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Coordination chemistry of unsaturated cyclic and acyclic PNS and PNSe ligands

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CONTENTS

ABSTRACT

This review is primarily concerned with the synthesis, structure and fluxional behaviour of cyclic and acyclic chalcogen–nitrogen systems containing phosphorus(V) or phosphorus(III). The cyclic $Ph_4P_2N_4S_2R^-$ and $Ph_4P_2N_4S_2^{2-}$ anions (and their selenium analogues) are versatile ligands for both early and late transition metals. Mono-, di-, tri- and tetradentate bonding modes have been established for the eight-membered $P_2N_4S_2$ ring in these inorganic heterocycles. Ligation occurs through sulphur (or selenium) and/or nitrogen, while the coordinatively saturated phosphorus(V) centres serve as an informative probe of fluxional processes. By contrast, coordination occurs exclusively through phosphorus in both the cyclic and acyclic phosphorus(III) systems.

In order to provide a background for the discussion of the coordination chemistry of hybrid P–N/S–N systems, the review begins with a short account of N-bonded complexes of cyclophosphazenes

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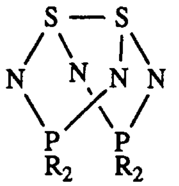
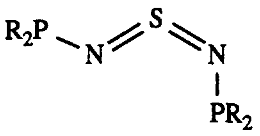
and S_4N_4, which is followed by a discussion of metal complexes of the $S_4N_4^{2-}$ dianion. The concluding section of the review describes metal complexes of some related anionic S—N ligands. In particular, the alkali metal derivatives of the acyclic $[RNS(R')NR'']^-$ anions and transition metal complexes of the cyclic radical $PhCN_2S_2^{\cdot}$ are discussed.

1. INTRODUCTION

This review is concerned with the synthesis and structures of metal complexes of cyclic and acyclic ligands containing phosphorus, nitrogen and sulphur (or selenium). An example of the cyclic system is the 1,5-diphosphadithiatetrazocine **1a*** and a representative of the acyclic ligands is the sulphur diimide **2**. In view of the number and diversity of heteroatoms in **1** and **2**, these ligands are likely to exhibit a variety of bonding modes with metals. The phosphorus(V) centres in **1** are coordinatively saturated so that metal coordination is restricted to the nitrogen and/or sulphur atoms. However, the NPN fragments in **1** serve two important functions. First, these units provide a structural brace that helps to maintain the integrity of the eight-membered $P_2N_4S_2$ ring in metal complexes. Secondly, ^{31}P nuclear magnetic resonance (NMR) spectroscopy supplies an invaluable probe for (a) monitoring reactions of **1** with metal reagents, (b) providing preliminary structural information and (c) elucidating the nature of fluxional processes exhibited by some metal complexes of **1**. In contrast with **1**, the phosphorus(III) centres in ligands of the type **2** are coordinatively unsaturated and metal complexation occurs preferentially at these atoms.



1a (E ≡ S)
1b (E ≡ Se)



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Since the ligand **1** is a hybrid of two well-known inorganic ring systems, namely cyclophosphazenes and tetrasulphur tetranitride (S_4N_4), the coordination chemistry of these classic inorganic heterocycles will be briefly discussed first. This introduction will be followed by an account of the various bonding modes adopted by unsaturated phosphorus–nitrogen–chalcogen heterocycles, primarily the $R_4P_2N_4E_2$ (E ≡ S, Se)

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* In view of the difficulty of representing the bonding in π-electron-rich rings and cages with valence bond structures, these inorganic heterocycles and their metal complexes are represented by *structural frameworks only* throughout this review, except where sulphur diimide units —N=S=N— are clearly involved on the basis of X-ray data.

ring and the related anion $Ph_4P_2N_4S_2R^-$ ($R \equiv$ alkyl, aryl). The next section deals with metal complexes of phosphorus(III) sulphur diimides **2** and acyclic phosphorus–nitrogen–chalcogen anions. The review concludes with some comments on related complexes derived from organolithium derivatives of sulphur diimides and the radical $PhCN_2S_2^{\cdot}$.

2. CYCLIC SYSTEMS

2.1. *N-bonded complexes of cyclophosphazenes*

Although the chemistry of cyclophosphazenes has been intensely scrutinized during the past 20 years, very few metal complexes of these rings exhibiting endocyclic nitrogen coordination have appeared in the literature [1]. This is probably due in large measure to the fact that the nitrogen atoms in most phosphazene rings, particularly those with electron-withdrawing substituents on phosphorus, are only weakly basic. In this review coverage is limited to some examples of metal complexes of cyclo- tri- and tetraphosphazenes involving endocyclic nitrogen atoms. For a more comprehensive treatise on the coordination chemistry of cyclophosphazenes the reader is referred to the review by Allcock et al. [2].

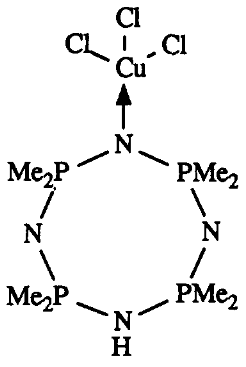
Stable metal adducts of hexaalkylcyclotriphosphazenes were first discovered in 1966 (eqn. (1)) [3]. These 1:1 adducts were assigned N-bonded structures on the basis of IR spectroscopic evidence, but it was not ascertained whether the P_3N_3 ring was acting as a monodentate or bidentate ligand (although the former seems more likely from a consideration of the ring geometry). Both monodentate and bidentate

$$(Me_2PN)_3 + MCl_4 \xrightarrow[CH_2Cl_2]{0^\circ C} (Me_2PN)_3MCl_4 \qquad (1)$$

$(M \equiv Sn, Ti)$

N-bonded adducts have been unequivocally established by X-ray crystallography for cyclotetraphosphazenes. The copper(II) complex **3**, which contains a protonated P_4N_4 ring, is prepared by treating $(NPMe_2)_4$ with $CuCl_2$ in methyl ethyl ketone [4], while the 1:1 adduct **4** is obtained from the reaction of K_2PtCl_4 with $[NP(NHMe)_2]_4$ in chloroform [5].

Some amino-substituted cyclophosphazenes engage in bidentate coordination to a metal via both an endocyclic and an exocyclic nitrogen atom. The complexes **5** [6] and **6** [7] are examples of this type of coordination. A general feature of these N-bonded complexes is the lengthening of the P–N bonds involving the coordinated endocyclic nitrogen atom. During the 1980s Allcock and co-workers undertook extensive investigations of the reactions of chlorocyclophosphazenes with organometallic anions. The products of these reactions embrace metal coordination to phosphorus as well as an endocyclic nitrogen atom (see ref. 2 for further details).



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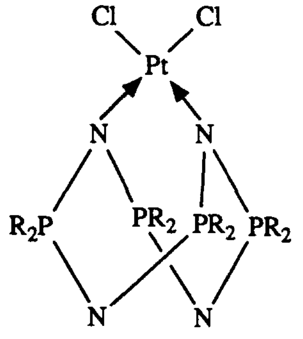
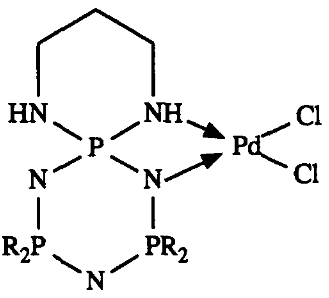
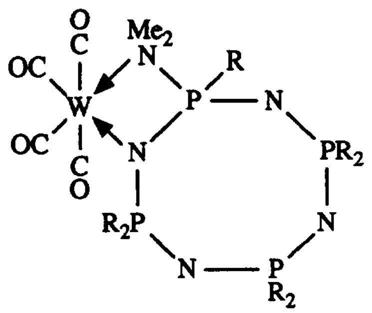


4 $(R \equiv MeNH)$



5 $(R \equiv NMe_2)$



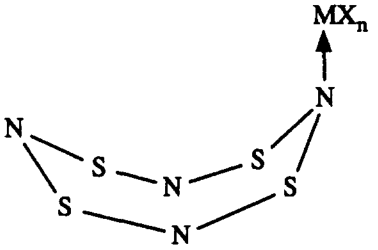
6 $(R \equiv NMe_2)$

2.2. *Complexes derived from S_4N_4 and Se_4N_4*

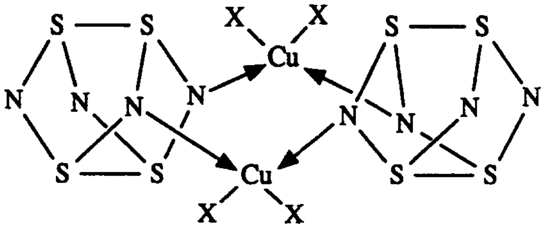
The cage compound S_4N_4 (and Se_4N_4) readily engages in redox reactions with transition metal reagents to give cyclometallathiazenes, i.e. complexes in which binary S–N anions formed by the reduction and fragmentation of S_4N_4 are chelated to the metal. The formation and structures of such complexes have been discussed in two reviews published in 1986 [8,9] and more recent developments are covered in articles by Woollins and co-workers [10]. In this subsection attention will be confined to complexes of the intact S_4N_4 ligand and the $S_4N_4^{2-}$ dianion. The corresponding complexes of $Se_4N_4^{2-}$ are unknown.

2.2.1. *N-bonded complexes of S_4N_4*

Until recently stable transition metal adducts of S_4N_4 have only been obtained with metal halides. In these N-bonded complexes the S_4N_4 ring acts as either a monodentate or a bidentate ligand, **7** or **8** respectively.



7 (MX$_n$≡TaCl$_5$ [11], FeCl$_3$ [12])



8 (X≡Cl, Br) [13]

In the monoadducts **7** coordination results in the disruption of the transannular S–S bonds of S_4N_4 to give a boat-shaped eight-membered ring with approximately coplanar sulphur atoms. The S–N distances involving the coordinated nitrogen atom are substantially longer (1.65–1.67 Å) than the other S–N bonds (1.54–1.60 Å) [11,12]. Surprisingly, the conformation and structural parameters of the bidentate S_4N_4 ligand in the copper complexes of type **8** are not significantly different from those of uncoordinated S_4N_4 [13].

