

How Not to Discover a New Reagent. The Evolution and Chemistry of Woollins' Reagent.

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Received: The date will be inserted once the manuscript is accepted.

This review is dedicated to the 'coworkers' (– in reality the workers) who performed the studies described here.

Abstract: The pathways in research can be complex. This review provides a personal account of the winding scientific and funding road which led to Woollins' Reagent. The synthesis and demonstrative reactions of Woollins' Reagent are summarized.

Keywords: Synthesis, heterocycle, phosphorus, selenium, group 16.

Whilst preparing this review I was acutely aware that the guidelines explicitly request that authors incorporate the background to their research and personal context and I have taken this seriously; I have provided a story, warts and all. . . This article will provide a review of the development of Woollins' Reagent – the zig zag story not the polished lecture! Inevitably there is some sense of autobiography and I set the scene with rather unrelated work which, I hope, illustrates the 'philosophy' and the joy of research in my labs. I must admit that I have also grasped the opportunity to review some simple S-N and Se-N chemistry – I am sure this area deserves more recognition and study than it currently receives.

I have been lucky enough to work with a range of very talented people over the past 35 years and certainly in the early days of my research career eccentricity often went hand in hand with brilliance. Sadly, in my view, there has been a leveling down in terms of behavior and style of academic staff and we, as a community, are poorer for it.

It is conventional to mention a burning desire to study chemistry that was instilled by a Damascus moment in which one had a blinding flash of inspiration igniting a lifelong desire to improve things for humanity through chemistry. I had none of this whilst at school and indeed slid through with the minimum of effort. As part of my general laziness and contrariness (and against lots of good advice) I chose to study chemistry, physics and religion as my three specialist subjects in sixth form. The consequence was that when I came to apply to university I didn't have enough maths to do physics or good enough English qualifications to study divinity so was left with chemistry as my only possible option. I started my university life at the University of East Anglia, UEA, (or as it was known back in 1973 for a variety of reasons, the University of Easy Access). I went to UEA for my BSc since I liked the prospect of watching Norwich City in the old English first

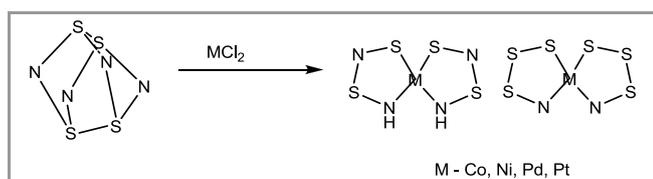
division and my school grades were really pretty marginal - indeed when I told my school chemistry teacher (an old school character Mr Gregory who was never without his sports coat, leather patches and moustache) that I was going to University to study chemistry he responded ominously 'Woollins, you won't last two weeks'

It turned out that UEA had a really rather good degree program taught with great enthusiasm by luminaries such as Alan Katrizky and Sandy McKillop amongst others and they did inspire and enthuse me greatly. At the end of my BSc I was offered a PhD place with Andrew Thomson and Roger Grinter to work on S-N systems. Neither Andrew or Roger knew anything much about the area but they had noticed the reports on the remarkable properties of (SN)_x and convinced Johnson Matthey to part-fund a project. Andrew has an intellect which still leaves me awestruck, whilst Roger has real depth and knowledge in theory coupled with an accent like a Dorset pig farmer. Two supervisors is a great boon – especially when they both go on sabbaticals during your PhD – I had a great time and largely pleased myself with the direction of the work with occasional nudges from one or other of my supervisors. Between them Roger and Andrew sparked an inquisitive nature coupled with the need to have long term goals whilst also training me in methodology and time management. After my PhD I was fortunate to undertake postdoctoral work in three quite disparate areas, [1] in asymmetric homogeneous catalysis with Bill Cullen at UBC, Vancouver [2] in platinum anti-cancer chemistry with Rosenberg at MSU, East Lansing and [3] in metallaborane chemistry with Norman Greenwood at Leeds. Norman Greenwood encouraged me to apply for a 'New Blood' lectureship and I was lucky enough to be offered a post at Imperial College by Geoffrey Wilkinson.

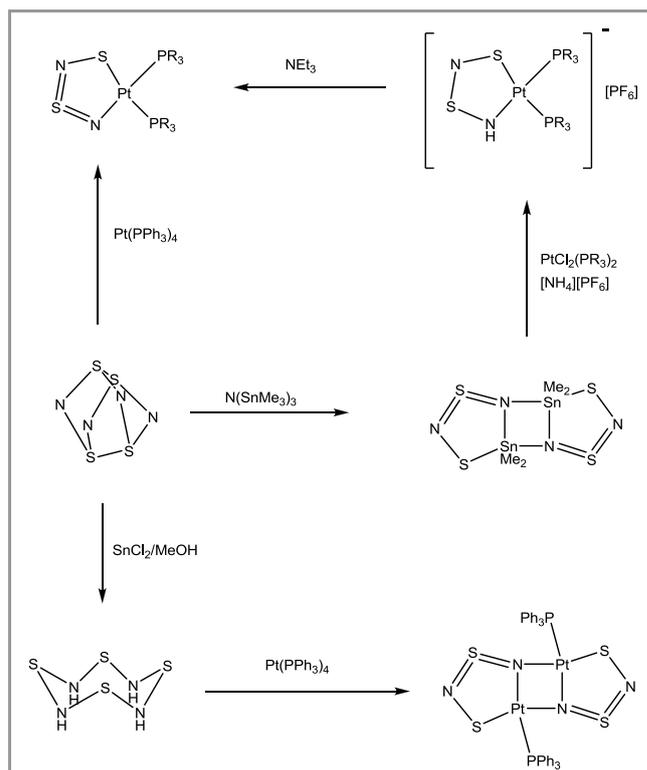
I started at IC in Oct 1984. IC was a very competitive environment but had a great 'can do' philosophy. Apart from Wilkinson, inorganic chemistry had some great talents including Denis Evans (originator of the Evans balance and the Evans NMR method) and William Griffith (a brilliant osmium chemist), whilst organic chemistry included young lecturers such as Steve Ley and William Motherwell. My research career started in earnest at IC and despite having been

appointed to a bioinorganic post I won my first research grant to work on M-S-N chemistry.

Our early work focused on trying to bring rational approaches to the synthesis of M-S-N systems. Although the chemistry of SN anions is now fairly well understood very few of these anions are available as 'off the shelf' salts. In the 1950's Becke-Goehring¹ showed that reaction of S_4N_4 with $Ni(CO)_4$ gives a solid of formula $Ni(NS)_4$ which when refluxed in methanol leads to $Ni(S_2N_2H)_2$.² Later, the reaction of simple metal halides with S_4N_4 was used to prepare Co, Ni, Pd and Pt complexes of the $[S_2N_2H]^-$ and $[S_3N]^-$ anions (eqn 1).³⁻⁵



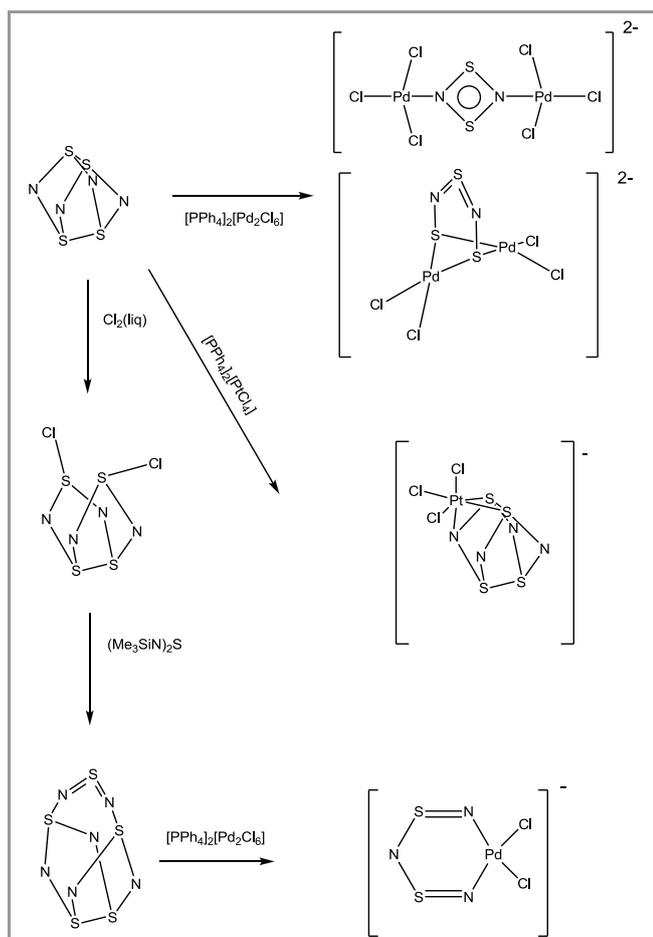
The published reactions were poor yield and hard to generalize. With the hope of developing interesting polymeric and/or stacking Pt-S-N systems we set about developing the area using two strategies, firstly developing the chemistry of S_4N_4 and secondly looking for reagents that could effect simple ligand transfer chemistry. The reaction chemistry of S_4N_4 is an elegant demonstration of the difficulties and complexity of main group chemistry. Its simplest reaction is decomposition to the elements, a thermodynamically favourable reaction which can be achieved with modest shock or heat. Notwithstanding this inherent difficulty S_4N_4 is almost certainly the most studied S-N molecule. It was first synthesized in 1835 and has undergone steady investigation for many years. In the early 70's interest in S-N chemistry received a boost when the unusual 1-D electrical and superconducting properties of $(SN)_x$ were uncovered.⁸ Sulfur-nitrogen chemistry remains a rather unfashionable area which given the unpredictable nature of reactions in this area is a great pity. There are some good reviews in the area which illustrate the beauty of this chemistry.^{9,10} In my early years at IC whilst my group worked on M-S-N and M-Se-N chemistry the organic chemist, Charles Rees (Derek Barton's successor at IC) uncovered a range of S-N aromatic C-S-N heterocycles first by reactions of S_4N_4 and later using more systematic methods.^{11,12} Charles' group were pretty hopeless at the synthesis of the purely inorganic starting materials but always seemed (unlike us) to have beautiful mechanisms; there was a healthy combination of complementarity and rivalry between us during this time.



