 2.1).



**Graph 2.1** Dynamic <sup>1</sup>H NMR spectra of complex **2.4**.

In the case of complex **2.3**, the broad doublet coalesced into a sharp singlet at higher temperature. The <sup>1</sup>H NMR spectrum of **2.2** displayed a broadening of the singlet as the temperature was reduced but two sharp equivalent singlets were not seen as low as 183K, the lowest temperature it was possible to go to before the NMR solvent froze, although it is believed that this would have happened had it possible to reduce the temperature further. The activation parameters of the chelate ring inversion of **2.1-2.4** were calculated and all necessary data are shown in Table 2.1.

Complex	$\delta$ (Cp) (ppm)	$T_{\text{cal}}$ (K)	$\Delta_{\text{v}}$ (Hz)	$\Delta G_{\text{c}}^*$ (kJ mol <sup>-1</sup> )
<b>2.1</b>	6.31	285	144.2	56.0
<b>2.2</b>	6.28	<183	-	-
<b>2.3</b>	5.90	303	60.9	61.9
<b>2.4</b>	6.31	268	148.9	52.5

**Table 2.1** The activation parameters of the chelate ring inversions of complexes

**2.1-2.4** (all NMR spectra were recorded at 270 MHz in CD<sub>2</sub>Cl<sub>2</sub>).

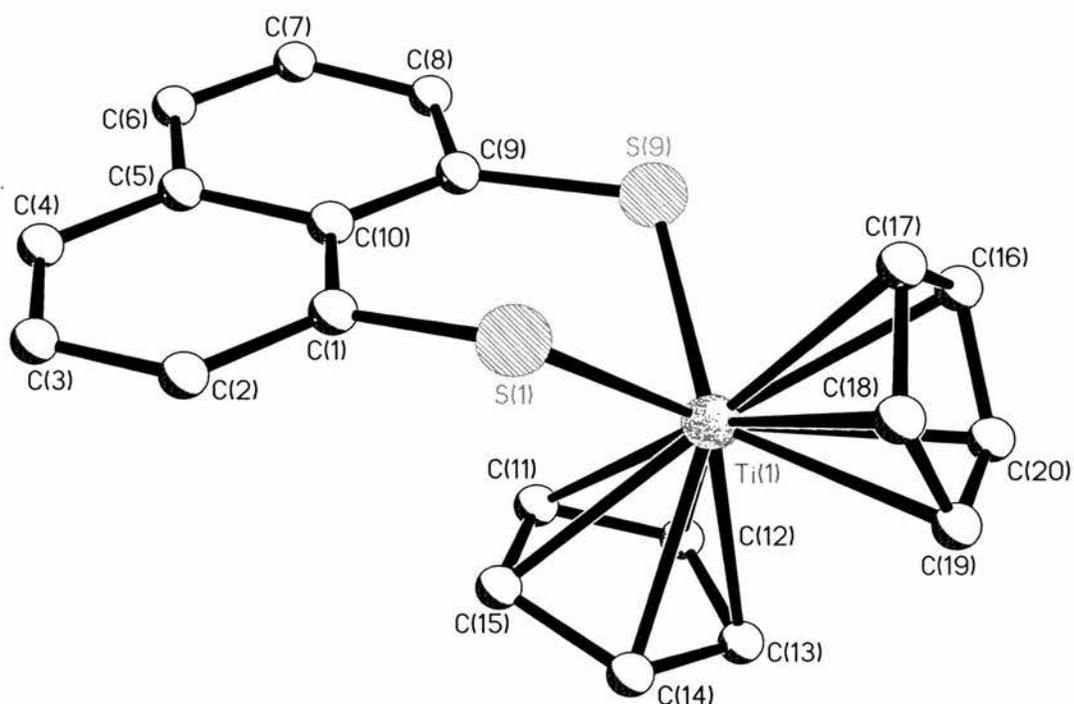
The value for  $\Delta G_{\text{c}}^*$  was calculated using Equation 2.3 where T is the temperature of coalescence of the two singlets into one peak (in Kelvin) and  $K_{\text{c}} = 2.22 \Delta V_{\text{c}}$ , where  $V_{\text{c}}$  is the gap between the two singlets at absence of exchange (in Hertz).

$$\Delta G_{\text{c}}^* = 8.314 T (23.760 + \ln T - \ln K_{\text{c}}) \quad \text{Equation 2.3}$$

Previously studied similar complexes which display this fluxionality in the backbone of the dithio ligand have yielded results close to these.<sup>(100, 101)</sup> While we cannot be sure of the exact  $\Delta G_{\text{c}}^*$  of complex **2.2**, the other values fall in the range 51 – 62 kJmol<sup>-1</sup>. There is no obvious trend such as the activation energy being proportional to the size of the group which is bridging the two sulfur atoms. This suggests that the activation energy is therefore probably influenced more by electronic effects than by steric effects.

The X-ray crystal structures of **2.1** and **2.3** show that the inequivalence of the two cyclopentadienyl groups occurs in the solid state of these four complexes

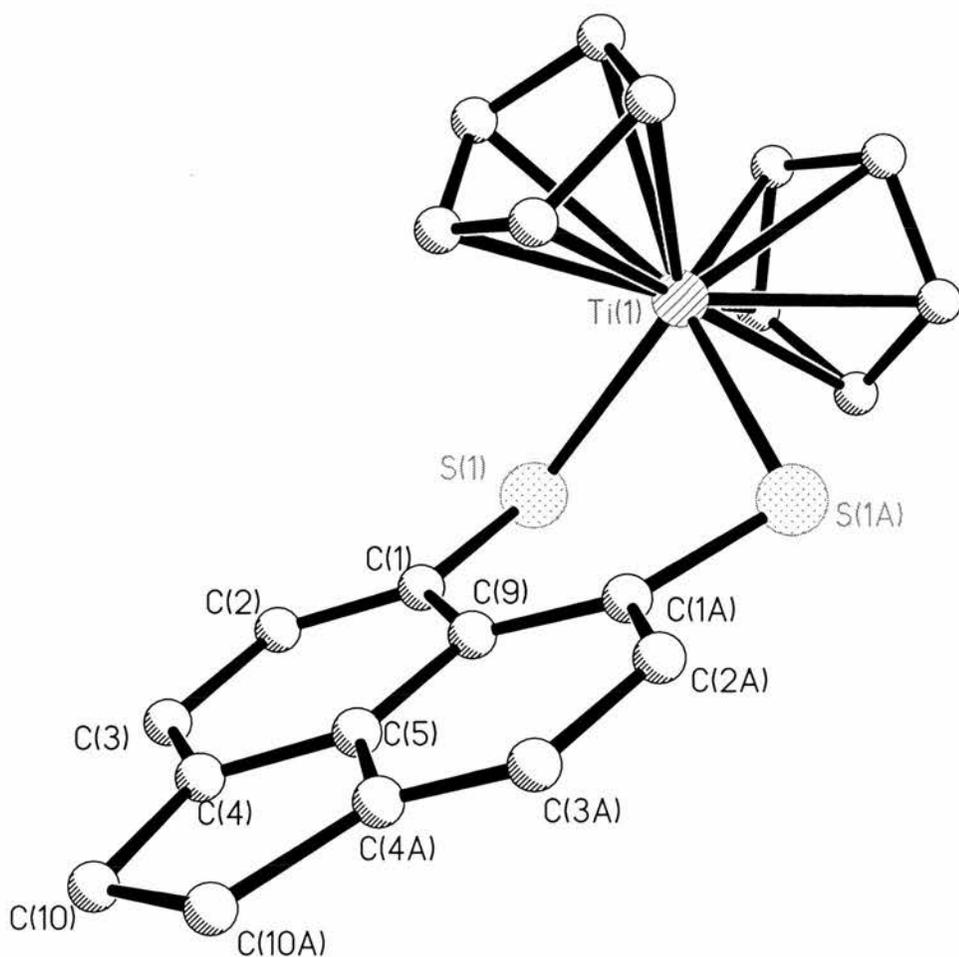
(Figures 2.1 and 2.2). Selected bond lengths and bond angles are also given (tables 2.2 and 2.3).



**Figure 2.1** Crystal structure of  $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{10}\text{H}_6)$  **2.1**.

Ti(1)-S(1)	2.3875(9)	S(1)-Ti(1)-S(9)	84.29(3)
Ti(1)-S(9)	2.3874(10)	Ti(1)-S(1)-C(1)	105.68(10)
Ti(1)-Cp(1)	2.371(3)-2.402(3)	Ti(1)-S(9)-C(9)	111.25(11)
Ti(1)-Cp(2)	2.356(3)-2.395(3)	S(1)-C(1)-C(10)	125.3(2)
S(1)-C(1)	1.774(3)	C(1)-C(10)-C(9)	126.7(3)
S(9)-C(9)	1.761(3)	S(9)-C(9)-C(10)	126.9(2)
C(1)-C(10)	1.457(4)	Splay angle	18.9
C(9)-C(10)	1.437(4)	C(4)-C(5)-C(10)-C(1)	-5.4(4)
		C(4)-C(5)-C(10)-C(9)	175.0(3)

**Table 2.2** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{10}\text{H}_6)$  **2.1**.



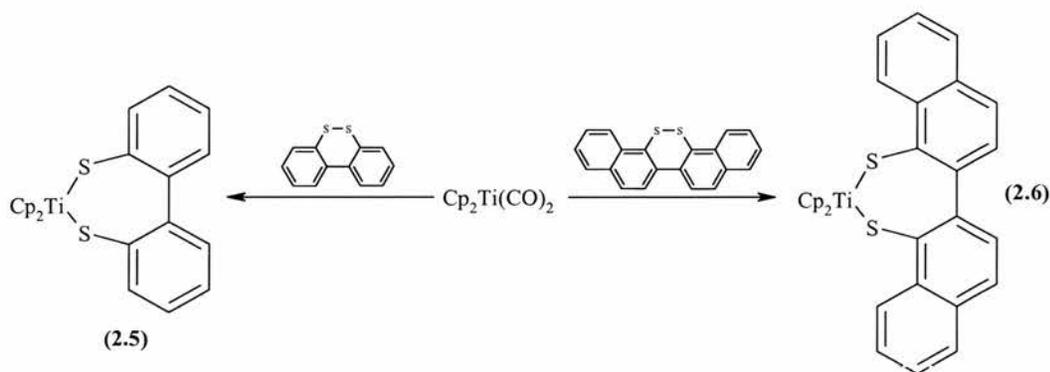
**Figure 2.2** Crystal structure of  $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{12}\text{H}_8)$  **2.3**.

Ti(1)-S(1)	2.4026(11)	S(1)-Ti(1)-S(1A)	84.80(5)
Ti(1)-Cp(1)	2.359(3)-2.376(3)	Ti(1)-S(1)-C(1)	107.64(7)
Ti(1)-Cp(2)	2.345(4)-2.386(4)	S(1)-C(1)-C(9)	125.2(2)
S(1)-C(1)	1.772(3)	C(1)-C(9)-C(1A)	129.6(4)
C(1)-C(9)	1.442(3)	Splay angle	20
		C(4)-C(5)-C(9)-C(1)	-0.1(6)
		C(4)-C(5)-C(9)-C(1A)	178.4(3)

**Table 2.3** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{12}\text{H}_8)$  **2.3**.

The Ti-S bond distances of **2.1** and **2.3** (2.3875(9) and 2.4026(11)Å respectively) closely resemble those of other related complexes.<sup>(21, 22, 93)</sup> The S(1)-C(1) bond lengths are similar to that of the pro-ligand, naphtho-[1,8-*cd*]-1,2-dithiole,<sup>(102)</sup> while the main difference between the pro-ligand and these complexes is the splay angle (the deviation from the two S-C bonds being parallel). The pro-ligand has a negative splay angle (-11.21°) due to the sulfur sulfur bond pulling the two atoms together. The two complexes however have positive splay angles (18.9° and 20.0° respectively) and this can be attributed to the absence of the sulfur sulfur bond and the insertion of the metal centre between the two sulfur atoms. This allows the two atoms to move further apart into a more comfortable position as it alleviates any strain which would have previously been present in the five membered ring.

The similar titanocene complexes **2.5** and **2.6** were synthesised in an identical manner to that described earlier for **2.1-2.4** (Scheme 2.3).



**Scheme 2.3** Oxidative addition reactions of disulfide pro-ligands to titanium species.

The <sup>1</sup>H NMR spectrum of complex **2.5** showed four sets of peaks in the aromatic region, each of equal intensity, corresponding to the four different aromatic

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proton environments of the biphenyl ligand. A singlet at 6.17 ppm represented the 10 cyclopentadienyl protons, showing that both groups were in an identical environment. The  $^{13}\text{C}$  NMR spectrum was as expected with two quaternary and four non-quaternary environments being identified and the cyclopentadienyl peak coming at 114.8 ppm. Again, microanalysis showed that the product was of high purity and the mass spectrum displayed the parent ion as expected at  $m/z$  394 ( $[\text{M}]^+$ ).

Similarly, complex **2.6** displays an appropriate  $^1\text{H}$  NMR spectrum. Five aromatic proton environments were observed in the relative intensity ratio of 2:2:2:4:2. These represent the 12 protons (in six different environments) of the aromatic backbone, with two of these environments overlapping and the others all being obvious on their own. A single peak at 6.14 ppm represents the 10 cyclopentadienyl protons. The  $^{13}\text{C}$  NMR shows 3 of the 4 expected quaternary peaks of the aromatic backbone and all six non-quaternary environments. A peak at 115 ppm represented the cyclopentadienyl carbons. Microanalysis proved the purity of the sample and the mass spectrum displayed the parent ion at  $m/z$  494 ( $[\text{M}]^+$ ), as expected.

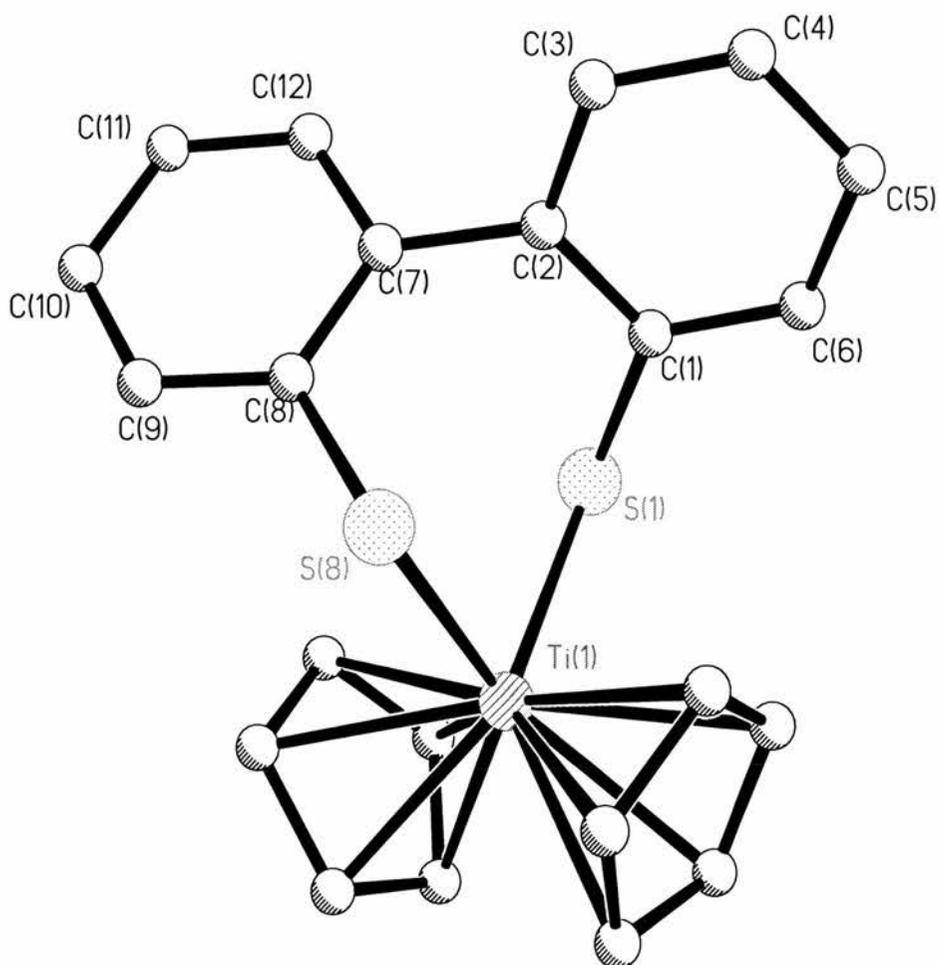
The  $^1\text{H}$  NMR spectra of **2.5** and **2.6** were recorded at lower temperature since the peaks representing the 10 cyclopentadienyl protons were singlets at a chemical shift close to that of complexes **2.1-2.4**. This was expected to show fluxionality like the previously discussed complexes and split into two sharp singlets of equal intensity. However, the peaks did not split, or indeed even broaden, at temperatures as low as 183 K. This suggests that there was no fluxionality in these complexes and that the ligand is held rigidly in place directly between the two cyclopentadienyl groups, causing them to be in similar environments at all

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times, even in solution. This was supported by X-ray crystallography which showed that the two phenyl rings of the backbone of **2.5** (or naphthalene rings of **2.6**) are twisted and held rigidly in place, being unable to flip back and forward like other examples and giving the complex a rotational axis of symmetry through the centre of the C(2)-C(7) bond and centre of the Ti atom (figures 2.3 and 2.4). Selected bond lengths and bond angles are also given (tables 2.4 and 2.5).

The crystal structures of **2.5** and **2.6** show the Ti-S bond distances [2.427(5)–2.442(5)Å] are very close to the Ti-S bond distances in complexes **2.1** and **2.3**. The S-C bond lengths are also very similar to those of the corresponding pro-ligands dibenzo[*ce*]-1,2-dithiine,<sup>(103)</sup> and 13,14-dithia-picene<sup>(104)</sup> and of other complexes **2.1** and **2.3**.

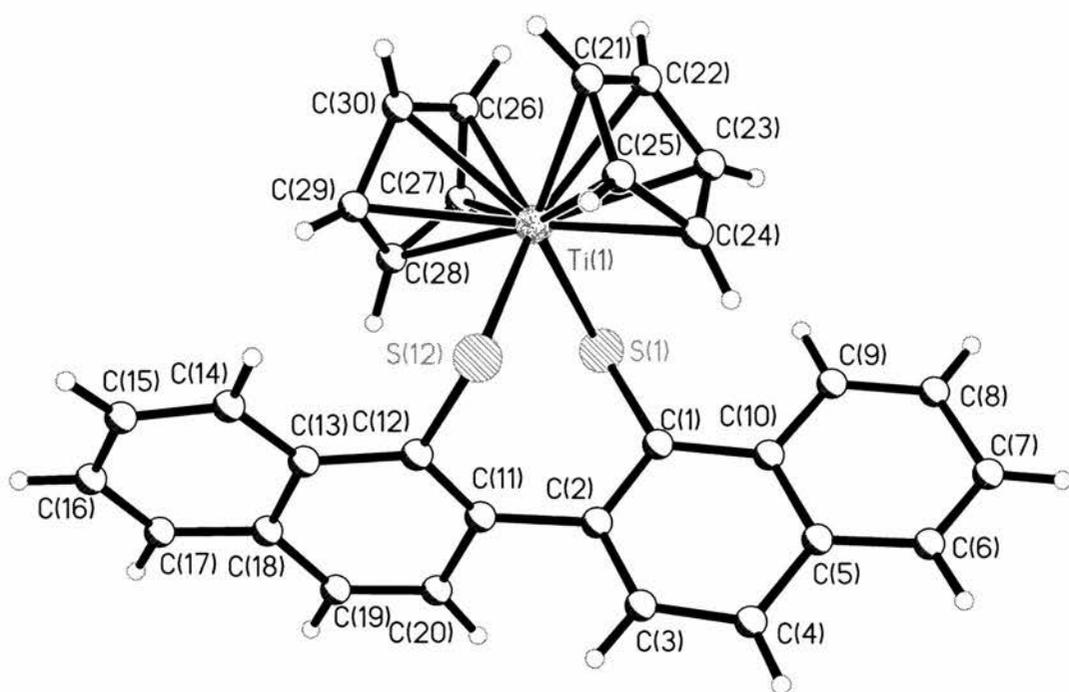
The S-Ti-S bond angles of complexes **2.5** and **2.6** [91.79(6) and 91.55(17)Å respectively] are greater than in titanocene 1,8-dithiolato naphthalene and titanocene 1,8-dithiolato-5,6-dihydroacenaphthalene but this is to be expected as they are part of a seven-membered ring instead of a six-membered ring in the case of the naphthalene complexes. The S-C-C angles are very similar to the S-C-C angles of the pro-ligands. This is unusual as the free ligands contain a six-membered ring and the insertion of the titanium atom between the two sulfur atoms should theoretically open up the S-C-C bond angles.



**Figure 2.3** Crystal structure of  $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{12}\text{H}_8)$  **2.5**.

Ti(1)-S(1)	2.428(3)	S(1)-Ti(1)-S(8)	91.79(6)
Ti(1)-S(8)	2.429(3)	Ti(1)-S(1)-C(1)	105.9(2)
Ti(1)-Cp(1)	2.357(6) – 2.412(6)	Ti(1)-S(8)-C(8)	105.02(19)
Ti(1)-Cp(2)	2.352(6) – 2.411(6)	S(1)-C(1)-C(2)	119.0(4)
S(1)-C(1)	1.782(6)	S(8)-C(8)-C(7)	118.6(4)
S(8)-C(8)	1.779(6)	C(1)-C(2)-C(7)	122.0(5)
C(1)-C(2)	1.389(8)	C(2)-C(7)-C(8)	122.2(5)
C(2)-C(7)	1.488(9)	C(1)-C(2)-C(7)-C(12)	64.6(6)
C(7)-C(8)	1.395(8)		

**Table 2.4** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{12}\text{H}_8)$  **2.5**.

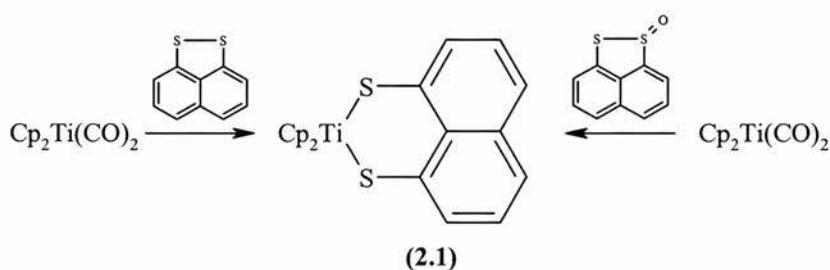


**Figure 2.4** Crystal structure of  $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{20}\text{H}_{12})$  **2.6**.

Ti(1)-S(1)	2.442(5)	S(1)-Ti(1)-S(12)	91.55(17)
Ti(1)-S(12)	2.427(5)	Ti(1)-S(1)-C(1)	106.7(6)
Ti(1)-Cp(1)	2.360(19) – 2.416(18)	Ti(1)-S(12)-C(12)	106.0(6)
Ti(1)-Cp(2)	2.372(18) – 2.405(19)	S(1)-C(1)-C(2)	119.9(12)
S(1)-C(1)	1.744(17)	S(12)-C(12)-S(11)	117.8(12)
S(12)-C(12)	1.776(17)	C(1)-C(2)-C(11)	120.0(15)
C(1)-C(2)	1.42(2)	C(2)-C(11)-C(12)	123.9(14)
C(2)-C(11)	1.52(2)	C(1)-C(2)-C(11)-C(20)	68.9(18)
C(11)-C(12)	1.35(2)		

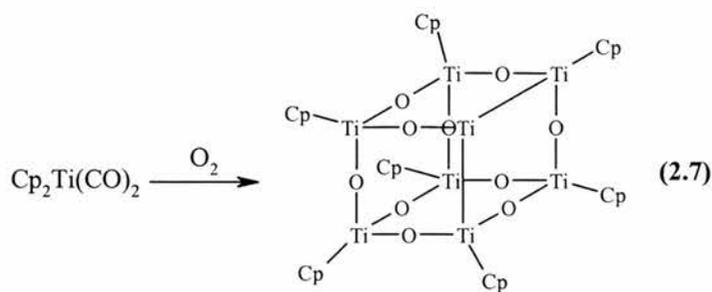
**Table 2.5** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{20}\text{H}_{12})$  **2.6**.

The reaction of titanocene dicarbonyl with the oxides of naphtho[1,8-*cd*]-1,2-dithiole yields a very interesting series of results. One equivalent of naphtho[1,8-*cd*]-1,2-dithiole-1-oxide was stirred with titanocene dicarbonyl in toluene at room temperature. Upon standard work up, the final product was found to actually be complex **2.1**. There was no evidence of any complex containing the original pro-ligand in its complete form (scheme 2.4).

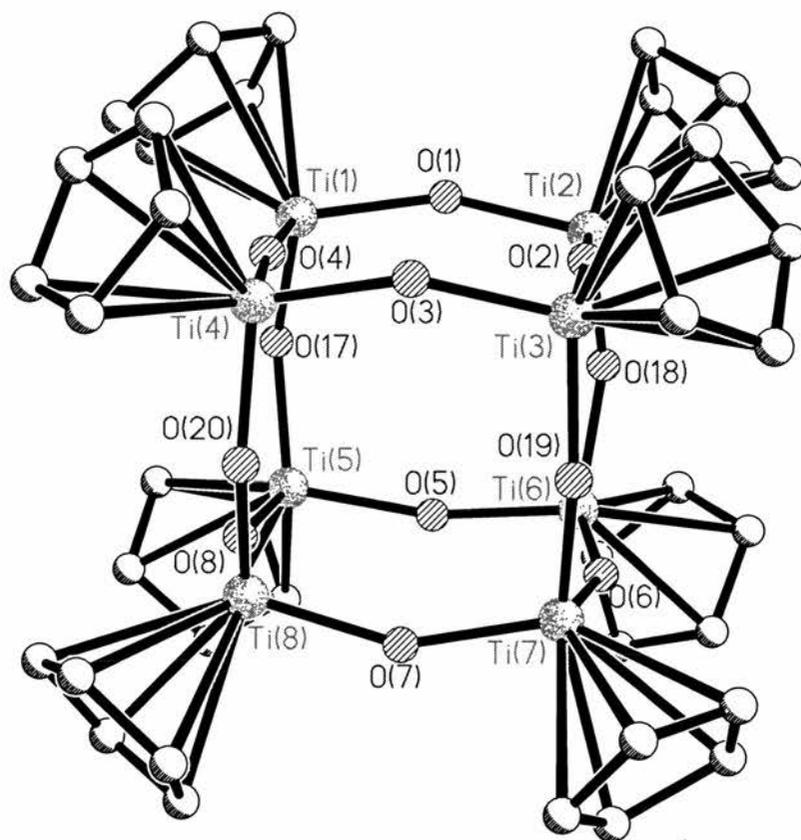


**Scheme 2.4** Synthesis of complex **2.1** using two different pro-ligands.

The loss of oxygen can most likely be attributed to the strong reducing power of Ti(II) in titanocene dicarbonyl. The oxygen which was lost appeared to stimulate the oligomerization of the air sensitive titanocene dicarbonyl as increased levels of orange insoluble solids were removed from the reaction mixture. This orange compound was characterized by X-ray crystallography and was shown to be a cubic structure with titanium at the 8 corners and the 12 edges of the cube being bridged by oxygen atoms, **2.7** (scheme 2.5). This compound has previously been seen as an acetonitrile solvated complex.<sup>(105)</sup> The X-ray crystal structure of this complex is shown in figure 2.5 and selected bond lengths and angles are given (table 2.6).



**Scheme 2.5** Synthesis of cubic titanocene compound **2.7**.

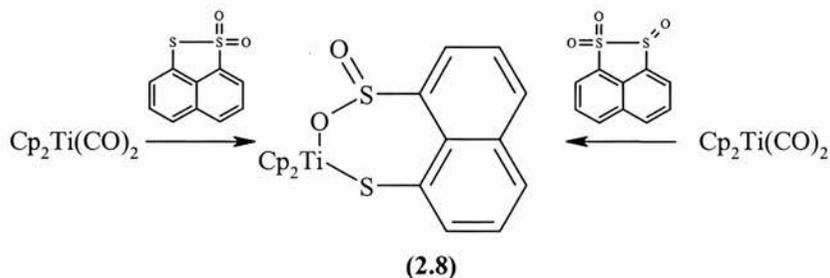


**Figure 2.5** Crystal structure of  $\text{Cp}_8\text{Ti}_8\text{O}_{12}$ , **2.7**.

Ti-O	1.794(6) - 1.829(6)	O-Ti-O	102.2(3) - 106.1(3)
Ti-C	2.359(12) - 2.431(11)	Ti-O-Ti	143.2(4) - 173.3(4)

**Table 2.6** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for titanocene cube **2.7**.

The reaction of titanocene dicarbonyl with one molar equivalent of naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide in toluene at room temperature yielded the Ti(IV) complex **2.8** (scheme 2.6).



**Scheme 2.6** Synthesis of complex **2.8** using two different pro-ligands.

In this case the ligand was found to be bound to the metal centre by a sulfur atom and also by an oxygen atom. Evidence for this is found in the infra-red spectra, which displays the characteristic peaks of a sulfinato-O bound complex<sup>(106)</sup> at 1092 (S=O) and 811 (S-O-Ti) wavenumbers. This mode of bonding can be explained by the fact that hard titanium prefers to complex to the hard oxygen atom rather than the soft sulfur (sulfinato) atom when offered the choice between the two.

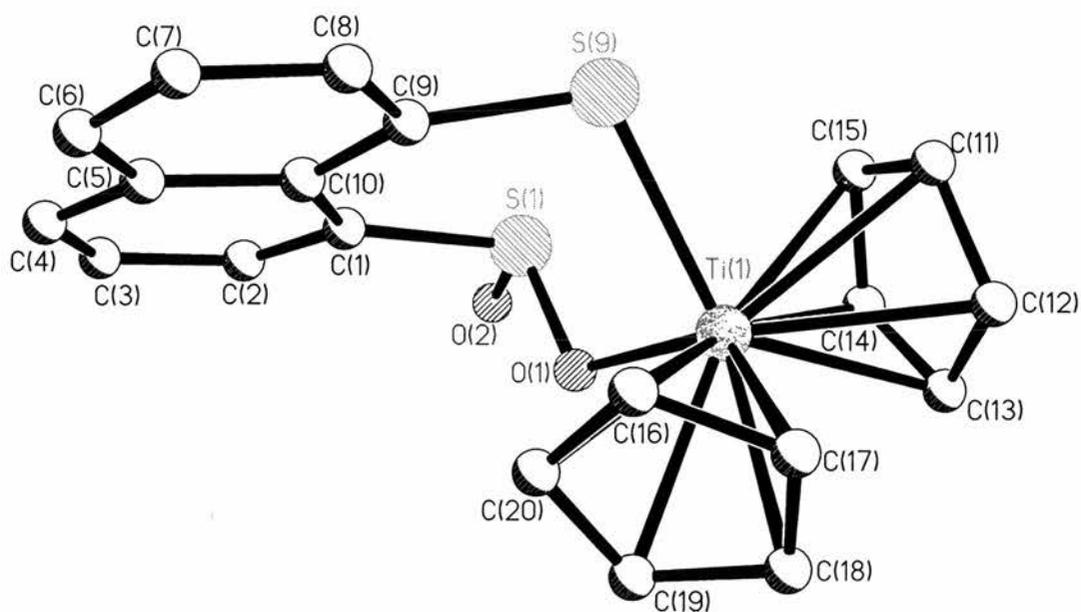
The <sup>1</sup>H NMR spectrum displays the expected peaks in the aromatic region and also a pair of singlets of equal intensity (6.52 and 5.75 ppm) which represent the two cyclopentadienyl groups, showing that these two groups are chemically inequivalent. The <sup>13</sup>C NMR was also as expected, microanalysis was satisfactory and the mass spectrum displayed the parent ion at *m/z* 401 ([M+H]<sup>+</sup>).

The two singlet peaks in the <sup>1</sup>H NMR did not merge or even broaden as the temperature at which the spectrum was measured was increased, as high as 363K

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(the maximum temperature afforded by the NMR solvent). This suggests that the two cyclopentadienyl groups are always in different chemical environments.

This hypothesis is supported by the X-ray crystal structure (figure 2.6, selected bond lengths and bond angles are given in table 2.7), which shows that the other oxygen atom (S=O) lies outwith the plane of the naphthalene ring, therefore lying closer to one of the cyclopentadienyl groups than the other. The result of this is that any backwards and forwards movement of the ligand between the two cyclopentadienyl groups (like that noticed in complexes **2.1-2.4**) will never allow these two groups to be in equivalent chemical environments and thus they will always show two separate singlets in the  $^1\text{H}$  NMR spectrum.



**Figure 2.6** Crystal structure of  $\text{Cp}_2\text{Ti}(\text{S}_2\text{O}_2\text{C}_{10}\text{H}_6)$  **2.8**.

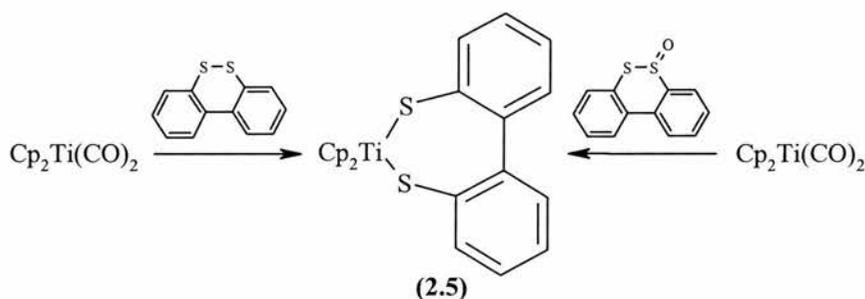
Ti(1)-S(9)	2.3920(10)	Ti(1)-S(9)-C(9)	108.49(11)
Ti(1)-Cp(1)	2.345(3)-2.402(4)	S(1)-C(1)-C(10)	126.2(2)
Ti(1)-Cp(2)	2.370(3)-2.402(4)	C(1)-C(10)-C(9)	125.9(3)
Ti(1)-O(1)	1.973(2)	S(9)-C(9)-C(10)	123.7(2)
O(1)-S(1)	1.582(2)	Splay angle	15.8
S(1)-O(2)	1.480(2)	O(1)-Ti(1)-S(9)	89.36(7)
S(1)-C(1)	1.836(3)	Ti(1)-O(1)-S(1)	119.09(12)
S(9)-C(9)	1.771(3)	O(1)-S(1)-O(2)	106.76(13)
C(1)-C(10)	1.442(4)	O(1)-S(1)-C(1)	97.10(13)
C(9)-C(10)	1.436(4)	O(2)-S(1)-C(1)	103.19(15)
		C(4)-C(5)-C(10)-C(1)	-3.3(4)
		C(4)-C(5)-C(10)-C(9)	175.6(3)

**Table 2.7** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\text{Cp}_2\text{Ti}(\text{S}_2\text{O}_2\text{C}_{10}\text{H}_6)$  **2.8**.

Complex **2.8** has a similar S(9)-C(9) bond distance (1.771(3)  $\text{\AA}$ ) to complexes **2.1** and **2.3** but the S(1)-C(1) bond is lengthened considerably (1.836(3)  $\text{\AA}$ ) compared to the same bond in the pro-ligand (1.768  $\text{\AA}$ ). This is probably due to the removal of the electron density away from the sulfur towards the titanium bound oxygen atom. The splay angle is also positive (15.8 $^\circ$ ) but not as large as complexes **2.1** and **2.3** as this angle is part of a seven-membered (Ti-O-S<sub>2</sub>-C<sub>3</sub>) ring in **2.8** compared with a six-membered (Ti-S<sub>2</sub>-C<sub>3</sub>) ring in **2.1** and **2.3**. The S=O bond distance in **2.8** (1.480(2)  $\text{\AA}$ ) is only slightly longer than that of the pro-ligand (1.436  $\text{\AA}$ ) but the S-O bond distance is significantly longer (1.582(2)  $\text{\AA}$ ) which is to be expected. The C(1)-S(1)-O(1) and C(1)-S(1)-O(2) bond angles of **7** (97.10(13) $^\circ$  and 103.19(15) $^\circ$  respectively) are considerably less than the C-S-O angle of the pro-ligand (108.9 $^\circ$  which is very close to the idealized 109.5 $^\circ$  tetrahedral geometry).

Complex **2.8** was also formed in the analogous reaction between titanocene dicarbonyl and naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide (scheme 2.6). Like the reaction of titanocene dicarbonyl and naphtho[1,8-*cd*]-1,2-dithiole-1-oxide discussed earlier, there was no evidence of any complex containing the original pro-ligand in its complete form. Again, there appeared to be an increased amounts of the orange insoluble solid mentioned earlier (**2.7**), whose production we believe was stimulated by the loss of oxygen from the pro-ligand. This pair of results suggests that the mono-oxidised sulfur atom of the pro-ligand always loses the oxygen atom and binds to the titanium centre through that sulfur atom.

In the same way that complex **2.1** was formed by reaction of titanocene dicarbonyl with the pro-ligand naphtho[1,8-*cd*]-1,2-dithiole-1-oxide, so too was complex **2.5** obtained from the reaction between titanocene dicarbonyl and dibenzo[*ce*]-1,2-dithiine-5-oxide.

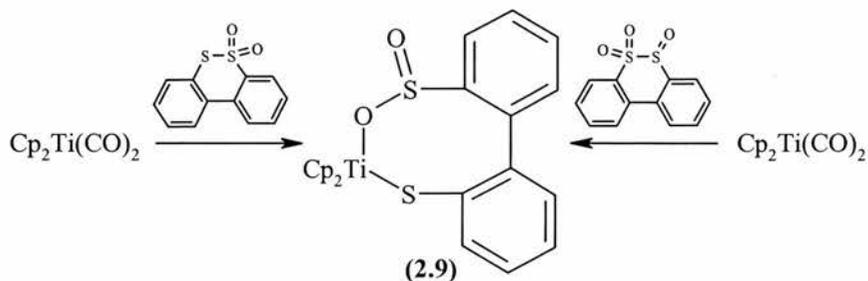


**Scheme 2.7** Synthesis of complex **2.5** using two different pro-ligands.

Again, there was no evidence of any complex containing the original pro-ligand in its complete form. This result suggests a general principle for these systems. This emerging trend was observed further when complex **2.9** was obtained by the

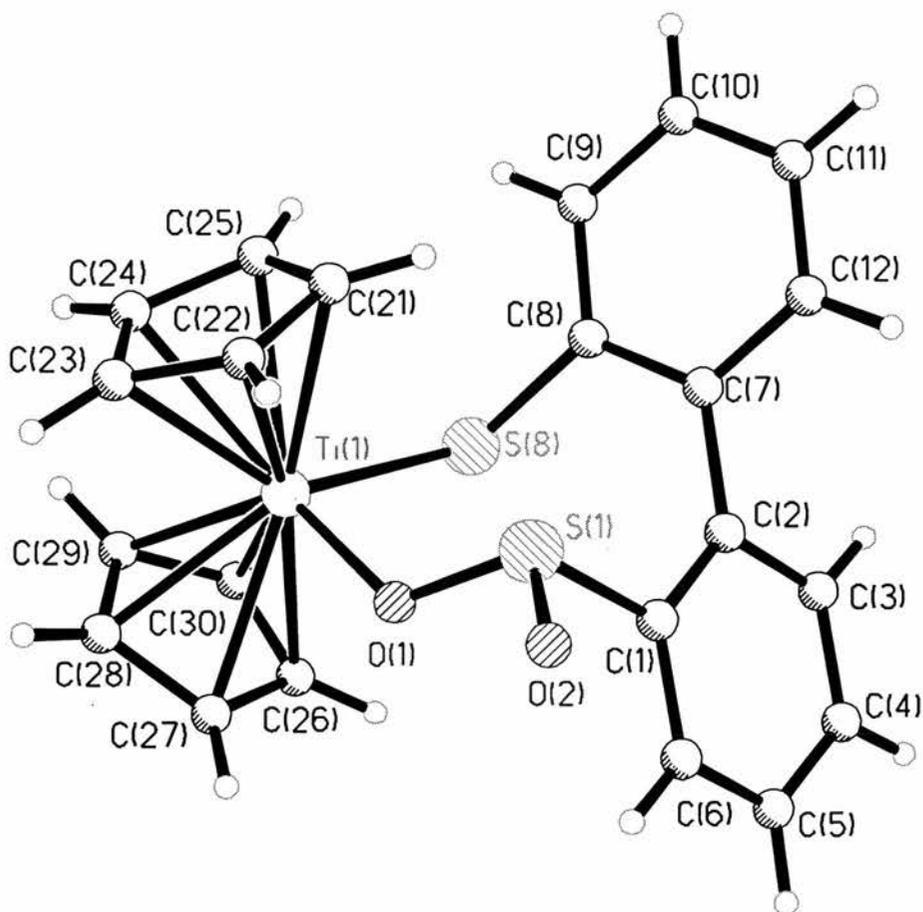
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reaction of titanocene dicarbonyl with either of the pro-ligands dibenzo[*ce*]-1,2-dithiine-5,5-dioxide or dibenzo[*ce*]-1,2-dithiine-5,5,6-trioxide (scheme 2.8).



**Scheme 2.8** Synthesis of complex **2.9** using two different pro-ligands.

The ligand in this case is bound to the titanium centre by one sulfur atom and one oxygen atom (figure 2.7), just as complex **2.8** is. Again, the infra-red spectrum supports this, showing peaks at 1108 and 824  $\text{cm}^{-1}$  which represent (S=O) and (S-O-Ti) stretches respectively. The  $^1\text{H}$  NMR of this complex displayed the expected peaks in the aromatic region and also a pair of singlets of equal intensity which represented the two inequivalent cyclopentadienyl groups (6.25 and 6.08 ppm). Like complex **2.8**, these two sharp singlets did not coalesce or even broaden when the spectrum was recorded at higher temperatures. The  $^{13}\text{C}$  NMR spectrum showed all eight aromatic C-H carbons, while microanalysis confirmed the purity of the sample. The mass spectrum (electrospray) displayed the parent ion at  $m/z$  449 ( $[\text{M}+\text{Na}]^+$ ). The X-ray crystal structure of this complex can be seen in figure 2.7. Selected bond lengths and bond angles are given in table 2.8.



**Figure 2.7** Crystal structure of  $\text{Cp}_2\text{TiC}_{12}\text{H}_8\text{S}_2\text{O}_2$  **2.9**.

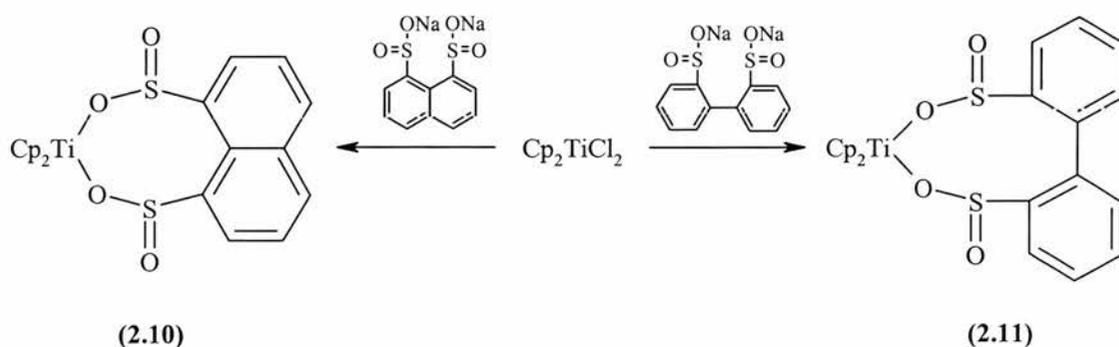
Ti(1)-S(8)	2.424(17)	S(8)-Ti(1)-O(1)	93.47(12)
Ti(1)-Cp(1)	2.362(6) – 2.392(6)	Ti(1)-S(8)-C(8)	112.44(17)
Ti(1)-Cp(2)	2.352(6) – 2.386(5)	S(1)-C(1)-C(2)	119.8(4)
Ti(1)-O(1)	1.976(4)	S(8)-C(8)-C(7)	119.8(4)
O(1)-S(1)	1.575(4)	C(1)-C(2)-C(7)	125.4(5)
S(1)-O(2)	1.475(4)	C(2)-C(7)-C(8)	121.7(5)
S(1)-C(1)	1.815(6)	Ti(1)-O(1)-S(1)	126.6(2)
S(8)-C(8)	1.783(5)	O(1)-S(1)-O(2)	107.3(2)
C(1)-C(2)	1.382(8)	O(1)-S(1)-C(1)	97.5(2)
C(2)-C(7)	1.481(8)	O(2)-S(1)-C(1)	104.0(2)
C(7)-C(8)	1.404(7)	C(1)-C(2)-C(7)-C(12)	66.4(6)

**Table 2.8** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\text{Cp}_2\text{Ti}(\text{S}_2\text{O}_2\text{C}_{12}\text{H}_8)$  **2.9**.

Complex **2.9** has similar S(8)-C(8) and Ti-S(8) bond lengths to **2.5** and **2.6** whereas the S(1)-C(1) bond has been lengthened in this complex in comparison with the pro-ligand. <sup>(103)</sup> The S-C-C bond angles are similar to those of complexes **2.5** and **2.6** and of the pro-ligand, but the Ti-S-C angle is greater than these two complexes since this angle is part of an eight-membered ring in **2.9** compared with seven-membered rings in **2.5** and **2.6**.

The S=O bond length in **2.9** [1.475(4)Å] is only slightly longer than that of the pro-ligand [1.438(2)Å] but the co-ordinated S-O bond length is, as is the case with **2.8**, significantly longer (1.575(4)Å). The C(1)-S(1)-O(1) and C(1)-S(1)-O(2) bond angles in **2.9** [97.5(2) and 104.0(2)° respectively] are considerably less than the C-S-O bond angles of the pro-ligand but are very similar to the same angles in complex **2.8**.

The salt elimination reaction of the disodium salts of naphthalene-1,8-disulfinic acid and biphenyl-2,2'-disulfinic acid with the titanium (IV) species titanocene dichloride in tetrahydrofuran at room temperature yielded the products titanocene 1,8-disulfinato-naphthalene and titanocene 2,2'-disulfinato-biphenyl (**2.10** and **2.11** respectively, scheme 2.9).