Recently Klapötke and co-workers have prepared a complex of the titanocene dication Cp_2Ti^{2+} which is thought to contain an intact S_4N_4 ligand (eqn. (2)) [14].

$$\mathrm{Cp_2Ti[AsF_6]_2 + S_4N_4 \xrightarrow{SO_2} [Cp_2Ti(S_4N_4)][AsF_6]_2} \tag{2}$$

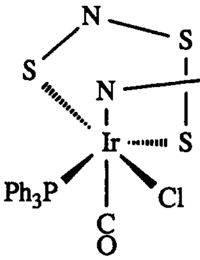
The presence of two equally intense resonances in the ^{14}N NMR spectrum of $Cp_2Ti(S_4N_4)^{2+}$ suggests that the S_4N_4 ligand is bonded symmetrically to titanium by two nitrogen atoms, but it has not been established whether this complex is monomeric or dimeric (cf. **8**).

2.2.2. *Complexes of the $S_4N_4^{2-}$ dianion*

Complexes of the hypothetical $S_4N_4^{2-}$ dianion have been prepared by the reaction of certain late, low valent transition metal reagents with S_4N_4. In these oxidative addition reactions the metal inserts into an S–N bond of S_4N_4. The first fully characterized metal complex of $S_4N_4^{2-}$ was prepared from Vaska's complex (eqn. (3)) [15].

$$\mathrm{[IrCl(CO)(PPh_3)_2] + S_4N_4 \xrightarrow{-PPh_3} [IrCl(CO)(PPh_3)(S_4N_4)]} \tag{3}$$

The crystal structure of the product **9** revealed an octahedral Ir(III) complex in which the $S_4N_4^{2-}$ ligand is coordinated facially to the metal centre via two sulphur atoms and one nitrogen atom [15b]. The two Ir–S bonds in **9** were found to differ in length by about 6 pm, reflecting the discrepancy in the trans influence between Cl and PPh_3. Subsequently Woollins and co-workers discovered that cleavage of the chloro-bridged dimer $[Pt_2Cl_4(PMe_2Ph)_2]$ with S_4N_4 in a 1:2 molar ratio afforded $[PtCl_2(PMe_2Ph)(S_4N_4)]$ (**10**) in high yield [16]. The relatively small single-bond ^{195}Pt—^{31}P coupling observed in the ^{31}P NMR spectrum of **10** suggested the complex might be a Pt(IV) species and this was later verified by an X-ray diffraction study, which showed the anticipated octahedral environment around Pt and tridentate (N,S,S′) coordination for the $S_4N_4^{2-}$ dianion. However, in this instance the S_4N_4 ligand is attached to the metal in a meridional fashion, and not facially as was observed in **9**.



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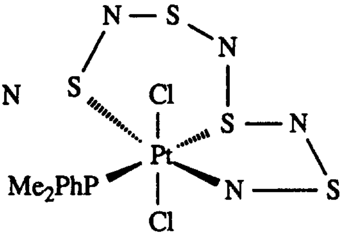

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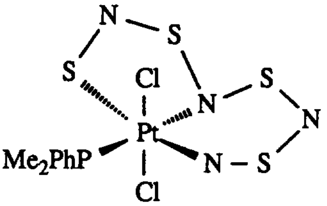

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On the basis of a ^{31}P NMR study alone, it was erroneously reported that mer-to-fac isomerization in **10** is readily accomplished by refluxing the complex in chloroform [17]. However, an investigation using ^{15}N-labelled S_4N_4 determined that, rather than simply inducing a change in conformation, heating **10** causes a [1,2] metallotropic shift to give a new structural isomer **11** in which the $S_4N_4^{2-}$ ligand is now bound to the metal by two nitrogen atoms and only one sulphur atom [18].

$$K[PtCl_3(CH_2{=}CH_2)] + S_4N_4 \xrightarrow[-C_2H_4]{THF} \underset{\mathbf{12}}{K[PtCl_3(S_4N_4)]} \tag{4}$$

Zeise's salt also reacts smoothly with S_4N_4 with the loss of ethylene to give the complex **12** (eqn. (4)) [19]. ^{195}Pt and ^{15}N NMR studies of the isotopomer with 100% ^{15}N enrichment at all four sites, $K[PtCl_3(S_4{}^{15}N_4)]$, showed quite convincingly that the $S_4N_4^{2-}$ ligand in **12** coordinates facially to the metal via two sulphur atoms and one nitrogen atom. The tetraphenylphosphonium salts of the bromo and iodo analogues of **12** are available from the reaction of $[PPh_4][Pt_2X_6]$ ($X \equiv Br, I$) with two equivalents of S_4N_4 in dichloromethane [19a]. An X-ray structural determination of $[NBu_4][PtBr_3(S_4N_4)]$ has confirmed the facial (S,S,N) coordination of the $S_4N_4^{2-}$ ligand [19b]. A poorly characterized actinide complex $[UCl_2(S_4N_4)]$ has been reported as the product of the reaction of S_4N_4 with UCl_4 [20].

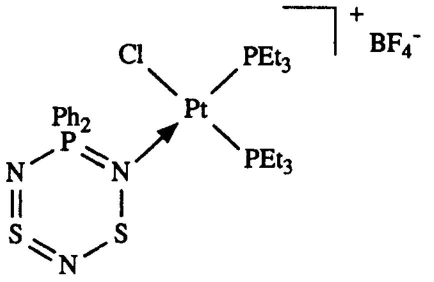
2.3. Complexes of P(V)NS and P(V)NSe ring systems

Cyclophosphathiazenes, which have the general formula $(R_2PN)_x(SN)_2$ ($x=1, 2$), can be considered as hybrids of the well-known cyclophosphazenes $(R_2PN)_n$ and a cyclothiazene, e.g. S_4N_4. The six-membered ring $Ph_2PN_3S_2$ ($x=1$) and two structural isomers of the eight-membered ring $Ph_4P_2N_4S_2$ ($x=2$) were first detected in product mixtures obtained from the nucleophilic degradation of S_4N_4 by PPh_2H or Ph_2PPPh_2 in boiling toluene [21]. The original synthesis produced 1,5-$Ph_4P_2N_4S_2$ (**1**, R ≡ Ph) in about 1% yield. However, much improved procedures for the preparation of **1** (R ≡ Ph) [22] and $Ph_2PN_3S_2$ [23] have been developed recently and so it has become possible to investigate the coordination chemistry of these hybrid ligands in detail. In view of the rich coordination chemistry of S_4N_4 [8–10], it was anticipated that **1** would act as a versatile ligand in metal complexes. Furthermore, the phosphorus(V) centres in **1** provide an informative structural probe via ^{31}P NMR spectroscopy, as well as acting as a stabilizing influence on the eight-membered ring.

2.3.1. N-bonded complexes

The reactions of cyclophosphathiazenes with transition metal electrophiles were investigated in order to establish the site of attachment and to determine the effect of adduct formation upon the geometry of the ring. The neutral and cationic dimers $[MCl_2(PEt_3)]_2$ (M ≡ Pt, Pd) and $[PtCl(PEt_3)_2]_2[BF_4]_2$, respectively were chosen for this study because the chloro bridges are readily cleaved by nucleophiles. The 1:1 adduct **13** was obtained according to eqn. (5) and complex **14** was prepared in a similar manner. The ^{31}P NMR data for **13** and **14** suggested that the platinum centres are datively bonded to a nitrogen atom adjacent to the PPh_2 group and this was confirmed by an X-ray structure of **14** [24]. The coordination of the platinum(II)

$$[PtCl(PEt_3)_2]_2[BF_4]_2 + Ph_2PN_3S_2 \xrightarrow{CH_2Cl_2} 2[PtCl(PEt_3)_2(Ph_2PN_3S_2)][BF_4] \qquad (5)$$



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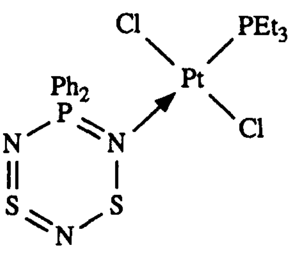
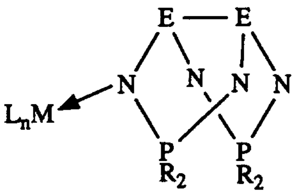


14

atom causes a lengthening of the S–N bond from 1.575(3) Å in the free ligand [25] to 1.67(2) Å in **14**. In addition, the coordinated nitrogen atom is displaced 0.63(2) Å out of the plane formed by the other five atoms in the heterocyclic ring. Similar structural perturbations are also observed for Lewis or Brønsted acid adducts of $Ph_2PN_3S_2$ [26]. The two S–N distances involving the sulphur atom opposite to the coordinated nitrogen atom are in the range 1.55–1.56 Å, indicative of a localized –N=S=N– unit. The Pt–N bond length of 2.12(2) Å in **14** is unusually long compared with the values of 2.01–2.05 Å found in Pt complexes of S–N ligands (see e.g. ref. 27). The weakness of the Pt–N interaction is also manifested by the facile dissociation of the adduct in solution.