Scheme 1 Examples of Metalla-sulfur-Nitrogen Complexes¹³⁻¹⁵.

Some early examples of routes to M-S-N complexes developed by my first PhD student, Paul Kelly, are shown in Scheme 1. Of particular interest are the $Pt(PR_3)_2(S_2N_2H)X$ systems which form stacked arrangements.¹⁶ Paul Kelly also later extended this work by making M-Se-N complexes using Se_4N_4 as starting material.¹⁷ This is very sensitive material; indeed the first time we prepared it (from a reaction in liquid ammonia) whilst washing the red solid with a solution of KCN the nitrogen was let into the flask fairly briskly – the resulting turbulence caused an explosion which destroyed the flask embedding pieces red selenium into the white shirt Paul was wearing – from a distance this looked like major bleeding. Bravery was not lacking in the group during that era and Paul Kelly also carried out what remains as the only published reaction of (extraordinarily explosive) S_5N_6 to give a complex of the $[S_2N_3]^-$ ligand.¹⁸ Scheme 2 illustrates the reaction of S_4N_4 and S_5N_6 with $[PPh_4]_2[Pd_2Cl_6]$. A mixture of compounds is formed, one containing the bridging, neutral S_2N_2 ring which is formally a 6π aromatic ring whilst the second product contains the $[S_3N_2]^{2-}$ dianion.¹⁹ Reaction of S_4N_4 with gaseous chlorine results in ring cleavage to give $(NSCl)_3$, whereas Roesky showed²⁰ very elegantly that treatment with liquid chlorine is milder and results in disubstitution to give $S_4N_4Cl_2$. This latter compound eliminates $MeSiCl$ when treated with $(Me_3SiN)_2S$ and gives the air sensitive and very explosive S_5N_6 . The reaction of S_5N_6 with $[PPh_4]_2[Pd_2Cl_6]$ gives $[PPh_4][PdCl_2(S_2N_3)]$ which contains the only known example of an $[S_2N_3]^-$ ligand. The complexity of this type of chemistry is

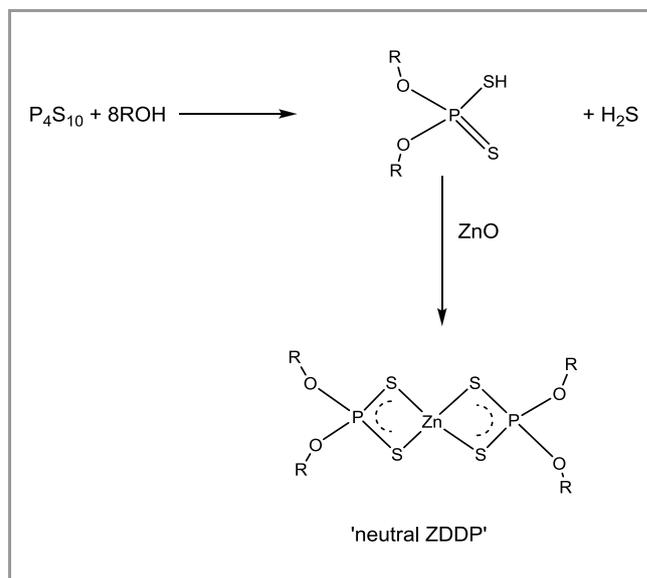
further illustrated by the reaction of S_4N_4 with $[PPh_4]_2[PtCl_4]$ which gives $[PPh_4][PtCl_3(S_4N_4)]$ containing Pt(IV) and the $[S_4N_4]^{2-}$ dianion. Our contribution to M-S-N chemistry has been reviewed.¹⁵ In subsequent years we developed M-Se-N chemistry but the main reason to discuss our M-S-N chemistry is to set the scene for our work on P-S and P-Se chemistry. Largely as a consequence of our published work on M-S-N chemistry and the dearth of other *p*-block chemists in the UK, I was approached by a division of EXXON and invited to work on P-S chemistry.



Scheme 2 Examples of M-S-N complexes prepared by us, illustrating the difference in reactivity of S_4N_4 and S_5N_6

A major use of P-S chemistry is the synthesis of zinc dialkyldithiophosphates which are added to engine oil as anti-oxidants. Although these compounds are made on quite large scale (multi-tonne) there can be problems with the synthetic route. The simplified synthesis is shown in scheme 3. Reaction of the cheap and readily available P_4S_{10} with alcohol gives the dialkyldithiophosphoric acid (DDP) which is neutralized to give the zinc complex (ZDDP). DDP with small R groups such as methyl are thermally unstable and thus both to improve the additive properties and avoid handling dangerous systems larger R groups and complexation with zinc are used to produce the commercial material which is added to

engine oils. In fact depending on the conditions it is also possible to prepare so called basic ZDDP of the formula $Zn_4O(DDP)_6$.



Scheme 3 Commercial synthesis of zinc dialkyldithiophosphates.

Although this chemistry has been in use since the 1950s there are still complexities and it was only fairly recently that we showed the structure of basic ZDDP is analogous to beryllium acetate with a tetrahedron of zinc atoms surrounding a central O^{2-} dianion and every edge of the zinc tetrahedron being chelated by a DDP ligand.²²

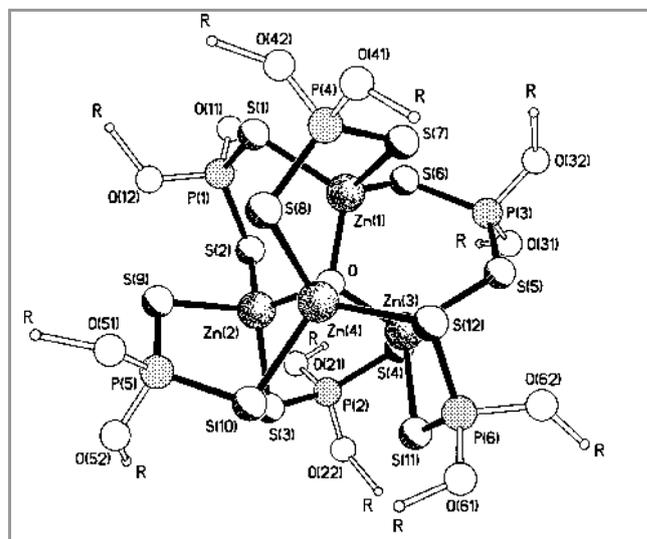


Figure 1 The crystal structure of basic $Zn_4O[S_2P(OBu^t)_2]_6$; only the first carbon atom of each Bu^t is illustrated (denoted R) for clarity.²²

The synthesis of DDP and ZDDP can be problematical with rather large variability in reaction rates. Careful examination of samples of P_4S_{10} showed that this material is often contaminated with traces of P_4S_9 and S_8 (almost certainly from incomplete reaction of P_4

and S₈ during the manufacturing process). This process (Scheme 3) is thus not ideal and also suffers from the environmental problem that it generates H₂S.

As part of this work with EXXON Paul Wood developed elegant routes to zinc dialkylmonothio phosphates (ZDMP, Equation 2).²³



Equation 2

These O,S ligands demonstrate classical hard soft ligand behaviour in complexation reactions²⁴ thus whilst reaction of ZDDP with Pt(PMe₂Ph)₂Cl₂ proceeds with elimination of ZnCl₂ to give [Pt(PMe₂Ph)₂(S₂P(OR)₂)] reaction of ZDMP results in insertion of the S-P-O backbone into the Pt-Cl bond to give (PMe₂Ph)₂Pt(SP(OR)₂O)₂ZnCl₂ (Figure 2).

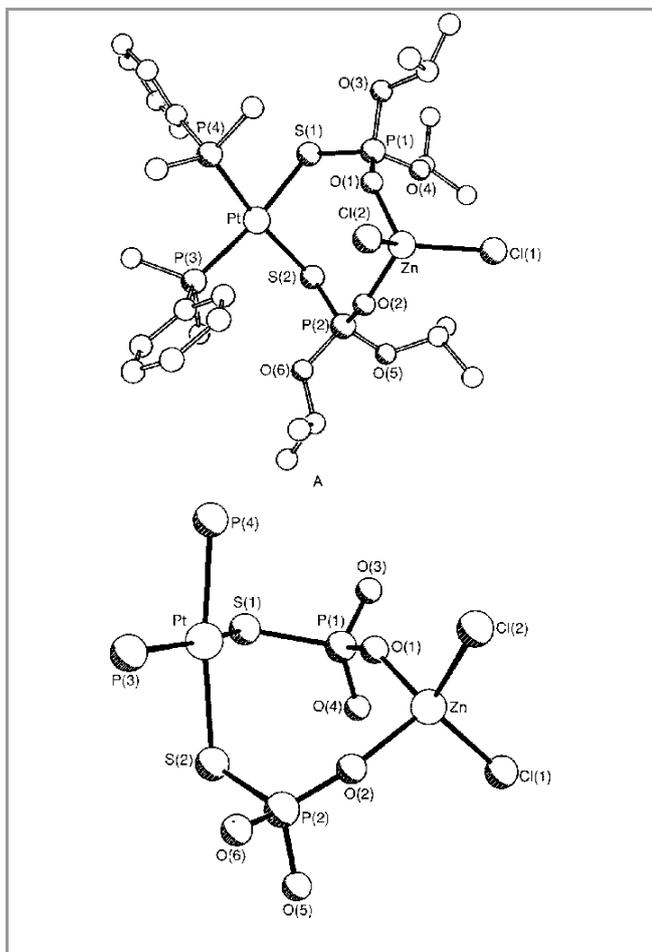
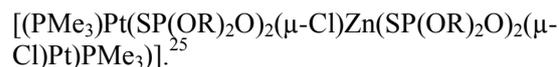
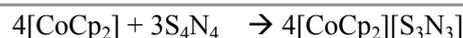


Figure 2 The X-Ray structure of (PMe₂Ph)₂Pt(SP(OR)₂O)₂ZnCl₂, upper complete molecule, lower core illustrating O coordination to Zn and S coordination to Pt.

