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The preparation and coordination chemistry of phosphorus–sulfur donor ligands

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Contents

Abbreviations: 8PS, see Figure 13; 9PS2, see Figure 13; 11P2S, see Figure 13; ape, $Ph_2AsCH_2CH_2PPh_2$; apeE, $Ph_2AsCH_2CH_2P(=E)Ph_2$ (b); dppbS, $Ph_2P(CH_2)_4P(=S)Ph_2$; dppeE, $Ph_2PCH_2CH_2P(=E)Ph_2$ (b); dppmE, $Ph_2PCH_2P(=E)Ph_2$ (b); dppmS, $Ph_2PCH_2P(=S)Ph_2$; dppmSe, $Ph_2PCH_2P(=Se)Ph_2$; dpppS, $Ph_2P(CH_2)_3P(=S)Ph_2$; *e*AsSMe, $Ph_2AsCH_2CH_2SMe$; *e*ESMe, $Ph_2ECH_2CH_2SMe$ (a); *e*ESR, $Ph_2ECH_2CH_2SR$ (a); *e*PEMe, $Ph_2PCH_2CH_2EMe$ (b); *e*PSEt, $Ph_2PCH_2CH_2SEt$; *e*PSH, $Ph_2PCH_2CH_2SH$; *e*PS_2H_2, $PhP(CH_2CH_2SH)_2$; *e*PS_3H_3, $P(CH_2CH_2SH)_3$; *e*PSMe, $Ph_2PCH_2CH_2SMe$; *e*PSPh, $Ph_2PCH_2CH_2SPh$; *e*PSR, $Ph_2PCH_2CH_2SR$; EtPTFH, $Ph_2PC(=S)NHEt$; L1, L2, L3, see Figure 11; MePTFH, $Ph_2PC(=S)NHMe$; MePTFMe, $Ph_2PC(=S)NMe_2$; *m*PSBz, $Ph_2PCH_2SCH_2Ph$; *m*PSMe, Ph_2PCH_2SMe; *m*PSPh, Ph_2PCH_2SPh; *m*PSR, Ph_2PCH_2SR; *ph*AsSH, $Ph_2AsC_6H_4SH$-2; *ph*AsSR, $Ph_2AsC_6H_4SR$-2; *ph*ESH, $Ph_2EC_6H_4SH$-2 (a); *ph*ESMe, $Ph_2EC_6H_4SMe$-2 (a); *ph*PEMe, $Ph_2PC_6H_4EMe$-2 (b); *ph*PSeH, $Ph_2PC_6H_4SeH$-2; *ph*PSeMe, $Ph_2PC_6H_4SeMe$-2; *ph*PSeR, $Ph_2PC_6H_4SeR$-2; *ph*PSEt, $Ph_2PC_6H_4SEt$-2; *ph*PSH, $Ph_2PC_6H_4SH$-2; *ph**PSH, $Ph_2P\{C_6H_4(SH\text{-}2)(SiMe_3\text{-}6)\}$; *ph*$PS_2H_2$, $PhP(C_6H_4SH\text{-}2)_2$; *ph**PS_2H_2, $PhP\{C_6H_4(SH\text{-}2)(SiMe_3\text{-}6)\}_2$; *ph*$PS_3H_3$, $P(C_6H_4SH\text{-}2)_3$; *ph*PSMe, $Ph_2PC_6H_4SMe$-2; *ph*PSR, $Ph_2PC_6H_4SR$-2; PhPTFH, $Ph_2PC(=S)NHPh$; PhPTFMe, $Ph_2PC(=S)NMePh$; $PhPTFSiMe_3$, $Ph_2PC(=S)NPh(SiMe_3)$; *pr*PSH, $Ph_2P(CH_2)_3SH$; *pr*PSPh, $Ph_2P(CH_2)_3SPh$; *pr*PSR, $Ph_2P(CH_2)_3SR$; RPTFH, $Ph_2PC(=S)NHR$; Tn = 2-thienyl; RPTFR′, $Ph_2PC(=S)NRR'$; R, R′ = alkyl or aryl; (a) E = P, As; (b) E = S, Se.

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Abstract

This article describes the synthesis and coordination chemistry of five broad types of ligands containing both phosphorus and sulfur donor centres, reviewing the literature up to the end of 1997. Phosphino–thiolate ligands combine a phosphine centre with a thiol functionality (usually deprotonated on coordination); phosphino–thioether ligands are similar in overall appearance, but contain a thioether group in place of the thiol functionality. Phosphino–thioformamides (of general formula $R_2PC(=S)NHR'$) and phosphino–dithioformates (of general formula $R_2PCS_2^-$) belong to the larger class of hetero-allylic ligands, being the phosphorus equivalents of thioureas and dithiocarbamates respectively. Finally, diphosphine monosulfides are related to the well-known diphosphine ligands (e.g. dppe) by the oxidation of one of the two phosphorus(III) centres to a phosphine sulfide. The review contains 340 references and 18 endnotes.

Keywords: P ligands; S ligands; Transition metals; Synthetic methods; Homogeneous catalysis; IR spectroscopy

1. Introduction

Much interest has been directed towards the chemistry of asymmetric multidentate ligands, in particular towards the phenomenon of hemilability [1]. In principle, a ligand containing one strongly binding donor centre and one weakly binding donor centre can be used to protect an active site at a metal centre until it is required to effect a transformation of a substrate. However, the chemistry of asymmetric ligands offers other significant possibilities:

- specific transformation of donor atoms can be carried out, potentially mirroring ligand reactivity in non-chelating complexes;
- ligand donor properties may be changed through chelation, conferring properties on a metal centre which are not available with monodentate ligands;
- chelate complexes are known to be particularly stable, and so the reactivity of a metal centre for one reaction (e.g. oxidative addition) may be studied without competing ligand substitution reactions.

Examples of all of these will be given in this review.

Ligands combining phosphorus centres and sulfur centres are especially interesting. Both phosphorus and sulfur are excellent ligand donor atoms for a wide range of metals, while the low ionisation energy of sulfur and the existence of several lone pairs of electrons (three in the case of a thiolate anion) offer the possibility of a rich sulfur-based chemistry of the complexes. Again, many examples will be given in the review, with a special discussion of the catalytic applications of certain complexes.

Five main types of phosphorus–sulfur donor ligand will be discussed, in approximate descending order of negative charge on the sulfur atom. Phosphino–thiols (Section 2) contain a phosphine group and a thiol function separated by an organic bridge; phosphino–thioformamides [2] and phosphino–dithioformates [3] (Section 3) are the phosphorus equivalents of thioureas and dithiocarbamates respectively; diphosphine monosulfides [4] (Section 4) are formally related to the well known diphosphine ligands (e.g. dppm, dppe) but with one of the phosphine centres oxidised to a phosphine sulfide; and phosphino–thioethers [5] (Section 5) contain a phosphine group and a thioether function separated by an organic bridge. All work published before December 1997 of which the authors are aware has been included.

2. Phosphino–thiols

2.1. Preparation of phosphino–thiols

The syntheses of phosphino–thiols, although not complicated by the standards of contemporary organic chemistry, present a number of challenges: many of the precursor compounds are not commercially available, or even chemically well-understood, often because they are highly unstable; the introduction of sulfur-containing groups brings with it the unwelcome possibility of the formation of phosphine sulfides; and, almost without exception, the compounds involved are toxic, malodiferous and air-sensitive.

The following is a brief survey of the strategies that have been used to prepare phosphino–thiols, along with an indication of the limits of their applicability.

2.1.1. Ring-opening reactions of thiiranes and thietanes

Thiiranes [6], and to a lesser extent thietanes [7], undergo ring-opening reactions on treatment with nucleophiles (e.g. the diphenylphosphide anion), especially in the presence of acid. However, this reaction is of limited synthetic utility unless the attacking species is a better nucleophile than the thiol formed on ring-opening, due to the ease of formation of poly(thioethers).

Another complication is the possibility of attack at sulfur rather than at carbon. This is rare in the case of thiiranes, although alkyl- and aryllithium compounds can cause desulfurisation [8]. However, initial attack at sulfur is the rule rather than the exception in ring-opening reactions of thietanes [9].

Phosphide ions formed from phosphine, or from primary or secondary organophosphines, will attack ethylene sulfide with ring opening to form phosphino–thiolate anions [10]. This is the standard method for the preparation of ethylene-bridged phosphino–thiols: it has also been extended to the synthesis of $PhHPC_6H_{10}SH$ or $Ph_2PC_6H_{10}SH$ from phenylphosphine [11] or diphenylphosphine [12] and (commercially available) cyclohexene sulfide, and to the preparation of β-mercapto-substituted stibines [13] and bismuthines [14].

2.1.2. Free-radical addition across carbon–carbon double bonds

Free radical addition of thioacetic acid across the double bond of allylphosphines and (3-butenyl)phosphines has been used to prepare the thioacetic *S*-esters of trimethylene- and tetramethylene- bridged phosphino–thiols [15]. These esters can be easily hydrolysed to the corresponding thiols; indeed the thioester linkage is cleaved under normal reaction conditions for coordination chemistry, allowing the thiol to be stored and handled conveniently as its thioacetate [16]. Unlike in the preparation of phosphino–thioethers (see Section 5.1.4), there are no reports of the production of phosphine sulfides as by-products, possibly due to the comparative instability of the acetyl radical which would be formed.

Similarly, phosphines will add to the C=C bond of 2-(vinylsulfanyl)-tetrahydropyran to give the tetrahydropyranyl-protected phosphino–thiol: the protecting group can be removed with dilute acid [17,18].

2.1.3. Nucleophilic substitution at sp^3-Carbon

A thiol that is ω-substituted with a good leaving group can in principle be converted into a phosphino–thiol by reaction with a phosphorus nucleophile. However this method of preparation has rarely been used, as the thiolate centre can compete with the incoming phosphorus nucleophile, leading to mixtures of products. For the same reason, the starting materials tend to be unstable with respect to cyclisation and/or oligomerisation, and present a substantial synthetic challenge. However, the route has been used to prepare 3-(phenylphosphino)propanethiol [11] and 3-(diphenylphosphino)propanethiol (*pr*PSH) [19] from commercially available 3-chloropropanethiol.

2.1.4. Addition reactions of thioketones

At first sight, the addition of a phosphorus-containing nucleophile to a thioketone appears a promising route to phosphino–thiols, especially those which are sterically-encombered α to the sulfur. However, the reactivity of thioketones with carbon nucleophiles is somewhat anomalous when compared with oxoketones [20,21], and 'thiophilic' addition is the norm [22]. There is one series of reports in which phosphorus nucleophiles attack at carbon rather than sulfur: phenylphosphine and diphenylphosphine react with thiobenzophenone to yield methylene-bridged phosphino–thiols. Trimethylsilylphosphines also react to give trimethylsilyl phosphino–thiols [23]. The coordination chemistry of these 1,1-phosphino–thiols has yet to be reported.

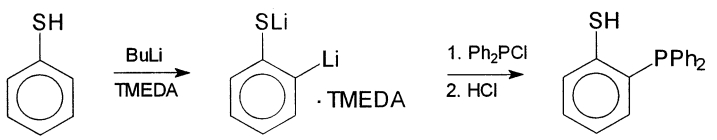
2.1.5. Ortho-lithiation and phenylene-bridged phosphino–thiols

Although a number of phenylene-bridged phosphino–thiols had been previously prepared by the metal-promoted dealkylation of phosphino–thioethers (see Section 2.1.7), the systematic study of their coordination chemistry was hampered by a lack of a general preparative route until the discovery of the *ortho*-lithiation of benzenethiol [24]. The 2-lithiobenzenethiolate can be quenched with chlorodiphenylphosphine to give 2-(diphenylphosphino)benzenethiol (*ph*PSH) [25] (see Scheme 1). A number of substituted phosphino–thiols can also be prepared, but the method is limited by the interference of several substituents with the initial lithiation step: for example, we were unable to prepare 4-(dimethylamino)-2-(diphenylphosphino)benzenethiol in acceptable yield via lithiation of 4-(dimethylamino)-benzenethiol because of the competing *ortho*-directing effects of the thiolate and dimethylamino groups [26,27].

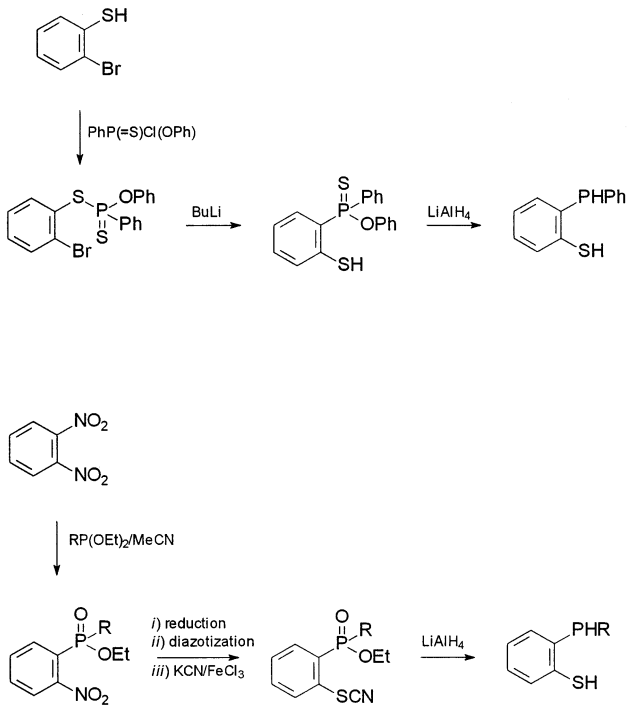
2.1.6. Arbuzov-type rearrangement of aryl dithiophosphonates

The reaction of 1,2-dinitrobenzene with a trialkyl phosphite in refluxing acetonitrile [28], or with a dialkyl organophosphonate in acetonitrile at room temperature, leads to an alkyl (2-nitrophenyl)organophosphonate which can be converted in high yield to a phosphino–thiol [29].

A modification of this route is shown in Scheme 2: this is reported to have the advantage that the phosphine sulfide is easier to reduce than the phosphine oxide [30].



Scheme 1. The preparation of 2-(diphenylphosphino)benzenethiol (*ph*PSH) by the *ortho*-lithiation of benzenethiol.



Scheme 2. Preparation of phosphino–thiols by Arbuzov-type rearrangements.

2.1.7. Preparation from thioethers

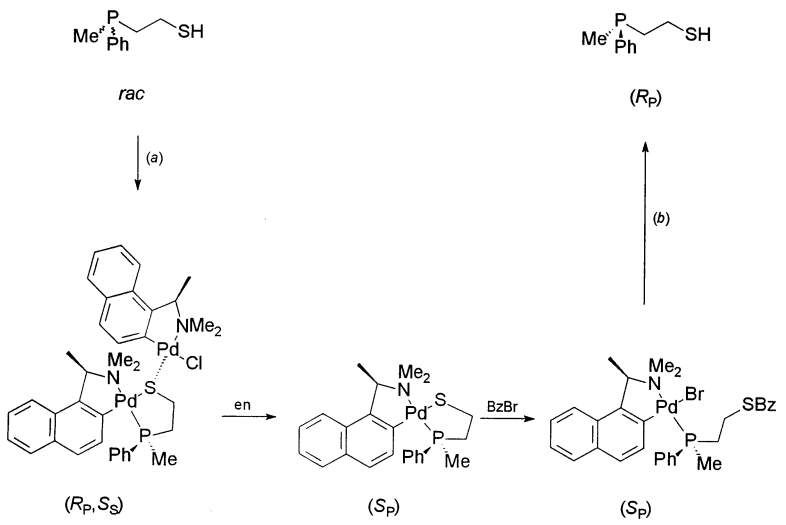
Coordinated phosphino–thioethers may be dealkylated under certain circumstances to yield the complexes of the corresponding phosphino–thiolates (see Section 5.2): this method led to the first complexes of phenylene-bridged phosphino–thiols [31], although it has limited applicability.

The reduction of (*R*)-(2-[benzylsulfanyl]ethyl)methylphenylphosphine with sodium in liquid ammonia is the final step in Leung and Wild's resolution of ($\pm$)-$MePhPCH_2CH_2SH$ [32] (see Scheme 3). A similar reductive dealkylation was used in the first preparation of $P(C_6H_4SH)_3$ ($ph PS_3H_3$) [33].

2.2. Organic reactivity of phosphino–thiols

2.2.1. Acidity and basicity

The addition of an ω-sulfanylalkyl group tends to reduce the basicity of the phosphine, as can be seen by the pK_a values of the phosphonium ions shown in Table 1. However, the acidity of the thiol is apparently little affected by the ω-phosphinoalkyl group, whether this is free or coordinated [34].



Scheme 3. The resolution of (±)-MePhPCH$_2$CH$_2$SH. [{PdCl[(*R*)-C$_{10}$H$_6$CHMeNMe$_2$-*C*^{2},*N*]}$_2$]: only the (R_C,S_P)-diastereomer can be crystallised, the (R_C,R_P)-diastereomer remaining in solution. (*b*) (*i*) (*R**,*R**)-C$_6$H$_4$(PMePh)$_2$; (*ii*) Na/NH$_3$. Redrawn from Ref. [32].

2.2.2. Photochemical sensitivity

It has been noted in the literature that ethylene-bridged phosphino–thiols are sensitive to photochemical rearrangement to the corresponding ethylphosphine sulfides [32,35]. This has been noted to proceed via the intermediate formation of ethylphosphines and thiophosphinyl–thiols, indicating that the process is intermolecular rather than intramolecular. The reaction proceeds with retention of configuration at the phosphorus centre [35].

It is this type of rearrangement which is undoubdtedly the cause of the 'nitrogen catalysed isomerisation' of *e*PSH [34], and the 'oxidation by molecular nitrogen' of PhHPC$_6$H$_{10}$SH [11]. The photochemical transfer of sulfur from an alkanethiol to a tertiary phosphorus centre has been noted in other systems [36], and it is highly likely that other alkylene-bridged phosphino–thiols are also sensitive to photochemical degradation, with obvious implications for their storage [37].

Photochemical degradation of phenylene-bridged phosphino–thiols has not been reported in the literature, nor has it been observed in our laboratory: this is possibly

Table 1
The acidity constants pK_a of the protonated triethyl phosphino-thiols

	pK_a	Ref.
Et_3PH^+	8.7	[311]
$[Et_2PHCH_2CH_2SH]^+$	7.4	[34]
$[EtPH(CH_2CH_2SH)_2]^+$	6.1	[34]
$[PH(CH_2CH_2SH)_3]^+$	4.2	[34]

because of the lower stability of the phenyl radical (formed after sulfur transfer) than the corresponding alkyl radical.

2.2.3. Other reactions

The phenylene-bridged phosphino–thiolate anions *ph*PS^-, *ph*PS_2^{2-}, $Cy_2PC_6H_4S^-$ and $Ph(C_6H_4MeO\text{-}o)PC_6H_4S^-$ react with $BH_2Cl{\cdot}SMe_2$ to give $H_2B(PS)$, with tetrahedral coordination at boron. The crystal structure of the compound resulting from reaction with PS_2^{2-} and subsequent methylation of the pendent thiolate has also been reported. The compounds dissociate in acid to give the phosphino–thiol ligands, but can be oxidised by *meta*-chloroperbenzoic acid (*m*-CPBA) to give the sulfone derivatives (*S*-coordinated phosphino–sulfinates) [38].

Condensation of primary and secondary phosphino–thiols with carbonyl compounds leads to the production of five-membered 1,3-thiaphospholane rings (from ethylene-bridged phosphino–thiols) and six-membered 1,3-thiaphosphinane rings (from trimethylene-bridged phosphino–thiols) [39].

*e*PSH is one of a number of organic ligands which have been used to catalyse the free-radical chlorination of phenoxytoluene derivatives on the methyl group: it is thought to stabilise the chlorine radical by the formation of a charge transfer complex [40].

2.3. Coordination chemistry of phosphino–thiols and related ligands

2.3.1. Group 1: lithium

Recrystallisation of the lithium salt of *ph**PS_2H_2 in the presence of dimethoxyethane (dme) yields a dimeric complex which has been crystallographically characterised [41] (see Fig. 1). The step-like structure is similar to that in other lithium thiolate oligomers, e.g. $[Li(SBz)(py)]_\infty$ [42], although the steric bulk of the

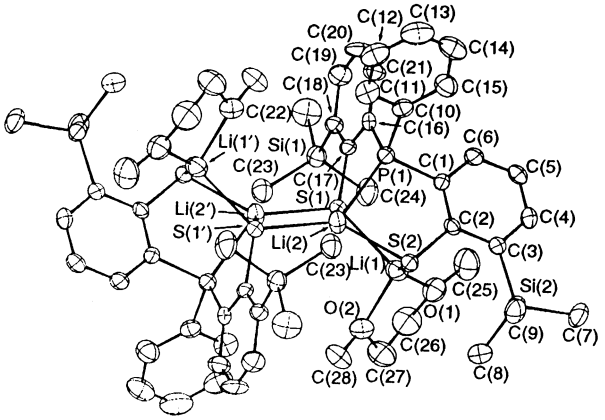


Fig. 1. The solid-state structure of $[\{Li_2(ph\text{*}PS_2)(dme)\}_2]$: trimethylsilyl groups have been omitted for clarity. Reproduced with permission from Ref. [41]: © Royal Society of Chemistry 1996.

trimethylsilyl substituents would appear to prevent higher oligomers forming in this case.

2.3.2. Group 4: titanium

The titanocene complex $[TiCp_2(ePS)_2]$ has been prepared as an air-sensitive purple solid [43]: the analogous complex of a trimethylene phosphino–thiolate ligand, $[TiCp_2(prPS)_2]$, has also been prepared [19]. X-ray diffraction studies on the latter complex, as well as chemical and spectroscopic properties, indicate that the phosphino–thiolate ligands are bound only by the sulfur atoms. These complexes have been used to prepare a number of heterobimetallic complexes (see Section 2.3.13 below).

2.3.3. Group 6: chromium, molybdenum, tungsten

The complexes $[M(ePS)(CO)_4]^-$ (M = Cr, Mo, W) were prepared by reaction of the phosphino–thiolate anion with $[MCl(CO)_5]^-$. The complexes are readily alkylated by iodomethane and by allyl halides [44]. An analogous cyclopentadienyl complex, $[MoCp(ePS)(CO)_2]$, has also been prepared [45].

Chatt et al. have prepared and crystallographically characterised [46] the oxomolybdenum(IV) complex $[MoO(ePS)_2]$. In common with similar complexes, the oxo-group could be protonated to water by strong acids, but the resulting aquo complex could not be isolated: unusually, the oxo-group was inert to condensation reactions with hydrazines. The complex shows an electrochemically reversible reduction process at $E_{1/2} = -1.86$ V in THF solution [47,48].

Reaction of the tridentate phosphino–thiolate ligand ePS_2^{2-} with $[MCl_4(PPh_3)_2]$ (M = Mo, W) leads to the homoleptic complexes $[M(ePS_2)_2]$, of which the molybdenum complex has been crystallographically characterised [49]. These show reversible one-electron oxidations at $E_{1/2} = +0.43$ V (M = Mo), $+0.36$ V (M = W) and reversible one-electron reductions at $E_{1/2} = -0.29$ V (M = Mo), -0.39 V (M = W) in dichloromethane solution: the values for $[Mo(ePS_2)_2]$ may be compared to those for the thioether–thiolate complex $[Mo\{S(CH_2CH_2S)_2\}_2]$ ($E_{1/2} = +0.59$ V, -0.34 V) [49] showing the greater donicity of the phosphine centre compared to the thioether centre.

Reaction of ePS_2^{2-} with the isodiazene complexes $[MCl(NNR_2)_2(PPh_3)_2]^+$ (M = Mo, W; $R_2 = Me_2$, MePh) yields the seven-coordinate complexes $[M(NNR_2)(ePS_2)_2]$. $[Mo(NNMe_2)(ePS_2)_2]$ has been crystallographically characterised [49] (see Fig. 2), as has the phenylene-bridged analogue $[Mo(NNMePh)(phPS_2)_2]$ [50].