The folded eight-membered rings, 1,5-$Ph_4P_2N_4E_2$ also form N-bonded 1:1 adducts **15** with platinum(II) (eqn. (6)) and the appropriate adjustment of stoichiometry produces the corresponding 1:2 adducts **16** or, in the case of E ≡ S, 1:3 adducts **17** [28,29]. The ^{31}P NMR chemical shifts of the folded rings **1a** and **1b** occur in an

$$2R_4P_2N_4E_2 + [MCl_2(PEt_3)]_2 \xrightarrow[\text{or THF}]{CH_2Cl_2} 2[MCl_2(PEt_3)(Ph_4P_2N_4E_2)] \quad (6)$$



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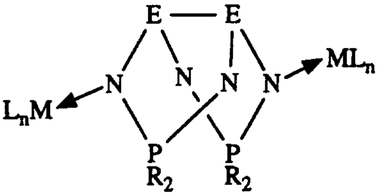

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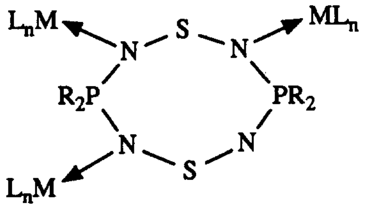

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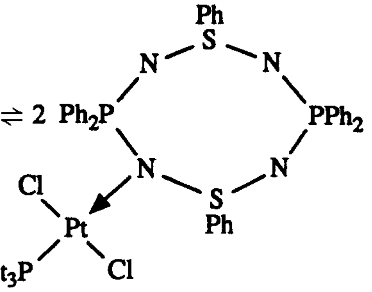
(E ≡ S, Se; M ≡ Pt, Pd; R ≡ Me, Et, Ph)

anomalously low field region (110–136 ppm) [23,29] and this parameter can be used to monitor the loss or retention of the cross-ring E–E interaction in **1a** or **1b** [30]. The ^{31}P NMR data for all the 1:1 adducts **15** indicate that the cross-ring E–E interaction is retained [28,29]. This conclusion has been confirmed by an X-ray structural determination of **15** (M ≡ Pt; E ≡ S; R ≡ Ph) [28], which reveals a contraction of the S–S distance from 2.528(1) Å in 1,5-$Ph_4P_2N_4S_2$ [21] to 2.41 Å and a lengthening of the P–N and S–N bonds involving the coordinated nitrogen atom. Similar structural changes occur upon methylation of the $P_2N_4S_2$ ring with $CH_3SO_3CF_3$ [30]. The Pt–N bond length of about 2.19 Å in this 1:1 adduct is indicative of a weak interaction consistent with the facile displacement of the $P_2N_4S_2$ ligand from platinum(II) by a THF molecule [28]. This displacement does not occur in THF solutions of the 1:1 adducts with the tetraalkyl derivatives $R_4P_2N_4S_2$ (R ≡ Me, Et), which also form 1:3 adducts with platinum(II) more readily than $Ph_4P_2N_4S_2$. Thus the replacement of phenyl groups on phosphorus by alkyl groups significantly enhances the Lewis basicity of the $P_2N_4S_2$ ring.

The distal arrangement of the platinum(II) centres in the 1:2 adduct **16** (E ≡ Se; M ≡ Pt) was indicated by the ^{31}P and ^{77}Se NMR spectra and confirmed by an X-ray structural investigation of the tetraphenyl derivative, which also established the presence of an Se–Se interaction (d(Se–Se) = 2.594(2) Å) [29]. The ^{31}P NMR spectra of the 1:3 adducts **17** (M ≡ Pt; R ≡ Ph, Et) show two signals for the heterocyclic phosphorus atoms in the region 70–80 ppm, which strongly suggest the disruption of the cross-ring S–S interaction. The S,S′ and Se,Se′ diorgano derivatives 1,5-$Ph_4P_2N_4E_2R_2$ also form N-bonded complexes with transition metals. For example, 1,5-$Ph_4P_2N_4S_2Ph_2$ cleaves the dimer $[PtCl_2(PEt_3)]_2$ to give the η^1-N-bonded 1:1 adduct **18**, but the yield is only about 30% [31]. The poor yield of **18** has been attributed to the equilibrium shown in eqn. (7).

$2Ph_4P_2N_4S_2Ph_2 + [PtCl_2(PEt_3)]_2 \rightleftharpoons 2$



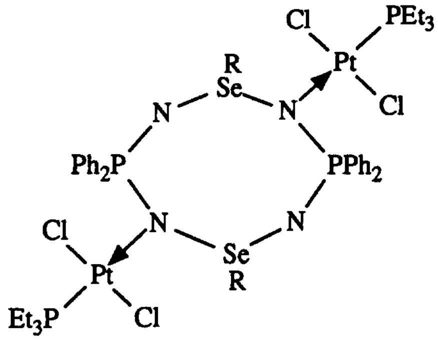
(7)

18

In contrast with the behaviour of 1,5-$Ph_4P_2N_4S_2Ph_2$, the Se,Se′ diorgano derivatives $Ph_4P_2N_4Se_2R_2$ (R ≡ Me, Et, Ph) afford only the 1:2 adducts **19** upon reaction with $[PtCl_2(PEt_3)]_2$ [31]. The two $PtCl_2(PEt_3)$ groups in **19** (R ≡ Me) are attached to distal nitrogen atoms of the (disordered) $P_2N_4Se_2$ ring with average Pt–N distances of 2.130(8) Å indicative of a weak interaction [31].

2.3.2. *Complexes of $Ph_4P_2N_4E_2^{2-}$ (E ≡ S, Se) anions*

The first reaction of 1,5-$Ph_4P_2N_4S_2$ with a transition metal reagent was reported in 1989 when it was shown that **1a** (R ≡ Ph) undergoes oxidative addition



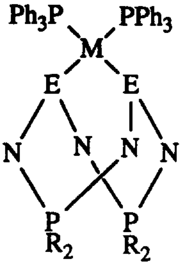
19 (R ≡ Me, Et, Ph)

with platinum(0) [32,33]. A similar reaction was reported for the related heterocycle 1,5-$(Me_2NC)_2N_4S_2$, which also has a transannular S–S bond [32]. Subsequently these oxidative addition reactions were extended to palladium(0) for both the $P_2N_4S_2$ and $P_2N_4Se_2$ ring systems (eqn. (8)) [29,34].

$$[M(PPh_3)_2L_2] + 1,5\text{-}R_4P_2N_4E_2 \xrightarrow{-L} \tag{8}$$

$$(M \equiv Pt;\ L \equiv C_2H_4) \quad (E \equiv S, Se;\ R \equiv Ph, Me, Et)$$

$$(M \equiv Pd;\ L \equiv 2PPh_3)$$



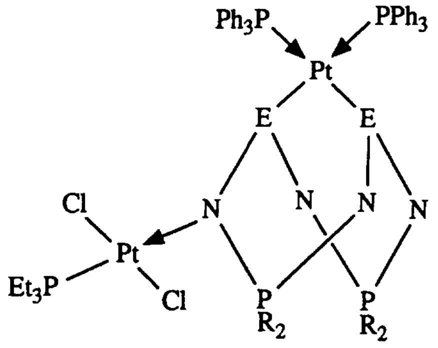
20

The products **20** can be regarded as platinum(II) or palladium(II) complexes of the dianions $Ph_4P_2N_4E_2^{2-}$. Alkali metal derivatives $M_2[Ph_4P_2N_4S_2]$ (M ≡ Li [35], Na [36]) may be prepared by the reduction of 1,5-$Ph_4P_2N_4S_2$ with the appropriate superhydride $M[Et_3BH]$ in THF. The dilithio derivative $Li_2[Ph_4P_2N_4S_2]$ reacts with *cis*-$PtCl_2(PPh_3)_2$ in THF to give **20** (M ≡ Pt; R ≡ Ph; E ≡ S) and this method has also been used to prepare η^2-S,S′ complexes of nickel(II), $[NiL_2(Ph_4P_2N_4S_2)]$ (L ≡ PPh_3, $\frac{1}{2}$diphos), which are unavailable from the reaction of 1,5-$Ph_4P_2N_4S_2$ with zero-valent nickel reagents [35]. The ^{31}P NMR data for **20** clearly indicate that the heterocyclic ligand in these complexes is symmetrically attached to the metal centre and that the E–E cross-ring bond has been ruptured. This was confirmed by the crystal structure for **20** (R ≡ Ph; M ≡ Pt; E ≡ S), which shows the $Ph_4P_2N_4S_2$ ring symmetrically bound to Pt via two strong Pt–S bonds

(2.408(4) and 2.341(4) Å) [34]. Each sulphur atom is trans to a PPh_3 ligand and the coordination at Pt is roughly square planar.

Density functional molecular orbital (MO) calculations for the model compound $Pt(PH_3)_2[1,5\text{-}(H_2NC)_2N_4S_2]$ have shown that the heterocyclic ligands in these η^2-S,S′ complexes engage in synergic bonding with the metal analogous to that established by Dewar, Chatt and Duncanson for η^2-alkene–metal complexes [32,37]. The major component of this interaction is back bonding from the metal to the empty σ^*(S–S) orbital of the ligand, i.e. the heterocyclic ligand behaves in a manner similar to an electron-deficient alkene [32].

The E–E bonds in the η^1-N-bonded 1:1 adducts of the type **15** also add oxidatively to $Pt(CH_2{=}CH_2)(PPh_3)_2$ to give the diplatinum complexes **21** [28,29], which combine the η^1-N and η^2-E,E′ coordination modes. Although these complexes can be isolated as air-stable solids, ^{31}P NMR evidence indicates that in solution **21** (E ≡ S; R ≡ Et) decomposes to the corresponding bimetallic dimer **22** and *cis*-$PtCl_2(PPh_3)(PEt_3)$. These bimetallic dimers are more conveniently formed by gentle heating of **20**, which causes the reversible dissociation of a triphenylphosphine ligand (eqn. (9)) [29,34,38]. The dimerization reaction is spontaneous at 25°C in dichloromethane for **20** (M ≡ Pt, Pd; R ≡ Et, Me), while heating at reflux in toluene is required to form the other bimetallic complexes. The crystal structure for **22** (M ≡ Pt; R ≡ Ph; E ≡ S), which is representative of all these bimetallic species, consists of a centrosymmetric dimer in which each $P_2N_4S_2$ ring is chelated to one Pt atom via nitrogen and sulphur atoms and forms a bridge to the second Pt atom through its other sulphur atom. Variable-temperature ^{31}P NMR spectroscopy revealed that all the dimers undergo a two-site dynamic exchange in solution. The intramolecular rearrangement probably proceeds via a pendular movement of the M–PPh_3 groups between vicinal nitrogen atoms in the ring, i.e. a [1,3] metallotropic shift (see Fig. 1). The relatively weak metal–nitrogen bonds in these complexes (d(Pt–N) = 2.089(7) Å



