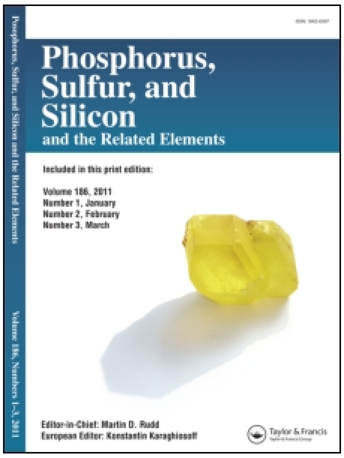

Phosphorus, Sulfur, and Silicon and the Related Elements

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Main Group Rings and Metallacycles

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The range of main group rings and cages is illustrated with examples of boron halide containing semi-conductors, P-N containing ligands, hemilabile phosphines, P-Se heterocycles and M-S-N compounds.

Keywords: Sulfur; Phosphorus; Selenium; Heterocycles

Introduction

Rings and cages are ubiquitous in inorganic chemistry. Apart from the synthetic challenges and the theoretical .difficulties that many of these compounds provide they may also offer exciting applications. Thus we have been involved in the general area with a number of possible outcomes, eg., 1-D conductors or materials with unusual magnetic properties, inorganic backbone ligands which allow control of the electronic effects compared to their organic analogues and thus offer potential in catalysis, lubricant additives, new metal extractants, catalysts for H_2S oxidation in environmental chemistry, thionation and selenation reagents. In this review I provide brief details of selected examples from our recent work.

Results and Discussion

The synthesis of charge transfer materials containing organic donors and acceptors is typified by systems such as TTF.TCNQ. These type of salts have been extensively studied by several groups[1] but most of the examples have involved small anions as replacements for TCNQ. We where interested to investigate the nature of compounds formed using large, spherical anions. In

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initial experiments wec attempted to electrocrystallise TTF with *closo*-$[B_{10}H_{10}]^{2-}$ but did not obtain useful materials. We postulated that a helpful strategy would be the use of large anions with 'soft' polarisable atoms and thus synthesised $[B_{10}I_{10}]^{2-}$ by reaction of the hydride with iodine. Interestingly during the course of the work we noted that varying the counterion influenced the outcome of the reaction and we were thus able to isolate $[B_{10}I_9H]^{2-}$ in good yield. The $[B_{10}I_{10}]^{2-}$ anion has proved to be a useful anion for the synthesis of new materials and we have been able to isolate a number of examples. The structure[2] of $ET_5[B_{10}I_{10}]$ is shown in Fig. 1. There are five crystallographically independent ET molecules denoted A-E which form repeat units to give a chain along the crystallographic *a* direction. Individual ET molecules differ somewhat in geometry as a result of differing amounts of oxidation. Conductivity measurements made with the four contact probe method reveal semiconductor properties with an activation energy of 156 meV.

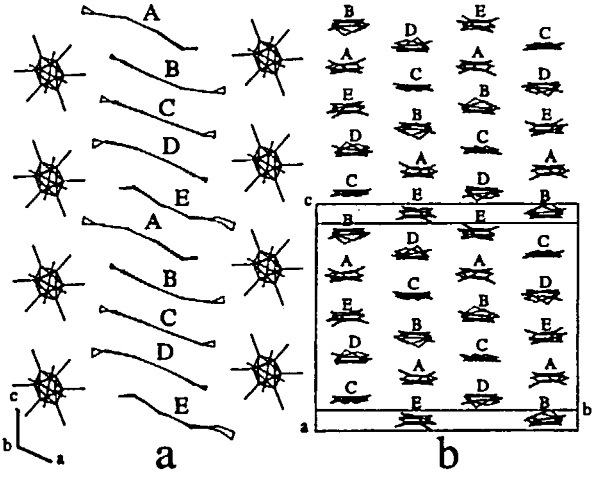


Figure 1 View showing (a) one of the ET chains and (b) the packing in the *bc* plane in the X-ray structure of $ET_5[B_{10}I_{10}]$.