**Scheme 2.9** Salt elimination reaction to synthesise complexes **2.10** and **2.11**.

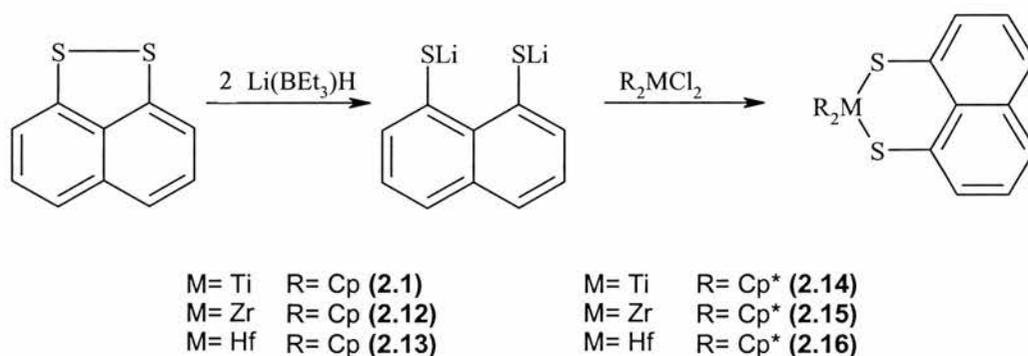
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The identity of complex **2.10** was confirmed by IR, NMR and mass spectroscopy. The infra-red spectra, like previously discussed for complexes **2.8** and **2.9**, display the characteristic peaks of a (S=O) stretch and a (S-O-Ti) stretch. The  $^1\text{H}$  NMR contains 3 aromatic environments of equal intensity and two equal peaks at 6.81 and 6.14 ppm which each represent 5 cyclopentadienyl protons. This shows that the two cyclopentadienyl groups exist in unequivalent environments, an expected result given the inequivalence of the two cyclopentadienyl groups in the related complex **2.8**. The  $^{13}\text{C}$  NMR shows 4 quaternary carbon environments and 2 non-quaternary carbons in the aromatic region and a solitary peak at 118.8 ppm. The parent ion was witnessed in the mass spectrum at  $m/z$  455 ( $[\text{M}+\text{Na}]^+$ ). Complex **2.11** was identified by similar methods, the  $^1\text{H}$  NMR displaying 4 aromatic environments of equal intensity and a solitary peak at 6.23 ppm which represents the 10 cyclopentadienyl protons, showing that in this case these two groups are equivalent, probably as a consequence of the twist in the biphenyl backbone holding the entire ligand rigidly in place with the two double-bonded oxygen atoms protruding out of the plane on opposite sides resulting in a symmetrical complex. The  $^{13}\text{C}$  NMR showed 6 environments in the range 131.4-120.4 ppm (4 non-quaternary environments and 2 quaternary environments, as expected) plus a peak at 119.4 ppm, which represents the cyclopentadienyl groups. The parent ion was found in the mass spectrum at  $m/z$  481 ( $[\text{M}+\text{Na}]^+$ ). In each case the purity of the complex was proved by elemental analyses.

A number of reactions were attempted with similar pro-ligands containing one or more chalcogen atoms other than sulfur (*ie.* selenium or tellurium) such as

naphtho[1,8-*cd*]-1,2-diselenole. These complexes were found to be unstable and were usually extremely impure and any attempts to obtain a pure sample by column chromatography on silica was futile as they broke down and no identifiable product was obtained.

Complexes **2.12-2.16** were synthesised by the salt elimination reaction of the group IV metallocene dichlorides with the di-lithium salt of naphtho[1,8-*cd*]-1,2-dithiole in tetrahydrofuran at room temperature (scheme 2.10).



**Scheme 2.10** Salt elimination reaction to yield complexes **2.1**, **2.12-2.16**.

Complexes **2.12** and **2.13** were found to be extremely air sensitive and could not be isolated or purified. They were dried, re-dissolved in toluene and filtered through a pad of Celite under nitrogen. The only possible analysis on these two complexes was NMR. Samples were prepared under nitrogen and the  $^1\text{H}$  NMR of these two complexes were collected. The NMR showed the products to be impure but the characteristic aromatic peaks were noticed, like complex **2.1**, plus the expected singlet of the cyclopentadienyl groups was seen at 6.24 and 6.14 ppm respectively. These spectra were re-recorded at lower temperature to investigate if, like **2.1**, the sharp singlet would broaden and split into two singlets

of equal intensity. This occurred as expected, coalescence occurring at 241 K and 246 K respectively. The activation parameters of the chelate ring inversion of **2.12** and **2.13** were calculated and all necessary data are shown in Table 2.9. Again, the value for  $\Delta G_c^*$  was calculated using Equation 2.3.

Complex	$\delta$ (cp) (ppm)	$T_{\text{cal}}$ (K)	$\Delta_{\text{v}}$ (Hz)	$\Delta G_c^*$ (kJ mol <sup>-1</sup> )
<b>2.11</b>	6.24	241	137.8	47.1
<b>2.12</b>	6.14	246	118.9	48.5

**Table 2.9** The activation parameters of the chelate ring inversions of complexes **2.12** and **2.13** (all NMR spectra were recorded at 270 MHz in CD<sub>2</sub>Cl<sub>2</sub>).

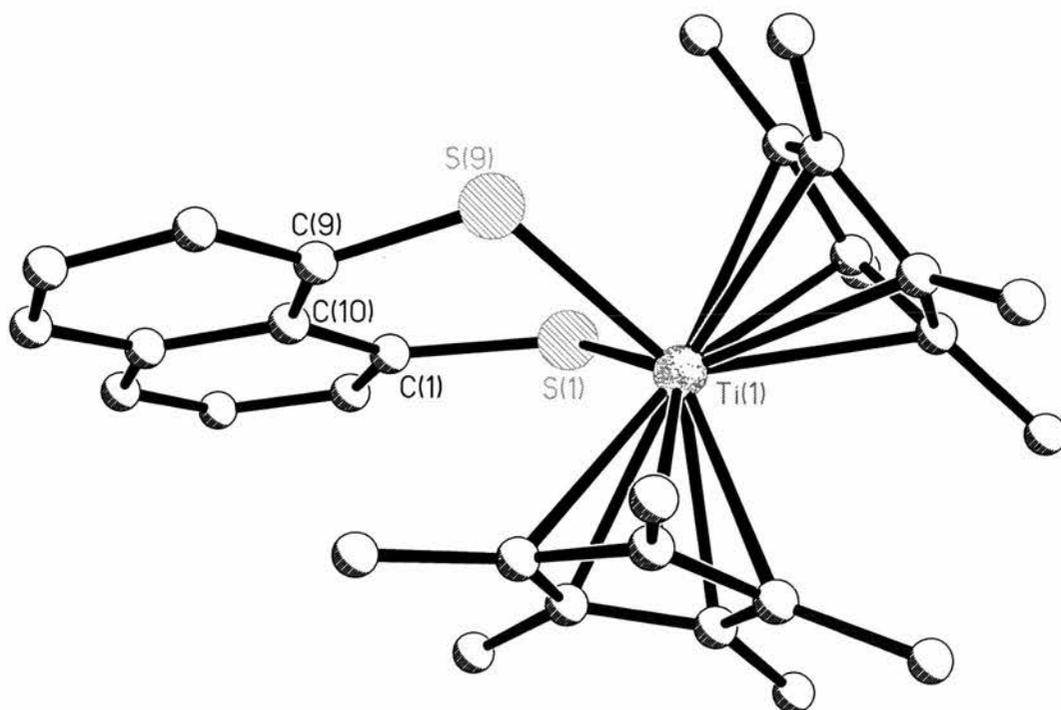
The purification and isolation of complexes **2.14-2.16** was performed by removing insoluble salts by re-dissolving in toluene and filtering through a pad of Celite. Recrystallisation from toluene/hexane gave crystals of extremely high purity which are stable in the solid state and in solution. The <sup>1</sup>H NMR data for these complexes all show the expected peaks, with three separate multiplets in the aromatic region (7.05–7.52 ppm) representing the three pairs of different protons on the naphthalene backbone and a singlet at 1.81, 1.84 and 1.87 ppm respectively due to the ten methyl groups on the cyclopentadienyl rings. No fluxionality was noticed in the <sup>1</sup>H NMR spectra of these complexes as low as 183 K, although the X-ray crystal structures of these complexes (figures 2.8-2.10) suggest that the two Cp\* groups are inequivalent. The most likely explanation for this absence of splitting is that the complexes are fluxional even at lower temperatures and that they would split if a lower temperature measurement could

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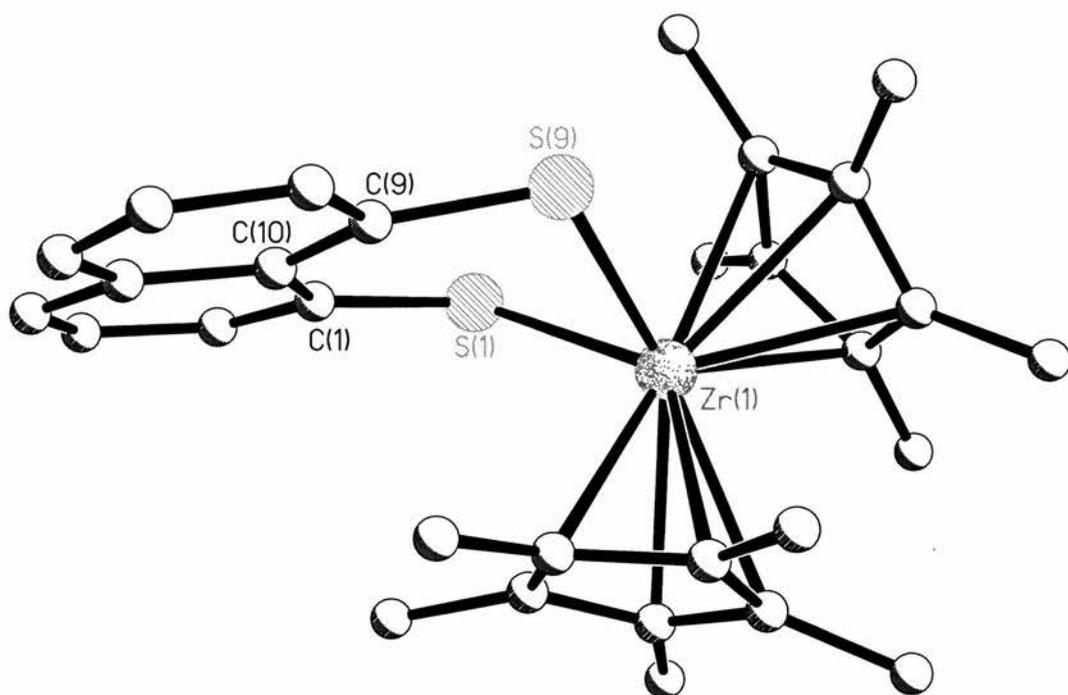
be achieved. The  $^{13}\text{C}$  NMR spectra are also clear cut, each displaying the three quaternary and three non quaternary peaks of the naphthalene backbone plus a peak representing the quaternary carbon atoms of the cyclopentadienyl rings and a single peak at 12.7, 11.6 and 10.5 ppm respectively representing the carbon of the ten methyl groups bound to the cyclopentadienyl rings.

Excellent elemental analyses were obtained for all complexes and electrospray mass spectral data were consistent with the proposed structures showing in each case  $[\text{M}]^+$  and  $[\text{M} + \text{Na}]^+$ .

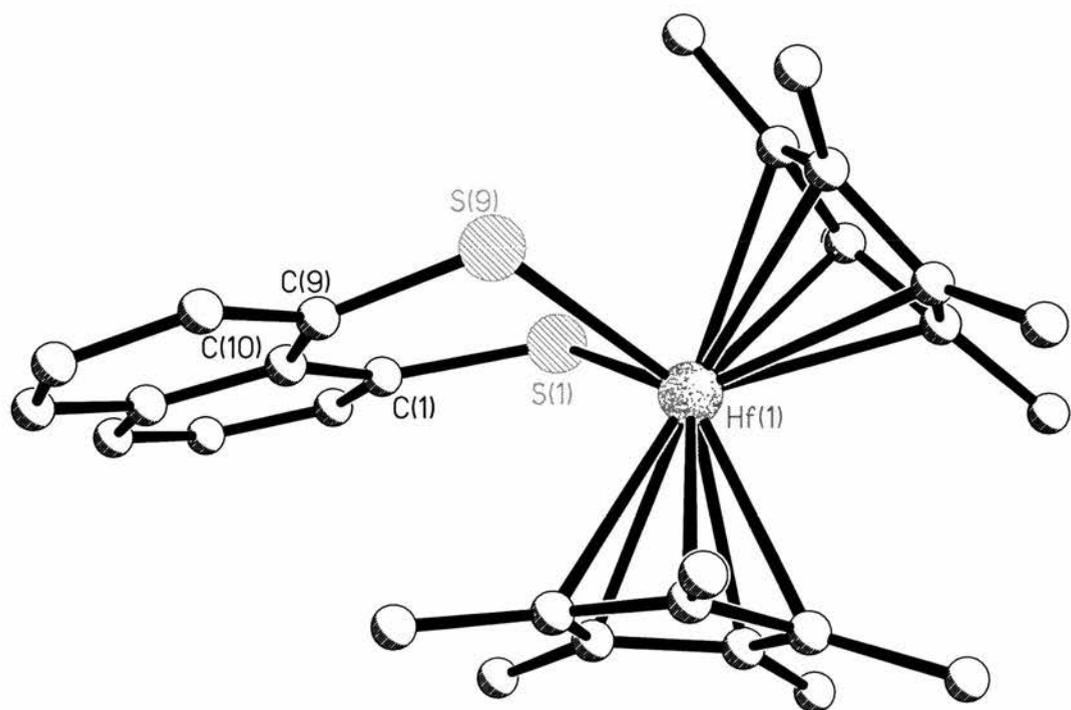
Selected bond lengths and angles are given in table 2.10.



**Figure 2.8** Crystal structure of  $\text{Cp}^*_2\text{Ti}(\text{S}_2\text{C}_{10}\text{H}_6)$  2.14.



**Figure 2.9** Crystal structure of Cp\*<sub>2</sub>Zr(S<sub>2</sub>C<sub>10</sub>H<sub>6</sub>) 2.15.



**Figure 2.10** Crystal structure of Cp\*<sub>2</sub>Hf(S<sub>2</sub>C<sub>10</sub>H<sub>6</sub>) 2.16.

Complex	2.14	2.15	2.16
M(1)-S(1)	2.406(2)	2.5033(7)	2.4832(13)
M(1)-S(9)	2.428(2)	2.5107(7)	2.4901(10)
S(1)-C(1)	1.788(6)	1.779(2)	1.781(4)
S(9)-C(9)	1.772(6)	1.779(2)	1.788(4)
C(1)-C(10)	1.440(8)	1.448(3)	1.464(5)
C(9)-C(10)	1.440(9)	1.445(3)	1.437(6)
M(1)-Cp <sup>*</sup> (1)	2.432(6)-2.490(6)	2.537(2)-2.579(2)	2.508(4)-2.564(4)
M(1)-Cp <sup>*</sup> (2)	2.418(6)-2.494(6)	2.520(3)-2.578(3)	2.509(6)-2.561(6)
S(1)-M(1)-S(9)	83.70(7)	82.40(2)	83.82(4)
M(1)-S(1)-C(1)	114.3(2)	112.32(8)	112.45(14)
M(1)-S(9)-C(9)	112.6(2)	110.73(8)	110.42(14)
S(1)-C(9)-C(10)	127.7(4)	128.25(18)	128.4(3)
S(9)-C(9)-C(10)	126.9(5)	127.11(18)	128.1(3)
C(1)-C(10)-C(9)	126.4(5)	127.4(2)	126.4(4)
Splay angle	21.0	22.8	22.9

**Table 2.10** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for complexes **2.14-2.16**.

The data for all three complexes are very similar. The S-M-S bond angles are in the range  $82.40(2)^\circ$  to  $83.82(4)^\circ$  which are similar to other complexes containing a six membered  $\text{TiS}_2\text{C}_3$  ring such as complexes **2.1-2.4**. The other angles in these six membered rings are also in accordance with these complexes. The splay angle (the deviation from the two S-C bonds being parallel) varies between the three complexes. The splay angles of complexes **2.14-2.16** are  $21.0^\circ$ ,  $22.8^\circ$  and  $22.9^\circ$  respectively. This can be explained by the size of the metal atom forcing the sulfur atoms apart and causing the S-C bonds to stray from being parallel. Zirconium has a greater atomic radius than titanium, therefore it forces the sulfur

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atoms further apart and gives a larger splay angle. Hafnium has a very similar atomic radius to zirconium so has a similar effect on the splay angle.

This effect is also seen in the M-S and M-Cp bond lengths. The M-S(1) bond lengths are 2.406(2)Å, 2.5033(7)Å and 2.4832(13)Å respectively while the M-S(9) bond lengths are 2.428(2)Å, 2.5107(7)Å and 2.4901(10)Å. These results are to be expected when the atomic radii of the three metal atoms are considered. The M-S bond lengths are very close to similar complexes.<sup>(107-115)</sup> This pattern where the Zr-S and Hf-S bond lengths are both very similar and noticeably longer than the Ti-S bond length has been noted before in a series of group IV metallocene complexes.<sup>(116)</sup> The M-Cp bond lengths show an identical pattern to that described above for the M-S bond lengths.

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## 2.3 Conclusion

In this chapter it has clearly been demonstrated that the oxidative addition of the general species  $RS_2R$ , where the two R groups are linked by an aromatic backbone, to the titanium (II) species  $Cp_2Ti(CO)_2$  occurs with ease in toluene at room temperature. The products are air stable and when the backbone is naphthalene based, the resulting product is unsymmetrical with the ligand being fluxional, folding along the S-S axis. This is seen clearly in the  $^1H$  NMR as the Cp singlet splits into two singlets of equal intensity at lower temperature. When the backbone is biphenyl based, the twist around the C(2)-C(7) bond causes the product to be symmetrical and no splitting is noticed in the  $^1H$  NMR.

Further it has been shown that ligands containing two oxygen atoms bound to a sulfur atom will bind to the metal centre through one of these oxygen atoms. In the case of the sulfur atom being mono-oxidised, the oxygen atom is lost and the ligand binds to the Ti centre through that sulfur atom. The lost oxygen atom stimulates the production of a cubic titanocene structure with Ti atoms at the 8 corners and oxygen atoms bridging the 12 edges.

The sulfur sulfur bond of these ligands can be reduced by super hydride to give the di-lithium salt which can then give complexes of the type  $Cp^*M(S_2R)$  by salt elimination reaction with  $Cp^*MCl_2$  ( $M = Ti, Zr, Hf$ ).

All of the isolated complexes have been characterised spectroscopically ( $^1H$ ,  $^{13}C$  NMR, IR, mass spectrometry), by elemental analysis and ten X-ray structures are reported.

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## 2.4 Experimental

### General

Unless otherwise stated, all operations were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Diethyl ether and tetrahydrofuran were purified by reflux over sodium and benzophenone and distilled under nitrogen. Toluene and hexane were purified by reflux over sodium and distilled under nitrogen. Dichloromethane was purified by reflux over calcium hydride and distilled under nitrogen. All other reagents were purchased from either Aldrich, Acros or Lancaster and used as received. Infra-red spectra were recorded as KBr discs in the range 4000-300  $\text{cm}^{-1}$  on a Perkin-Elmer System 2000 Fourier transform spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded using a Jeol GSX Delta 270 or Bruker Avance 300 MHz spectrometer. Microanalyses were performed by the University of St Andrews microanalysis service. Mass spectra were recorded by both the University of St Andrews mass spectrometry service and the EPSRC National Mass Spectrometry Service Centre, Swansea.

The pro-ligands naphtho[1,8-*cd*]-1,2-dithiole, <sup>(31, 32)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1-oxide, <sup>(48)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide, <sup>(32, 33)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide, <sup>(42)</sup> 2,7-di(*tert*-butyl)naphtho[1,8-*cd*]-1,2-dithiole, <sup>(38)</sup> 5,6-dihydroacenaphtho[1,8-*cd*]-1,2-dithiole, <sup>(37)</sup> 4,5-dithioacephenanthrylene, <sup>(117)</sup> dibenzo[*ce*]-1,2-dithiine, <sup>(43)</sup> dibenzo[*ce*]-1,2-dithiine-5-oxide, <sup>(118)</sup> dibenzo[*ce*]-1,2-dithiine-5,5-dioxide, <sup>(42)</sup> dibenzo[*ce*]-1,2-dithiine-5,5,6-trioxide, <sup>(42)</sup> disodium

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biphenyl-2,2'-disulfinate<sup>(42)</sup> and 13,14-dithiapicene<sup>(119)</sup> were prepared according to literature procedures as was the complex titanocene dicarbonyl.<sup>(120)</sup>

## Synthesis

### Titanocene 1,8-dithiolato naphthalene (2.1)

Naphtho[1,8-*cd*]-1,2-dithiole (264 mg, 1.38 mmol) was added in one portion to a solution of titanocene dicarbonyl (323 mg, 1.38 mmol) in toluene and was stirred for 1 h. The resulting red solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The resulting filtrate was concentrated under vacuum to *ca.* 3 cm<sup>3</sup> and hexane (20 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a red solid (0.277 g, 55%). Microanalysis: Found (Calc. for (TiS<sub>2</sub>C<sub>20</sub>H<sub>16</sub>)<sub>4</sub>.C<sub>7</sub>H<sub>8</sub>): C 66.10 (66.74), H 4.41 (4.63), S 16.85 (16.39)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.45-7.18 (m, 6H, aromatics), 6.31 (broad s, 10H, Cp groups). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 147.9 (quaternary aromatic), 137.2 (quaternary aromatic), 132.0 (aromatic C-H), 126.8 (aromatic C-H), 124.4 (aromatic C-H), 114.9 (Cp groups). Mass Spec (FAB): [M]<sup>+</sup> 368.

### Method B

Naphtho[1,8-*cd*]-1,2-dithiole-1-oxide (200 mg, 0.97 mmol) was added in one portion to a solution of titanocene dicarbonyl (227 mg, 0.97 mmol) in toluene and was stirred for 1 h. The resulting red solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble

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impurities. The resulting filtrate was concentrated under vacuum to *ca.* 3 cm<sup>3</sup> and hexane (20 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a red solid (0.026 g, 7%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.47-7.18 (m, 6H, aromatics), 6.30 (broad s, 10H, Cp groups). Mass Spec (FAB): [M]<sup>+</sup> 368.

### **Titanocene 1,8-dithiolato-2,7-di(*tert*-butyl)naphthalene (2.2)**

2,7-di(*tert*-butyl)naphtho[1,8-*cd*]-1,2-dithiole (258 mg, 0.86 mmol) was added in one portion to a solution of titanocene dicarbonyl (200 mg, 0.86 mmol) in toluene and was stirred for 1 hr. The resulting dark red solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to *ca.* 3 cm<sup>3</sup> and hexane (20 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a purple solid (0.154 g, 38%). Microanalysis: Found (Calc. for TiC<sub>28</sub>H<sub>32</sub>S<sub>2</sub>): C 70.21 (69.98), H 6.68 (6.71)%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ= 7.54-7.51 (d, 2H, aromatics), 7.41-7.38 (d, 2H, aromatics), 6.28, (s, 10H, Cp groups), 1.50 (s, 18H, *t*-Bu groups). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ= 139.6 (quaternary aromatic), 139.1 (quaternary aromatic), 132.8 (quaternary aromatic), 125.8 (aromatic C-H), 121.9 (aromatic C-H), 120.2 (Cp groups), 35.6 (quaternary *t*-Bu), 28.2 (Me groups). FAB<sup>+</sup> MS: *m/z* [M]<sup>+</sup> 480.

### **Titanocene 1,8-dithiolato-5,6-dihydroacenaphthalene (2.3)**

5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dithiole (185 mg, 0.86 mmol) was added in one portion to a solution of titanocene dicarbonyl (200 mg, 0.86 mmol) in toluene and was stirred for 1 h. The resulting red solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any

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insoluble impurities. The resulting filtrate was concentrated under vacuum to *ca.* 3 cm<sup>3</sup> and the product started to precipitate as a red solid (0.270 g, 80%). Microanalysis: Found (Calc. for TiC<sub>22</sub>H<sub>18</sub>S<sub>2</sub>): C 68.34 (67.0), H 5.19 (4.6)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ= 7.20 (m, 4H, aromatics), 6.8-6.0 (broad d, 10H, Cp groups), 3.31 (s, 4H, CH<sub>2</sub> x 2). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ= 144.0 (quaternary aromatic), 143.4 (quaternary aromatic), 140.8 (quaternary aromatic), 132.7 (Cp groups), 118.8 (aromatic C-H), 114.7 (aromatic C-H), 30.0 (CH<sub>2</sub>). EI<sup>+</sup> MS: *m/z* [M]<sup>+</sup> 394.

#### **Titanocene 1,8-dithiolato-acephenanthrylene (2.4)**

4,5-dithioacephenanthrylene (205 mg, 0.86 mmol) was added in one portion to a solution of titanocene dicarbonyl (200 mg, 0.86 mmol) in toluene and was stirred for 1 h. The resulting dark solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The resulting filtrate was concentrated under vacuum to *ca.* 3 cm<sup>3</sup> and hexane (20 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a brown solid (0.066 g, 19%). Microanalysis: Found (Calc. for TiC<sub>24</sub>H<sub>18</sub>S<sub>2</sub>): C 69.14 (68.9), H 4.09 (4.3)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ= 8.48 (m, 2H, aromatics), 7.71-7.35 (m, 6H, aromatics), 6.31 (s, 10H, Cp groups). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ= 133.4, 131.3, 127.2, 127.1, 126.0, 124.8, 123.1, 120.8 (all aromatic C-H), 128.5, 125.5, 122.9, 118.5, 118.2, 112.6 (all quaternary aromatics), 114.9 (Cp groups). FAB<sup>+</sup> MS: *m/z* [M]<sup>+</sup> 418.

#### **Titanocene 2,2'-dithiolato biphenyl (2.5)**

Dibenzo[*ce*]-1,2-dithiine (200 mg, 0.93 mmol) was added in one portion to a solution of titanocene dicarbonyl (216 mg, 0.93 mmol) in toluene and was stirred

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for 1 h. The resulting green solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The resulting filtrate was concentrated under vacuum to ca. 3 cm<sup>3</sup> and hexane (20 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a green solid. Yield 0.302 g (83 %). Microanalysis: Found (Calc. for TiC<sub>22</sub>H<sub>18</sub>S<sub>2</sub>): C 66.70 (67.0), H 4.80 (4.6)%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ= 7.74-7.71 (dd, 2H, aromatics), 7.39-7.32 (td, 2H, aromatics), 7.25-7.17 (td, 2H, aromatics), 7.09-7.06 (dd, 2H, aromatics), 6.17 (s, 10H, Cp groups). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ= 151.1, 142.0 (both 2C, quaternary aromatics), 133.4, 130.0, 127.5, 126.3 (all 2C, aromatic C-H), 114.8 (10C, Cp groups). FAB<sup>+</sup> MS: *m/z* [M]<sup>+</sup> 394.

### Method B

Dibenzo[*ce*]-1,2-dithiine-5-oxide (198 mg, 0.86 mmol) was added in one portion to a solution of titanocene dicarbonyl (200 mg, 0.86 mmol) in toluene and was stirred overnight. The resulting green solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to ca. 3 cm<sup>3</sup> and hexane (20 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a green solid. Yield 0.069 g (21 %). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ= 7.71-7.68 (dd, 2H, aromatics), 7.38-7.31 (td, 2H, aromatics), 7.25-7.16 (td, 2H, aromatics), 7.02-6.98 (dd, 2H, aromatics), 6.17 (s, 10H, Cp groups). FAB<sup>+</sup> MS: *m/z* [M]<sup>+</sup> 394.

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### **Titanocene 1,1'-dithiolato[2,2']binaphthalene (2.6)**

13,14-dithia-picene (270 mg, 0.86 mmol) was added in one portion to a solution of titanocene dicarbonyl (200 mg, 0.86 mmol) in toluene and was stirred for 1 h. The resulting green solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The resulting filtrate was removed under vacuum and the remaining solid was purified by chromatography through silica, using dichloromethane as an elutant. The green layer was collected, dried and recrystallised from hot toluene to give dark crystals 0.091 g (22 %). Microanalysis: Found (Calc. for  $\text{TiC}_{30}\text{H}_{22}\text{S}_2$ ): C 72.54 (72.9), H 4.19 (4.5)%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$ = 8.66 (d, 2H, aromatics), 7.92 (d, 2H, aromatics), 7.72 (d, 2H, aromatics), 7.68-7.58 (m, 4H, aromatics), 7.14 (d, 2H, aromatics), 6.14 (s, 10H, Cp groups).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$ = 140.6, 134.3, 133.2 (all 2C, quaternary aromatics), 128.6, 128.0, 127.3, 125.9, 125.8, 125.7 (all 2C, aromatic C-H), 114.4 (10C, Cp groups).  $\text{EI}^+$  MS:  $m/z$   $[\text{M}]^+$  494.

### **Titanocene 1-sulfinato-8-thiolato-naphthalene (2.8)**

Naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide (200 mg, 0.90 mmol) was added in one portion to a solution of titanocene dicarbonyl (211 mg, 0.90 mmol) in toluene and was stirred for 1 h. The resulting dark red solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The resulting filtrate was concentrated under vacuum to *ca.* 3  $\text{cm}^3$  and hexane (30  $\text{cm}^3$ ) was slowly added with stirring to precipitate the product as a dark red-purple solid (0.161 g, 45%). Microanalysis: Found (Calc. for  $(\text{TiC}_{20}\text{H}_{16}\text{S}_2\text{O}_2)_2 \cdot \text{C}_7\text{H}_8$ ): C 62.92 (63.22), H 4.51 (4.52)%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )

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$\delta$ : 8.42 (dd, 1H, aromatic), 8.01 (dd, 1H, aromatic), 7.87 (dd, 1H, aromatic), 7.74 (dd, 1H, aromatic), 7.57 (dt, 2H, aromatics), 6.52 (s, 5H, Cp group) and 5.75 (s, 5H, Cp group).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 148.1, 143.0, 135.5, 133.4, 133.0, 131.7, 129.2, 125.7, 125.6, 123.4 (all aromatics) and 117.0 (Cp groups). Selected IR data (KBr): 1092  $\nu(\text{S}=\text{O})$ , 811  $\nu(\text{S}-\text{O}-\text{M})$   $\text{cm}^{-1}$ . Mass Spec (FAB):  $[\text{M}+\text{H}]^+$  401.

### Method B

Naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide (290 mg, 1.21 mmol) was added in one portion to a solution of titanocene dicarbonyl (284 mg, 1.21 mmol) in toluene and was stirred for 1 h. The resulting dark red solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The resulting filtrate was concentrated under vacuum to *ca.* 3  $\text{cm}^3$  and hexane (20  $\text{cm}^3$ ) was slowly added with stirring to precipitate the product as a dark red-purple solid (0.197 g, 40%). Mass Spec (FAB):  $[\text{M}+\text{H}]^+$  401.

### Titanocene 2-sulfinato 2'-thiolato biphenyl (2.9)

Dibenzo[*ce*]-1,2-dithiine-5,5-dioxide (200 mg, 0.81 mmol) was added in one portion to a solution of titanocene dicarbonyl (189 mg, 0.81 mmol) in toluene and was stirred for 1 h. The resulting brown solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The solvent was removed under reduced pressure and the remaining brown solid was purified by chromatography through silica. Dichloromethane was used to elute a green layer which was characterised as

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complex **2.5** and then acetone was used to elute an orange layer. The orange layer was recrystallised from hot toluene. Yield 0.068 g (20 %). Microanalysis: Found (Calc. for  $(\text{TiC}_{22}\text{H}_{18}\text{S}_2\text{O}_2)_3\text{C}_7\text{H}_8$ ): C 63.33 (63.93), H 4.68 (4.56)%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$ = 7.83-7.16 (m, 8H, aromatics), 6.25 (s, 5H, Cp group), 6.08 (s, 5H, Cp group).  $^{13}\text{C}$  NMR:  $\delta$ = 133.4, 130.7, 130.2, 129.1, 128.7, 128.3, 126.6, 120.4 (all 1C, aromatic C-H), 117.0 (5C, Cp group), 115.1 (5C, Cp group). Selected IR data (KBr): 1108  $\nu(\text{S}=\text{O})$ , 824  $\nu(\text{S}-\text{O}-\text{M})$   $\text{cm}^{-1}$ .  $\text{ES}^+$  MS:  $m/z$   $[\text{M}+\text{Na}]^+$  449.

### Method B

Dibenzo[*ce*]-1,2-dithiine-5,5,6-trioxide (150 mg, 0.57 mmol) was added in one portion to a solution of titanocene dicarbonyl (133 mg, 0.57 mmol) in toluene and was stirred for 1 h. The resulting brown solution was filtered through a shallow pad of Celite to remove any unreacted starting material and any insoluble impurities. The solvent was removed under reduced pressure and the brown solid was purified by chromatography through silica. Dichloromethane was used to elute a green layer which was characterised as complex **2.5** and then acetone was used to elute an orange layer. The orange layer was recrystallised from hot toluene. Yield 0.106 g (44 %).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$ = 8.01-6.79 (m, 8H, aromatics), 6.18 (s, 5H, Cp group), 6.01 (s, 5H, Cp group).  $\text{ES}^+$  MS:  $m/z$   $[\text{M}+\text{Na}]^+$  449.

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### **Titanocene 1,8-disulfinato-naphthalene (2.10)**

A mixture of titanocene dichloride (150 mg, 0.60 mmol) and the di-sodium salt of naphthalene-1,8-disulfinic acid (181 mg, 0.60 mmol) in tetrahydrofuran was stirred for 24 hrs. The resulting orange solution was dried under vacuum and the product extracted into dichloromethane. This was filtered through a shallow pad of Celite to remove any insoluble impurities and NaCl and dried under vacuum. The remaining solid was dissolved in minimum volume of hot dichloromethane (3 cm<sup>3</sup>) and hexane (20 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as an orange solid (0.128 g, 49%). Microanalysis: Found (Calc. for (TiS<sub>2</sub>O<sub>4</sub>C<sub>20</sub>H<sub>16</sub>): C 55.79 (55.56), H 3.66 (3.73)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 8.51 (d, 2H, aromatic), 8.06 (d, 2H, aromatics), 7.71 (t, 2H, aromatic), 6.81 (s, 5H, Cp group) 6.14 (s, 5H, Cp group). <sup>13</sup>C NMR δ: 132.4, 125.8, 124.0, 121.1 (all 2C, aromatic C-H), 120.7, 120.2 (both 1C, quaternary aromatic), 118.8 (10C, Cp groups). Selected IR data (KBr): 1097 ν(S=O), 824 ν(S-O-M) cm<sup>-1</sup>. ES<sup>+</sup> MS: *m/z* [M+Na]<sup>+</sup> 455.

### **Titanocene 2,2'-disulfinato-biphenyl (2.11)**

A mixture of titanocene dichloride (285 mg, 1.15 mmol) and the di-sodium salt of biphenyl-2,2'-disulfinic acid (373 mg, 1.15 mmol) in tetrahydrofuran was stirred for 24 hrs. The resulting orange solution was dried under vacuum and the product extracted into dichloromethane. This was filtered through a shallow pad of Celite to remove any insoluble impurities and NaCl and dried under vacuum. The remaining solid was dissolved in minimum volume of hot dichloromethane (3 cm<sup>3</sup>) and hexane (20 cm<sup>3</sup>) was slowly added with stirring to precipitate the

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product as an orange solid (0.280 g, 54%). Microanalysis: Found (Calc. for  $(\text{TiS}_2\text{O}_4\text{C}_{22}\text{H}_{18})$ ): C 57.59 (57.64), H 3.61 (3.96)%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 8.08 (dd, 2H, aromatic), 7.58 (dt, 2H, aromatics), 7.45 (dt, 2H, aromatic), 7.25 (dd, 2H, aromatic) 6.23 (s, 10H, Cp groups).  $^{13}\text{C}$  NMR  $\delta$ : 131.4, 130.8, 129.5, 123.4 (all 2C, aromatic C-H), 121.2, 120.4 (both 2C, quaternary aromatic), 119.4 (10C, Cp groups). Selected IR data (KBr): 1090  $\nu(\text{S}=\text{O})$ , 819  $\nu(\text{S}-\text{O}-\text{M})$   $\text{cm}^{-1}$ .  $\text{ES}^+$  MS:  $m/z$   $[\text{M}+\text{Na}]^+$  481.

### **Zirconocene 1,8-dithiolato-naphthalene (2.12)**

Naphtho[1,8-*cd*]-1,2-dithiole (0.143 g, 0.76 mmol) was dissolved in tetrahydrofuran ( $10\text{cm}^3$ ) and a 1.0 M solution of  $\text{LiBEt}_3\text{H}$  ( $1.50\text{ cm}^3$ , 1.50 mmol) was added via syringe. Upon addition an immediate colour change from red to yellow was observed along with the evolution of gas. Biscyclopentadienyl zirconium dichloride (0.220 g, 0.76 mmol) was added and this solution was allowed to stir for 1 h. An immediate colour change to bright pink was noticed. The solvent was removed under reduced pressure and the remaining residue had its  $^1\text{H}$  NMR recorded.

### **Hafnocene 1,8-dithiolato-naphthalene (2.13)**

Naphtho[1,8-*cd*]-1,2-dithiole (0.143 g, 0.76 mmol) was dissolved in tetrahydrofuran ( $10\text{cm}^3$ ) and a 1.0 M solution of  $\text{LiBEt}_3\text{H}$  ( $1.50\text{ cm}^3$ , 1.50 mmol) was added via syringe. Upon addition an immediate colour change from red to yellow was observed along with the evolution of gas. Biscyclopentadienyl hafnium dichloride (0.220 g, 0.76 mmol) was added and this solution was

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allowed to stir for 1 h. An immediate colour change to orange was noticed. The solvent was removed under reduced pressure and the remaining residue had its  $^1\text{H}$  NMR recorded.

#### **Decamethyl titanocene 1,8-dithiolato-naphthalene (2.14)**

Naphtho[1,8-*cd*]-1,2-dithiole (0.072 g, 0.38 mmol) was dissolved in tetrahydrofuran (10 cm<sup>3</sup>) and a 1.0 M solution of LiBEt<sub>3</sub>H (0.75 cm<sup>3</sup>, 0.75 mmol) was added via syringe. Upon addition an immediate colour change from red to pale yellow was observed along with the evolution of gas. Bis(pentamethyl)cyclopentadienyl titanium dichloride (0.147 g, 0.38 mmol) was added and this solution was allowed to stir for 24 h. The solvent was removed under reduced pressure and the residue extracted into hot toluene. This was filtered through a shallow pad of Celite, dried and recrystallised from toluene/hexane to give green crystals. Yield 0.125 g, 64 %. Microanalysis: Found (Calc. for (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiS<sub>2</sub>C<sub>10</sub>H<sub>6</sub>): C 70.79 (70.84), H 7.55 (7.13), S 12.36 (12.58)%.  $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.41 (dd, 2H, aromatics), 7.33 (dd, 2H, aromatics), 7.05 (td, 2H, aromatics), 1.81 (s, 30H, 10 x Me).  $^{13}\text{C}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 147.8, 137.0, 120.6 (all quaternary aromatic), 134.4, 124.6, 123.6 (all aromatic), 125.1 (aromatic Cp groups), 12.7 (methyl). ES<sup>+</sup> MS: *m/z*, [M+Na]<sup>+</sup> 531, [M]<sup>+</sup> 508.

#### **Decamethyl zirconocene 1,8-dithiolato-naphthalene (2.15)**

Naphtho[1,8-*cd*]-1,2-dithiole (0.072 g, 0.38 mmol) was dissolved in tetrahydrofuran (10 cm<sup>3</sup>) and a 1.0 M solution of LiBEt<sub>3</sub>H (0.75 cm<sup>3</sup>, 0.75 mmol)

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was added via syringe. Upon addition an immediate colour change from red to pale yellow was observed along with the evolution of gas. Bis(pentamethyl)cyclopentadienyl zirconium dichloride (0.164 g, 0.38 mmol) was added and this solution was allowed to stir for 24 h. The solvent was removed under reduced pressure and the residue extracted into hot toluene. This was filtered through a shallow pad of Celite, dried and recrystallised from toluene/hexane to give dark red crystals. Yield 0.071 g, 34 %. Microanalysis: Found (Calc. for  $(C_5Me_5)_2ZrS_2C_{10}H_6$ ): C 65.26 (65.43), H 6.58 (6.59), S 11.83 (11.62)%.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  = 7.52 (dd, 2H, aromatics), 7.38 (dd, 2H, aromatics), 7.07 (td, 2H, aromatics), 1.84 (s, 30H, 10 x Me).  $^{13}C$  NMR ( $CD_2Cl_2$ ):  $\delta$  = 144.8, 139.9, 121.8 (all quaternary aromatic), 136.4, 123.8, 122.1 (all aromatic), 125.8 (aromatic Cp groups), 11.6 (methyl).  $ES^+$  MS:  $m/z$ ,  $[M+Na]^+$  573,  $[M]^+$  550.

#### **Decamethyl hafnocene 1,8-dithiolato-naphthalene (2.16)**

Naphtho[1,8-*cd*]-1,2-dithiole (0.072 g, 0.38 mmol) was dissolved in tetrahydrofuran (10 cm<sup>3</sup>) and a 1.0 M solution of  $LiBEt_3H$  (0.75 cm<sup>3</sup>, 0.75 mmol) was added via syringe. Upon addition an immediate colour change from red to pale yellow was observed along with the evolution of gas. Bis(pentamethyl)cyclopentadienyl hafnium dichloride (0.197 g, 0.38 mmol) was added and this solution was allowed to stir for 24 h. The solvent was removed under reduced pressure and the residue extracted into hot toluene. This was filtered through a shallow pad of Celite, dried and recrystallised from toluene/hexane to give green crystals. Yield 0.087 g, 36 %. Microanalysis: Found

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(Calc. for  $(C_5Me_5)_2HfS_2C_{10}H_6$ ): C 56.70 (56.23), H 5.91 (5.66), S 9.99 (9.52)%.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  = 7.51 (dd, 2H, aromatics), 7.34 (dd, 2H, aromatics), 7.08 (td, 2H, aromatics), 1.87 (s, 30H, 10 x Me).  $^{13}C$  NMR ( $CD_2Cl_2$ ):  $\delta$  = 137.4, 126.2, 123.7 (all quaternary aromatic), 128.0, 121.7, 116.0 (all aromatic), 117.3 (aromatic Cp groups), 10.5 (methyl).  $ES^+$  MS:  $m/z$ ,  $[M+Na]^+$  663,  $[M]^+$  640.

### X-ray Crystallography

Tables 2.11-2.14 list details of data collections and refinements. For **2.1**, **2.3**, **2.5**, **2.7** and **2.9**, data were collected at 125 K using Mo-K $\alpha$  radiation with a Rigaku Mercury system and for **2.2** at room temperature on a Bruker SMART diffractometer using Mo-K $\alpha$  radiation. Data for **2.6** were collected at 125 K on a Rigaku MM007/Saturn diffractometer. Data for **2.8** were collected at 298 K on a Rigaku Mercury diffractometer. Complex **2.6** was refined isotropically while in **2.5** C(1) and C(8) were refined isotropically; in all other structures all non-H atoms were refined anisotropically. The large residual electron densities in **2.9** are located about the titanium atoms. Refinements were by full-matrix least squares based on  $F^2$  using SHELXTL.<sup>(121)</sup>

	2.1	2.3
Empirical formula	C <sub>21.75</sub> H <sub>18</sub> S <sub>2</sub> Ti	C <sub>25.50</sub> H <sub>22</sub> S <sub>2</sub> Ti
<i>M</i>	391.38	440.45
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/m
<i>a</i> /Å	30.827(5)	21.939(7)
<i>b</i> /Å	15.229(3)	12.009(4)
<i>c</i> /Å	15.027(3)	7.764(3)
$\alpha$ /°	90	90
$\beta$ /°	94.288(3)	91.461(5)
$\gamma$ /°	90	90
<i>U</i> /Å <sup>3</sup>	7035(2)	2044.7(12)
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	1.478	1.431
$\mu$ /mm <sup>-1</sup>	0.724	0.832
Reflections measured	17446	6153
Independent reflections	5033	1928
Final <i>R</i> <sub>1</sub> ,	0.0362,	0.0418,
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0820	0.0851

**Table 2.11** Details of the X-ray data collections and refinements for complexes 2.1 and 2.3.

	<b>2.5</b>	<b>2.6</b>
Empirical formula	C <sub>22</sub> H <sub>18</sub> S <sub>2</sub> Ti	C <sub>30</sub> H <sub>22</sub> S <sub>2</sub> Ti
<i>M</i>	394.38	494.50
Crystal system	Monoclinic	Orthorhombic
Space group	P2 <sub>1</sub> /c	Pbca
<i>a</i> /Å	7.850(7)	10.8920(13)
<i>b</i> /Å	16.344(14)	10.8871(12)
<i>c</i> /Å	14.429(13)	38.317(5)
$\alpha$ /°	90	90
$\beta$ /°	92.167(17)	90
$\gamma$ /°	90	90
<i>U</i> /Å <sup>3</sup>	1850(3)	4543.7(9)
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	1.416	1.466
$\mu$ /mm <sup>-1</sup>	0.689	0.578
Reflections measured	7761	25174
Independent reflections	2597	3953
Final <i>R</i> <sub>1</sub> ,	0.0650,	0.2185,
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1551	0.4432

**Table 2.12** Details of the X-ray data collections and refinements for complexes **2.5** and **2.6**.

	2.7	2.8	2.9
Empirical formula	C <sub>46</sub> H <sub>52</sub> Cl <sub>12</sub> O <sub>12</sub> Ti <sub>8</sub>	C <sub>23.50</sub> H <sub>20</sub> S <sub>2</sub> O <sub>2</sub> Ti	C <sub>22.50</sub> H <sub>19</sub> C <sub>10.50</sub> O <sub>2</sub> S <sub>2</sub> Ti
<i>M</i>	1605.48	446.42	451.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	C2/c	P2 <sub>1</sub> /c
<i>a</i> /Å	20.265(4)	22.998(5)	7.7413(11)
<i>b</i> /Å	16.343(3)	12.703(3)	11.5820(17)
<i>c</i> /Å	38.350(8)	14.269(3)	23.933(4)
$\alpha$ /°	90	90	90
$\beta$ /°	103.036(4)	105.689(7)	98.693(3)
$\gamma$ /°	90	90	90
<i>U</i> /Å <sup>3</sup>	12373(4)	4013.3(14)	2121.1(5)
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	1.724	1.478	1.413
$\mu$ /mm <sup>-1</sup>	1.550	0.652	0.679
Reflections measured	73549	7516	10558
Independent reflections	22644	3105	3793
Final <i>R</i> <sub>1</sub> ,	0.1110,	0.0425,	0.0711,
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1702	0.0807	0.1603

**Table 2.13** Details of the X-ray data collections and refinements for complexes 2.7, 2.8 and 2.9.

	2.14	2.15	2.16
Empirical formula	C <sub>30</sub> H <sub>36</sub> S <sub>2</sub> Ti	C <sub>30</sub> H <sub>36</sub> S <sub>2</sub> Zr	C <sub>30</sub> H <sub>36</sub> S <sub>2</sub> Hf
<i>M</i>	508.61	551.93	639.20
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pna2(1)	Pna2(1)	Pna2(1)
<i>a</i> /Å	17.873(10)	18.1276(19)	18.074(2)
<i>b</i> /Å	8.468(5)	8.4311(13)	8.4295(11)
<i>c</i> /Å	16.735(9)	16.722(3)	16.721(2)
$\alpha^\circ$	90	90	90
$\beta^\circ$	90	90	90
$\gamma^\circ$	90	90	90
<i>U</i> /Å <sup>3</sup>	2533(2)	2555.7(6)	2547.5(6)
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	1.334	1.434	1.667
$\mu$ /mm <sup>-1</sup>	0.520	0.611	4.276
Reflections measured	13438	14822	14755
Independent reflections	3640	4132	4039
Final <i>R</i> <sub>1</sub> ,	0.0678,	0.0215,	0.0195,
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1456	0.0513	0.0438

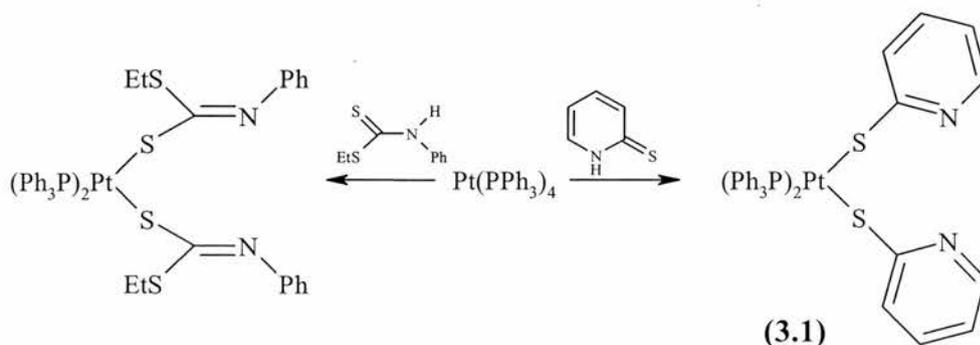
**Table 2.14** Details of the X-ray data collections and refinements for complexes 2.14, 2.15 and 2.16.