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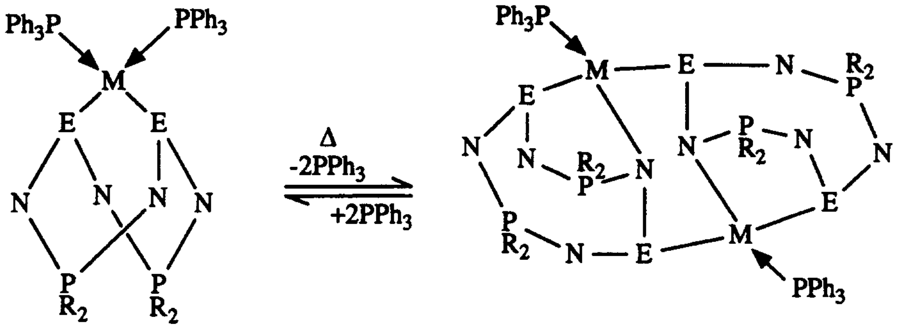


(E ≡ S, Se; M ≡ Pt, Pd; R ≡ Ph, Me, Et)

22

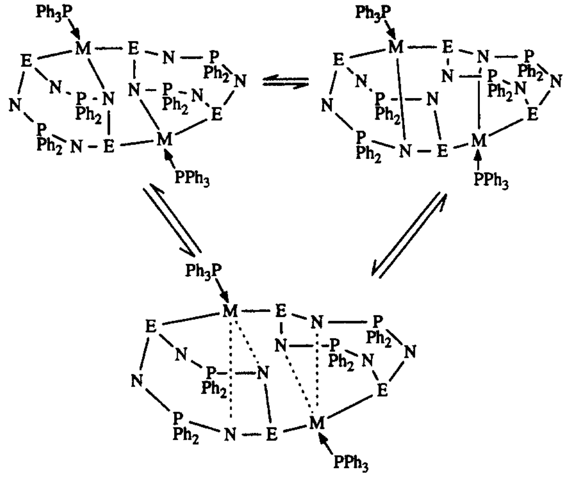
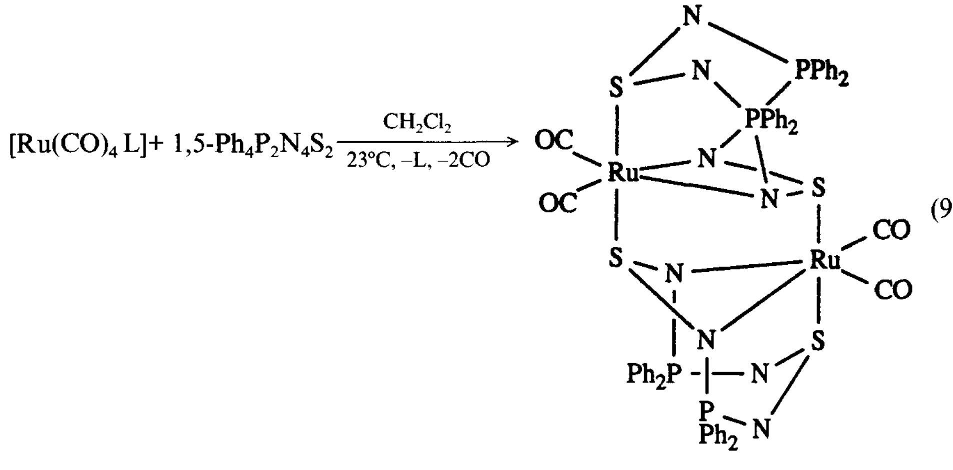


Fig. 1. Proposed mechanism for the [1,3] metallotropic rearrangement in $[M(PPh_3)(R_4P_2N_4E_2)]_2$, **22** (M ≡ Pt, Pd; E ≡ S, Se).

for **22** (M ≡ Pt; E ≡ S; R ≡ Ph)) probably account for the observed fluxional behaviour in solution.

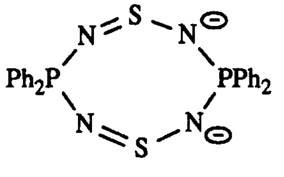
The proposed intermediate in this [1,3] metallotropic rearrangement involves a tetradentate bonding mode for the $P_2N_4S_2$ ring, i.e. the metal is bonded (symmetrically) to two vicinal nitrogen atoms and the remote sulphur atom while the second sulphur atom forms a bridge to the other metal atom (see Fig. 1). Very recently a ruthenium dimer **23** with exactly this type of coordination mode for the $P_2N_4S_2$ ligand (η^3-N,N′,S-μ,η^1-S′) has been obtained by the oxidative addition of 1,5-$Ph_4P_2N_4S_2$ to $Ru(CO)_4(C_2H_4)$ or $Ru(CO)_5$ (eqn. (9)) [39]. The crystal structure of **23** showed that the $P_2N_4S_2$ ring is coordinated in a tridentate (S,N,N′) fashion to one ruthenium atom and in a monodentate (S′) mode to the other ruthenium atom to give a centrosymmetric dimer. The trends in the P–N and S–N bond



(9)

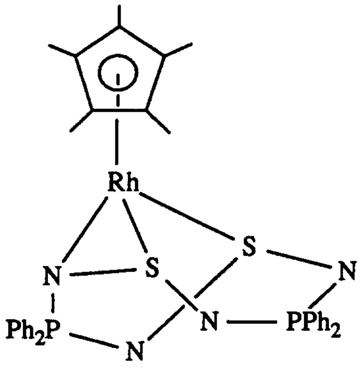
23

lengths suggest that the $Ph_4P_2N_4S_2^{2-}$ ligand in **23** can be represented approximately by the valence bond structure **24a**. The Ru–N distances are equal (about 2.15 Å) [39]. Mono- or dimethylation of **23** with $MeSO_3CF_3$ occurs at two-coordinate nitrogen sites without a change in the bonding mode between the heterocyclic ligand and the metal [40].

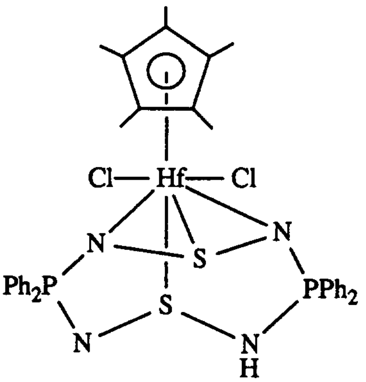


24a

An alternative to the oxidative addition approach to metal complexes of the $Ph_4P_2N_4S_2^{2-}$ dianion is the direct reaction of alkali metal derivatives of the dianion with organometallic halides. Although these reactions frequently result in the regeneration of the eight-membered ring **1a** via a redox process, the complexes $[RhCp^*(Ph_4P_2N_4S_2)]$ (**24b**) and $[MCp^*Cl_2(Ph_4P_2N_4S_2H)]_2$ (M ≡ Zr, Hf) have recently been obtained by this route [36]. The reaction of $Na_2[Ph_4P_2N_4S_2]$ with $[RhCp^*(\mu\text{-}Cl)Cl]_2$ produces **24b** in which the $P_2N_4S_2$ ring acts as a tridentate (η^3-N,S,S′) ligand. The hafnium complex **24c**, which exists as a hydrogen-bonded dimer in the solid state, was prepared by the treatment of Cp^*HfCl_3 with $Na_2[Ph_4P_2N_4S_2]$ in DME followed by filtration through Celite. The heterocyclic ligand in **24c** is formally the N-protonated dianion $Ph_4P_2N_4S_2H^-$, which adopts a tetradentate (η^4-N,N′,S,S′) bonding mode [36].



24b



24c

2.3.3. *Complexes of* $Ph_4P_2N_4E_2R^-$ *(E ≡ S, Se) anions*

The reaction of organolithium reagents with 1,5-$Ph_4P_2N_4S_2$ results in nucleophilic attack at sulphur to give the organolithium derivatives $Li[Ph_4P_2N_4S_2R]$, **25** (eqn. (10)), in which the integrity of the eight-membered ring is retained [41,42].

$$1{,}5\text{-}Ph_4P_2N_4S_2 + RLi \xrightarrow{THF} \underset{\mathbf{25}}{Li[Ph_4P_2N_4S_2R]} \qquad (10)$$

(R ≡ Ph, Me, ^{t}Bu, ^{n}Bu, CH_2PPh_2, $CH_2P(S)Ph_2$).

As indicated in Fig. 2, the derivative **25** (R ≡ Ph) exists as a centrosymmetric dimer in the solid state with a step-shaped structure reminiscent of that found for organolithium derivatives of sulphur diimides (see Section 4.1). Each of the two equivalent lithium atoms in **25** is bonded almost symmetrically to two vicinal nitrogen atoms of one $P_2N_4S_2$ ring. One of these nitrogen atoms is also coordinated to the other lithium atom, so that the phosphorus atoms of each $P_2N_4S_2$ ring, which adopts a boat conformation, are inequivalent. The three Li–N distances are quite similar,

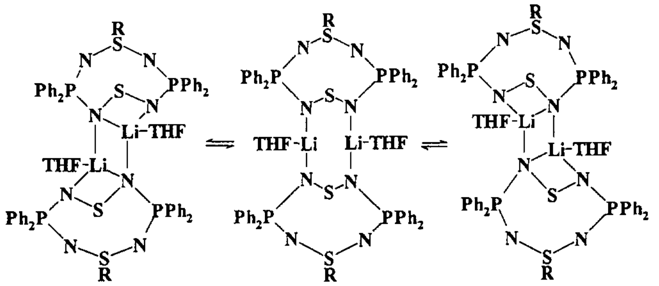


Fig. 2. Proposed mechanism for the [1,3] metallotropic rearrangement of the organolithium derivatives $[Li(Ph_4P_2N_4S_2R)\cdot THF]_2$, **25**.

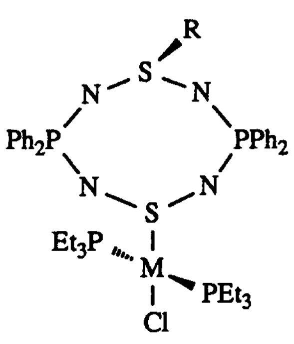
with values of 2.03(2), 2.08(2) and 2.10(2) Å, and a THF molecule occupies the fourth coordination site for each Li atom [42].