As mentioned above we have also been interested in lubricant additives – in particular zinc dialkyldithiophosphate (ZDDP) and zinc dialkylmonothiophosphate (ZDMP) complexes.[3] ZDDP complexes have been known for many years and exist in two forms of empirical formula ZnL_2 and Zn_4OL_6 [L = $(RO)_2PSS^-$] – the so called 'neutral' and 'basic' forms respectively. Surprisingly the structure of the basic form has not been unequivocally established. We have determined the structure of both forms for R = Bu. Interestingly the neutral form exists as Zn_2L_4 (Fig. 2) with a central core which has one particularly open face suitable for surface coordination [especially important in its activity as a lubrcant anti-oxidant]. The basic form exists as a Zn_4 tetrahedron (Fig. 3) with bridging ligands along each edge. In the case of ZDMP we have only been able to isolate a 'basic' form (R = Ph, Me) and the difficulties with the structural analysis perhaps explain why it has taken so long to solve this structural problem. The Zn_4 core exists in two interpenetrating 50% weight disordered occupancies even though the light atoms are not disordered! In the ZDMP case there is also the opportunity for isomerism (Fig. 4) – to date we have observed only one isomer for each of the Me and Ph cases but they are different to each other.[4]

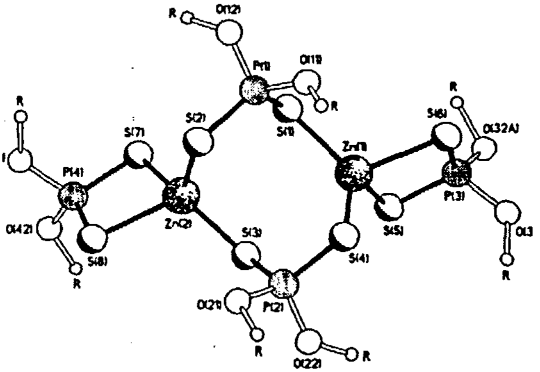


Figure 2 X-Ray crystal structure of $Zn[S_2P(OBu)_2]_2$.

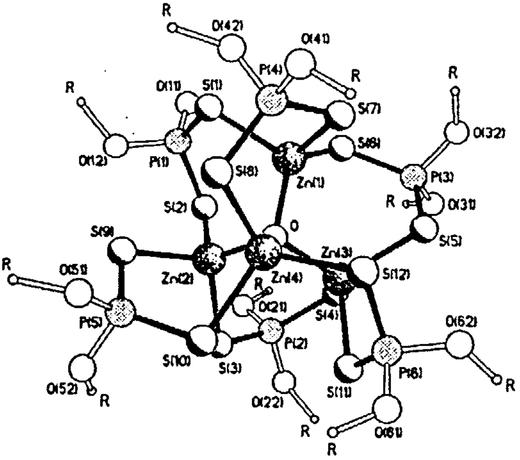


Figure 3 X-Ray crystal structure of $Zn_4O[S_2P(OBu)_2]_6$

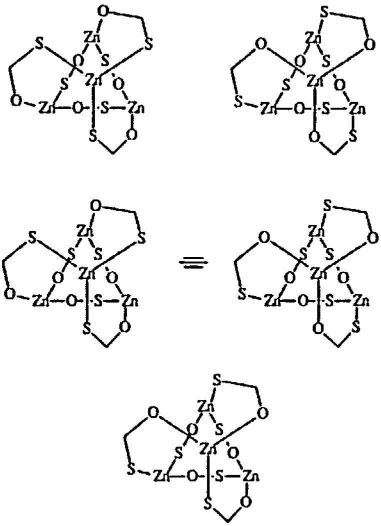
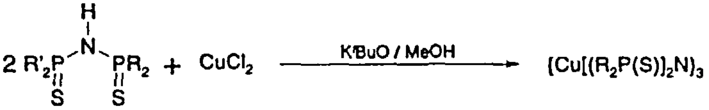


Figure 4 Examples of structural isomers in ZDMP.

In attemts to develop new lubricant additives we undertook investigations into simple imidophosphinates. These may be synthesised by a variety of routes including simple coupling of R_2PCl with $NH(SiMe_3)_2$ to give $R_2P\text{-}NH\text{-}PR_2$ which can be oxidised using sulfur or selenium to give $R_2P(E)\text{-}NH\text{-}(E)PR_2$ [5] or by coupling of P^V species[6,7] and we have reviewed our early work in this area.[8] We have noted that the MEPNPE rings adopt a variety of geometries in the solid state but are totally fluxional even at low temperatures in solution - in accord with density functional calculations which imply very small barriers to conformational change in these rings even though there is considerable multiple bond character in the rings. Recently we have reported the reaction of $R_2P(E)\text{-}NH\text{-}(E)PR_2$ with copper salts.[9] Interestingly, trimeric Cu_3L_3 systems are formed (Fig. 5). The X-Ray structures reveal that the molecules contain a six membered Cu_3S_3 ring in their core with each copper atom being tricordinate in approximately trigonal geometry as a result of two bridging and one terminal sulfur donor atoms.