Reaction of the phenylene-bridged phosphino–thiolate ligand $phPS^-$ with molybdenum pentachloride yields a mixture of $[Mo_2Cl_3(phPS)_3]$ and $[MoCl_2(phPS)_2]$. The former has been crystallographically characterised, and shows the thiolate sulfur atoms triply bridging a molybdenum–molybdenum triple bond. The complex shows a reversible one-electron reduction at $E_{1/2} = -2.08$ V in dichloromethane solution [51] (see Table 2).

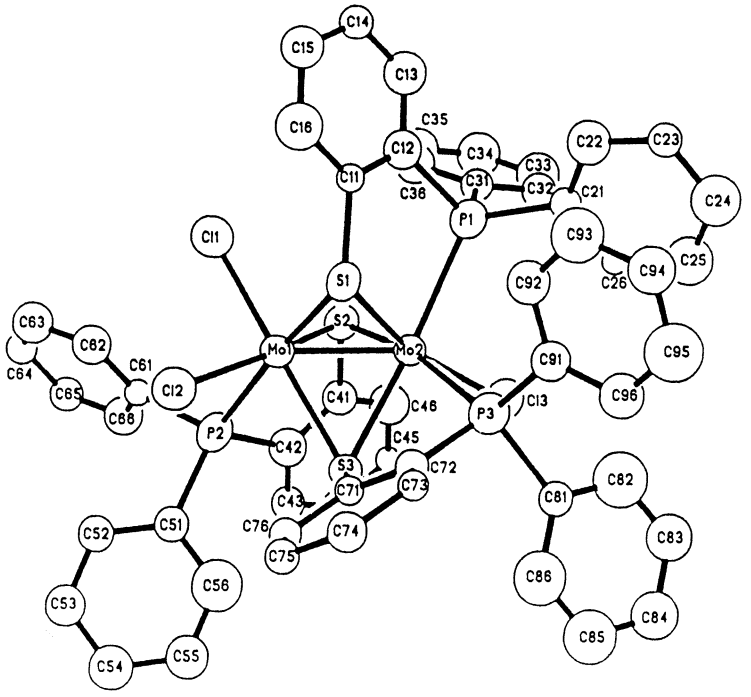


Fig. 2. The solid-state structure of $[Mo_2Cl_3(phPS)_3]$. Reproduced with permission from Ref. [51]: © Elsevier Science 1989.

2.3.4. Group 7: manganese, technetium, rhenium

A dimeric carbonyl–manganese(I) phosphino–thiolate complex has been prepared by the reaction of $[MnBr(CO)_5]$ with ePS^-: its exact formulation is uncertain, but it is thought to be $[\{Mn(ePS\text{-}P,\mu\text{-}S)(CO)_3\}_2]$ by comparison of its IR spectrum with those of other $[\{Mn(\mu\text{-}SR')(CO)_3(PR_3)\}_2]$ complexes [45].

The homoleptic technetium(III) complex of $phPS^-$, $[Tc(phPS)_3]$, has been prepared and crystallographically characterised by both Bolzati et al. [52] (from TcO_4^-) and by Dilworth et al. [53] (from $[TcCl_4(PPh_3)_2]$): the preparation and crystal structure of the rhenium(III) analogue is included in the latter paper, along with a discussion of the electrochemistry of the two complexes. Both complexes show two reversible one-electron oxidations and one reversible one-electron reduction: $E_{1/2} = +1.75$ V, $+1.00$ V, -0.10 V (M = Tc); $+1.52$ V, $+0.74$ V, -0.48 V (M = Re).

Reaction of $[TcOCl_4]^-$ with exactly two equivalents of *ph*PSH at -80°C yields the technetium(V) complex $[TcOCl(phPS)_2]$. Once formed, the complex shows no tendency to disproportionate into technetium(III) species and oxidised ligand ($[Tc(phPS)_3]$ is formed when an excess of ligand is used), although the chloride ligand appears to be relatively labile in polar solvents [53]. However, the rhenium analogue cannot be prepared, as $phPS^-$ always reduces rhenium(V) to rhenium(III)

Table 2
A summary of the known phosphino–thiolate complexes of metals from Groups 6 and 7

	Electrochemistry	Crystal structure	Ref.
$[M(ePS)(CO)_4]^-$ (M = Cr, Mo, W)			[44]
$[(OC)_4Mo(ePS)_2Ni]$		*	[87]
$[MoCp(ePS)(CO)_2]$			[45]
$[Mo(ePS_2)_2]$	*	*	[49]
$[W(ePS_2)_2]$	*		[49]
$[MoO(ePS)_2]$	*	*	[46]
$[Mo(NNMe_2)(ePS_2)_2]$		*	[49]
$[Mo(NNMePh)(ePS_2)_2]$			[49]
$[Mo_2Cl_3(phPS)_3]$	*	*	[51]
$[MoCl_2(phPS)_2]$			[51]
$[Mo(NNMe_2)(phPS_2)_2]$		*	[50]
$[W(NNMeR)(ePS_2)_2]$ (R = Me, Ph)			[49]
$[\{Mn(ePS)(CO)_3\}_2]$[a]			[45]
$[Tc(ePS)_2(SCH_2CH_2POPh_2)]$		*	[55]
$[Tc(prPS)_2\{S(CH_2)_3POPh_2\}]$			[55]
$[M(phPS)_3]$ (M = Tc, Re)	*	*	[52,53,55]
$[Tc(phPS_3)(CNPr^i)_n]$ ($n = 1,2$)		*	[33]
$[Re(ePS)_3]$			[54]
$[Re(ePS)_2(SBz)]$			[54]
$[Re(ePS)_2(SR)]$ (R = Pr^n, Ph, $CH_2CH_2POPh_2$)			[54]
$[Re(ePS_2)(ePS_2H)]$[a]			[49]
$[Re(ePS_2)(ePS_2H)(CO)]$[a]			[49]
$[TcOCl(phPS)_2]$	*		[49,53]
$[TcN(phPS)_2]$	*		[53]
$[ReOCl(ePS)_2]$			[49]

[a] Formulation uncertain.

[53], although the complex with the ethylene-bridged phosphino–thiolate ligand, $[ReOCl(ePS)_2]$, has been prepared [49]. Reaction of $[TcNBr_2(PPh_3)_2]$ with *ph*PSH yields the nitrido–technetium(V) complex $[TcN(phPS)_2]$. The oxo-technetium(V) complex shows an irreversible reduction process at ca. -0.2 V in dichloromethane at room temperature, which becomes pseudo-reversible on cooling to -80°C ($E_{1/2} = -0.05$ V, $\Delta E_p = 0.185$ V). The nitrido-complex is redox-inactive between $+1.5$ V and -1.5 V [53].

Reaction of *e*PSH with $[ReCl_3(MeCN)(PPh_3)_2]$ yields five coordinate rhenium(III) bis(phosphino–thiolate) complexes, in which the fifth coordination site can be occupied by a monodentate thiolate ligand. Hence, $[Re(ePS)_3]$ is five coordinate with one phosphino–thiolate ligand bound by sulfur alone, as is indicated by the upfield ^{31}P-NMR signal (δ_P -16.0: c.f. -20.0 for *e*PSH) and the ease of oxidation of the pendant phosphine group. The analogous complex $[Re(ePS)_2(SBz)]$ has been crystallographically characterised [54]. Reaction of $[TcO_4]^-$ with ePS^- or $prPS^-$ is similar, with the conditions leading to the oxidation of the pendant thiolate group during reaction giving $[Tc(PS)_2\{S(CH_2)_nPOPh_2\}]$ ($n = 2$, 3) [55].

Reaction of $[ReOCl_3(PPh_3)_2]$ with the tridentate phosphino–thiolate anion ePS_2^{2-} leads to reduction of the rhenium centre, giving $[Re(ePS_2)(ePS_2H)]$ (c.f. $phPS^-$, which also leads to reduction and ePS^-, which can form a stable rhenium(V) complex). In the absence of a crystal structure, it is not clear whether the protonated thiol is coordinated or pendant, but the complex reacts rapidly with carbon monoxide to give a carbonyl complex, $[Re(ePS_2)(ePS_2H)(CO)]$ as a mixture of three isomers with the carbonyl *trans* to sulfur [49].

On reaction with $[TcOCl_4]^-$, $phPS_3^{3-}$ gives an unstable dark green complex which reacts with isopropyl isocyanide to give the complexes $[Tc(phPS_3)(CNPr^i)_n]$ ($n = 1$, 2). These complexes show a unique tetradentate binding of the $phPS_3^{3-}$ ligand (see Fig. 3) [33].

2.3.5. Group 8: iron, ruthenium, osmium

Reaction of $[FeBrCp(CO)_2]$ with ePS^- gives the monomeric complex $[FeCp(ePS)(CO)]$ although, as with the dicarbonyl molybdenum complex, the yield is low [45]. The homoleptic iron(III) complexes $[Fe(phPS)_3]$ and $[Fe(phPS_2)_2]^-$ have been prepared, although few properties have been reported [56].

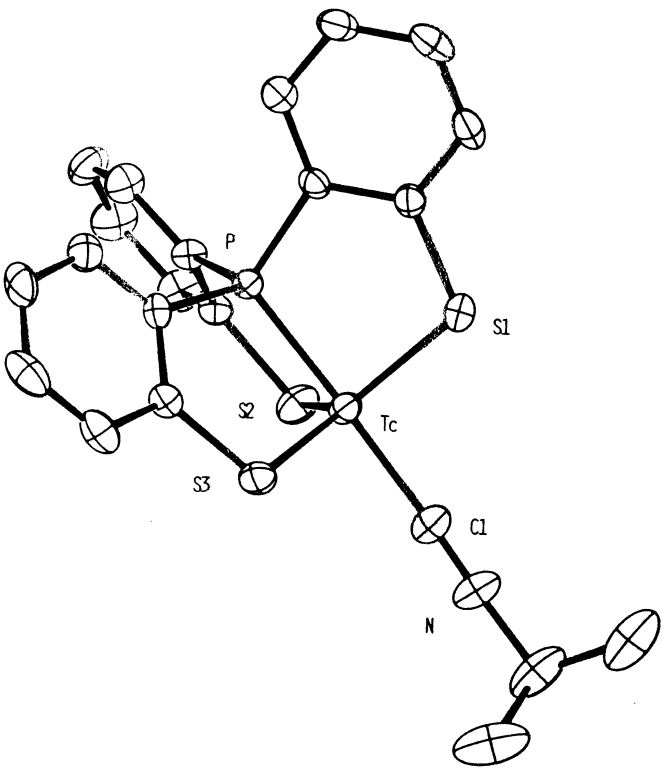


Fig. 3. The solid-state structure of $[Tc(phPS_3)(CNPr^i)]$, showing the unique tetradentate coordination of the phosphino–thiolate ligand. Reproduced with permission from Ref. [33]: © Elsevier Science 1989.

Reaction of $[RuCl_2(PPh_3)_3]$ with $phPS^-$ yields the anionic ruthenium(II) complex $[Ru(phPS)_3]^-$: this is readily oxidised in air, first to the neutral ruthenium(III) analogue $[Ru(phPS)_3]$, and then to the sulfur oxidised complex $[Ru(phPS)(Ph_2PC_6H_4SO\text{–}P,S)(Ph_2PC_6H_4SO_2\text{–}P,S)]$ [57]. This latter complex, which has been crystallographically characterised (see Fig. 4), shows rare examples of *S*-coordinated sulfenate and sulfinate groups [58]. The electrochemistry of these complexes in dichloromethane solution has also been studied: $[Ru(phPS)_3]^-$ shows a pseudo-reversible oxidation at $E_{1/2} \approx +0.05$ V; $[Ru(phPS)_3]$ shows a reversible oxidation at $E_{1/2} = +0.73$ V and a reversible reduction at $E_{1/2} = -0.07$ V; $[Ru(phPS)(Ph_2PC_6H_4SO)(Ph_2PC_6H_4SO_2)]$ shows a reversible oxidation at $E_{1/2} = +0.76$ V and a reversible reduction at $E_{1/2} = -0.14$ V [57].

$[MCl_2(PPh_3)_3]$ (M = Ru, Os) react with the tridentate ligand $phPS_2^{2-}$ to give the M^{III} homoleptic complexes $[M(phPS_2)_2]^-$. The osmium complex $[OsCl_2(PPh_3)_3]$ reacts with $phPS_3H_3$ in the presence of base to give $[Os(phPS_3H)_2]^-$, which rapidly transforms on attempted recrystallisation to a complex of a novel hexadentate ligand formed from the oxidation of the two $phPS_3H^{2-}$ units with the formation of

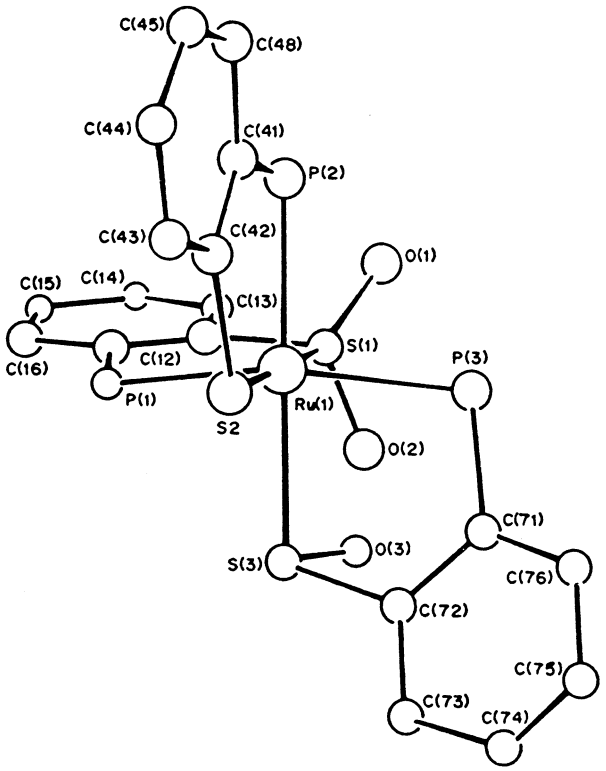


Fig. 4. The solid-state structure of $[Ru(phPS)(Ph_2PC_6H_4SO)(Ph_2PC_6H_4SO_2)]$, formed by atmospheric oxidation of $[Ru(phPS)_3]$. Reproduced with permission from Ref. [57]: © Kluwer Academic Publishers 1994.

two disulfide bridges. The reaction of $[RuCl_2(PPh_3)_3]$ with $phPS_3H_3$ in the presence of base is thought to be analogous [59].

2.3.6. Group 9: cobalt, rhodium, iridium

$CoCl_2$ reacts with $H_2PCH_2CHRS^-$ (R = H, Me) to give the cobalt(III) complexes $[Co(H_2PCH_2CHRS)_3]$, along with dihydrogen. The latter complex reacts with CoX_2 (X = Cl, Br, I, SCN) to give hetero-dimeric complexes $[Co(H_2PCH_2CHMeS)CoX_2]$, which are assumed to be thiolate-bridged. The complex also reacts with dimethyl sulfate or Et_3O^+ to give the corresponding phosphino–thioether complexes (see Section 5.1.3 and Table 3). $[Co(H_2PCH_2CH_2S)_3]$ can be *P*-deprotonated by potassium in liquid ammonia to give the phosphido–thiolate complex $[Co(HPCH_2CH_2S)_3]^{3-}$, which was isolated as the potassium salt. This reacts with 1-bromobutane, chlorotrimethylsilane and chlorotriethyltin to give the corresponding secondary phosphino–thiolate complexes $[Co(RHPCH_2CH_2S)_3]$ (R = Bu^n, Me_3Si, Et_3Sn) [60,61].

$[CoBr_3(NH_3)_3]$ reacts with the tetradentate phosphino–thiol ligand $HSCH_2CH_2PH(CH_2)_3PHCH_2CH_2SH$ to give the complex $[CoBr\{SCH_2CH_2PH(CH_2)_3PHCH_2CH_2S)(NH_3)]$: the analogous rhodium complex has been claimed, but has not been well characterised [60,61].

Table 3
Phosphino–thiolate complexes of rhodium and iridium

	Crystal structure	Ref.
$[Rh(H_2PCH_2CHRS)_3]$ (R = H, Me)[a]		[60]
$[Rh(RHPCH_2CH_2S)_3]$ (R = Me_3Si, Et_3Sn)[a]		[60]
$[\{Rh(ePS)(CO)\}_2]$		[62]
$[\{Rh(phPS)(CO)\}_2]$	*	[62]
$[\{Rh(ph*PS)(CO)\}_2]$		[12]
$[\{Rh(Ph_2PC_6H_{11}S)(CO)\}_2]$		[12]
$[\{M(phPS)(\eta^1\text{-cod})\}_2]$ (M = Rh, Ir)		[12]
$[M(phPS)(CO)(PPh_3)]$ (M = Rh, Ir)		[66]
$[M(phPS)(SO_2)(CO)(PPh_3)]$ (M = Rh, Ir)		[66]
$[Rh(phPS)_3]$		[68]
$[Rh(ph*PS)_3]$		[56,68]
$[Rh(phPS_2)_2]^-$		[56,59]
$[Ir(H_2PCH_2CH_2S)_3]$[a]		[60]
$[Ir(ePS)(CO)(PPh_3)]$		[67]
$[IrH(ePS)(ePSH)(CO)]^+$	*	[67]
$[IrH_2(phPS)(CO)(PPh_3)]$		[66]
$[Ir(phPS)_3]$	*	[68]
$[IrH(phPS)_2(CO)]$		[56,68]
$[IrH(ph*PS)_2(CO)]$		[56,68]
$[IrCl_2(phPS)(PMe_2Ph)_2]$	*	[68]
$[Ir(phPS_2)_2]^-$		[56,59]

[a] Formulation uncertain [61].

$RhCl_3 \cdot 3H_2O$ reacts with the primary phosphino–thiolate ligands $H_2PCH_2CHRS^-$ (R = H, Me) to form $[Rh(H_2PCH_2CHRS)_3]$: the chemistry of these complexes is analogous to that of the cobalt(III) analogues described above. $[IrCl_6]^{3-}$ reacts with $H_2PCH_2CH_2S^-$ to give $[Ir(H_2PCH_2CH_2S)_3]$ [60,61].

The present authors have prepared the complexes $[\{Rh(PS)(CO)\}_2]$ (PS– = *e*PS$^-$, *ph*PS$^-$, *ph**PS$^-$, $Ph_2PC_6H_{10}S^-$) by reaction of a stoichiometric quantity of PS$^-$ with a methanolic solution of $[\{RhCl(CO)_2\}_2]$: the *ph*PS$^-$ complex has been crystallographically characterised. $[\{M(phPS)(cod)\}_2]$ (M = Rh, Ir) were prepared by the reaction of *ph*PS$^-$ with $[\{MCl(cod)\}_2]$: the cyclooctadiene ligand is monodentate, and the complexes are assumed to be sulfur-bridged dimers as are the carbonyl species [12,62].

$[\{Rh(ePS)(CO)\}_2]$ and $[\{Rh(phPS)(CO)\}_2]$ are highly efficient catalysts for the carbonylation of methanol to acetic acid, showing up to four times the activity of the classical catalyst $[RhI_2(CO)_2]^-$ [62,63]. The cause of this increased reactivity is not entirely apparent, but may be due to increased electron density on the rhodium atom or to participation by the sulfur in the catalytic cycle. It has been suggested [64] that a salt effect (from phosphonium salts formed by degradation of the complex) may be responsible for the enhanced rates: although specific salt effects have been observed in the carbonylation of iodomethane [65], particularly with tetraphenylarsonium salts, ^{31}P-NMR studies indicate that the phosphino–thiolate ligand remains coordinated to the rhodium.

The mononuclear rhodium(I) and iridium(I) phosphino–thiolate complexes $[M(phPS)(CO)(PPh_3)]$ have been prepared from the reaction of *ph*PS$^-$ and $[MCl(CO)(PPh_3)_2]$. These complexes reversibly bind sulfur dioxide, and the iridium complex reversibly adds dihydrogen [66].

Stephan [67] has prepared the Vaska-type compound $[Ir(ePS)(CO)(PPh_3)]$ by reaction of *e*PS$^-$ with $[IrCl(CO)(PPh_3)_2]$. This compound reacted with *e*PSH to give an iridium(III) complex containing a coordinated phosphino–thiol ligand, $[IrH(ePS)(ePSH)(CO)]^+$, which was crystallographically characterised (see Fig. 5). In an analogous reaction, *ph*PSH and *ph**PSH react with $[IrCl(CO)(PPh_3)_2]$ in methanol in the presence of NEt_3 to give $[IrH(phPS)_2(CO)]$ and $[IrH(ph*PS)_2(CO)]$, with the more acidic arenethiol ligands both being deprotonated [56,68].

Reaction of an excess of *ph*PS$^-$ or *ph*PS$_2^{2-}$ with $MCl_3 \cdot xH_2O$ (M = Rh, Ir) leads to the production of $[M(phPS)_3]$ and $[M(phPS_2)_2]^-$ respectively: $[Rh(phPS_2)_2]^-$ and $[Rh(ph*PS)_3]$ can also be prepared by reaction of *ph*PS$_2^{2-}$ or *ph**PS$^-$ respectively with $[RhCl(PPh_3)_3]$ [56,68]. The crystal structure of $[Ir(phPS)_3]$ has been determined, and is analogous to that of other tris(phosphino–thiolate) complexes: the complex also shows a broad, irreversible oxidation process at $E \approx +0.89$ V. Reaction of *ph*PS$^-$ with $[IrCl_3(PMe_2Ph)_3]$ leads to the mixed ligand iridium(III) complex $[IrCl_2(phPS)(PMe_2Ph)_2]$ which has also been crystallographically characterised [68].

2.3.7. Group 10: nickel, Palladium, Platinum

The coordination chemistry of nickel(II) with various phosphino–thiolate ligands has been extensively studied (see Table 4). For the most part, it is completely analogous to the chemistry of palladium(II) discussed below. Particularly note-

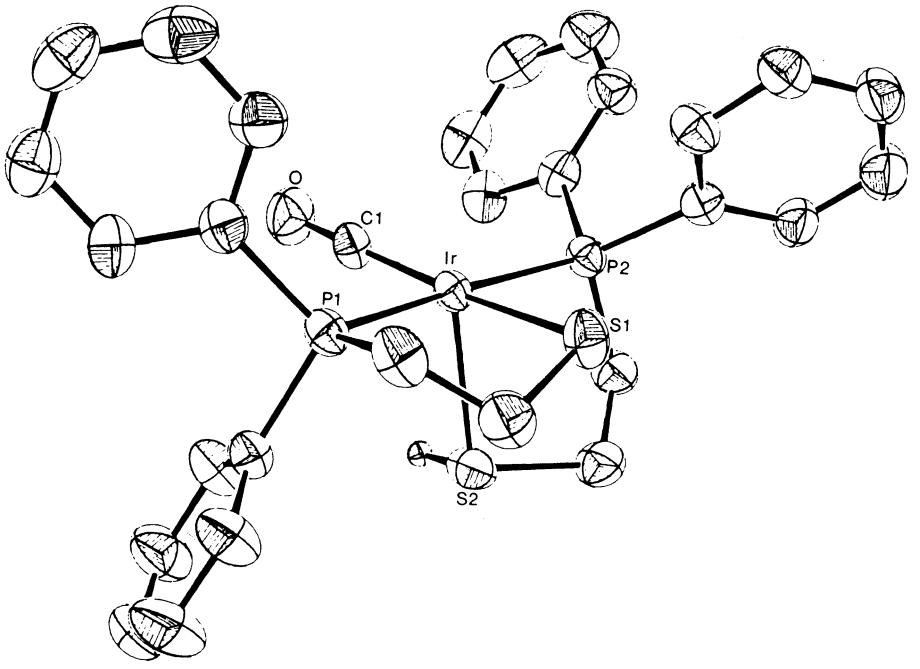


Fig. 5. The solid-state structure of $[IrH(ePS)(ePSH)(CO)]^+$. Reproduced with permission from Ref. [67]: © American Chemical Society 1984.

worthy reactions include the formation of the thiolate-bridged complexes $[Ni(ePS)_2Ni(ePS)]^+$ and $[\{Ni(Et_2PCH_2CH_2S)_2\}_2Ni]^{2+}$ from $[Ni(H_2O)_6]^{2+}$ and the bis(phosphino–thiolate) complexes [34,69]. These reactions appear to involve the isomerisation of the original monomeric complex from the *trans*- to the *cis*-isomer: such solution isomerisation is also seen in $[Ni(MePhECH_2CH_2S)_2]$ (E = P, As) [70].