Variable-temperature ^{7}Li and ^{31}P NMR studies have revealed that all the organolithium derivatives **25** undergo a rapid two-site exchange in solution above 0°C which averages the two inequivalent phosphorus environments on the NMR time scale. A mechanism in which the lithium atoms undergo a [1,3] metallotropic shift between nitrogen atoms of two $P_2N_4S_2$ rings has been proposed to account for this fluxional behaviour (see Fig. 2) [42]. The ^{7}Li and ^{31}P NMR studies of **25** also provide evidence for a symmetrical species in solution. On the basis of the trends observed in these spectra as a function of concentration, a more highly solvated form of the intermediate shown in Fig. 2 has been suggested for this symmetrical species, i.e. two molecules of THF coordinated to each lithium atom [42].

The organolithium derivatives **25** are potential sources of the monoanions $Ph_4P_2N_4S_2R^-$ and recent investigations indicate that these anions will be highly versatile ligands in transition metal complexes. The first transition metal complexes of the $Ph_4P_2N_4S_2R^-$ anions were prepared by treating either *cis*- or *trans*-$[MCl_2(PEt_3)_2]$ ($M \equiv Pt$ or Pd) with $[Li(Ph_4P_2N_4S_2R)]_2$ ($R \equiv Me$, ^{t}Bu, Ph, CH_2PPh_2) in THF [41]. The products **26** were identified as η^1-S-bonded derivatives on the basis of ^{31}P NMR spectroscopy. Complexes of the corresponding selenium anion $Ph_4P_2N_4Se_2R^-$ have been obtained in a similar manner [29].

Crystallographic studies performed on **26** ($M \equiv Pd$; $R \equiv Me$) have confirmed that the heterocyclic ligand in these complexes is attached to the metal through a solitary sulphur atom (d(Pd–S) = 2.253(1) Å) [41]. The P_2N_4 plane of the chair-shaped heterocyclic ring in **26** ($M \equiv Pd$; $R \equiv Me$) is aligned perpendicularly to the square plane of coordination about palladium. In addition, the methyl group on the remote sulphur atom points towards one PEt_3 ligand and away from the other. This type of orientation renders the two phosphorus atoms of the ring equivalent while making the PEt_3 groups on the metal inequivalent. ^{31}P NMR spectra consistent with this structure were observed below −50°C in toluene. However, when solutions of **26** were warmed from −50 to +90°C, the two signals for the inequivalent PEt_3 groups were found to collapse to give a single resonance at the mean position. These changes have been attributed to an intramolecular two-site exchange which involves a simple rotation of the $P_2N_4S_2$ ligand about the metal–sulphur bond. A narrow range of activation energies (40–46 kJ mol^{-1}) were found for **26** [41,42b] and a related selenium complex [29], indicating that the barrier to rotation is not dramatically affected by the nature of the metal, the chalcogen or the remote R group.

Early transition metals also form stable, albeit very air sensitive, complexes with the $Ph_4P_2N_4S_2R^-$ anions. The metallocene dichlorides MCp_2Cl_2 react cleanly with **25** in THF to afford the crystalline complexes $MClCp_2(Ph_4P_2N_4S_2R)$ ($M \equiv Ti$, Zr, Hf; $R \equiv Me$, ^{t}Bu, Ph, CH_2PPh_2) [43a]. The crystal structure of the zirconium derivative **27a** shows that the heterocyclic ring is η^2-N,S bonded to the metal centre.



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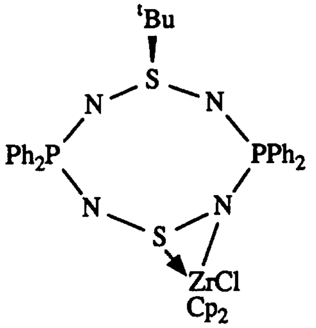
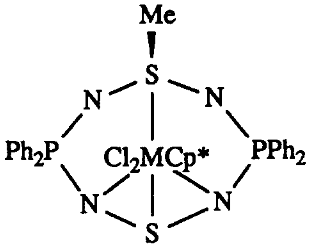


27a



27b

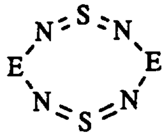
In contrast, the reaction of MCp^*Cl_3 (M ≡ Zr, Hf) with $Li(Ph_4P_2N_4S_2Me)$ produces the complexes $MCp^*Cl_2(Ph_4P_2N_4S_2Me)$ (**27b**) in which the $Ph_4P_2N_4S_2Me^-$ anion is bonded to the metal in a tetradentate (η^4-N,N′,S,S′) fashion [36]. Another type of ligand behaviour is observed for the $Ph_4P_2N_4S_2R^-$ ion in the complexes formed by the displacement of a PPh_3 ligand from Wilkinson's catalyst (eqn. (11)) [43b].

$$Li[Ph_4P_2N_4S_2R] + RhCl(PPh_3)_3 \xrightarrow[THF]{-PPh_3} [RhCl(PPh_3)_2(Ph_4P_2N_4S_2R)]Li \qquad (11)$$

(R ≡ Me, ^{n}Bu, ^{t}Bu)

2.4. Complexes of P(III)NS ring systems

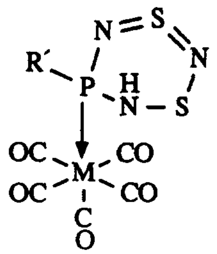
Eight-membered rings of the type $E_2N_4S_2$, **28** (E ≡ AsR, SbR), are readily prepared from K_2SN_2 with organoarsenic(III) or organoantimony(III) dichlorides [44,45] and the metal complexes of these cyclic sulphur diimides are limited to mono- or bidentate coordination via the pnictogen atoms [45–49]. The corresponding phosphorus(III) compounds **28** (E ≡ PR) are not accessible by this route [50]. Furthermore, the reaction of $RPCl_2$ adducts of $M(CO)_5$ (M ≡ Cr, W) with K_2SN_2 produces metal complexes of the six-membered PNSNSNH ring **29** rather than the expected complexes of **28** (E ≡ PR) (eqn. (12)) [50–52].



28

$M(CO)_5(RPCl_2) + K_2SN_2 \xrightarrow{CH_3CN}$

(M ≡ Cr, W; R ≡ Cl, ^{t}Bu, Ph)



(12)

29

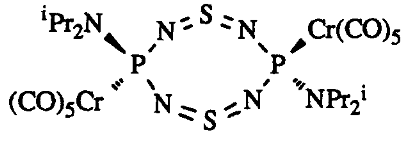
(M ≡ Cr, W; R′ ≡ NH_2, ^{t}Bu, Ph)

An alternative approach to complexes of the type **29** (M ≡ Cr; R′ ≡ Me_3SiNH) involves the reaction of $Cr(CO)_5[P(NSiMe_3)N(SiMe_3)_2]$ with S_4N_4 followed by treatment with isopropanol [53]. Initially, the structural assignment for **29** was based upon chemical analyses and spectroscopic data. In particular, reverse 2D $^1H\{^{15}N\}$ NMR experiments yielded ^{15}N chemical shifts (relative to CH_3NO_2) of −259.3 and −311.0 ppm for the NH nitrogen atoms in **29**, R′ ≡ ^{t}Bu and NH_2, respectively, and single-bond $J(^{31}P–^{15}NH)$ couplings of 60.2 and 54.4 Hz respectively [51]. This structure was subsequently confirmed by X-ray structural analyses of two adducts **29** (M ≡ Cr; R′ ≡ ^{t}Bu) [52] and **29** (M ≡ Cr; R ≡ Me_3SiNH) [54]. In both cases the $P^{III}N_3S_2$ ring is attached to the $Cr(CO)_5$ fragment through phosphorus. The ring in each structure adopts a half-boat conformation which has the NH nitrogen atom lifted out of the plane containing the other five heterocyclic ring atoms. Within each ring there are localized –N=S=N– (d(S–N) = 1.52–1.57 Å; ∠NSN ≈ 120°) and –HN–S–N= (d(S–N) = 1.65–1.69 Å, ∠NSN ≈ 108°) units. The elusive eight-membered phosphorus(III) rings **28** (E ≡ PR) were finally isolated as the bis-$Cr(CO)_5$ complexes **30a** and **30b** in low yields by exploiting the well-known base-promoted conversion of thionylimides (–NSO) into sulphur diimides (–N=S=N–) with the elimination of SO_2 (eqn. (13)) [53,55].

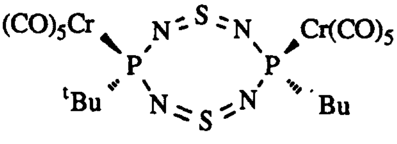
$$2[Cr(CO)_5(RPCl_2)] + 4MNSO \xrightarrow[-2SO_2,\ -4MCl]{CH_3CN} [(CO)_5Cr[RP(NSN)_2PR]Cr(CO)_5] \quad (13)$$

(R ≡ ^{t}Bu, iPr$_2$N) (M ≡ K, $(Me_2N)_3S$) **30a** (R ≡ ^{i}Pr$_2$N) **30b** (R ≡ ^{t}Bu)

X-Ray structures were obtained for **30a** and **30b**. In contrast with the boat-shaped $As_2N_4S_2$ ring in **28** (E ≡ As^{t}Bu) [44], which is unaffected by metal coordination, the $P_2^{III}N_4S_2$ ring in **30a** is essentially planar. The $Cr(CO)_5$ substituents are located on opposite sides of the $P_2N_4S_2$ plane and the bulky ^{i}Pr$_2$N groups are also trans to each other. In contrast, the $P_2^{III}N_4S_2$ ring in **30b**, in which the two $Cr(CO)_5$ substituents are cis to each other, deviates from planarity towards a boat conformation. The endocyclic bond angles at nitrogen in **30a** are remarkably large (150°–153°)



30a



30b

as a result of the enforced planarity of the $P_2N_4S_2$ ring. However, the S–N bond lengths (1.50–1.52 Å) and the endocyclic bond angles at sulphur of 124°–125° are typical for cyclic sulphur diimides. The structural parameters for the $P_2N_4S_2$ ring in **30b** are essentially the same as those in **30a**, except for the minor warping of the ring plane.