R, R' = ^iPr 1. R = EtO, R' = OPh 2. R = Ph, R' = ^iPr 3. R = OPh, R' = ^iPr 4.

The central Cu_3S_3 core in these molecules is oxidisable electrochemically but as yet we do not fully understand the processes involved which may be relevant to some metalloenzymes.

We have also recently reported on tellurium complexes of imidophosphinates jointly with Novosad and Husebeye.[10,11] The simple TeL_2 complexes adopt 4-coordinate and pseudo 2-coordinate [with weak coordination of the two 'non-coordinate' chalcogenides] depending on the electronic properties of the donor atoms. The solid state structure of a two cordinate example is shown in Fig 6. It reveals the Te(1)-S(1) and Te(1)-S(3) distances are 2.5267(11) and 2.5131(12) Å respectively with the Te(1)–S(2) and Te(1)-S(4) contacts being considerably longer (~ 2.9 Å). The

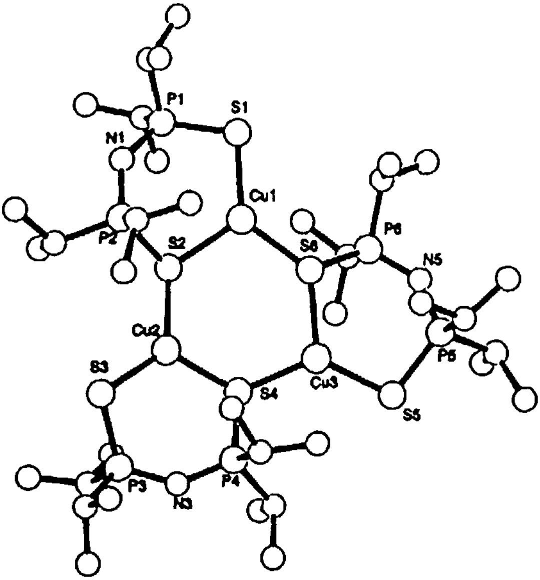


Figure 5 The X-Ray structure of $Cu_3[N(SPPr_2)_2]_3$.

bond lengths in the SPNPS 'ring' suggest that the negative charge is localised on the tellurium bound sulfur - P(4)-S(4) is 1.968(2) Å, typical for a P=S while the bonded P(1)-S(1) is longer at 2.046(2)Å indicating a bond order lower than 2. Including all four sulfur atoms the geometry about tellurium is distorted square planar. The two pendant sulfur atoms are attached to the OPh substituted phosphorus atoms whilst the coordinated sulfur atoms are closest to Et substituents. The OPh groups are not as sterically demanding as the cyclohexyl substituents in a 4-coordinate cyclohexyl analogue. It can be concluded that the electronic nature of the R groups is more significant in affecting coordination number/fluxionallity in these complexes than the steric requirements of the phosphorus substituents. Apart from their intersting structural properties wec are now investigating imidophosphinates as metal selective extractants and in catalysis.

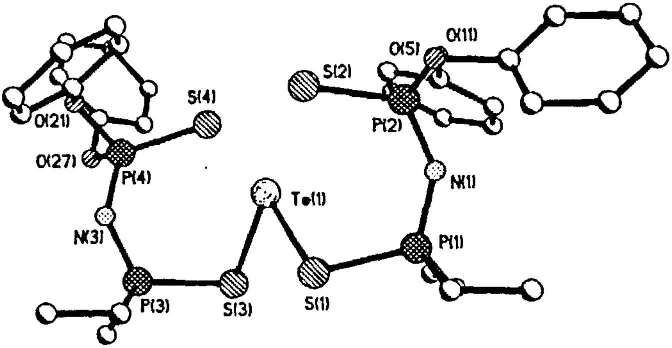
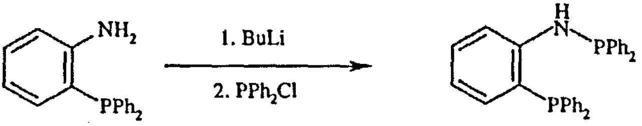


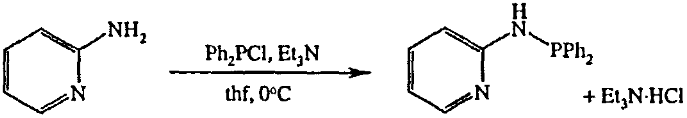
Figure 6 The X-Ray structure of a 'two-coordinate' TeL_2 complex.