Palladium(II) and platinum(II) complexes of the primary phosphino–thiolate ligands $H_2PCH_2CHRS^-$ (R = H, Me) [71] and the secondary phosphino–thiolate ligands $[SCHRCH_2PH(CH_2)_2PHCH_2CHRS]^{2-}$ (R = H, Me) [60] and $Bu^nHPCH_2CH_2S^-$ [71] have been prepared (see Table 5). The complexes are readily *S*-alkylated on one or both sulfurs to prepare phosphino–thioether complexes (see Section 5.1.3 and 5.2.5). The complexes $[M(H_2PCH_2CHMeS)_2]$ (M = Ni, Pd, Pt) can be *P*-deprotonated by potassium in liquid ammonia: the resulting phosphido–thiolate species are readily *P*-alkylated by 1-bromobutane to give $[M(Bu^nHPCH_2CHMeS)_2]$.

Most of the known complexes of nickel(II) and palladium(II) with phenylene–bridged phosphino–thiolate ligands have been formed by the dealkylation of coordinated phosphino–thioethers. Hence $[PdCl_2(phPSMe)]$ is dealkylated by benzylamine or phenethylamine to give $[\{PdCl(phPS)\}_2]$, and $[Pd(phPSMe)_2]^{2+}$ is similarly demethylated to give $[Pd(phPS)_2]$ [72]. $[PdI_2(phPSMe)]$ demethylates on standing overnight in ethanol solution [73]. $[M(Ph_2PC_6F_4S)_2]$ (M = Ni, Pd) are

prepared by the demethylation of $[MX_2(Ph_2PC_6F_4SMe)]$ (X = Cl, Br, SCN): the nickel complex demethylates on standing in dichloromethane solution alone or in the presence of iodide ions, whereas the palladium complex requires refluxing in DMF in the presence of excess ligand. If this excess ligand is not present, the dimeric complex $[\{PdCl(Ph_2PC_6F_4S)\}_2]$ is formed instead [74]. $[M\{PhP(C_6F_4SMe)(C_6F_4S)\}_2]$ and $[\{Pd\{PhP(C_6F_4SMe)(C_6F_4S)\}(SCN)\}_2]$ are prepared by dealkylation of $[MX_2\{PhP(C_6F_4SMe)_2\}]$: the remaining thioether group is presumably pendant, and shows no tendency to demethylate [74].

The complexes $[\{PdI(phES)\}_2]$ and $[\{PdI[PhE(C_6H_4SMe)(C_6H_4S)]\}_2]$ (E = P, As) were prepared by demethylation of the phosphino– and arsino–thioether complexes $[PdI_2(phESMe)]$ and $[PdI_2\{PhE(C_6H_4SMe)_2\}]$ in DMF solution. $[Pd(phES)_2]$ and $[Pd\{PhE(C_6H_4SMe)(C_6H_4S)\}_2]$ were similarly prepared from $[Pd(phESMe)_2]^{2+}$ and $[Pd\{PhE(C_6H_4SMe)_2\}_2]^{2+}$. Alkylation of $[Pd\{PhAs(C_6H_4SMe)(C_6H_4S)\}_2]$ with *p*-nitrobenzyl bromide gave $[PdBr_2\{PhAs(C_6H_4SMe)(C_6H_4SCH_2C_6H_4NO_2)\}]$, which could be demethylated to give $[\{PdBr[PhAs(C_6H_4SCH_2C_6H_4NO_2)(C_6H_4S)]\}_2]$ [75].

All four possible diastereomers are formed when (±)-$MePhECH_2CH_2SH$ (E = P, As) is reacted with $[Pd(MeCN)_4]^{2+}$ in acetonitrile in the presence of base. When the racemic ligand is reacted with $[PtCl_4]^{2-}$, only the two *cis*-diasteromers are formed initially: the phosphino–thiolate complex does not isomerise at room temperature, but an equilibrium mixture of the four diastereomers of the arsino–thiolate complex is formed within 18 h in $CDCl_3$ solution [70]. In contrast, reaction of (±)-$(MeOCH_2C_6H_4)MePCH_2CH_2SH$ with $[PtCl_4]^{2-}$ gives all four diasteromers of $[Pt(ArMePCH_2CH_2S)_2]$, with a 7:2 preference for the *trans*-diastereomers: again, there is no evidence of isomerism [76].

Table 4
Phosphino–thiolate and arsino–thiolate complexes of nickel

	Crystal structure	Ref.
$[Ni(H_2PCH_2CHRS)_2]$ (R = H, Me)[a]		[71]
$[Ni(Bu^nHPCH_2CHMeS)_2]$[a]		[71]
$[Ni(SCHRCH_2PH(CH_2)_2PHCH_2CHRS)]$ (R = H, Me)[a]		[60]
$[Ni(SCH_2CH_2PH(CH_2)_4PHCH_2CH_2S)]$[a]		[60]
$[Ni(ePS)_2]$	*	[34,69,87,243,312]
$[Ni(R_2PCH_2CH_2S)_2]$ (R = Et, $HSCH_2CH_2$)		[34]
$[Ni\{SCH_2CH_2P(CH_2CH_2SHgMe)_2\}_2]$		[34]
$[Ni(MePhECH_2CH_2S)_2]$ (E = P, As)		[70]
$[(OC)_4Mo(ePS)_2Ni]$	*	[87]
$[Ni(ePS)_2Ni(ePS)]^+$		[69]
$[\{NiBr(ePS)\}_2]$	*	[313]
$[\{Ni(Et_2PCH_2CH_2S)_2\}_2Ni]^{2+}$		[34]
$[\{Ni[RP(CH_2CH_2S)_2]\}_2]$ (R = Et, Ph)		[34]
$[\{Ni(ePS_3H)\}_2]$	*	[34]
$[Ni(Ph_2PC_6F_4S)_2]$		[74]
$[Ni\{PhP(C_6F_4SMe)(C_6F_4S)\}_2]$		[74]

[a] Formulation uncertain [61].

Table 5
Phosphino– and arsino–thiolate complexes of palladium and platinum[a]

	Crystal structure	Ref.
$[M(H_2PCH_2CHRS)_2]$ (R = H, Me)[b]		[71]
$[M(Bu^nHPCH_2CHMeS)_2]$[b]		[71]
$M(SCHRCH_2PH(CH_2)_2PHCH_2CHRS)]$ (R = H, Me)[b]		[60]
$[M(R_2PCH_2CH_2S)_2]$ (R = Et, Ph, $HSCH_2CH_2$)		[34]
$[Pd(MePhECH_2CH_2S)_2]$ (E = P, As)		[70]
[LPd(MePhPCH$_2$CH$_2$S-P,μ-S)PdClL][c]		[32]
[LPd(MePhPCH$_2$CH$_2$S)][c]		[32]
$[Pd(phPS)_2]$	*	[72,73,82]
$[Pd(Ph_2PC_6F_4S)_2]$		[74]
$[Pd\{PhE(C_6H_4SMe)(C_6H_4S)\}_2]$ (E = P, As)		[75]
$[Pd\{PhP(C_6F_4SMe)(C_6F_4S)\}_2]$		[74]
[LPd(MePhAsCH$_2$CH$_2$S-As,μ-S)PdClL][c]	*	[77]
[LPd(MePhAsCH$_2$CH$_2$S)][c]		[77]
$[Pd\{(MeOCH_2C_6H_4)MeAsCH_2CH_2S\}_2]$	*	[78,314]
[LPd{(MeOCH$_2$C$_6$H$_4$)MeAsCH$_2$CH$_2$S-As,μ-S}PdClL][c]		[78]
[LPd{(MeOCH$_2$C$_6$H$_4$)MeAsCH$_2$CH$_2$S}][c]		[78]
$[Pd(phAsS)_2]$		[75]
$[\{PdCl(phPS)\}_2]$		[72]
$[\{PdI(phPS)\}_2]$	*	[75]
$[\{PdI[PhE(C_6H_4SMe)(C_6H_4S)]\}_2]$ (E = P, As)		[75]
$[\{PdCl(Ph_2PC_6F_4S)\}_2]$		[74]
$[\{Pd[PhP(C_6F_4SMe)(C_6F_4S)](SCN)\}_2]$		[74]
$[\{PdI(phAsS)\}_2]$		[75]
$[\{PdBr[PhAs(C_6H_4SCH_2C_6H_4NO_2)(C_6H_4S)]\}_2]$		[75]
$[Pt(MePhECH_2CH_2S)_2]$ (E = P, As)		[70]
$[Pt\{(MeOCH_2C_6H_4)MeAsCH_2CH_2S\}_2]$		[76]
$[Pt(Et_2PCH_2CH_2S)_2Pt(CN)_2]$		[69]
$[Pt(phPS)_2]$		[82]

[a] Throughout this table, M = Pd, Pt unless otherwise stated.
[b] Formulation uncertain [61].
[c] L = (C^2,κ*N*-(*R*)-1-(1-dimethylaminoethyl)-2-naphthyl.

The resolution of (±)-$MePhPCH_2CH_2SH$ via the diastereomeric complex [{(*R*)-$C_{10}H_6CHMeNMe_2$–*C*,*N*}Pd(MePhPCH$_2$CH$_2$S)PdCl{(*R*)-$C_{10}H_6CHMeNMe_2$–*C*,*N*}] has been described above (see Section 2.1.7 and Scheme 3). The arsenic analogue (±)-$MePhAsCH_2CH_2SH$ can also be resolved by a similar procedure, although in this case benzylation of the thiolate group is unnecessary as the arsino–thiol may be liberated from the complex [Pd($C_{10}H_6CHMeNMe_2$)(MePhAsCH$_2$CH$_2$S)] by treatment with cyanide [77]. (±)-($MeOCH_2C_6H_4$)$MeAsCH_2CH_2SH$ may be resolved by a similar method [78].

2.3.8. Group 11: gold

A number of phosphino–thiolate complexes of gold(I), $[\{Au[S(CH_2)_nPR_2]\}_2]$ (R = Et, Ph; *n* = 2–4) have been prepared. The complexes exist as head-to-tail

dimers with linear two-coordinate gold(I) centres: the $n = 2$ complex (R = Et) has been crystallographically characterised [79] (see Fig. 6). These complexes have been shown to inhibit the development of adjuvent arthritis in rats [80,81]. When $ph\mathrm{PS}^-$ is used as the ligand, polymeric products are formed [82].

Reaction of $ph\mathrm{PS}^-$ with $[\mathrm{AuCl_4}]^-$ gives the square-planar gold(III) complex $[\mathrm{Au}(ph\mathrm{PS})_2]^+$, which has been crystallographically characterised. The complex shows a reversible one-electron reduction at $E_{1/2} = -1.40$ V in acetonitrile solution [82].

2.3.9. Group 12: mercury

The only known phosphino–thiolate complex of a group 12 element is $[\mathrm{Ni}\{\mathrm{SCH_2CH_2P(CH_2CH_2SHgMe)_2}\}_2]$, formed by reaction of MeHgCl with $[\mathrm{Ni}(e\mathrm{PS_3H_2})_2]$ [34].

2.3.10. Group 13: gallium, indium

The group 13 phosphino–thiolate complexes $[\mathrm{Ph_2M}(e\mathrm{PS})]$ and $[\mathrm{Ph_2M(SCHMeCH_2PPh_2)}]$ (M = Ga, In) and the stibino–thiolate complexes $[\mathrm{Ph_2M(SCH_2CH_2SbPh_2)}]$ have been prepared as possible MOCVD precursors of III–V semiconductors [83]. The latter are the only known complexes of a stibino–thiolate ligand.

2.3.11. Group 14: tin

Reaction of $ph^*\mathrm{PS_2H_2}$ with $[\mathrm{Sn}\{\mathrm{N(SiMe_3)_2}\}_2]$ yields the tin(II) complex $[\{\mathrm{Sn}(ph^*\mathrm{PS_2})\}_2]$, which has been crystallographically characterised [41]. The stability of the tin(II) complex in this case contrasts with the instability of (pyridine-2-thiolato)tin(II) complexes, which disproportionate to metallic tin and tin(IV) complexes [84].

2.3.12. The lanthanides

Reaction of samarium(III) iodide with $ph\mathrm{PS_2H_2}$ or $ph^*\mathrm{PS_2H_2}$ in the presence of excess triethylamine and pyridine yields the eight-coordinate complexes

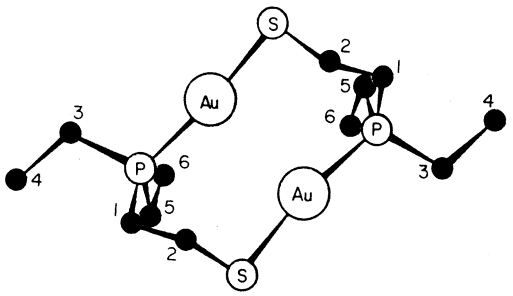


Fig. 6. The solid-state structure of $[\{\mathrm{Au(SCH_2CH_2PEt_2)}\}_2]$. Reproduced with permission from Ref. [79]: © Elsevier Science 1978.

$[Sm(phPS_2)_2(py)_2]^-$ and $[Sm(ph*PS_2)_2(py)_2]^-$, which have been crystallographically characterised. Reaction of the lithium salt of $phPS_2H_2$ with ytterbium(II) iodide yields a black ytterbium(II) complex which is rapidly oxidised by adventitious oxygen to a red ytterbium(III) complex (also air-sensitive): neither complex has been fully characterised [41].

2.3.13. Heterobimetallic complexes

The complexes $[TiCp_2\{Ph_2P(CH_2)_nS\}_2]$ ($n=2$, 3), in which the phosphino–thiolate ligands are bound solely by the sulfur atoms leaving two pendant phosphine groups (see Section 2.3.2), have been used as precursors for a number of heterobimetallic phosphino–thiolate complexes.

Reaction with $[Cu(MeCN)_4]^+$ yields the complex $[Cp_2Ti(ePS)_2Cu]^+$, which has been crystallographically characterised [43]. Although the question of metal–metal bonding in this type of 'early–late' heterobimetallic compound is still open [85,86], the appearance of a number of low energy bands in the electronic spectrum suggest that a Cu–Ti interaction may possibly exist in this system. The complex also exhibits a rare electrochemically reversible Ti^{IV}–Ti^{III} couple at $E_{1/2} = -0.99$ V.

Reaction of the trimethylene-bridged titanium complex $[Cp_2Ti(prPS)_2]$ with $[\{RhCl(nbd)\}_2]$ yielded a brown–black heterobimetallic complex $[Cp_2Ti(prPS)_2Rh]^+$ [19]. It is not clear whether there is any significant Ti–Rh interaction in this complex, although again the appearance of low energy bands in the electronic spectrum would suggest that this is possible. The complex undergoes a reversible reduction at $E_{1/2} = -0.87$ V: the reduction can also be effected chemically with Cp_2Co, yielding a neutral complex $[CpTi(prPS)_2Rh]$. The ESR spectrum showed parameters consistent with the unpaired electron residing primarily on the titanium centre ($g = 1.979$, $a < {}^{47}Ti/{}^{49}Ti > = 0.90$ mT), as well as hyperfine coupling to the ^{103}Rh nucleus ($a = 0.28$ mT) and to two equivalent ^{31}P nuclei ($a = 0.18$ mT).

The compound $[(OC)_4Mo(ePS)_2Ni]$, formed by the reaction of $[Mo(CO)_4(nbd)]$ and *trans*-$[Ni(ePS)_2]$ shows a short M–M′ distance (2.998 Å) and a dihedral angle between the MoS_2 and NiS_2 planes of 103.4°, at the smaller end of the range for thiolate bridged complexes of d^8 metals [87].

2.3.14. Phosphino–selenolate complexes

$[NiCl_2(phPSeMe)]$ readily demethylates in refluxing butanol to give $[Ni(phPSe)_2]$ [88], which has been crystallographically characterised [89].

$[Pd(SCN)_2(phPSeMe)]$ also readily dealkylates on refluxing in butanol to give a species formulated as $[\{Pd(SCN)(phPSe)\}_2]$, thought to be a selenolato-bridged dimer. $[\{Pd(phPSe)_2\}_n]$ can be formed from the reaction of $phPSeMe$ with $K_2[Pd(NO_3)_4]$ in the presence of DMF: it is highly insoluble in common solvents and is thought to be a selenolato-bridged polymer [88].

Table 6
The physical and infrared spectroscopic properties of some phosphino–thioformamides[a]

	m.p. (°C)	ν_1(NCS) (cm^{-1})	ν_2(NCS) (cm^{-1})	ν(N–H) (cm^{-1})
MePTFH	118–20	1502	1337	3360 3340
MePTFMe		1479	1377	
PhPTFH	107–10	1523	1384	3300
PhPTFMe		unresolved	1355	
$PhPTFSiMe_3$	94–96	1530	1320	
$Cy_2PCSNHPh$	114–16	1495	1330	3200

[a] See text for a discussion of ν_1(NCS) and ν_2(NCS).

3. Hetero-allylic ligands: phosphino–thioformamides and phosphino–dithioformates

3.1. Preparation of phosphino–thioformamides and phosphino–dithioformates

3.1.1. Preparation of phosphino–thioformamides

Phosphino–thioformamides were first prepared in 1964, by the addition of diphenylphosphine across the C=N double bond of an aryl isothiocyanate [90]. *N*-Alkyl analogues can be prepared, although here the nucleophilic attack of a secondary phosphide anion is preferred to the addition reaction. The reaction of alkali metal phosphides with thiocarbamoyl chlorides has also been used to prepare phosphino–thioformamide ligands [91], and this method can be used to prepare *N*,*N*-disubstituted ligands. The *N*-silylated ligands have been prepared by the insertion of isothiocyanates into the P–Si bond of Ph_2PSiMe_3 [92].

A related ligand, *N*,*N*-dimethyl-2-(diphenylphosphino)acetothioamide, $Ph_2PCH_2CSNMe_2$, has been prepared by the deprotonation of CH_3CSNMe_2 with butyllithium followed by reaction with chlorodiphenylphosphine: the coordination chemistry of this compound has not been studied [93].

The free thioformamides are usually considered to exist primarily in the *N*-protonated form, although the C–N bond has been shown to have considerable double bond character, and geometric (*E*/*Z*) isomers of simple thioamides can be separated by thin-layer chromatography [94].

The physical and spectroscopic propeties of some phosphino–thioformamides are given in Tables 6 and 7.

3.1.2. Preparation of phosphino–dithioformates

Phosphino–dithioformates are prepared by the reaction of secondary phosphines with carbon disulfide in the presence of a base such as potassium hydroxide [95] or triethylamine [96], or by the reaction of an alkali metal phosphide with carbon disulfide [97,98]. The trimethylsilyl ester $Ph_2PCS_2SiMe_3$ has been prepared by the insertion of carbon disulfide into the P–Si bond of Ph_2PSiMe_3 [92]. The crystal-structure of the free anionic ligand $Ph_2PCS_2^-$ (as its tetraethylammonium salt) has been determined [99].

3.2. Coordination chemistry of phosphino–thioformamides

3.2.1. Modes of coordination

The phosphino–thioformamide ligand contains three atoms — nitrogen, phosphorus and sulfur — with a lone pair capable of coordination to a metal centre, and hence a large number of binding modes can be envisaged.

Of the monodentate modes, only (*P*)-monodentate coordination has been unequivocally identified. It has often been proposed for the binding of neutral ligands by analogy with complexes of phosphino–thioethers (see Section 5.2) — examples include [M(CO)(RPTFR′)] (M = Cr, Mo, W; R′ = H, Me, $SiMe_3$) [100] and [RhCl(CO)$(PhPTFH)_2$] [101] — and it has been crystallographically characterised in cadmium and mercury complexes of $Cy_2PCSNHPh$.

(*N*)-Monodentate coordination seems possible in the compound [Ph_3Sn(PhPTF)], with the infrared spectrum showing ν(C=S) at 1158 cm^{-1} (see Section 3.2.2) and no apparent band corresponding to ν(Sn–S) but, in the absence of ^{31}P-NMR data, a zwitterionic structure with (*P*)-coordination cannot be ruled out [103]. The assignment of (*N*)-monodentate coordination for the complexes [R′Zn(RPTF)] must be considered speculative given the absence of any positive evidence in favour of the supposition [104]. (*S*)-monodentate coordination has yet to be claimed for a phosphino–thioformamide complex.

All three of the possible bidentate modes — (*N*,*P*), (*N*,*S*) and (*P*,*S*) — have been identified in X-ray structure determinations. Of these, the first two have only been shown in the two isomers of [Mo_2(MePTF)$_4$] (see Fig. 7), although it is likely that the *N*-phenyl analogue also contains (*N*,*S*)-coordinated ligands: in these compounds, the phosphino–thioformamide ligands are bridging a molybdenum–molybdenum quadruple bond [105].

(*P*,*S*)-chelation is by far the most common binding mode for phosphino–thioformamide ligands, both neutral and deprotonated. Four examples have been crystallographically characterised [106]: [$Cr(CO)_4$(MePTFH)] [107], [Mn(Ph-

Table 7
NMR spectroscopic properties of some phosphino–thioformamides[a]

	δ_H	δ_C	$^1J_{CP}$ (Hz)	δ_P
MePTFH	8.42	206.7	34	+15.9[c]
		208.5	37	
MePTFMe		208.9	33.0	+17.9[c]
EtPTFH	9.50	205.7	34	
PhPTFH	8.70	208.9	37	+19.2[b]
				+23.2[c]
$PhPTF^-K^+$				+9.2[c]
$Cy_2PCSNHPh$				+44.3[b]

[a] δ_H is given only for the N–*H* proton, δ_C is given only for *C*=S.
[b] $CDCl_3$ solution.
[c] THF-d_8 solution.

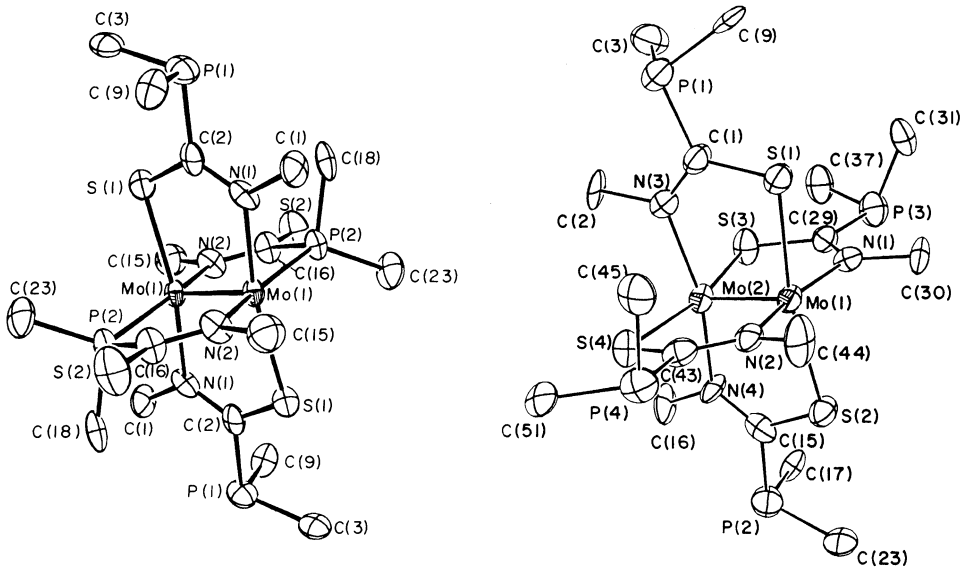


Fig. 7. The solid-state structures of the two isomers of $[Mo_2(MePTF)_4]$. Reproduced with permission from Ref. [105]: © American Chemical Society 1984.