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# CHAPTER 3. THE PLATINUM CHEMISTRY OF NAPHTHO[1,8-*cd*]-1,2-DITHIOLE, DIBENZO[*ce*]-1,2- DITHIINE AND THEIR OXIDISED DERIVATIVES

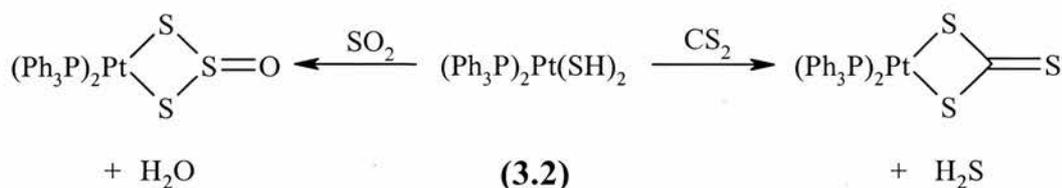
## 3.1 Introduction

Thiolato complexes of platinum are well documented and a number of examples are known. Amongst the simplest of these complexes,  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{SH})_2$ , is prepared by reaction of  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{N}_3)_2$  with  $\text{H}_2\text{S}$ .<sup>(122)</sup> This same platinum precursor can be reacted with disulfides,  $\text{RS-SR}$ , to yield  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{SR})_2$  ( $\text{R} = \text{Me}, n\text{-Bu}, \text{Ph}$ ). Platinum *cis*-chlorides can also be used instead of *cis*-azides. These are reacted with a selection of thiols ( $\text{RSH}$ ) in the presence of triethylamine to yield  $(\text{R}'_3\text{P})_2\text{Pt}(\text{SR})_2$ <sup>(123)</sup> which are found to exist in the *cis* configuration when  $\text{R}$  is an alkyl group and in the *trans* configuration when  $\text{R}$  is an aryl group. Oxidative addition of a  $\text{RS-SR}$  compound to  $\text{Pt}(\text{PPh}_3)_4$  [ $\text{Pt}(0)$ ], a method which is of particular interest to this thesis, has also been successful. For example,  $\text{Pt}(\text{PPh}_3)_4$  reacts with  $\text{F}_3\text{CS-SCF}_3$  to yield  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{SCF}_3)_2$ <sup>(124)</sup> and also with ethyl *N*-phenyldithiocarbamate<sup>(125)</sup> and pyridine-2-thione<sup>(126)</sup> as shown in equation 3.1.

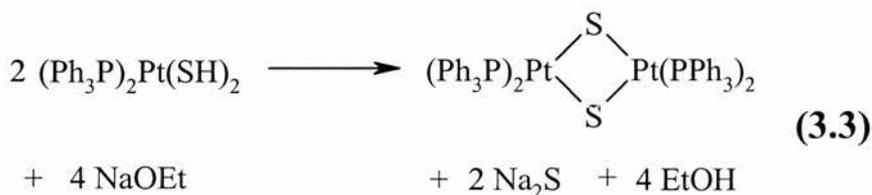


Oxidative addition can also be used to incorporate the  $(\text{Ph}_3\text{P})_2\text{Pt}$  moiety into the sulfur sulfur bond of a cyclic compound to give a platinum containing ring. This has previously been shown in equation 1.38 where the  $(\text{Ph}_3\text{P})_2\text{Pt}$  unit is inserted into the S-S bond of tetrathionaphthalene and other similar compounds.

Other cyclic platinum sulfur containing complexes include  $(\text{R}_3\text{P})_2\text{Pt}(\text{S}_2\text{C}_2(2\text{-pyridyl}))$ , <sup>(127)</sup>  $(\text{Ph}_3\text{P})_2\text{PtS}_4$  (formed by reaction of  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{SH})_2$  and elemental sulfur <sup>(128)</sup> or from reaction of  $[\text{Pt}(\text{S}_5)_3]^{2-}$  with triphenylphosphine <sup>(122)</sup>) and  $(\text{R}_3\text{P})_2\text{Pt}(\text{S}_2\text{CH}_2)$ . <sup>(129)</sup> Shaver and co-workers have also demonstrated that novel cyclic platinum sulfur complexes can be developed by taking  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{SH})_2$  and closing the ring by inserting a new group between the two sulfur atoms. This has been successful with both  $\text{SO}_2$  <sup>(130)</sup> and  $\text{CS}_2$  <sup>(131)</sup> as shown in equation 3.2.



$(\text{Ph}_3\text{P})_2\text{Pt}(\text{SH})_2$  has also been converted into an interesting homo-bimetallic complex containing a four-membered  $\text{Pt}_2\text{S}_2$  ring <sup>(128)</sup> by reaction with NaOEt (equation 3.3).



These previous examples have all involved platinum thiolato complexes. However, a few sulfenato complexes of platinum are also known such as those

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cyclic examples previously described in chapter 1. <sup>(71-77)</sup> The majority of other examples use a dialkyl sulfoxide as a ligand, most involving dimethylsulfoxide, <sup>(132-134)</sup> although examples containing tetramethylenesulfoxide, ethylmethylsulfoxide, di-*n*-propylsulfoxide, benzylmethylsulfoxide and dibenzylsulfoxide have also been reported. <sup>(135)</sup> Some of these sulfoxide containing platinum complexes have been shown to display anti-tumour activity. <sup>(136, 137)</sup> In each case these ligands have been shown to be sulfur bound to the metal centre and never oxygen bound.

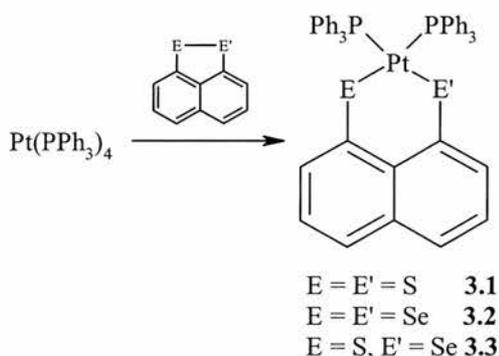
A few examples of platinum sulfinato complexes are also known.  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{N}_3)(\text{SO}_2\text{C}_6\text{F}_{13})$  and  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{N}_3)_2(\text{SO}_2\text{C}_6\text{F}_{13})_2$  are formed by reaction of  $\text{F}_{13}\text{C}_6\text{SO}_2\text{N}_3$  with  $\text{Pt}(\text{PPh}_3)_4$  and  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$  respectively. <sup>(138)</sup>

In this chapter, we have studied the insertion of the  $(\text{Ph}_3\text{P})_2\text{Pt}$  group into the sulfur-sulfur bond of those aromatic disulfides previously studied in chapter 2. Again, we have used a variety of compounds whose sulfur atoms have been mono- and di-oxidised in an attempt to find out whether these ligands, like the titanium complexes in chapter 2, will be oxygen bound to the metal centre, or if they will bind through sulfur. We also discuss an alternative route to a variety of these complexes, by reducing the chalcogen chalcogen bond with super-hydride and then forming the final complex via salt elimination reaction with a platinum dichloride.

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### 3.2 Results and Discussion

Oxidative addition reactions of naphtho[1,8-*cd*]-1,2-dithiole, its selenium analogue naphtho[1,8-*cd*]-1,2-diselenole and the mixed chalcogen derivative naphtho[1,8-*cd*]-1,2-selenathiole with the Pt(0) complex [Pt(PPh<sub>3</sub>)<sub>4</sub>] all proceed smoothly in toluene at room temperature (Scheme 3.1) to give Pt(II) complexes [Pt(1,8-S<sub>2</sub>-nap)(PPh<sub>3</sub>)<sub>2</sub>] **3.1**, [Pt(1,8-Se<sub>2</sub>-nap)(PPh<sub>3</sub>)<sub>2</sub>] **3.2** and [Pt(1-S,8-Se-nap)(PPh<sub>3</sub>)<sub>2</sub>] **3.3** respectively in excellent yields (84-95%).



**Scheme 3.1** Oxidative addition reactions of dichalcogen pro-ligands to platinum species.

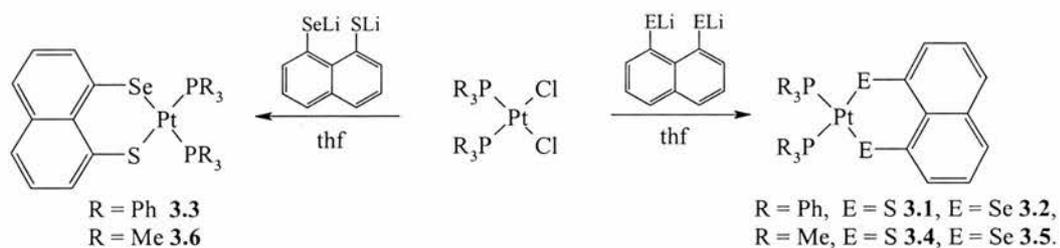
In each case, the pro-ligand was prepared by literature methods. Two equivalents of triphenylphosphine were evolved resulting in the oxidative addition of the (Ph<sub>3</sub>P)<sub>2</sub>Pt unit into the sulfur sulfur bond, and a new complex with a greater ring size being formed. The purification and isolation of the compounds is straightforward and is achieved via filtration through a shallow pad of silica and elution with dichloromethane followed by evaporation of the filtrate and precipitation of the product with diethyl ether and hexane.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $\text{CD}_2\text{Cl}_2$ ) of complexes **3.1** and **3.2** display the anticipated single resonances with platinum satellites at  $\delta(\text{P})$  23.4 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2966$  Hz] and  $\delta(\text{P})$  20.5 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3016$  Hz] respectively with additional  $^{77}\text{Se}$  satellites [ $^2J(^{31}\text{P}-^{77}\text{Se}) = 51$  Hz] being observed in the spectrum of complex **3.2**. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ ) of **3.3** is of the AX type with both platinum and selenium satellites. Although it is impossible to assign the two distinct phosphorus doublets as being *trans* to either sulfur or selenium with absolute certainty the similarity of the two shifts when compared to those of complexes **3.1** and **3.2** suggests that the phosphorus at  $\delta(\text{P})$  20.1 ppm [ $^1J(^{31}\text{P}_{(\text{A})}-^{195}\text{Pt}) = 2984$  Hz,  $^2J(^{31}\text{P}_{(\text{A})}-^{77}\text{Se}) = 58$  Hz] is *trans* to the selenium and that at  $\delta(\text{P})$  22.6 ppm [ $^1J(^{31}\text{P}_{(\text{X})}-^{195}\text{Pt}) = 2989$  Hz,  $^2J(^{31}\text{P}_{(\text{X})}-^{77}\text{Se}) = 47$  Hz] *trans* to the sulfur of the (1-S,8-Se-nap) ligand. An additional  $^2J(^{31}\text{P}_{(\text{A})}-^{31}\text{P}_{(\text{A})})$  coupling constant of 25 Hz is typical for platinum complexes bearing two inequivalent phosphine ligands in a *cis* configuration. The  $^{195}\text{Pt}$  NMR spectra ( $\text{CD}_2\text{Cl}_2$ ) show triplets at  $\delta(\text{Pt})$  -4799 (**3.1**) and  $\delta(\text{Pt})$  -4912 (**3.2**) which also shows selenium satellites,  $^1J(^{195}\text{Pt}-^{77}\text{Se}) = 165$  Hz which is within the range of previously reported examples of  $^1J(^{195}\text{Pt}-^{77}\text{Se})$  couplings of 61-298 Hz<sup>(139-143)</sup> while that of **3.3** is a double doublet at  $\delta(\text{Pt})$  -4820 ppm.

In each case the purity of the sample was confirmed by elemental analysis and the parent ion  $[\text{M}]^+$  observed at  $m/z$  910 and 1004 in the case of **3.1** and **3.3** and at  $m/z$  958 ( $[\text{M}+\text{H}]^+$ ) for **3.3**. In all three cases  $[\text{M}-\text{dichalcogen ligand}]^+$  was seen at 719/720.

An alternative approach was adopted to synthesise complexes **3.1-3.3** in slightly lower yields but with equal purity. This method involved the *in situ* generation of the dilithio-1,8-dichalcogenato naphthalenes, by reduction of the parent

dichalcogen compound with two equivalents of super hydride ( $\text{LiBEt}_3\text{H}$ ) followed by salt elimination reaction with *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  (scheme 2). This method was also utilised to synthesise the similar trimethylphosphine derivatives, complexes **3.4-3.6**.



**Scheme 3.2** Salt elimination reactions of dichalcogen pro-ligands to platinum species.

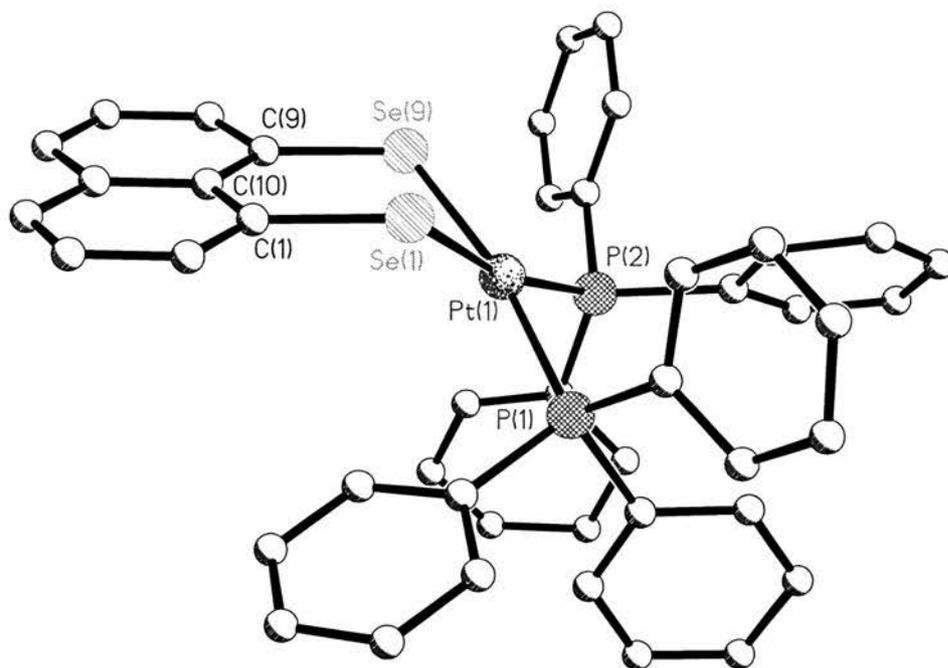
The trimethylphosphine derivatives were found to be unstable in chlorinated solvents but decomposition was prevented by addition of a small amount of triethylamine (to act as an acid scavenger) to all chlorinated workup and NMR solvents. This suggests that the decomposition is due to free HCl present in the solvent.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $\text{CD}_2\text{Cl}_2/\text{Et}_3\text{N}$ ) of complexes **3.4-3.6** exactly mirrored those of complexes **3.1-3.3** respectively. **3.4** and **3.5** displayed the anticipated single resonances with platinum satellites at  $\delta(\text{P})$  -23.1 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2801$  Hz] and  $\delta(\text{P})$  -28.7 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2840$  Hz] respectively. Complex **3.6** displayed two distinct doublets like **3.3**, again it is impossible to assign either of these as being *trans* to either sulfur or selenium with absolute certainty. However, the similarity of the two shifts when compared to those of complexes **3.4** and **3.5** suggests that the phosphorus at  $\delta(\text{P})$  -27.3 ppm [ $^1J(^{31}\text{P}_{(\text{A})}-^{195}\text{Pt}) =$

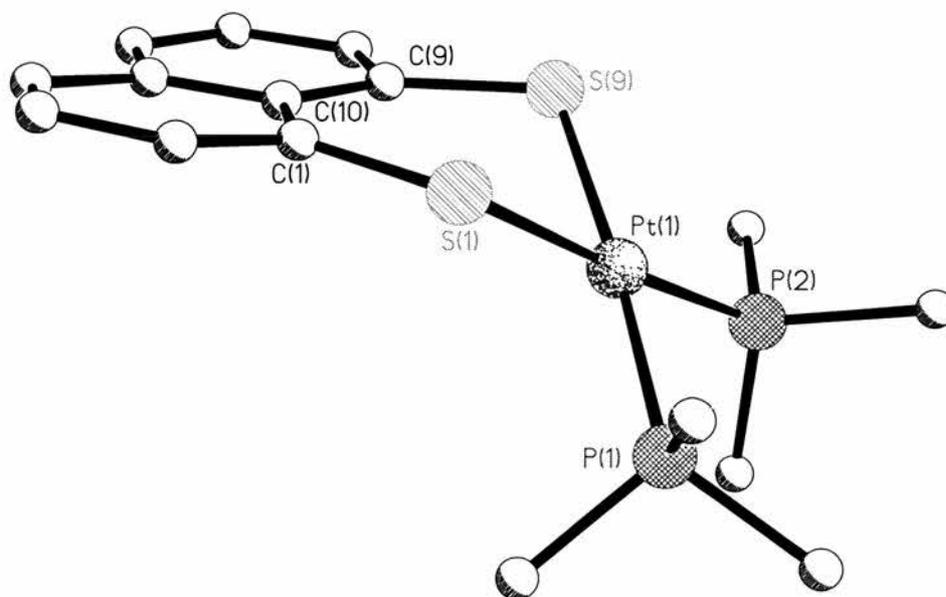
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2805 Hz,  ${}^2J({}^{31}\text{P}_{(\text{A})}-{}^{77}\text{Se}) = 58$  Hz] is *trans* to the selenium and that at  $\delta(\text{P})$  -23.6 ppm [ ${}^1J({}^{31}\text{P}_{(\text{X})}-{}^{195}\text{Pt}) = 2834$  Hz,  ${}^2J({}^{31}\text{P}_{(\text{X})}-{}^{77}\text{Se}) = 63$  Hz] *trans* to the sulfur of the (1-S,8-Se-nap) ligand.

The X-ray crystal structures of **3.2** and **3.4** (figures 3.1 and 3.2 respectively) show that the platinum core lies at the centre of a distorted square-planar coordination sphere, consisting of two equivalent phosphorus atoms and either two selenium or two sulfur atoms respectively. Complex **3.2** was found to crystallise with two independent molecules in the unit cell, only one molecule has been shown in figure 3.1.



**Figure 3.1** Crystal structure of  $[\text{Pt}(1,8\text{-Se}_2\text{-nap})(\text{PPh}_3)_2]$  **3.2**



**Figure 3.2** Crystal structure of  $[\text{Pt}(1,8\text{-S}_2\text{-nap})(\text{PMe}_3)_2]$  **3.4**

	3.2 (molecule 1)	3.2 (molecule 2)	3.4
Pt(1)-E(1)	2.447(1)	2.4301(7)	2.320(1)
Pt(1)-E(9)	2.436(1)	2.4595(7)	2.326(1)
Pt(1)-P(1)	2.289(2)	2.292(2)	2.284(1)
Pt(1)-P(2)	2.283(2)	2.287(2)	2.273(1)
E(1)-C(1)	1.938(7)	1.940(6)	1.754(4)
E(9)-C(9)	1.912(7)	1.915(7)	1.760(4)
E(1)-E(1)	3.37(1)	3.36(1)	3.22(1)
E(1)-Pt(1)-E(9)	87.36(2)	86.65(2)	87.62(4)
P(1)-Pt(1)-P(2)	98.40(6)	98.84(6)	96.55(4)
P(1)-Pt(1)-E(1)	87.50(5)	90.04(4)	85.88(4)
P(2)-Pt(1)-E(9)	88.34(5)	85.11(5)	89.97(4)
P(1)-Pt(1)-E(9)	169.80(5)	174.16(4)	173.45(4)
P(2)-Pt(1)-E(1)	167.74(5)	168.47(5)	176.83(4)
Pt(1)-E(1)-C(1)	109.2(2)	111.30(19)	113.24(14)
E(1)-C(1)-C(10)	126.4(5)	129.0(5)	128.4(3)
C(1)-C(10)-C(9)	126.4(6)	126.1(6)	125.8(3)
C(10)-C(9)-E(9)	131.0(5)	124.9(5)	127.1(3)
C(9)-E(9)-Pt(1)	110.81(19)	103.38(19)	110.28(14)
E(1)-C(1) ... C(9)- E(9)	9	25	9
(PtE <sub>2</sub> ) ... (E <sub>2</sub> Nap)	135	130	136
C(4)-C(5)-C(10)- C(9)	178.9(6)	177.7(6)	174.7(4)
C(6)-C(5)-C(10)- C(1)	177.6(6)	173.9(7)	179.1(4)
C(4)-C(5)-C(10)- C(1)	1.7(9)	3.4(9)	3.5(6)
C(6)-C(5)-C(10)- C(9)	1.7(9)	5.0(1)	2.7(6)
Splay angle	23.8	20.0	21.3

**Table 3.1** Selected bond lengths [Å] and angles [°] for complexes **3.2** and **3.4**.

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The P(1)-Pt(1)-P(2) angles are in the range 96.55(4)-98.84(6)°, showing considerable deviation from perfect square planar geometry. They are very similar to the corresponding angles in the known complex [(Ph<sub>3</sub>P)<sub>2</sub>Pt(ttn)Pt(PPh<sub>3</sub>)<sub>2</sub>] (ttn = tetrathiolatonaphthalene), 98.5°. <sup>(53)</sup> Likewise, the E(1)-Pt(1)-E(9) are in the range 86.65(2)-87.62(4)° as a result of this distortion and again are similar to those of [(Ph<sub>3</sub>P)<sub>2</sub>Pt(ttn)Pt(PPh<sub>3</sub>)<sub>2</sub>]. <sup>(53)</sup> The *cis* P(1)-Pt(1)-E(1), P(2)-Pt(1)-E(9) (85.11(5)-90.04(4)°) and *trans* P(1)-Pt(1)-E(9), P(2)-Pt(1)-E(1) (167.74(5)-176.83(4)°) angles lie within reasonable ranges and are unremarkable other than to further highlight the distortion from square planarity. The Pt(1)-P(1) [2.289(2), 2.292(2)Å] and Pt(1)-P(2) [2.283(2), 2.287(2)Å] bond lengths of **3.2** closely resemble those of the related species *cis*-[Pt(SePh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (2.290(6), 2.294(6)Å), <sup>(144)</sup> *cis*-[Pt(Se<sub>2</sub>CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (2.274(2), 2.290(2)Å) <sup>(145)</sup> and the diseleno-oxalate complex *cis*-[Pt(Se<sub>2</sub>C<sub>2</sub>O<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (2.288(1), 2.303(1)Å). <sup>(146)</sup> The Pt(1)-Se(1) (2.447(1), 2.43(1)Å), and Pt(1)-Se(9) (2.436(1), 2.460(1)Å) distances of **3.2** can also be compared with the corresponding bonds in *cis*-[Pt(SePh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (2.489(1), 2.451(1)Å) <sup>(144)</sup> and *cis*-[Pt(Se<sub>2</sub>C<sub>2</sub>O<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (2.446(1), 2.461(1)Å) <sup>(146)</sup> but are longer than those found in [Pt(Se<sub>2</sub>CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (2.418(1), 2.435(1)Å) <sup>(145)</sup> although this may be due to the latter complex bearing an aliphatic rather than aromatic diselenolato ligand. The average distance between the two selenium atoms of **3.2** is 3.365(1)Å which is 88% of the van der Waals radii of selenium and implies that there is a significant interaction between the two Se atoms. The non-bonded Se...Se distance of **3.2** is over 1Å larger than bonded Se-Se distance of naphtho[1,8-*cd*]-1,2-diselenole <sup>(102)</sup> (2.357(1)Å).

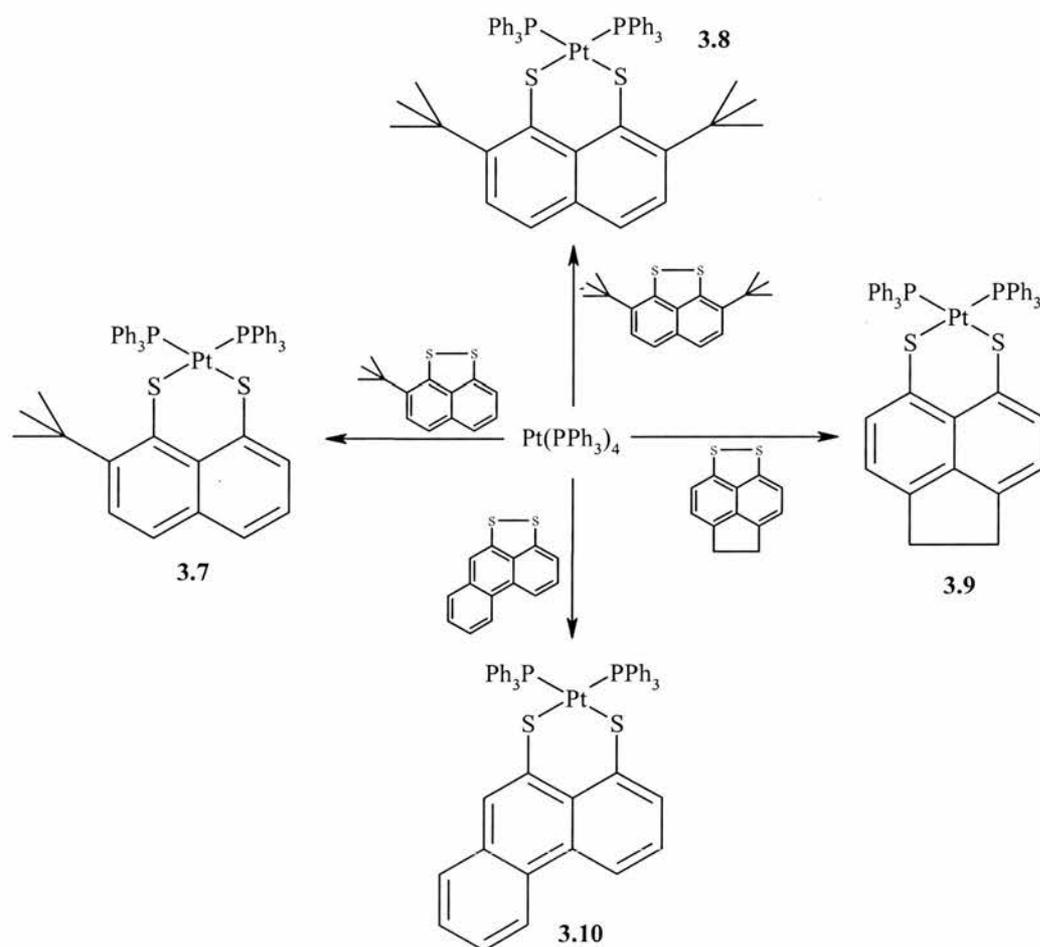
The Pt-P (2.284(1), 2.273(1)Å) and Pt-S (2.320(1), 2.326(1)Å) bond distances of [Pt(1,8-S<sub>2</sub>-nap)(PMe<sub>3</sub>)<sub>2</sub>] **3.4** are as expected and bear direct comparison to the

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equivalent bonds in [(PPh<sub>3</sub>)<sub>2</sub>Pt(ttn)Pt(PPh<sub>3</sub>)<sub>2</sub>] (Pt-P = 2.293(3), 2.296(3) and Pt-S = 2.298(3), 2.315(3)Å).<sup>(53)</sup> The non-bonded S...S distance of **3.4** (3.22(1)Å) is also more than 1Å more than that in the free ligand,<sup>(102)</sup> and is slightly less than the non-bonded Se...Se distance of **3.2**.

The C(1)-E(1) and C(9)-E(9) bond lengths of these two complexes are both similar to those of the free ligands and are unremarkable. However, like the titanium complexes of these compounds, the main difference is the splay angle (the deviation from the two S-C bonds being parallel). The pro-ligands have a negative splay angle (-3.6° and -11.21° respectively) due to the chalcogen chalcogen bond pulling the two atoms together. These two complexes however have positive splay angles (23.8°/20.0° and 21.3° respectively) and this can be attributed to the absence of the chalcogen chalcogen bond and the insertion of the metal centre between the two chalcogen atoms. This allows the two atoms to move further apart into a more comfortable position as it alleviates any strain which would have previously been present in the five membered ring. The size of the splay angle of **3.4** is surprising, given that platinum has a slightly smaller atomic radius than titanium, yet **3.4** displays a greater splay angle than the titanium complex of this ligand, complex **2.1** (18.9°). The splay angle of **3.2** (23.8°/20.0°) is the greatest seen yet but this is a result of the two larger selenium atoms being present rather than sulfur atoms in the other examples.

The similar *tert*-butyl, di-*tert*-butyl, acenaphthalene and phenanthrene complexes (3.7-3.10) were synthesized in the same manner to complexes 3.1-3.3, by oxidative addition of the pro-ligands 2-*tert*-butyl-naphtho[1,8-*cd*]-1,2-dithiole, 2,7-di-*tert*-butyl-naphtho[1,8-*cd*]-1,2-dithiole, 5,6-dihydroacenaphtho[5,6-*c,d*]-1,2-dithiole and 4,5-dithia-acephenanthrylene to [Pt(PPh<sub>3</sub>)<sub>4</sub>] in toluene at room temperature (Scheme 3.3) to give Pt(II) complexes [Pt(1,8-S<sub>2</sub>-2-<sup>t</sup>Bu-nap)(PPh<sub>3</sub>)<sub>2</sub>] 3.7, [Pt(1,8-S<sub>2</sub>-2,7-di-<sup>t</sup>Bu-nap)(PPh<sub>3</sub>)<sub>2</sub>] 3.8 [Pt(1,2-S<sub>2</sub>-acenap)(PPh<sub>3</sub>)<sub>2</sub>] 3.9 and [Pt(4,5-S<sub>2</sub>-phenan)(PPh<sub>3</sub>)<sub>2</sub>] 3.10 respectively in excellent yields (76-94%).

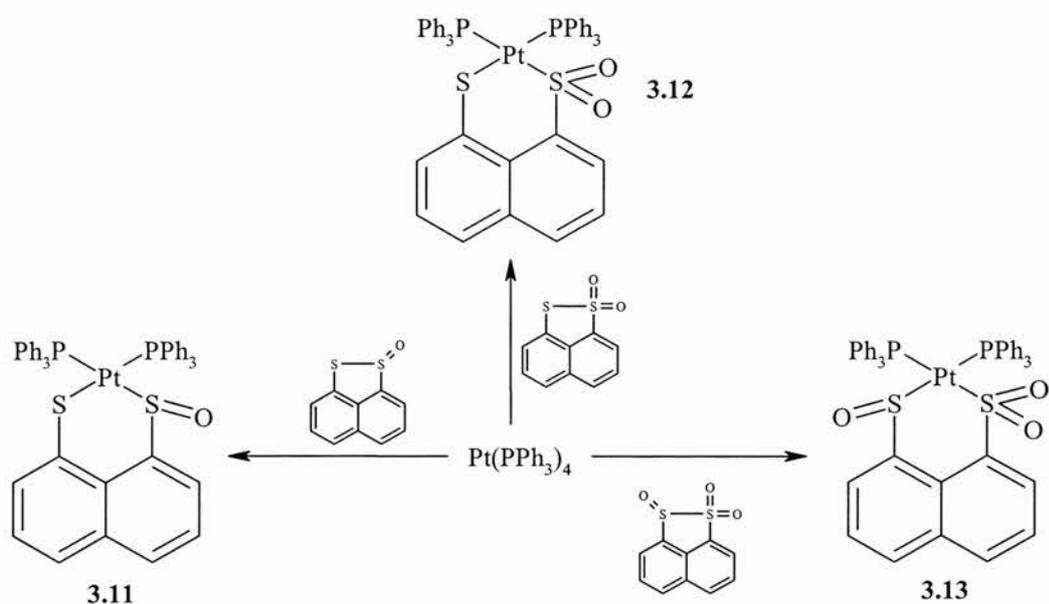


**Scheme 3.3** Oxidative addition reactions of disulfur pro-ligands to platinum species.

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The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) data for complexes **3.7-3.10** are consistent with the proposed structures, those of **3.8** and **3.9** consisting of a singlet with platinum satellites at  $\delta(\text{P})$  21.3 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt})$  2949 Hz] and 23.0 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt})$  2981 Hz] respectively while the asymmetrically substituted complexes **3.7** and **3.10** display AX type spectra with resonances in the range of  $\delta(\text{P})$  19.5 and 25.5 ppm,  $^1J(^{31}\text{P}-^{195}\text{Pt})$  and  $^2J(^{31}\text{P}_{(\text{A})}-^{31}\text{P}_{(\text{X})})$  coupling constants with typical values of around 3000 and 26/27 Hz.  $^{195}\text{Pt}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta(\text{Pt})$  values are in accordance with those of complexes **3.1-3.6** and characteristically lie within the -4900 to -4600 Hz range and appear as a well resolved triplet for **3.8** and **3.9** and double doublets for **3.7** and **3.10**. The mass spectra of these complexes displayed the parent ion at  $m/z$  967 ( $\text{M}+\text{H}$ ) $^+$ , 1022 ( $\text{M}$ ) $^+$ , 936 ( $\text{M}$ ) $^+$  and 961 ( $\text{M}+\text{H}$ ) $^+$  respectively while elemental analysis was satisfactory.

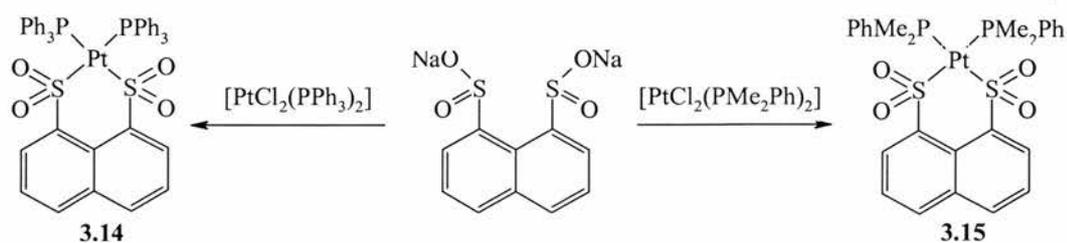
Complexes **3.11**, **3.12** and **3.13** were also prepared by oxidative addition of the S-S bridged mono, di and tri- oxides of naphtho[1,8-*cd*]-1,2-dithiole to  $[\text{Pt}(\text{PPh}_3)_4]$  in toluene at room temperature (scheme 3.4).



**Scheme 3.4** Oxidative addition reactions of oxidised disulfur pro-ligands to platinum species.

The yellow/orange microcrystalline solids were obtained in almost quantitative yields (91-96%).

The tetra-oxide derivatives **3.14** and **3.15** were prepared from the appropriate *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] complex and the disodium salt of naphthalene-1,8-disulfinic acid (scheme 3.5) as attempted oxidative addition reactions of the tetra-oxide naphtho[1,8-*cd*]-1,2-dithiole-1,1,2,2-tetraoxide failed.



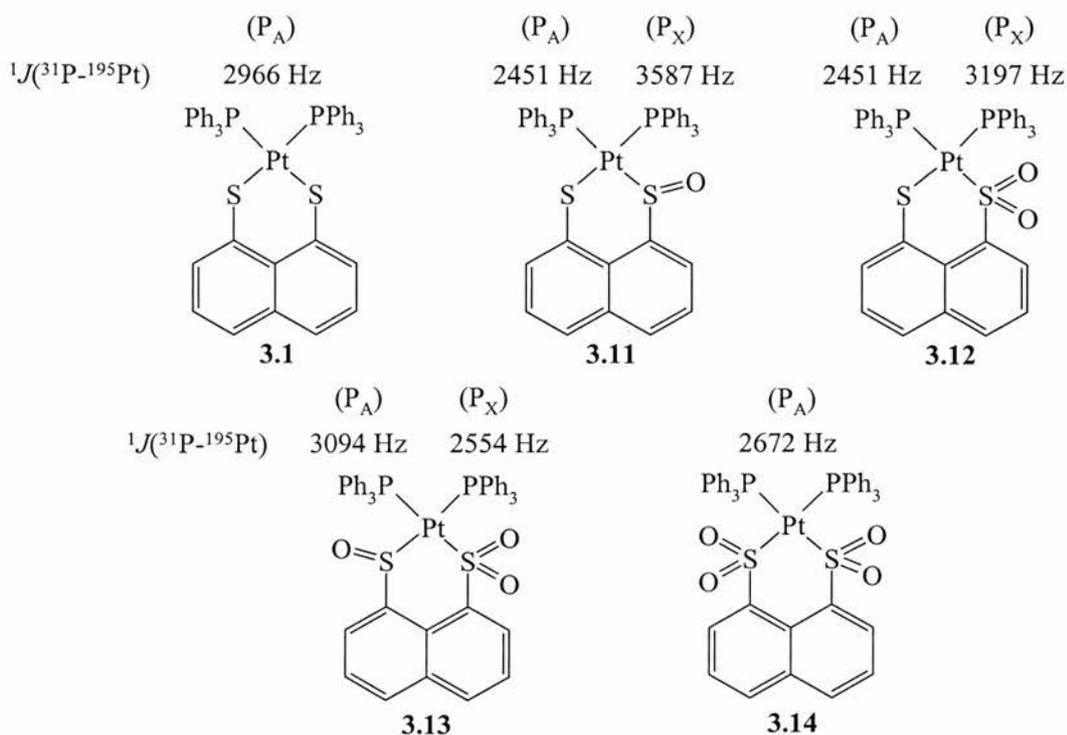
**Scheme 3.5** Salt elimination reactions of disulfinic acid pro-ligands to platinum species.

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Compound **3.14** was isolated as a yellow solvent free powder. The dimethylphenylphosphine analogue **3.15** was isolated as yellow crystals which were found by microanalysis and X-ray crystallography to contain a half molecule of dichloromethane per molecule of product. In common with complexes **3.4**, **3.5** and **3.6**, the tetra-oxide derivatives were prone to degradation in chlorinated solvents – the decomposition products in both cases were identified as *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (PR<sub>3</sub> = PPh<sub>3</sub> **3.14**, PMe<sub>2</sub>Ph **3.15**) confirmed by comparison of the <sup>31</sup>P{<sup>1</sup>H} δ(P) and <sup>1</sup>J(<sup>31</sup>P-<sup>195</sup>Pt) values to those of authentic samples. The addition of triethylamine to chlorinated solvents used in their preparation prevented decomposition.

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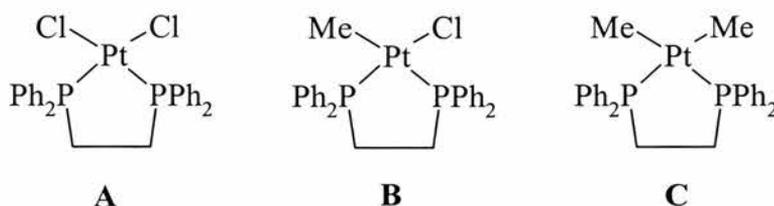
The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) data for complexes **3.11-3.13** are similar in that the spectra are all of the AX type with corresponding platinum satellites. The phosphorus resonances and  $^1J(^{31}\text{P}-^{195}\text{Pt})$  coupling constants of complex **3.11**,  $\delta(\text{P}_\text{A})$  20.8 ppm (2451 Hz) and  $\delta(\text{P}_\text{X})$  26.4 ppm (3587 Hz) have been assigned to the phosphines *trans* to the sulfenato ( $-\text{S}(\text{O})\text{R}$ ) and the thiolato ( $-\text{SR}$ ) groups respectively. In previously characterised examples of  $[(\text{PPh}_3)_2\text{Pt}]$  complexes bearing thiolato/sulfenato ligand systems phosphines *trans* to the sulfenato moiety have much smaller  $^1J(^{31}\text{P}-^{195}\text{Pt})$  coupling constants due to the larger *trans* influence of the ( $-\text{S}(\text{O})\text{R}$ ) ligand.<sup>(71-78)</sup> Assuming that ( $-\text{S}(\text{O})_2\text{R}$ ) ligands have a higher *trans* influence than ( $-\text{SR}$ ) (see crystallographic discussion below) the phosphine ligands of complex **3.12** can be assigned thus, P *trans* to ( $-\text{S}(\text{O})_2\text{R}$ )  $\delta(\text{P}_\text{A})$  18.4 ppm,  $^1J(^{31}\text{P}_\text{(A)}-^{195}\text{Pt})$  2451 Hz and P *trans* to ( $-\text{SR}$ )  $\delta(\text{P}_\text{X})$  22.4 ppm,  $^1J(^{31}\text{P}_\text{(X)}-^{195}\text{Pt})$  3197 Hz. The assignment of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **3.13** is more complicated but it is believed that  $\delta(\text{P}_\text{A})$  20.0 ppm  $^1J(^{31}\text{P}_\text{(A)}-^{195}\text{Pt})$  3094 Hz is the  $\text{Ph}_3\text{P}$  group *trans* to the ( $-\text{S}(\text{O})_2\text{R}$ ) and  $\delta(\text{P}_\text{X})$  22.1 ppm  $^1J(^{31}\text{P}_\text{(X)}-^{195}\text{Pt})$  2554 Hz is the  $\text{Ph}_3\text{P}$  ligand *trans* to the ( $-\text{S}(\text{O})\text{R}$ ) function. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $\text{CD}_2\text{Cl}_2/\text{Et}_3\text{N}$ ) of **3.14** and **3.15** are both single resonances with platinum satellites at  $\delta(\text{P})$  14.2, ( $^1J(^{31}\text{P}-^{195}\text{Pt})$  2672 Hz) and -10.6, ( $^1J(^{31}\text{P}-^{195}\text{Pt})$  2599 Hz) respectively. These assignments were all based upon a quantitative comparison of the  $^1J(^{31}\text{P}-^{195}\text{Pt})$  coupling constants of complexes **3.1**, **3.11**, **3.12**, **3.13** and **3.14** (Figure 3.3).



**Figure 3.3** Comparison of coupling constants of complexes **3.1** and **3.11-3.14**.

The  $^1J(^{31}\text{P}-^{195}\text{Pt})$  coupling constant of the dithiolate complex **3.1** is 2966 Hz, while the  $\text{PPh}_3$  ligand *trans* to the thiolate group of **3.11** is 3587 Hz, 600 Hz larger than in **3.1**, an increase that is believed to be due to an effect of the *cis* ligand ( $-\text{S}(\text{O})\text{R}$ ) in **3.11**. In complex **3.12** the coupling constants are 2451 Hz for  $\text{P}_{(\text{A})}$ ,  $\text{PPh}_3$  *trans* to  $(-\text{SO})_2\text{R}$ ) and 3197 Hz for  $\text{P}_{(\text{X})}$ ,  $\text{PPh}_3$  *trans* to  $(-\text{SR})$ . Once more there is an increase, although smaller than in **3.11**, in the coupling constant magnitude for the  $\text{PPh}_3$  *trans* to the  $(-\text{SR})$  ligand, again as a consequence of the “*cis* effect” of a ligand with a higher *trans* influence. If this argument is applied to **3.13** then the ligand *trans* to  $(-\text{S}(\text{O})_2\text{R})$  should have a coupling constant that is substantially higher than that observed in **3.12**, which is what we find in **3.13**, 3094 vs 2451, an increase of over 640 Hz. There is also an increase in the *trans* to  $(-\text{S}(\text{O})\text{R})$   $^1J(^{31}\text{P}_{(\text{X})}-^{195}\text{Pt})$  coupling of **3.13** (2554 Hz) in comparison to **3.11**

(2451 Hz) which we also observe in **3.12**. Further evidence for the proposed “*cis* effect” of highly *trans* influencing ligands can be seen by comparison of the  $^{31}\text{P}\{^1\text{H}\}$  NMR data ( $\text{CD}_2\text{Cl}_2$ ) for a series of Pt(II) complexes bearing DPPE (1,2-bis(diphenylphosphino)ethane), Me and Cl ligands (figure 3.4).