Interestingly, changing the phosphine on the platinum influences the reaction as well so reaction of ZDMP with Pt(PMe₃)₂Cl₂ gives a trimetallic complex



This period in my research group was very lively, apart from Paul Kelly (now Reader at Loughborough) working on M-S/Se-N chemistry, Ivan Parkin (now Professor and Head of Dept at UCL, London) Paul Wood (now Lecturer at Cambridge University) were competing to deliver exciting new work. Parkin developed some very direct routes to M-S-N and M-Se-N complexes using reactions in liquid ammonia,^{17b,26} whilst Kelly continued to show his skill and imagination by using an imaginative route to isolate the [S₃N₃]⁻ anion.²⁷ Chivers published elegant work on S-N anions and our engagement in this area learnt on his work whilst occasionally causing uncomfortable tensions and these could have been quite destructive especially since the US and UK editors of *Polyhedron* independently commissioned reviews on M-S-N chemistry from us both.^{13,14} Although Chivers pioneered S-N anion chemistry Paul Kelly prepared this anion by a neat reduction using cobaltocene²⁷



Equation 3

The resulting material forms infinite stacks of alternating cations and anions with weak C-H...N hydrogen bonds (Figure 3) with the solid material being dark red but solutions being yellow indicating strong charge transfer interactions.

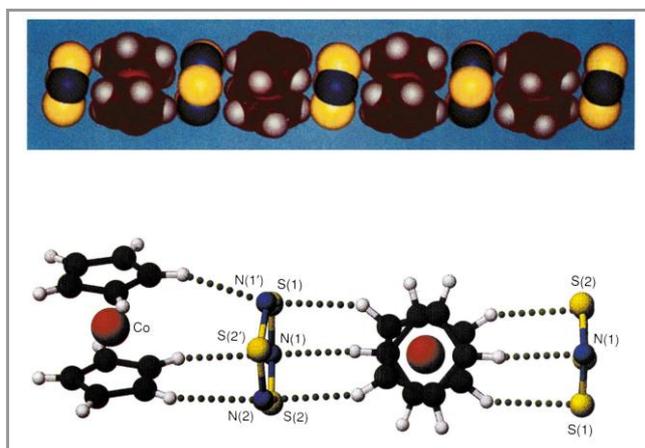


Figure 3 The X-Ray structure of [CoCp₂][S₃N₃]. Upper is the space filling representation, lower is detail of the packing showing the cation-anion interactions.²⁷

Against the backdrop of strong competition from others in my group, Paul Wood rose to the challenge in two different ways which have both had lasting impact on the direction of our research. Firstly, as mentioned above we had found that P₄S₁₀ had variable rates of reaction because of the presence of P₄S₉. During attempts to make pure samples of P₄S₉ Paul Wood serendipitously prepared a peri substituted

naphthalene system. Reaction of P_4S_3 with S_8 in α -bromonaphthalene at 240 °C was reported to give P_4S_9 in moderate yield.²⁸ However the reaction is very sensitive to the conditions used. We found that in order to maximise the yield of P_4S_9 , a slightly lower temperature is preferable. If the temperature is raised to 240 °C, and above, naphthalenedithiadiphosphatanedisulfide **NapP₂S₄** is obtained (Figure 4).²⁹

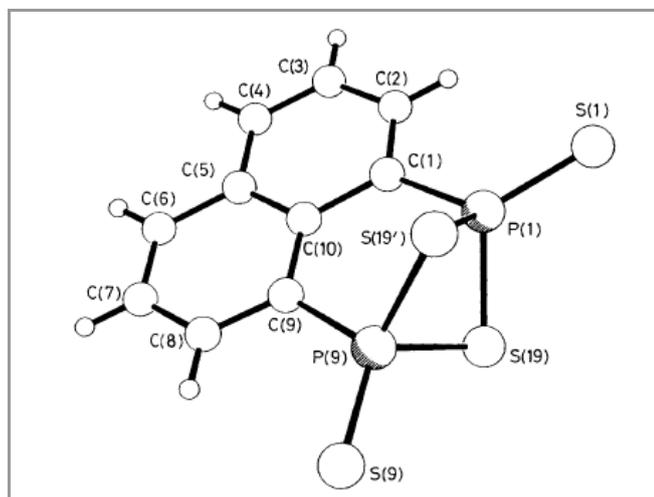
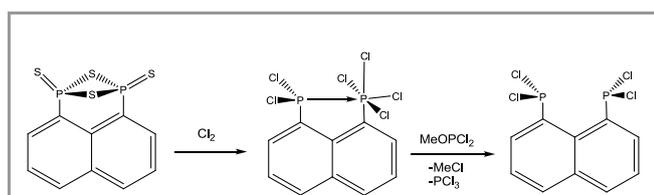


Figure 4 The X-Ray structure of naphthalenedithiadiphosphatanedisulfide²⁹

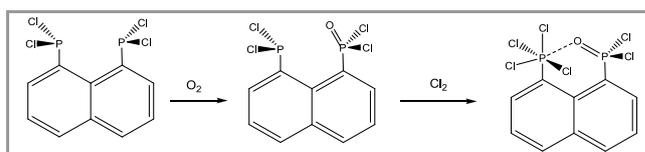
The identity of **NapP₂S₄** baffled us for a while and we needed X-Ray crystallography to settle this problem. Alexandra Slawin started her long collaboration with me around this time. This has been very fruitful - she is a genuinely brilliant crystallographer who will tackle any problem even with lousy crystals. To paraphrase the advert 'I liked the crystallographer so much I married her'. **NapP₂S₄** can be thought of as a *cis* analogue of Lawesson's Reagent and was our first forage into organic reaction chemistry – we showed it is capable of sulfur transfer reaction. Over the twenty years since we made **NapP₂S₄**, we recognized how hard it is to make 1,8 (*peri*) substituted naphthalenes and used the *peri* arrangement to isolate some unusual systems as well as developing insight into weak bonding/repulsive effects using the naphthalene backbone as a molecular scaffolding. This work has been reviewed³⁰ but here I mention one or two highlights.



Equation 4

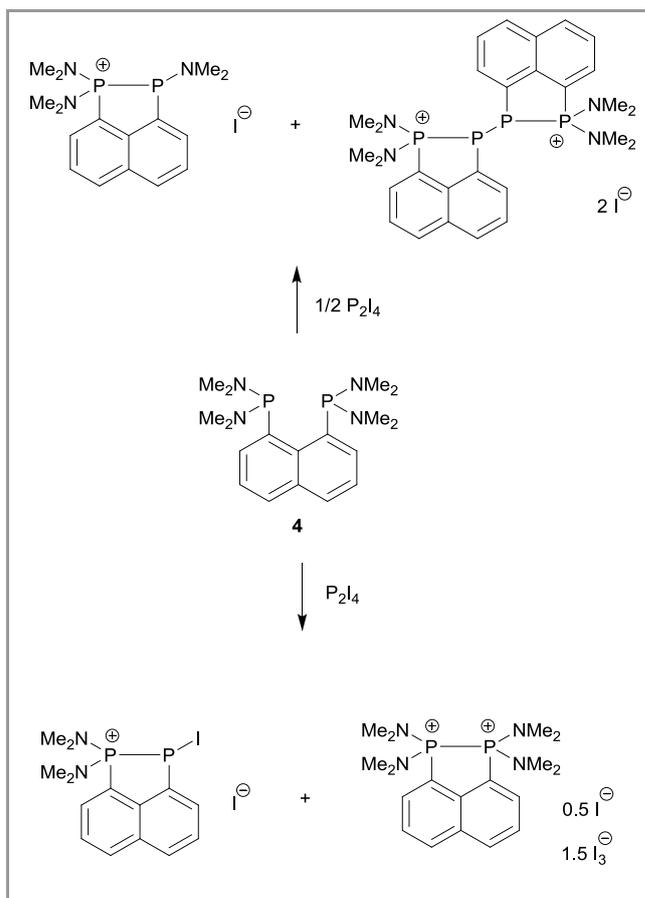
Preparation of 1,8 Nap(PR₂)₂ systems is surprisingly difficult with the expected dilithiation giving poor yields but we found that chlorination of **NapP₂S₄** gives Nap(PCl₂)(PCl₄) containing a rare intra-

molecular P(III)→P(V) dative covalent bond.³¹ Removal of the chlorine to give Nap(PCl₂)₂ was surprisingly difficult until we used (MeO)PCl₂ which eliminates PCl₃ and MeCl to give the desired bis phosphine chloride in quantitative yield.³² This material represents the ideal synthon for making a wide range of alkyl and aryl substituted naphthalene *bis* phosphines. Reaction of Nap(PCl₂)₂ with oxygen results in oxidation of one phosphorus centre to give Nap(POCl₂)(PCl₂) and subsequent reaction with chlorine generates Nap(POCl₂)(PCl₄) (equation 5) containing two P(V) centres.³³ The bridging P=O group results in hypercoordination of the R₂PCl₄ centre with a P...O distance of 1.505(2) Å.