PTF)$(CO)_4$] and *fac*-[MnBr$(CO)_3$(PhPTFH)] [108], and [RuCp′(PhPTF)(PPh_3)] [109]. One isomer of $[Mo_2(MePTF)_4]$ provides an example of (*P*,*S*)-coordination across a metal–metal bond [110].

A single example of tridentate coordination of a phosphino–thioformamide ligand has been unequivocally indenified: in $[\{Mo(MePTF)_2(CO)_2\}_2]$, one of the phosphino–thioformamide ligands is (*P*,*S*)-chelated to a single metal centre while the other is (*N*,*S*)-chelated to one metal centre and (*P*)-bound to the other, creating a bridged structure (see Fig. 8) [111,112]. A similar structure has been proposed [101] for the rhodium(I) complex $[\{Rh(RPTF)(CO)\}_4]$ but, in the absence of a crystal structure or any precedent for such coordination to a rhodium(I) centre, the ascription must be considered tentative.

One further bonding mode has been described: there is strong evidence that the phosphino–thioformamide ligand in [Pt$(PPh_3)_2$(PhPTFH)] is bound in a η^2-C=S fashion (see Fig. 9), although it is impossible to grow crystals due to its decomposition to a hydrido–platinum(II) complex [113].

Although many crystal structure determinations have been carried out on phosphino–thioformamide complexes, in the majority of cases the structure has been assigned by a combination of spectroscopic analysis and chemical intuition. While chemical intuition is usually recognised as such and justified by the authors in their reports, the assumptions underlying the spectroscopic analysis of phosphino–thioformamide complexes have not been critically discussed to date. These assumptions, particularly those concerning the effect of coordination on the IR spectrum, may prove to be invalid, casting doubt on structural assignments made on that basis.

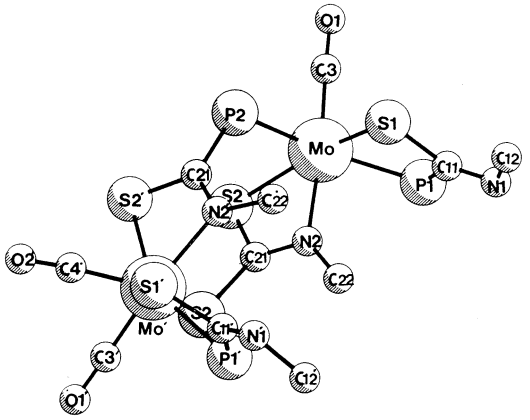


Fig. 8. The solid-state structure of [{Mo(MePTF)$_2$(CO)$_2$}$_2$]. Reproduced with permission from Ref. [112]: © American Chemical Society 1984.

3.2.2. IR spectra of phosphino–thioformamide complexes

The infrared spectra of the free ligands can be assigned by comparison with the fully assigned spectra of simpler analogues (see Table 8). The two thioamide stretching modes are strongly coupled, and it is not possible to assign one to ν(C–N) and the other to ν(C=S). The higher frequency band is referred to as the B-band or ν_1(NCS), while the lower frequency band is known as the C-band or ν_2(NCS). ν_1(NCS) is sometimes obscured by an aromatic stretching band in *N*-aryl thioamides [114], and is sometimes of low intensity in *N*-silylated derivatives [115].

The assignment of the infrared spectra of phosphino–thioformamide complexes is not so clear cut. ν(N–H) occurs between 3160 and 3361 cm^{-1} in protonated complexes, although the absorption is often weak and/or broad, and its presence or absence is occasionally not reported.

The situation regarding the thioamide B- and C-bands, where one might hope to find structurally suggestive information, is somewhat confused. In most cases, the frequency of ν_1(NCS) increases on coordination, and, in general, the increase is greater when the phosphino–thioformamide ligand is chelating than when it is monodentate, but the range of values for $\Delta\nu_1$ is so large as to make it virtually useless in determining binding mode. $\Delta\nu_1$ is greater for *N*-alkyl ligands than for *N*-aryl ligands, although the free *N*-alkyl phosphino–thioformamides have lower values of ν_1(NCS) before ligation. There is no significant difference in $\Delta\nu_1$ between neutral and deprotonated ligands, although this could be an artefact arising from the lack of comparison values of ν_1(NCS) for the deprotonated ligands.

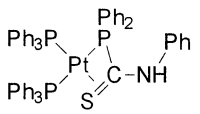


Fig. 9. The proposed structure of [Pt(PPh$_3$)$_2$(PhPTFH)].

Table 8
Characteristic vibrational frequencies in simple thioamides, their cations and metal complexes[a]

	ν(N–H) (cm^{-1})	ν_1(NCS) (cm^{-1})	ν_2(NCS) (cm^{-1})	Ref.
$HCSNH_2$[b]	3276, 3160	1443	1288	[315]
	3280, 3165	1443	1325*	[117]
HCSNHMe	3160	1550	1440	[316]
H_3CCSNH_2	3290, 3165	1478*	1306	[317]
	3290, 3085	1482	1307	[318]
$H_3CSNH_3^+$	3285, 3140	1548	1312	[318]
$[Cu\{H_3CCSNH_2\}_4]$	3195, 3060	1515	1318	[318]
$H_3CSNHMe$	3207	1565	1357	[316]
F_3CSNH_2	3400, 3200	1465	1348	[319]
H_2NCSNH_2	3390, 3349	1473	1416	[318]
$[ZnCl_2\{SC(NH_2)_2\}_2]$	3360, 3290	1445	1408	[320]
$[Pt\{SC(NH_2)_2\}_4]^{2+}$	3360, 3290	1406	1386	[320]
$H_2NCSNH_3^+$	3208, 3080	1440	1349	[321]
	3280, 3100	1548	1447	[318]

[a] Spectra determined from mineral oil mulls unless otherwise stated. Peaks marked with an asterisk were assigned to different vibrations by the original authors.
[b] Liquid sample.

The situation concerning ν_2(NCS) is even more confused. The assignment of bands between 1320 and 1384 cm^{-1} in the spectra of the free ligands as ν_2(NCS) is strongly supported by the data in Table 8; many bound phosphino–thioformamides, both monodentate and chelating also, show a band between 1350 and 1415 cm^{-1}. However, many authors have assigned a band at between 900 and 947 cm^{-1} in the spectra of deprotonated ligands to ν_2(NCS): this is based on the hypothesis that, while the free thioamides are primarily in the *N*-protonated form, deprotonation leads to isomerisation to the mercapto–imidinate form.

The situation is also confused by disagreements over the force constant of the C=S bond [116], with Suzuki assigning a band at 843 cm^{-1} in the IR spectrum of thioformamide to ν(C=S) [117]. Other idiosyncratic assignments of ν_2(NCS) are in $[MClCp(CO)_2(MePTFH\text{–}P)]$ ($\nu = 1495$ cm^{-1} (M = Mo), 1489 cm^{-1} (M = W)) [118] and in $[RuCp'(PhPTF\text{–}P)(dppe)]$ ($\nu = 1185$ cm^{-1}) [109].

Studies in the authors' laboratory on the tris(phosphino–thioformamide) complexes of technetium and rhenium refute the assignment of bands in the 900–950 cm^{-1} range to ν_2(NCS). The complexes $[M(RPTF)_3]$ contain chelating deprotonated phosphino–thioformamide ligands, as shown by the X-ray crystal structure of $[Tc(PhPTF)_3]$, but display no notable absorption band in the 900–950 cm^{-1} region. A strong absorption in the region 1225–1230 cm^{-1} displayed by all the complexes seems a more likely candidate for ν_2(NCS) [12,119].

This hypothesis of a mercapto–imidinate type anion has received strong support from X-ray crystal structure determinations (see Table 9). The crystal structures of PhPTFH and $Cy_2PCSNHPh$ have been determined [120], and show that the carbon–nitrogen and carbon–sulfur bond lengths are as would be expected for a

C–N single bond and a C=S double bond, respectively [121,122]. As deprotonated ligands in [Mn(PhPTF)$(CO)_4$] and [RuCp′(PhPTF)(PPh_3)], the distances are as would be expected for a C=N double bond and a C–S single bond [123], and can be compared to those in (diphenylthiophosphinyl)-*N*-methyl(methylsulfanyl)-methanimine, $Ph_2P(=S)C(=NMe)SMe$ [91,124]. The bond distances in [Mn-$Br(CO)_3$(PhPTFH)], in which the phosphino–thioformamide ligand is protonated and chelating, are intermediate, with an increase in r(C–S) of 0.034(13) Å over the free ligand: however, the authors have assigned a band at 1411 cm^{-1} as ν_2(NCS), some 27 cm^{-1} higher than in the free ligand. In brief:

- it seems difficult to reconcile the huge change in ν_2(NCS) with the rather more modest changes seen in ν_1(NCS), and indeed there is no correlation in the published values;
- on the simplest of models, a compound such as [$MnBr(CO)_3$(PhPTFH)] which shows bond lengths intermediate between the free ligand and the deprotonated ligand should similarly show intermediate behaviour in its IR spectrum [125].

Hence its should be noted that the assignment of very low frequency bands to ν_2(NCS) may be erroneous, and care should be taken before assigning a coordination mode on this basis.

3.2.3. NMR spectra of phosphino–thioformamide complexes

Very little indication of the coordination mode can be gained from chemical shift measurements in the ^{31}P-NMR spectrum, as the ligand shift on coordination (Δ) is highly dependent on the metal, being negative for some tungsten and rhenium complexes: in general, Δ decreases on descending the group. A ring-shift (Δ_R) [126] is observable, decreasing slightly on descending the group (see Table 10), but this is swamped by the variation in Δ.

In the case of tungsten, rhodium, platinum and mercury complexes, the existence of a spin-half metal nucleus allows the observation of phosphorus–metal coupling

Table 9
A comparison of crystallographically-determined bond lengths and observed IR bands for two phosphino-thioformamides and their complexes

	r(C–N) (Å)	r(C–S) (Å)	ν_1(NCS) (cm^{-1})	ν_2(NCS) cm^{-1}	Ref.
PhPTFH	1.334(3)	1.650(3)	1525	1384	[120]
[$MnBr(CO)_3$(PhPTFH-*P*)]	1.30(2)	1.68(1)	1532	1411	[110,108]
[Mn(PhPTF-*P*,*S*)$(CO)_4$]	1.290(5)	1.760(5)	1550	n.r. [a]	[108]
[RuCp′(PhPTF-*P*,*S*)(PPh_3)]	1.263(6)	1.762(5)	1585	925	[109]
Ph_2P(=S)C(=NMe)SMe	1.286(8)	1.765(9)	1569	n.r. [a]	[91]
Cy_2PCSNHPh	1.356(8)	1.661(6)	1495	1330	[120]
	1.349(9)	1.658(7)			
[{CdI_2(Cy_2PCSNHPh-*P*)}$_2$]	1.364(2)	1.620(1)	1500	1375	[102]
[{$HgCl_2$(Cy_2PCSNHPh-*P*)}$_2$]	1.37(4)	1.65(3)	1500	1375	[102]
	1.32(4)	1.63(3)			
[$HgCl_2$(Cy_2PCSNHPh-*P*)$_2$]	1.33(3)	1.63(3)	1500	1375	[102]

[a] n.r. not resolved.

Table 10
A ring-shift in the ^{31}P chemical shifts for some group 6 phosphino–thioformamide complexes [100][a1]

	M = Cr	M = Mo	M = W
δ_P ([M(CO)$_5$(PhPTFH-*P*)])	+78.0	+60.2	+44.3
δ_P ([M(CO)$_4$(PhPTFH-*P*,*S*)])	+63.3	+38.9	+20.4
Δ_R	−13.3	−17.1	−20.2

[a] The ring shift is significantly smaller than the variation in coordination shift between the metals: mean values are $\Delta = +48(7)$ [Cr], $+23(8)$ [Mo], $+5(9)$ [W].

in the ^{31}P-NMR spectrum. Only in the case of tungsten are the trends in the magnitude of the coupling constants sufficiently clear for generalisations to be made. However, observation of $^1J_{PM}$ is strong evidence for (*P*)-coordination to the metal centre if this is in doubt (see Section 3.2.8).

3.2.4. Group 6: chromium, molybdenum, tungsten

The complexes [M(CO)$_5$(PhPTFH)] (M = Cr, Mo, W) and [Cr(CO)$_5$(MePTFH)] have been synthesised by the reaction of [M(CO)$_5$(thf)] with the corresponding phosphino–thioformamide ligand in the absence of light [100]. The phosphino–thioformamide ligand is bound solely through the phosphorus atom. Photolysis leads to the (*P*,*S*)-chelated complexes [M(CO)$_4$(RPTFH)] (R = Me, Ph), [M(CO)$_4$(PhPTFSiMe$_3$)] and [M(CO)$_4$(MePTFMe)], which can also be prepared directly from [M(CO)$_6$] (M = Mo, W). [Cr(CO)$_4$(MePTFH)] has been crystallographically characterised [107]. The bis(phosphino–thioformamide) complexes [M(CO)$_4$(MePTFH)$_2$] can also be prepared in low yield by photolytic substitution of carbon monoxide, but the complexes are labile, with the ligand being bound in a (*P*)-monodentate fashion [100].

Reaction of [M(CO)$_4$(py)$_2$] (M = Mo, W) with PhPTFH in the presence of base yields [M(PhPTF)(CO)$_4$]$^-$, which contain (*P*,*S*)-chelating phosphino–thioformamide ligands [127].

Phosphino–thioformamide ligands will replace a single carbonyl ligand of [MClCp(CO)$_3$] (M = Mo, W) to give [MClCp(CO)$_2$(RPTFH)] (R = Ph, Me), in which the phosphino–thioformamide ligand is bound only through the phosphorus atom [118]. If base is present in the reaction mixture, the (*P*,*S*)-chelate complexes [MCp(RPTF)(CO)$_2$] (R = Me, Ph, (*R*/*S*)-CHMePh) are formed [118,128].

[Mo$_2$(OAc)$_4$] reacts with RPTFH (R = Me, Ph) in the presence of base to give [Mo$_2$(RPTF)$_4$]. When the reactions are conducted in ethanol with potassium hydroxide as the base, the products are associated with two molecules of water, which cannot be removed by common ligands such as THF or MeCN. However, when the reactions are carried out in benzene with butyllithium as the base, the anhydrous products are formed. The *N*-methyl derivative exists as two isomers, which have both been crystallographically characterised: one contains solely (*S*,*N*)-bridging ligands, which each molybdenum having a *trans*-S_2N_2 donor set, while the other has two (*S*,*N*)-bridging ligands and two (*P*,*N*)-bridging ligands, giving each

molybdenum a *cis*-SN_2P donor set. On the basis of its UV–visible spectrum, the *N*-phenyl derivative is thought to be isostructural with the former isomer. The electrochemistry of the complexes has been examined, with all three showing an irreversible one-electron oxidation process at $E \approx +0.67$ V [105].

Reaction of RPTFH (R = Ph, Me) with $[MCl_2(CO)_4]$ or $[MCl_2(CO)_2(PPh_3)_2]$ (M = Mo, W) yields compounds formulated as $[MCl_2(CO)_2(RPTFH)_2]$: the complexity of the $^{31}P\{^1H\}$-NMR spectra indicates that there is a dynamic equilibrium between linkage isomers occurring in solution, which is markedly solvent dependent. Deprotonation of the RPTFH ligand can be effected with triethylamine, yielding complexes of the formulation $[M(RPTF)_2(CO)_2]$ and, depending on the reaction conditions, a molecule of triethylamine or triphenylphosphine can also bind, yielding a seven coordinate complex. A small amount of a second complex is also formed in the reaction. When R = Me, this is the dimer $[\{Mo(MePTF)_2(CO)_2\}_2]$, which has been crystallographically characterised, but the formulation of the second complex when R = Ph is uncertain [111,112].

As was mentioned above, coupling between ^{31}P and ^{183}W ($I = 1/2$, 14.4%) nuclei can be diagnostic for the binding mode of phosphino–thioformamide ligands. It can be seen from Table 11 that the magnitude of $^1J_{PW}$ is 30–40 Hz lower in (*P*,*S*)-chelated complexes than in (*P*)-monodentate complexes. However, comparisons are only valid within related classes of compound, as this difference is within the range of variation of $^1J_{PW}$ (note particularly that $[W(PhPTF–P,S)(CO)_4]^-$ shows $^1J_{PW} =$ 250 Hz, greater than that for $[W(CO)_5(PhPTFH–P)]$, $^1J_{PW} = 245.2$ Hz).

3.2.5. Group 7: manganese, rhenium

Reaction of the phosphino–thioformamide ligands with $[MX(CO)_5]$ (M = Mn, Re; X = Cl, Br) in the presence of triethylamine yields the complexes $[M(RPTF)(CO)_4]$ (R = Ph, Me, Et) and $[Mn(Cy_2PCSNPh)(CO)_4]$. When the reac-

Table 11
Coordination shifts and ^{31}P–^{183}W coupling in the assignment of coordination mode in phosphino–thioformamide complexes of tungsten

	δ_P	Δ	$^1J_{PW}$ (Hz)	Ref.
(*P*)-monodentate				
$[W(CO)_5(PhPTFH)]$	+44.3	+25.1	245.2	[100]
$[WClCp(CO)_2(MePTFH)]$	+41.5	+25.6	261	[118]
$[WClCp(CO)_2(PhPTFH)]$	+45.8	+26.6	260	[118]
(*P*,*S*)-chelating				
$[W(CO)_4(MePTFH)]$	+16.4	+0.5	199.4	[100]
$[W(CO)_4(MePTFMe)]$	+24.6	+6.7	199.0	[100]
$[W(CO)_4(PhPTFH)]$	+20.4	+1.2	202.5	[100]
$[W(CO)_4(PhPTFSiMe_3)]$	+19.0	−0.3	199.4	[100]
$[WCp(MePTF)(CO)_2]$	+3.4	−12.5	230	[118]
$[WCp(PhPTF)(CO)_2]$	+3.7	−15.5	231	[118]
$[W(PhPTF)(CO)_4]^-$	+18.4	−0.8	250	[127]

tion is carried out in the absence of base, the halide complexes $[MX(CO)_3(RPTFR')]$ (R = Ph, Me; R′ = H, Me) and $[MnBr(CO)_3(Cy_2PCSNHPh)]$ are formed. During the preparation of the bromo–manganese complexes, significant amounts of $[Mn(PhPTF)(CO)_4]$ (37%) or $[MnBr(CO)_4(PCy_2H)]$ (ca. 40%) are formed. In all cases, the phosphino–thioformamide ligands bind in a (*P*,*S*)-chelating manner [110,128–131]. The crystal structures of *fac*-$[MnBr(CO)_3(PhPTFH)]$ and $[Mn(PhPTF)(CO)_4]$ have been reported [108].

^{55}Mn-NMR data has been collected for $[MnBr(CO)_3(RPTFH)]$ (R = Me, Et, Ph) and $[MnL(CO)_4]$ (L = $MePTF^-$, $PhPTF^-$, $Cy_2PCSNPh^-$; also $Ph_2PCS_2^-$ and $Cy_2PCS_2^-$, see Section 3.3.3) [132]: the chemical shifts occupy a small range ($\delta_{Mn} = -1545$ to -1620) just downfield of the range for pentacarbonyl–manganese(I) complexes.

3.2.6. Group 8: iron, ruthenium

Reaction of $[FeCpI(CO)_2]$ with RPTFH (R = Me, Et, Ph) leads to replacement of one carbonyl ligand and the isolation of [FeCpI(CO)(RPTFH)], in which the phosphino–thioformamide ligand is thought to be (*P*)-monodentate: reaction of the same precursor with the silyl derivatives $RPTFSiMe_3$ (R = Me, Et, Ph) leads to elimination of iodotrimethylsilane and isolation of the chelate complexes [FeCp(RPTF)(CO)] [133].

$[RuCl_2(PPh_3)_3]$ reacts with $PhPTF^-$ to give the six-coordinate complex $[Ru(PhPTF)_2(PPh_3)_2]$. The two triphenylphosphine ligands can be easily displaced by other phosphines, forming $[Ru(PhPTF)_2L_2]$ ($L_2 = \{P(CH_2CH_2CN)_3\}_2$, dppe). $[\{RuCl_2(CS)(PPh_3)_2\}_2]$ reacts with $PhPTF^-$ to give the thiocarbonyl complex $[Ru(PhPTF)_2(CS)(PPh_3)]$, while $[RuCl_2(CO)(CS)(PPh_3)]$ reacts to give $[RuCl(PhPTF)(CO)(CS)(PPh_3)]$. Reaction of the nitrosyl precursor $[RuCl(NO)(CO)(PPh_3)_2]$ with $PhPTF^-$ leads to substitution of the nitrosyl to give $[RuX(PhPTF)(CO)(PPh_3)_2]$ (X = Cl): the analogous hydride complex (X = H) can be formed from $[RuHCl(CO)(PPh_3)_3]$ [134].

Reaction of PhPTFH with $[RuClCp'(PPh_3)_2]$ in the presence of base yields $[RuCp'(PhPTF)(PPh_3)]$, which has been crystallographically characterised. Reaction with [RuClCp′(dppe)] yields [RuCp′(PhPTF)(dppe)]: this compound shows an infrared absorption band at 1185 cm^{-1} attributed to ν(C=S), and the phosphino–thioformamide ligand is thought to be bound solely through the phosphorus atom. However, the broad ^{31}P-NMR resonances at room temperature may be indicative of some sort of exchange process. When PhPTFH is reacted with $[RuClCp'(PPh_3)_2]$ in the absence of base, the complex $[RuClCp'(PhPTFH)(PPh_3)]$ is formed. The PhPTFH ligand is thought to be bound through phosphorus alone, athough infrared absorption bands at 934 and 2320 cm^{-1}, attributed to ν(C–S) and ν(S–H), respectively, suggest that the ligand is in the *S*-protonated form rather than the more usual *N*-protonated form [109].

3.2.7. Group 9: rhodium, iridium

Reaction of $[\{RhCl(CO)_2\}_2]$ with one equivalent of RPTFH (R = Ph, Me) in the absence of base leads to the evolution of carbon monoxide to yield complexes

formulated as [{RhCl(CO)(RPTFH)}$_2$]. In the reaction with PhPTFH, a substantial quantity of a tetrameric species is also formed, although the structure of this is unknown. Reaction of [{RhCl(CO)$_2$}$_2$] with two equivalents of RPTFH yields the Vaska-type compounds [RhCl(CO)(RPTFH)$_2$], with the phosphino–thioformamide ligands bound solely through phosphorus. Reaction with RPTFH in the presence of triethylamine yields tetrameric species [{Rh(RPTF)(CO)}$_4$], which are thought to be bridged by the phosphino–thioformamide ligands in a manner similar to that in [{Mo(MePTF)$_2$(CO)$_2$}$_2$] (see Section 3.2.1 and Fig. 10). Reaction of these tetramers with further RPTFH in the absence of base, or reaction of [{RhCl(CO)(RPTFH)}$_2$] with RPTF$^-$, leads to the monomeric species [Rh(RPTF)(CO)(RPTFH)], in which the deprotonated ligand is thought to be chelating and the protonated ligand to be bound solely thorough phosphorus. The *N*-phenyl compound was found to undergo intramolecular oxidative addition of the N–H bond under certain (unquoted) conditions to give [RhH(PhPTF)$_2$(CO)] [101].