3. ACYCLIC SYSTEMS

3.1. *Complexes of phosphorus(III) sulphur diimides*

The coordination chemistry of acyclic sulphur diimides was reviewed in 1980 [56]. As indicated in Fig. 3, sulphur diimides can bind as a monodentate ligand via N, for which three configurations are possible, as a bidentate ligand via two N atoms, very rarely as a monodentate ligand via the S atom, and in an η^2 fashion via the π-N=S bond. The RN=S=NR ligand may also bridge two metal atoms as depicted in Fig. 3(g). Several of these metal complexes exhibit fluxional behaviour involving 1,3-nitrogen shifts in which the intermediate may involve either of the bonding modes (d) or (e) shown in Fig. 3.

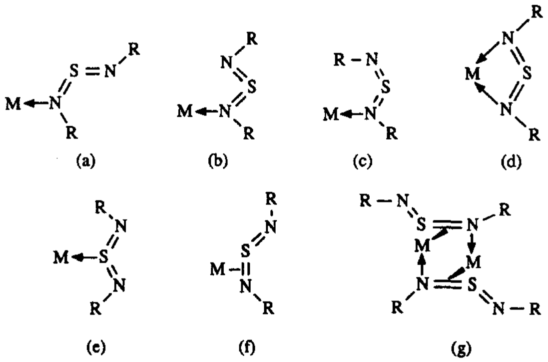
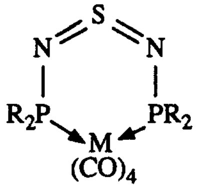


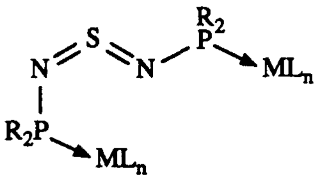
Fig. 3. Principal bonding modes for acyclic sulphur diimides: (a)–(c) monodentate nitrogen coordination; (d) bidentate nitrogen coordination; (e) monodentate sulphur coordination; (f) monodentate π-N=S coordination; (g) bridging metal–σ-N and metal–π-N=S coordination.

Phosphorus(III) derivatives of sulphur diimides, $R_2PNSNPR_2$ have been known for 10 years [57], but their coordination chemistry has developed quite slowly, primarily because most of these compounds are unstable as free ligands. Only di-, tri- and tetra-*t*-butyl-substituted derivatives R^tBuENSNER$'_2$ (R ≡ phenyl or ^{t}Bu; R′ ≡ ^{t}Bu or Ph; E ≡ P) can be isolated and reacted directly with transition metal reagents. The sterically demanding *t*-butyl groups apparently impart stability to these molecules by shielding the reactive NSN core from external nucleophiles and electrophiles. It is not surprising therefore that phosphino-substituted sulphur diimides only bind to metals via their two phosphorus atoms. Thus, in so far as their coordination chemistry is concerned, these molecules behave more like bisphosphine ligands (cf. $^tBu_2PCH_2CH_2CH_2P^tBu_2$) than classical *N,N′*-diorganosulphur diimides. For instance, Herberhold and co-workers have found that phosphino-substituted sulphur diimides bearing at least one *t*-butyl group react cleanly with metal carbonyl complexes such as $M(CO)_5THF$ (M ≡ Cr, Mo, W), $Fe_2(CO)_9$ or $CpMn(CO)_2(THF)$ to give either 1:1 or 1:2 metal adducts in high yields [58–61]. The 1:1 adducts involve chelation of the ligand to the metal through the two phosphorus(III) atoms, which enforces a cis,cis (*Z,Z*) arrangement of the sulphur diimide. The 1:2 metal adducts, on the other hand, invariably adopt a cis,trans (*Z,E*) geometry as in **32**.



31

(R ≡ ^{t}Bu; M ≡ Cr, Mo, W) [59]



32

(R ≡ ^{t}Bu; ML_n ≡ $M'(CO)_5$ (M′ ≡ Cr, Mo,W), $Fe(CO)_4$, $MnCp(CO)_2$) [59,60]

Metal complexes of bis-phosphino-sulphur diimides bearing substituents other than ^{t}Bu can be prepared by the reaction of coordinated R_2PCl ligands with the sulphur diimide dianion NSN^{2-} (eqns. (14) and (15)) [62,63]. The S–N bond lengths of 1.52–1.54 Å and the angles at sulphur of about 125° for complexes of the types **31** and **32** are typical values for sulphur diimides.

$$cis\text{-}[M(CO)_4(PPh_2Cl)_2] + K_2SN_2 \xrightarrow[-2KCl]{CH_2Cl_2,\ -40°C} \mathbf{31} \quad (R \equiv Ph;\ M \equiv Cr,\ Mo) \quad (14)$$

$$2[M(CO)_5(PPh_2Cl)] + K_2SN_2 \xrightarrow[-2KCl]{MeCN,\ -40°C} \mathbf{32} \quad (R \equiv Ph;\ M \equiv Cr,\ Mo) \quad (15)$$

The base-catalysed extrusion of SO_2 from coordinated R_2PNSO ligands has also been used to prepare bimetallic complexes (eqn. (16)) and this method had been adapted for the generation of complexes of the type **32** in which the two metals are different [63,64].

$$2M(CO)_5(R_2PNSO) \xrightarrow[-SO_2]{2KO^tBu/C_6H_6} \mathbf{32} \quad (R \equiv Me, Ph;\ M \equiv Cr, Mo) \qquad (16)$$

Complexes of the type **32** exhibit fluxional behaviour in solution. A variable-temperature ^{31}P NMR study of **32** ($R \equiv Ph$; $M \equiv Cr$, Mo) showed that the bridging $Ph_2PNSNPPh_2$ ligand undergoes a cis,trans → trans,cis intramolecular rearrangement in solution [63,64] (see Fig. 4). Band shape analysis of the ^{31}P NMR spectra at various temperatures afforded activation energies of 10.1 kcal mol^{-1} ($M \equiv Cr$) and 9.8 kcal mol^{-1} ($M \equiv Mo$) for the fluxional process. These values are about 1.5 kcal mol^{-1} smaller than that calculated for the cis,trans → trans,cis interconversion in the less sterically demanding model sulphur diimide MeNSNMe [56].

3.2. *Complexes of P(V)NE ($E \equiv S$, Se) anions*

Complexes of the dithiophosphinate **33a** and, to a lesser extent, diselenophosphinate **33b** anions with transition metals and main group elements have been studied in great detail [65]. The anionic ligand $Ph_2P(NSiMe_3)_2^-$ **34** ($R \equiv Ph$), is readily prepared and the structure of all the alkali metal derivatives have been determined recently [66]. The lithium and potassium compounds are monomers whereas the rubidium and caesium derivatives adopt step-shaped dimeric structures. Interestingly, the sodium derivative $[Na(THF)_6]\{Na[(NSiMe_3)_2PPh_2]_2\}$ has a unique structure in which two anions chelate to one sodium ion and the cation is a hexasolvated sodium ion. The hybrid anions $Ph_2P(E)NSiMe_3^-$, **35a** and **35b** ($R \equiv Ph$), represent potentially versatile ligands since they combine hard and soft coordination sites with a reactive Si–N bond. There have been very few reports of metal complexes of these hybrid ligands [65]. The aminophosphorane chalcogenides $R_2P(E)N(SiMe_3)_2$ ($E \equiv S$, Se) are potential sources of the anionic ligands **35a** and **35b** and the corresponding dianions $R_2P(E)N^{2-}$. Roesky et al. have recently de-

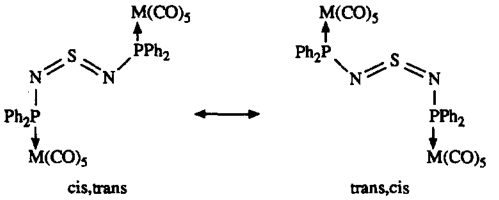
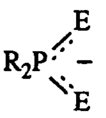
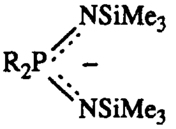


Fig. 4. Cis,trans → trans cis isomerization of $(CO)_5MPPh_2NSNPh_2PM(CO)_5$ ($M \equiv Cr$, Mo).



33a (E ≡ S)

33b (E ≡ Se)



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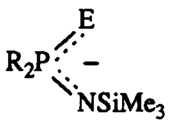
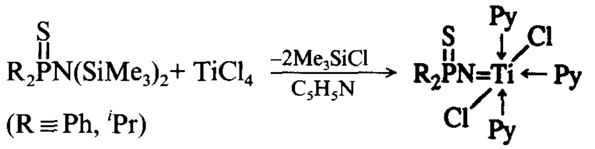


35a (E ≡ S)

35b (E ≡ Se)

scribed the synthesis of titanium(IV) complexes of the dianion $Ph_2P(S)N^{2-}$ (eqn. (17)) [67,68].

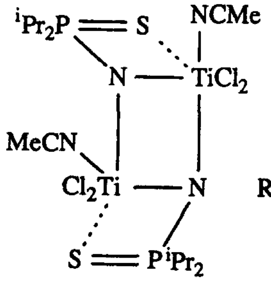


$$R_2P(S)N(SiMe_3)_2 + TiCl_4 \xrightarrow[C_5H_5N]{-2Me_3SiCl} R_2P(S)N{=}TiCl_2(Py)_3 \quad (17)$$

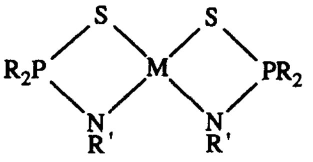
(R ≡ Ph, ${}^iPr$)

36a (Py ≡ C_5H_5N)

The complexes **36a** exhibit short Ti–N distances of about 1.72 Å indicative of metal–nitrogen multiple bonding. Moreover, the Ti–N–P bond linkages are almost linear (171°–172°), suggesting that the nitrogen is acting as a four-electron donor (i.e. –N≡Ti) to give a 16-electron configuration at titanium. When pyridine is replaced by acetonitrile in eqn. (17), the product is a dimer **36b** with unequal Ti–N bond lengths of 1.86 and 2.06 Å. Each $TiCl_2$ group is also coordinated to an acetonitrile molecule and a long-range Ti–S interaction (2.64 Å) completes the octahedral coordination at each Ti centre [68]. Four-membered spirocycles of the type **37** in which the hybrid ligand $R_2P(S)NR^-$ chelates to cobalt or nickel [69] or tin [70] have also been reported.