Equation 5

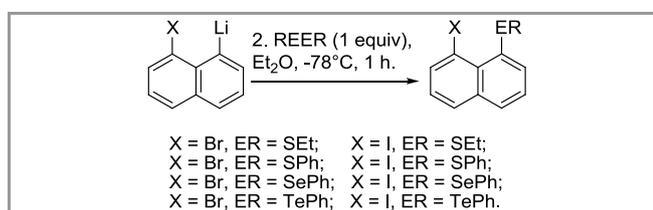
More recent work on phosphorus systems has included using the naphthalene backbone to stabilize unusual cations and dications (scheme 4).³⁴



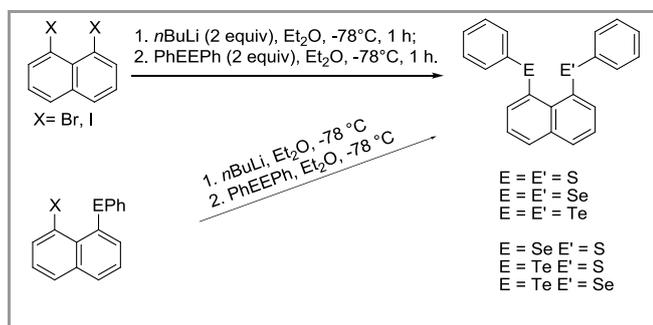
Scheme 4 Reactions of *peri* substituted phosphine to give cationic and chain species.³⁴

This early work by Paul Wood also ultimately led via some convoluted routes to our interest in group 16

peri substituted systems. We have prepared an extensive range of *peri* substituted naphthalene systems investigating the repulsive and attractive effects associated with forcing two heavy elements into close proximity (schemes 5, 6).³⁵ Weak attractive forces are apparent, depending on the orientation of the substituents. Reactions of these *peri* substituted systems with halogens have proved particularly exciting. Thus, A range of diverse compounds {Nap[SPh]₂·Br₄ (Nap = naphthalene-1,8-diyl); Nap[SePh][EPh]·Br₄ (E = Se, S); Nap[SePh]₂·I₂; Nap[SePh][EPh]·3/2I₂ (E = Se, S); Nap[TePh][G]·X₂ (G = SePh, SPh, Br, I; X = Br, I); [Nap(PPh₂OH)(SPh)]⁺Br₃⁻} formed from *peri*-substituted naphthalene chalcogen-donors {Nap[ER][E'R] (ER/E'R = SPh, SePh, TePh); Nap[TePh][X] (X = Br, I); Nap[PPh₂][SPh]} and dibromine and diiodine were studied by X-ray crystallography.^{35d}



Scheme 5 The preparation of 1-halo-8-(alkylchalcogeno)naphthalenes



Scheme 6 The preparation of 1,8-dialkylchalcogenonaphthalenes

In general the conformation of the final products obeyed the rule based on charge-transfer i.e. 'see-saw' adducts arise when the halogen (X) is more electronegative than the chalcogen (E) and if the converse is true then C.-T. 'spoke' adducts are formed (scheme 7). Upon treatment with dibromine, selenium containing compounds {Nap[SePh]₂} and {Nap[SePh][SPh]} afford unusual tribromide salts of bromoselenyl cations containing a hypervalent X-E...E' 3c-4e type interaction. These adducts form complex structures in the solid state e.g. short intermolecular contacts exist in the TeX adducts constructing planar Te₂X₂ squares (Figure 5)

Peri substitution is hard to direct synthetically and after developing the naphthalene systems we found that acenaphthene systems are synthetically much more readily prepared and provide an excellent backbone or

molecular scaffolding for studying weak interactions between heavier elements.³⁷

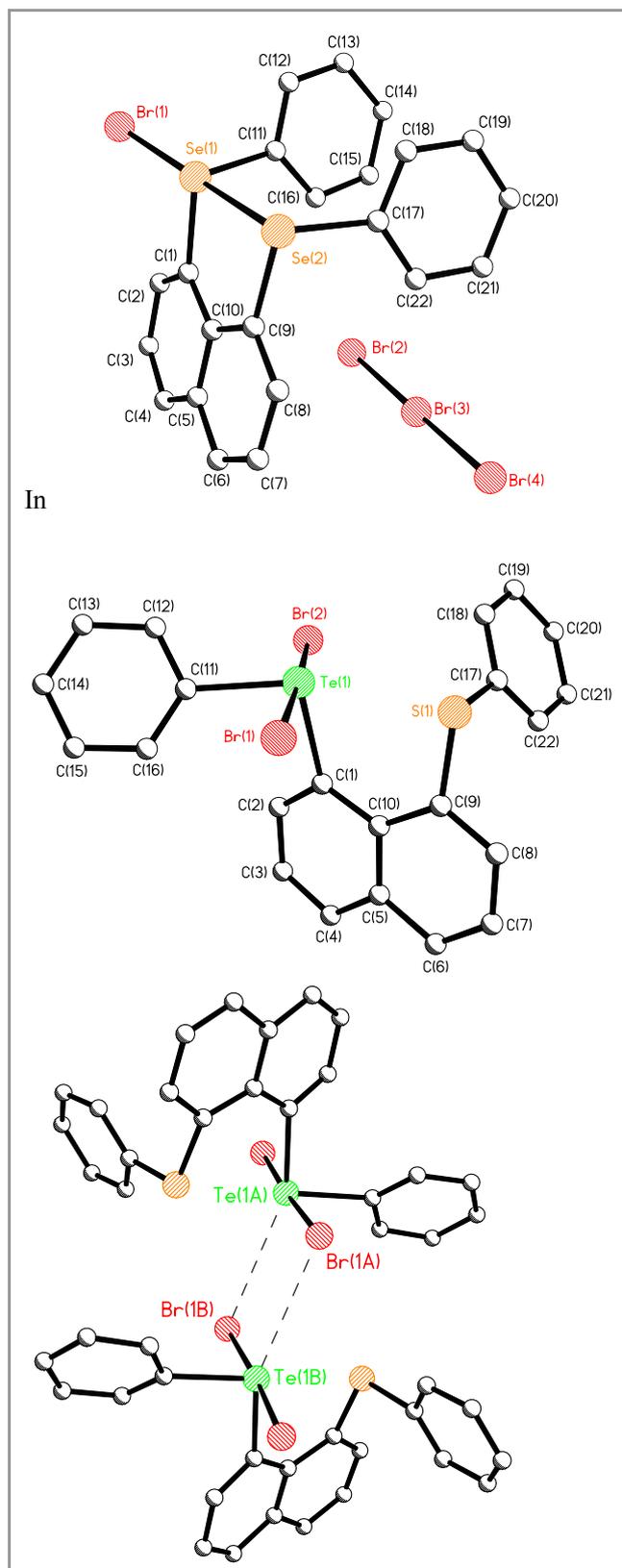
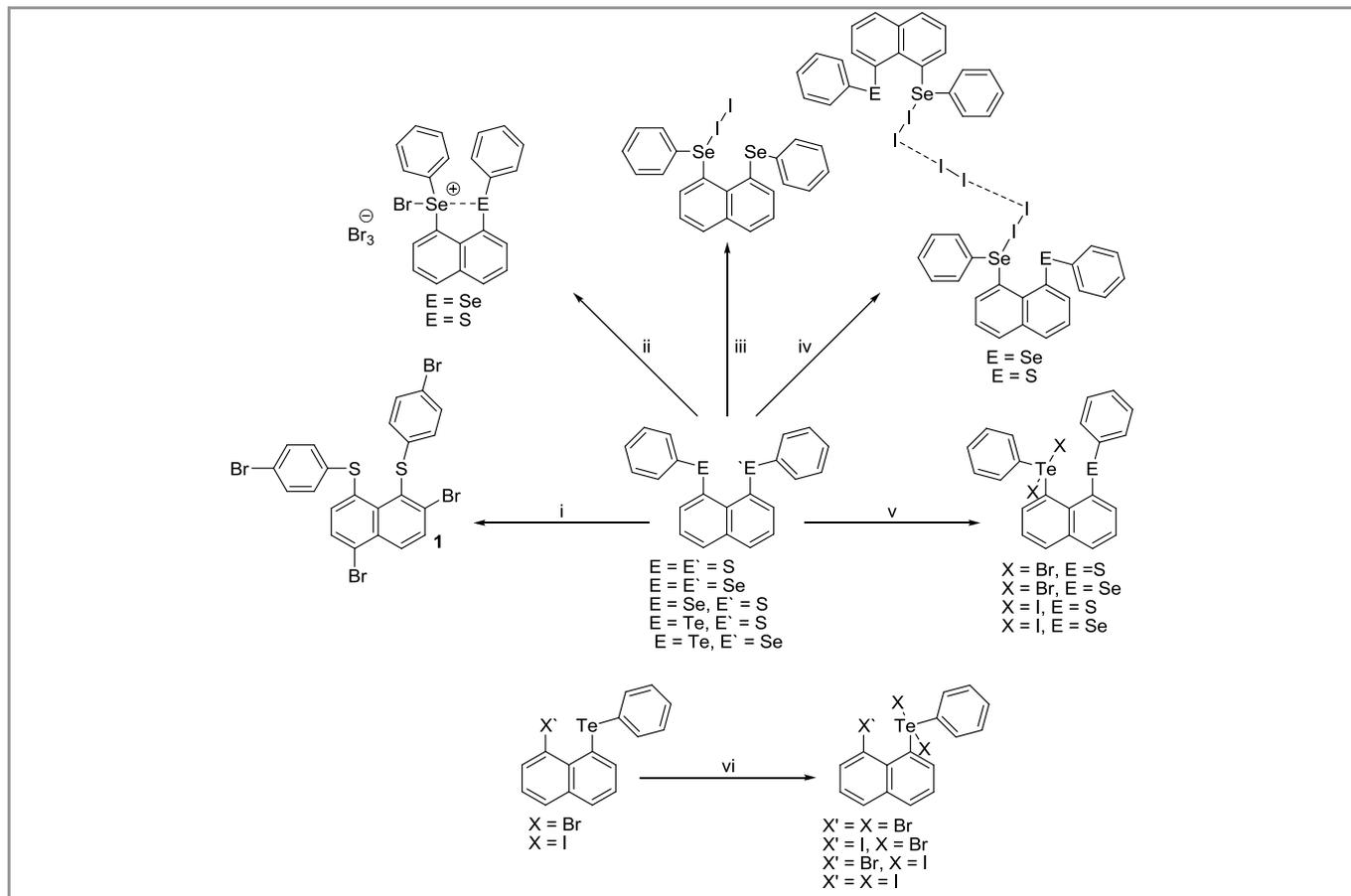


Figure 5 Upper The X-ray structure of a typical ionic C.-T. 'extended spoke' adduct, middle a typical 'see-saw' adduct formed from Nap(EPh)₂. And lower intramolecular packing in see-saw adducts.