The complexes [M(PhPTF)(PPh$_3$)$_2$] and [M(PhPTF)(CO)(PPh$_3$)] (M = Rh, Ir) have been prepared from [MCl(PPh$_3$)$_3$] and [MCl(CO)(PPh$_3$)$_2$] respectively [98,135]. [Rh(PhPTF)(PPh$_3$)$_2$] reacts with excess isothiocyanate, RNCS (R = Me, Ph), to give the complexes [Rh(PhPTF)(RNCS$_2$)(RNC)(PPh$_3$)] [136], and with carbon disulfide to give [Rh(PhPTF)(CS)(PPh$_3$)] [137].

The complexes [Rh(RPTF)$_3$] (R = Ph, Me) show a variation with temperature in their ^{31}P{^{1}H}-NMR spectra which has not been fully explained: the iridium analogues do not show this temperature dependence [138]. The electrochemistry of these complexes has also been investigated: the complexes are irreversibly oxidised at potentials close to those for the free ligand ($E = +1.65$ V (R = Ph), $+1.61$ V (R = Me)), and are irreversibly reduced ($E = -1.11$ V (R = Ph), -1.14 V (R = Me)) in what is assumed to be a two electron process on the basis of peak current [139]. The resulting rhodium(I) complexes, formulated as [Rh(RPTF–*P*,*S*)-(RPTFH–*P*)$_2$], are irreversibly oxidised at around $E = +0.16$ V [140].

The dimeric rhodium(I) complexes [{RhCl(RPTFH)}$_2$] (R = Ph, Me) have been prepared in low yield, but it is not clear whether these complexes are bridged by sulfur or by chlorine [138].

A number of rhodium(III) complexes containing PhPTF$^-$ along with other heteroallylic ligands have been prepared, but little structural information is available [138,140].

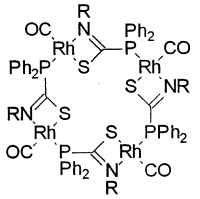


Fig. 10. The proposed structure of [{Rh(RPTF)(CO)}$_4$]: redrawn from Ref. [101].

3.2.8. Group 10: platinum

The hydrido–platinum(II) complex [PtH(PhPTF)(PPh_3)] has been prepared by the reaction of [Pt(PPh_3)$_4$] with PhPTFH in the absence of base [98]. The formulation of the hydride has been taken as evidence that an early stage in the formation of late transition metal complexes of phosphino–thioformamide ligands is the oxidative addition of the N–H bond. Carr et al. cast doubt on this suggestion by showing that the first product of the reaction of [Pt(C_2H_4)(PPh_3)$_2$] with PhPTFH is a η^2-C=S bound complex [Pt(PhPTFH)(PPh_3)$_2$] (see Fig. 9). This complex isomerises in solution to give the hydrido–platinum(II) complex [PtH(PhPTF)(PPh_3)] and free triphenylphosphine. The isomerisation could be conveniently followed by ^{31}P-NMR, using the magnitude of J_{PPt} to indicate bonding mode (see Table 12). An intermediate in the isomerisation could be detected by NMR, but could not be isolated. The *N*-trimethylsilyl ligand PhPTFSiMe_3 also formed an η^2-C=S complex on initial reaction, but this isomerised to a (*P*,*S*)-chelate complex without migration of the trimethylsilyl group [113].

3.2.9. Group 12: zinc, mercury

R$ZnPPh_2$ (R = Et, Ph) is reported to react with organic isothiocyanates, R′NCS (R = Me, Ph), to give RZn(R′PTF), but no structural details are given. Hydrolysis affords the free phosphino-thioformamide ligands [104].

Mercury(II) halides HgX_2 (X = Cl, Br, I) react with Cy_2PCSNHPh to give either [{HgX_2(Cy_2PCSNHPh)}$_2$] or [HgX_2(Cy_2PCSNHPh)$_2$], depending on the ratio of reactants. These complexes, as well as their cadmium analogues, can also be prepared by the reaction of phenyl isothiocyanate with [MX_2($PHCy_2$)$_2$] (X = Cl, Br, I). [CdX_2(Cy_2PCSNHPh)$_2$] spontaneously dimerises in solution with loss of one phosphino–thioformamide ligand [141]. [{CdI_2(Cy_2PCSNHPh)}$_2$], [{$HgCl_2$(Cy_2PCSNHPh)}$_2$] and [$HgCl_2$(Cy_2PCSNHPh)$_2$] have been crystallographically characterised: all three complexes show tetrahedral coordination of the metal centre, with the two dimeric complexes being bridged by halide ligands [102].

3.2.10. Group 14: tin

The tin(IV) phosphido complex [Ph_3Sn(PPh_2)] reacts with phenyl isothiocyanate to give [Ph_3Sn(PhPTF)]: an IR absorption at 1158 cm^{-1} was assigned to ν(C=S), but no other structual details were given [103].

Table 12
The difference in magnitude between $^1J_{PPt}$ and $^2J_{PPt}$ was important in determining the unprecedented η^2-C=S binding mode in platinum(0) phosphino–thioformamide complexes [113]

	δ_P	$^1J_{PPt}$ (Hz)	$^2J_{PPt}$ (Hz)
[Pt(PhPTFH-*P*,*S*)(PPh_3)$_2$]	+10.8	1400	
[Pt(PhPTFH-η^2-*C*=*S*)(PPh_3)$_2$]	+33.1		34
[Pt(PhPTFSiMe_3-*P*,*S*)(PPh_3)$_2$]	+13.1	1423	
[Pt(PhPTFSiMe_3-η^2-*C*=*S*)(PPh_3)$_2$]	+34.2		30
[Pt(Cy_2PCSNHPh-*P*,*S*)(PPh_3)$_2$]	+18.2	1387	
[PtH(Cy_2PCSNPh)(PPh_3)]	+30.0	2906	

Table 13
The characteristic IR absorption bands of phosphino–dithioformate complexes

	ν_1 (cm^{-1})	ν_2 (cm^{-1})	Ref.
KS_2CPCy_2	980	865	[150]
KS_2CPPh_2	1005	870	[150]
(*S*,*S*′)-coordination			
$[ZrClCp_2\{S_2CP(SiMe_3)_2\}]$	978	923	[142]
$[ZrCp_2Me\{S_2CP(SiMe_3)_2\}]$	979	930	[142]
$[Mn(S_2CPPh_2)_2]$	981	891	[147]
$[Fe(S_2CPCy_2)_2(PHCy_2)_2]$	951	897	[148]
$[Cu(S_2CPCy_2)(PHCy_2)]$	995	908	[148]
$[TlMe_2(S_2CPCy_2)]$	1000	885	[150]
$[TlMe_2(S_2CPPh_2)(thf)]$	1000	890	[150]
(*P*,*S*)-coordination			
$[Mn(S_2CPPh_2)(CO)_4]$	1080	835	[110]
$[Mn(S_2CPPh_2)(CO)_4]$			[129]
$[RuCp'(S_2CPPh_2)(PPh_3)]$	1030	[a]	[109]
$[Rh(S_2CPPh_2)(PPh_3)_2]$	1082	847	[98]
$[Rh(S_2CPPh_2)(CO)(PPh_3)]$	1094	842	[98]
$[Ni(S_2CPPh_2)_2]$			[95]
$[Ni(S_2CPCy_2)_2]$	1081	857	[95,148]
$[Ni(S_2CPBz_2)_2]$			[95]
$[Pd(S_2CPCy_2)_2]$	1081	860	[148,149]
$[Pt(S_2CPCy_2)_2]$	1081	860	[148,149]
$[Zn(S_2CPCy_2)_2]$	1021	845	[148]

[a] The authors' assignment of a band at 1135 cm^{-1} as ν(C=S) is inconsistent with other reports.

3.3. Coordination chemistry of phosphino–dithioformates

Phosphino–dithioformates are the phosphorus equivalents of dithiocarbamates, but the weakness of the carbon–phosphorus π-bonding and the ligating power of a phosphorus(III) centre combine to lead to a prevalence of (*P*,*S*)-coordination rather than the (*S*,*S*′)-coordination which is so characteristic of dithiocarbamates. IR spectroscopy has been the main tool used to determine the mode of coordination in the absence of a crystal structure: the characteristic bands of the ligand occur at 951–1000 cm^{-1} and 885–930 cm^{-1} in (*S*,*S*′)-coordinated ligands and at 1021–1094 cm^{-1} and 835–860 cm^{-1} in (*P*,*S*)-coordinated ligands (see Table 13).

3.3.1. Group 4: zirconium

Carbon disulfide reacts with the terminal phosphido complexes $[ZrCp_2X\{P(SiMe_3)_2\}]$ to give $[ZrCp_2X\{S_2CP(SiMe_3)_2\}]$ (X = Cl, Me), of which the chloro complex has been crystallographically characterised. The unusual steric bulk of the phosphorus centre, and the hard nature of the zirconium(IV) centre lead to (*S*,*S*′)-coordination of the phosphino–dithioformate ligand. Both complexes decompose on heating to give $[\{ZrCp_2(\mu\text{-}S)\}_2]$ [142].

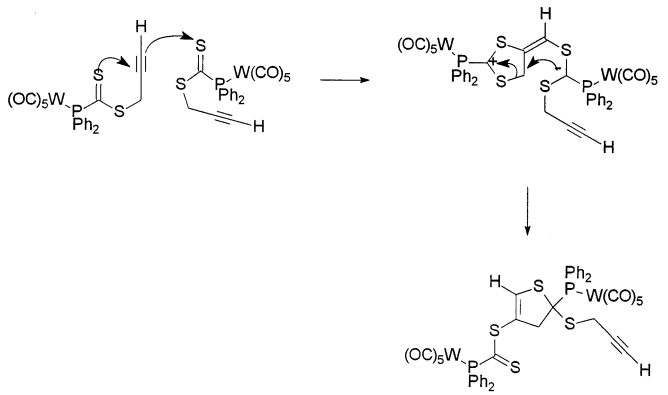
3.3.2. Group 6: molybdenum, tungsten

Reaction of $[W(CO)_5(PHPh_2)]$ with CS_2 and butyllithium yields $[W(S_2CPPh_2)(CO)_5]^-$, which has been crystallographically characterised and shown to have (*P*)-monodentate coordination [99,143]. The same complex has also been reported from the reaction of $[W(CO)_5(NC_5H_4Me)]$ and $Ph_2PCS_2^-$ [144]: it is reported to lose carbon monoxide in acetone solution or on heating in THF solution, presumably to form the chelated tetracarbonyl complex [99,127].

The dithioformate groups can be readily alkylated with iodomethane, vinyl or propargyl bromide, or iodoacetonitrile, yielding complexes of phosphino–dithioformate esters, $[W(CO)_5(Ph_2PCS_2R)]$, of which that of the methyl ester has been crystallographically characterised [99]. Reaction with organic diiodides gives the bridged dimeric species $[(OC)_5W(Ph_2PCS_2(CH_2)_nS_2CPPh_2)W(CO)_5]$ ($n = 1–3$). The complex of the propargyl ester is unstable at room temperature, and undergoes spontaneous intermolecular cycloaddition to yield a dimeric complex (see Scheme 4), which has been crystallographically characterised [145]. The cycloaddition can be effected without dimerisation by protonation of the complex: a similar cycloaddition occurs on protonation of the complex of the cyanomethyl ester, but in this case the reaction is readily reversible.

In another cyclodimerisation, in the presence of catalytic amounts of triethylamine, $[M(CO)_5(Ph_2PCS_2C \equiv CH)]$ (M = Mo, W) is converted to $[\{(CO)_5M\}_2(\mu\text{-}Ph_2PC_5H_2S_3PPh_2)]$, in which the two metal centres are linked by a bis(diphenylphosphino)-substituted 6a-thiathiophthen. Reaction with a primary amine forms the phosphino–thioformamide complexes $[M(CO)_5(RPTFH)]$ (R = Et, Bz) [146].

Reaction of $[W(Ph_2PCS_2)(CO)_5]^-$ with $[ReBr(CO)_5]$ gives the heterobimetallic complex $[(OC)_5W(\mu\text{-}Ph_2PCS_2)Re(CO)_5]$. (*P*)-coordination to tungsten (as in the parent complex) was shown by the observation of $^1J_{PW}$ satellites in the ^{31}P-NMR spectrum ($J = 240.9$ Hz): the authors have postulated (*S*)-monodentate coordination to rhenium, although (*S*,*S*′)-chelation (leading to a 7-coordinate rhenium



Scheme 4. The cyclodimerisation of $[W(CO)_5(Ph_2PCS_2CH_2C{\equiv}CH)]$: redrawn from Ref. [145].

centre) is also a possibility. The strength of the phosphino–dithioformate bridge is indicated by the observation of the $[W(Ph_2PCS_2)Re]^+$ peak in the FAB mass spectrum [99].

3.3.3. Group 7: manganese, rhenium

The carbonyl–manganese(I) complexes $[Mn(S_2CPR_2)(CO)_4]$ (R = Ph, Cy) have been prepared by the reaction of phosphino–dithioformate anions with $[MnX(CO)_5]$ (X = Cl, Br) [110,129]. The diphenyl compound is reported to be light-sensitive. The ^{55}Mn chemical shifts have been measured ($\delta_{Mn} = -1450$ (R = Ph), -1480 (R = Cy)), and are very close to those of the corresponding phosphino–dithioformate complexes (see Section 3.2.5) [132].

The preparation of $[Mn(S_2CPPh_2)_2]$ has been reported: it is thought to have (*S*,*S*′)-coordination [147].

The heterobimetallic complex $[(OC)_5W(\mu\text{-}Ph_2PCS_2)Re(CO)_5]$ has been mentioned in the previous section.

3.3.4. Group 8: iron, ruthenium

The reaction of $FeSO_4$ with dicyclohexylphosphine and carbon disulfide in the presence of triethylamine gives $[Fe(S_2CPCy_2)_2(PHCy_2)_2]$, an (*S*,*S*′)-coordinated complex [148].

$Ph_2PCS_2^-$ reacts with $[RuClCp'(PPh_3)_2]$ to give $[RuCp'(S_2CPPh_2)(PPh_3)]$, but reaction with [RuClCp′(dppe)] does not yield stable products, in contrast to the behaviour of phosphino–thioformamides [109].

3.3.5. Group 9: rhodium

$[Rh(S_2CPPh_2)(PPh_3)_2]$ has been prepared by the reaction of the phosphino–dithioformate anion with $[RhCl(PPh_3)_3]$, and it can be carbonylated to form a complex formulated as $[Rh(S_2CPPh_2)(CO)(PPh_3)]$ [98].

3.3.6. Group 10: nickel, palladium, platinum

Kopf et al. have prepared a range of nickel(II) phosphino–dithioformate complexes $[Ni(S_2CPR_2)_2]$ (R = Ph, Cy, Bz). The complex with R = Cy has been crystallographically characterised and shown to have *trans* (*P*,*S*)-coordination [95,148]. The analogous complexes $[M(S_2CPCy_2)_2]$ (M = Pd, Pt) have also been prepared, and structure determinations showed that, in these cases, the two (*P*,*S*)-chelated ligands adopt a *cis*-configuration [149].

3.3.7. Group 11: copper

The copper(I) complex $[Cu(S_2CPCy_2)(PHCy_2)]$ is formed by the reaction of $CuCl_2$ with dicyclohexylphosphine and carbon disulfide in the presence of base: its structure is uncertain, but (*S*,*S*′)-coordination of the phosphino–dithioformate ligand ($\nu = 995$, 908 cm^{-1}) is proposed [148].

3.3.8. Group 12: zinc

Zinc chloride reacts with dicyclohexylphosphine and carbon disulfide to give $[Zn(S_2CPCy_2)_2]$, a complex with (*P*,*S*)-coordination of the phosphino–

dithioformate ligand [148]. $PhZnPPh_2$ is reported to react with carbon disulfide to give $PhZn(S_2CPPh_2)$, but no structural details are given [104].

3.3.9. Group 13: thallium

Dimethylthallium phosphino–dithioformates $[Me_2Tl(S_2CPR_2)]$ (R = Cy, Ph) have been prepared by reacting $Ph_2PCS_2^-$ with $Me_2Tl(NO_3)$. The *P*,*P*-diphenyl derivative forms initially as a THF adduct, which slowly loses THF on storage. There is no indication of $^{31}P-^{205}Tl$ coupling in either the ^{31}P- or ^{205}Tl-NMR spectra, and the X-ray crystal structure of $[Me_2Tl(S_2CPPh_2)(thf)]$ confirms that the phosphino–dithioformate ligand is bound through the two sulfur atoms [150].

3.3.10. Group 14: tin

Ph_3SnPPh_2 reacts with carbon disulfide to give $[Ph_3Sn(S_2CPPh_2)]$: the IR spectrum shows bands at 349 and 1125 cm^{-1}, assigned as $\nu(Sn-S)$ and $\nu(C=S)$, respectively, but no other structural information was reported. $Sn(PPh_2)_4$ is also reported to react with carbon disulfide to give $[Sn(S_2PPh_2)_4]$ [103].

3.3.11. Group 16: tellurium

Triphenyltelluronium chloride reacts with carbon disulfide and secondary phosphines in the presence of base to give phosphino–dithioformate compounds $[Ph_3Te(S_2CPR_2)]$ (R = Ph, Bz, Pr^i): these are thought to contain a tellurium–sulfur single bond [151].

4. Diphosphine monosulfides and monoselenides

4.1. Preparation of diphosphine monosulfides and monoselenides

The most direct route to diphosphine monosulfides is the reaction of one equivalent of sulfur with the diphosphine in a suitable solvent [152–154]. Careful control of the conditions is required to avoid excessive contamination with the disulfide. Reaction of $Ph_2AsCH_2CH_2PPh_2$ (ape) with one equivalent of elemental sulfur in dichloromethane at ambient temperature leads to the oxidation only of the phosphorus [152], and this has led to apeE being preferred to dppeE as a tool to examine the ethylene-bridged ligands of this type (see below). Diphosphine monoselenides can also be obtained by a similar route, either by reaction with KSeCN or with red elemental selenium [155].

The monosulfide of dppm, dppmS, can be prepared by an organometallic route [156] (Table 14).

$$Ph_3P{=}S + MeLi \rightarrow Ph_2P(=S)CH_2Li$$

$$Ph_2P(=S)CH_2Li + Ph_2PCl \rightarrow Ph_2P(=S)CH_2PPh_2$$

The mechanism of the first step is thought to involve substitution followed by deprotonation [157]. Although this route was originally reported to be effective for

Table 14
Transition metal complexes of diphosphine monosulfides and monoselenides.

Crystal structure	Crystal structure	Ref.
$[WI(CO)_2(NO)(dppmE)]$ (E = S, Se)		[166]
$[WI(CO)_2(NO)(apeE)]$ (E = S, Se)		[166]
$[M(CO)_4(Ph_2PCH_2PSRR')]$ (M = Cr, Mo, W; R, R′ = Ph, Bu^t, Pr^i, Me)		[152,155,163–165]
$[M(CO)_4(dppmSe)]$ (M = Cr, Mo, W)		[152,155,167]
$[M(CO)_5(dppmSe)]$ (M = Mo, W)		[167]
$[M(CO)_5(apeSe)]$ (M = Mo, W)		[167]
$[MX_2(CO)_3(dppmSe)]$ (M = Mo, W; X = Cl, Br)		[167]
$[MX_2(CO)_3(apeSe)]$ (M = Mo, W; X = Cl, Br)		[167]
$[MoX_2(CO)_2(apeSe)_2]$ (X = Cl, Br)		[167]
$[MnX(CO)_3(dppmE)]$ (X = Cl, Br; E = S, Se)		[152]
$[ReBr(CO)_3(dppmE)]$ (E = S, Se)		[152]
$[\{MnX(CO)_3(apeE)\}_2]$ (X = Cl, Br; E = S, Se)		[152]
$[MnX(CO)_3(apeE)_2]$ (X = Cl, Br; E = S, Se)		[152]
$[ReBr(CO)_3(apeE)_n]$ (E = S, Se; n = 1, 2)		[152]
$[RuCl(\eta^6\text{-}C_6H_6)(dppmS)]^+$		[159]
$[RuCl_2L(dppmS)]$ (L = η^6-C_6H_6, η^6-cymene)	*	[159]
$[RuCl_2(\eta^6\text{-}C_6Me_6)(dppmSe)]$		[168]
$[RuCl(\eta^6\text{-}C_6Me_6)(dppmSe)]^+$		[168]
$[RuCl(Ph_2PCHPSPh_2)(\eta^6\text{-cymene})]$		[159]
$[M(cod)(dppmE)]^+$ (M = Rh, Ir; E = S, Se)	*	[159]
$[ML_2(Ph_2PCH_2PSBu^t_2)]^+$ (M = Rh, Ir; L_2 = cod, $(CO)_2$)		[159]
$[M(cod)(Ph_2PCHPSBu^t_2)]$ (M = Rh, Ir)		[159]
$[RhL_2(Ph_2PCH_2PSBu^t_2)]^+$ ($L_2 = (CNBu^t)_2$, dppm)		[159]
$[M(Ph_2PCHPEPh_2)(cod)]$ (M = Rh, Ir; E = S: M = Rh; E = Se)	*	[159,169]
$[RhClCp^*(dppmSe)]^+$		[168]
$[RhIMe(Ph_2PCHPSPh_2)(cod)]$		[169]
$[RhIMe(Ph_2PCHMePSPh_2)(cod)]^+$		[169]
$[M\{C(PPh_2)(PSPh_2)_2\}L_2]$ (M = Rh, Ir; $L_2 = (CNBu^t)_2$, cod)		[170]
$[RhX(CO)(dppmS)]$ (X = Cl, I)	*	[171]
$[RhI_2\{C(PPh_2)(PSPh_2)_2\}(CNBu^t)_2]$	*	[170]
$[RhBrBz\{C(PPh_2)(PSPh_2)_2\}(CNBu^t)_2]$		[170]
$[Pt(dppmSe)]^{2+}$		[160]
$[Pt\{S_2P(OEt)_2\}_2(dppmE)]$ (E = S, Se)		[172]
$[Pt\{S_2P(OEt)_2\}_2(apeE)]$ (E = S, Se)	*	[172]
$[Pd(CN)(SeCN)(dppmSe)]$		[161]
$[MCl(PEt_3)(Ph_2PCH_2PSR_2)]^+$ (M = Pd, Pt; R = Ph, Pr^i, Bu^t)	*	[173]
$[PtCl(PEt_3)(Ph_2PCHPEPh_2)]$ (E = S, Se)		[173]
$[PtCl(PEt_3)(Ph_2PCHPSBu^t_2)]$		[173]
$[MCl(PR_3)(dppmSe)]^+$ (M = Pd, Pt; R = Et, Bu^n)		[173]
$[Au(C_6F_5)_2Cl(dppmS)]$		[174]
$[Au(C_6F_5)_2(dppmS)]^+$		[174]
$[Au(C_6F_5)_2(Ph_2PCHPSPh_2)]$		[174]
$[Au(C_6F_5)_2\{Ph_2PCH(AuX)PSPh_2\}]$ (X = Cl, C_6F_5)		[174]
$[Au(C_6F_5)_2\{Ph_2PCH(AuX_3)PSPh_2\}]$ ($X_3 = (C_6F_5)_3$, $(C_6F_5)_2Cl$)		[174]
$[Au(C_6F_5)_2\{Ph_2PCH(AgPPh_3)PSPh_2\}]^+$		[174]
$[\{Au(C_6F_5)_2(Ph_2PCHPSPh_2)\}_2M]^+$ (M = Ag, Au)		[174]
$[\{Au(C_6F_5)_2(Ph_2PCHPSPh_2)\}_2Au(C_6F_5)_2]^+$		[174]

Table 14 (Continued)

Crystal structure	Crystal structure	Ref.
$[Hg(Ph_2PCHPEPh_2)_2]$ (E = S, Se, Te)		[162]
$[HgX_2(dppeE)]$ (X = Cl, Br, I; E = S, Se)		[175]
$[Hg(dppmE)_2]^{2+}$ (E = S, Se)		[177]
$[HgI_2(dppmS)]$	*	[154]

the production of dppmSe, $Ph_2P(=Se)CH_2PPh_2$ [156], it was later reported to lead to the production of volatile selenium species, malodiferous and probably highly toxic [155].