We have developed the use of P-N bond forming reactions for a range of new P^{III} and P^{V} ligands which are currently being tested as catalysts. Details of P-N-Si-N-P and P-piperazine-P backbone ligands are provided elsewhere in this issue. Recent other examples from our work include phosphines based on organic diamines[12] and unsymmetrical systems such as that shown below[13]



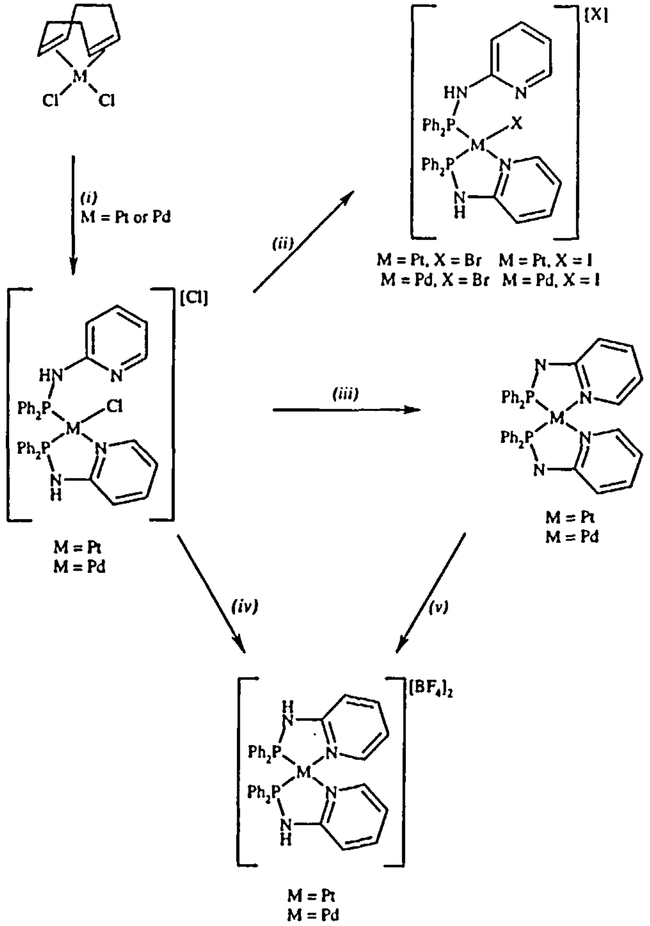
This *bis*phosphine does display differing coordination properties for the two P^{III} centres asa result of steric factors.

It is also very straightforward to prepare new hemilabile ligands



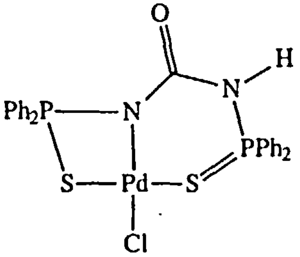
based on pyridine by similar, simple P-N bond forming reactions.

We have used this pyyridyl phosphine ligand in a range of complexation reactions and some examples are shown below.[14]



Scheme 1 *(i)* Ph$_2$PNHpy, MeCN; *(ii)* KBr or NaI, acetone; *(iii)* ^{t}BuOK, MeOH; *(iv)* Ag[BF$_4$], CH$_2$Cl$_2$; *(v)* HBF$_4$·OEt$_2$, CH$_2$Cl$_2$.

We have also developed routes to urea and thiourea based *bis*-phosphines[15] and amino acid derivatives.[16] Perhaps the most remarkable aspect of the P-N based phosphine chemistry is the relatively high stability of the P-N bond under many circumstances. There is also a rich and diverse chemistry of mixed donor systems based on ureas. For example, the reaction between $[PdCl_2(PhCN)_2]$ and $[Ph_2P(S)NH]_2C{=}O$ (H_2L) proceeds with monodeprotonation of an amine group in the disulfide ligand to give [Pd(HL)Cl] (shown below) , in which the $(HL)^-$ anion supplies an *S,N,S'* donor set to palladium(II), leading to disparate *S,N* chelate ring sizes at the metal.[17]



There has not been enough space in this brief review to illiustrate all of the apsects of our work on main group rings and cages, The most notable omissions are developments in organo-phosphorus—sulfur/selenium chemistry and new Sn-S-N reagents for ring synthesis but these are described elsewhere[18,19] and in this issue.

Acknowledgements
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