Scheme 7. Synthesis of halogen adducts. Conditions: i-vii X_2 ($X = Br, I$), CH_2Cl_2 , 2 h, RT; i (4 equiv) Br_2 ; ii (2 equiv) X_2 ; iii/iv (1 equiv) I_2 ; v/vi (1 equiv) X_2 .

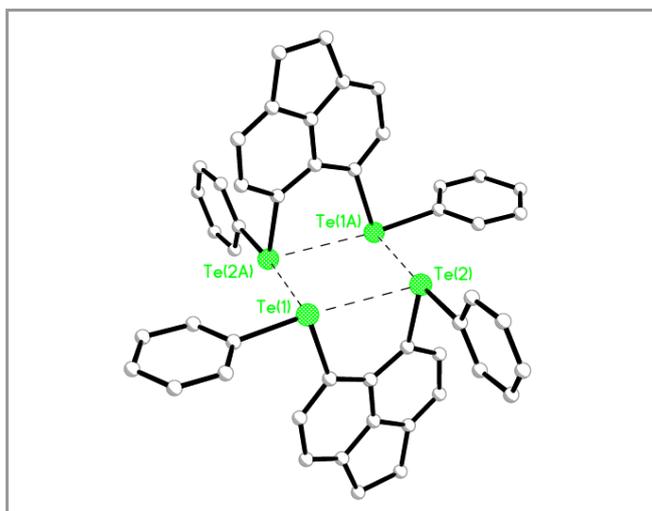


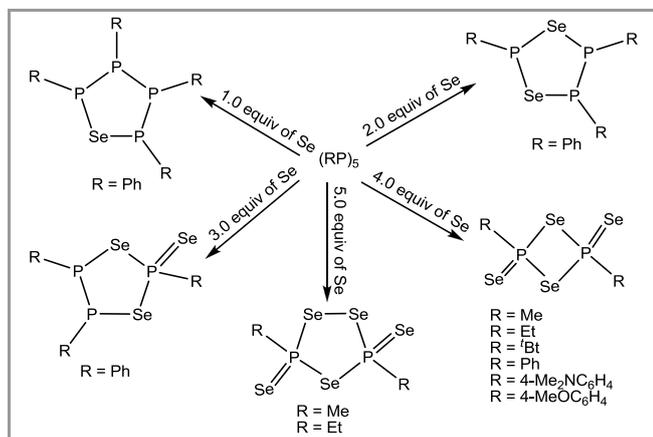
Figure 6 The X-ray structure of $acen(TePh)_2$; short intermolecular contacts between neighbouring molecules form planar Te_4 rhombus units

The propensity of group sixteen elements to catenate is illustrated neatly in the X-ray structure of $acen(TePh)_2$. Short intermolecular contacts operating between neighbouring molecules of this bis-telluride construct Te_4 parallelograms. As a consequence of the

symmetry, the Te_4 rhombus core is strictly planar containing two unequal $Te \cdots Te$ non-bonded distances and with interior angles combining to 360° . The larger intermolecular separation ($3.853(1) \text{ \AA}$) is longer than the non-bonded intramolecular *peri*-distance ($3.3674(19) \text{ \AA}$), though both are shorter than twice the van der Waals radius of tellurium (4.12 \AA) (Figure 6).

I hope it is clear from the above that the late 80s and early 90s helped develop a number of themes that have carried threaded through our research. Paul Wood was also responsible for the start of our interest in P-Se chemistry. The organic-P-S chemistry developed well but the attraction of P-Se chemistry was enormous, the opportunity to make use of ^{77}Se nmr proved irresistible. We³⁷ set about reacting cyclophosphines with selenium in efforts to form analogues of the more well known sulfur systems. In parallel (but unknown to us) Karaghiosoff was developing related systems.³⁸ We found that cyclophosphines react under mild conditions to give a variety of P-Se heterocycles (scheme 8) and that the outcome could be influenced by adjusting the stoichiometry of the reaction. The P-Se heterocycles represent simple valence isoelectronic replacement of RP by Se and oxidation of P(III) centres to P(V)=Se centres. The four membered rings were a possible

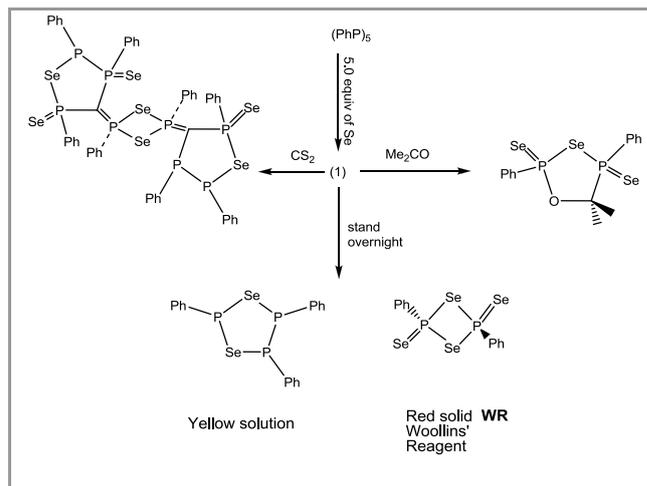
anticipated product though to date no one has been able to directly react P_4Se_{10} with RH to give these analogues of Lawesson's reagent. In general we restricted ourselves to reactions with phenyl phosphines since we found reactions with eg $(PMe)_x$ systems are extremely complex³⁹ whilst Karaghiosoff tested the reactions with a wider range of alkyl phosphines (scheme 8).



Scheme 8 Examples of syntheses of P-Se heterocycles.^{37,38}

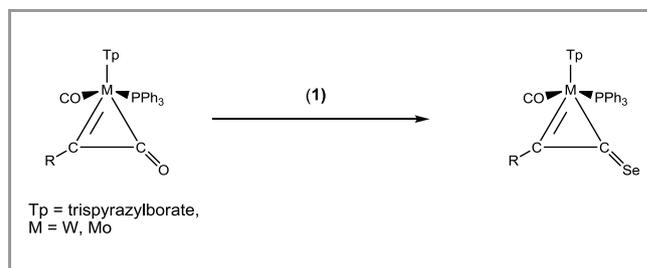
In 1988 we established the syntheses of some new P-Se heterocycles and largely characterized them by multielement NMR.³⁷ However, this preliminary work was not complete. The early organic reactivity was tested using a solution of (1) in scheme 9 and showed immediate promise with two new organo -P-Se heterocycles being isolated and characterized crystallographically.³⁷ Emboldened by our exciting results I submitted abstracts on both M-S-N and P-Se chemistry to the 5th Inorganic Rings International Symposium in Amherst. Whilst my presentation on M-S-N chemistry went well I was rather dismayed to sit through a lecture by Karagiosoff which summarized at least half of my groups work in the area. I hastily rewrote my overheads and presented somewhat different material but this was a serious shock and salutary warning as to the need to publish or perish!

After our initial flurry of activity we quickly established a synthesis that gave pure $PhP(Se)(\mu-Se_2)P(Se)Ph$ and prepared⁴⁰ an example of a coordination compound by reaction with $Pt(dppe)Cl_2$ but then there set this system to one side. In 1994 I moved, along with Alex Slawin (and our three children) to Loughborough. At that time there was little interest in funding P-Se chemistry from UK research councils and our work moved on to imidophosphinate ligands⁴¹ including synthesizing the first six membered true heterocycle..(ie a hetrocycle in which every atom is different)⁴² and ferrocenyl analogues of Lawesson's reagent.⁴³



Scheme 9 Early syntheses and organic reactivity developed at Imperial College.³⁷

Our interest and enthusiasm was, however, suddenly reawakened when Tony Hill, an ex colleague from Imperial College, published a manuscript with the tongue in cheek title 'Selenoketenyl and selenoalkyne complexes *via* the reactions of ketenyl complexes with Woollins' reagent'⁴⁴ This paper described the transformation of some organometallic complexes to their selenium analogues. Although the organic C=O group was converted to C=Se the coordinated CO remained unchanged (eqn 6).



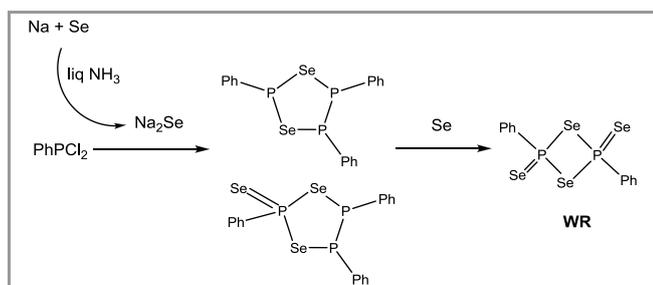
Equation 6

This paper by Hill suggested that the four membered ring system should be called Woollins' reagent **WR** and reactivated our interest and within a week a proposal was submitted to the EPSRC seeking funds to develop the chemistry of 'this important system'. Luckily, almost certainly because of the Hill paper, this was funded and we set about establishing the nature and the utility of this new material.

Our work developed syntheses of ring systems and established that **WR** was the active species in reactions that had already been reported. We also found that **WR** was the most readily isolated heterocycle and so this soon became the main focus of our work. A major obstacle to developing the chemistry of **WR** was the unwieldy synthesis from the (incredibly smelly) cyclophosphine whose preparation could not be readily scaled up.