Aladzheva et al. have prepared dpppS and dppbS in yields of ca. 30% by the reaction of one equivalent of diphenylphosphine sulfide with $BrCH_2(CH_2)_nCH_2X$ (X = Cl, Br; $n = 1$, 2) followed by substitution of the other halogen by lithium diphenylphosphide [158]. The same authors also describe a preparation of dppeS in 88% yield by the reaction of diphenylphosphine with diphenylvinylphosphine sulfide [158]. Although the reaction was carried out under phase-transfer conditions in the presence of base, it seems likely that it proceeds by a radical mechanism.

The diselenide of dppm has been reported to spontaneously extrude selenium on attempted complexation to iridium [159] or platinum [160], forming complexes of the monoselenide, dppmSe. The reverse reaction, insertion of selenium into a phosphorus–metal bond of a dppm complex, has been observed in the reaction of dppm with $[Pt(SeCN)_4]^{2-}$ and on heating $[Pt(SeCN)_2(dppm)]$, both of which yield [Pt(CN)(SeCN)(dppmSe)] [161].

As with dppm itself, the monochalcogenides of dppm show a certain acidity of the methylene carbons. The monosulfide, dppmS, can be deprotonated directly with butyllithium, but attempted deprotonationation of the monoselenide is reported to lead to deselenisation and the formation of $BuSe_nLi$ [162]. The anions of the monoselenide and the monotelluride can be formed by the reaction of $[Ph_2PCHPPh_2]Li$ with elemental selenium or tellurium, respectively [162]. The methylene protons are more acidic still when the ligand is coordinated, and may be removed with sodium hydride or exceptionally by organic amines (see below).

4.2. Coordination chemistry of diphosphine monosulfides and monoselenides

4.2.1. Groups 6 and 7

Grim et al. have prepared a number of tetracarbonyl complexes of group 6 metals, $[M(CO)_4L]$ (M = Cr, Mo, W), with diphosphine monosulfide and monoselenide ligands [155,163–165]. Reaction of dppmE or apeE (E = S, Se) with $[WI(CO)_4(NO)]$ gives the chelated complexes $[WI(CO)_2(NO)L]$ [166].

Reaction of dppmSe and apeSe with the halocarbonyl anions $[MX(CO)_5]^-$ gave the species $[M(CO)_5L]$, with the phosphine selenide group pendent. The chelated complexes of dppmSe could be prepared from $[M(CO)_6]$, but the phosphine selenide group of apeSe could not be made to coordinate, illustrating the relatively weak

donor ability of the selenium centre to these M^0 centres. In contrast, both ligands formed chelate complexes $[MX_2(CO)_3L]$ on reaction with the M^{II} halocarbonyl complexes $[MX_2(CO)_4]$ [167].

Reaction of $[MnX(CO)_5]$ (X = Cl, Br) with dppmE (E = S, Se) leads to the chelated complexes $[MnX(CO)_3(dppmE)]$, while the corresponding apeE (E = S, Se) complexes spontaneously dimerise to give $[\{Mn(\mu\text{-}X)(CO)_3(apeE\text{-}As)\}_2]$. Reaction of either set of ligands with the rhenium(I) complex $[ReBr(CO)_5]$ gives the chelated complexes $[ReBr(CO)_3L]$. Both manganese and rhenium complexes of apeE react with a second equivalent of ligand to give $[MX(CO)_3(apeE\text{-}As)_2]$ [152].

In both Group 6 M^0 complexes $[M(CO)_4(L–L)]$ and Group 7 M^I complexes $[MX(CO)_3(L–L)]$, the replacement of a phosphorus donor atom by a sulfur or a selenium leads to a 250–300 mV reduction in the one-electron oxidation potential measured by cyclic voltammetry. However, the kinetic lability of the oxidised species is such that attempts to isolate them were unsuccessful [152].

4.2.2. Platinum group metals

Reaction of $Ph_2PCH_2P(=E)R_2$ (E = S, Se; R = Ph, Bu^t) with $[\{RuCl_2(\eta^6\text{-}L)\}_2]$ (L = benzene, cymene) gives $[RuCl_2(\eta^6\text{-}L)\{Ph_2PCH_2P(=E)R_2\text{-}P\}]$ of which one has been crystallographically characterized. The chloride ion can be removed by $AgClO_4$ to give the chelated cationic complexes [159]. Use of the deprotonated ligands [159] or suitably polar solvents [168] also leads to displacement of the chloride by the group 16 centre.

$[M(cod)(dppmS)]^+$ (M = Rh, Ir) and related complexes can be easily prepared by reaction of $[\{MCl(cod)\}_2]$ with the free ligand in acetone or dichloromethane [159,169]. The methylene group can be deprotonated by sodium hydride in THF. The deprotonated complexes show a double reactivity with iodomethane, both at the methylene carbon and at the metal center: for the rhodium complex, attack occurs first at the metal, while the inverse is true for the iridium complex [169].

The enhancement of the acidity of the C–H bond vicinal to a phosphine sulfide group is amply demonstrated by the ligand $HC(PPh_2)(PSPh_2)_2$, which is deprotonated by diethylamine in forming the complexes $[M\{C(PPh_2)(PSPh_2)_2\text{-}P,S\}(cod)]$ (M = Rh, Ir). The rhodium complex shows only metal-centred reactivity on reaction with iodine or benzyl bromide [170].

The rhodium carbonyl complexes [RhX(CO)(dppmS)] (X = Cl, I) have been shown to be excellent catalysts for the carbonylation of methanol to acetic acid, being eight times more active than $[RhI_2(CO)_2]^-$. The complex is stable for several repeated batch experiments under the very agressive reaction conditions (185°C, 70 bar CO, in the presence of iodomethane and acetic acid), and shows no signs of hemilabile behaviour [63,171].

Reaction of one equivalent of dppmE (E = S, Se) with $[Pt\{S_2P(OEt)_2\}_2]$ leads to $[Pt\{S_2P(OEt)_2\}(dppmE)]^+$, while reaction with an excess of ligand causes complete substitution of the dithiophosphate, giving $[Pt(dppmE)_2]^{2+}$. Use of apeE (E = S, Se) leads to the substitution of only one of the four sulfur centres, giving $[Pt\{S_2P(OEt)_2\text{-}S\}\{S_2P(OEt)_2\text{-}S,S'\}(apeE\text{-}As)]$, of which the apeS complex has been crystallographically characterised [172].

The complexes $[MCl(PR'_3)(Ph_2PCH_2PER_2)]^+$ (M = Pd, Pt; E = S, Se; R = Ph, Pr^i, Bu^t, R′ = Et, Bu^n) can be prepared, usually as a mixture of *cis*- and *trans*-isomers, by the reaction of the free ligand with $[\{MCl_2(PR'_3)\}_2]$, and *trans*-$[PtCl(PEt_3)(Ph_2PCH_2PSPBu^t_2)]^+$ has been crystallographically characterised [173]. The platinum complexes can be deprotonated with sodium hydride to yield the neutral complexes of the $[Ph_2PCHPER_2]^-$ anion.

4.2.3. Groups 11 and 12

The pendent diphenylphosphino group of $[Au(C_6F_5)_2Cl(\eta^1\text{-dppm})]$ can be specifically oxidised with one equivalent of sulfur to give $[Au(C_6F_5)_2Cl(dppmS)]$ in 86% yield. This complex exists in solution as an equilibrium mixture of $[Au(C_6F_5)_2Cl(dppmS\text{-}P)]$ and $[Au(C_6F_5)_2(dppmS\text{-}P,S)]^+Cl^-$: the chloride ligand can easily be removed with silver perchlorate and the anionic species has been crystallographically characterised as its perchlorate salt. Deprotonation of this chelated complex gives the neutral species $[Au(C_6F_5)_2(Ph_2PCHPSPh_2)]$: the methanide carbon can be coordinated to a variety of silver(I), gold(I) and gold(III) centres by halide metathesis [174].

Reaction of mercury(II) halides with dppmS or dppeE (E = S, Se) leads to the four-coordinate adducts $[HgX_2L]$ (X = Cl, Br, I) [175], of which $[HgI_2(dppmS)]$ has been crystallographically characterised [176]. However, use of the anions $[Ph_2PCHPEPh_2]^-$ (E = S, Se, Te) leads to substitution of the halide ions giving $[Hg(Ph_2PCHPEPh_2)_2]$ [162]. The *C*-protonated versions of these complexes (E = S, Se) can be formed from the neutral ligands and mercury(II) perchlorate [177].

5. Phosphino–thioethers

5.1. Preparation of acyclic phosphino–thioethers

The disconnection approach [178] suggests that there are three general routes to the synthesis of phosphino–thioethers. The initial disconnection can be either

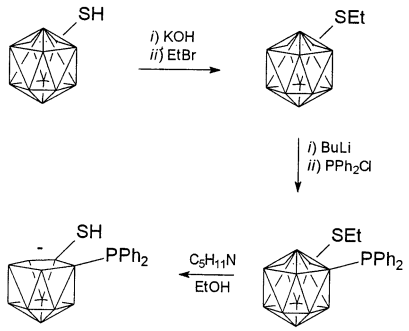
- at the phosphorus–carbon bond, leading to either a carbanion or a carbocation; or
- at the sulfur–carbon bond, leading to a thiolate anion and an electrophilic carbon centre.

There are also free radical routes to phosphino–thioethers.

5.1.1. Reaction of organometallic reagents with electrophilic phosphorus centres

This strategy involves the preparation of a sulfur-containing organolithium or Grignard reagent and its subsequent ‘quenching’, usually with a chlorophosphine (e.g., chlorodiphenylphosphine).

The organolithium reagent can be prepared either by direct lithiation of an aromatic C–H bond using butyllithium, or by reaction of lithium metal with an organic halide. The latter route is preferred in the preparation of 2-(methylsulfanyl)phenyllithium [179] as direct lithiation of methyl phenyl sulfide leads mainly



Scheme 5. The preparation of *o*-carborane bridged phosphino–thioethers: redrawn from Ref. [187].

to the 'laterally metallated' product (phenylsulfanyl)methyllithium [180,181]. The lateral metallation of the fluorinated derivative 1,2,3,4-tetrafluoro-6-(methylsulfanyl)benzene on reaction with butyllithium was not noted, although the yield of the final product, $Ph_2PC_6F_4SMe$-2, was relatively low (60%) [182]. The direct lithiation of other alkyl phenyl sulfides gives mostly the *o*-lithio derivatives [183], whereas benzyl methyl sulfide lithiates exclusively at the benzylic position [184]. Other alkyl methyl sulfides can be directly metallated on the methyl group by butyllithium in the presence of TMEDA [185].

Other phosphorus electrophiles apart from chlorophosphines can be used. The reaction of 2-(methylsulfanyl)methylmagnesium bromide with methyl methylphenylphosphinate, MePhP(=O)OMe, is stereospecific, allowing the preparation of optically active phosphino–thioethers (after reduction of the resulting phosphine oxide with phenylsilane) from resolved phosphinate esters [186]. (Methylsulfanyl)methyllithium reacts with trialkyl phosphites to give tris[(methylsulfanyl)methyl]phosphine [185].

This procedure has been used to prepared the *o*-carborane bridged phosphino–thioethers *closo*-1-Ph_2P-2-EtS-1,2-$C_2B_{10}H_{10}$ and *nido*-7-Ph_2P-8-SEt-7,8-$C_2B_9H_{10}^-$ (see Scheme 5) [187].

5.1.2. Reaction of organophosphide anions with electrophilic carbon centres

While phosphino–thioethers with a phenylene or substituted-phenylene bridge are usually prepared by organometallic routes as above, the most common procedure for the preparation of methylene-, ethylene- and trimethylene-bridged phosphino–thioether ligands is the reaction of organophosphide anions with the corresponding ω-chloroalkyl alkyl sulfides [187].

SAFETY NOTE: 2-Chloroethyl alkyl sulfides ('hemisulfur mustards') are potent vesicants [189], and under no circumstances should they be allowed to come into contact with the skin. Procedures involving bis(2-chloroethyl) sulfide ('mustard gas'), including the hitherto standard preparation of $Ph_2PCH_2CH_2SCH_2CH_2PPh_2$ [190], have been severely restricted in many countries following the signing of the Chemical Weapons Convention.

γ-Phosphino-thioethers with a benzyl bridge have been prepared by the reaction of the corresponding substituted benzyltrimethylammonium iodide with sodium diphenylphosphide [191].

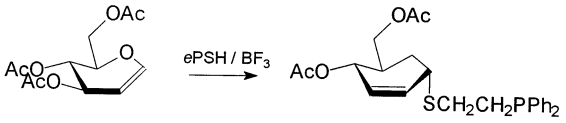
5.1.3. The sulfur–carbon disconnection

Although there are a number of feasible reactions corresponding to the disconnection of the sulfur–carbon bond at the bridgehead, they inevitably require the use of either ω-chloroalkylphosphines or phosphinoalkylmetal reagents, neither of which are trivial synthetic targets in themselves [192].

An alternative sulfur–carbon disconnection leads to the alkylation of a phosphino–thiol, and thereto to the problems of preparation of phosphino–thiols themselves (see Section 2.1). However, this is a very convenient route to the ethylene-bridged phosphino–thioethers, avoiding the need to use 2-chloroethyl alkyl sulfides. Ethylene-bridged phosphino–thiols are usually prepared by reaction of an organophosphide anion with ethylene sulfide (see Section 2.1.1), and the resulting phosphino–thiolate anion can be alkylated in situ to give the corresponding phosphino–thioether [193]. Notable examples of this are the formation of the phosphino–thioether ligands, *e*PSR; (*a*) where R is a β-cyclodextrin, by the reaction of *e*PSH with 6-tosyl-β-cyclodextrin [194]; and (*b*) where R is a mono- or disaccharide, by the Ferrier rearrangement of glycals in the presence of a Lewis acid (see Scheme 6) [195].

5.1.4. Free radical routes to phosphino–thioether ligands

The alternative to the polar reactions corresponding to the sulfur–carbon disconnection is to use a free-radical addition of the sulfur-containing group. Ethylene-bridged phosphino–thioethers can be prepared by the free radical addition of thiols across the C=C bond of diphenylvinylphosphine [196]. Formation of phosphorus(V) species is related to the ease of cleavage of the C–S bond, with benzyl mercaptan and tert-butyl mercaptan giving exclusively phosphine sulfide and propane-2-thiol yielding a significant proportion of the phosphorus(V) species. Other thiols, including ethanethiol and benzenethiol, gave primarily the phosphino–thioether product [197]. There is no reason to suggest that this reaction could not be used to prepare trimethylene- and tetramethylene-bridged phosphino–thioethers from allylphosphines and (2-butenyl)phosphines, respectively [198] (see Section 2.1.2). The addition of radicals derived from secondary phosphines to alkyl allyl sulfides has also been used to prepare phosphino–thioethers [93].



Scheme 6. The Ferrier rearrangement of glycals with a phosphino–thiol as the *S*-nucleophile: redrawn from Ref. [195].

5.2. Coordination chemistry of acyclic phosphino–thioethers and related ligands

5.2.1. Group 6: chromium, molybdenum, tungsten

The reaction of *e*PSR (R = Me, Et, Ph) with $[Cr(CH_2SOMe_2)(CO)_5]$ leads to $[Cr(CO)_5(e\text{PSR}–P)]$: the *e*PSMe complex will lose carbon monoxide under UV irradiation to give $[Cr(CO)_4(e\text{PSMe}–P,S)]$ [199].

Liu et al. have shown that the complexes of the (P_2,*S*)-donor ligand 2,2-bis(diphenylphosphinomethyl)-1-(phenylsulfanyl)propane (L1, see Fig. 11) with chromium, molybdenum and tungsten carbonyls have (*P*,*P*)-coordination [200], having crystallographically characterised the carbonylmolybdenum(0) complex $[Mo(CO)_4(L1)]$. By contrast, complexes of the (*O*,*P*,*S*)-donor ligand 2-(diphenylphosphinomethyl)-2-(phenylsulfanylmethyl)-1-methoxypropane (L2, see Fig. 11) have (*P*,*S*)-coordination [201]. The X-ray crystal structures of the carbonylchromium(0) and carbonyltungsten(0) complexes $[M(CO)_4(L2)]$ were reported.

The complexes $[M(CO)_4(e\text{PSMe})]$ (M = Mo, W) have been prepared either by the reaction of *e*PSMe with $[M(CO)_6]$ [202] or by *S*-methylation of $[M(e\text{PS})(CO)_4]^-$ with iodomethane [44]. The latter route has also been used to prepare $[Cr(CO)_4(e\text{PSMe})]$ and, by reaction with allyl chloride or methallyl chloride, $[M(CO)_4(e\text{PSR})]$ ($R = CH_2CH{=}CH_2$; M = Mo, W: $R = CH_2CMe{=}CH_2$; M = W). $[Mo(CO)_4(e\text{PSMe})]$ has been crystallographically characterised [203].

$[Mo(CO)_4(e\text{PSMe})]$ reacts with Me_3O^+ to yield $[Mo(CO)_4(Ph_2PCH_2CH_2SMe_2)]^+$, in which the molybdenum is coordinated by both a phosphorus and by a positively-charged sulfur centre. The X-ray crystal structure showed that the molybdenum–sulfur distance is 0.135(4) Å shorter in the sulfonium complex (r(Mo–S) = 2.425(4) Å) than in the corresponding thioether complex (r(Mo–S) = 2.560(1) Å), a consequence of the greater π-acceptor strength of the R_3S^+ centre [203].

5.2.2. Group 7: manganese

The complexes *fac*-$[MnBr(CO)_3(L1\text{-}P,P')]$, *fac*-$[MnBr(CO)_3(L2\text{-}P,S)]$ and *fac*-$[MnBr(CO)_3(L3\text{-}P,S)]$ have been prepared by displacement of carbon monoxide from $[MnBr(CO)_5]$ [201,204]. The complexes with L1 and L3 (see Fig. 11) are formed as pairs of isomers, with the pendant arm of the tripodal ligand being either *syn* or *anti* to the bromine atom. Both isomers of the L1 complex and the *syn*-isomer of the L3 complex have been crystallographically characterised.

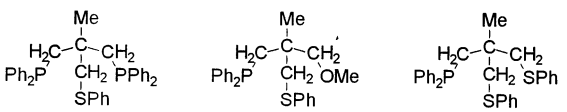


Fig. 11. The ligands L1, L2 and L3.

5.2.3. Group 8: ruthenium

Sanger and Day have reported a series of ruthenium(II) complexes of *e*PSPh [205] from reaction of $[\{RuCl_2(CO)_3\}_2]$ with *e*PSPh at room temperature which yields *mer*-$[RuCl_2(e\text{PSPh-}P)(CO)_3]$. Reaction in refluxing benzene leads to further substitution, yielding $[RuCl_2(CO)_2(e\text{PSPh-}P)_2]$. Reaction of *e*PSPh with $RuCl_3{\cdot}3H_2O$ under an atmosphere of carbon monoxide yielded the ruthenium(II) complex $[RuCl_2(CO)(e\text{PSPh-}P)(e\text{PSPh-}P,S)]$.

The ruthenium(II) complexes $[RuCl_2(ph\text{PEMe})_2]$ (E = S, Se) have been prepared by reaction of the ligand with $RuCl_3{\cdot}xH_2O$, but the stereochemistry of the products could not be determined [206].

5.2.4. Group 9: cobalt, rhodium, iridium

Reaction of *m*PSR (R = Me, Ph) with the dicobalt complexes $[Co_2(R'C{\equiv}CCO_2Me)(CO)_6]$ (R′ = H, CO_2Me) leads to the replacement of a single carbonyl to give $[Co_2(R'C{\equiv}CCO_2Me)(CO)_5(m\text{PSR-}P)]$ (Table 15). A further carbonyl can be reversibly substituted on heating in touene solution to give the bridged species $[Co_2(R'C{\equiv}CCO_2Me)(CO)_4(\mu\text{-}m\text{PSR-}P,S)]$, of which the *m*PSMe (R′ = CO_2Me) complex has been crystallographically characterised. However, reaction with the trinuclear cluster $[Co_2Fe(\mu_3\text{-S})(CO)_9]$ gave only the bridged species $[Co_2Fe(\mu_3\text{-S})(CO)_7(\mu\text{-}m\text{PSR-}P,S)]$, with the phosphino–thioether ligand attached to the cobalt centres [207].

Alkylation of the primary phosphino–thiolate complexes $[M(H_2PCH_2CHMeS)_3]$ (M = Co, Rh) with dimethyl sulfate or Et_3O^+ yields the primary phosphino–thioether complexes $[M(H_2PCH_2CHMeSR)_3]^{3+}$ (R = Me, Et) [60,61].

The cobalt(II) complexes $[Co(e\text{PSR})_2]^{2+}$ (R = Me, Et) can be prepared by reaction of *e*PSR with $Co(BF_4)_2$, but the product of the reaction of *e*PSPh with $Co(BF_4)_2$ could not be isolated in pure form [208]. The magnetic moments of the complexes ($\mu_{eff} = 1.87\mu_B$ (R = Me), $2.19\mu_B$ (R = Et)) are rather low for square-planar cobalt(II) complexes, but similar to those of analogous $[Co(L{-}L)_2]^{2+}$ complexes [209].

Table 15
Phosphino–thioether and phosphino–selenoether complexes of cobalt

	Magnetic properties	Ref.
$[Co(H_2PCH_2CHMeSR)_3]^{3+}$ (R = Me, Et)[a1]		[60]
$[Co(e\text{PSR})_2]^{2+}$ (R = Me, Et)	*	[208]
$[Co(CO)_2(e\text{PSR})_2]^{+}$ (R = Me, Et, Ph)		[208]
$[Co(NO)_n(e\text{PSR})_2]$ (R = Me, Et; $n = 1, 2$)		[210]
$[CoBr(ph\text{PEMe})_2]$ (E = S, Se)	*	[212]
$[CoX\{Ph_2PC_6H_4S(CH_2)_3SC_6H_4PPh_2\}]$ (X = Cl, Br, I)	*	[213]
$[CoI_2\{(Ph_2PCH_2CH_2)_2S\}]$	*	[214,190]
$[CoX_2(PPh_{3-x}Tn_x)_2]$ (X = Cl, Br, I; $x = 1$–3)	*	[215]

[a] Formulation uncertain [61].

The complexes $[Co(ePSR)_2]^{2+}$ (R = Me, Et) react with NO at room temperature to give five-coordinate mononitrosyl complexes $[Co(NO))(ePSR–P,S)_2]^{2+}$, which decompose in refluxing methanol to form four coordinate dinitrosyl complexes $[Co(NO)_2(ePSR–P)_2]^{+}$ [210]. This $\{Co(NO)\}^8$ to $\{Co(NO)_2\}^{10}$ transformation [211] is promoted by bases or halide or psuedohalide anions.

$[Co(ePSR)_2]^{2+}$ can also be reductively carbonylated to yield carbonylcobalt(I) complexes $[Co(CO)_2(ePSR)_2]^{+}$ (R = Me, Et, Ph), which are thought to have a trigonal-bipyramidal geometry with one phosphino–thioether ligand chelating [208].

Reaction of *ph*PEMe (E = S, Se) with cobalt(II) bromide leads to the five-coordinate complexes $[CoBr(phPEMe)_2]$ [212]. Similar complexes are also formed with the tetradentate ligand $Ph_2PC_6H_4S(CH_2)_3SC_6H_4PPh_2$ [213].