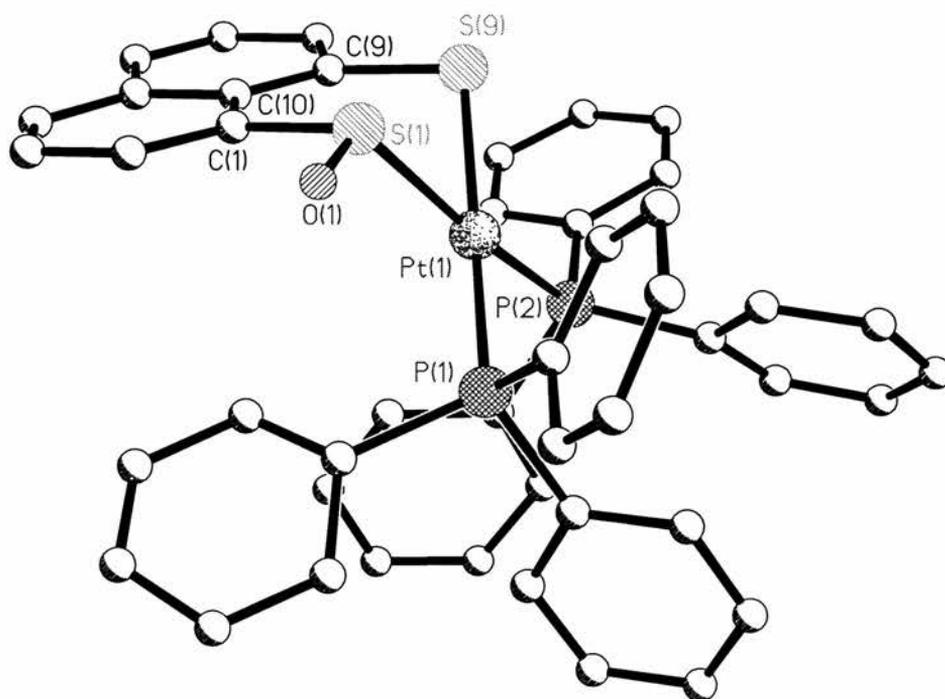


**Figure 3.4** Platinum (II) complexes containing chlorine and methyl groups for comparison of  $^{31}\text{P}$  NMR.

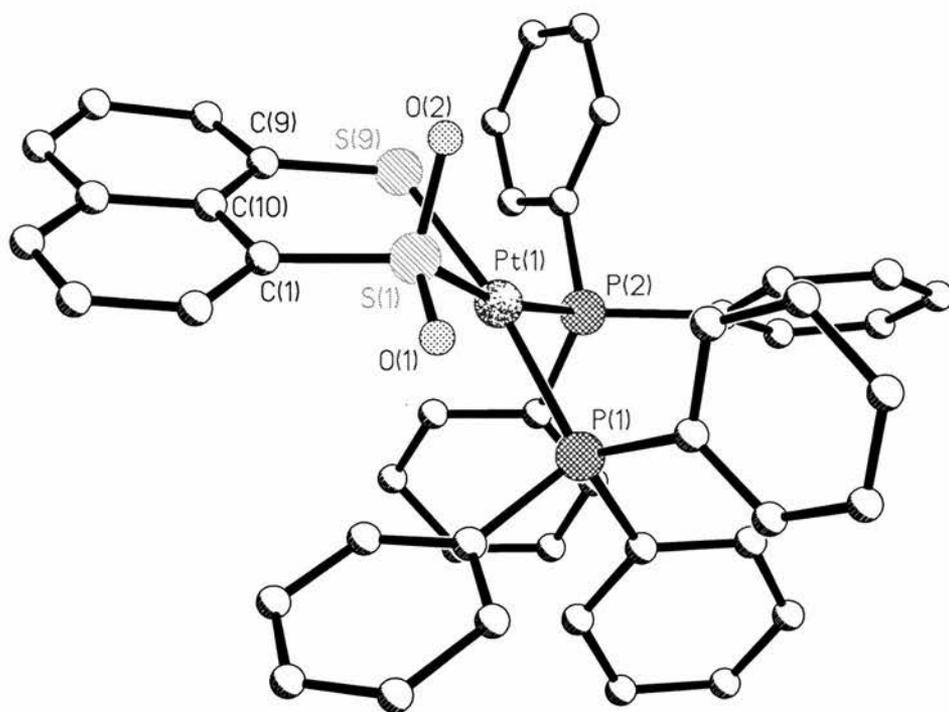
The  $^1J(^{31}\text{P}-^{195}\text{Pt})$  coupling constant of the chloride complex **A** is 3620 Hz,<sup>(147)</sup> while that of **C** with Me ligands (the *trans* effect of Me is much greater than that of Cl ligands) has a coupling of 1797 Hz.<sup>(148)</sup> The couplings in **B** are 1738 Hz for the phosphorus *trans* to the Me ligand and 4211 Hz for phosphorus *trans* to Cl, an increase of nearly 600 Hz compared to that of dichloride **A**.<sup>(148)</sup> The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **3.11**, **3.12** and **3.13** also show the characteristic  $^2J(^{31}\text{P}_{(\text{A})}-^{31}\text{P}_{(\text{X})})$  couplings of 19, 23 and 16 Hz respectively which are consistent with asymmetrically substituted *cis*-platinum diphosphine complexes. The  $^{195}\text{Pt}$  NMR data ( $\text{CD}_2\text{Cl}_2$ ) of complexes **3.11-3.13** are also consistent with the proposed structures, each spectra being displayed as a double doublet in the expected range -4529 to -4097 ppm, while the  $^{195}\text{Pt}$  NMR spectra ( $\text{CD}_2\text{Cl}_2/\text{Et}_3\text{N}$ ) of **3.14** and **3.15** are triplets centered at  $\delta(\text{Pt})$  -4250 and  $\delta(\text{Pt})$  -4352 ppm respectively. IR (KBr disc) data for complexes **3.11-3.15** were consistent with the structural

assignments showing  $\nu(\text{S}=\text{O})$  bands for complexes **3.11** and **3.13** at *ca.*  $1100\text{ cm}^{-1}$  and  $\nu(\text{S}\{\text{=O}\}_2)$  bands for **3.12**, **3.13**, **3.14** and **3.15** at approximately  $1200$ ,  $1060\text{ cm}^{-1}$ . Satisfactory microanalyses were obtained for all of these complexes and mass spectral data in all cases showed  $m/z$  corresponding to  $[\text{M}+\text{H}]^+$  at  $927$ ,  $943$ ,  $959$ ,  $975$  and  $727$  respectively, plus mass peak profiles matching  $[\text{Pt}(\text{PR}_3)_2]^{2+}$  ( $\text{PR}_3 = \text{PPh}_3$ ,  $\text{PMe}_3$  or  $\text{PMe}_2\text{Ph}$ ).

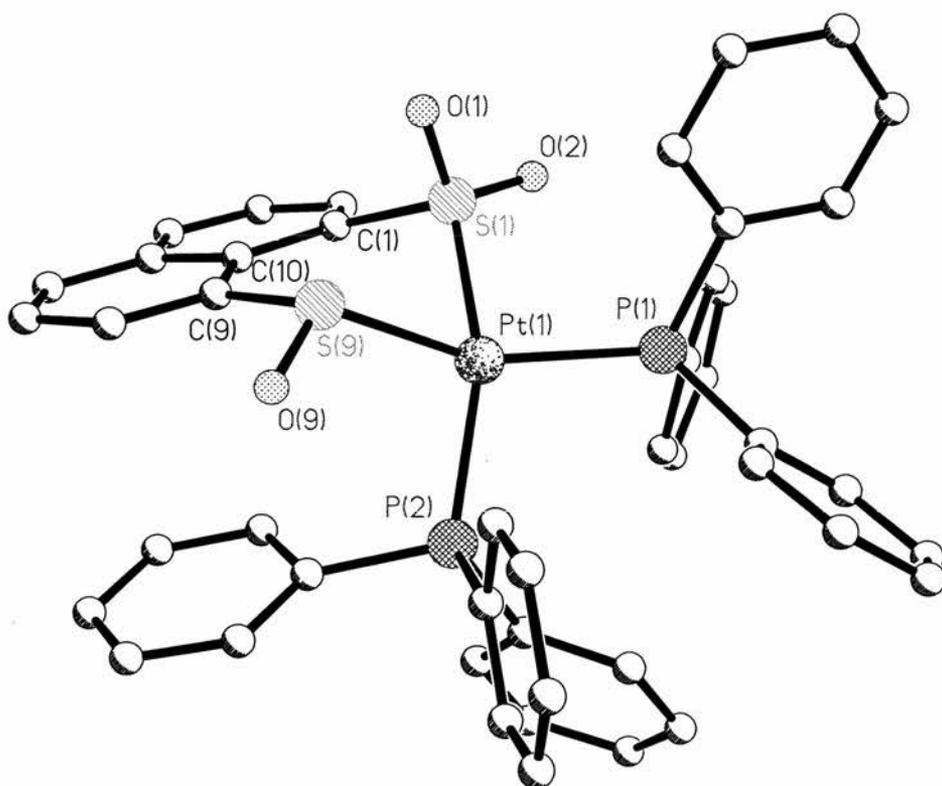
The X-ray crystal structures of complexes **3.11**, **3.12**, **3.13** and **3.15** (figures 3.5-3.8) show that these oxide ligands are always bound to the platinum core through the sulfur atoms, in contrast to the analogous titanium complexes mentioned in chapter 2, which are bound through the oxygen atom. This is explained by the fact that platinum is considered a soft metal and will therefore prefer to bind to the soft sulfur atom rather than the hard oxygen atom.



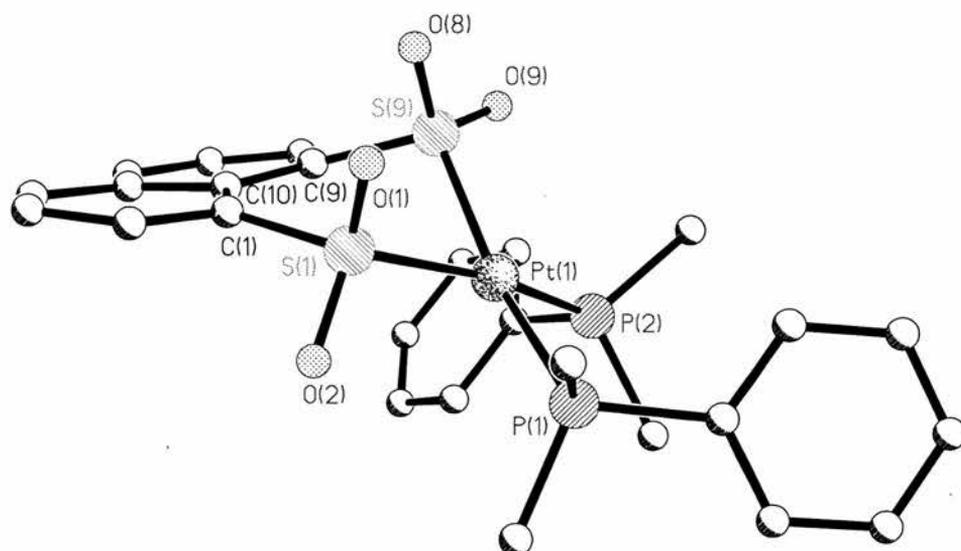
**Figure 3.5** Crystal structure of  $[\text{Pt}(1\text{-S},8\text{-}\{\text{S}(\text{O})\}\text{-nap})(\text{PPh}_3)_2]$  **3.11**.



**Figure 3.6** Crystal structure of  $[\text{Pt}(1\text{-S},8\text{-}\{\text{S}(\text{O})_2\}\text{-nap})(\text{PPh}_3)_2]$  **3.12**.



**Figure 3.7** Crystal structure of  $[\text{Pt}(1\text{-}\{\text{S}(\text{O})\},8\text{-}\{\text{S}(\text{O})_2\}\text{-nap})(\text{PPh}_3)_2]$  **3.13**.



**Figure 3.8** Crystal structure of [Pt(1,8- $\{S(O)_2\}_2$ -nap)(PMe<sub>2</sub>Ph)<sub>2</sub>] **3.15**.

	<b>3.11</b>	<b>3.12(mol 1)</b>	<b>3.12(mol 2)</b>	<b>3.13</b>	<b>3.15</b>
Pt(1)-E(1)	2.344(2)	2.310(5)	2.291(5)	2.306(2)	2.313(1)
Pt(1)-E(9)	2.338(2)	2.308(5)	2.332(5)	2.327(2)	2.288(1)
Pt(1)-P(1)	2.308(2)	2.308(5)	2.295(5)	2.331(2)	2.336(1)
Pt(1)-P(2)	2.316(2)	2.321(5)	2.337(5)	2.323(2)	2.327(1)
E(1)-C(1)	1.829(8)	1.789(19)	1.806(18)	1.792(8)	1.835(4)
E(9)-C(9)	1.767(10)	1.78(2)	1.791(17)	1.813(7)	1.770(5)
E(1)-E(1)	2.94(1)	3.19(1)	3.17(1)	3.03(1)	3.14(1)
S(1)-O(1)	1.450(6)	1.436(14)	1.458(14)	1.452(5)	1.454(3)
S(1)-O(2)	-	1.455(13)	1.495(14)	1.466(5)	1.478(3)
S(9)-O(8)	-	-	-	-	1.469(3)
S(9)-O(9)	-	-	-	1.501(5)	1.437(3)
E(1)-Pt(1)-E(9)	77.87(8)	87.25(18)	86.54(18)	81.69(6)	85.91(4)
P(1)-Pt(1)-P(2)	97.86(6)	96.50(18)	96.53(18)	103.64(6)	98.12(4)
P(1)-Pt(1)-E(1)	93.36(7)	90.45(18)	89.09(18)	90.01(6)	88.79(3)
P(2)-Pt(1)-E(9)	91.14(7)	86.98(18)	88.58(17)	92.99(6)	90.36(4)
P(1)-Pt(1)-E(9)	169.86(7)	171.95(18)	170.59(18)	152.29(6)	164.71(4)
P(2)-Pt(1)-E(1)	168.56(7)	168.97(18)	172.61(19)	158.17(7)	165.56(3)

Pt(1)-E(1)-C(1)	97.2(3)	110.3(6)	106.0(6)	103.0(2)	110.92(12)
E(1)-C(1)-C(10)	126.3(7)	124.8(15)	122.3(14)	122.1(5)	127.9(3)
C(1)-C(10)-C(9)	125.0(8)	126.9(16)	124.5(16)	127.0(6)	126.4(4)
C(10)-C(9)-E(9)	122.5(7)	127.4(15)	131.8(15)	125.0(5)	120.1(3)
C(9)-E(9)-Pt(1)	103.1(3)	114.7(7)	111.0(7)	106.3(2)	106.77(14)
Pt(1)-S(1)-O(1)	117.9(3)	115.1(6)	114.9(5)	113.3(2)	115.28(11)
Pt(1)-S(1)-O(2)	-	104.6(6)	109.6(6)	114.7(2)	107.84(10)
C(1)-S(1)-O(1)	106.0(4)	104.9(9)	105.8(9)	103.9(3)	107.02(15)
C(1)-S(1)-O(2)	-	104.7(9)	104.3(8)	106.0(3)	101.22(16)
O(1)-S(1)-O(2)	-	116.9(8)	115.1(8)	114.3(3)	113.66(15)
Pt(1)-S(9)-O(8)	-	-	-	-	108.64(13)
Pt(1)-S(9)-O(9)	-	-	-	115.64(19)	114.75(16)
C(9)-S(9)-O(8)	-	-	-	-	103.56(19)
C(9)-S(9)-O(9)	-	-	-	105.8(3)	107.4(2)
O(8)-S(9)-O(9)	-	-	-	-	114.78(19)
S(1)-C(1) ...	3	14	24	9	24
C(9)-S(9)					
(PtE <sub>2</sub> ) ...	111	137	131	119	129
(E <sub>2</sub> Nap)					
C(4)-C(5)-C(10)- C(9)	177.2(9)	178.8(17)	170.3(18)	175.5(7)	171.6(4)
C(6)-C(5)-C(10)- C(1)	176.4(9)	179.0(18)	177.4(17)	179.3(6)	173.7(4)
C(4)-C(5)-C(10)- C(1)	0.9(13)	1.0(3)	4.0(3)	2.3(10)	7.5(6)
C(6)-C(5)-C(10)- C(9)	5.6(13)	3.0(3)	8.0(3)	2.9(10)	7.2(6)

**Table 3.2** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for complexes **3.11-3.13** and **3.15**.

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Like the earlier examples, the central platinum atom of these complexes are shown to exist in a distorted square planar co-ordination sphere consisting of two phosphorus atoms and two sulfur atoms. The P(1)-Pt(1)-P(2) angles are in the range 96.50(18)-98.12(4)° with the exception of **3.13** which has a significantly larger angle of 103.64(13)°. Correspondingly, the distortion from square planarity is shown by the S(1)-Pt(1)-S(9) angles of these complexes, in the range 85.91(4)-87.25(18)° with the exception of **3.13** again, which has an angle of 81.69(6)° and also **3.11**, which displays the smallest S(1)-Pt(1)-S(9) angle (77.87(8)°). Like **3.2** and **3.4**, the *cis* P(1)-Pt(1)-S(1), P(2)-Pt(1)-S(9) (86.98(18)-93.36(7)°) and *trans* P(1)-Pt(1)-S(9), P(2)-Pt(1)-S(1) (164.71(4)-172.61(19)°) angles lie within reasonable ranges and are unremarkable, with the exception of **3.13** which has a much narrower *trans* bond angle (152.29(6)° and 158.17(7)°).

The non-bonded S...S distances of these complexes are in the range 2.94(1)-3.19(1)Å, which are slightly shorter than that of complex **3.4**, possibly as a consequence of the presence of the oxygen atom(s) on one or both sulfur atoms, the preferred position of the oxidised sulfur atom being pushed slightly closer to the other sulfur atom to help accommodate the oxygen atom(s) around it although there is no trend noticed between the non-bonded S...S distance and the number of oxygen atoms in the complex. Pt-S bond lengths are unremarkable and are in accord with **3.4** and other similar complexes.<sup>(53)</sup>

A previous study of the Ni-S bond distances of a series of symmetrically derivatised complexes showed the following bond length trend: Ni-S(O)R > Ni-SR > Ni-S(O)<sub>2</sub>R (this was rationalized by invoking a combination of competing factors such as the  $\sigma$ -donor ability, a contraction in the size of the sulfur atom with increasing oxidation state, and destabilization of the M-S bond due to

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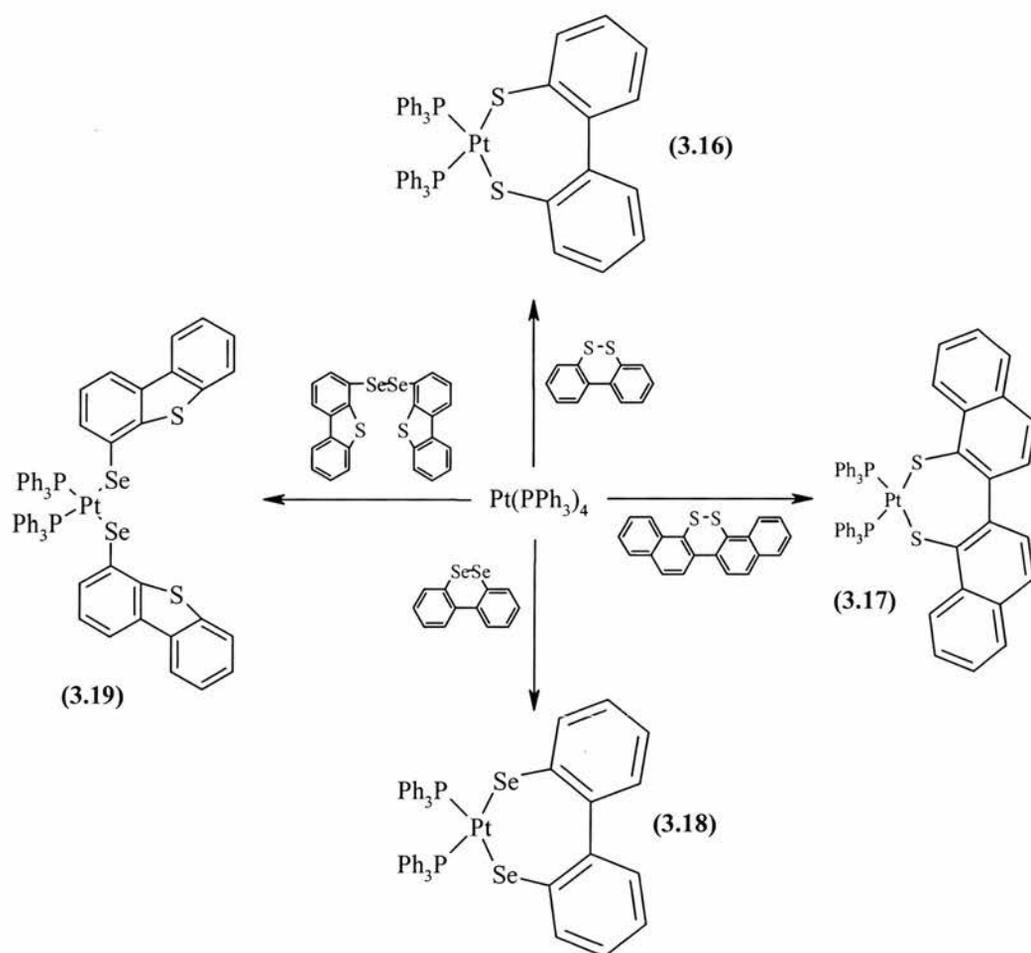
repulsion between the filled *d* orbitals of the metal and lone pairs on the ligand.<sup>(85)</sup> It has also been observed that the Pt-P bond distance increases with the increasing *trans* influence of the co-ligand, the sulfenato –S(O)R ligand having a larger *trans* influence than the thiolato –SR ligand.<sup>(71-78)</sup> As there are no reported examples of platinum complexes with mixed phosphine-sulfinato ligand donor sets a comparison of the *trans* influence of sulfinato vs sulfenato vs thiolato ligands is not possible. Examination of the Pt-S bond distances of the oxidized naphtho-1,8-dithiolate derivatives **3.11**, **3.12**, **3.13** and **3.15** shows no obvious Pt-S bond length trend; the Pt-S<sub>(thiolato)</sub> distances of **3.11** and **3.12** are in the range 2.308(5)-2.338(2)Å, the Pt-S<sub>(sulfenato)</sub> bond lengths of **3.11** 2.338(2)Å and **3.13** 2.332(5)Å and Pt-S<sub>(sulfinato)</sub> distance range of **3.12**, **3.13** and **3.15** 2.291(5)-2.313(1)Å show considerable overlap. The *trans* influence of the sulfur ligand in relation to Pt-P bond length trend as discussed above is observed in complexes **3.11**, **3.12** and **3.13**; Pt-P<sub>(*trans* to thiolato)</sub> **3.11** 2.308(2), **3.12** 2.308(5) and 2.295(5)Å are noticed to be shorter than Pt-P<sub>(*trans* to sulfenato)</sub> **3.11** 2.316(2), **3.13** 2.337(5)Å. Additionally we find that the Pt-P<sub>(*trans* to sulfinato)</sub> distances **3.12** 2.321(5) and 2.337(5), **3.13** 3.323(2) and **3.15** 2.336(1) and 2.327(1)Å are greater than the Pt-P<sub>(*trans* to thiolato)</sub> bond lengths implying that (-S(O)<sub>2</sub>R) has a stronger *trans* influence than (-SR). However there appears to be no significant difference in Pt-P<sub>(*trans* to sulfenato)</sub> vs Pt-P<sub>(*trans* to sulfinato)</sub> bond distances. The S-O bond lengths appear to be independent of sulfur oxidation state and fall within a narrow range 1.436(14)-1.501(5) Å; previous studies of average S-O distances in –S(O)R and –S(O)<sub>2</sub>R complexes found that sulfinato S-O lengths were typically 0.1 Å shorter than those of sulfenato ligands.<sup>(85)</sup> The X-ray structures of **3.11**, **3.12** and **3.13** show the oxygen atoms of the sulfenato groups in **3.11** and **3.13** and one oxygen atom

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of the sulfinato moiety's of **3.12** and **3.13** lies approximately within the plane of the naphthalene ring. A similar situation is observed in the S(9) sulfinato group of complex **3.15** where O(9) and the naphthalene ring are co-planar whereas the O(1) and O(2) oxygen atoms of the S(1) sulfinato group lie above and below the naphthalene ring plane respectively which may be a consequence of the distortion observed in the ligand (see below). The naphthalene-E<sub>2</sub> ligands are hinged with respect to the coordination plane and the angles defined by the Pt(1)-E(1)-E(9) and the E(1)-E(9)-naphthalene mean planes are variable and range from 111° in **3.11** to 137° in **3.12** the most bent examples (those with a hinge angle closest to 90°) being molecules containing a sulfenato -S(O)R moiety **3.11** (111°) and **3.13** (119°). Another interesting feature of these complexes is observed in the naphthalene ring which although planar when the di-sulfur bridge is intact, <sup>(102)</sup> becomes twisted when incorporated in to a six-membered platinacycle. Upon coordination the naphthalene backbone of the ligand becomes "twisted" – the extent of the naphthalene ring distortion is variable (see dihedral S(1)-C(1) ... C(9)-S(9) and naphthalene ring torsion angles in Table 3.2) the most planar example is **3.12**<sub>(molecule 1)</sub> and the most twisted is **3.15**.

Oxidative addition reactions of dibenzo[*ce*]-1,2-dithiine, 13,14-dithiapicene, 9,10-diselena-phenanthrene and 4-selena-dibenzothiophene dimer with the Pt(0) complex [Pt(PPh<sub>3</sub>)<sub>4</sub>] all proceed smoothly (Scheme 3.6) to give Pt(II) complexes [Pt(2,2'-S<sub>2</sub>-biphen)(PPh<sub>3</sub>)<sub>2</sub>] **3.16**, [Pt(2,2'-S<sub>2</sub>-binap)(PPh<sub>3</sub>)<sub>2</sub>] **3.17**, [Pt(2,2'-Se<sub>2</sub>-biphen)(PPh<sub>3</sub>)<sub>2</sub>] **3.18** and [Pt(4-Se-dbt)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] **3.19**, respectively in reasonable to excellent yield (55-92%).



**Scheme 3.6** Oxidative addition reactions of dichalcogeno-proligands to platinum species.

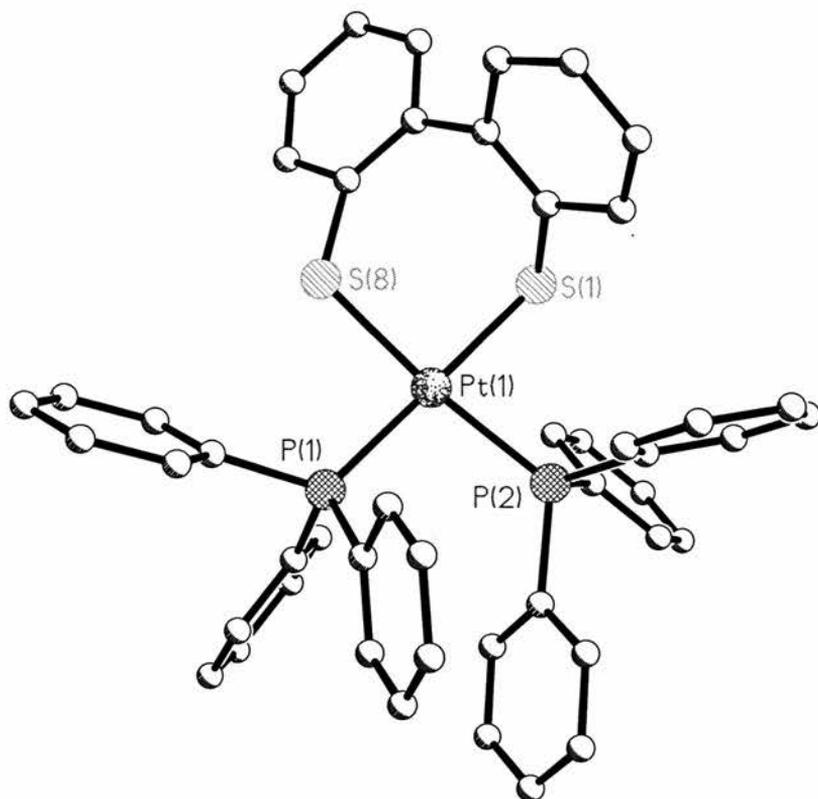
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The isolation and purification of these complexes is straight-forward and similar to the method used for other complexes mentioned earlier.

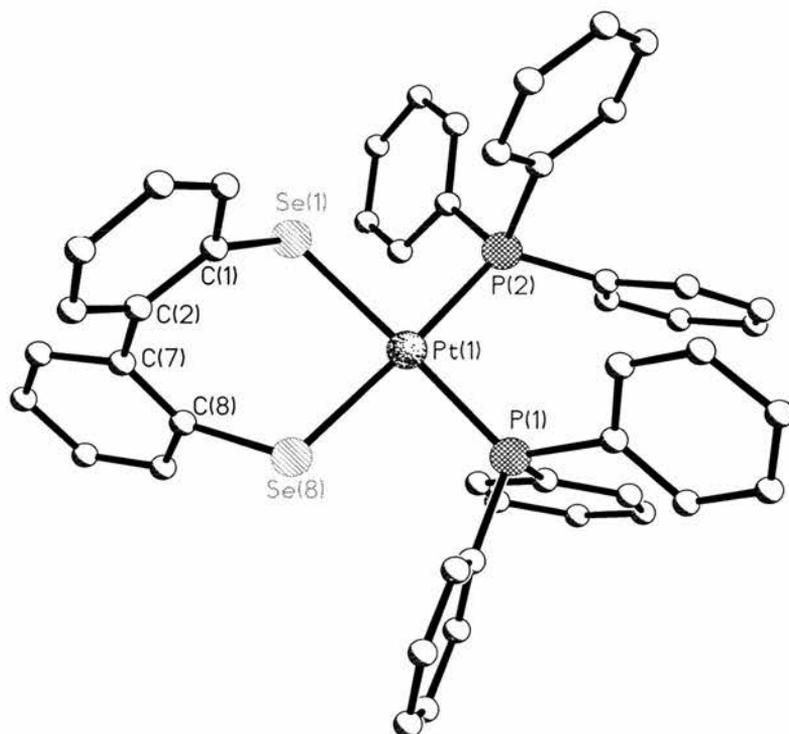
The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $\text{CD}_2\text{Cl}_2$ ) of complexes **3.16**, **3.17**, **3.18** and **3.19** display the anticipated single resonances with platinum satellites at  $\delta(\text{P})$  23.1 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2956$  Hz],  $\delta(\text{P})$  23.0 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2971$  Hz],  $\delta(\text{P})$  18.7 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt}) = 2990$  Hz] and  $\delta(\text{P})$  16 ppm [ $^1J(^{31}\text{P}-^{195}\text{Pt}) = 3046$  Hz] respectively with additional  $^{77}\text{Se}$  satellites [ $^2J(^{31}\text{P}-^{77}\text{Se}) = 49$  Hz] being observed in the spectrum of complex **3.18**. The expected selenium satellites in **3.19** are not observed, probably due to the poor solubility of this sample in dichloromethane causing a weaker spectrum. The  $^{195}\text{Pt}$  NMR spectra ( $\text{CD}_2\text{Cl}_2$ ) show triplets at  $\delta(\text{Pt}) = -4553$  ppm,  $\delta(\text{Pt}) = -4530$  ppm,  $\delta(\text{Pt}) = -4785$  ppm and  $\delta(\text{Pt}) = -4843$  ppm for **3.16-3.19** respectively. These values are all very similar to those of the related naphthalene complexes described earlier such as complexes **3.1** and **3.2**.

In each case the purity of the sample was confirmed by elemental analysis and the parent ion was witnessed as  $[\text{M}]^+$  at  $m/z$  936 in the case of **3.16**, at  $m/z$  1031 ( $[\text{M}+\text{H}]^+$ ) for **3.18** and  $[\text{M}+\text{Na}]^+$  at 1058 and 1267 for **3.17** and **3.19** respectively.

The X-ray analyses of complexes **3.16** and **3.18** (figures 3.9 and 3.10) show that the platinum core, like their naphthalene backboned equivalents, lie at the centre of a distorted square planar co-ordination sphere, consisting of two phosphorus and two chalcogen atoms.



**Figure 3.9** Crystal structure of  $[\text{Pt}(2,2'\text{-S}_2\text{-biphen})(\text{PPh}_3)_2]$  **3.16**.



**Figure 3.10** Crystal structure of  $[\text{Pt}(2,2'\text{-Se}_2\text{-biphen})(\text{PPh}_3)_2]$  **3.18**.

	<b>3.16</b>	<b>3.18</b>
Pt(1)-E(1)	2.368(6)	2.4830(8)
Pt(1)-E(8)	2.330(10)	2.4555(8)
Pt(1)-P-(1)	2.283(6)	2.2775(17)
Pt(1)-P(2)	2.295(9)	2.2895(17)
E(1)-C(1)	1.769(10)	1.915(8)
C(8)-E(8)	1.797(10)	1.925(7)
P(1)-Pt(1)-P(2)	97.21(12)	97.28(6)
P(1)-Pt(1)-E(8)	88.11(12)	86.37(5)
P(2)-Pt(1)-E(8)	174.51(11)	174.10(5)
P(1)-Pt(1)-E(1)	178.72(14)	177.67(5)
P(2)-Pt(1)-E(1)	83.64(13)	84.79(5)
E(1)-Pt(1)-E(8)	91.07(13)	91.47(3)
C(1)-E(1)-Pt(1)	102.8(4)	103.6(2)
C(8)-E(8)-Pt(1)	115.7(4)	107.6(2)
E(1)-C(1)-C(2)	121.0(8)	122.7(6)
C(1)-C(2)-C(7)	122.5(9)	120.1(7)
C(2)-C(7)-C(8)	125.4(9)	123.4(7)
C(7)-C(8)-E(8)	125.3(7)	122.8(6)
C(1)-C(2)-C(7)-C(12)	56.2(9)	62.0(8)

**Table 3.3** Selected bond lengths [Å] and angles [°] for complexes **3.16** and **3.18**.

These two complexes display many similarities in their X-ray structures. The P(1)-Pt(1)-P(2) angles are 97.21(12) and 97.28(6)°, showing considerable deviation from idealized 90° square planar geometry, similar to the naphthalene derivatives described earlier. The corresponding E(1)-Pt(1)-E(8) angles 91.07(13) and 91.47(3)°, close to idealized square planar geometry and larger than those corresponding angles in (PMe<sub>3</sub>)<sub>2</sub>Pt(S<sub>2</sub>C<sub>10</sub>H<sub>6</sub>) **3.4** and (PPh<sub>3</sub>)<sub>2</sub>Pt(Se<sub>2</sub>C<sub>10</sub>H<sub>6</sub>) **3.2**. This can be explained as this angle is part of a seven-

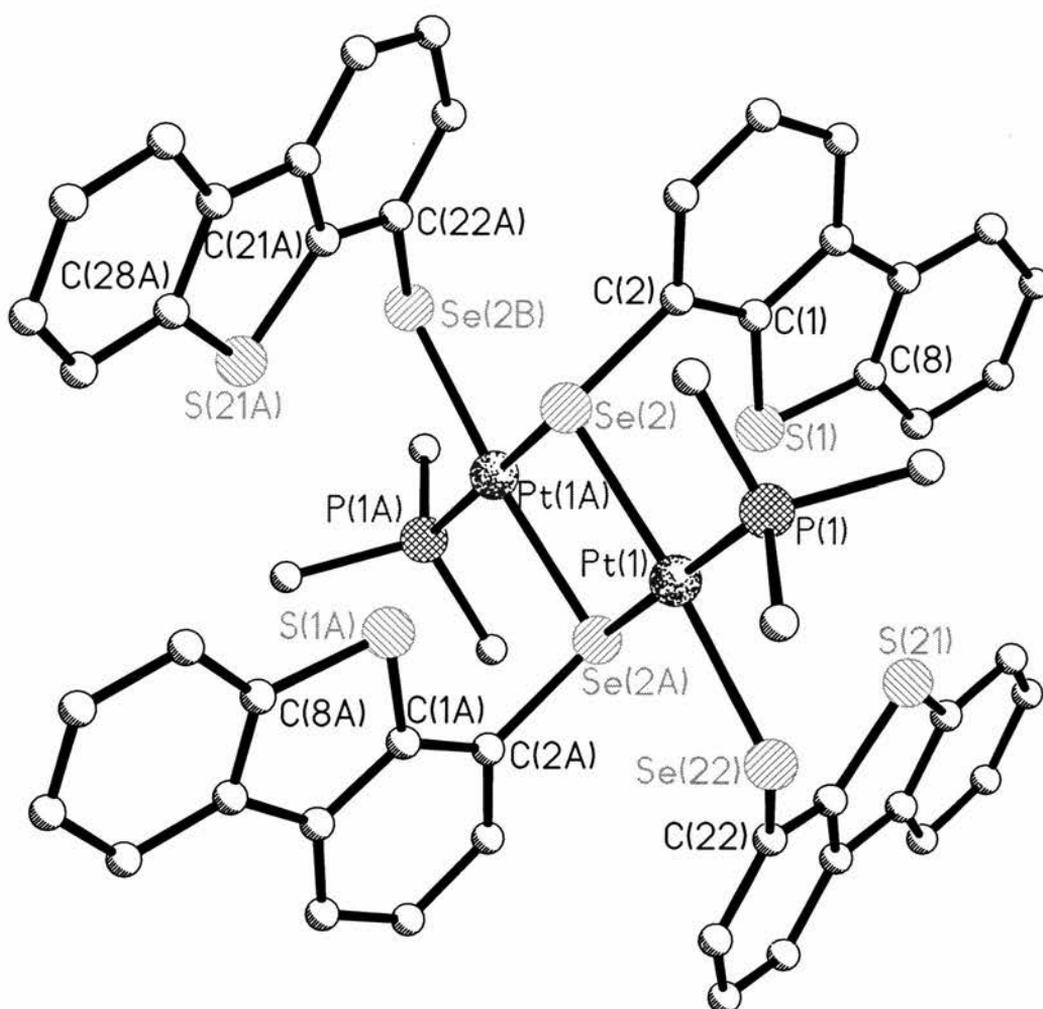
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membered (PtE<sub>2</sub>C<sub>4</sub>) ring rather than a six-membered (PtE<sub>2</sub>C<sub>3</sub>) ring, the presence of the extra carbon in the ring reduces strain and allows the chalcogen atoms more flexibility to settle in a square planar geometry. The Pt-E-C bond angles are found to be vastly different on each side of these complexes (102.8(4)<sup>o</sup> and 115.7(4)<sup>o</sup> (**3.16**) and 103.6(2)<sup>o</sup> and 107.6(2)<sup>o</sup> (**3.18**)). This is explained by the flexibility in the biphenyl backbone, which is also noticed in the free ligand,<sup>(103)</sup> where the two C<sub>6</sub> rings are not co-planar. In fact, the two C<sub>6</sub> rings are angled more notably than in the free ligands, with the C(1)-C(2)-C(7)-C(12) angle of **3.16** (56.2(9)<sup>o</sup>) being much greater than the ligand (34.2(7)<sup>o</sup>).<sup>(103)</sup> The C(1)-C(2)-C(7)-C(12) angle of **3.18** is even greater than that of the sulfur containing derivative (62.0(8)<sup>o</sup>).

The non-bonded S...S distances of **3.16**, 3.353(10)Å, is much larger than in the S-S bonded prologues,<sup>(103)</sup> and is significantly larger than the corresponding distances in the previously mentioned naphthalene backbone derivatives, in accord with the greater S(1)-Pt(1)-S(8) bond angle forcing the two sulfur atoms further apart, an expected result which suggests that there is no bonding interaction between the two sulfur atoms. The same is noticed in the non-bonded Se...Se distance of **3.18**, 3.54(1)Å, which is much greater than the bonded distance of the free ligand, 2.323(2)Å.<sup>(47)</sup> This non-bonded distance is greater than that of the complex (PPh<sub>3</sub>)<sub>2</sub>Pt(Se<sub>2</sub>C<sub>10</sub>H<sub>6</sub>), **3.2**, and is close to the van der Waals radius of selenium, implying that there might be a significant interaction between the two Se atoms.

The Pt-S distances of **3.16** are unremarkable and are similar to those seen in previous platinum complexes. Similarly, the Pt-Se bond distances of complex **3.17** are very close to those of known Pt-Se containing complexes.<sup>(144, 146)</sup>

Complex **3.19** was found by X-ray crystallography to exist as a bimetallic platinum complex containing a four-membered ( $\text{Pt}_2\text{Se}_2$ ) ring (figure 3.11). This is in contrast to the spectral data of this complex in solution; mass spectrometry and  $^{31}\text{P}$  NMR suggests that it exists as a monomer with the formula  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{SeC}_{12}\text{H}_7\text{S})_2$  suggesting that this dimeric complex is only found in the solid state.



**Figure 3.11** Crystal structure of  $[\text{Pt}(4\text{-Se-dbt})_2(\text{PPh}_3)]_2$  **3.19**.

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Pt(1)-P(1)	2.2644(18)	P(1)-Pt(1)-Se(22)	87.43(5)
Pt(1)-Se(2)	2.4667(7)	P(1)-Pt(1)-Se(2)	96.15(5)
Pt(1)-Se(2A)	2.4595(7)	P(1)-Pt(1)-Se(2A)	175.27(5)
Pt(1)-Se(22)	2.4403(8)	Se(2)-Pt(1)-Se(22)	174.82(3)
Se(2)-C(2)	1.917(7)	Se(2)-Pt(1)-Se(2A)	82.82(2)
Se(22)-C(22)	1.916(7)	Se(2A)-Pt(1)-Se(22)	93.92(2)
		Pt(1)-Se(2)-C(2)	105.5(2)
		Pt(1)-Se(2)-Pt(1A)	97.18(2)
		C(2)-Se(2)-Pt(1A)	105.9(2)

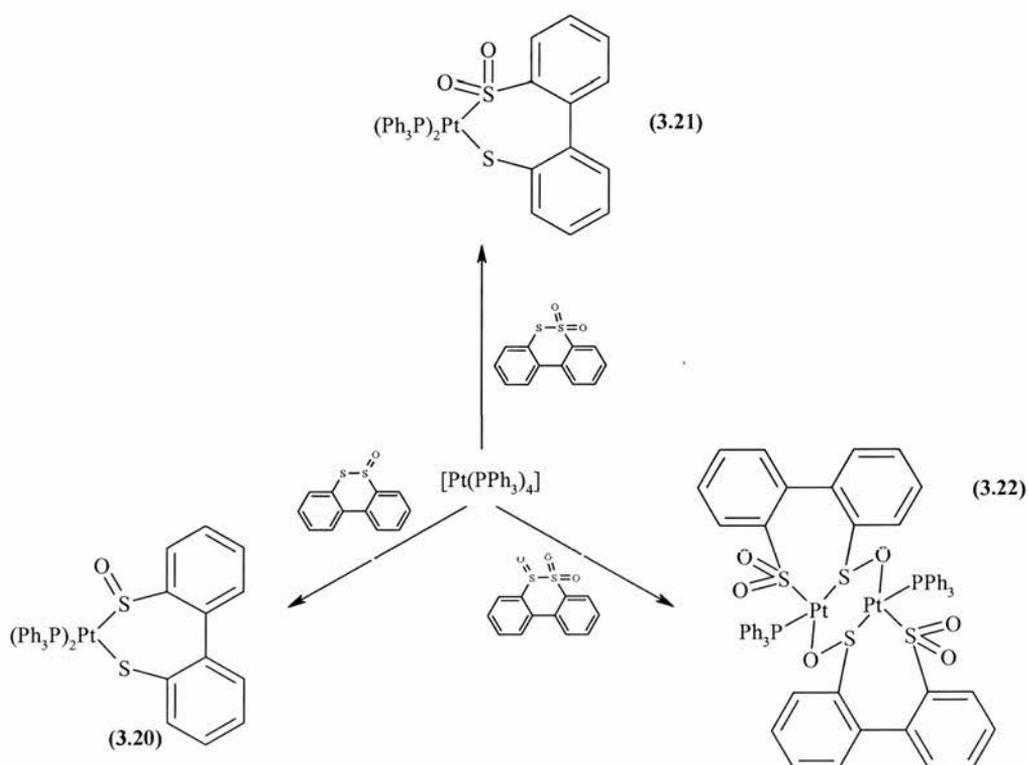
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**Table 3.4** Selected bond lengths (Å) and angles (°) for complex **3.19**.

The platinum atoms lie at the centre of a distorted square planar co-ordination sphere, consisting of three selenium atoms and one phosphorus atom. Two of the three selenium atoms are bridging between the two platinum atoms and belong to a molecule of 4-selena-dibenzothiophene. The other selenium atom also belongs to a molecule of 4-selena-dibenzothiophene but this ligand is terminal rather than bridging. These ligands are one half of the pro-ligand 4-selena-dibenzothiophene dimer, showing that the platinum atom has undergone oxidative addition between the two selenium atoms. The C(2)-Se(2)-Pt(1) and C(2)-Se(2)-Pt(1A) angles are very close ( $105.5(2)^\circ$  and  $105.9(2)^\circ$  respectively) showing that the C(2) atom does not sit in the plane of the four-membered ring but rather sits above the plane, with the Se-C bond almost perpendicular to the two Se-Pt bonds. The Se(2)-Pt(1)-Se(22) bond angle ( $174.82(3)^\circ$ ) and the Se(2A)-Pt(1)-P(1) angle ( $175.27(5)^\circ$ ) show that the selenium atom of the terminal 4-selena-

dibenzothiophene and the phosphorus atom of the  $\text{PPh}_3$  group both lie in the plane of the  $\text{Pt}_2\text{Se}_2$  group. The Pt-Se and Pt-P bond distances of complex **3.19** are unremarkable and are found to be close to the other selenium bound platinum complex  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{Se}_2\text{C}_{10}\text{H}_6)$ , **3.2**.

The biphenyl analogues of the oxygen containing complexes **3.11-3.13** were synthesized in a similar manner, by reaction of the ligands dibenzo[*ce*]-1,2-dithiine-5-oxide, dibenzo[*ce*]-1,2-dithiine-5,5-dioxide and dibenzo[*ce*]-1,2-dithiine-5,5,6-trioxide with  $[\text{Pt}(\text{PPh}_3)_4]$  in toluene at room temperature (scheme 3.7) to yield the complexes  $[\text{Pt}(2\text{-S},2'\text{-}\{\text{S}(\text{O})\}\text{-biphen})(\text{PPh}_3)_2]$  **3.20**,  $[\text{Pt}(2\text{-S},2'\text{-}\{\text{S}(\text{O})_2\}\text{-biphen})(\text{PPh}_3)_2]$  **3.21** and  $[\text{Pt}(2\text{-}\{\text{S}(\text{O})\},2'\text{-}\{\text{S}(\text{O})_2\}\text{-biphen})(\text{PPh}_3)_2]$  **3.22** respectively in good yield (78-89%).