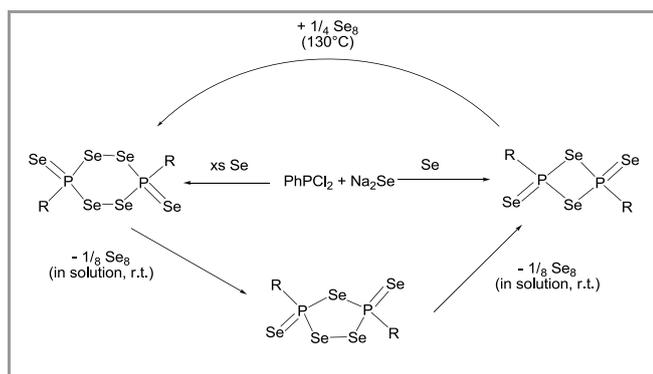
Leaning on our previous work in liquid ammonia we prepared Na_2Se by simple reduction of selenium with sodium in liquid ammonia to give material which is

much more soluble than that prepared by the solid state route though it is worth noting that this wonderfully finely divided solid is also very pyrophoric; on one occasion around 75 g caught fire in the port of our glove box with rather unpleasant consequences. Reaction of Na_2Se with PhPCl_2 gives a mixture of five membered rings (scheme 10) which can be converted to **WR** by reaction with grey selenium.⁴⁵



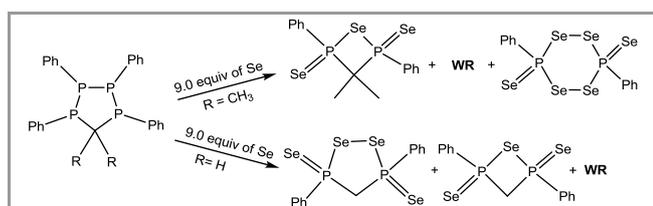
Scheme 10 Large scale synthesis of **WR** capable of scale up to ca 150 g in normal lab glassware.

We extended this preparative route to ferrocenyl systems and also obtained even more selenium rich heterocycles both directly and by conversion from **WR** (scheme 11).⁴⁶



Scheme 11 Formation of selenium rich P-Se heterocycles R = Ph, Fc.

In subsequent work we studied the formation of carbon substituted analogues⁴⁷ starting from organocyclophosphines (scheme 12).



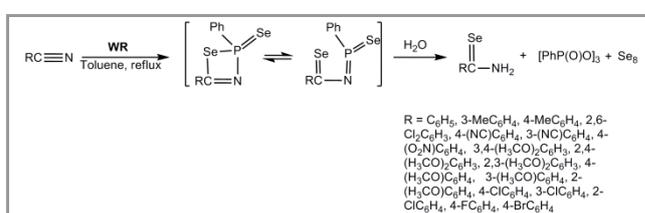
Scheme 12 Synthesis of organo-P-Se heterocycles from organocyclophosphines R = H, Me..

The reactivity of Woollins' reagent in many respects mirrors that of Lawesson's reagent except that often the resulting organo-selenium compounds rapidly react to form new species. In the following there is a summary of different reaction types but no discussion

of metal complex formation though Rothenberger has developed direct reactions of **WR** with metal salts to good effect⁴⁹ and we have carried out some studies relating to our earlier work on ZDDP.⁵⁰

We have reviewed the reactivity of **WR** previously^{51,52} and in the following provide a brief summary together with more recent results.

Selenoamides^{53,54} and selenoaldehydes⁵⁵ have been obtained by simple oxygen/selenium exchange or reaction with aryl nitriles (ArCN) followed by hydrolysis. Thus the reaction of **WR** with aryl nitriles in refluxing toluene followed by addition of water gives primary arylselenoamides in 60 – 100% yield (eg eqn 7).



Equation 7

We examined the structural motifs and hydrogen bonding of selenoamides.⁵⁶ Whilst H-bonding is well understood in amides the heavier chalcogenides are less well studied. We broadly classified the pattern of hydrogen bonding in compounds **A** - **L** (selected parameters in Table 1) with illustrative examples in Figure 7. The H-bonding can be classified (1) **A**: Ladder; (2) **B**: Linked dimer; (3) **F**: Tetrameric sheets; (4) **G**: Herringbone dimers; (5) **I**: Helical chains and (6) **J**: Linear chains. It is clear that N-H...Se hydrogen bonding is an important feature of the solid state packing of these molecules and may be a significant influence in biological systems

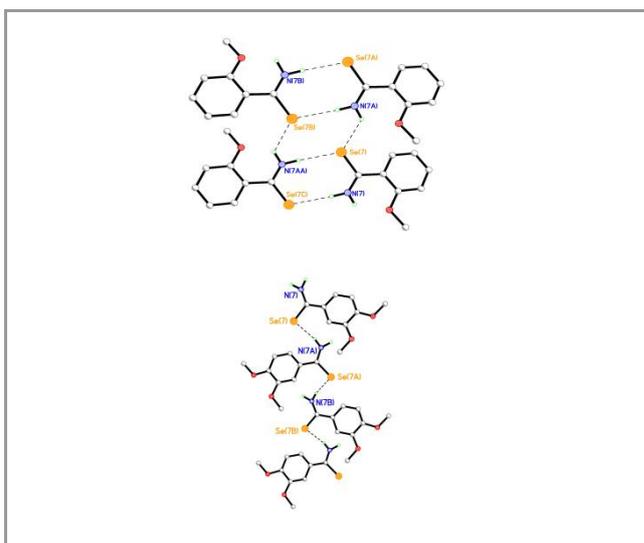
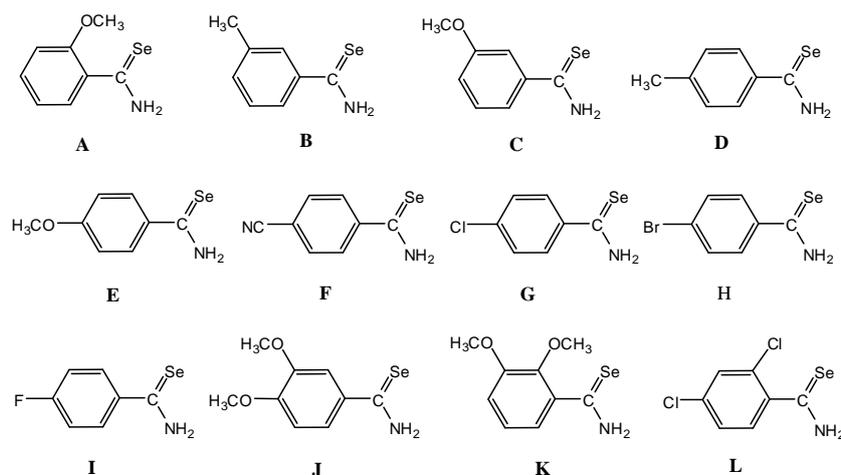
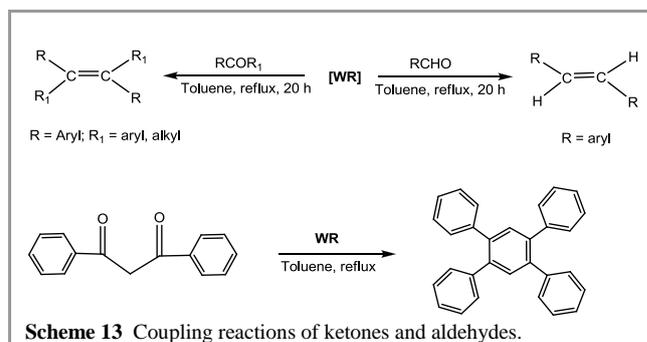


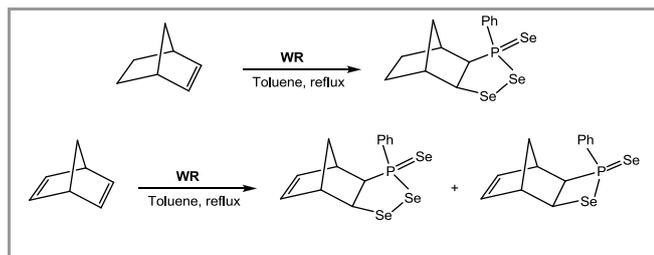
Figure 7 Examples of N-H...Se bonding patterns in selenoamides., upper Compound **A**: Ladder, lower, Compound **J**: Linear chains

Table 1. Major N-H...Se hydrogen bonding distances (Å) in selenoamides.