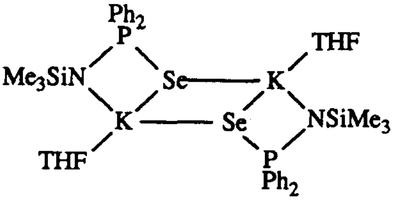


36b



37a (M ≡ Co, Ni; R, R′ ≡ alkyl or aryl)

37b (M ≡ $SnCl_2$; R ≡ ${}^iPr$; R′ ≡ $SeMe_3$)



38b

The monoanions **35a** and **35b** may be otained as potassium salts by the reaction of $Ph_2P(E)N(SiMe_3)_2$ with one molar equivalent of potassium *t*-butoxide (eqn. (18)) [71]. The use of two molar equivalents of KO^tBu does not, however, generate the corresponding dianions $Ph_2P(E)N^{2-}$, even in boiling dimethoxyethane.

$$Ph_2P(E)N(SiMe_3)_2 + KO^tBu \xrightarrow[23^\circ C]{THF} K[Ph_2P(E)N(SiMe_3)] + {}^tBuOSiMe_3 \qquad (18)$$

$$\mathbf{38a}\ (E \equiv S)$$
$$\mathbf{38b}\ (E = Se)$$

In the solid state the selenide **38b** exists as a step-shaped, centrosymmetric dimer. Each potassium atom is bonded to the selenium and nitrogen atoms of one $Ph_2P(Se)N(SiMe_3)^-$ anion and to the selenium atom of the other anion. The coordination sphere at potassium is completed by a THF molecule. The P–N bond lengths of 1.56(1) and 1.59(1) Å are intermediate between single and double bonds and the P–Se distances of 2.181(5) Å are about 0.1 Å longer than a typical P=Se double bond [71a]. In addition, the ^{77}Se–^{31}P NMR coupling constant in **39** is about 160 Hz smaller than that in $Ph_2P(Se)N(SiMe_3)_2$. Taken together, the structural and spectroscopic evidence suggests substantial charge delocalization in $Ph_2P(Se)NSiMe_3^-$, **35b** (R ≡ Ph). The structure of the sulphur analogue **35a** (R ≡ Ph) has been determined as the Ph_4As^+ salt [71b]. The P–N and P–S bond lengths are 1.56 and 1.98 Å respectively, indicating substantial charge delocalization on to the sulphur atom.

4. RELATED SYSTEMS

This final section deals with the metal complexes of some anionic ligands that are closely related to the P(V)NE (E ≡ S, Se) ligands discussed in Sections 2 and 3. Organolithium derivatives of *N,N'*-diorganosulphur diimides (Section 4.1) can in some ways be regarded as acyclic analogues of the organolithium derivatives of the $P_2N_4S_2$ rings described in Section 2.3.3. They exhibit structural resemblances and may be expected to show some similarities in their coordination chemistry.

4.1. *Organolithium derivatives of sulphur diimides*

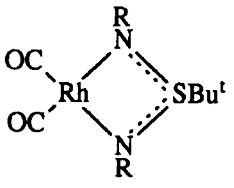
Organolithium derivatives of sulphur diimides have been known for nearly 20 years [72]. They are readily prepared in diethyl ether or THF solutions at low temperatures (eqn. (19)) [72–74]. These S-organolithium derivatives form metal

$$RNSNR + R'Li \xrightarrow[-20^\circ C]{Et_2O} Li[RNS(R')NR] \qquad (19)$$

(R ≡ alkyl, aryl)

complexes in which the sulphur diimide undergoes *N,N'*-bidentate coordination with the metal, e.g. **39** [75]. However, the solid state structures of the lithium sulphinimidamides themselves have been established only in the last few years by Stalke and co-workers [73,74]. Several structural types as illustrated by the four examples **40–43** have been established.

The structures are dependent on the nature of the solvent as well as the groups attached to sulphur or nitrogen. For example, the diethyl ether adducts **40** are



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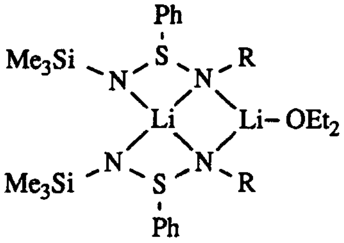
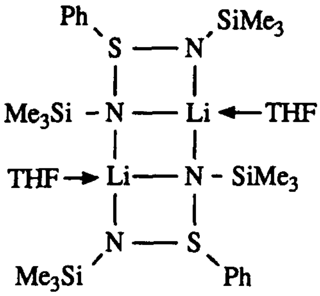


40 ($R \equiv SiMe_3$, ^tBu)



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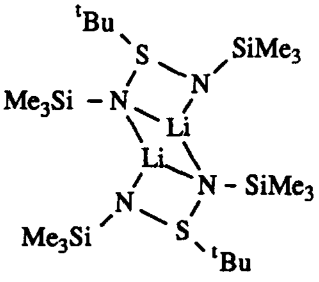

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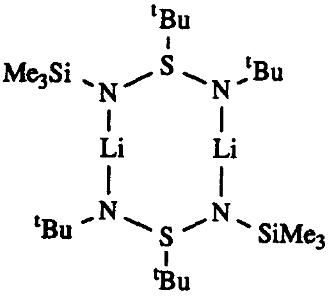

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composed of two monoanionic sulphinimido groups linked by two N-bonded lithium cations. Somewhat surprisingly, the coordination spheres of the two lithium atoms in these structures are not equivalent. One lithium atom is coordinated to all four nitrogen atoms of the dimer, while the other lithium atom is attached to just two nitrogen atoms and the oxygen atom of a diethyl ether molecule. In contrast, a centrosymmetric structure **41** with one solvent molecule coordinated to each lithium atom is found when THF is used as a solvent.

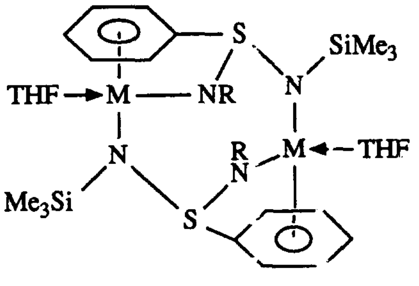
The replacement of the phenyl group on sulphur with a more bulky ^{t}Bu group results in structures without coordinated solvent molecules, **42** and **43**. The former has a step-shaped arrangement of three four-membered rings with tricoordinate lithium atoms whereas the structure of **43** more closely resembles an eight-membered ring. The connection between the structures **41**–**43** and those described for the dimers $[\mathrm{Li(THF)(Ph_4P_2N_4S_2R)}]_2$, **23** (Fig. 2), is readily apparent. An eight-membered ring structure of the type **43** has recently been established for the copper(I) dimer $\{\mathrm{Cu[(Me_3SiN)_2SPh]}\}_2$ [74b]. Heavier alkali metal sulphinimidamides may be prepared by the reaction of sulphiniminamines (obtained by the hydrolysis of lithium sulphiniminamides) with an alkali metal (eqn. (20)) or alkali metal hydride (eqn. (21)) [74].

$$2\mathrm{Me_3SiNS(Ph)NHSiMe_3} + 2\mathrm{M} \xrightarrow[-\mathrm{H_2}]{\mathrm{THF}} [\mathrm{Me_3SiNS(Ph)NSiMe_3(THF)M}]_2 \qquad (20)$$

$$(\mathrm{M} \equiv \mathrm{Rb, Cs})$$

$$2\mathrm{Me_3SiNS(Ph)NH{}^tBu} + 2\mathrm{MH} \xrightarrow[-2\mathrm{H_2}]{\mathrm{THF}} [\mathrm{Me_3SiNS(Ph)N{}^tBu(THF)M}]_2 \qquad (21)$$

$$(\mathrm{M} \equiv \mathrm{Na, K})$$



44 (M $\equiv$ Na K, Rb, Cs; R $\equiv$ ^{t}Bu or $\mathrm{SiMe_3}$)

A generalized structure **44** for these dimeric alkali metal derivatives is represented below. Each metal atom is bonded to two nitrogen atoms, the oxygen atom of a THF molecule and, somewhat unexpectedly, the π cloud of the phenyl group attached to sulphur. As indicated in Table 1, the metal atom moves closer to the

TABLE 1
Selected X-ray structural data for the alkali metal complexes of sulphinimidamides (**40** and **41** [73], **42**–**44** [74])