The complex $[CoI_2\{(Ph_2PCH_2CH_2)S\}]$ can be prepared from CoI_2 and bis(diphenylphosphinoethyl) sulfide. It is a non-electrolyte in nitrobenzene solution and its magnetic moment, $\mu_{eff} = 2.18\mu_B$, is consistent with a single unpaired electron with a relatively large orbital contribution to the moment: the cobalt centre is thought to be five-coordinate [190,214].

The cobalt(II) complexes $[CoX_2(PPh_{3-x}Tn_x)_2]$ (X = Cl, Br, I, NCS; Tn = 2-thienyl; $x = 1–3$) have been prepared and shown to be very similar in their magnetic and spectroscopic properties to the triphenylphosphine derivatives, suggesting (*P*)-monodentate coordination of the thienylphosphines [215].

Reaction of an excess of phosphino–thioether with $[\{MClL\}_2]$ (M = Rh, Ir; L = cod, nbd) leads to the bis-chelate complexes $[M(PSR)_2]^{+}$ [216,217]. If stoichiometric quantities of ligand are used, $[RhL(PSR)]^{+}$ may be isolated in some cases. One exception is the ligand 2-(diphenylphosphino)thiophene (dppt), which will not form chelate complexes. $[Rh(cod)(dppt\text{-}P)_2]^{+}$ and $[Rh(ePSMe–P,S)_2]^{+}$ have been crystallographically characterised [193]. In a similar reaction, *e*PSR ligands in which R is a mono- or disaccharide will displace the acac ligand of [Rh(acac)(cod)] to give cationic $[Rh(cod)(ePSR)]^{+}$ complexes: the circular dichroism spectra of these complexes have been reported [195].

$[M(ePSR)_2]^{+}$ (M = Rh, Ir; R = Me, Et, Ph) readily form dioxygen adducts $[M(O_2)(ePSR)_2]^{+}$, and are effective catalysts for the oxidation of terminal alkenes to methyl ketones [218,219]. The size of the chelate ring appears to be important, as $[Rh(mPSPh)_2]^{+}$ and $[Rh(prPSPh)_2]^{+}$ are poor catalysts. Anderson and Kumar also found no reaction between $[Rh(ePSMe)_2]^{+}$ and dihydrogen at room temperature [220].

Reaction of *m*PSMe with $[\{RhCl(CO)_2\}_2]$ yields the A-frame type complex $[\{RhCl(CO)(mPSMe)\}_2]$: It is postulated that the phosphino–thioether ligands bridge in a head-to-tail manner, with each phosphine *trans* to a thioether group [221].

Reaction of *e*ESMe (E = P, As) with $[\{RhCl(CO)_2\}_2]$ yields [RhCl(CO)(*e*ESMe)], while reaction with $[RhCl_2(CO)_2]^{-}$ apparently leads to oxidation of rhodium(I) to rhodium(II) to form the dimeric complexes $[\{RhCl_2(CO)(eESMe)\}_2]$. Reaction of $RhCl_3\cdot 3H_2O$ with *e*ESMe leads to reduction of rhodium(III) to rhodium(II) and the formation of $[\{RhCl_2(eESMe)\}_2]$, which is readily carbonylated to $[\{RhCl_2(CO)(eESMe)\}_2]$ [222] (Table 16).

Table 16
Phosphino–thioether and arsino–thioether of rhodium and iridium[a1]

	Crystal structure	Ref.
$[M(m\text{PSPh})_2]^+$		[220,226][*218*,*219*]
$[Rh(e\text{PSR})_2]^+$ (R = Me, Et, Ph)	*	[193,216,226][*218–220*]
$[Rh(pr\text{PSPh})_2]^+$		[*218*,*219*][220]
$[Rh(CO)(e\text{PSPh})_2]^+$		[226]
$[Rh(cod)(dppt)_2]^+$	*	[193]
$[Rh(nbd)(m\text{PSPh})]^+$		[220]
$[Rh(nbd)(e\text{PSR})]^+$ (R = Me, Et, Ph, Cd)[b1]		[194,220]
$[Rh(nbd)(pr\text{PSPh})]^+$		[220]
$[M(O_2)(e\text{PSR})_2]^+$ (R = Me, Et, Ph)		[216]
$[RhCl(CO)(m\text{PSPh})_2]$		[223,226][*225*]
$[RhCl(CO)(m\text{PSPh})_2HgCl]$		[225]
$[\{RhCl(CO)(m\text{PSPh})\}_2]$		[221]
[RhCl(cod)(*m*PSPh-*P*,*S*)]		[226]
[RhCl(CO)(*e*PSR)] (R = Me, Ph)		[221,222,226]
$[RhCl(CO)(e\text{PSPh})_2]$		[223,226][*225*]
[RhCl(CO)(*e*AsSMe)]		[222]
$[RhCl(CO)_2(dppt)_2]$		[224]
$[RhCl(H_2O)(e\text{PSMe})]$		[222]
$[\{RhCl_2(e\text{ESMe})\}_2]$ (E = P, As)		[222]
$[\{RhCl_2(CO)(e\text{ESMe})\}_2]$ (E = P, As)		[222]
$[Rh(H_2PCH_2CHMeSMe)_3]$[c1]		[60]
$[Ir(e\text{PSR})_2]^+$ (R = Me, Et, Ph)		[216,226][*218*,*219*]
$[Ir(CO)(e\text{PSR})_2]^+$ (R = Me, Et, Ph)		[226,227]
$[Ir(CO)_2(e\text{PSR})_2]^+$ (R = Me, Et)		[227]
$[IrH(CO)(e\text{PSEt})_2]^+$		[227]
$[IrH(COOMe)(e\text{PSEt})_2]^+$	*	[227]
$[IrCl(cod)(m\text{PSPh-}P)_2]$		[226]
$[IrCl(e\text{PSPh})_2]$		[226]
$[IrCl(CO)(e\text{PSPh})_2]$		[226]

[a] References in italics are concerned with the reactivity of complexes rather than their preparation and characterisation.

[b] Cd = β-cyclodextrin-6-yl.

[c] Formulation uncertain [61].

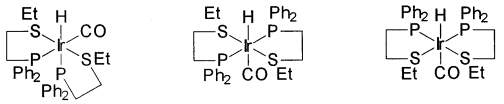
Reaction of $[\{RhCl(CO)_2\}_2]$ with an excess of *e*PSPh or *m*PSPh leads to the Vaska-type complexes $[RhCl(CO)(\text{PSPh–}P)_2]$ [223]. Careful reaction with an excess of dppt leads to the dicarbonyl complex $[RhCl(CO)_2(dppt)_2]$, which readily loses carbon monoxide to form $[RhCl(CO)(dppt)_2]$ [224].

The oxidative addition of mercury(II) chloride to $[RhCl(CO)(m\text{PSPh})_2]$ yields a white product $[RhCl(CO)(m\text{PSPh})_2HgCl]$, in which the phosphino–thioether ligands are bound to rhodium through phosphorus and to mercury through sulfur. The presence of a rhodium–mercury bond is inferred from the observation of $^2J_{PHg} = 306$ Hz in the ^{31}P-NMR spectrum. The nature of the oxidative addition product of $HgCl_2$ and $[RhCl(CO)(e\text{PSPh})_2]$ could not be ascertained [225].

Reaction of $[\{RhCl(cod)\}_2]$ with excess *m*PSPh under an atmosphere of nitrogen yielded the complex [RhCl(*m*PSPh)(cod)]: an examination of the ^{1}H- and ^{31}P-NMR spectra showed that it is the phosphino–thioether and not the cyclooctadiene which is chelating in this four-coordinate complex. However, in the analogous reaction with $[\{IrCl(cod)\}_2]$, the five-coordinate complex [IrCl(*m*PSPh-*P*)$_2$(cod)] is formed, containing chelating cyclooctadiene. Reaction of $[\{MCl(cod)\}_2]$ with *e*PSPh yields $[Rh(ePSPh)_2]^+$ (see above) and $[IrCl(ePSPh)_2]$, confirming the stronger binding ability of the ethylene-bridged ligand. If sodium tetraphenylborate is added to ethanolic solutions of $[IrCl(mPSPh)_2(cod)]$ or $[IrCl(ePSPh)_2]$, the bis(phosphino–thioether) complexes $[Ir(PSPh)_2]^+$ are precipitated. $[M(ePSPh)_2]^+$ (M = Rh, Ir) complexes are readily carbonylated to give $[M(CO)(ePSPh)_2]^+$, which appear to be five-coordinate on the basis of their ^{31}P-NMR spectra [226].

Reaction of *e*PSR (R = Me, Et) with $[IrCl(CO)(PPh_3)_2]$ in dichloromethane–methanol at room temperature yields the products $[Ir(CO)(ePSR)_2]^+$, although *e*PSPh does not give a single species under these conditions. The complexes are stereochemically non-rigid on the NMR time scale, but are thought to have a five-coordinate trigonal-bipyramidal structure with an equatorial carbonyl ligand. The complexes could be carbonylated to give the dicarbonyl species $[Ir(CO)_2(ePSR)_2]^+$, which are thought to be five coordinate with a pendant thioether group [227].

$[Ir(CO)(ePSEt)_2]^+$ can be protonated by strong acids to give hydrido–iridium(III) complexes $[IrH(CO)(ePSEt)_2]^{2+}$ [227]. The (*OC*-6-43)-isomer, with the hydride *cis* to the carbonyl (see Fig. 12), is formed by protonation with HBF_4 while one of the two isomers with the hydride *trans* to the carbonyl (*OC*-6-12, *OC*-6-22), expected to be the more stable arrangement [228], is formed by protonation with HCl. The *cis*-isomer slowly yields the *trans*-isomer on standing in dichloromethane solution, and the isomerisation is promoted by chloride ions. $[IrH(CO)(ePSEt)_2]^{2+}$ reacts with methanol to give the methoxycarbonyl complex $[IrH(COOMe)(ePSEt)_2]^+$, which has been crystallographically characterised. Ethanol reacts similarly, but the more basic Pr^{i}OH and Bu^{t}OH and the more acidic CF_3CH_2OH do not react [227]. Although this reaction represents a formal carbonylation of methanol, no evidence for the reductive elimination of methyl formate was observed.



(*OC*-6-43) (*OC*-6-12) (*OC*-6-22)

Fig. 12. Three of the possible isomers of $[IrH(CO)(ePSEt)_2]^{2+}$.

5.2.5. Group 10: nickel, palladium, platinum

Methylene-bridged phosphino–thioethers *m*PSR (R = Me, Ph) do not form chelate complexes with nickel(II) centres, but instead form $[NiX_2(m\text{PSR}\text{–}P)_2]$ complexes which show an equilibrium in solution between square-planar and pseudo-tetrahedral geometries [229]. The reaction of other bidentate phosphino–thioethers with nickel(II) precursors such as nickel(II) perchlorate, or alkylation of nickel(II) phosphino–thiolate complexes with dimethyl sulfate or Et_3O^+, leads to a variety of four-coordinate complexes $[Ni(PSR)_2]^{2+}$ [71,190,230,231]. Addition of halide or pseudohalide anions to the reaction, either in the form of a nickel halide precursor or a haloalkane alkylating agent, leads to the five-coordinate species $[NiX(PSR)_2]^+$ [71,231,232]. Four-coordinate $[NiX_2(PSR)]$ may also be formed if the amount of phosphino–thioether is limiting [233], and similar complexes $[NiX_2(Me_2AsC_6H_4SMe)]$ (X = Cl, Br, I) are formed with an arsino–thioether ligand [234] (Table 17).

The iodo complex $[NiI\{(Ph_2PCH_2CH_2SCH_2)_2\}]^+$ displays remarkable temperature dependent magnetic behaviour. Below 150 K, it behaves as a normal paramagnet with $\mu_{eff} = 0.7\mu_B$ (0 K); above 240 K it displays temperature-independent paramagnetism with $\chi_m = 570$ cm^3 mol^{-1}. Between those temperatures, μ_{eff} rises sharply from 1.0 to $1.7\mu_B$ before falling back again. The crystal structure of the complex has been determined both at 295 and at 120 K, but there is no significant difference between the two determinations [232,235].

$[Ni(e\text{PSR})_2]^{2+}$ (R = Me, Et, Ph) react with excess cyanide to give $[Ni(CN)_2(e\text{PSR})_2]$. The coordination number of these complexes varies with the nature of R, being five for R = Me (one monodentate and one chelating phosphino–thioether ligand), four for R = Ph (both phosphino–thioether ligands monodentate) and four in the solid-state and five in solution for R = Et. $[Ni(CN)_2(e\text{PSPh})_2]$ reacts with excess *e*PSPh to give a five-coordinate complex $[Ni(CN)_2(e\text{PSPh-}P)_3]$: an analogous equilibrium can be observed for $[Ni(CN)(e\text{PSEt})_n]$ ($n = 2$, 3) in the presence of large excesses of *e*PSEt [188].

$[NiX_2(Ph_2PC_6F_4SMe)_2]$ can be prepared by reacting NiX_2 with an excess of the ligand: the complexes are green and paramagnetic ($\mu_{eff} = 3.15\mu_B$ for X = Br), suggesting six-coordinate nickel(II). The green complexes (X = Cl, Br) dissolve in dichloromethane and other solvents to give red diamagnetic solutions, presumably through dissociation of one phosphino–thioether ligand to form square-planar $[NiX_2(Ph_2PC_6F_4SMe)]$: the electronic spectra of solutions of $[NiBr_2(Ph_2PC_6F_4SMe)]$ and $[NiBr_2(Ph_2PC_6F_4SMe)_2]$ are indistinguishable. $[NiCl_2(Ph_2PC_6F_4SMe)]$ cannot be isolated in the solid state, though it is thought to be present in solution, and $[Ni(NCS)_2(Ph_2PC_6F_4SMe)]$ readily decomposes to give $[Ni(NCS)_2(Ph_2PC_6F_4SMe)_2]$ on exposure to moisture or polar solvents. $[NiX_2(Ph_2PC_6F_4SMe)_n]$ ($n = 1$, 2) complexes spontaneously demethylate in the presence of iodide ions to give $[Ni(Ph_2PC_6F_4S)_2]$ [233].

Reaction of $Et_2PCH_2CH_2SEt$ with nickel(II) thiocyanate yields $[Ni(NCS)_2(Et_2PCH_2CH_2SEt)_2]$, which exists as a diamagnetic yellow form and a paramagnetic green form in the solid state. The diamagnetic form, which is the only one which persists in solution, is thought to be a square-planar complex with

Table 17
Complexes of nickel with acyclic phosphino–thioether, phosphino–selenoether and arsino–thioether ligands

	Magnetic properties	Crystal structure	Ref.[a1]
$[Ni(ePSEt)_2]$			[243,244]
$[Ni\{Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2\}]$			[243]
$[Ni(CO)_2(ePSEt)_2]$			[243,244]
$[Ni(fn)(ePSEt)_2]$			[244]
$[Ni(Ph_2PCH_2CH_2SCH_2C_5H_4N)_2]^+$			[246]
$[Ni(H_2PCH_2CHRSR')_2]^{2+}$ (R = H, Me; R′ = Me, Et)[b1]			[71]
$[Ni(ePSR)_2]^{2+}$ (R = Me, Et, Ph)		*	[231,243,244][*188*]
$[Ni(Ph_2PCH_2CH_2SCH_2COO)_2]$			[246]
$[Ni(Ph_2PCH_2CH_2SCH_2C_5H_4N)_2]^{2+}$		*	[246]
$[Ni\{(Ph_2PCH_2CH_2SCH_2)_2\}]^{2+}$		*	[190,230,243]
$[Ni(MePhPCH_2CH_2SMe)_2]^{2+}$			[231]
$[Ni(Et_2PCH_2CH_2SR)_2]^{2+}$ (R = Me, Et)			[231,236]
$[Ni\{(Et_2PCH_2CH_2SCH_2)_2C_6H_4\}]^{2+}$			[231]
$[Ni\{Ph_2PC_6H_4S(CH_2)_3SC_6H_4PPh_2\}]^{2+}$			[213]
$[Ni(phPEMe)_2]^{2+}$ (E = S, Se)			[237]
$[Ni\{PhP(C_6H_4SMe)_2\}(phPSMe)]^{2+}$	*		[237]
$[Ni\{PhP(C_6H_4SMe)_2\}_2]^{2+}$			[237]
$[Ni\{P(C_6H_4SMe)_3\}_2]^{2+}$	*		[240]
$[Ni(H_2PCH_2CH_2S)(H_2PCH_2CH_2SR)]^+$ (R = Me, Et)[b1]			[71]
$[Ni(H_2PCH_2CHMeS)(H_2PCH_2CH_2SR)]^+$ (R = Me, Et)[b1]			[71]
$[Ni\{PhP(C_6H_4SMe)_2(L–L)]^{2+}$ (L–L = dppe, ape)	*		[237]
$[NiX_2(Ph_2PC_6F_4SMe)]$ (X = Cl, Br, NCS)	*		[233]
$[NiX_2(mPSR\text{-}P)_2]$ (X = Cl, Br, I, NCS; R = Me, Ph)	*		[229]
$[NiX_2(PPh_{3-x}Tn_x)_2]$ (X = Br, I, NCS; x = 1–3)	*		[215]
$[NiCl_2(phPEMe)]$ (E = S, Se)			[237]
$[NiX_2(Me_2AsC_6H_4SMe)]$ (X = Cl, Br, I)			[234]
$[NiBr\{(H_2PCH_2CHRSCH_2)_2C_6H_4\}]^+$ (R = H, Me)[b1]			[71]
$[NiH(ePSEt)_2]^+$			[243,244]
$[Ni(CN)(ePSR)_2]^+$ (R = Me, Et, Ph)			[188]
$[NiX(ePSEt)_2]^+$ (X = Me, Ac)			[243]
$[NiH\{(Ph_2PCH_2CH_2SCH_2)_2\}]^+$		*	[243]
$[NiX\{(Ph_2PCH_2CH_2SCH_2)_2\}]^+$ (X = Me, Ac)			[243]
$[NiI(Et_2PCH_2CH_2SR)_2]^+$ (R = Me, Et)	*		[231,236]
$[NiX\{Ph_2PC_6H_4S(CH_2)_3SC_6H_4PPh_2\}]^+$ (X = Cl, Br, I)			[213]
$[NiX\{(Ph_2PCH_2CH_2)_2S\}]^+$ (X = Cl, Br, I)			[190]
$[NiBr\{(Ph_2AsCH_2CH_2)_2S\}]^+$			[239]
$[NiX\{(Ph_2PCH_2CH_2SCH_2)_2\}]^+$ (X = Br, I)	*	*	[190,232,235]
$[NiX(phPEMe)_2]^+$ (X = Cl, Br; E = S, Se)			[237]
$[NiX\{P(C_6H_4SMe)_3\}]^+$ (X = Cl, Br, I, NCS)			[240]
$[NiL\{P(C_6H_4SMe)_3\}]^{2+}$ (L = PPh_3, $PMePh_2$, tu)			[240]
$[NiI_2\{(Ph_2PCH_2CH_2)_2S\}]$		*	[190,238]

Table 17 (Continued)

	Magnetic properties	Crystal structure	Ref.[a1]
$[NiX_2\{(Ph_2AsCH_2CH_2)_2S\}]$ (X = Br, I)			[239]
$[Ni(NCS)_2(Et_2PCH_2CH_2SEt)_2]$	*		[236]
$[NiCl_2(ph PEMe)_2]$ (E = S, Se)			[237]
$[NiX_2\{PhP(C_6H_4SMe)_2\}]$ (X = Cl, Br, I)			[237]
$[Ni(CN)_2(e PSR)_2]$ (R = Me, Et, Ph)			[188]
$[Ni(NCS)_2(Ph_2PC_6F_4SMe)_2]$	*		[233]
$[Ni(Ph_2PCH_2CH_2SCH_2COO)_2]^+$			[246]
$[Ni(Ph_2PCH_2CH_2SCH_2C_5H_4N)_2]^{3+}$			[246]

[a] References in italics are concerned with the reactivity of the complexes rather than their preparation and characterisation.

[b] Formulation uncertain [61].

(*P*)-monodentate coordination of the phosphino–thioether ligands, whereas the paramagnetic form is thought to be six-coordinate with chelating phosphino–thioether ligands [236].

The complex $[Ni(NCS)_2(Ph_2PC_6F_4SMe)_2]$ shows a magnetic moment of $\mu_{eff} = 2.25\mu_B$ at room temperature, unusually low for a six-coordinate nickel(II) complex. Curie–Weiss behaviour was observed between 73 K and room temperature ($\theta_W = -4$ K), precluding either magnetic coupling or spin equilibrium phenomena. The observation of infrared absorption bands characteristic of ionic thiocyanate suggests that the correct formulation of this complex is $[Ni(NCS)_2(Ph_2PC_6F_4SMe\text{-}P,S)_2]$ $[Ni(Ph_2PC_6F_4SMe\text{-}P,S)_2](NCS)_2$, assuming the four-coordinate species to be square-planar and diamagnetic: this would imply a magnetic moment $\mu_{eff} = 3.08\mu_B$ for the six-coordinate centre [233].

$[NiCl(ph PEMe)_2]$ (E = S, Se) will react with excess chloride to yield $[NiCl_2(ph PEMe)_2]$, which the authors formulate as six-coordinate with chelating ligands on the basis of magnetic and spectroscopic data. These complexes lose ligand in solution to give the four-coordinate species $[NiCl_2(ph PEMe)]$ [237].

Reaction of $(Ph_2PCH_2CH_2)_2S$ with NiX_2 (X = Cl, Br, I) in ethanol yields products analysing as $[NiX_2\{(Ph_2PCH_2CH_2)_2S\}]$: these change colour on dissolution in polar solvents, and addition of a suitable counter-anion leads to isolation of salts of the $[NiX\{(Ph_2PCH_2CH_2)_2S\}]^+$ cation (X = Cl, Br, I) [190]. Of the neutral species, only the diiodide is well characterised, and has been crystallographically characterised; it is isomorphous with its cobalt analogue [238]. The reaction of NiX_2 with the analogous arsino–thioether $(Ph_2AsCH_2CH_2)_2S$ is similar [239]. Nickel(II) halides will react with $PhP(C_6H_4SMe)_2$ to give five-coordinate complexes, $[NiX_2\{PhP(C_6H_4SMe)_2\}]$ (X = Cl, Br, I) [237].

The tridentate ligand $PhP(C_6H_4SMe)_2$ reacts with nickel perchlorate to give $[Ni\{PhP(C_6H_4SMe)_2\}_2]^{2+}$: mixed-ligand complexes such as $[Ni\{PhP(C_6H_4SMe)_2\}(ape)]^{2+}$ (ape = 1-(diphenylarsino)-2-(diphenylphosphino)ethane) have also been prepared. The structure of these complexes could not be determined with certainty, but five-coordination was proposed on the basis of spectroscopic data [237].

The tripodal ligand $P(C_6H_4SMe)_3$ reacts with NiX_2 to give intensely-coloured complexes $[NiX\{P(C_6H_4SMe)_3\}]^+$ (X = Cl, Br, I, NCS) which are thought to be trigonal-bipyramidal: similar complexes $[NiL\{P(C_6H_4SMe)_3\}]^{2+}$ (L = PPh_3, $PMePh_2$, tu) were obtained from the reaction of the ligand with nickel perchlorate in the presence of L. The diamagnetic complex $[Ni\{P(C_6H_4SMe)_3\}_2]^{2+}$ was also prepared, although its structure could not be ascertained [240]. The selenium analogue of the ligand, $P(C_6H_4SeMe)_3$ formed a similar series of complexes [241], although the arsenic analogue, $As(C_6H_4SMe)_3$, did not coordinate to nickel(II) [240]. The absorption coefficient for the first visible band of the selenoether complexes (λ_{max} = ca. 630–675 nm) was ca. 50% higher than that of the corresponding band in the thioether complexes (ε = ca.1100 mol^{-1} dm^3 cm^{-1} (S), 1700 mol^{-1} dm^3 cm^{-1} (Se)).