	Type	Se...H	Se...N	Se...H-N	Se...H	Se...N	Se...H-N
A	Ladder	2.55(1)	3.512(3)	167(3)	2.72(4)	3.403(3)	127(3)
B	Linked dimers	2.527(7)	3.489(2)	168(2)	2.539(10)	3.491(2)	164(3)
C	Linked dimers	2.59(3)	3.510(6)	156(6)	2.58(3)	3.491(5)	155(5)
D	Linked dimers (sheets)	2.55(1)	3.517(4)	170(5)	2.71(5)	3.408(4)	129(4)
E	Linked dimers (sheets)	2.55(7)	3.527(4)	174(4)	2.82(5)	3.415(4)	120(4)
F	Tetramers (sheets)	2.57(2)	3.58(11)	171(11)	2.63(6)	3.527(11)	152(11)
		2.90(14)	3.430(12)	115(1)	2.69(10)	3.466(10)	136(10)
G	Herringbone dimers	2.68(10)	3.502(8)	142(12)	2.85(12)	3.509(8)	125(1)
H	Dimers	2.50(17)	3.43(4)	158(4)	2.49(16)	3.43(3)	160(4)
		2.48(9)	3.45(5)	169(5)	2.58(8)	3.43(3)	169(5)
I	Helical chain	2.63(3)	3.513(5)	150(4)	2.97(3)	3.628(5)	125(4)
		2.74(4)	3.566(5)	143(5)	2.62(3)	3.512(5)	151(5)
J	Chain	2.52(2)	3.483(6)	168(6)			
K	Dimers	2.69(1)	3.63(3)	162(3)			
L	Linked dimers	2.535(8)	3.511(4)	174(5)	2.579(14)	3.533(4)	165(4)

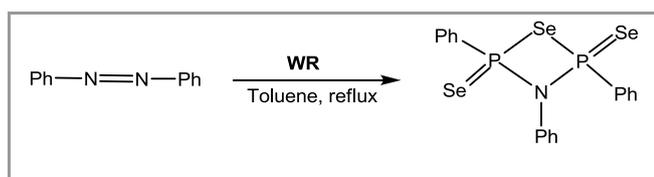
In contrast to the original reactions we studied for the formation of selenoketones we observed self-coupling of a wide range of ketones and aldehydes was achieved by treatment with **WR** in refluxing toluene, which yields symmetrical and unsymmetrical (*E*)-olefins in high yield (Scheme 13).¹The method has potential for a variety of systems and may prove especially beneficial where base sensitive substituents are present. Its speculative mechanism involves a Wittig-like reaction intermediate rather than a decomposition of a selenoketone.⁵⁷





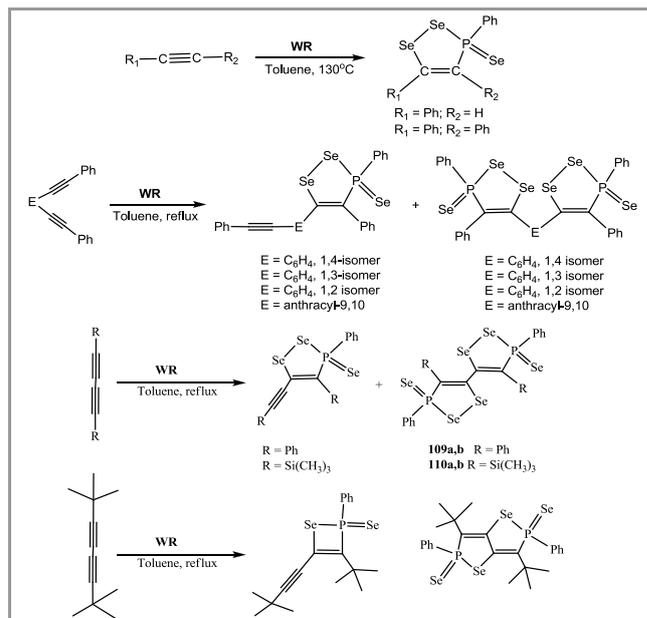
Scheme 14

WR undergoes a wide range of cycloaddition reactions and we have already mentioned the reaction with acetone and carbon disulfide (scheme 9). **WR** reacts with trinorbornene in refluxing toluene to give a five-membered C_2PSe_2 ring (confirmed by X-ray crystallography).⁵⁸ However, reaction of **WR** with trinorboradiene yields the five-membered C_2PSe_2 ring and a four-membered C_2PSe heterocycle analogous to the thiaphosphetane (C_2PS) rings (Scheme 14).⁴³ Reaction of **WR** with azobenzene⁵⁸ gives a PSe_2N heterocycle (eqn 8)

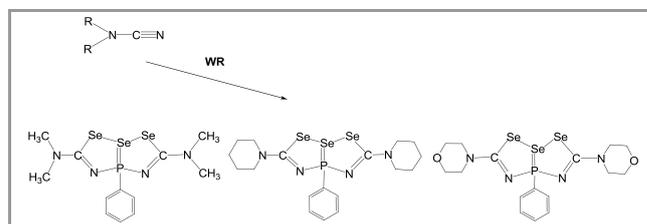


Eqn 8

Reaction of **WR** with alkynes has been extensively studied in particular by Pravat Bhattacharyya and Guoxiong Hua and some key examples are summarized in scheme 15. The reactions predominantly lead to five membered C_2PSe_2 rings.^{45,59} Refluxing **WR** with symmetrically disubstituted alkynes ($RC\equiv C-C\equiv CR$, $R = Ph, Si(CH_3)_3$) in 2:1 molar ratio in toluene gave two product both containing five-membered $P(Se)Se_2C_2$ heterocycles either with one unreacted triple bond 'dangling' or *bis*-heterocycles with two five-membered $P(Se)Se_2C_2$ rings are connected through a C-C single bond. However, **WR** and $tBu-C\equiv C-C\equiv C-tBu$ react differently to afford an unprecedented four-membered $P(Se)Se_2C_2$ heterocycle with one unreacted triple bond together with a fused *bis*-heterocycle containing two five-membered $P(Se)Se_2C_3$ rings fused at the middle two carbons of the diyne to give a heteropentalene analogue of pentalene, [3.3.0]octa-1-6-diene (Scheme 15).⁶⁰

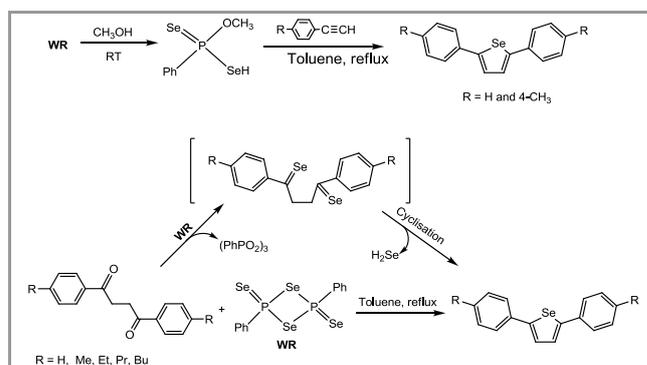
Scheme 15 Reaction of alkynes and dialkynes with **WR**

Refluxing a toluene solution of **WR** with a ten-fold excess of dialkylcyanamides R_2NCN [$R_2 = Me_2, -CH_2CH_2OCH_2CH_2-$, or $-(CH_2)_5-$] led to fused ring 1,6,6γ⁴-triseleno-3a-phospha 3,4-diazapentalenes in ca. 5% yield (Scheme 16).⁶¹

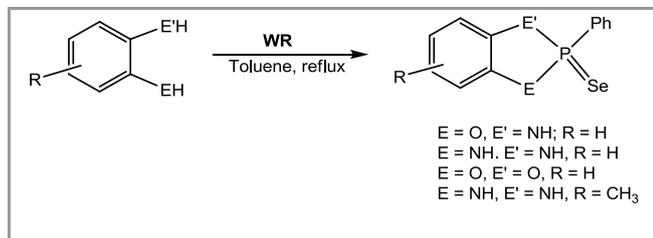


Scheme 16

Selenophenes⁶² (and related 2,5-Disubstituted 1,3,4-selenadiazoles⁶³) can be obtained by direct reaction of the diketone (or the diamide) with **WR** or via the treatment of *O*-methyl *Se*-hydrogen phenylphosphonodiselenoate with arylacetylenes

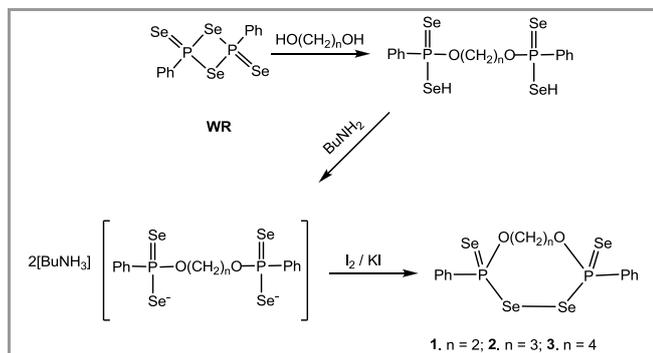
Scheme 17 Synthesis of 2,5-Diarylselenophenes by reaction of *O*-methyl *Se*-hydrogen phenylphosphonodiselenoate with arylacetylenes or by direct reaction of Woollins' reagent with 1,4-dialkylbutane-1,4-diones.

Other simple heterocycles can be readily formed from diols or diamines. Thus, treatment of **WR** with 2-aminophenol, 1,2-phenylene-diamine, catechol or 3,4-diaminotoluene gives the simple 5-membered heterocycles (eqn 9) formed by asymmetric cleavage of the selenium compound.⁶⁴



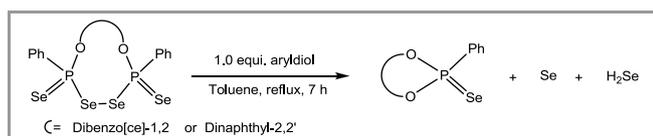
Eqn 9

Cleavage of the four-membered P_2Se_2 ring in **WR** by alkyl diols affords the bisdiselenophosphonic acids quantitatively, the latter can be converted into the corresponding ammonium salts by treatment with butyl amine, followed by addition of I_2/KI to give eight-, nine- and ten-membered ring diselenides in good to excellent yield (70 – 90%) (Scheme 18), examples of each of these rings were characterized crystallographically (Figure 8).⁶⁵