**Scheme 3.7** Oxidative addition reactions of oxidised disulfur pro-ligands to platinum species.

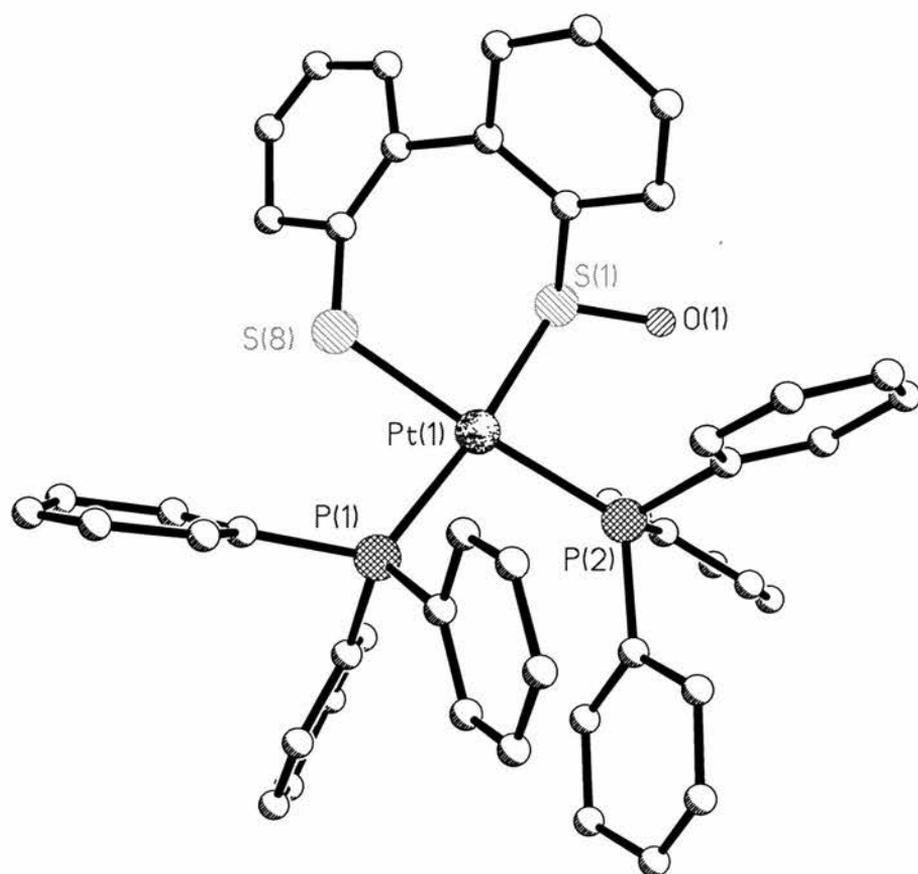
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The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) data for **3.20** and **3.21** are both of the AX type with corresponding platinum satellites. The phosphorus resonances and  $[^1J(^{31}\text{P}-^{195}\text{Pt})]$  coupling constants of complex **3.20**,  $\delta(\text{P}_\text{A}) = 19.2$  ppm (2295 Hz) and  $\delta(\text{P}_\text{X}) = 23.7$  (3542 Hz) are assigned to the phosphine groups *trans* to the sulfenato ( $-\text{S}(\text{O})\text{R}$ ) and the thiolato ( $-\text{SR}$ ) groups, respectively, in accordance with the previously discussed mixed thiolato sulfenato platinum complex **3.11**. For complex **3.21**, the phosphorus resonances and  $[^1J(^{31}\text{P}-^{195}\text{Pt})]$  coupling constants,  $\delta(\text{P}_\text{A}) = 14.2$  ppm (2436 Hz) and  $\delta(\text{P}_\text{X}) = 20.5$  (3130 Hz) are assigned to the phosphine groups *trans* to the sulfinato ( $-\text{S}(\text{O})_2\text{R}$ ) and the thiolato ( $-\text{SR}$ ) groups, respectively. The dimeric **3.22** shows only one resonance in the phosphorus NMR with phosphorus satellites at  $\delta(\text{P}_\text{A}) = 23.2$  ppm ( $[^1J(^{31}\text{P}-^{195}\text{Pt})] = 3303$  Hz). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **3.20** and **3.21** also show the characteristic  $[^2J(^{31}\text{P}_\text{(A)}-^{31}\text{P}_\text{(X)})]$  couplings of 26 Hz and 22 Hz respectively, which are consistent with asymmetrically substituted *cis*-platinum diphosphine complexes. The  $^{195}\text{Pt}$  NMR data ( $\text{CD}_2\text{Cl}_2$ ) are all consistent with the proposed structures of **3.20**, **3.21** and **3.22**. The spectra of **3.20** and **3.21** are both a doublet of doublets with the appropriate coupling constants centred at  $-4234$  ppm and  $-4374$  ppm respectively, while the spectrum of **3.22** shows a doublet centred at 5515 (3300 Hz). IR (KBr disc) data for complexes **3.19-3.21** were consistent with the structural assignments showing  $\nu(\text{S}=\text{O})$  bands for complex **3.19** at *ca.*  $1100\text{ cm}^{-1}$  and  $\nu(\text{S}\{=\text{O}\}_2)$  bands for **3.20** at approximately  $1200, 1060\text{ cm}^{-1}$ , as was the case for the similar complexes **3.11** and **3.12**. Complex **3.21** is slightly different from the trioxide complex **3.13** and thus displays a slightly different IR spectrum. The  $\nu(\text{S}\{=\text{O}\}_2)$  bands are still present at  $1208$  and  $1071\text{ cm}^{-1}$  but there is no  $\text{S}=\text{O}$  bond. Instead, this complex contains a  $\text{S}-\text{O}-\text{Pt}$  bond (similar to complexes

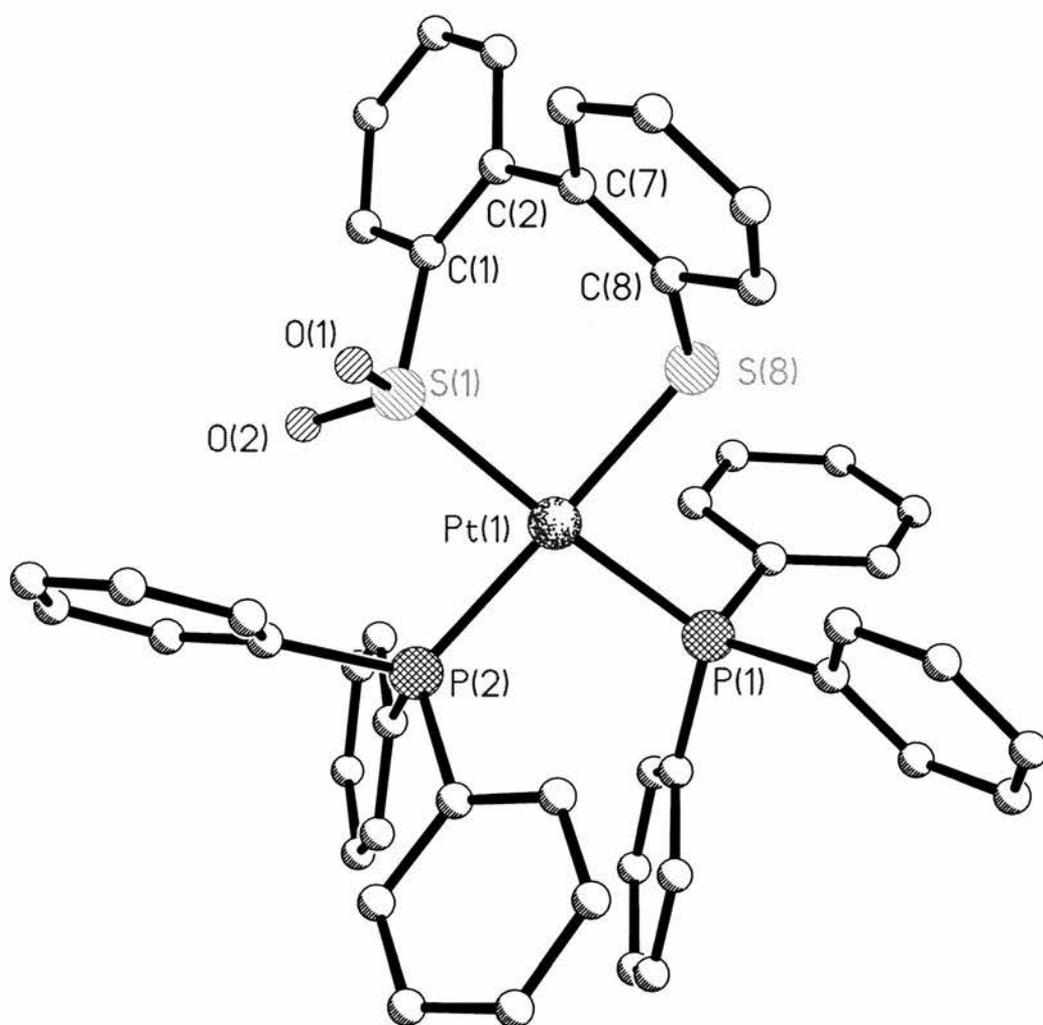
described in chapter 2) and therefore the band at  $843\text{ cm}^{-1}$  is assigned to this stretch.

The elemental analyses obtained for these complexes were satisfactory and the mass spectra showed the parent ion at  $m/z$  953, 969 and 1465 corresponding to  $[M+H]^+$  (3.20 and 3.21) and  $[M+Na]^+$  (3.22).

The X-ray crystal structures of complexes 3.20 and 3.21 (figures 3.12 and 3.13) show that the platinum core lies at the centre of a distorted square planar coordination sphere, consisting of two phosphorus and two sulfur atoms, with the sulfenato/sulfinato groups being bound to the platinum atom via sulfur.



**Figure 3.12** Crystal structure of  $[Pt(2-S,2'-\{S(O)\}-biphen)(PPh_3)_2]$  3.20.



**Figure 3.13** Crystal structure of  $[\text{Pt}(2\text{-S},2'\text{-}\{\text{S}(\text{O})_2\}\text{-biphen})(\text{PPh}_3)_2]$  **3.21**.

	<b>3.20</b>	<b>3.21</b>
Pt(1)-S(1)	2.338(3)	2.3249(16)
Pt(1)-S(8)	2.319(3)	2.3548(15)
Pt(1)-P-(1)	2.328(3)	2.3254(14)
Pt(1)-P(2)	2.306(3)	2.3181(15)
S(1)-C(1)	1.834(15)	1.798(8)
S(1)-O(1)	1.480(8)	1.337(7)
S(1)-O(2)	-	1.580(8)
C(8)-S(8)	1.784(17)	1.796(6)
P(1)-Pt(1)-P(2)	96.90(11)	96.13(5)
P(1)-Pt(1)-S(8)	87.05(12)	86.03(5)
P(2)-Pt(1)-S(8)	175.78(12)	177.24(5)
P(1)-Pt(1)-S(1)	174.04(13)	170.75(6)
P(2)-Pt(1)-S(1)	88.66(11)	87.26(5)
S(1)-Pt(1)-S(8)	87.46(12)	90.86(6)
C(1)-S(1)-Pt(1)	102.3(4)	112.9(2)
O(1)-S(1)-C(1)	102.1(8)	102.1(4)
O(1)-S(1)-Pt(1)	115.2(4)	112.9(2)
O(2)-S(1)-C(1)	-	93.4(4)
O(2)-S(1)-Pt(1)	-	107.1(3)
O(1)-S(1)-O(2)	-	115.8(2)
C(8)-S(8)-Pt(1)	116.3(6)	106.0(2)
S(1)-C(1)-C(2)	117.7(17)	122.1(5)
C(1)-C(2)-C(7)	122.9(17)	124.2(6)
C(2)-C(7)-C(8)	124.4(15)	122.2(5)
C(7)-C(8)-S(8)	125.0(14)	122.8(5)
C(1)-C(2)-C(7)-C(12)	56.0(8)	54.6(7)

**Table 3.5** Selected bond lengths (Å) and angles (°) for complexes **3.20** and **3.21**.

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The P(1)-Pt(1)-P(2) angles (96.90(11) and 96.13(5)<sup>o</sup> respectively) show considerable deviation from idealized 90<sup>o</sup> square planar geometry. The corresponding S(1)-Pt(1)-S(8) angles (87.46(12) and 90.86(6)<sup>o</sup>) are close to idealized square planar geometry and larger than those corresponding angles in (PPh<sub>3</sub>)<sub>2</sub>Pt(S<sub>2</sub>OC<sub>10</sub>H<sub>6</sub>) **3.11** and (PPh<sub>3</sub>)<sub>2</sub>Pt(S<sub>2</sub>O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>) **3.12**. This is explained like complexes **3.16** and **3.18**, as this angle is part of a seven-membered (PtS<sub>2</sub>C<sub>4</sub>) ring rather than a six-membered (PtS<sub>2</sub>C<sub>3</sub>) ring and the extra carbon atom in the ring reduces strain and allows the sulfur atoms more flexibility to settle in a square planar geometry. The Pt-S-C bond angles are found to be vastly different on each side of these complexes (102.3(4)<sup>o</sup> and 116.3(6)<sup>o</sup> (**3.20**) and 112.9(2)<sup>o</sup> and 106.0(2)<sup>o</sup> (**3.21**)). This, as mentioned earlier, is due to the flexibility in the biphenyl backbone, which is also noticed in the free ligand,<sup>(103)</sup> where the two C<sub>6</sub> rings are not co-planar. The C(1)-C(2)-C(7)-C(12) angles of **3.20** (56.0(8)<sup>o</sup>) and **3.21** (54.6(7)<sup>o</sup>) are similar to that of **3.16**, greater than the free ligand.

The non-bonded S...S distances of 3.219(6)Å (**3.20**) and 3.334(6)Å (**3.21**) are much larger than in the S-S bonded prologues,<sup>(103)</sup> and are significantly larger than the corresponding distances in the previously mentioned naphthalene backbone derivatives due to the greater S(1)-Pt(1)-S(8) bond angle forcing the two sulfur atoms further apart, an expected result which suggests that there is no bonding interaction between the two sulfur atoms.

The Pt-S<sub>(thiolato)</sub> distances of **3.16**, **3.20** and **3.21** (in the range 2.319(2)-2.368(6)Å), the Pt-S<sub>(sulfenato)</sub> distance of **3.20** (2.338(3)Å) and the Pt-S<sub>(sulfinato)</sub> distance of **3.21** (2.3249(16)Å) are all very similar and close to those seen in previous platinum complexes **3.1**, **3.11** and **3.12**.

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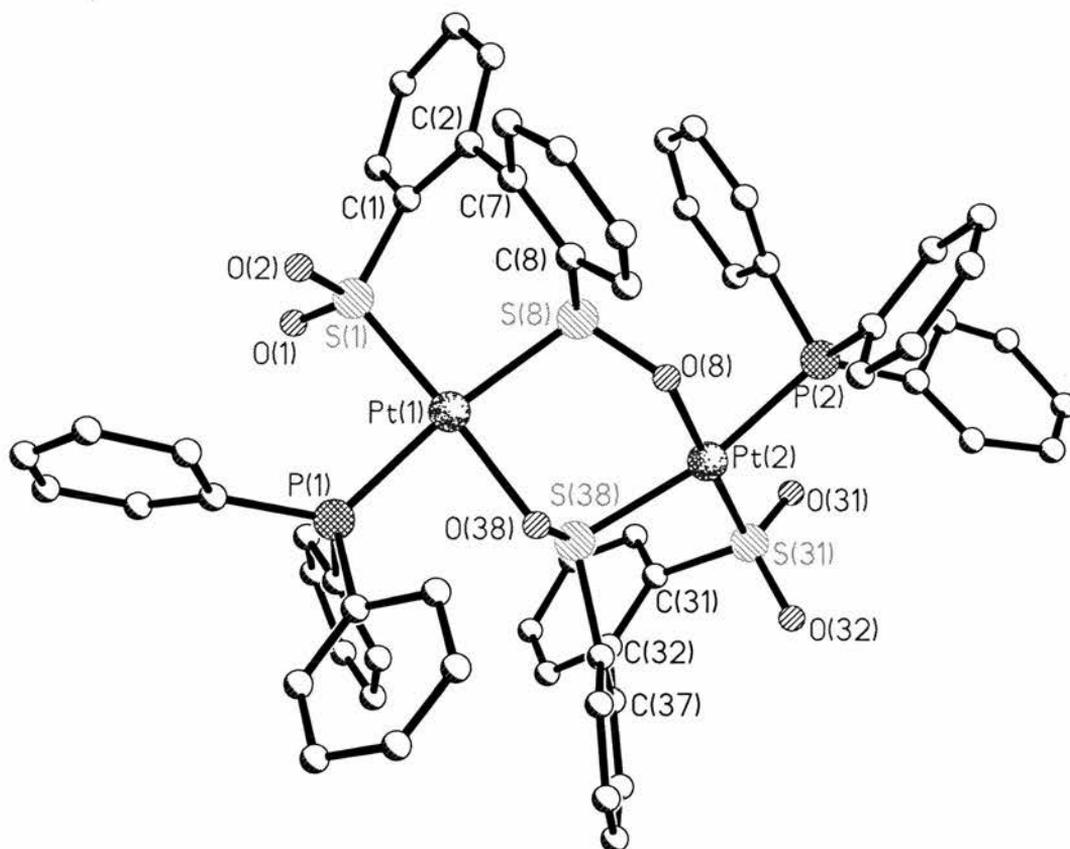
The *trans* influence of the sulfur ligand in relation to Pt-P bond lengths has been comprehensively discussed previously and this argument can be applied to the bond lengths in these complexes. Complexes **3.16**, **3.20** and **3.21** have Pt-P<sub>(trans to thiolato)</sub> bond lengths in the range 2.283(6)-2.3181(15)Å. The Pt-P<sub>(trans to sulfenato)</sub> bond length of **3.20** (2.328(3)Å) and the Pt-P<sub>(trans to sulfinato)</sub> bond length of **3.21** (2.3254(14)Å) are both longer than the Pt-P<sub>(trans to thiolato)</sub> bond lengths. This is in accordance with these previously discussed complexes, and like these complexes, there is no significant difference or trend between Pt-P<sub>(trans to sulfenato)</sub> and Pt-P<sub>(trans to sulfinato)</sub> bond lengths.

The S=O bond length of **3.20** is 1.480(8)Å, a value very similar to other complexes containing a metal centre bound to a sulfenato group and also virtually identical to the same distance in the free ligand.<sup>(149)</sup> However, the two S=O bond lengths of **3.21** are quite different, (1.337(7)Å and 1.580(8)Å). These values are much smaller and greater respectively than the normal values seen in complexes such as **3.20** or the analogous complex Pt(PPh<sub>3</sub>)<sub>2</sub>(S<sub>2</sub>O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>) **3.12**, an observation which does not seem to fit with the trends of previous complexes.

Complex **3.22** exists as a platinum dimer complex containing a six-membered (Pt<sub>2</sub>S<sub>2</sub>O<sub>2</sub>) ring with two seven membered (PtS<sub>2</sub>C<sub>4</sub>) rings on either side (figure 3.14). The platinum cores are both found to lie at the centre of a distorted square planar co-ordination sphere, consisting of two sulfur atoms, one phosphorus atom and one oxygen atom. This six-membered ring is very rare as soft platinum usually preferentially bonding to soft sulfur. Only one other example of a six-membered (Pt<sub>2</sub>S<sub>2</sub>O<sub>2</sub>) ring is known, formed by hydrolysis of [Pt(NSO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] to give [{Pt(SO<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>]<sub>2</sub>}.<sup>(150)</sup> The six-membered

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ring of complex **3.22** is found to have very similar bond lengths and angles to that of  $[\{\text{Pt}(\text{SO}_3)(\text{PMe}_2\text{Ph})_2\}_2]$ .



**Figure 3.14** Crystal structure of  $[\text{Pt}(2\text{-}\{\text{S}(\text{O})\},2'\text{-}\{\text{S}(\text{O})_2\}\text{-biphen})(\text{PPh}_3)]_2$  **3.22**.

Pt(1)-E(1)	2.212(8)	Pt(2)-S(31)	2.214(9)
Pt(1)-E(8)	2.347(8)	Pt(2)-S(38)	2.334(8)
Pt(1)-P(1)	2.316(8)	Pt(2)-O(8)	2.09(2)
Pt(1)-O(38)	2.11(2)	Pt(2)-P(2)	2.316(8)
S(1)-C(1)	1.78(3)	S(31)-C(31)	1.82(3)
S(1)-O(1)	1.46(2)	S(31)-O(31)	1.47(2)
S(1)-O(2)	1.48(2)	S(31)-O(32)	1.44(2)
C(8)-S(8)	1.79(4)	C(38)-S(38)	1.81(3)
S(8)-O(8)	1.58(2)	S(38)-O(38)	1.62(2)
P(1)-Pt(1)-S(8)	173.0(3)	P(2)-Pt(2)-S(38)	168.5(3)
P(1)-Pt(1)-S(1)	94.4(3)	P(2)-Pt(2)-S(31)	97.6(3)
S(1)-Pt(1)-S(8)	92.6(3)	S(31)-Pt(2)-S(38)	92.1(3)
P(1)-Pt(1)-O(38)	82.9(6)	P(2)-Pt(2)-O(8)	81.6(6)
S(1)-Pt(1)-O(38)	176.8(6)	S(31)-Pt(2)-O(8)	179.2(6)
S(8)-Pt(1)-O(38)	90.1(6)	O(8)-Pt(2)-S(38)	88.7(6)
C(1)-S(1)-Pt(1)	113.4(11)	Pt(2)-S(31)-C(31)	107.6(11)
O(1)-S(1)-Pt(1)	107.4(10)	Pt(2)-S(31)-O(31)	110.8(10)
O(2)-S(1)-Pt(1)	115.7(7)	Pt(2)-S(31)-O(32)	109.4(11)
O(1)-S(1)-C(1)	105.7(14)	O(31)-S(31)-C(31)	101.7(14)
O(2)-S(1)-C(1)	102.5(14)	O(32)-S(31)-C(31)	107.4(15)
O(1)-S(1)-O(2)	117.7(12)	O(31)-S(31)-O(32)	119.1(15)
C(8)-S(8)-Pt(1)	95.7(12)	C(38)-S(38)-Pt(2)	109.4(11)
C(8)-S(8)-O(8)	99.8(14)	C(38)-S(38)-O(38)	99.0(13)
O(8)-S(8)-Pt(1)	106.5(9)	O(38)-S(38)-Pt(2)	106.2(8)
S(1)-C(1)-C(2)	124(2)	S(31)-C(31)-C(32)	121(2)
C(1)-C(2)-C(7)	122(3)	C(31)-C(32)-C(37)	129(3)
C(2)-C(7)-C(8)	120(3)	C(32)-C(37)-C(38)	118(3)
C(7)-C(8)-S(8)	119(3)	C(37)-C(38)-S(38)	118(2)
Pt(2)-O(8)-S(8)	119.0(11)	Pt(1)-O(38)-S(38)	108.3(10)
C(1)-C(2)-C(7)-C(12)	53(4)	C(31)-C(32)-C(37)-C(42)	49(4)

**Table 3.6** Selected bond lengths (Å) and angles (°) for complex **3.22**.

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The S-Pt-O angles ( $90.1(6)^\circ$  and  $88.7(6)^\circ$ ) are very close to idealized square planar geometry. The S-Pt-S angles ( $92.6(3)^\circ$  and  $92.1(3)^\circ$ ) are marginally wider than those of **3.16**, **3.20** and **3.21**. The other angles around platinum (S-Pt-P  $94.4(3)^\circ$  and  $97.6(3)^\circ$ , P-Pt-O  $82.9(6)^\circ$  and  $81.6(6)^\circ$ ) demonstrate that the geometry is distorted square planar. Like complexes **3.16**, **3.20** and **3.21**, complex **3.22** has vastly different Pt-S-C angles ( $113.4(11)^\circ$  and  $95.7(12)^\circ$ ) at Pt(1) whilst the same angles at Pt(2) are closer to each other ( $107.6(11)^\circ$  and  $109.4(11)^\circ$ ). The reason for the vast difference at Pt(1) is the same as mentioned earlier: the flexibility in the biphenyl backbone ( $53^\circ$ ) causes twisting which removes any similarity between these two angles. The biphenyl backbone of the ligand bound at Pt(2) is closer to being planar (C(31)-C(32)-C(37)-C(42) =  $49(4)^\circ$ ), giving a less drastic difference between the two Pt-S-C bond angles.

The non-bonded S...S distances (S(1)-S(8) =  $3.30(1)\text{\AA}$  and S(31)-S(38) =  $3.28\text{\AA}$ ) are close to complexes **3.16**, **3.20** and **3.21** and suggests there is no bonding interaction between the two sulfur atoms. This is again due to the increased S-Pt-S angle forcing the two sulfur atoms apart.

The Pt(1)-S<sub>(sulfenato)</sub> and Pt(1)-S<sub>(sulfinato)</sub> distances of **3.22** are  $2.347(8)\text{\AA}$  and  $2.212(8)\text{\AA}$  respectively. The Pt-S<sub>(sulfenato)</sub> distance is similar to the corresponding bond in **3.20** but the Pt-S<sub>(sulfinato)</sub> distance is markedly shorter than the corresponding distance in **3.21**. This may be explained as a consequence of the *trans* influence of the opposite oxygen atom. The oxygen atom is a poor  $\pi$  acceptor, resulting in a shortening of the Pt-S bond length as the sulfur atom accepts the electron density of the metal d orbitals. This shortened Pt-S distance is also noticed on the opposite side of the molecule (Pt(2)-S(38) =  $2.334(8)\text{\AA}$ , Pt(2)-S(31) =  $2.214(9)\text{\AA}$ ) for the same reason.

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The Pt-P bond lengths of **3.22** are both 2.316(8)Å, similar to other Pt-P bond lengths described within this paper and close to the Pt-P length in [ $\text{Pt}(\text{SO}_3)(\text{PMe}_2\text{Ph})_2$ ]<sub>2</sub> (2.305(5)Å).<sup>(150)</sup>

The S=O bond lengths of **3.22** (1.44(2)-1.48(2)Å) are very similar to those of **3.20** and also to other platinum complexes containing a mixture of thiolato, sulfenato or sulfinato groups and of the free ligand.<sup>(103)</sup> The S-O bond lengths (1.58(2)Å and 1.62(2)Å) are longer than the S=O bond lengths and are typical of sulfur oxygen single bonds. These values are very similar to those of other S-O-M complexes (M=Ti) discussed in chapter 2.

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### 3.3 Conclusion

We have successfully developed a series of platinum dichalcogenato complexes by oxidative addition of the dichalcogenide bridged pro-ligand to the Pt(0) species Pt(PPh<sub>3</sub>)<sub>4</sub>. These complexes are air stable both in solution and in the solid state and are shown to adopt a square planar geometry, typical of a d<sup>8</sup> metal complex. Further, we have shown a slightly different method of synthesising these Pt(II) complexes, namely by reduction of the chalcogen-chalcogen bond with super hydride to give a di-lithium salt followed by salt elimination reaction with a platinum(II) dichloride to give the final product.

The oxides of naphtho[1,8-*cd*]-1,2-dithiole and dibenzo[*ce*]-1,2-dithiine have been shown to complex to platinum via the sulfur atom rather than the oxygen atom, without the loss of any oxygen atoms, to give monomeric species. The exception to this is dibenzo[*ce*]-1,2-dithiine 1,1,2-trioxide, which gives a dimeric complex which is bound via one sulfur atom and one oxygen atom in a six-membered ring. Developing this series has allowed us to carry out a comprehensive analysis of the *cis* and *trans* effects of thiolato, sulfenato and sulfinato ligands on the <sup>1</sup>J(<sup>31</sup>P-<sup>195</sup>Pt) coupling constant in the <sup>31</sup>P NMR.

The new selenium ligand, 4-seleno-dibenzothiophene dimer also gives an interesting structure which is shown by NMR and mass spectrometry to be a monomer but which crystallises as a dimer with both terminal and bridging selenium atoms.

All of the isolated complexes have been characterised spectroscopically (<sup>31</sup>P, <sup>195</sup>Pt NMR, IR, mass spectrometry), by elemental analysis and twelve X-ray structures are reported.

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### 3.4 Experimental

#### General

Unless otherwise stated, all operations were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Diethyl ether and tetrahydrofuran were purified by reflux over sodium and benzophenone and distilled under nitrogen. Toluene and hexane were purified by reflux over sodium and distilled under nitrogen. Dichloromethane was purified by reflux over calcium hydride and distilled under nitrogen. All other reagents were purchased from either Aldrich, Acros or Lancaster and used as received. Infra-red spectra were recorded as KBr discs in the range 4000-300  $\text{cm}^{-1}$  on a Perkin-Elmer System 2000 Fourier transform spectrometer.  $^{31}\text{P}$  and  $^{195}\text{Pt}$  NMR were recorded using a Jeol GSX Delta 270 or Bruker Avance 300 MHz spectrometer. Microanalyses were performed by the University of St Andrews microanalysis service. Mass spectra were recorded by both the University of St Andrews mass spectrometry service and the EPSRC National Mass Spectrometry Service Centre, Swansea.

The pro-ligands naphtho[1,8-*cd*]-1,2-dithiole, <sup>(31, 32)</sup> naphtho[1,8-*cd*]-1,2-diselenole, <sup>(151)</sup> naphtho[1,8-*cd*]-1,2-thiaselenole, <sup>(152)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1-oxide, <sup>(48)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide, <sup>(32, 33)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide, <sup>(42)</sup> 2,7-di(*tert*-butyl)naphtho[1,8-*cd*]-1,2-dithiole, <sup>(38)</sup> 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dithiole, <sup>(37)</sup> 4,5-dithioacephenanthrylene, <sup>(117)</sup> dibenzo[*ce*]-1,2-dithiine, <sup>(43)</sup> dibenzo[*ce*]-1,2-dithiine-5-oxide, <sup>(118)</sup> dibenzo[*ce*]-1,2-dithiine-5,5-dioxide, <sup>(42)</sup> dibenzo[*ce*]-1,2-

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dithiine-5,5,6-trioxide, <sup>(42)</sup> disodium biphenyl-2,2'-disulfinate <sup>(42)</sup> and 13,14-dithiapicene <sup>(119)</sup> were prepared according to literature procedures as was the complex  $\text{Pt}(\text{PPh}_3)_4$ . <sup>(153)</sup> *Cis*- $[\text{PtCl}_2(\text{PR}_3)_2]$  were synthesised by the addition of two equivalents of the appropriate phosphine ligand to  $[\text{PtCl}_2(\text{cod})]$  in dichloromethane.

## Synthesis

### **$[\text{Pt}(1,8\text{-S}_2\text{-nap})(\text{PPh}_3)_2]$ (3.1)**

Naphtho[1,8-*cd*]-1,2-dithiole (0.066 g, 0.347 mmol) was added in one portion to a solution of  $[\text{Pt}(\text{PPh}_3)_4]$  (0.433 g, 0.348 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 2 hours. The resulting dark yellow solution was filtered through a silica pad and further eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and diethyl ether (25 cm<sup>3</sup>) followed by hexane (50 cm<sup>3</sup>) were slowly added with stirring to precipitate the product as a bright yellow micro-crystalline solid (0.293 g, 92 %). Microanalysis: Found (Calc. for  $\text{Pt}(\text{S}_2\text{C}_{10}\text{H}_6)(\text{PPh}_3)_2$ ): C 60.45 (60.72), H 4.00 (3.99), S 6.88 (7.05)%. <sup>31</sup>P NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 23.4 (<sup>1</sup>*J*(P<sub>A</sub>,Pt) 2966 Hz). <sup>195</sup>Pt NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : -4799. FAB<sup>+</sup> MS: *m/z*  $[\text{M}]^+$  910,  $[\text{M}-(\text{S}_2\text{C}_{10}\text{H}_6)]^{2+}$  719/720.

### **Method B**

Naphtho[1,8-*cd*]-1,2-dithiole (0.071 g, 0.373 mmol) was dissolved in tetrahydrofuran and a 1.0 M solution of LiBEt<sub>3</sub>H (0.75 ml, 0.75 mmol) was added via syringe. Upon addition an immediate colour change from red to pale

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yellow was observed accompanied by the evolution of gas. This solution of  $\text{Li}_2[1,8\text{-S}_2\text{-naphthalene}]$  was transferred via a stainless steel canula to a tetrahydrofuran suspension ( $10\text{ cm}^3$ ) of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  (0.293 g, 0.371 mmol) and the mixture was rapidly stirred for 2.5 hours giving a dark yellow solution. This solution was filtered through a silica pad and further eluted with dichloromethane ( $100\text{ cm}^3$ ). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.*  $5\text{ cm}^3$  and diethyl ether ( $25\text{ cm}^3$ ) followed by hexane ( $50\text{ cm}^3$ ) were slowly added with stirring to precipitate the product as a bright yellow micro-crystalline solid (0.288 g, 85 %). The analytical and spectroscopic properties of this material were identical to those of material prepared by method A.

### **$[\text{Pt}(1,8\text{-Se}_2\text{-nap})(\text{PPh}_3)_2]$ (3.2)**

Naphtho[1,8-*cd*]-1,2-diselenole (0.101 g, 0.356 mmol) was added in one portion to a solution of  $[\text{Pt}(\text{PPh}_3)_4]$  (0.440 g, 0.354 mmol) in toluene ( $20\text{ cm}^3$ ) and stirred for 2 hours. The resulting dark yellow solution was filtered through a silica pad and further eluted with dichloromethane ( $100\text{ cm}^3$ ). The filtrate was evaporated to *ca.*  $5\text{ cm}^3$ , precipitating the product as a bright orange crystalline solid (0.299 g, 84 %). Microanalysis: Found (Calc. for  $\text{Pt}(\text{Se}_2\text{C}_{10}\text{H}_6)(\text{PPh}_3)_2$ ): C 54.89 (55.04), H 3.66 (3.62)%.  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 20.5 ( $^1J(\text{P}_A, \text{Pt})$  3016 Hz).  $^{195}\text{Pt}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : -4912. FAB<sup>+</sup> MS:  $m/z$   $[\text{M}]^+$  1004,  $[\text{M}-(\text{Se}_2\text{C}_{10}\text{H}_6)]^{2+}$  719/720.

### **$[\text{Pt}(1\text{-S},8\text{-Se-nap})(\text{PPh}_3)_2]$ (3.3)**

Naphtho[1,8-*cd*]-1,2-selenathiole (0.074 g, 0.312 mmol) was added in one portion to a solution of  $[\text{Pt}(\text{PPh}_3)_4]$  (0.390 g, 0.313 mmol) in toluene ( $20\text{ cm}^3$ )

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and stirred for 2 hours. The resulting dark yellow solution was filtered through a silica pad and further eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to *ca.* 5 cm<sup>3</sup>, precipitating the product as an orange solid (0.279 g, 95 %). Microanalysis: Found (Calc. for Pt(SeSC<sub>10</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 57.63 (57.74), H 3.82 (3.79) S 3.19 (3.35)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 20.1 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2984 Hz), 22.6 (<sup>1</sup>J(P<sub>X</sub>,Pt) 2989 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4820. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 958, [M-(SeSC<sub>10</sub>H<sub>6</sub>)]<sup>2+</sup> 719/720.

#### **[Pt(1,8-S<sub>2</sub>-nap)(PMe<sub>3</sub>)<sub>2</sub>] (3.4)**

Naphtho[1,8-*cd*]-1,2-dithiole (0.053 g, 0.279 mmol) was dissolved in tetrahydrofuran and a 1.0 M solution of LiBEt<sub>3</sub>H (0.56 ml, 0.56 mmol) was added via syringe. Upon addition an immediate colour change from red to pale yellow was observed accompanied by the evolution of gas. This solution of Li<sub>2</sub>[1,8-S<sub>2</sub>-naphthalene] was transferred via a stainless steel canula to a tetrahydrofuran suspension (10 cm<sup>3</sup>) of *cis*-[PtCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (0.116 g, 0.277 mmol) and the mixture was rapidly stirred for 2.5 hours giving a dark yellow solution. This solution was filtered through a silica pad and further eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and diethyl ether (25 cm<sup>3</sup>) followed by hexane (50 cm<sup>3</sup>) were slowly added with stirring to precipitate the product as a yellow solid (0.104 g, 70 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)(PMe<sub>3</sub>)<sub>2</sub>): C 35.61 (35.75), H 4.46 (4.50) S 11.91 (11.93)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -23.1 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2801 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4663. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 539, [M-(S<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)]<sup>2+</sup> 347.

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**[Pt(1,8-Se<sub>2</sub>-nap)(PMe<sub>3</sub>)<sub>2</sub>] (3.5)**

Naphtho[1,8-*cd*]-1,2-diselenole (0.073 g, 0.257 mmol) was dissolved in tetrahydrofuran and a 1.0 M solution of LiBEt<sub>3</sub>H (0.52 ml, 0.52 mmol) was added via syringe. Upon addition an immediate colour change from red to pale yellow was observed accompanied by the evolution of gas. This solution of Li<sub>2</sub>[1,8-S<sub>2</sub>-naphthalene] was transferred via a stainless steel canula to a tetrahydrofuran suspension (10 cm<sup>3</sup>) of *cis*-[PtCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (0.107 g, 0.256 mmol) and the mixture was rapidly stirred for 2.5 hours giving an orange solution. This solution was filtered through a silica pad and further eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and diethyl ether (25 cm<sup>3</sup>) followed by hexane (50 cm<sup>3</sup>) were slowly added with stirring to precipitate the product as an orange solid (0.206 g, 89 %). Microanalysis: Found (Calc. for Pt(Se<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)(PMe<sub>3</sub>)<sub>2</sub>): C 30.51 (30.44), H 3.89 (3.83)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -28.7 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2840 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4767. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 632, [M-(Se<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)<sup>2+</sup> 347.

**[Pt(1-S,8-Se-*nap*)(PMe<sub>3</sub>)<sub>2</sub>] (3.6)**

Naphtho[1,8-*cd*]-1,2-selenathiole (0.065 g, 0.274 mmol) was dissolved in tetrahydrofuran and a 1.0 M solution of LiBEt<sub>3</sub>H (0.55 ml, 0.55 mmol) was added via syringe. Upon addition an immediate colour change from red to pale yellow was observed accompanied by the evolution of gas. This solution of Li<sub>2</sub>[1,8-S<sub>2</sub>-naphthalene] was transferred via a stainless steel canula to a tetrahydrofuran suspension (10 cm<sup>3</sup>) of *cis*-[PtCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (0.114 g, 0.273 mmol) and the mixture was rapidly stirred for 2.5 hours giving an orange solution. This

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solution was filtered through a silica pad and further eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and diethyl ether (30 cm<sup>3</sup>) followed by hexane (70 cm<sup>3</sup>) were slowly added with stirring to precipitate the product as an orange solid (0.122 g, 71 %). Microanalysis: Found (Calc. for Pt(SSeC<sub>10</sub>H<sub>6</sub>)(PMe<sub>3</sub>)<sub>2</sub>): C 32.64 (32.88), H 4.04 (4.14), S 5.45 (5.49)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -27.3 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2805 Hz), -23.6 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2834 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4716. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 586, [M-(Se<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)]<sup>2+</sup> 347.

### **[Pt(1,8-S<sub>2</sub>-2-<sup>t</sup>Bu-nap)(PPh<sub>3</sub>)<sub>2</sub>] (3.7)**

2-*tert*-butyl-naphtho[1,8-*cd*]-1,2-dithiole (0.058 g, 0.234 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.290 g, 0.233 mmol) in toluene (20 cm<sup>3</sup>) and stirred at 80°C for 30 minutes. The resulting red solution was filtered through a silica pad and further eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and hexane (30 cm<sup>3</sup>) was added. This was then reduced in volume to *ca.* 20 cm<sup>3</sup> and the product precipitated as an orange solid (0.172 g, 76 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>C<sub>14</sub>H<sub>14</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 62.61 (62.16), H 4.50 (4.59), S 6.23 (6.64)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 19.5 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2923 Hz), 25.5 (<sup>1</sup>J(P<sub>X</sub>,Pt) 3017 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4664. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 967, [M-(C<sub>14</sub>H<sub>14</sub>S<sub>2</sub>)]<sup>2+</sup> 719/720.

### **[Pt(1,8-S<sub>2</sub>-2-<sup>t</sup>Bu-nap)(PPh<sub>3</sub>)<sub>2</sub>] (3.8)**

2,7-di-*tert*-butyl-naphtho[1,8-*cd*]-1,2-dithiole (0.071 g, 0.234 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.290 g, 0.233 mmol) in toluene (20

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cm<sup>3</sup>) and stirred at 80°C for 2 hours. The resulting red solution was filtered through a silica pad and further eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was added. This was then reduced in volume to *ca.* 20 cm<sup>3</sup> and the product precipitated as a yellow solid (0.194 g, 81 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>C<sub>18</sub>H<sub>22</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 63.70 (63.45), H 5.02 (5.13), S 6.13 (6.27)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 21.3 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2949 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4562. FAB<sup>+</sup> MS: *m/z* [M]<sup>+</sup> 1022, [M-(C<sub>14</sub>H<sub>14</sub>S<sub>2</sub>)]<sup>2+</sup> 719/720.

#### **[Pt(1,2-S<sub>2</sub>-acenap)(PPh<sub>3</sub>)<sub>2</sub>] (3.9)**

5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dithiole (0.061 g, 0.282 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.350 g, 0.281 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 2 hours. The resulting orange solution was filtered through a silica pad and further eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and diethyl ether (25 cm<sup>3</sup>) followed by hexane (50 cm<sup>3</sup>) were slowly added with stirring to precipitate the product as a bright orange crystalline solid (0.246 g, 94 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>C<sub>12</sub>H<sub>8</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 61.64 (61.60), H 4.05 (4.09), S 6.65 (6.85)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 23.3 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2981 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4836. FAB<sup>+</sup> MS: *m/z* [M]<sup>+</sup> 936, [M-(S<sub>2</sub>C<sub>12</sub>H<sub>8</sub>)]<sup>2+</sup> 719/720.

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**[Pt(4,5-S<sub>2</sub>-phenan)(PPh<sub>3</sub>)<sub>2</sub>] (3.10)**

4,5-dithia-acephenanthrylene (0.035 g, 0.146 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.180 g, 0.145 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 2 hours. The resulting dark yellow solution was filtered through a silica pad and further eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and diethyl ether (25 cm<sup>3</sup>) followed by hexane (50 cm<sup>3</sup>) were slowly added with stirring to precipitate the product as a yellow solid (0.111 g, 80 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 62.24 (62.56), H 4.11 (3.99), S 6.53 (6.88)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 21.9 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2944 Hz), 24.6 (<sup>1</sup>J(P<sub>X</sub>,Pt) 2984 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4736. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 961, [M-(S<sub>2</sub>C<sub>14</sub>H<sub>8</sub>)]<sup>2+</sup> 719/720.

**[Pt(1-S,8-{S(O)}-nap)(PPh<sub>3</sub>)<sub>2</sub>] (3.11)**

Naphtho[1,8-*cd*]-1,2-dithiole-1-oxide (0.057 g, 0.276 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.341 g, 0.274 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 30 minutes. A yellow precipitate started to separate and stirring was continued for a further 1.5 hours. The precipitate was dissolved by the addition of dichloromethane (20 cm<sup>3</sup>) and the solution was filtered through silica eluting first with dichloromethane (150 cm<sup>3</sup>), which was discarded and then with a 1:3 mixture of acetone/dichloromethane (150 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and diethyl ether (30 cm<sup>3</sup>) followed by hexane (70 cm<sup>3</sup>) were slowly added with stirring to precipitate the product as a yellow/orange micro-crystalline solid (0.214 g, 91 %). Microanalysis: Found

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(Calc. for Pt(S<sub>2</sub>OC<sub>10</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 59.45 (59.67), H 3.84 (3.92), S 6.72 (6.93)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 20.8 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2451 Hz), 26.4 (<sup>1</sup>J(P<sub>X</sub>,Pt) 3587 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4530. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 927, [M-(S<sub>2</sub>OC<sub>10</sub>H<sub>6</sub>)]<sup>2+</sup> 719/720. Selected IR data (KBr): 1095 ν(S=O) cm<sup>-1</sup>.

**[Pt(1-S,8-{S(O)}<sub>2</sub>)-nap)(PPh<sub>3</sub>)<sub>2</sub>] (3.12)**

Naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide (0.057 g, 0.256 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.318 g, 0.256 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 5 minutes. A yellow precipitate started to separate and stirring was continued for a further 30 minutes. The precipitate was dissolved by the addition of dichloromethane (20 cm<sup>3</sup>) and the solution was filtered through silica eluting first with dichloromethane (150 cm<sup>3</sup>), which was discarded and then with a 1:1 mixture of acetone/dichloromethane (150 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a bright yellow/orange micro-crystalline solid (0.230 g, 95 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 58.44 (58.66), H 3.80 (3.85), S 6.42 (6.81)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 18.4 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2451 Hz), 22.4 (<sup>1</sup>J(P<sub>X</sub>,Pt) 3197 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4529. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 943, [M-(S<sub>2</sub>O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)]<sup>2+</sup> 719/720. Selected IR data (KBr): 1185, 1063 ν(S{=O}<sub>2</sub>) cm<sup>-1</sup>.

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**[Pt(1-{S(O)},8-{S(O)}<sub>2</sub>-nap)(PPh<sub>3</sub>)<sub>2</sub>] (3.13)**

Naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide (0.079 g, 0.332 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.411 g, 0.330 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 17 hours. A yellow precipitate formed which was filtered off (0.302 g, 96 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>O<sub>3</sub>C<sub>10</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 57.61 (57.68), H 3.57 (3.79), S 6.43 (6.70)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 20.0 (<sup>1</sup>J(P<sub>A</sub>,Pt) 3094 Hz), 22.1 (<sup>1</sup>J(P<sub>X</sub>,Pt) 2554 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4097. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 959, [M-(S<sub>2</sub>O<sub>3</sub>C<sub>10</sub>H<sub>6</sub>)]<sup>2+</sup> 719/720. Selected IR data (KBr): 1101 ν(S=O), 1212, 1061 ν(S{=O}<sub>2</sub>) cm<sup>-1</sup>.

**[Pt(1,8-{S(O)}<sub>2</sub>)<sub>2</sub>-nap)(PPh<sub>3</sub>)<sub>2</sub>] (3.14)**

A mixture of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.132 g, 0.167 mmol) and di-sodium naphthalene-1,8-disufinic acid (0.067 g, 0.223 mmol) were stirred in methanol (20 cm<sup>3</sup>) for 24 hours. The resulting yellow solution was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane containing approximately 0.5% by volume of triethylamine (3 x 15 cm<sup>3</sup>). The pale orange/yellow extracts were combined and filtered through a shallow pad of Celite and evaporated to *ca.* 3 cm<sup>3</sup>. Diethyl ether (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a pale yellow solid (0.117 g, 72 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>O<sub>4</sub>C<sub>10</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 56.42 (56.73), H 3.43 (3.73), S 6.60 (6.59)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 14.2 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2672 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4250. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 975, [M-(S<sub>2</sub>O<sub>4</sub>C<sub>10</sub>H<sub>6</sub>)]<sup>2+</sup> 719/720. Selected IR data (KBr): 1214, 1058 ν(S{=O}<sub>2</sub>) cm<sup>-1</sup>.