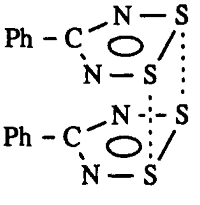
	Compound								
	40 (R $\equiv$ SiMe$_3$) (M $\equiv$ Li)	**40** (R $\equiv$ ^{t}Bu) (M $\equiv$ Li)	**41** (M $\equiv$ Li)	**42** (M $\equiv$ Li)	**43** (M $\equiv$ Li)	**44** (M $\equiv$ Na)	**44** (M $\equiv$ K)	**44** (M $\equiv$ Rb)	**44** (M $\equiv$ Cs)
Bond length (Å)									
S–N (av.)	1.609(3)	1.618(6)	1.610(2)	1.615(3)	1.615(3)	1.615(3)	1.609(3)	1.602(4)	1.598(3)
S–C	1.808(4)	1.826(8)	1.803(3)	1.854(3)	1.865(3)	1.801(3)	1.805(3)	1.807(3)	1.809(3)
M–N	1.994(3)	1.983(8)	2.022(5)	1.916(7)	1.904(7)	2.399(3)	2.752(3)	2.877(4)	3.045(3)
	2.245(5)	2.23(1)	2.393(5)	1.965(6)	1.912(7)	2.632(3)	2.880(2)	3.083(3)	3.250(3)
	2.033(5)	2.01(1)	2.054(5)	2.374(8)		2.409(3)	2.834(3)	2.922(2)	3.187(3)
M–O	1.879(9)	1.92(2)	1.974(5)	—	—	2.350(2)	2.716(3)	2.916(3)	3.101(5)
M–centre of phenyl ring on S	—			—	—	3.863	3.698	3.699	3.551
Bond angles (°)									
NSN	105.7(1)	105.6(3)	105.9(1)	105.7(1)	107.1(1)	110.7(1)	110.4(1)	110.4(2)	108.3(2)
N(1)–S(1)–C	104.4(2)	104.1(3)	104.7(1)	104.1(1)	104.1(1)	103.1(1)	103.5(1)	102.7(2)	103.3(2)
N(2)–S(1)–C	101.5(3)	101.5(3)	104.0(1)	103.4(1)	102.0(2)	98.5(1)	99.3(1)	99.4(1)	99.7(2)

centre of the phenyl ring as the size of the alkali metal increases. Thus, at least in these dimeric systems, the heavier alkali metals apparently engage in a stronger interaction with the phenyl π cloud. As expected, the average metal–nitrogen distance and the metal–oxygen distances to the coordinated THF molecules increase with expanding radius of the alkali metal. However, the size of M does not affect the bond lengths and angles within the sulphur diimide ligands of **44**. The S–N distances of 1.57–1.62 Å are somewhat longer than the value of 1.536(3) Å found for $Me_3SiN{=}S{=}NSiMe_3$ in the gas phase and the NSN angles of 105°–114° are more acute than that observed in $Me_3SiNSNSiMe_3$ [76].

The reaction of $Me_3SiNSNSiMe_3$ with PhMgBr in THF produces the dimer $\{MgBr[(Me_3SiN)_2SPh]\cdot THF\}_2$ in which the monomer units are bridged by slightly asymmetric Mg–Br contacts [74b]. The monomer $Mg[(Me_3SiN)_2SPh)]_2\cdot THF$ has a central five-coordinate magnesium atom bonded to all four nitrogen atoms of the two anions and a THF molecule [74b].

4.2. *Metal complexes of the acyclic $SNC(Ph)NS^{2-}$ ligand*

Recently electrochemical evidence has been presented for the formation of the $PhCN_2S_2^-$ ion by an irreversible one-electron reduction of the corresponding radical $PhCN_2S_2^{\cdot}$ [77] which exists as the dimer **45** in the solid state [78]. The S–S bonds within the five-membered CN_2S_2 rings have normal bond lengths (2.09 Å), while the inter-dimer S–S interactions are of length 3.11 Å. Although the PhC and Ph_2P groups are isolobal as substituents in cyclic S–N systems, the corresponding phosphorus-containing five-membered ring $Ph_2PN_2S_2$ is unknown. However, metal complexes of $PhCN_2S_2^{\cdot}$ are formed by the rupture of the S–S bond and in this respect resemble complexes of the $P_2N_4S_2$ ring formed by oxidative addition reactions (see Section 2.3.2).



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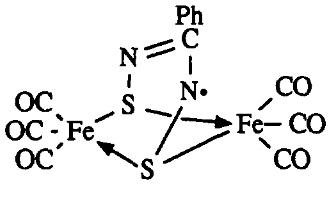

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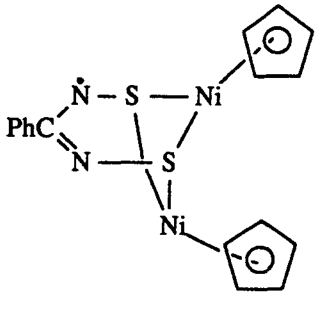
Banister et al. have recently shown that $PhCN_2S_2^{\cdot}$ radical undergoes oxidative addition reactions with a variety of zero-valent transition metal centres to give complexes in which the metal has inserted into the S–S bond of the ligand (see e.g.

$$(\mathrm{Ph\overline{CNSSN}})_2 + \mathrm{Fe_3(CO)_{12}} \xrightarrow[\text{(or THF)}]{\text{toluene}} \mathbf{46} \tag{22}$$

eqn. (22)) [79]. The CN_2S_2 plane of the bridging ligand in **46** is perpendicular to the Fe–Fe vector and each sulphur atom forms a dative coordinate ($2e^-$) bond with one iron atom and one-electron σ bond with the other. The S–S distance is opened up to 2.93 Å in **46** from 2.09 Å in **45** consistent with reduction to the $PhCN_2S_2^{2-}$ radical dianion. There are relatively short N–N and S–S intermolecular contacts in the crystal lattice of **46**, which have been ascribed to radical–radical interactions [79]. A structurally similar paramagnetic nickel complex **47** was prepared by the reaction of $[NiCpCO]_2$ with $(\mathrm{Ph\overline{CNSSN}})_2$ in toluene [80] and the tripalladium complex **48** was obtained in a similar manner from $Pd(PPh_3)_4$ [81]. Once again the metal centres in **47** are held together by bridging sulphur-bonded $PhCN_2S_2^{2-}$ ligands.



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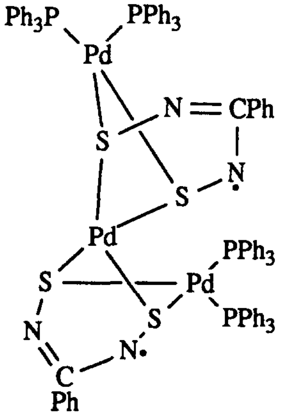

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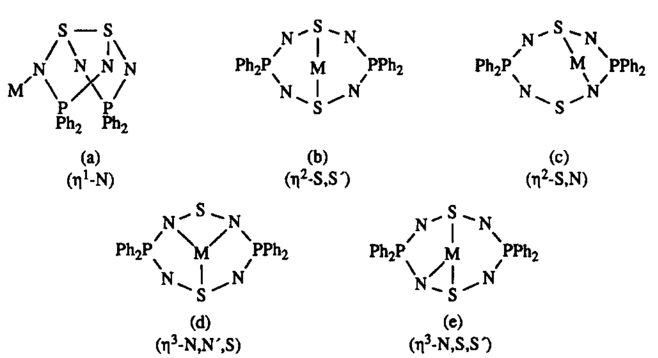
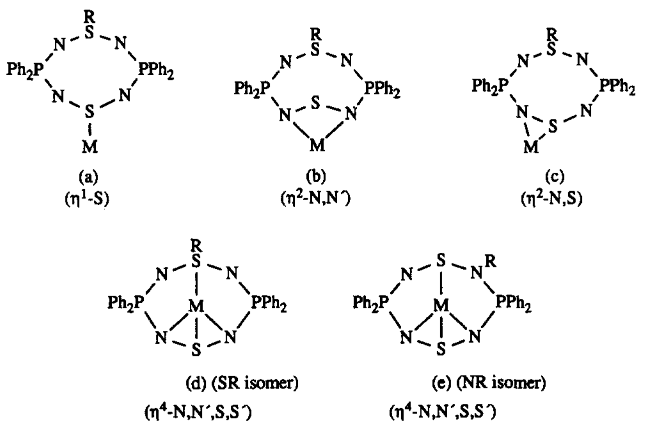
5. CONCLUSIONS

Whereas the coordination chemistry of cyclic and acyclic phosphorus(III) sulphur diimides is limited to the phosphorus(III) centre, the structural variety of complexes formed by cyclic phosphorus(V)–nitrogen–sulphur systems is extensive. The coordination modes that have been established to date for the $P_2N_4S_2$ ring are summarized in Figs. 5 and 6 for the ligands $Ph_4P_2N_4S_2^{2-}$ and $Ph_4P_2N_4S_2R^-$ respectively. The diversity of interactions that can be achieved with the combination of both hard and soft coordination sites is readily apparent. To date most studies have involved the late transition metals. It is conceivable that additional bonding modes will be identified, particularly for the anionic ligands, when investigations of these



(a) (η^1-N)
(b) (η^2-S,S′)
(c) (η^2-S,N)
(d) (η^3-N,N′,S)
(e) (η^3-N,S,S′)

Fig. 5. Coordination modes in metal complexes of $Ph_4P_2N_4S_2^{2-}$, where M represents the metal and ancillary ligands. The uncoordinated sulphur atom in (c) and (d) acts as a bridge to give centrosymmetric dimeric structures (see Section 2.3.2. for specific examples of each coordination mode).



(a) (η^1-S)
(b) (η^2-N,N′)
(c) (η^2-N,S)
(d) (SR isomer) (η^4-N,N′,S,S′)
(e) (NR isomer) (η^4-N,N′,S,S′)

Fig. 6. Coordination modes in metal complexes of $Ph_4P_2N_4SR^-$, where M represents the metal and ancillary ligands. One of the coordinated nitrogens in (b) also serves as a bridge to another metal to give a dimeric structure (see Section 2.3.3 for specific details).

ligands are extended to include the lanthanide and actinide elements. In all these metal complexes the retention of the integrity of the $P_2N_4S_2$ ring is a common feature, which can be attributed to the structural stability imposed by the NPR_2N units. ^{31}P NMR spectroscopy provides an important structural tool as well as a probe for the mechanistic study of fluxional processes for these complexes. As expected for the late transition metals, bonding to sulphur is stronger than the interaction with the nitrogen centres of these hybrid ligands and metallotropic shifts between vicinal nitrogen centres occur in some cases. The possibility of making use of these weak M–N bonds in certain multidentate coordination modes for the generation of reactive metal centres is worth considering.

The metal complexes of acyclic P(V)NS/Se anions have not been extensively investigated. Since these ligands are limited to one soft (S or Se) and one hard (N) centre, a multimode coordinate chemistry rivalling that of the cylic P(V)NS/Se ligands is not anticipated. Nevertheless, the combination of coordination sites with different metal affinities and the use of ^{31}P NMR spectroscopy as a structural probe is likely to be fruitful.

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