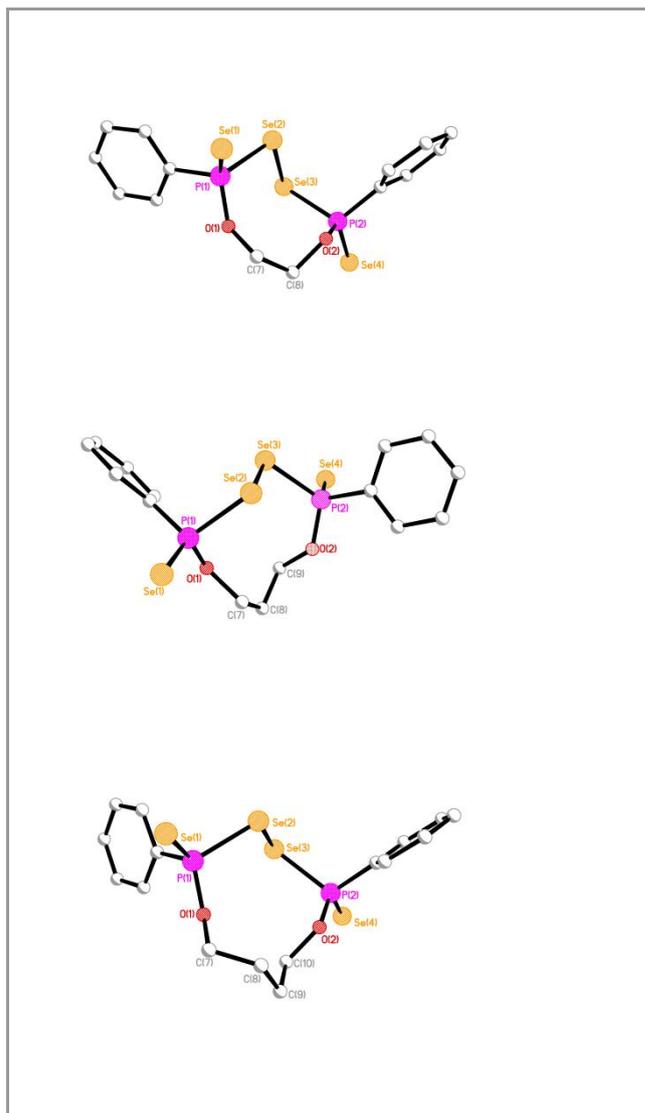
Scheme 18

Interestingly these large rings are readily converted to smaller rings by elimination/reaction of a PhPSe_2 unit (eqn 10).⁶⁶

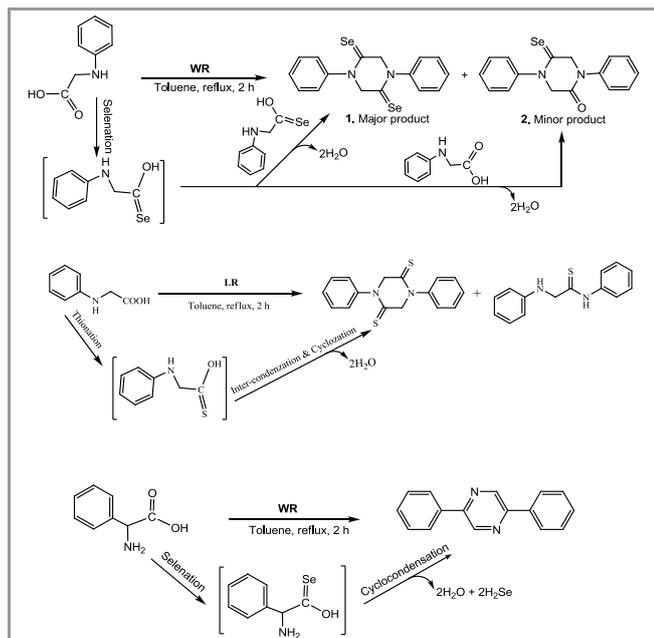


Eqn 10

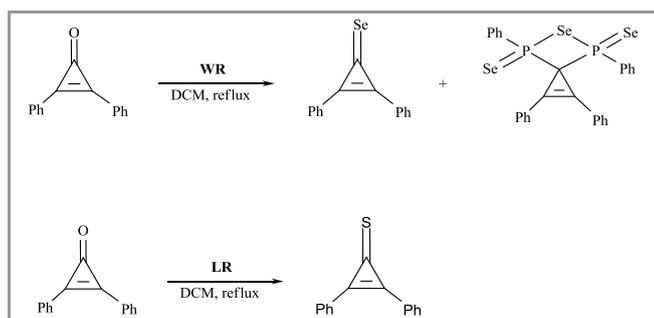
It is interesting to consider the difference in reactivity between **WR** and Lawesson's Reagent (**LR**). *N*-phenylglycine reacts with an equivalent of **WR** to give as the major product planar 1,4-diphenylpiperazine-2,5-diselenone and as the minor product boat conformation 1,4-diphenyl-5-selenoxopiperazin-2-one.

Figure 8 X-rays structures of 8,9 and 10 membered heterocycles⁶⁵

DFT-B3LYP calculations suggest that the planar conformation is around 2 kcal/mol less stable than the puckered conformation for the dideleno derivative. In contrast to **WR**, reacting *N*-phenylglycine with an equivalent of **LR** gives 1,4-diphenylpiperazine-2,5-dithione and *N*-phenyl-2-(phenylamino)ethanethioamide. Surprisingly, 2-phenylglycine treated with an equivalent of **WR** under identical reaction conditions leads to only the formation of 2,5-diphenylpyrazine.⁶⁷ We also examined the reaction of **WR** and **LR** with diphenylcyclopropanone, where there is opportunity for reaction at the $\text{C}=\text{C}$ or the $\text{C}=\text{O}$ functionality. Interestingly, whilst **LR** simply thionated the substrate **WR** gave the selenketone derivative together with an unusual spirobicyclic system containing two four membered rings (eqn 11, Figure 9).⁴⁵



Scheme 19 Reaction of **WR** and **LR** with glycine and *N*-phenylglycine.



Eqn 11

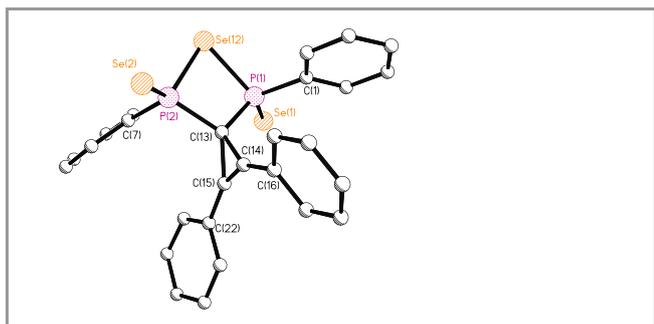
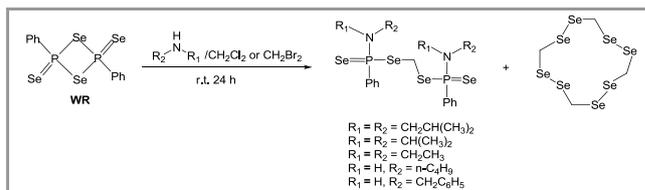


Figure 9 The X-ray structure of the bicyclic product from eqn 11. Selected bond lengths (Å) and angles (°): P(1)-Se(1) 2.089(3), P(1)-Se(12) 2.265(2), P(1)-C(1) 1.826(10), P(1)-C(13) 1.840(9), C(13)-C(15) 1.507(12), C(14)-C(15), 1.290(12) P(1)-Se(12)-P(2) 78.83(9), P(1)-C(13)-P(2) 102.0(4).

One final example that deserves mention is the remarkable reaction of **WR** with secondary amines.

Reaction of **WR** with secondary amines in the presence of CH_2Cl_2 or CH_2Br_2 proceeds to give, predictably, Bis(*N,N*-dialkyl-*P*-phenylphosphonamidodiselenoates (scheme 20).

More excitingly, we also obtained the new heterocycle 1,2,4,5,7,8,10,11-octaselenacyclododecane⁶⁸



Scheme 20

The new 12-membered C_4Se_8 ring is remarkably stable and even when heated does not eliminate selenium. Interestingly, in the structure of (Figure 10) the Se(2) atom lies over the face of the central Se_2C unit with an Se(2)...Se(1A) distance of 3.880(2) Å

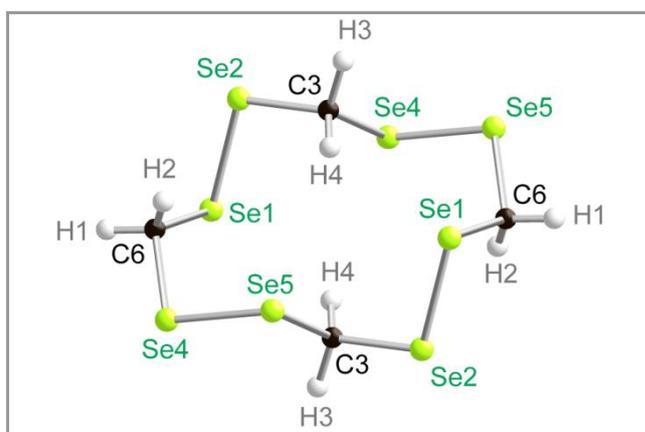


Figure 10 The X-ray structure of 1,2,4,5,7,8,10,11-octaselenacyclododecane. Selected bond lengths (Å) and angles (°): Se(1)-Se(2) 2.3162(9), Se(4)-Se(5) 2.3094(8), Se(2)-C(3) 1.931(5), Se(1)-C(6) 1.945(5), Se(5)-C(6) 1.940(5), Se(4)-C(3) 1.954(5); C(6)-Se(1)-Se(2) 102.04(16), C(3)-Se(2)-Se(1) 100.06(17), Se(2)-C(3)-Se(4) 112.2(3), C(3)-Se(4)-Se(5) 100.79(17), C(6)-Se(5)-Se(4) 99.80(16), Se(5)-C(6)-Se(1) 106.7(2).

In conclusion, this review has aimed to demonstrate the non linear nature of research and the enjoyment that an unexpected diversion might engender. The utility of Woollins' reagent is established and it is reasonable to anticipate that more unusual reactions will be developed with this system since it is now sold commercially. Current work in our laboratories includes studies into **WR** and efforts to prepare stable *P*-Te systems.

Acknowledgment

I am grateful to the many researchers at all levels, who have contributed to this work. Special acknowledgement has to go to Prof Alexandra Slawin who is the finest crystallographer I have ever met.

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