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**[Pt(1,8-{S(O)}<sub>2</sub>)-nap)(PMe<sub>2</sub>Ph)<sub>2</sub>] (3.15).**

A mixture of *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.105 g, 0.194 mmol) and di-sodium naphthalene-1,8-disulfonic acid (0.072 g, 0.240 mmol) were stirred in methanol (20 cm<sup>3</sup>) for 24 hours. The resulting yellow solution was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane containing approximately 0.5% by volume of triethylamine (3 x 15 cm<sup>3</sup>). The pale orange/yellow extracts were combined and filtered through a shallow pad of Celite and evaporated to *ca.* 3 cm<sup>3</sup>. Diethyl ether (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a pale yellow solid (0.109 g, 78 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>O<sub>4</sub>C<sub>10</sub>H<sub>6</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 41.79 (41.46), H 3.71 (3.81), S 8.46 (8.34)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -10.6 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2599 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4352. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 726/727, [M-(S<sub>2</sub>O<sub>4</sub>C<sub>10</sub>H<sub>6</sub>)]<sup>2+</sup> 471. Selected IR data (KBr): 1186, 1051 ν(S{=O}<sub>2</sub>) cm<sup>-1</sup>.

**[Pt(2,2'-S<sub>2</sub>-biphen)(PPh<sub>3</sub>)<sub>2</sub>] (3.16)**

Dibenzo[*ce*]-1,2-dithiine (0.134 g, 0.619 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.772 g, 0.620 mmol) in toluene (20 cm<sup>3</sup>) and refluxed for 4 hours, at which point a fine yellow precipitate started to appear. This was refluxed for another 16 hours. The resulting dark yellow solution was filtered through a silica pad and further eluted with toluene (100 cm<sup>3</sup>), which was discarded. This was then eluted with dichloromethane (300 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of toluene *ca.* 20 cm<sup>3</sup> and diethyl ether (100 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a yellow solid (0.533 g, 92 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>C<sub>12</sub>H<sub>8</sub>)(PPh<sub>3</sub>)<sub>2</sub>): C 61.60 (61.45), H 4.09

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(4.05), S 6.85 (6.90)%.  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 23.1 ( $^1J(\text{P}_A, \text{Pt})$  2956 Hz).  $^{195}\text{Pt}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : -4553. FAB<sup>+</sup> MS:  $m/z$   $[\text{M}]^+$  936,  $[\text{M}-(\text{S}_2\text{C}_{12}\text{H}_8)]^{2+}$  719/720.

### **[Pt(2,2'-S<sub>2</sub>-binap)(PPh<sub>3</sub>)<sub>2</sub>] (3.17)**

13,14-dithia-picene (0.075 g, 0.237 mmol) was added in one portion to a solution of  $[\text{Pt}(\text{PPh}_3)_4]$  (0.295 g, 0.237 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 3 hours. The resulting yellow solution was filtered through a silica pad and further eluted with toluene (100 cm<sup>3</sup>), which was discarded. This was then eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 3 cm<sup>3</sup> and diethyl ether (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a yellow solid (0.161 g, 66 %). Microanalysis: Found (Calc. for  $\text{Pt}(\text{S}_2\text{C}_{20}\text{H}_{12})(\text{PPh}_3)_2$ ): C 65.20 (64.91), H 4.04 (4.09), S 6.33 (6.18)%.  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 23.0 ( $^1J(\text{P}_A, \text{Pt})$  2971 Hz).  $^{195}\text{Pt}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : -4530. ES<sup>+</sup> MS:  $m/z$   $[\text{M}+\text{Na}]^+$  1058.

### **[Pt(2,2'-Se<sub>2</sub>-biphen)(PPh<sub>3</sub>)<sub>2</sub>] (3.18)**

9,10-diselena-phenanthrene (0.168 g, 0.542 mmol) was added in one portion to a solution of  $[\text{Pt}(\text{PPh}_3)_4]$  (0.676 g, 0.543 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 30 minutes. The resulting orange solution was filtered through a silica pad and eluted with dichloromethane (200 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of toluene *ca.* 10 cm<sup>3</sup>, giving a suspension, and diethyl ether (30 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as an orange microcrystalline solid (0.480 g, 86 %). Microanalysis: Found (Calc. for  $\text{Pt}(\text{Se}_2\text{C}_{12}\text{H}_8)(\text{PPh}_3)_2$ ): C 55.99 (56.12), H

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3.72 (3.77)%.  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 18.7 ( $^1J(\text{P}_A, \text{Pt})$  2990 Hz).  $^{195}\text{Pt}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : -4785. FAB<sup>+</sup> MS:  $m/z$   $[\text{M}+\text{H}]^+$  1031,  $[\text{M}-(\text{Se}_2\text{C}_{12}\text{H}_8)]^{2+}$  719/720.

### **Pt(4-Se-dbt)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (3.19)**

4-selena-dibenzothiophene dimer (0.066 g, 0.125 mmol) was added in one portion to a solution of  $[\text{Pt}(\text{PPh}_3)_4]$  (0.311g, 0.250 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 2 hours. The resulting orange solution was filtered through a silica pad and eluted with dichloromethane (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 2 cm<sup>3</sup>, and diethyl ether (25 cm<sup>3</sup>), followed by hexane (50 cm<sup>3</sup>) were slowly added with stirring to precipitate the product as an orange solid (0.135 g, 55 %). Microanalysis: Found (Calc. for  $\text{Pt}(\text{SeSC}_{12}\text{H}_7)_2(\text{PPh}_3)_2$ ): C 57.49 (57.93), H 3.60 (3.56), S 5.03 (5.15)%.  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 19.7 ( $^1J(\text{P}_A, \text{Pt})$  3046 Hz).  $^{195}\text{Pt}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : -4843. FAB<sup>+</sup> MS:  $m/z$   $[\text{M}+\text{Na}]^+$  1267,  $[(\text{M}-\text{PPh}_3)+\text{Na}]^+$  1006.

### **[Pt(2-S,2'-{S(O)}-biphen)(PPh<sub>3</sub>)<sub>2</sub>] (3.20)**

Dibenzo[*ce*]-1,2-dithiine-5-oxide (0.105 g, 0.452 mmol) was added in one portion to a solution of  $[\text{Pt}(\text{PPh}_3)_4]$  (0.563 g, 0.453 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 18 hours. The resulting golden-orange solution was filtered through a silica pad and eluted with dichloromethane (150 cm<sup>3</sup>), which was discarded. This was then eluted with acetone (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 3 cm<sup>3</sup>, and diethyl ether (150 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a bright yellow solid (0.369 g, 86

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%). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>OC<sub>12</sub>H<sub>8</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>): C 60.23 (60.65), H 3.85 (4.02), S 6.61 (6.74)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 19.2 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2295 Hz), 23.7 (<sup>1</sup>J(P<sub>X</sub>,Pt) 3542 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4234. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 953, [M-(S<sub>2</sub>OC<sub>12</sub>H<sub>8</sub>)]<sup>+</sup> 719/720. Selected IR data (KBr): 1098 ν(S=O) cm<sup>-1</sup>.

### **[Pt(2-S,2'-{S(O)}<sub>2</sub>)-biphen)(PPh<sub>3</sub>)<sub>2</sub>] (3.21)**

Dibenzo[*ce*]-1,2-dithiine-5,5-dioxide (0.064 g, 0.257 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.322 g, 0.259 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 18 hours. The resulting golden-orange solution was filtered through a silica pad and eluted with dichloromethane (150 cm<sup>3</sup>), which was discarded. This was then eluted with acetone (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 3 cm<sup>3</sup>, and diethyl ether (150 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a bright yellow solid (0.195 g, 78 %). Microanalysis: Found (Calc. for Pt(S<sub>2</sub>O<sub>2</sub>C<sub>12</sub>H<sub>8</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>): C 60.01 (59.56), H 4.01 (3.96), S 6.43 (6.63)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 14.2 (<sup>1</sup>J(P<sub>A</sub>,Pt) 2436 Hz), 20.5 (<sup>1</sup>J(P<sub>X</sub>,Pt) 3130 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -4374. FAB<sup>+</sup> MS: *m/z* [M+H]<sup>+</sup> 969, [M-(S<sub>2</sub>O<sub>2</sub>C<sub>12</sub>H<sub>8</sub>)]<sup>+</sup> 719/720. Selected IR data (KBr): 1180, 1066 ν(S{=O}<sub>2</sub>) cm<sup>-1</sup>.

### **[Pt(2-{S(O)},2'-{S(O)}<sub>2</sub>)-biphen)(PPh<sub>3</sub>)<sub>2</sub>] (3.22)**

Dibenzo[*ce*]-1,2-dithiine-5,5,6-trioxide (0.087 g, 0.330 mmol) was added in one portion to a solution of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (0.410 g, 0.329 mmol) in toluene (20 cm<sup>3</sup>) and stirred for 18 hours. The resulting yellow solution was filtered through a silica pad and eluted with dichloromethane (100 cm<sup>3</sup>), which was discarded. This

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was then eluted with acetone (100 cm<sup>3</sup>). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane *ca.* 3 cm<sup>3</sup>, and diethyl ether (100 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a bright yellow solid (0.212 g, 89 %). Microanalysis: Found (Calc. for [Pt(S<sub>2</sub>O<sub>3</sub>C<sub>12</sub>H<sub>8</sub>)(PPh<sub>3</sub>)<sub>2</sub>]: C 50.16 (49.93), H 3.28 (3.21), S 8.76 (8.88)%. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 23.3 (<sup>1</sup>J(P<sub>A</sub>,Pt) 3303 Hz). <sup>195</sup>Pt NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: -5515. ES<sup>+</sup> MS: *m/z* [M+Na]<sup>+</sup> 1465, [1/2M+Na]<sup>+</sup> 744. Selected IR data (KBr): 1208, 1071 ν(S{=O}<sub>2</sub>), 843 ν(S-O-Pt) cm<sup>-1</sup>.

### X-ray Crystallography

Tables 3.7-3.10 list details of data collections and refinements. For **3.2**, **3.4**, **3.10** and **3.17**, data were collected at 293 K and for **3.11**, **3.12** and **3.14** data were collected at 125 K on a Bruker SMART diffractometer using Mo-K $\alpha$  radiation. Data for **3.21** were collected at 93 K on a Rigaku MM007/Saturn diffractometer. Data for **3.15**, **3.17**, **3.18** and **3.20** were collected at 93 K on a Rigaku Mercury diffractometer. In complex **3.11** the carbon atoms were refined isotropically; in all other structures all non-H atoms were refined anisotropically. Refinements were by full-matrix least squares based on  $F^2$  using SHELXTL.<sup>(121)</sup>

	<b>3.2</b>	<b>3.4</b>	<b>3.10</b>
Empirical Formula	C <sub>46</sub> H <sub>36</sub> P <sub>2</sub> PtSe <sub>2</sub> · 0.25CH <sub>2</sub> Cl <sub>2</sub>	C <sub>16</sub> H <sub>24</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>46</sub> H <sub>36</sub> OP <sub>2</sub> PtS <sub>2</sub>
<i>M</i>	1024.94	537.50	925.90
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/n	P2(1)/c
<i>a</i> /Å	11.9003(9)	12.8530(4)	10.6497(12)
<i>b</i> /Å	14.7985(11)	8.8142(3)	18.967(2)
<i>c</i> /Å	25.0528(18)	17.9522(6)	19.186(2)
$\alpha^\circ$	74.2800(10)	90	90
$\beta^\circ$	86.6290(10)	109.4390(10)	95.726(2)
$\gamma^\circ$	76.4220(10)	90	90
<i>U</i> /Å <sup>3</sup>	4128.2(5)	1917.85(11)	3856.0(8)
<i>Z</i>	4	4	4
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	1.649	1.862	1.595
$\mu/\text{mm}^{-1}$	5.303	7.693	3.866
Reflections measured	20900	7981	19176
Independent reflections	11717	2722	5492
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0346, 0.0895	0.0178, 0.0434	0.0343, 0.0749
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]			

**Table 3.7** Details of the X-ray data collections and refinements for complexes **3.2**, **3.4** and **3.10**.

	3.11	3.12	3.14
Empirical Formula	C <sub>46</sub> H <sub>36</sub> O <sub>2</sub> P <sub>2</sub> PtS <sub>2</sub> · 0.25CHCl <sub>3</sub>	C <sub>46</sub> H <sub>36</sub> O <sub>3</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>26</sub> H <sub>28</sub> O <sub>4</sub> P <sub>2</sub> PtS <sub>2</sub> · 0.5CH <sub>2</sub> Cl <sub>2</sub>
<i>M</i>	971.74	957.90	768.10
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/c	C2/c
<i>a</i> /Å	11.855(2)	15.068(3)	18.865(4)
<i>b</i> /Å	14.613(3)	17.579(3)	15.201(3)
<i>c</i> /Å	24.799(5)	15.198(3)	19.066(5)
$\alpha^\circ$	74.707(4)	90	90
$\beta^\circ$	86.638(4)	103.771(3)	95.114(19)
$\gamma^\circ$	74.177(4)	90	90
<i>U</i> /Å <sup>3</sup>	3996.7(13)	3909.8(11)	5446(2)
<i>Z</i>	4	4	8
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	1.615	1.627	1.874
$\mu$ /mm <sup>-1</sup>	3.784	3.819	5.555
Reflections measured	20280	19030	11506
Independent reflections	11375	5556	3884
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0796, 0.1715	0.0406, 0.0896	0.0214, 0.0506
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]			

**Table 3.8** Details of the X-ray data collections and refinements for complexes **3.11**, **3.12** and **3.14**.

	3.15	3.17	3.18
Empirical Formula	C <sub>48</sub> H <sub>38</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>49</sub> H <sub>40</sub> C <sub>12</sub> P <sub>2</sub> PtSe <sub>2</sub>	C <sub>91</sub> H <sub>66</sub> P <sub>2</sub> Pt <sub>2</sub> S <sub>4</sub> Se <sub>4</sub>
<i>M</i>	935.93	1114.66	2055.64
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2(1)/c	P2(1)/c	P-1
<i>a</i> /Å	10.23(3)	12.994(3)	12.8759(7)
<i>b</i> /Å	17.32(9)	20.561(4)	13.0591(8)
<i>c</i> /Å	22.62(5)	17.698(4)	13.2920(7)
$\alpha^\circ$	90	90	103.912(5)
$\beta^\circ$	99.11(5)	93.326(4)	97.926(5)
$\gamma^\circ$	90	90	112.460(4)
<i>U</i> /Å <sup>3</sup>	3956(25)	4720.3(17)	1938.02(19)
<i>Z</i>	4	4	1
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	1.571	1.568	1.761
$\mu$ /mm <sup>-1</sup>	3.767	4.727	5.680
Reflections measured	24407	28227	10770
Independent reflections	7128	7824	6201
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0666, 0.1886	0.0484, 0.1080	0.0408, 0.0811
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]			

**Table 3.9** Details of the X-ray data collections and refinements for complexes **3.15**, **3.17** and **3.18**.

	3.19	3.20	3.21
Empirical Formula	C <sub>48</sub> H <sub>38</sub> OP <sub>2</sub> PtS <sub>2</sub>	C <sub>49</sub> H <sub>40</sub> Cl <sub>2</sub> O <sub>2</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>63</sub> H <sub>52</sub> Cl <sub>6</sub> O <sub>6</sub> P <sub>2</sub> Pt <sub>2</sub> S <sub>4</sub>
<i>M</i>	951.93	1052.86	1698.11
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	P2(1)/c
<i>a</i> /Å	10.2583(8)	13.0888(16)	13.354(5)
<i>b</i> /Å	17.3039(14)	20.565(3)	14.952(5)
<i>c</i> /Å	23.0113(19)	17.767(2)	31.510(11)
$\alpha^\circ$	90	90	90
$\beta^\circ$	100.566	92.614(4)	100.266(6)
$\gamma^\circ$	90	90	90
<i>U</i> /Å <sup>3</sup>	4015.4(6)	4777.4(10)	6191(4)
<i>Z</i>	4	4	4
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	1.575	1.464	1.822
$\mu$ /mm <sup>-1</sup>	3.715	3.240	5.012
Reflections measured	17285	28166	28639
Independent reflections	5727	8513	8805
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0497,	0.0467,	0.1367,
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0922	0.1165	0.3692

**Table 3.10** Details of the X-ray data collections and refinements for complexes 3.19, 3.20 and 3.21.

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# CHAPTER 4. THE IRIDIUM CHEMISTRY OF NAPHTHO[1,8-*cd*]-1,2-DITHIOLE AND ITS OXIDISED DERIVATIVES

## 4.1 Introduction

There are many examples of complexes containing iridium sulfur bonds in the literature. A number of these involve octahedral iridium (III) complexes such as  $\text{IrCl}_3(\text{SMe}_2)_3$  <sup>(154)</sup> where a neutral sulfur atom is co-ordinated to the metal centre or  $\text{IrH}(\text{PPh}_3)_2(\text{CO})(\text{S}_3\text{N}_2\text{C}_2\text{H}_3)_2$  <sup>(155)</sup> where a sulfur anion is bound to iridium (figure 4.1).

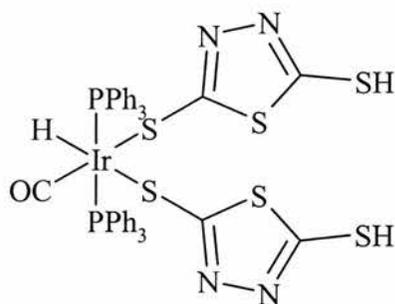


Figure 4.1

Other examples such as that seen previously in equation 1.40 are also known, for example an octahedral complex formed by oxidative addition of the disulfide ligand to the Ir(I) complex  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ .

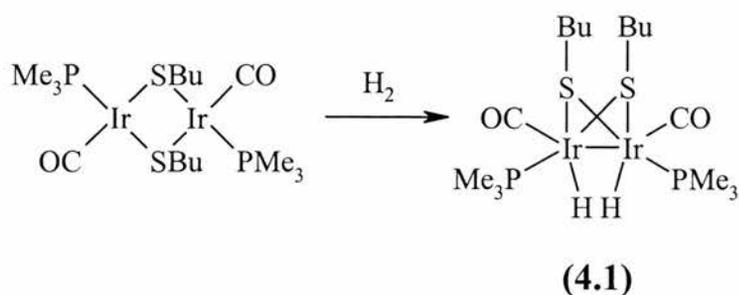
A common bonding mode in iridium sulfur chemistry is the bridging sulfur ligand which links two iridium atoms. A good example of this is  $[\text{IrCp}^*]_3(\mu\text{-S}_2)]^{2+}[\text{BF}_4^-]_2$  which has a bridging sulfur atom above and below the plane of the

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metal atoms. <sup>(156)</sup> Similar to this is the cubic structure  $(Cp^*IrS)_4$  with iridium and sulfur atoms at alternating corners of the cube. <sup>(157)</sup>

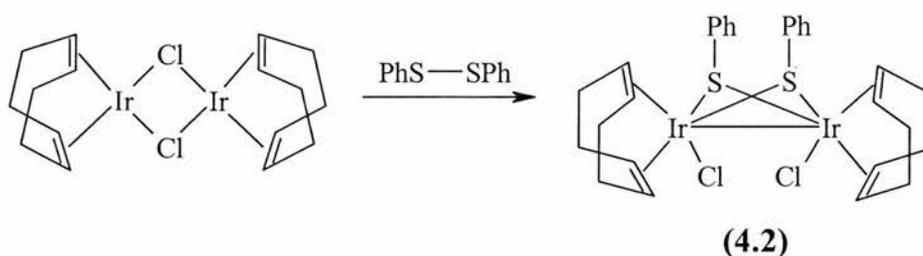
Poilblanc and co-workers have developed several poly-iridium complexes with sulfur bridging ligands of the general formula  $[Ir(SR)(CO)_2]_2$  with terminal carbonyl groups and bridging SR groups <sup>(158, 159)</sup> and the similar complex  $\{Ir(SBu^t)(CO)(PPh_3)\}_2$ , with terminal carbonyl and phosphine groups and bridging thiolato groups. <sup>(160)</sup> Six co-ordinate examples with bridging sulfur atoms are also known such as  $[Ir(\mu-SBu)(CO)(PPh_3)]_2[\mu-CH_2]$ . <sup>(161)</sup> Larger bridging groups than a solitary sulfur atom are also known. An excellent example of this is the tetra-metallic complex  $Ir_4(CO)_6(1,3,5-trithiane)$  which has the four metal atoms in a trigonal pyramidal alignment, with the top iridium atom being bound to three terminal carbonyl groups and the other three iridium atoms having one carbonyl group each. The molecule of 1,3,5-trithiane lies parallel to the plane of the three lower iridium atoms with the sulfur atoms bound to a single iridium atom giving a five-membered  $Ir_2S_2C$  ring. <sup>(162)</sup> The tri-metallic complex  $[Ir_3(\mu-SC_6F_5)_3(\mu-CO)(CO)_4(PPh_3)_2]$  with three bridging  $SC_6F_5$  groups in a six-membered  $Ir_3S_3$  ring is another fine example. <sup>(163)</sup>

The Ir(I) dimer complexes developed by Poilblanc can be converted into an octahedral Ir(II) complex containing a metal metal bond, for example by addition of hydrogen to give  $[Ir(SBu^t)(CO)(PR_3)H]_2$  as shown in equation 4.1. <sup>(164, 165)</sup> Similar complexes have been prepared by addition of iodine rather than hydrogen but the method is essentially the same. <sup>(166, 167)</sup>



Teo and Snyder-Robinson have produced a number of interesting iridium sulfur dimer complexes such as that seen in equation 1.39 where tetrathionaphthalene reacts with *trans*-Ir(PPh<sub>3</sub>)<sub>2</sub>(CO)Br to give the sulfur bridged dimer with two octahedral iridium (II) centres. <sup>(54)</sup> They also took this further to produce the tetrameric iridium complex using more of the iridium (I) complex to react with both sulfur sulfur bridges on the opposite sides of the naphthalene molecule as demonstrated in equation 1.41. <sup>(55)</sup>

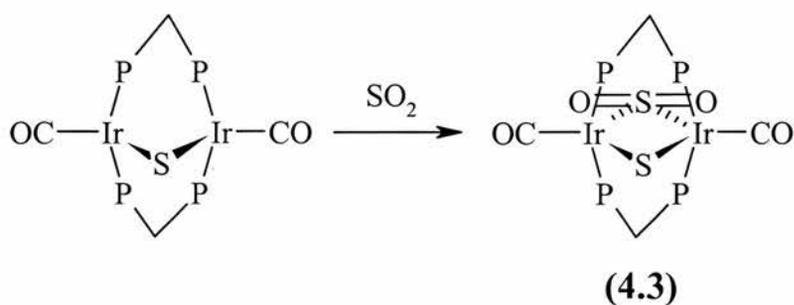
A similar reaction to those described which is of particular interest to this thesis is that of [IrCl(cod)]<sub>2</sub> with PhS-SPh which results in the complex displayed in equation 4.2 by oxidative addition of the disulfide compound to iridium (I). <sup>(168)</sup>



This reaction is very similar to those which we have studied in this chapter. Interestingly, this can also be produced by ligand exchange reaction of PhSH with [Ir(OMe)(cod)]<sub>2</sub> to give [Ir(SPh)(cod)]<sub>2</sub> followed by addition of Cl<sub>2</sub> to give the final product.

As in previous chapters, we are also interested in metal sulfenato and metal sulfinato complexes as well as metal thiolato complexes although there are not

many examples of either known. The only sulfenato examples are similar to those mentioned in chapter 3, where dimethylsulfoxide is used as a ligand to give complexes such as  $\text{IrHCl}_2(\text{DMSO})_3$ ,<sup>(169)</sup>  $\text{IrCl}(\text{DMSO})_3$ <sup>(170)</sup> and  $\text{IrCl}_2(\text{C}_{15}\text{H}_{13}\text{O})(\text{DMSO})_2$ .<sup>(171)</sup> In each case these sulfenato ligands are sulfur bound. There are also a few examples of sulfinato ligands in iridium complexes, such as  $\text{IrCl}(\text{CO})(\text{SO}_2)(\text{PPh}_3)_2$  where the  $\text{SO}_2$  group can reversibly bind, always through the sulfur atom.<sup>(172)</sup> Randall and co-workers have studied the binding of  $\text{SO}_2$  to  $\text{Ir}(\text{CO})\text{Cl}(\text{PR}_3)_2$  and have found these always to be S bound to the metal centre.<sup>(173)</sup>  $\text{SO}_2$  has also been proven to react with  $[\text{Ir}(\text{CO})_2\text{X}_2]^-$  ( $\text{X} = \text{Br}, \text{I}$ ) to give complexes of general formula  $[\text{Ir}(\text{SO}_2)_2\text{X}(\text{H}_2\text{O})_2]$  where the sulfur dioxide moiety is S bound.<sup>(174)</sup> Another example of an iridium sulfinato complex,  $[(\text{IrCp}^*)_2(\mu\text{-CH}_2)_2(\mu\text{-SSO}_2)]$ , (S, S bound) is known which has been prepared by oxidising the parent disulfide complex.<sup>(175)</sup> Finally, a bridging  $\text{SO}_2$  ligand has also been seen. The sulfur bridged complex  $[\text{Ir}(\text{dppm})(\text{CO})]_2\text{S}$  accepts an  $\text{SO}_2$  ligand which bridges the two iridium atoms via the sulfur atom (figure 4.3).<sup>(176)</sup>

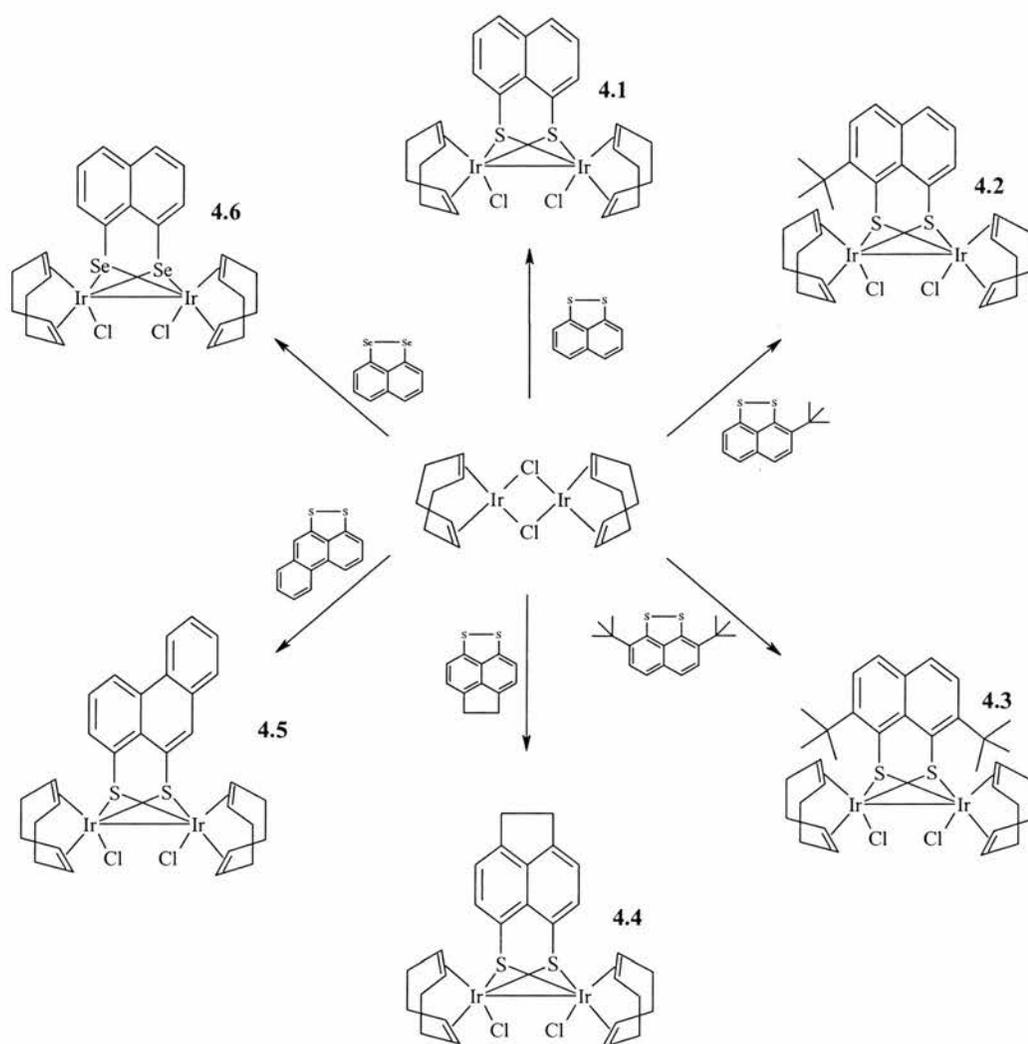


In this chapter, we have studied the reactions of a number of naphthalene backboned disulfides with the iridium (I) complex  $[\text{IrCl}(\text{cod})]_2$ . We have also used the oxides of naphtho[1,8-*cd*]-1,2-dithiole in an attempt to find out whether these ligands will be bound to the metal centre through sulfur as expected, or through oxygen.

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## 4.2 Results and discussion

The oxidative addition reactions of naphtho[1,8-*cd*]-1,2-dithiole, 2-*tert*-butylnaphtho[1,8-*cd*]-1,2-dithiole, 2,7-di-*tert*-butylnaphtho[1,8-*cd*]-1,2-dithiole, 5,6-dihydroacenaphtho[1,8-*cd*]-1,2-dithiole, 4,5-dithioacephenanthrylene and naphtho[1,8-*cd*]-1,2-diselenole to  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$  proceed smoothly in dichloromethane at room temperature via sulfur-sulfur or selenium-selenium bond cleavage to give  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1,8-S}_2\text{-nap})]$  **4.1**,  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1,8-S}_2\text{-2-}^t\text{Bu-nap})]$  **4.2**,  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1,8-S}_2\text{-2,7-di-}^t\text{Bu-nap})]$  **4.3**,  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1,8-S}_2\text{-acenap})]$  **4.4**,  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-4,5-S}_2\text{-phenan})]$  **4.5** and  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1,8-Se}_2\text{-nap})]$  **4.6** in moderate to excellent (57-90%) yields (Scheme 4.1).



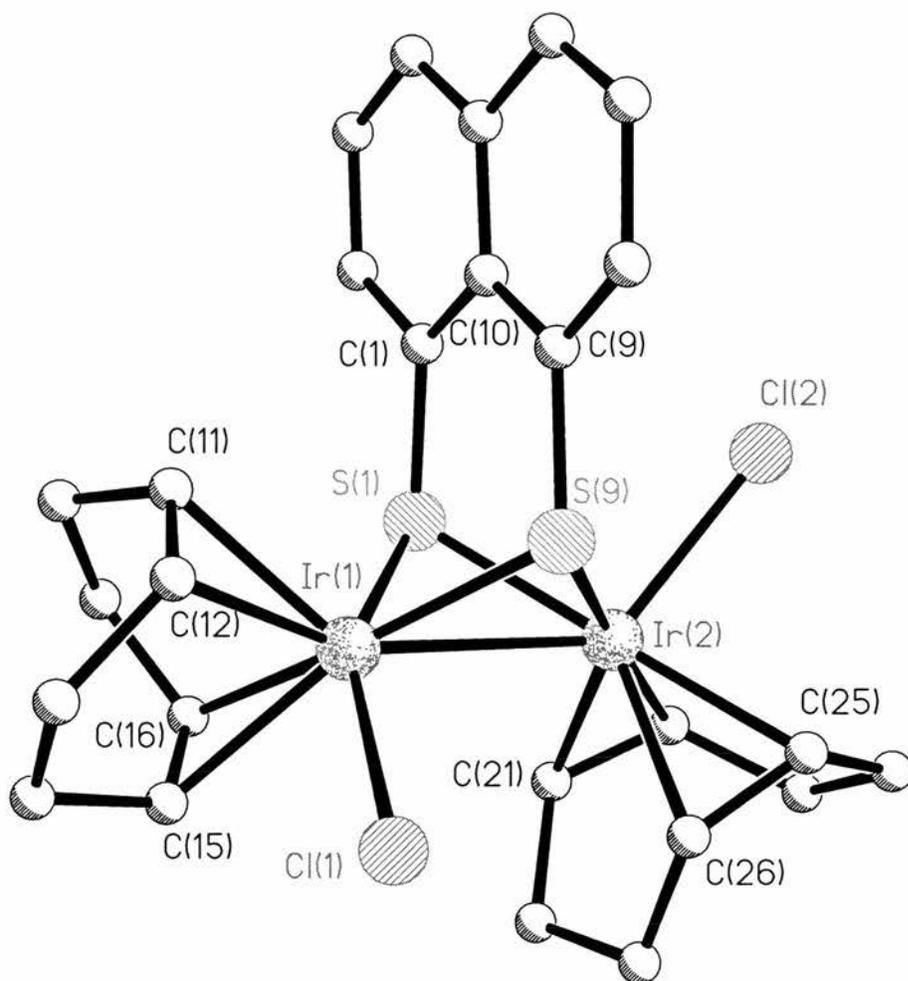
**Scheme 4.1** Oxidative addition reactions of di-sulfide (and di-selenide) proligands to  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ .

In each case the sulfur-sulfur (or selenium-selenium in **4.6**) bond is cleaved and both iridium atoms insert between these sulfur atoms. These complexes are all found to be air stable both in the solid state and in solution. The purification and isolation of these compounds is straight forward and is done by chromatography on silica (eluting with dichloromethane/diethyl ether mixtures) followed by concentration of the eluent and precipitation of the product with hexane.

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The  $^1\text{H}$  NMR of complex **4.1** is very complicated but shows that the two 1,5-cyclooctadiene ligands are inequivalent in solution, displaying a number of complex multiplets in the ranges 5.78-3.47 ppm (olefinic) and 3.01-1.64 ppm (aliphatic), along with typical peaks in the aromatic region (8.44-7.34 ppm) relating to the six naphthalene protons. The  $^{13}\text{C}$  NMR data backs up the  $^1\text{H}$  NMR data, displaying the nonequivalence of the 1,5-cyclooctadiene ligands and showing eight olefinic carbons in the range 106.2-76.1 ppm and eight methylene carbon environments (38.5-30.5 ppm) plus ten aromatic environments in the naphthalene backbone. Elemental analysis proved the purity of the sample while mass spectral data displayed  $[\text{M}-\text{Cl}]^+$  as the highest molecular weight fragment at  $m/z$  826.

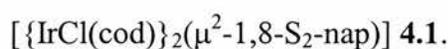
The X-ray crystal structure of **4.1** shows that the iridium centres are both in a distorted octahedral environment consisting of the two olefinic moieties of the 1,5-cyclooctadiene ligand, a chlorine ligand, the two sulfur atoms of the bridging ligand and the other iridium atom (Figure 4.2). Selected bond lengths and bond angles are also given (table 4.1).



**Figure 4.2** Crystal structure of  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-}1,8\text{-S}_2\text{-nap})]$  **4.1**.

Ir(1)-Ir(2)	2.7663(5)	S(1)-Ir(1)-S(9)	82.42(7)
Ir(1)-S(1)	2.315(2)	S(1)-Ir(2)-S(9)	81.44(7)
Ir(1)-S(9)	2.321(2)	Ir(1)-S(1)-Ir(2)	73.11(5)
Ir(2)-S(1)	2.329(2)	Ir(1)-S(9)-Ir(2)	72.57(5)
Ir(2)-S(9)	2.353(2)	Ir(1)-Ir(2)-S(1)	53.22(5)
Ir(1)-Cl(1)	2.442(2)	Ir(2)-Ir(1)-S(1)	53.67(5)
Ir(2)-Cl(2)	2.442(2)	Ir(1)-Ir(2)-S(9)	53.18(5)
Ir(1)-olefinic C	2.197(8)-2.302(8)	Ir(2)-Ir(1)-S(9)	54.25(5)
Ir(2)-olefinic C	2.182(8)-2.192(7)	Cl(1)-Ir(1)-S(1)	151.94(7)
S(1)-C(1)	1.780(8)	Cl(1)-Ir(1)-S(9)	84.21(7)
S(9)-C(9)	1.769(8)	Cl(2)-Ir(2)-S(1)	92.79(7)
Splay angle	16.4	Cl(2)-Ir(2)-S(9)	93.57(7)
		Cl(1)-Ir(1)-Ir(2)	98.71(6)
		Cl(2)-Ir(2)-Ir(1)	131.97(6)
		Ir(1)-S(1)-C(1)	109.6(3)
		Ir(2)-S(1)-C(1)	112.9(3)
		Ir(1)-S(9)-C(9)	112.8(3)
		Ir(2)-S(9)-C(9)	110.6(3)
		Cl-Ir-Ir-Cl	131.7

**Table 4.1** Selected bond lengths [Å] and angles [°] for



The inter-metallic distance of **4.1** (2.7663(5)Å) is typical of other known Ir-Ir(II) thiolato bridged compounds;  $[\{\text{PPh}_3\}\text{IrBr}(\text{CO})\}_2(\mu^2\text{-C}_{10}\text{H}_4\text{S}_4)]$  Ir-Ir = 2.676(1)Å ( $\mu^2\text{-C}_{10}\text{H}_4\text{S}_4$  = naphtho[1,8-*cd*]dithiol-4,5-dithiolato),<sup>(54)</sup>  $[\{\text{IrCl}(\text{cod})\}_2(\mu\text{-SPh})_2]$  Ir-Ir = 2.800(1)Å,<sup>(177)</sup>  $[\{\text{PPh}_3\}\text{Ir}(\text{NO})\}_2(\mu\text{-S}^t\text{Bu})_2]$  Ir-Ir = 2.665(1)Å<sup>(178)</sup> and  $[\{\text{IrI}(\text{CO})_2\}_2(\mu\text{-S}^t\text{Bu})_2]$  Ir-Ir = 2.637(1)Å.<sup>(179)</sup> The Ir-S bond distances of **4.1** are in the range 2.315-2.353Å, close to those of the similar complex  $[\{\text{PPh}_3\}\text{IrBr}(\text{CO})\}_2(\mu^2\text{-C}_{10}\text{H}_4\text{S}_4)]$  (2.340-2.372Å).<sup>(54)</sup> These values are slightly

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shorter than other complexes mentioned earlier which displayed Ir-S bond lengths closer to 2.4Å which is probably a consequence of the two thiolato groups being linked in this example compared with other complexes where the thiolato groups are not connected in any way. <sup>(178, 179)</sup> The transannular S...S distance is 3.05Å, considerably greater than that of the free ligand which has a S-S bond distance of approximately 2.1Å. This is further backed up by the splay angle of this complex (the deviation from the two S-C bonds being parallel). As mentioned in previous chapters, the pro-ligand has a negative splay angle (-11.21°) due to the sulfur sulfur bond pulling the two atoms together. However, this complex has a splay angle of 16.4°, showing that the insertion of the iridium atoms between the two sulfur atoms forces them apart. This splay angle is less than the splay angle noticed in chapter 2 when titanium is inserted between the sulfur atoms of this ligand. This is explained by the fact that iridium has a smaller atomic radius than titanium (due to the lanthanide contraction) and the insertion of a smaller iridium atom between the sulfur atoms forces them less far apart than when a larger titanium atom is inserted.

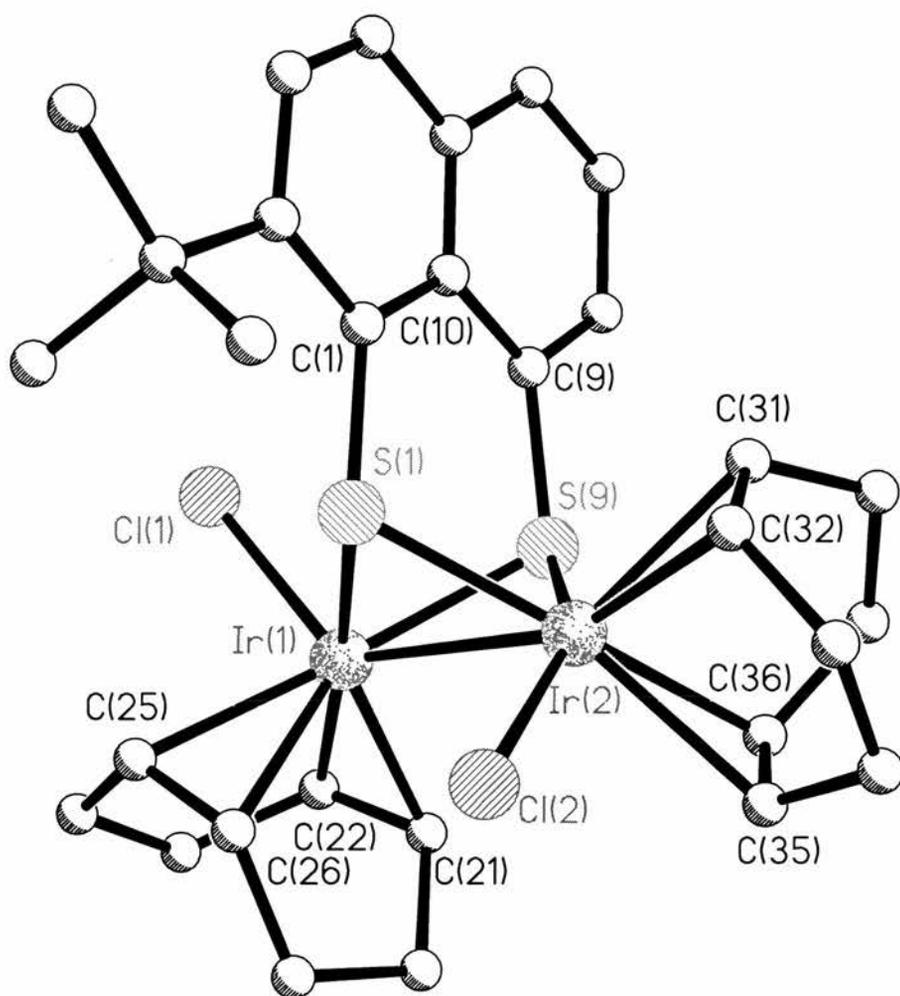
The internal angles of the Ir<sub>2</sub>S<sub>2</sub> core of **4.1** demonstrate the distortion from perfect octahedral geometry around iridium, the S-Ir-S angles being 82.42(7)° and 81.44(7)°, a considerable deviation from perfect 90° octahedral geometry, possibly because the naphthalene backbone pulls the two sulfur atoms together, although these bond angles are similar to those in the complex [ $\{\text{IrCl}(\text{cod})\}_2(\mu\text{-SPh})_2$ ] <sup>(177)</sup> whose thiolato groups are unconnected. The Ir-S-Ir angles of complex **4.1** (73.11(5)° and 72.57(5)°) are narrower than 90° as the metal metal bond pulls the two iridium atoms together.

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The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of complexes **4.2-4.5** were similar to those of complex **4.1**. In each case they show that the two 1,5-cyclooctadiene ligands are inequivalent, with the exception of **4.4**, where only four regions each of intensity 2 are noticed instead of eight regions of intensity 1 in the other examples. The naphthalene region also suggests that there is more symmetry in this complex. The  $^1\text{H}$  NMR spectra of the other three complexes all show a series of peaks in the aromatic region corresponding to the naphthalene peaks in the range 8.97-7.34 ppm. Further to this, a series of multiplets are noticed for the olefinic protons (5.94-3.21 ppm) and the aliphatic protons (3.19-1.57 ppm). The  $^{13}\text{C}$  NMR spectra of these complexes mirror the  $^1\text{H}$  NMR spectra. The *tert*-butyl group of **4.2** occurs at  $\delta(\text{H})$  1.63 and the quaternary  $-\underline{\text{C}}(\text{CH}_3)_3$  and methyl  $-\text{C}(\underline{\text{C}}\text{H}_3)_3$  carbons at  $\delta(\text{C})$  38.5 and 32.2 ppm respectively. Interestingly the *tert*-butyl groups of **4.3** are observed as two singlets,  $\delta(\text{H})$  1.72 and 1.62 ppm in the  $^1\text{H}$  NMR spectra, a result which is also reflected in the  $^{13}\text{C}$  NMR spectra where the two quaternary  $-\underline{\text{C}}(\text{CH}_3)_3$  and methyl  $-\text{C}(\underline{\text{C}}\text{H}_3)_3$  carbons are shown at  $\delta(\text{C})$  38.7, 38.5 and 32.6, 32.3 ppm respectively. The NMR spectra of complex **4.6** were exceptionally messy and proved difficult to extract useful information from due to the high number of overlapping peaks. This is believed to be due to the presence of starting material as well as desired product, making an already complicated NMR spectrum even more over-crowded. This allows us to surmise that complex **4.6** is not pure. However, all other spectroscopic data leads us to believe that we have successfully produced this complex in low yield. Excellent elemental analysis were obtained for all compounds except **4.6** and positive ion mass spectral data were consistent with the proposed structures showing in all cases  $[\text{M}-\text{Cl}]^+$  as the highest molecular weight fragment at  $m/z$  883, 939, 853,

842 and 921 respectively, while complex **4.4** and **4.6** also showed  $[M]^+$  at  $m/z$  888 and 956.

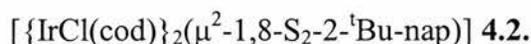
The X-ray crystal structures of complexes **4.2** and **4.3** show that they are very similar to complex **4.1** (figures 4.3 and 4.4). Selected bond lengths and bond angles are also given (tables 4.2 and 4.3).

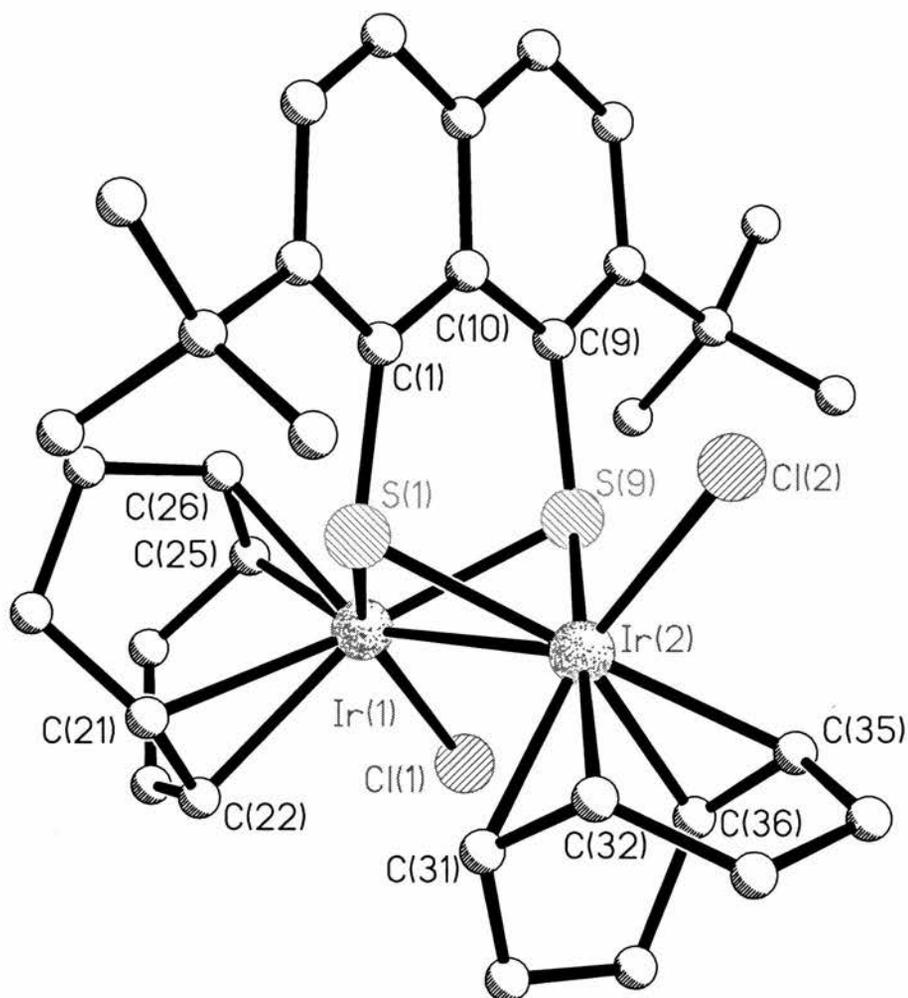


**Figure 4.3** Crystal structure of  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-}1,8\text{-S}_2\text{-}2\text{-}^t\text{Bu-nap})]$  **4.2**.

Ir(1)-Ir(2)	2.7630(8)[2.7572(7)]	S(1)-Ir(1)-S(9)	80.75(12)[82.42(13)]
Ir(1)-S(1)	2.352(4)[2.308(4)]	S(1)-Ir(2)-S(9)	81.82(12)[81.33(13)]
Ir(1)-S(9)	2.316(3)[2.308(4)]	Ir(1)-S(1)-Ir(2)	72.74(10) [72.54(11)]
Ir(2)-S(1)	2.307(3)[2.315(3)]	Ir(1)-S(9)-Ir(2)	73.33(10)[73.22(10)]
Ir(2)-S(9)	2.311(4)[2.351(4)]	Ir(1)-Ir(2)-S(1)	54.38(9) [52.99(8)]
Ir(1)-Cl(1)	2.455(4)[2.446(4)]	Ir(2)-Ir(1)-S(1)	52.88(8) [54.47(9)]
Ir(2)-Cl(2)	2.429(4)[2.463(4)]	Ir(1)-Ir(2)-S(9)	53.42(9) [53.28(9)]
Range of Ir(1)-olefinic C	2.155(15)-2.207(15)	Ir(2)-Ir(1)-S(9)	53.25(9) [53.50(8)]
Range of Ir(2)-olefinic C	2.218(15)-2.317(14)	Cl(1)-Ir(1)-S(1)	94.43(14) [81.65(13)]
S(1)-C(1)	1.766(14)[1.796(15)]	Cl(1)-Ir(1)-S(9)	93.63(14) [93.21(12)]
S(9)-C(9)	1.762(14)[1.797(14)]	Cl(2)-Ir(2)-S(1)	82.67(12) [94.96(13)]
Splay angle	15.4	Cl(2)-Ir(2)-S(9)	152.31(13) [152.75(12)]
		Cl(1)-Ir(1)-Ir(2)	133.22(11) [133.11(9)]
		Cl(2)-Ir(2)-Ir(1)	98.98(10) [99.30(9)]
		Ir(1)-S(1)-C(1)	114.8(5) [116.2(5)]
		Ir(2)-S(1)-C(1)	113.7(5) [110.6(5)]
		Ir(1)-S(9)-C(9)	111.4(4) [111.9(5)]
		Ir(2)-S(9)-C(9)	108.9(5) [109.0(5)]
		Cl-Ir-Ir-Cl	128.9

**Table 4.2** Selected bond lengths [Å] and angles [°] for





**Figure 4.4** Crystal structure of  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-}1,8\text{-S}_2\text{-}2,7\text{-di-}^t\text{Bu-nap})]$  **4.3**.

Ir(1)-Ir(2)	2.7805(3)	S(1)-Ir(1)-S(9)	81.36(5)
Ir(1)-S(1)	2.308(1)	S(1)-Ir(2)-S(9)	80.44(5)
Ir(1)-S(9)	2.296(1)	Ir(1)-S(1)-Ir(2)	74.06(4)
Ir(2)-S(1)	2.309(1)	Ir(1)-S(9)-Ir(2)	73.72(4)
Ir(2)-S(9)	2.339(1)	Ir(1)-Ir(2)-S(1)	52.95(3)
Ir(1)-Cl(1)	2.433(2)	Ir(2)-Ir(1)-S(1)	53.00(3)
Ir(2)-Cl(2)	2.456(2)	Ir(1)-Ir(2)-S(9)	52.45(3)
Range of Ir(1)-olefinic C	2.190(5)-2.306(5)	Ir(2)-Ir(1)-S(9)	53.83(4)
Range of Ir(2)-olefinic C	2.177(6)-2.211(6)	Cl(1)-Ir(1)-S(1)	150.61(5)
S(1)-C(1)	1.774(6)	Cl(1)-Ir(1)-S(9)	83.44(5)
S(9)-C(9)	1.769(6)	Cl(2)-Ir(2)-S(1)	94.56(5)
Splay angle	12.9	Cl(2)-Ir(2)-S(9)	94.22(5)
		Cl(1)-Ir(1)-Ir(2)	97.89(4)
		Cl(2)-Ir(2)-Ir(1)	133.22(4)
		Ir(1)-S(1)-C(1)	114.19(18)
		Ir(2)-S(1)-C(1)	111.30(18)
		Ir(1)-S(9)-C(9)	111.42(18)
		Ir(2)-S(9)-C(9)	114.27(18)
		Cl-Ir-Ir-Cl	129.4

**Table 4.3** Selected bond lengths [Å] and angles [°] for

[{IrCl(cod)}<sub>2</sub>(μ<sup>2</sup>-1,8-S<sub>2</sub>-2,7-di-<sup>t</sup>Bu-nap)] **4.3**.

Complex **4.2** is found to crystallise with two independent molecules in the unit cell. In both cases the iridium centres are in a distorted octahedral environment consisting of the two olefinic moieties of the 1,5-cyclooctadiene ligand, a chlorine ligand, the two sulfur atoms of the bridging ligand and the other iridium atom. The iridium-iridium distances of **4.2** and **4.3** (2.7630(8)[2.7572(7)]Å and

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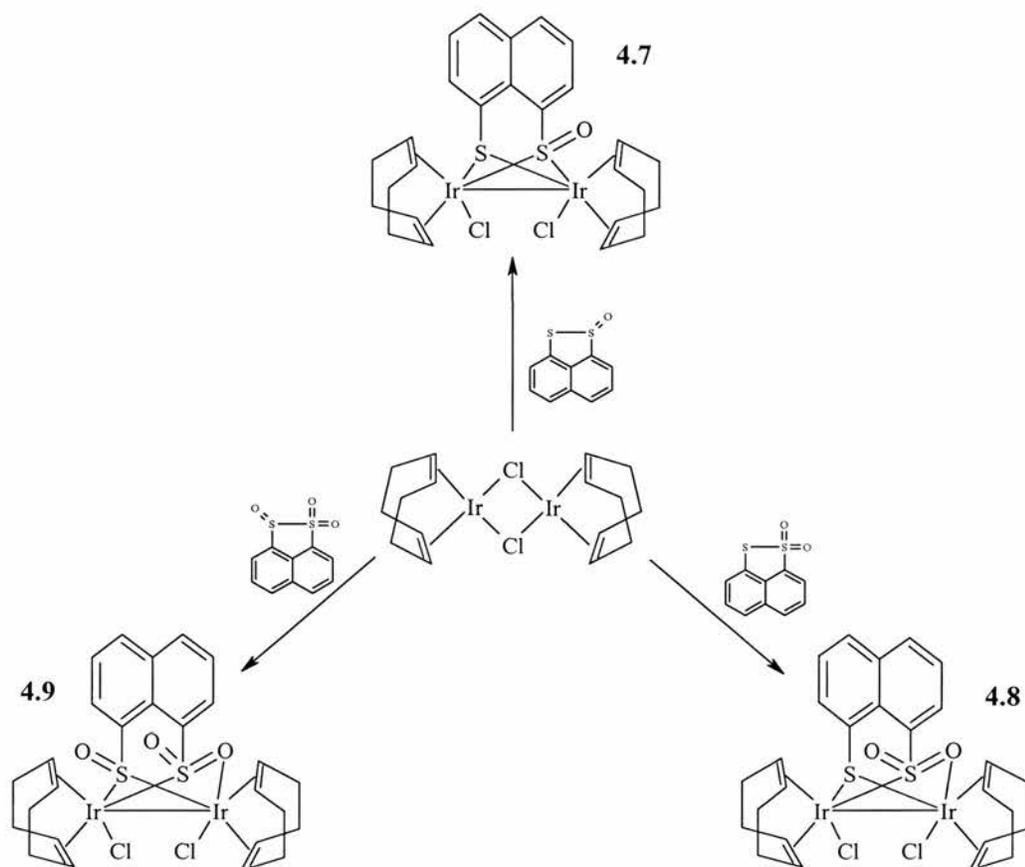
2.7805(3)Å respectively) are similar to that of **4.1** and are unremarkable as are the Ir-S distances (2.307(4)-2.352(4)Å and 2.296(1)-2.339(1)Å respectively) which are slightly shorter than previously studied Ir-S containing complexes. Again this is believed to be due to the two thiolato groups being linked to each other. The transannular S...S distances are both approximately 3.05Å, again, considerably greater than that of the free ligand and identical to that seen in **4.1**. The splay angles of these complexes are 15.4 ° and 12.9° respectively, showing that the two S-C bonds are slightly closer to planarity than **4.1** but are still positive in contrast to the starting ligands.

The S-Ir-S angles of complexes **4.2** and **4.3** show the deviation from perfect octahedral geometry, coming in the range 80.44-82.42°. Again, the Ir-S-Ir angles are considerably less than 90° as a consequence of the presence of the iridium-iridium bond pulling the two atoms closer together.

The oxidative addition reactions of the oxides of naphtho[1,8-*cd*]-1,2-dithiole, namely naphtho[1,8-*cd*]-1,2-dithiole-1-oxide, naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide and naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide to [ $\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2$ ] also proceed smoothly in dichloromethane at room temperature via sulfur-sulfur bond cleavage to give [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-S,8-}\{\text{S}(\text{O})\}\text{-nap})$ ] **4.7**, [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-S,8-}\{\text{S}(\text{O})_2\}\text{-nap})$ ] **4.8** and [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-}\{\text{S}(\text{O})\},8\text{-}\{\text{S}(\text{O})_2\}\text{-nap})$ ] **4.9** in moderate (56-69%) yields (Scheme 4.2).

Again, the sulfur-sulfur bond is cleaved and both iridium atoms insert between these sulfur atoms. These complexes are all found to be air stable both in the solid state and in solution. The purification and isolation of these compounds is straight forward and is done by chromatography on silica (eluting with

dichloromethane/diethyl ether mixtures) followed by concentration of the eluent and precipitation of the product with hexane.



**Scheme 4.2** Oxidative addition reactions of oxidised di-sulfide pro-ligands to  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ .

The  $^1\text{H}$  NMR spectra of complexes **4.7-4.9** are complicated but, like earlier complexes, prove that the two 1,5-cyclooctadiene ligands are inequivalent in solution, displaying a number of complex multiplets in the ranges 6.32-3.06 ppm (olefinic) and 3.19-1.57 ppm (aliphatic). These spectra also display typical peaks in the aromatic region (8.84-7.36 ppm) which correspond to the six protons in the naphthalene backbone. The  $^{13}\text{C}$  NMR data mirrors the  $^1\text{H}$  NMR data, displaying

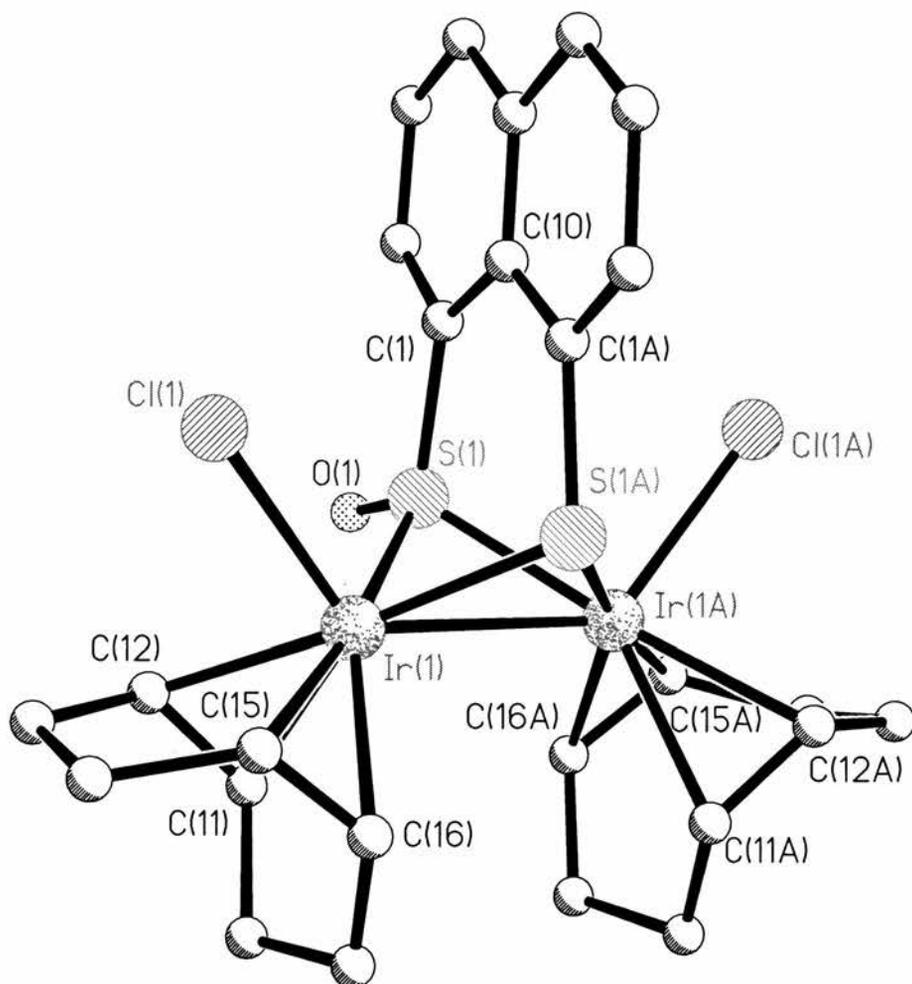
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the non-equivalence of the 1,5-cyclooctadiene ligands and showing eight olefinic carbons in the range 107.8-77.0 ppm and eight methylene carbon environments (37.1-25.5 ppm) plus ten aromatic environments in the naphthalene backbone. Elemental analysis of these samples was satisfactory while mass spectral data displayed  $[M-Cl]^+$  as the highest molecular weight fragment at  $m/z$  842, 858 and 875 respectively and  $[M]^+$  at  $m/z$  910 for **4.9**. IR data for complexes **4.7-4.9** were consistent with the structural assignments, complexes **4.7** and **4.9** displaying the obvious S=O peaks while **4.8** and **4.9** also display the S-O-Ir peak at 824 and 826  $\text{cm}^{-1}$  respectively. The X-ray crystal structures of **4.7** and **4.8** have been determined, removing any doubt about the mode of bonding, while the infra-red spectrum of **4.9** suggests that it is S bound to both iridium atoms at the sulfenato moiety and S, O bound to the iridium atoms at the sulfinato moiety.

The X-ray crystal structures of **4.7** and **4.8** are shown in figures 4.5 and 4.6. Selected bond lengths and bond angles are also given (table 4.4 and 4.5). The iridium centres of complex **4.7**, like the previously discussed complexes, exist in a distorted octahedral environment consisting of the two olefinic moieties of the 1,5-cyclooctadiene ligands, a chlorine ligand, the other iridium atom and the two sulfur atoms of the bridging naphthalene ligand while only one of the iridium atoms of complex **4.8** exists like this. The other iridium atom also exists in a distorted octahedral environment but rather than consisting of two sulfur atoms, this consists of only one sulfur atom (of the thiolato group) and one oxygen atom, from the sulfinato group. Complex **4.7** contains a centre of symmetry down the Ir-Ir bond and the oxygen atom of the S=O group has a 50% occupancy on either side of the molecule, only one of these is shown in figure 4.4 for the sake of clarity.

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The Ir-Ir, and Ir-S bond distances and the splay angle of both complexes are similar to those of the previously discussed complexes and are unremarkable as is the transannular S...S distance of 4.7. This distance in 4.8 is elongated as a result of the S-O-Ir bonding.

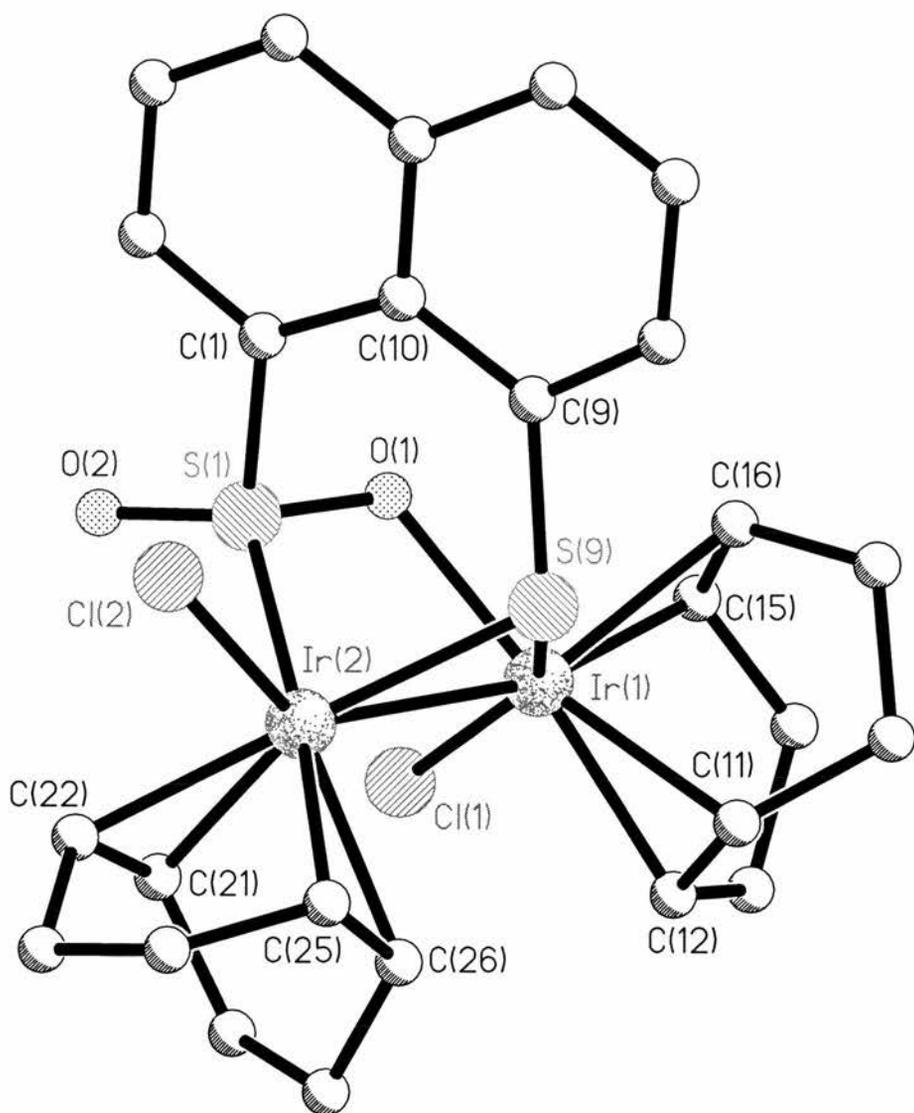


**Figure 4.5** Crystal structure of  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-S,8-\{S(O)\}}\text{-nap})]$  4.7.

Ir(1)-Ir(2)	2.811(1)	S(1)-Ir(1)-S(9)	81.94(12)
Ir(1)-S(1)	2.307(3)	Ir(1)-S(1)-Ir(2)	75.16(9)
Ir(1)-S(9)	2.303(3)	Ir(2)-Ir(1)-S(1)	52.36(7)
Ir(2)-S(1)	2.303(3)	Ir(2)-Ir(1)-S(9)	52.48(8)
Ir(2)-S(9)	2.307(3)	Cl(1)-Ir(1)-S(1)	93.58(11)
Ir(1)-Cl(1)	2.418(3)	Cl(1)-Ir(1)-S(9)	91.44(11)
Ir(2)-Cl(2)	2.418(3)	Cl(1)-Ir(1)-Ir(2)	129.43(8)
Range of Ir(1)-olefinic C	2.179(1)-2.231(1)	Cl(2)-Ir(2)-Ir(1)	129.43(8)
Range of Ir(2)-olefinic C	2.179(1)-2.231(1)	Ir(1)-S(1)-O(1)	121.1(7)
S(1)-C(1)	1.791(12)	Ir(2)-S(1)-O(1)	124.2(7)
S(9)-C(9)	1.791(12)	Ir(1)-S(1)-C(1)	111.5(4)
S(1)-O(1)	1.409(2)	Ir(2)-S(1)-C(1)	109.9(3)
Splay angle	15.2	C(1)-S(1)-O(1)	110.6(8)
		Cl-Ir-Ir-Cl	-4.0

**Table 4.4** Selected bond lengths [Å] and angles [°] for  
 [{IrCl(cod)}<sub>2</sub>(μ<sup>2</sup>-1-S,8-{S(O)}-nap)] **4.7**.

It should be noted here that complex **4.7** has a Cl-Ir-Ir-Cl torsion angle close to 0°, while the other complexes have a torsion angle close to 130°. This is believed to be a result of the S=O group restricting rotation of the 1,5-cyclooctadiene molecules, thus imposing this geometry. The Ir(1)-S(1)-O(1) and Ir(1A)-S(1)-O(1) angles are 121.1(7)° and 124.2(7)° respectively while the S(1)-O(1) bond length is 1.409(2)Å. This is significantly shorter than the S-O bond length in the mononuclear platinum complexes **3.11** and **3.13** (1.450(6)Å and 1.501(5)Å respectively).



**Figure 4.6** Crystal structure of  $[\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-S,8-}\{\text{S}(\text{O})_2\}\text{-nap})]$  **4.8**.

Ir(1)-Ir(2)	2.8053(3)	S(1)-Ir(2)-S(9)	85.60(5)
Ir(1)-S(9)	2.322(1)	Ir(1)-S(9)-Ir(2)	74.35(4)
Ir(2)-S(1)	2.262(1)	Ir(1)-Ir(2)-S(1)	70.00(3)
Ir(2)-S(9)	2.321(1)	Ir(1)-Ir(2)-S(9)	52.85(3)
Ir(1)-Cl(1)	2.406(1)	Ir(2)-Ir(1)-S(9)	52.81(4)
Ir(2)-Cl(2)	2.469(1)	Cl(1)-Ir(1)-S(9)	150.29(5)
Range of Ir(1)-olefinic C	2.203(6)-2.236(5)	Cl(2)-Ir(2)-S(1)	85.23(5)
Range of Ir(2)-olefinic C	2.171(6)-2.266(5)	Cl(2)-Ir(2)-S(9)	94.78(5)
S(1)-C(1)	1.784(5)	Cl(1)-Ir(1)-Ir(2)	97.70(4)
S(9)-C(9)	1.799(5)	Cl(2)-Ir(2)-Ir(1)	139.28(4)
S(1)-O(1)	1.536(4)	Ir(2)-S(1)-O(1)	106.07(13)
S(1)-O(2)	1.453(4)	O(1)-Ir(1)-S(9)	87.22(10)
Ir(1)-O(1)	2.085(3)	O(1)-Ir(1)-Cl(1)	81.10(10)
Splay angle	15.7	Ir(2)-S(1)-C(1)	112.40(17)
		Ir(1)-S(9)-C(9)	113.37(17)
		Ir(2)-S(9)-C(9)	113.5(2)
		Ir(2)-S(1)-O(2)	118.34(17)
		Ir(1)-O(1)-S(1)	107.62(17)
		Ir(2)-Ir(1)-O(1)	76.06(9)
		C(1)-S(1)-O(1)	98.4(2)
		C(1)-S(1)-O(2)	106.8(2)
		O(1)-S(1)-O(2)	113.1(2)
		Cl-Ir-Ir-Cl	132

**Table 4.5** Selected bond lengths [Å] and angles [°] for

[{IrCl(cod)}<sub>2</sub>(μ<sup>2</sup>-1-S,8-{S(O)<sub>2</sub>}-nap)] **4.8**.

Complex **4.8** contains a highly unusual Ir<sub>2</sub>S<sub>2</sub>O core where the two iridium atoms are bridged by both a thiolato and a sulfinato function. There are very few examples of crystallographically characterized complexes containing a bridged sulfinato ligand. The S(1)-O(2) bond length of **4.8** is 1.453(4)Å, which is comparable with the S-O (non-bridging oxygen) bond distance in the homo and hetero-bimetallic complexes

[{μ <sup>2</sup> (1-(SO <sub>2</sub> )-2-CMe(O)-3,4,5-(OMe) <sub>3</sub> C <sub>6</sub> H)Mn(CO) <sub>3</sub> } <sub>2</sub> ]	(1.464(7)Å),	<sup>(180)</sup>	[(μ <sup>2</sup> -EtS)(μ <sup>2</sup> -p-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )Fe <sub>2</sub> (CO) <sub>6</sub> ]	(1.454(4)Å),	<sup>(181)</sup>	[(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )WRe(μ <sup>2</sup> -SO <sub>2</sub> Ph)(CCPh)(CO) <sub>5</sub> ]	(1.456(5)Å)	<sup>(182)</sup>	and	[(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )WRe(μ <sup>2</sup> -SO <sub>2</sub> Ph)(CCPh)(CO) <sub>5</sub> ]	(1.455(5)Å).
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<sup>(182)</sup> The S-O (bridging oxygen) bond length of **4.8**, 1.536(4)Å, is marginally longer than those found in the above complexes (1.495(5)-1.526(4)Å).

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### 4.3 Conclusion

In this chapter it has clearly been demonstrated that the oxidative addition of naphtho[1,8-*cd*]-1,2-dithiole and several similar dithio compounds to the Ir(I) dimeric complex  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$  occurs with ease in dichloromethane at room temperature. The products are air stable both in the solid state and in solution. These complexes have been shown to be asymmetrical by NMR and X-ray-crystallography which has also proved the existence of an interesting four-membered  $\text{Ir}_2\text{S}_2$  ring.

The oxides of naphtho[1,8-*cd*]-1,2-dithiole have been shown to add oxidatively to  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ , binding through a thiolato and a sulfenato sulfur in the case of naphtho[1,8-*cd*]-1,2-dithiole-1-oxide and via a thiolato sulfur and sulfinato oxygen atom in the case of naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide. The exact mode of bonding of naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide can only be speculated as no X-ray crystallography data is available.

All of the isolated complexes have been characterised spectroscopically ( $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR and mass spectroscopy), by elemental analysis and five X-ray structures are reported.

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## 4.4 Experimental

### General

Unless otherwise stated, all operations were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Diethyl ether and tetrahydrofuran were purified by reflux over sodium and benzophenone and distilled under nitrogen. Toluene and hexane were purified by reflux over sodium and distilled under nitrogen. Dichloromethane was purified by reflux over calcium hydride and distilled under nitrogen. All other reagents were purchased from either Aldrich, Acros or Lancaster and used as received. Infra-red spectra were recorded as KBr discs in the range 4000-300  $\text{cm}^{-1}$  on a Perkin-Elmer System 2000 Fourier transform spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded using a Jeol GSX Delta 270 or Bruker Avance 300 MHz spectrometer. Microanalyses were performed by the University of St Andrews microanalysis service. Mass spectra were recorded by both the University of St Andrews mass spectrometry service and the EPSRC National Mass Spectrometry Service Centre, Swansea.

The pro-ligands naphtho[1,8-*cd*]-1,2-dithiole,<sup>(31, 32)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1-oxide,<sup>(48)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide,<sup>(32, 33)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide,<sup>(42)</sup> naphtho[1,8-*cd*]-1,2-dithiole-1,1,2,2-tetraoxide,<sup>(49)</sup> 2,7-di(*tert*-butyl)naphtho[1,8-*cd*]-1,2-dithiole,<sup>(38)</sup> 5,6-dihydroacenaphtho[1,8-*cd*]-1,2-dithiole,<sup>(37)</sup> 4,5-dithioacephenanthrylene,<sup>(117)</sup> and naphtho[1,8-*cd*]-1,2-diselenole<sup>(151)</sup> were prepared by literature methods as was the complex  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ .<sup>(183, 184)</sup>

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## Synthesis

### **[{IrCl(cod)}<sub>2</sub>(μ<sup>2</sup>-1,8-S<sub>2</sub>-nap)] (4.1)**

Naphtho[1,8-*cd*]-1,2-dithiole (61 mg, 0.320 mmol) was added in one portion to a solution of [{Ir(μ-Cl)(cod)}<sub>2</sub>] (214 mg, 0.319 mmol) in dichloromethane and was stirred for 2 h. The resulting red solution was dried under vacuum and the residue taken up in approximately 3 cm<sup>3</sup> of dichloromethane and applied to the top of a column (2.5 x 25 cm) of silica (in hexane) and eluted first with dichloromethane giving a weak pale orange band which was discarded and then eluted with a 95:5 mixture of dichloromethane/diethyl ether. The resulting broad deep red fraction was concentrated under vacuum to *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a dark red crystalline solid (0.244 g, 89%). Microanalysis: Found (Calc. for [{IrCl(cod)}<sub>2</sub>(μ<sup>2</sup>-1,8-S<sub>2</sub>-nap)].H<sub>2</sub>O): C 35.29 (35.45), H 3.47 (3.66), S 7.11 (7.27)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 8.44 (dd, 1H, naphthalene), 8.22 (d, 2H, naphthalene), 8.16 (d, 1H, naphthalene), 7.43 (t, 1H, naphthalene), 7.34 (t, 1H, naphthalene), 5.78 (m, 1H, =CH), 5.36 (m, 1H, =CH), 5.05 (m, 1H, =CH), 4.86 (m, 1H, =CH), 4.76 (m, 1H, =CH), 4.43 (m, 1H, =CH), 4.35 (m, 1H, =CH), 3.47 (m, 1H, =CH), 3.01-1.64 (m, 16H, CH<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 134.6, 130.4, 130.2, 129.9, 129.7, 126.9, 126.7, 126.1, 124.7, 124.4 (all naphthalene), 106.2, 97.7, 82.9, 82.6, 81.8, 76.2, 76.1 (all =CH), 38.5, 34.5, 31.9, 31.3, 31.2, 30.9, 30.8, 30.5 (all CH<sub>2</sub>). Mass Spec (FAB): [M-Cl]<sup>+</sup> 826.

### **[{IrCl(cod)}<sub>2</sub>(μ<sup>2</sup>-1,8-S<sub>2</sub>-2-<sup>t</sup>Bu-nap)] (4.2)**

2-*tert*-butyl-naphtho[1,8-*cd*]-1,2-dithiole (96 mg, 0.390 mmol) was added in one portion to a solution of [{Ir(μ-Cl)(cod)}<sub>2</sub>] (261 mg, 0.389 mmol) in

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dichloromethane and was stirred for 2 h. The resulting red solution was dried under vacuum and the residue taken up in approximately 3 cm<sup>3</sup> of dichloromethane and applied to the top of a column (2.5 x 25 cm) of silica (in hexane) and eluted first with dichloromethane giving a weak pale orange band which was discarded and then eluted with a 95:5 mixture of dichloromethane/diethyl ether. The resulting broad red fraction was concentrated under vacuum to *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a dark red solid (0.295 g, 83%). Microanalysis: Found (Calc. for [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1,8-S}_2\text{-2-}^t\text{Bu-nap})\} \cdot 0.75\text{H}_2\text{O}$ ): C 38.44 (38.64), H 4.13 (4.27), S 6.80 (6.86)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 8.41 (dd, 1H, naphthalene), 8.14 (dd, 1H, naphthalene) 8.06 (d, 1H, naphthalene), 7.64 (d, 1H, naphthalene), 7.34 (dd, 1H, naphthalene), 5.71 (m, 1H, =CH), 5.51 (m, 1H, =CH), 5.31 (m, 1H, =CH), 4.87 (m, 1H, =CH), 4.42 (m, 2H, =CH), 4.34 (m, 1H, =CH), 3.44 (m, 1H, =CH), 2.99-1.65 (m, 16H, CH<sub>2</sub>), 1.63 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 133.2, 130.7, 130.6, 129.7, 128.8, 126.8, 126.0, 125.6, 125.0, 124.8 (all naphthalene), 105.5, 97.2, 83.3, 81.7, 76.8, 76.3, 75.7 (all =CH), 38.7, 34.5, 31.9, 31.5, 31.2, 30.7, 30.4 (all CH<sub>2</sub>), 38.5 (-C(CH<sub>3</sub>)<sub>3</sub>), 32.2 (-C(CH<sub>3</sub>)<sub>3</sub>). Mass Spec (FAB): [M-Cl]<sup>+</sup> 883.

### **[ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1,8-S}_2\text{-2,7-di-}^t\text{Bu-nap})\} \text{ (4.3)}$**

2,7-di-*tert*-butylnaphtho[1,8-*cd*][1,2]dithiole (95 mg, 0.314 mmol) was added in one portion to a solution of [ $\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2$ ] (214 mg, 0.319 mmol) in dichloromethane and was stirred for 2 h. The resulting red solution was dried under vacuum and the residue taken up in approximately 3 cm<sup>3</sup> of dichloromethane and applied to the top of a column (2.5 x 25 cm) of silica (in

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hexane) and eluted first with dichloromethane giving a weak pale orange band which was discarded and then eluted with a 95:5 mixture of dichloromethane/diethyl ether. The resulting red fraction was concentrated under vacuum to *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a dark red micro-crystalline solid (0.249 g, 80%). Microanalysis: Found (Calc. for [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-}1,8\text{-S}_2\text{-}2,7\text{-di-}^t\text{Bu-nap})\} \cdot 0.5\text{CHCl}_3$ ): C 39.88 (40.07), H 4.39 (4.54), S 6.20 (6.19)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 7.98 (t, 2H, naphthalene), 7.66 (d, 1H, naphthalene) 7.57 (d, 1H, naphthalene), 5.85 (m, 1H, =CH), 5.48 (m, 2H, =CH), 4.80 (m, 1H, =CH), 4.49 (m, 1H, =CH), 4.26 (m, 1H, =CH), 3.61 (m, 1H, =CH), 3.21 (m, 1H, =CH), 2.95-1.75 (m, 16H, CH<sub>2</sub>), 1.72 (s, 9H, CH<sub>3</sub>), 1.62 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 133.5, 131.8, 131.5, 129.2, 128.7, 126.2, 126.0, 125.9, 123.3, 122.9 (all naphthalene), 105.7, 100.7, 84.3, 83.9, 82.0, 77.3, 76.7, 76.1 (all =CH), 39.7, 36.7, 34.5, 33.6, 31.1, 29.7, 28.7, 28.4 (all CH<sub>2</sub>), 38.7, 38.5 (both -C(CH<sub>3</sub>)<sub>3</sub>), 32.6, 32.3 (both -C(CH<sub>3</sub>)<sub>3</sub>). Mass Spec (FAB): [M-Cl]<sup>+</sup> 939.

#### **[ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-}1,8\text{-S}_2\text{-acenap})$ ] (4.4)**

5,6-dihydroacenaphtho[1,8-*cd*]-1,2-dithiole (64 mg, 0.298 mmol) was added in one portion to a solution of [ $\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2$ ] (200 mg, 0.298 mmol) in dichloromethane and was stirred for 2 h. The resulting orange solution was dried under vacuum and the residue taken up in approximately 3 cm<sup>3</sup> of dichloromethane and applied to the top of a column (2.5 x 25 cm) of silica (in hexane) and eluted first with dichloromethane giving a weak pale orange band which was discarded and then eluted with a 90:10 mixture of dichloromethane/diethyl ether. The resulting orange fraction was concentrated

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under vacuum to *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as an orange powder (0.209 g, 79%). Microanalysis: Found (Calc. for [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1,8-S}_2\text{-acenap})$ ]): C 37.39 (37.84), H 3.49 (3.63), S 7.02 (7.20)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 8.33 (d, 2H, acenaphthene), 8.08 (d, 2H, acenaphthene), 7.20 (t, 4H, CH<sub>2</sub>), 5.64 (m, 2H, =CH), 4.98 (m, 2H, =CH), 4.84 (m, 2H, =CH), 4.73 (m, 2H, =CH), 3.12-2.32 (m, 16H, CH<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 149.1, 148.8, 130.9, 130.8, 130.6, 121.1, 120.8, 120.3, 120.1, (all acenaphthene), 106.1, 97.2, 85.2, 82.2, 81.7, 81.2, 76.1, 75.5 (all =CH), 38.6, 34.2, 31.7, 31.4, 31.2, 30.9, 30.3, 29.2 (all CH<sub>2</sub> cod), 31.1 (CH<sub>2</sub> nap backbone). Mass Spec (FAB): [M]<sup>+</sup> 888, [M-Cl]<sup>+</sup> 853.

#### **[ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-4,5-S}_2\text{-phenan})$ ] (4.5)**

4,5-dithia-acephenanthrylene (93 mg, 0.387 mmol) was added in one portion to a solution of [ $\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2$ ] (260 mg, 0.387 mmol) in dichloromethane and was stirred for 2 h. The resulting red solution was dried under vacuum and the residue taken up in approximately 3 cm<sup>3</sup> of dichloromethane and applied to the top of a column (2.5 x 25 cm) of silica (in hexane) and eluted first with dichloromethane giving a weak pale orange band which was discarded and then eluted with a 90:10 mixture of dichloromethane/diethyl ether. The resulting broad red fraction was concentrated under vacuum to *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a dark red powder (0.319 g, 90%). Microanalysis: Found (Calc. for [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-4,5-S}_2\text{-phenan})$ ]): C 39.40 (39.47), H 3.26 (3.54), S 6.79 (7.01)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 8.97 (m, 1H, phenanthrene), 8.78 (d, 1H, phenanthrene), 8.62 (m, 1H, phenanthrene), 8.29 (m, 1H, phenanthrene), 8.03-7.41 (m, 4H, phenanthrene), 5.79 (m, 1H, =CH), 5.40

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(m, 1H, =CH), 5.07 (m, 1H, =CH), 4.88 (m, 1H, =CH), 4.77 (m, 1H, =CH), 4.45 (m, 1H, =CH), 4.37 (m, 1H, =CH), 3.61 (m, 1H, =CH), 2.99-1.58 (m, 16H, CH<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 132.1, 131.6, 131.5, 131.1, 130.7, 129.0, 128.5, 127.8, 127.0, 126.3, 125.0, 124.8, 124.7, 122.2 (all phenanthrene), 106.1, 99.2, 85.5, 85.1, 82.9, 81.7, 80.3, 76.5 (all =CH), 38.3, 34.5, 31.9, 31.3, 31.1, 31.0, 30.8, 29.7 (all CH<sub>2</sub>). Mass Spec (FAB): [M-Cl]<sup>+</sup> 877.

#### **[{IrCl(cod)}<sub>2</sub>(μ<sup>2</sup>-1,8-Se<sub>2</sub>-nap)] (4.6)**

Naphtho[1,8-*cd*]-1,2-diselenole (85 mg, 0.298 mmol) was added in one portion to a solution of [{Ir(μ-Cl)(cod)}<sub>2</sub>] (200 mg, 0.298 mmol) in dichloromethane and was stirred for 24 h. The resulting red solution was dried under vacuum and the residue taken up in approximately 3 cm<sup>3</sup> of dichloromethane and applied to the top of a column (2.5 x 25 cm) of silica (in hexane) and eluted first with dichloromethane giving a weak pale orange band which was discarded and then eluted with a 95:5 mixture of dichloromethane/diethyl ether. The resulting broad deep red fraction was concentrated under vacuum to *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a brown powder (0.177 g, 62%). Microanalysis: Found (Calc. for [{IrCl(cod)}<sub>2</sub>(μ<sup>2</sup>-1,8-Se<sub>2</sub>-nap)]): C 34.89 (32.57), H 3.97 (3.16)%. Mass Spec (FAB): [M]<sup>+</sup> 956 [M-Cl]<sup>+</sup> 921.

#### **[{IrCl(cod)}<sub>2</sub>(μ<sup>2</sup>-1-S,8-{S(O)}-nap)] (4.7)**

Naphtho[1,8-*cd*]-1,2-dithiole-1-oxide (69 mg, 0.334 mmol) was added in one portion to a solution of [{Ir(μ-Cl)(cod)}<sub>2</sub>] (225 mg, 0.335 mmol) in dichloromethane and was stirred for 2 h. The resulting light red/orange solution was dried under vacuum and the residue taken up in approximately 3 cm<sup>3</sup> of

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dichloromethane and applied to the top of a column (2.5 x 25 cm) of silica (in hexane) and eluted first with hexane, which was discarded, and then eluted with a 80:20 mixture of dichloromethane/diethyl ether. The resulting orange fraction was concentrated under vacuum to *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as an orange powder (0.231 g, 69%). Microanalysis: Found (Calc. for [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-S,8-}\{\text{S}(\text{O})\}\text{-nap})$ ]): C 35.73 (35.53), H 3.27 (3.44), S 7.18 (7.28)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 8.74 (dd, 1H, naphthalene), 8.27 (dd, 2H, naphthalene), 8.12 (m, 2H, naphthalene), 7.76 (t, 1H, naphthalene), 7.36 (dd, 1H, naphthalene), 5.85 (m, 1H, =CH), 5.48 (m, 1H, =CH), 5.23 (m, 1H, =CH), 4.93 (m, 1H, =CH), 4.83 (m, 1H, =CH), 4.54 (m, 1H, =CH), 4.39 (m, 1H, =CH), 3.73 (m, 1H, =CH), 3.19-1.57 (m, 16H, CH<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 134.6, 132.3, 131.5, 131.3, 129.5, 128.9, 126.7, 126.5, 125.7, 122.7 (all naphthalene), 107.8, 102.7, 86.8, 85.8, 85.1, 84.6, 77.4, 77.0 (all =CH), 37.1, 34.5, 33.8, 33.0, 30.5, 30.3, 28.4, 27.0 (all CH<sub>2</sub>). Mass Spec (FAB): [M-Cl]<sup>+</sup> 842. Selected IR data (KBr): 1109  $\nu(\text{S}=\text{O})$  cm<sup>-1</sup>.

#### **[ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-S,8-}\{\text{S}(\text{O})_2\}\text{-nap})$ ] (4.8)**

Naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide (76 mg, 0.342 mmol) was added in one portion to a solution of [ $\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2$ ] (231 mg, 0.344 mmol) in dichloromethane and was stirred for 5 h. The resulting dark red/purple solution was filtered through a shallow pad of Celite to remove a small quantity of insoluble impurity. This was dried under vacuum and the residue taken up in approximately 3 cm<sup>3</sup> of dichloromethane and applied to the top of a column (2.5 x 25 cm) of silica (in hexane) and eluted first with hexane, which was discarded, and then eluted with a 75:25 mixture of dichloromethane/diethyl ether. The

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resulting orange/red fraction was concentrated under vacuum to *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as an orange/red powder (0.174 g, 57%). Microanalysis: Found (Calc. for [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-S,8-}\{\text{S}(\text{O})_2\text{-nap})\}].\text{CHCl}_3$ ): C 31.95 (32.02), H 3.02 (3.09), S 6.19 (6.32)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 8.48 (dd, 1H, naphthalene), 8.13 (dd, 1H, naphthalene), 7.98 (dd, 1H, naphthalene), 7.88 (dd, 1H, naphthalene), 7.57 (q, 2H, naphthalene), 5.94 (m, 1H, =CH), 5.25 (m, 1H, =CH), 4.86 (m, 1H, =CH), 4.73 (m, 1H, =CH), 4.46 (m, 1H, =CH), 4.35 (m, 1H, =CH), 4.23 (m, 1H, =CH), 3.38 (m, 1H, =CH), 3.05-1.68 (m, 16H, CH<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 142.2, 137.5, 135.6, 133.0, 132.7, 130.7, 125.8, 125.3, 124.6, 123.8 (all naphthalene), 96.4, 95.2, 91.7, 85.9, 84.9, 84.6, 83.4, 81.3 (all =CH), 35.5, 34.0, 32.9, 31.5, 31.3, 31.0, 27.6, 26.5 (all CH<sub>2</sub>). Mass Spec (FAB): [M-Cl]<sup>+</sup> 858. Selected IR data (KBr): 1185  $\nu$ (S=O), 824  $\nu$ (S-O-M) cm<sup>-1</sup>.

#### **[ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-}\{\text{S}(\text{O})\},8\text{-}\{\text{S}(\text{O})_2\}\text{-nap})$ ] (4.9)**

Naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide (71 mg, 0.298 mmol) was added in one portion to a solution of [ $\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2$ ] (200 mg, 0.298 mmol) in dichloromethane and was stirred for 2 h. The resulting orange solution was dried under vacuum and the residue taken up in approximately 3 cm<sup>3</sup> of dichloromethane and applied to the top of a column (2.5 x 25 cm) of silica (in hexane) and eluted first with hexane, which was discarded, and then eluted with a 80:20 mixture of dichloromethane/diethyl ether. The resulting orange fraction was concentrated under vacuum to *ca.* 5 cm<sup>3</sup> and hexane (50 cm<sup>3</sup>) was slowly added with stirring to precipitate the product as a yellow/orange powder (0.152 g, 56%). Microanalysis: Found (Calc. for [ $\{\text{IrCl}(\text{cod})\}_2(\mu^2\text{-1-S}(\text{O}),8\text{-S}(\text{O})_2\text{-nap})$ ]):

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C 34.51 (34.29), H 3.47 (3.32), S 6.81 (7.03)%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 8.84 (d, 1H, naphthalene), 8.25 (d, 1H, naphthalene), 8.03 (d, 1H, naphthalene), 7.83 (m, 2H, naphthalene), 7.62 (t, 1H, naphthalene), 6.32 (m, 1H, =CH), 5.61 (m, 1H, =CH), 4.92 (m, 1H, =CH), 4.68 (m, 1H, =CH), 4.43 (m, 1H, =CH), 3.71 (m, 1H, =CH), 3.34 (m, 1H, =CH), 3.06 (m, 1H, =CH), 2.89-1.74 (m, 16H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 141.5, 136.8, 134.5, 134.2, 132.9, 129.2, 126.0, 125.8, 125.2, 124.8 (all naphthalene), 96.7, 95.4, 95.2, 91.7, 88.4, 87.9, 85.7, 85.2 (all =CH), 36.0, 34.7, 33.2, 30.8, 30.4, 28.2, 27.4, 25.5 (all  $\text{CH}_2$ ). Mass Spec (FAB):  $[\text{M}]^+$  910  $[\text{M}-\text{Cl}]^+$  875. Selected IR data (KBr): 1187, 1106  $\nu(\text{S}=\text{O})$ , 826  $\nu(\text{S}-\text{O}-\text{M})$   $\text{cm}^{-1}$ .

### X-ray Crystallography

Tables 4.6 and 4.7 list details of data collections and refinements. For **4.1**, **4.2**, **4.3**, **4.7** and **4.8**, data were collected at 293 K on a Bruker SMART diffractometer using Mo- $\text{K}\alpha$  radiation. In complex **4.2**, C(21) was refined isotropically; in all other structures all non-H atoms were refined anisotropically. Refinements were by full-matrix least squares based on  $F^2$  using SHELXTL.<sup>(121)</sup>

	4.1	4.2	4.3
Empirical Formula	C <sub>26</sub> H <sub>30</sub> Cl <sub>2</sub> Ir <sub>2</sub> S <sub>2</sub> ·H <sub>2</sub> O	C <sub>30</sub> H <sub>38</sub> Cl <sub>2</sub> Ir <sub>2</sub> S <sub>2</sub> ·0.75H <sub>2</sub> O	C <sub>34</sub> H <sub>46</sub> Cl <sub>2</sub> Ir <sub>2</sub> S <sub>2</sub> ·0.5CHCl <sub>3</sub>
<i>M</i>	879.93	931.54	1033.81
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/n	P-1	C2/c
<i>a</i> /Å	7.0783(7)	10.6793(7)	22.6861(17)
<i>b</i> /Å	21.462(2)	16.9968(12)	13.4258(10)
<i>c</i> /Å	16.9298(16)	17.5776(12)	23.1736(17)
$\alpha^\circ$	90	87.4420(10)	90
$\beta^\circ$	91.505(2)	83.9950(10)	95.2940(10)
$\gamma^\circ$	90	87.6090(10)	90
<i>U</i> /Å <sup>3</sup>	2570.9(4)	3167.7(4)	7028.1(9)
<i>Z</i>	4	4	8
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	2.273	1.953	1.954
$\mu/\text{mm}^{-1}$	10.731	8.715	7.975
Reflections measured	10987	16129	14944
Independent reflections	3640	8957	5027
Final <i>R</i> 1, <i>wR</i> 2	0.0298,	0.0460,	0.0245,
[ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.0698	0.0915	0.0547

**Table 4.6** Details of the X-ray data collections and refinements for complexes **4.1**, **4.2** and **4.3**.

	4.7	4.8
Empirical Formula	C <sub>26</sub> H <sub>30</sub> Cl <sub>2</sub> Ir <sub>2</sub> OS <sub>2</sub>	C <sub>26</sub> H <sub>30</sub> Cl <sub>2</sub> Ir <sub>2</sub> O <sub>2</sub> S <sub>2</sub> ·CHCl <sub>3</sub>
<i>M</i>	877.92	1013.29
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2(1)/n
<i>a</i> /Å	16.087(5)	12.2588(8)
<i>b</i> /Å	12.956(5)	21.3037(14)
<i>c</i> /Å	12.922(4)	12.5784(8)
$\alpha$ /°	90	90
$\beta$ /°	110.938(7)	114.6910(10)
$\gamma$ /°	90	90
<i>U</i> /Å <sup>3</sup>	2515.4(14)	2984.6(3)
<i>Z</i>	4	4
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	2.318	2.255
$\mu$ /mm <sup>-1</sup>	10.968	9.522
Reflections measured	5749	12786
Independent reflections	1727	4237
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0422,	0.0221,
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0813	0.0463

**Table 4.7** Details of the X-ray data collections and refinements for complexes 4.7 and 4.8.

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## CHAPTER 5. ADDITIONAL CHEMISTRY OF NAPHTHO[1,8-*cd*]-1,2-DITHIOLE AND RELATED COMPOUNDS

### 5.1 Introduction

This chapter deals with some further reactions of naphtho[1,8-*cd*]-1,2-dithiole and dibenzo[*ce*]-1,2-dithiine. The synthesis of two new dichalcogen bridged compounds are described, firstly 2-*tert*-butylnaphtho[1,8-*cd*]-1,2-dithiole which is actually a by-product of the synthesis of 2,7-di-*tert*-butylnaphtho[1,8-*cd*]-1,2-dithiole. <sup>(38)</sup> The second compound is 4-selena-dibenzothiophene dimer which was prepared as the major product in the attempted synthesis of the as yet unknown compound naphtho[1,8-*cd*]-1,2-selenathiole.

The exchange reactions between titanocene dithiolato complexes and platinum dichlorides have been studied before <sup>(99)</sup> and shown to successfully yield titanocene dichloride and a platinum dithiolato complex. This chapter deals with the reaction of titanocene thiolato/sulfinato and titanocene disulfinato complexes with platinum dichlorides, in which the sulfur containing ligands are believed to be bound more strongly to the titanium centre as they are bound via hard oxygen atoms rather than soft sulfur atoms.

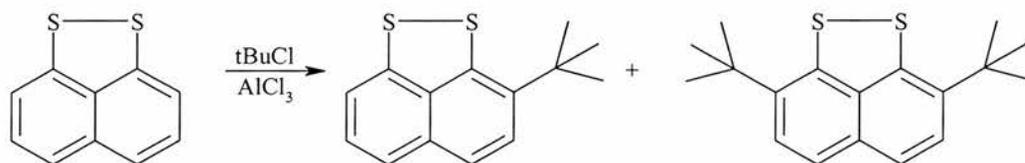
Dimeric rhodium and iridium complexes have been studied by the salt elimination reactions of the di-lithium salts of naphtho[1,8-*cd*]-1,2-dithiole and dibenzo[*ce*]-1,2-dithiine with the chlorine bridged complexes  $[\text{Cp}^*\text{MCl}_2]_2$ . Reactions of this type have been seen before with a di-potassium salt of cyanodithioimidocarbonate. <sup>(185)</sup>

Finally, the electrocrystallisation of naphtho[1,8-*cd*]-1,2-dithiole with a counter anion, namely boron tetrafluorate, has been studied. This is in an attempt to produce a simple charge transfer salt as those known in the literature so far have involved much larger, more complicated molecules.

## 5.2 Results and discussion

### Synthesis of new ligands

The disulfide pro-ligand 2-*tert*-butylnaphtho[1,8-*cd*]-1,2-dithiole (**5.1**) was synthesised during the literature synthesis of the similar pro-ligand 2,7-di(*tert*-butyl)naphtho[1,8-*cd*]-1,2-dithiole (Scheme 5.1).<sup>(38)</sup>

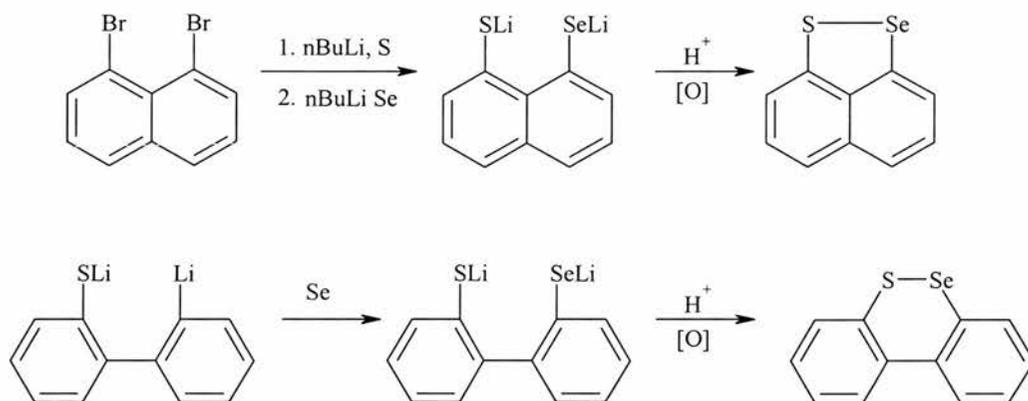


**Scheme 5.1** Synthesis of 2-*tert*-butylnaphtho[1,8-*cd*]-1,2-dithiole **5.1**.

Size exclusion chromatography on the sample of supposedly pure 2,7-di(*tert*-butyl)naphtho[1,8-*cd*]-1,2-dithiole using dichloromethane as an elutant gives three bands which we found to be the expected di-*tert*-butyl compound, the new mono-*tert*-butyl compound and the starting material, naphtho[1,8-*cd*]-1,2-dithiole respectively. The identity of compound **5.1**, a red oil at room temperature, was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, the  $^1\text{H}$  NMR showing a multiplet in the aromatic region and a singlet at 1.47 ppm in the expected

intensities of 5:9. The  $^{13}\text{C}$  NMR showed 5 quaternary carbon environments, 5 non-quaternary environments and peaks at 35.5 and 28.2 ppm representing the  $\underline{\text{C}}(\text{CH}_3)_3$  and  $\text{C}(\underline{\text{C}}\text{H}_3)_3$  carbons respectively. The mass spectrum displayed the expected parent ion at  $m/z$  246.

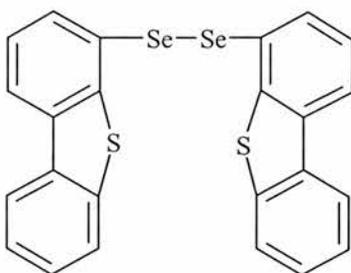
The compound 4-selena-dibenzothiophene dimer (**5.2**) was synthesised by the addition of 1 equivalent of selenium to the literature compound 2,2'-Li(LiS) $\text{C}_{12}\text{H}_8$ .<sup>(70)</sup> This was done in an attempt to synthesise the as yet unknown compound dibenzo[*ce*]-1,2-selenathiine. The reason for this line of synthesis was the close proximity to the literature synthesis of the analogous naphthalene backboneed mixed chalcogen complex naphtho[1,8-*cd*]-1,2-selenathiole (Scheme 5.2).<sup>(152)</sup>



**Scheme 5.2** The literature synthesis of naphtho[1,8-*cd*]-1,2-selenathiole (top) and the similar projected synthesis of the biphenyl backboneed analogue dibenzo[*ce*]-1,2-selenathiine (bottom).

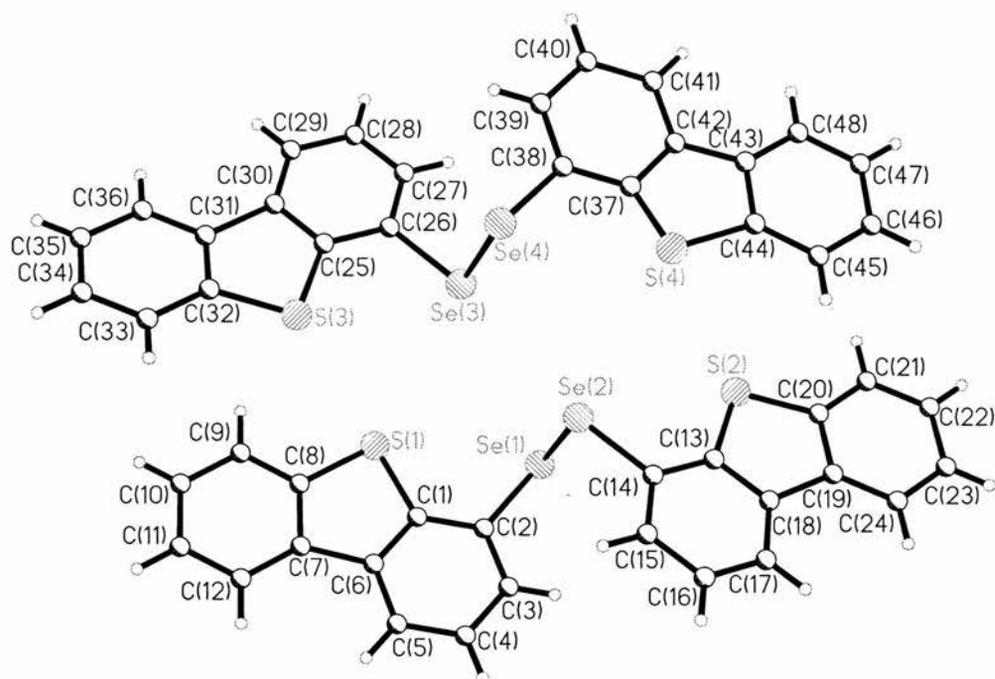
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This synthesis never produced a sample of dibenzo[*ce*]-1,2-selenathiole but actually produced a spectroscopically similar dimer compound 4-selenadibenzothiophene dimer (**5.2**), figure 5.1.



**Figure 5.1**

The structure of compound **5.2** was established primarily by X-ray crystallography as other methods were inconclusive.  $^1\text{H}$  and  $^{13}\text{C}$  NMR showed the typical peaks of compounds such as this, both spectra not showing anything distinctive. The mass spectrum was also inconclusive, the predominant peak being shown at  $m/z$  263 (1/2M) plus another peak at 526 (M). This was inconclusive as the mass of 1/2M is virtually identical to that of the desired product, dibenzo[*ce*]-1,2-selenathiine. However, the X-ray crystal structure (figure 5.2) showed that the compound did indeed exist as a dimer containing a di-selenium bridge. This structure was further confirmed when compound **5.2** was used to synthesise the platinum complex **3.18**, described earlier in chapter 3.



**Figure 5.2** X-ray crystal structure of compound **5.2**.

Se(1)-Se(2)	2.332(9)	Se(1)-Se(2)-C(14)	100.1(18)
Se(1)-C(2)	1.88(3)	Se(2)-Se(1)-C(2)	101.1(12)
Se(2)-C(14)	1.91(3)	C(2)-Se(1)-Se(2)-C(14)	86.0(18)
Se(3)-Se(4)	2.352(9)	Se(3)-Se(4)-C(38)	94.4(18)
Se(3)-C(26)	1.92(3)	Se(4)-Se(3)-C(26)	100.1(12)
Se(4)-C(38)	1.95(3)	C(26)-Se(3)-Se(4)-C(38)	-87.6(17)

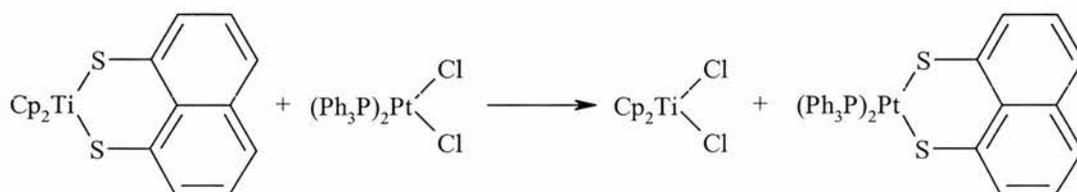
**Table 5.1** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $(\text{C}_{12}\text{H}_8\text{SSe})_2$ , **5.2**.

The selenium selenium bond lengths (2.332(9) and 2.352(9) $\text{\AA}$ ) are almost identical to those of naphtho[1,8-*cd*]-1,2-diselenole<sup>(102)</sup> and dibenzo[*ce*]-1,2-diselenin.<sup>(47)</sup> All other bond lengths are standard for a compound such as this

and are unremarkable. The most interesting bond angles of these molecules are the splay angles ( $86.0(18)$  and  $-87.6(17)^\circ$ ) which show that the molecules of dibenzothiophene are almost perpendicular to each other and that the two molecules are mirror images of each other since one of these angles is positive while the other is negative.

### Exchange reactions

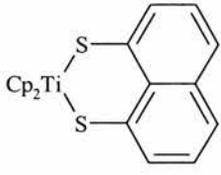
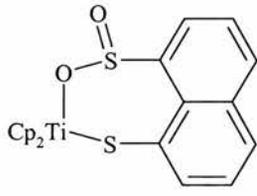
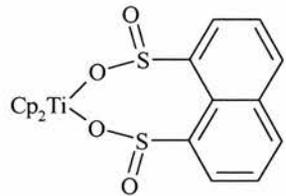
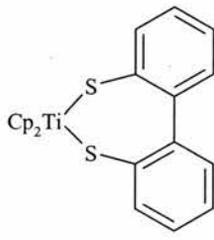
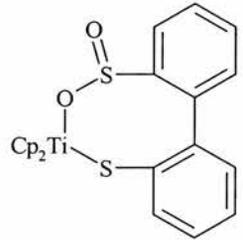
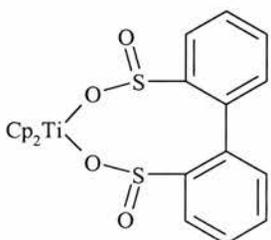
It has previously been shown that bis(thiolato)titanocene complexes (such as those mentioned in chapter 2) can react with dichloro-platinum complexes in a ligand exchange reaction to yield titanocene dichloride and a new platinum thiolato complex.<sup>(99)</sup> This has been shown to be the case whether the two thiolato groups are linked to each other or not. The reason for the success of such a reaction can be attributed to hard and soft mismatching of co-ordination between titanium and sulfur in the starting material being thermodynamically unfavourable when compared with titanium-chlorine co-ordination in the product, driving the reaction forward.



**Scheme 5.3** Ligand exchange reactions between bis(thiolato)titanocene complex and dichloro-platinum complex.

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We have studied the ability of the titanocene complexes titanocene 1,8-dithiolato naphthalene (**2.1**), titanocene 2,2'-dithiolato biphenyl (**2.5**), titanocene 1-sulfinato-8-thiolato-naphthalene (**2.8**), titanocene 2-sulfinato 2'-thiolato biphenyl (**2.9**), titanocene 1,8-disulfinato-naphthalene (**2.10**) and titanocene 2,2'-disulfinato-biphenyl (**2.11**) to undergo ligand exchange with the dichloro-platinum complex *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] in an attempt to discover if the desire of titanium to bond to chlorine and give the product titanocene dichloride is greater or less than the desire to remain as starting material with the hard titanium atom bound to hard oxygen atom(s) of the ligand. The progress of these reactions is particularly easy to monitor as the platinum thiolato complexes are already known (chapter 3). This means that NMR can be used to determine whether exchange has occurred or not by comparing the <sup>1</sup>H and <sup>31</sup>P NMR of the product with those of the expected products and with the starting materials.

Starting material	$^1\text{H}$ NMR of starting material	$^{31}\text{P}$ NMR of expected product	$^1\text{H}$ NMR of product	$^{31}\text{P}$ NMR of product
	6.31	23.4 (2966 Hz)	6.54	23.3 (2985 Hz)
	6.52 5.75	18.4 (2451 Hz) 22.4 (3197 Hz)	6.54	15.5 18.4 (2450 Hz) 22.4 (3194 Hz)
	6.81 6.14	14.2 (2956 Hz)	6.81 6.14	15.5
	6.17	23.1 (2956 Hz)	6.53	23.1 (2955 Hz)
	6.25 6.08	14.2 (2436 Hz) 20.5 (3130 Hz)	6.25 6.08	15.5
	6.23	-	6.23	15.5

**Table 5.2** NMR data for exchange reactions.

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If exchange takes place then the  $^1\text{H}$  NMR should display a peak at 6.54 ppm (the characteristic peak of the 10 aromatic protons of the cyclopentadienyl rings of  $\text{Cp}_2\text{TiCl}_2$ ) and the  $^{31}\text{P}$  NMR should display a peak representing the new platinum complex as described in chapter 3. If no reaction occurs then the  $^1\text{H}$  NMR should show characteristic peak(s) relating to the original titanocene complex (chapter 2) and the  $^{31}\text{P}$  NMR should display a peak at 15.5 ppm (the shift of  $\text{Cl}_2\text{Pt}(\text{PPh}_3)_2$ ).

The NMR data for the six reactions are shown in table 5.2. The  $^{31}\text{P}$  NMR spectrum of reaction 1 shows the characteristic peak at 23.3 ppm, with platinum satellites and a coupling constant of 2985 Hz, while the  $^1\text{H}$  NMR is messy but displays a distinct peak at 6.54 ppm, the shift for  $\text{Cp}_2\text{TiCl}_2$ . There is also no evidence of the starting material  $\text{Cp}_2\text{TiS}_2\text{C}_{10}\text{H}_6$ . This evidence suggests that exchange has taken place and that the platinum complex  $(\text{Ph}_3\text{P})_2\text{PtS}_2\text{C}_{10}\text{H}_6$  has been formed. This is not an unsurprising result given that thiolato ligand transfer from titanium to platinum has been shown to occur previously. A similar result is noticed in the fourth reaction, that between the dithiolato dibenzo complex of titanocene and  $\text{Cl}_2\text{Pt}(\text{PPh}_3)_2$ . Again, the  $^1\text{H}$  NMR is messy but the distinct peak of  $\text{Cp}_2\text{TiCl}_2$  is noticed at 6.53 ppm while the  $^{31}\text{P}$  NMR shows a peak at 23.1 ppm with the appropriate satellites and a coupling constant of 2955 Hz.

Reactions 2 and 5, which are between the titanocene thiolato-sulfinato complexes and  $\text{Cl}_2\text{Pt}(\text{PPh}_3)_2$  give contrasting results. In the case of reaction 5 (the dibenzo example) there is absolutely no evidence of any exchange having occurred as the NMR spectra only display peaks corresponding to the starting material. However, the  $^1\text{H}$  NMR of the product of reaction 2 displays the characteristic peak of  $\text{Cp}_2\text{TiCl}_2$  while the  $^{31}\text{P}$  NMR shows 3 distinct peaks, the predominant

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one occurring at 15.5 ppm (starting material) while two smaller peaks occurring at 18.4 and 22.4 ppm with coupling constants of 2450 and 3194 Hz respectively. This suggests that a slight amount of exchange has occurred as these two peaks correspond to the expected product but since the predominant peak is of the starting material it is fair to assume that the majority of the starting material is unreacted.

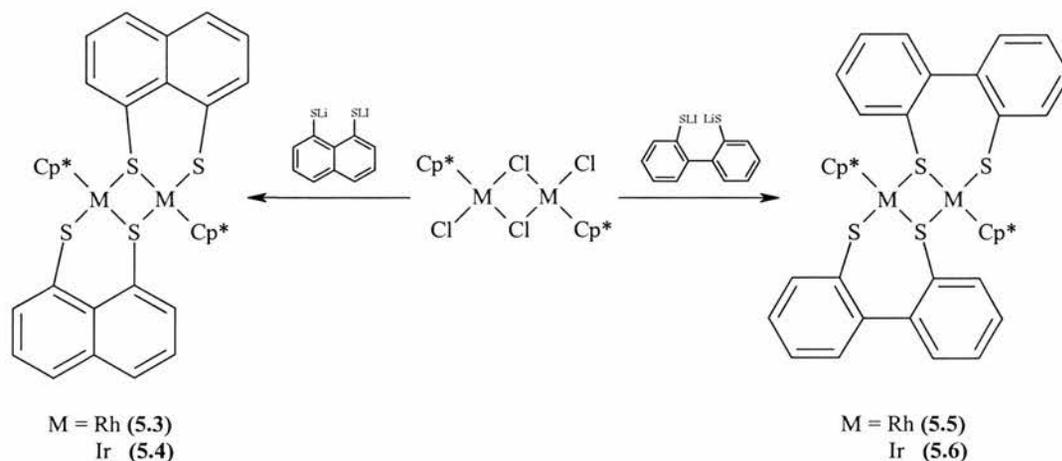
Reactions 3 and 6, which are between the disulfinato titanocene complexes and  $\text{Cl}_2\text{Pt}(\text{PPh}_3)_2$  are shown to not undergo exchange by NMR spectroscopy. In each case the starting materials are seen in the spectra while there is no evidence of any of the expected products.

The success of reactions 1 and 4 and the failure of reactions 3 and 6 are all expected and can be attributed to the desire of titanium to bond to chlorine rather than soft sulfur (in the case of reactions 1 and 4) and the desire of titanium to remain bound to hard oxygen rather than chlorine (in the case of reactions 3 and 6). The partial success of reaction 2 suggests that the strength of the Ti-O bond is marginally weaker than that of the Ti-Cl bond while the failure of reaction 5 suggests that the Ti-O bond is stronger than the corresponding Ti-Cl bond, preventing any exchange from taking place.

### **Dimeric complexes**

The dimeric complexes **5.3-5.6** were synthesised in adequate yield (57–66%) by the salt elimination reaction of two equivalents of the lithium salts of naphtho[1,8-*cd*]-1,2-dithiole and dibenzo[*ce*]-1,2-dithiine with the metal complexes  $[\text{M}(\mu\text{-Cl})\text{ClCp}^*]_2$  (M = Rh, Ir) as demonstrated in scheme 5.4. The

lithium salts were prepared by reaction of two equivalents of super hydride with one equivalent of the parent disulfide bridged compound to reduce the sulfur-sulfur bond and give a di-lithium salt.



**Scheme 5.4** Synthesis of complexes 5.3-5.6

These complexes are all air stable both in the solid state and in solution. The purification and isolation of these compounds is straight forward and is done by removing insoluble impurities by filtration through Celite followed by concentration of the eluent and precipitation of the product with hexane.

The  $^1\text{H}$  NMR spectra display the expected peaks in the aromatic region belonging to the aromatic protons of the disulfide backbone with a small degree of overlap due to the number of different aromatic proton environments in these complexes (6 for the naphthalene complexes and 8 for the biphenyl complexes). Further, a sharp singlet is seen at 1.13 and 1.20 (naphthalene complexes) and at 1.78 and 1.66 ppm (biphenyl complexes). The  $^{13}\text{C}$  NMR spectra concur with the  $^1\text{H}$  NMR spectra, showing aromatic carbons in the region of 139-123 ppm, the quaternary carbon of the pentamethylcyclopentadienyl group (98.5-91.1 ppm) and the Me carbon of the pentamethylcyclopentadienyl group (1.78-1.13 ppm).

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Elemental analysis proved the purity of the samples while mass spectral data (FAB) displayed  $[M+H]^+$  as the highest molecular weight fragment at  $m/z$  857, 1036, 909 and 1089 respectively.

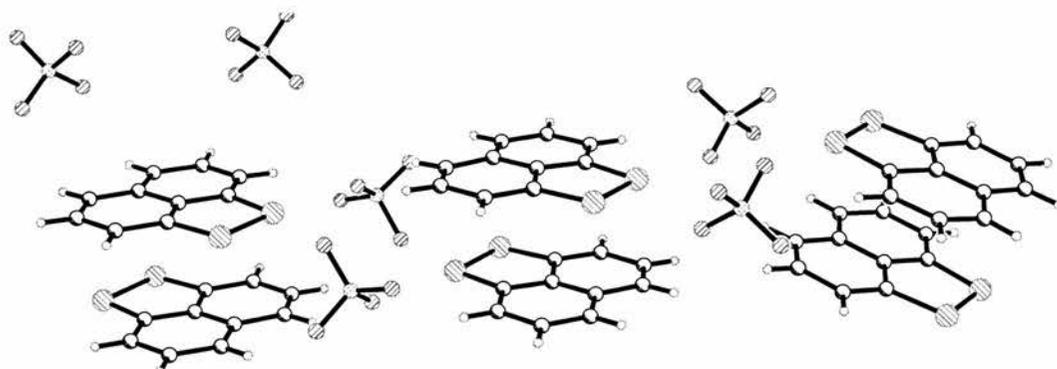
### **Electrocrystallisation**

Electrocrystallisation is an excellent technique for the synthesis of charge transfer salts. This method yields crystals of the highest purity. For electrocrystallisation to be successful, slow nucleation and the minimum of disturbances such as temperature variation and intermittent intense light are desired. Extremely clean and dry containers and electrodes, highly purified and dried materials are prerequisites for successful crystal growth.

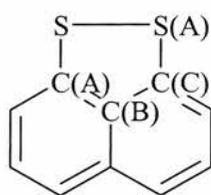
A typical experimental setup involves dissolving a small amount of the donor compound (typically around 10 mg) in the chosen solvent ( $5\text{ cm}^3$ ) and placing this in the anode compartment (the donor compound is that which will give up an electron while the acceptor is that which will accept the electron in the final product). A vast excess of the acceptor compound (up to 500 mg) in  $10\text{ cm}^3$  of solvent is prepared and  $7.5\text{ cm}^3$  is added to the cathodic compartment while the remaining  $2.5\text{ cm}^3$  is added to the anodic compartment to make the volume on both sides equal. These solutions are degassed for 30 seconds and the platinum wire electrodes are placed in the H- cell. A current density is applied using a constant current source and this is left in a temperature controlled environment in the dark (to avoid possible photochemical decomposition of the donor).

We used the technique of electrocrystallisation to study the possibility of naphtho[1,8-*cd*]-1,2-dithiole being used as an inorganic donor with a number of

different anions. This proved successful with  $\text{BF}_4^-$  as the anion as crystals of  $[\text{C}_{10}\text{H}_6\text{S}_2^+]_3 [\text{BF}_4^-]_3$  (compound **5.7**) were obtained which were found by DC conductivity studies to be insulating. These crystals had their X-ray crystal structure determined as shown in figure 5.3. A selection of important bond lengths and angles can be seen in table 5.3.



**Figure 5.3** X-ray crystal structure of  $[\text{C}_{10}\text{H}_6\text{S}_2^+]_3 [\text{BF}_4^-]_3$ , **5.7**.



**Figure 5.4** Naming of atoms for table 5.3.

S-S(A)	2.033(2)-2.053(2)	S(A)-S-C(A)	95.75(14)-96.52(15)
S-C(A)	1.701(5)-1.730(5)	S-C(A)-C(B)	113.9(3)-115.9(4)
C(A)-C(B)	1.385(5)-1.434(5)	C(A)-C(B)-C(C)	115.6(5)-119.2(5)

**Table 5.3** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $[\text{C}_{10}\text{H}_6\text{S}_2^+]_3 [\text{BF}_4^-]_3$ , **5.7**.

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It is worth mentioning here that this product is not actually a donor acceptor complex but is the first step in the synthesis of one, which would be obtained by exchanging the  $\text{BF}_4$  anion with a molecule such as TCNQ to give a stacked compound. This molecule was found to crystallize with six independent halves in the unit cell as shown in figure 5.2. This means that each molecule of  $\text{C}_{10}\text{H}_6\text{S}_2^+$  has an axis of symmetry down the middle and therefore bonds such as S-C(A) are identical in length to the analogous one on the other side of the axis of symmetry, *ie* S(A)-S(C). This is also shown in the bond angles.

The main difference between this molecule and a molecule of naphtho[1,8-*cd*]-1,2-dithiole is the missing electron in the sulfur sulfur bond. One might expect that the sulfur sulfur bond would be slightly longer in this case than in the neutral molecule. However, this elongation is not noticed as the bond length is very similar to that of the neutral molecule.<sup>(102)</sup> All other bond lengths and angles in this cationic species are virtually identical to those of the neutral species.

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### 5.3 Conclusion

In this chapter we have described the synthetic route to two new dichalcogen bridged compounds, namely 2-*tert*-butylnaphtho[1,8-*cd*]-1,2-dithiole and 4-selena-dibenzothiophene dimer. These compounds have subsequently been used as pro-ligands in the preparation of platinum and iridium complexes (described in chapters 3 and 4 respectively).

We have also demonstrated that while titanocene dithiolato complexes will undergo ligand exchange with a dichloro platinum species to yield a titanocene dichloride and a platinum dithiolato complex, titanocene thiolato sulfinato complexes are much less keen to undergo such exchange while absolutely no exchange will occur when using a titanocene disulfinato complex. This is attributed to the increased strength of the titanium-oxygen bonds as opposed to titanium-sulfur bonds which are weaker as a result of the hard-soft mismatch between titanium and sulfur.

A variety of rhodium and iridium complexes of naphtho[1,8-*cd*]-1,2-dithiole and dibenzo[*ce*]-1,2-dithiine have been prepared by salt elimination reaction of the dithium salts of these pro-ligands with the starting complex  $[\text{Cp}^*\text{MCl}_2]_2$  and these complexes have been identified by spectroscopic methods.

Finally, the sulfur sulfur bond of naphtho[1,8-*cd*]-1,2-dithiole is shown to give up an electron upon electrocrystallisation with  $\text{BF}_4$  as a counter-ion to give a 1:1 adduct. The crystal structure of this is reported, showing three molecules of both ions in the unit cell.

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## 5.4 Experimental

### General

Unless otherwise stated, all operations were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Diethyl ether and tetrahydrofuran were purified by reflux over sodium and benzophenone and distilled under nitrogen. Toluene and hexane were purified by reflux over sodium and distilled under nitrogen. Dichloromethane was purified by reflux over calcium hydride and distilled under nitrogen. All other reagents were purchased from either Aldrich, Acros or Lancaster and used as received. Infra-red spectra were recorded as KBr discs in the range 4000-300  $\text{cm}^{-1}$  on a Perkin-Elmer System 2000 Fourier transform spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR were recorded using a Jeol GSX Delta 270 or Bruker Avance 300 MHz spectrometer. Microanalyses were performed by the University of St Andrews microanalysis service. Mass spectra were recorded by both the University of St Andrews mass spectrometry service and the EPSRC National Mass Spectrometry Service Centre, Swansea.

### Synthesis

#### **2-*tert*-butylnaphtho[1,8-*cd*]-1,2-dithiole (5.1)**

Naphtho[1,8-*cd*]-1,2-dithiole (3 g, 15.8 mmol) was dissolved at 50°C in a mixture of nitromethane (37 mL) and *tert*-butyl chloride (4.38g, 47.3 mmol). Anhydrous  $\text{AlCl}_3$  (400mg, 3.00 mmol) was added and the mixture was stirred at

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50°C for 20 minutes. This was then extracted with water. The water was washed with dichloromethane and discarded while the organic fractions were combined and dried over anhydrous magnesium sulphate. This was then filtered and the solvent removed under reduced pressure. The remaining solid was dissolved in hexane and passed through a silica column to give an orange coloured solution. This was further purified by size exclusion chromatography using bio beads and eluting with dichloromethane. The first fraction removed was found to be 2,7-di-*tert*-butylnaphtho[1,8-*cd*]-1,2-dithiole. Fraction 2 was the desired product while fraction 3 was the starting material, naphtho[1,8-*cd*][1,2]dithiole. The desired product was obtained as a red oil, yield 1.126 g (29%). Microanalysis: Found (Calc. for S<sub>2</sub>C<sub>14</sub>H<sub>14</sub>): C 67.50 (68.24), H 6.07 (5.72) %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ= 7.70-7.10 (m, 5H, aromatics), 1.47 (s, 9H, 3 x Me). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ= 142.7, 140.2, 139.4, 134.4, 127.9 (all quaternary aromatic), 126.9, 125.8, 122.4, 121.9, 121.2 (all aromatic), 35.5 (quaternary) and 28.2 (CH<sub>3</sub>). EI<sup>+</sup> MS: *m/z*, 246.0 [M]<sup>+</sup>, 230.9 [M-CH<sub>3</sub>]<sup>+</sup>.

#### 4-selena-dibenzothiophene dimer (5.2)

A solution of 2,2'-Li(LiS)C<sub>12</sub>H<sub>8</sub> was prepared. <sup>(70)</sup> 1 equivalent of Selenium was added and this was allowed to stir overnight. 25% glacial acetic acid in tetrahydrofuran was added (30 cm<sup>3</sup>) and this was allowed to stir in air overnight. This was then dried under pressure and purified by chromatography on silica using hexane/dichloromethane (50:50) as eluant. The yellow fraction was collected and recrystallised from dichloromethane/hexane to give the final product as a yellow microcrystalline solid. Yield 0.232 g, 26 %. EI MS: *m/z* 526 [M]<sup>+</sup> and 263 [1/2M]<sup>+</sup>.

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## Exchange reactions

Titanocene 1,8-dithiolato naphthalene (complex 2.01) (0.070 g, 0.190 mmol) and *cis*-Cl<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub> (0.150 g, 0.190 mmol) were refluxed in 20 cm<sup>3</sup> of tetrahydrofuran for 24 hours. The resulting solution was dried under vacuum and studied by <sup>1</sup>H and <sup>31</sup>P NMR. This reaction was repeated using the related oxide complexes titanocene 1-sulfinato-8-thiolato-naphthalene (complex 2.8) and titanocene 1,8-disulfinato-naphthalene (2.10) and the similar biphenyl complexes titanocene 2,2'-dithiolato biphenyl (2.5), titanocene 1-sulfinato-8-thiolato-naphthalene (2.8) and titanocene 2,2'-disulfinato-biphenyl (2.11).

### [Cp\*<sub>2</sub>RhS<sub>2</sub>C<sub>10</sub>H<sub>6</sub>]<sub>2</sub> (5.3)

Naphtho[1,8-*cd*]-1,2-dithiole (100 mg, 0.53 mmol) was dissolved in 10 ml of tetrahydrofuran and a 1.0 M solution of LiBEt<sub>3</sub>H (1.06 ml, 1.06 mmol) was added via syringe. Upon addition an immediate colour change from red to pale yellow was observed accompanied by the evolution of gas. To this was added [Cp\*<sub>2</sub>RhCl<sub>2</sub>]<sub>2</sub> (162 mg, 0.26 mmol) and this was allowed to stir overnight. The solvent was removed under reduced pressure and the remaining solid was extracted into dichloromethane, filtered through a shallow pad of Celite to remove any insoluble salts and reduced in volume to approximately 3 cm<sup>3</sup>. Hexane (40 cm<sup>3</sup>) was slowly added to precipitate the final product as a red powder (0.140 g, 63 %). Microanalysis: Found (Calc. for [Cp\*<sub>2</sub>RhS<sub>2</sub>C<sub>10</sub>H<sub>6</sub>]<sub>2</sub>): C 56.32 (56.07), H 5.06 (4.94), S 15.40 (14.94)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 8.06 (dd, 1H, aromatic), 7.75 (dt, 2H, aromatic), 7.50 (dd, 1H, aromatic), 7.15 (dt, 2H, aromatic), 1.13 (s, 15H, Me groups). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 132.0, 129.3, 129.1,

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124.9, 123.8, 123.4 (all aromatic C-H), 96.6 (quaternary Cp groups), 7.8 (Me groups). Mass Spec (FAB):  $[M+H]^+$  857,  $[M]^+$  856.

#### **$[Cp^*IrS_2C_{10}H_6]_2$ (5.4)**

Naphtho[1,8-*cd*]-1,2-dithiole (100 mg, 0.53 mmol) was dissolved in 10 ml of tetrahydrofuran and a 1.0 M solution of  $LiBEt_3H$  (1.06 ml, 1.06 mmol) was added via syringe. Upon addition an immediate colour change from red to pale yellow was observed accompanied by the evolution of gas. To this was added  $[Cp^*IrCl_2]_2$  (209 mg, 0.26 mmol) and this was allowed to stir overnight. The solvent was removed under reduced pressure and the remaining solid was extracted into dichloromethane, filtered through a shallow pad of Celite to remove any insoluble salts and reduced in volume to approximately 3 cm<sup>3</sup>. Hexane (40 cm<sup>3</sup>) was slowly added to precipitate the final product as an orange powder (0.153 g, 57 %). Microanalysis: Found (Calc. for  $[Cp^*IrS_2C_{10}H_6]_2$ ): C 46.10 (46.33), H 4.01 (4.09), S 12.85 (12.34)%. <sup>1</sup>H NMR ( $CD_2Cl_2$ )  $\delta$ : 8.05 (dd, 1H, aromatic), 7.72 (dt, 2H, aromatic), 7.48 (dd, 1H, aromatic), 7.11 (dt, 2H, aromatic), 1.20 (s, 15H, Me groups). <sup>13</sup>C NMR ( $CD_2Cl_2$ )  $\delta$ : 130.2, 129.2, 128.4, 124.9, 124.0, 123.3 (all aromatic C-H), 130.5, 128.7, 126.4 (all quaternary aromatic), 91.1 (quaternary Cp groups), 7.5 (Me groups). Mass Spec (FAB):  $[M+H]^+$  1036.

#### **$[Cp^*RhS_2C_{12}H_8]_2$ (5.5)**

Dibenzo[*ce*]-1,2-dithiine (100 mg, 0.46 mmol) was dissolved in 10 ml of tetrahydrofuran and a 1.0 M solution of  $LiBEt_3H$  (0.92 ml, 0.92 mmol) was added via syringe. Upon addition the solution immediately changed colour from

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yellow to colourless accompanied by the evolution of gas. To this was added  $[\text{Cp}^*\text{RhCl}_2]_2$  (143 mg, 0.23 mmol) and this was allowed to stir overnight. The solvent was removed under reduced pressure and the remaining solid was extracted into dichloromethane, filtered through a shallow pad of Celite to remove any insoluble salts and reduced in volume to approximately 3 cm<sup>3</sup>. Hexane (40 cm<sup>3</sup>) was slowly added to precipitate the final product as a brown powder (0.121 g, 58 %). Microanalysis: Found (Calc. for  $[\text{Cp}^*\text{RhS}_2\text{C}_{12}\text{H}_8]_2$ ): C 58.10 (58.15), H 4.91 (5.11), S 13.85 (14.08)%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 8.30 (dd, 1H, aromatic), 8.06 (dt, 2H, aromatic), 7.83 (dd, 1H, aromatic), 7.73 (m, 2H, aromatic), 7.41 (m, 2H, aromatic), 1.78 (s, 15H, Me groups). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 138.6, 137.6, 137.2, 136.6, 136.0, 128.9, 128.4, 126.3 (all aromatic C-H), 134.8, 132.0, 130.7 (all quaternary aromatic) 98.5 (quaternary Cp groups), 8.5 (Me groups). Mass Spec (FAB):  $[\text{M}+\text{H}]^+$  909.

### **$[\text{Cp}^*\text{IrS}_2\text{C}_{12}\text{H}_8]_2$ (5.6)**

Dibenzo[*ce*]-1,2-dithiine (100 mg, 0.46 mmol) was dissolved in 10 ml of tetrahydrofuran and a 1.0 M solution of LiBEt<sub>3</sub>H (0.92 ml, 0.92 mmol) was added via syringe. Upon addition the solution immediately changed colour from yellow to colourless accompanied by the evolution of gas. To this was added  $[\text{Cp}^*\text{IrCl}_2]_2$  (185 mg, 0.23 mmol) and this was allowed to stir overnight. The solvent was removed under reduced pressure and the remaining solid was extracted into dichloromethane, filtered through a shallow pad of Celite to remove any insoluble salts and reduced in volume to approximately 3 cm<sup>3</sup>. Hexane (40 cm<sup>3</sup>) was slowly added to precipitate the final product as a yellow powder (0.165 g, 66 %). Microanalysis: Found (Calc. for  $[\text{Cp}^*\text{RhS}_2\text{C}_{12}\text{H}_8]_2$ ): C

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48.10 (48.52), H 4.40 (4.26), S 11.85 (11.75)%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 8.13 (dd, 1H, aromatic), 8.09 (dd, 1H, aromatic), 7.88 (dd, 1H, aromatic), 7.80 (dd, 1H, aromatic), 7.49 (m, 2H, aromatic), 7.36 (m, 2H, aromatic), 1.66 (s, 15H, Me groups).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 138.9, 137.2, 137.1, 136.7, 135.9, 129.4, 129.2, 126.5 (all aromatic C-H), 144.2, 133.9, 131.9, 127.2 (all quaternary aromatic), 92.5 (quaternary Cp groups), 8.3 (Me groups). Mass Spec (FAB):  $[\text{M}+\text{H}]^+$  1089.

### **Electrocrystallisation, $[\text{S}_2\text{C}_{10}\text{H}_6^+]_3 [\text{BF}_4^-]_3$ (5.7)**

10 cm<sup>3</sup> of a 0.15 M tetrabutylammonium tetrafluoroborate salt solution (0.494 g) in 1,1,2-trichloroethane and 5 cm<sup>3</sup> of a  $1.2 \times 10^{-2}$  M solution of naphtho[1,8-*cd*]-1,2-dithiole in 1,1,2-trichloroethane were prepared. 5 cm<sup>3</sup> of the naphtho[1,8-*cd*]-1,2-dithiole solution was added to the anode compartment of a glass H-cell (containing a fine porosity glass frit between the two compartments and two platinum wire electrodes) and 5 cm<sup>3</sup> of the tetrabutylammonium tetrafluoroborate was added to the cathode compartment. The remaining 5 cm<sup>3</sup> of the tetrabutylammonium tetrafluoroborate solution was added in equal amounts to the anode and cathode compartments to produce equal solution heights on both sides. Both solutions were purged for 30 seconds with nitrogen and the platinum electrodes were placed in their respective compartments and adjusted in height so that they were immersed in the solutions but not touching the bottom. The apparatus was covered in aluminium foil to exclude light and the current was adjusted to 3  $\mu\text{A}$ .

After 4 weeks the crystals were harvested. This was done by carefully lifting the anode from the solution and brushing the crystals onto a suction filter where they

were washed with some cold TCE and dried under vacuum. The resulting crystals were of very high quality and were suitable for X-ray diffraction.

	5.2	5.7
Empirical Formula	C <sub>24</sub> H <sub>14</sub> S <sub>2</sub> Se <sub>2</sub>	C <sub>10</sub> H <sub>6</sub> S <sub>2</sub> BF <sub>4</sub>
<i>M</i>	524.39	277.08
Crystal system	Monoclinic	Orthorhombic
Space group	Cc	Pmn2(1)
<i>a</i> /Å	10.757(6)	10.1272(12)
<i>b</i> /Å	10.701(7)	6.6216(8)
<i>c</i> /Å	32.93(2)	47.129(6)
$\alpha$ /°	90	90
$\beta$ /°	93.98(4)	90
$\gamma$ /°	90	90
<i>U</i> /Å <sup>3</sup>	3781(4)	3160.4(6)
<i>Z</i>	8	12
$\rho_{\text{calcd}}$ g/cm <sup>3</sup>	1.842	1.747
$\mu$ /mm <sup>-1</sup>	4.140	4.889
Reflections measured	8036	23747
Independent reflections	5099	3128
Final <i>R</i> 1, <i>wR</i> 2	0.2223,	0.0507,
[ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.4616	0.1224

**Table 5.4** Details of the X-ray data collections and refinements for complexes **5.2** and **5.7**.

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