$[Ni(ePSEt)_2]^{2+}$ and $[Ni\{Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2\}]^{2+}$ show two reversible reduction processes, at $E_{1/2} = +0.182$, -0.399 V and $E_{1/2} = +0.126$, -0.426 V, respectively in acetonitrile solution [242]. The reduction to nickel(0) can also be effected chemically with sodium amalgam. The nickel(0) species reacts with carbon monoxide to form dicarbonyl complexes, and $[Ni(ePSEt)_2]$ reacts with fumaronitrile (fn) to give $[Ni(fn)(ePSEt)_2]$: these complexes are thought to be four-coordinate with (*P*)-bonded ligands. Protonation of the nickel(0) species with fluoroboric acid yielded hydride complexes, and $[NiH\{Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2\}]^+$ has been crystallographically characterised. $[NiH(ePSEt)_2]^+$ is a catalyst for the isomerisation of terminal alkenes to internal alkenes [243,244].

The five-coordinate nickel(II) complex $[Ni\{Ph_2P(CH_2)_2S(CH_2)_2NH(CH_2)_2S(CH_2)_2PPh_2\}]^{2+}$ has been prepared and crystallographically characterised. Reduction with $NaBH_4$ yields the corresponding nickel(I) complex, which reacts with acids in non-aqueous media to give nearly quantitative yields of dihydrogen. The kinetics and mechanism of this reaction, which is a possible model for nickel–iron hydrogenase enzymes, have been discussed at some length [245].

$[Ni(Ph_2PCH_2CH_2SCH_2COO)_2]$ cannot be reversibly reduced, but shows a reversible oxidation at $E_{1/2} = +0.66$ V in methanol solution: the oxidation can be effected chemically with cerium(IV). $[Ni(Ph_2PCH_2CH_2SCH_2C_5H_4N)_2]^{2+}$ shows a reversible oxidation and two reversible reductions at $E_{1/2} = +0.93$, -0.47, -1.01 V in propylene carbonate solution: the nickel(III) and nickel(I) complexes can be prepared chemically by reaction with cerium(IV) and Cp_2Co, respectively [246].

Reaction of a stoichiometric quantity of *m*PSPh with $[PdCl_2(PhCN)_2]$ gives a polymeric product $[\{PdCl_2(mPSPh)\}_n]$, belived to be a cyclic tetramer in solution. Reaction of an excess of *m*PSPh with $[MCl_2(PhCN)_2]$ (M = Pd, Pt) yields the complexes $[MCl_2(mPSPh–P)_2]$: the palladium complex has *trans* geometry while the isolated platinum complex is the *cis*-isomer [226].

Reaction of mercury(II) chloride with $[MCl_2(mPSPh)_2]$ (M = Pd, Pt) yields the product $[MCl_2(mPSPh)_2HgCl_2]$ in which the phosphino–thioether ligand is bound to palladium or platinum through phosphorus and to mercury through the initially pendant thioether group. In contrast to the corresponding rhodium complex (see

Section 5.2.4), there is no oxidative addition or metal–metal bond formation. The platinum complex in particular is very labile, extruding $HgCl_2$ on recrystallisation [225] (Tables 18 and 19).

Reaction of $[PdCl_2(PhCN)_2]$ with a stoichiometric quantity of *e*PSPh yielded the chelate complex $[PdCl_2(e\text{PSPh–}P,S)]$, while reaction with an excess of ligand yielded *trans*-$[PdCl_2(e\text{PSPh–}P)_2]$. Reaction with the analogous platinum(II) precursor $[PtCl_2(PhCN)_2]$ with excess *e*PSPh yielded *cis*-$[PtCl_2(e\text{PSPh–}P)_2]$. The chelated platinum complex, $[PtCl_2(e\text{PSPh–}P,S)]$, can be prepared by recrystallisation of the polymeric product obtained from the reaction of a stoichiometric quantity of *e*PSPh with $[PtCl_4]^{2-}$. Addition of one equivalent of $NaBPh_4$ to an ethanolic solution of $[MCl_2(e\text{PSPh–}P)_2]$ leads to precipitation of $[MCl(e\text{PSPh})_2]BPh_4$, in which one of the phosphino–thioether ligands is chelating and the other is bound solely through the phosphorus atom: use of an excess of tetraphenylborate leads to the isolation of $[M(e\text{PSPh–}P,S)_2]^{2+}$ [226].

The complexes $[PdCl_2(R_2PCH_2CH_2SEt)]$ (R = Et, Pr^i, Ph) have been crystallographically characterised. the R = Et, Pr^i complexes are active catalysts for the photochemical carbonylation of benzene to benzaldehyde, as are $[PdCl_2(e\text{PSPh})]$ and the corresponding platinum complexes, but the *e*PSMe and *e*PSEt complexes are inactive. The mechanism of catalysis is thought to involve photochemical cleavage of the M–S bond [247].

Anderson and Kumar have prepared the complexes $[PtX_2(e\text{PSMe})]$ (X = Cl, I) by reaction of $[PtX_2(\text{cod})]$ with one equivalent of ligand. These complexes react with a second equivalent of ligand to produce products which appear to retain coordinated halide, but which could not be fully characterised: on removal of halide with $AgBF_4$, the complex $[Pt(e\text{PSMe})_2]^{2+}$ was formed quantitatively [248].

A number of alkylpalladium(II) and alkylplatinum(II) complexes of phosphino–thioethers and arsino–thioethers, *e*ESR, have been prepared by halide metathesis or by displacement of neutral ligands such as 1,5-cyclooctadiene [249–251]. The complex $[PtClPh(e\text{PSMe})]$ reacts slowly with carbon monoxide, forming the benzoyl–platinum(II) complex $[PtCl(COPh)(e\text{PSMe})]$ [252].

A variety of $[Pd(PSR)_2]^{2+}$, $[PdX_2(PSR)]$ and (with potentially tridentate ligands) $[PdX(PSR)]^{+}$ complexes have been prepared. Complexes of the ligands $E(C_6H_4SMe)_3$ (E = P, As) have a tendency to polymerise [253].

Reaction of $[M(SCH_2CH_2PEt_2)_2]$ (M = Pd, Pt) with iodomethane gives $[PdI_2(Et_2PCH_2CH_2SMe)]$ or $[Pt(Et_2PCH_2CH_2SMe)_2]^{2+}$ (c.f. the nickel(II) analogue, which gives $[NiI(Et_2PCH_2CH_2SMe)_2]^{+}$). $[Pd(Et_2PCH_2CHMeSEt)_2]^{2+}$ has been prepared by ethylation of the corresponding phosphino–thiolate complex with Et_3O^{+} [231]. The strong tendency for palladium to form $[PdX_2(PSR)]$ complexes can be seen in the formation of $[Cl_2Pd\{Ph_2P(CH_2)_2S(CH_2)_3S(CH_2)_2PPh_2\}PdCl_2]$ from $PdCl_2$ and the tetradentate ligand [254]: nickel and platinum form mononuclear $[ML]^{2+}$ complexes.

The complexes $[PdX_2(ph\text{ESMe})]$ and $[PdX_2\{PhE(C_6H_4SMe)_2\}]$ (X = Cl, I; E = P, As) were prepared by reacting the ligands with PdX_2: all are four-coordinate species, with the complexes of $PhE(C_6H_4SMe)_2$ having a pendant thioether group. These complexes were readily demethylated by heating in DMF solution to give

Table 18
Complexes of palladium and platinum with acyclic phosphino–thioethers and phosphino-selenoethers

	Crystal structure	Ref.
[M(*e*PSPh)$_2$]		[259,261]
[PtCl(*m*PSMe-*P*)(*m*PSMe-*P*,*S*)]		[221]
[{PdX(*m*PSBz)}$_2$] (X = Cl, I)	*	[257]
[{Pd(NC$_5$H$_4$Me)(*m*PSBz)}$_2$]$^{2+}$		[257]
[{PtCl(*m*PSMe)}$_2$]		[221]
[M(SCH$_2$CH$_2$PH$_2$)(H$_2$PCH$_2$CH$_2$SR)] (R = Me, Et)[a1]		[71]
[M(SCHMeCH$_2$PH$_2$)(H$_2$PCH$_2$CHMeSR)] (R = Me, Et)[a1]		[71]
[M(H$_2$PCH$_2$CHR′SR)$_2$]$^{2+}$ (R = Me, Et; R′ = H, Me)[a1]		[71]
[M(H$_2$PCH$_2$CH$_2$SCH$_2$C$_6$H$_4$CH$_2$SCH$_2$CH$_2$PH$_2$)]$^{2+}$[a1]		[71]
[M(H$_2$PCH$_2$CHMeSCH$_2$C$_6$H$_4$CH$_2$SCHMeCH$_2$PH$_2$)]$^{2+}$[a1]		[71]
[M(Et$_2$PCH$_2$CH$_2$SMe)$_2$]$^{2+}$ (M = Pd, Pt)		[231]
[Pd(Ph$_2$PCH$_2$CH$_2$SCH$_2$CH$_2$SCH$_2$CH$_2$PPh$_2$)]$^{2+}$		[190]
[M{Ph$_2$PC$_6$H$_4$S(CH$_2$)$_3$SC$_6$H$_4$PPh$_2$}]$^{2+}$		[213]
[Pt(*e*PSR)$_2$]$^{2+}$ (R = Me, Et, Ph)		[226,248]
[M(*ph*PSR)$_2$]$^{2+}$ (M = Pd, R = Me, Et: M = Pt; R = Et)		[72,75,253,255]
[Pd{P(C$_6$H$_4$SMe)$_3$}$_2$]$^{2+}$		[253]
[Pd{PhP(C$_6$H$_4$SMe)$_2$}$_2$]$^{2+}$		[75]
[MCl(*e*PSPh-*P*)(*e*PSPh-*P*,*S*)]$^+$		[226]
[Pd{MeCH(1-C$_{10}$H$_6$)NMe$_2$-*C*^{2},*N*}(*e*PSMe)]$^+$	*	[263]
[PdBr{Me$_2$NCMe(1-C$_{10}$H$_6$)}(MePhPCH$_2$CH$_2$SBz-*P*)]	*	[32]
[MI{Ph$_2$PC$_6$H$_4$S(CH$_2$)$_3$SC$_6$H$_4$PPh$_2$}]$^+$		[213]
[PdCl{PhP(C$_6$H$_4$SMe)$_2$}]$^+$		[253]
[Pt(*ph*PS)(*ph*PSEt)]$^+$		[255]
[PdI$_2$(Et$_2$PCH$_2$CH$_2$SMe)]		[231]
[Cl$_2$Pd{Ph$_2$P(CH$_2$)$_2$S(CH$_2$)$_3$S(CH$_2$)$_2$PPh$_2$}PdCl$_2$]	*	[254]
[PdI$_2${(Ph$_2$PCH$_2$CH$_2$)$_2$S}]		[190]
[PdX{(Ph$_2$PCH$_2$CH$_2$)$_2$S}]$^+$ (X = Cl, Br)		[190]
[PdCl$_2$(L2-*P*,*S*)][b1]	*	[201]
[PdCl$_2$(L3-*P*,*S*)][b1]		[266]
[MCl$_2$(*m*PSPh)$_2$HgCl$_2$]		[225]
[MCl$_2$(*m*PSR-*P*)$_2$] (M = Pd; R = Bz, Ph: M = Pt; R = Me, Ph)		[221,226,257]
[PdCl$_2$(*m*PSPh)]$_n$		[226]
[Pd$_2$Cl$_2$(μ-PhC=CH)(μ-*m*PSBz)$_2$]		[257]
[Pd$_2$Cl$_2$(μ-MeO$_2$CC=CCO$_2$Me)(μ-*m*PSBz)$_2$]		[257]
[Pd$_2$X$_2$(μ-C$_6$H$_4$)(μ-*m*PSBz)$_2$] (X = AcO, I)		[258]
[PtCl(COPh)(*e*PSMe)]		[252]
[PtCl(η^1-C$_3$H$_5$)(*e*PSR)] (R = Me, Ph)		[261]
[Pt(η^3-C$_3$H$_5$)(*e*PSR)]$^+$ (R = Me, Ph)		[261]
[Pd(η^3-CH$_2$CMeCH$_2$)(*e*PSR)]$^+$ (R = Me, Et, Ph)		[259]
[PdCl$_2$(R$_2$PCH$_2$CH$_2$SEt)] (R = Et, Pr^i, Ph)	*	[247]
[MCl$_2$(*e*PSPh)]		[226,247]
[MCl$_2$(*e*PSPh-*P*)$_2$]		[226]
[MX$_2$(*e*PSMe)] (X = Cl, I, Me, Ph)	*	[247–251,267]
[PtX$_2$(BF$_3$)(*e*PSMe)] (X = Cl, I)		[267]
[PdCl$_2${P(C$_6$H$_4$SMe)$_3$}]		[253]
[Pd$_2$Cl$_4${P(C$_6$H$_4$SMe)$_3$}]		[253]
[PdX$_2$(Ph$_2$PC$_6$F$_4$SMe)] (X = Cl, Br, I, SCN)		[233]
[PdX$_2${PhP(C$_6$F$_4$SMe)$_2$}] (X = Cl, Br, I, SCN)		[233]

Table 18 (Continued)

	Crystal structure	Ref.
$[\{PdX[PhP(C_6F_4SMe)(C_6F_4S)]\}_2]$ (X = Cl, Br, I, SCN)		[233]
$[MX_2(phPSR)]$ (R = Me, Et; X = Cl, I)	*	[253,75,72,256]
$[Pd\{PhP(C_6H_4SMe)(C_6H_4S)\}_2]$		[75]
$[PdI_2\{PhP(C_6H_4SMe)(C_6H_4SR)\}]$ (R = Me, Et)		[253,75]
$[Pd(SCN)_2(phPEMe)]$ (E = S, Se)		[206]

[a] Formulation uncertain [61]
[b] See Fig. 11.

dimeric species $[\{PdX(phES)\}_2]$ and $[\{PdX[PhE(C_6H_4SMe)(C_6H_4S)]\}_2]$. Reaction of PdX_2 with an excess of the phosphino– or arsino–thioether ligands gave the bis chelate complexes $[Pd(phESMe)_2]^{2+}$ and $[Pd\{PhE(C_6H_4SMe)_2\}_2]^{2+}$. These can be demethylated in DMF solution to give $[Pd(phES)_2]$ and $[Pd\{PhE(C_6H_4SMe)(C_6H_4S)\}_2]$ [72,75]. Similarly, $[Pt(phPSEt)_2]^{2+}$ undergoes a stepwise dealkylation in DMF solution [255].

Table 19
Complexes of palladium and platinum with acyclic arsino-thioether ligands.

	Ref.
$[PdCl_2\{As(C_6H_4SMe)_3\}]$	[253]
$[Pd_2Cl_4\{As(C_6H_4SMe)_3\}]$	[253]
$[Pd\{As(C_6H_4SMe)_3\}_2]^{2+}$	[253]
$[PdX_2\{Ph_2AsC_6H_4S(CH_2)_nSC_6H_4AsPh_2\}]$ (X = Cl, Br, I, SCN; $n = 2, 3$)	[268,269]
$[X_2Pd\{Ph_2AsC_6H_4S(CH_2)_nSC_6H_4AsPh_2\}PdX_2]$ (X = Cl, I; $n = 2$–4)	[269,270]
$[PdCl\{Ph_2AsC_6H_4S(CH_2)_2SC_6H_4AsPh_2\}]^+$	[269]
$[PdX\{Ph_2AsC_6H_4S(CH_2)_3SC_6H_4AsPh_2\}]^+$ (X = Cl, Br, I)	[269]
$[PdX\{Ph_2AsC_6H_4S(CH_2)_4SC_6H_4AsPh_2\}]^+$ (X = Cl, Br)	[270]
$[Pd\{Ph_2AsC_6H_4S(CH_2)_nSC_6H_4AsPh_2\}]^{2+}$ ($n = 2, 3$)	[269]
$[PdI_2(phAsSR)]$ (R = Me, $CH_2C_6H_4NO_2$-*p*)	[75]
$[PdX_2(Me_2AsC_6H_4SMe)]$ (X = Cl, Br, I, SCN)	[234]
$[PdX_2(Me_2AsC_6H_4SMe)_2]$ (X = Cl, Br, I, SCN)	[234]
$[Pd(Me_2AsC_6H_4SMe)_2]^{2+}$	[234]
$[PdI_2\{PhAs(C_6H_4SMe)_2\}]$	[75]
$[\{PdI[PhAs(C_6H_4SMe)(C_6H_4S)]\}_2]$	[75]
$[Pd(phAsSMe)_2]^{2+}$	[75]
$[Pd\{PhAs(C_6H_4SMe)_2\}_2]^{2+}$	[75]
$[Pd\{PhAs(C_6H_4SMe)(C_6H_4S)\}_2]$	[75]
$[PdBr_2\{PhAs(C_6H_4SMe)(C_6H_4SR)\}]$ (R = Bu^n, $CH_2C_6H_4NO_2$-p)	[75]
$[\{PdBr[PhAs(C_6H_4SCH_2C_6H_4NO_2\text{-}4)(C_6H_4S)]\}_2]$	[75]
$[PdX_2(eAsSMe)]$ (X = Cl, Me)	[251]
$[PdClMe(eAsSMe)]$	[251]
$[Pd\{MeCH(1\text{-}C_{10}H_6)NMe_2\text{-}C^2,N\}(R_2AsCH_2CH_2SMe)]^+$ (R = Me, Ph)	[263]
$[PtX_2(eAsSMe)]$ (X = Cl, Me, Ph)	[249,250,267]
$[PtCl_2(BF_3)(eAsSMe)]$	[267]

[PdI_2(*ph*PSEt)] was formed by alkylation of [Pd(*ph*$PS)_2$] with iodoethane, and [$PdBr_2(Ph_2AsC_6H_4SCH_2C_6H_4NO_2)$] was formed from reaction of [Pd(*ph*$AsS)_2$] with *p*-nitrobenzyl bromide. [$PdBr_2${$PhAs(C_6H_4SMe)(C_6H_4SBu^n)$}] and a number of similar complexes have been prepared by alkylation of [Pd{PhE-$(C_6H_4SMe)(C_6H_4S)\}_2$] (E = P, As) with the corresponding alkyl halide: no attempt was made to determine which of the distinct thioether groups was coordinated to the palladium centre [75].

[PdI_2(*ph*PSMe)] has been crystallographically characterised: the chelated phosphine group shows an unusually large *trans* influence (r(Pd–I) = 2.602(1) Å *trans* to S, 2.658(1) Å *trans* to P) [256].

Reaction of *m*PSBz with $[PdCl_4]^{2-}$ yields [$PdCl_2$(*m*PSBz-*P*)$_2$]: this complex reacts with [Pd(dba)$_2$] (dba = dibenzylideneacetone, PhCH=CHCOCH=CHPh) to give the dimeric palladium(I) complex [{PdCl(*m*PSBz)}$_2$], which has been crystallographically characterised. The terminal chlorides can be replaced by iodide or 4-methylpyridine ligands, and the complex will also react with substituted acetylenes to give A-frame type complexes [257,258].

Reaction of [$PtCl_2$(*m*PSMe–*P*)$_2$] with [Pt(dba)$_2$] yields [{PtCl(*m*PSMe)}$_2$], an A-frame type complex with a platinum(I)–platinum(I) bond. based on the ^{31}P-NMR spectrum ($^1J_{PPt}$ = 4080 Hz), it was postulated that the phosphino–thioether ligands bridge head to tail with each phosphorus *trans* to a thioether group, as for the palladium complex [221].

The allyl–palladium(II) complexes [Pd(η^3-CH_2CMeCH_2)(*e*PSR)]$^+$ (R = Me, Et, Ph) have been prepared from [{Pd(η^3-CH_2CMeCH_2)Cl}$_2$] [259]. Reaction of [{Pt(C_3H_5)Cl}$_4$] with *e*PSR (R = Me, Ph) yields the η^1-allyl complexes [PtCl-(η^1- C_3H_5)(*e*PSR)]: NMR data indicate that the phosphorus of the phosphino–thioether ligand is *trans* to the allyl group ($^1J_{PPt}$ = 4600 Hz) [260]. The η^1-allyl complexes readily extrude chloride in polar solvents to give the η^3-allyl complexes [Pt(η^3-C_3H_5)(*e*PSR)]$^+$ [261]. The *e*PSPh complexes (M = Pd, Pt) were reduced by excess ligand to give [M^0(*e*$PSPh)_2$]: these do not react with dioxygen in solution, nor promote the oxidation of alkenes, in contrast to similar complexes (see Section 5.2.8 and Ref. [262]).

The stereodynamics of phosphino–thioether (*e*PSMe) and arsino–thioether (*e*AsSMe, $Me_2AsCH_2CH_2SMe$) complexes of [(*R*)-dimethyl{1-(1-naphthyl)ethyl}aminato–C^2,*N*]palladium(II) units has been investigated, with a particular interest in the rate of inversion at the epimeric sulfur centre [263]. The barrier to inversion at sulfur in these complexes is very low, with a coalescence temperature for the NMR signals of the two epimers of ca. −90°C, which compares to an inversion barrier for terminal thioethers bound to palladium(II) centres of 50–70 kJ mol^{-1} [264]. It is postulated that the lowering of the inversion barrier is an effect of the *trans* ligand, here an aryl carbon, as in the platinum(II) dithioether complexes [$PtX_2(EtSCH_2CH_2SEt)$] [265]. The X-ray crystal structure of the phosphino–thioether complex [Pd(aminate)(*e*PSMe)]$^+$ (aminate = (*R*)-dimethyl-{1-(1-naphthyl)ethyl}aminato–C^2,*N*), has been determined: the asymmetric contains two diastereomers with enantiomorphic configuration at the sulfur centre.

Reaction of L2 (see Fig. 11) with palladium(II) chloride yields the complex $[PdCl_2(L2\text{-}P,S)]$, which has been crystallographically characterised [201]. Reaction of the related tripod ligand 2,2-bis[(phenylsulfanyl)methyl]-1-(diphenylphosphino)propane (L3) yields the expected dichloro complex $[PdCl_2(L3\text{-}P,S)]$: this complex shows a dynamic exchange of coordinated and uncoordinated thioether groups [266].

Platinum(II) phosphino–thioether and arsino–thioether complexes $[PtX_2(e\text{ESMe})]$ (E = P; X = Cl, I: E = As; X = Cl) form stable adducts with boron trifluoride $[PtX_2(BF_3)(e\text{ESMe})]$ [267].

The potentially quadridentate ligands $Ph_2AsC_6H_4S(CH_2)_nSC_6H_4AsPh_2$ ($n = 2$–4) display a range of coordination modes to palladium(II):

- $[PdX_2L]$ ($n = 2$; X = Cl, Br, I: $n = 3$; X = Cl, Br, I, SCN), where the ligand is (*As*,*As′*)-bidentate with pendant thioether groups;
- $[X_2PdLPdX_2]$ ($n = 2$, 3, 4; X = Cl, I), where the ligand is (*As*,*S*)-bidentate to each palladium centre;
- $[PdXL]^+$ ($n = 2$; X = Cl: $n = 3$; X = Cl, Br, I: $n = 4$; X = Cl, Br), where the ligand is (*As*,*As′*,*S*)-tridentate with a dynamic exchange of coordinated and uncoordinated thioether groups;
- $[PdL]^{2+}$ ($n = 2$, 3), where the ligand is tetradentate.

The solution equilibria between the various forms are complex, and the nature of the isolated complex is dependent on the relative solubilities [268–270].

5.2.6. Group 11: copper, silver, gold

The complexes $[Cu(e\text{PSR})_2]^+$ (R = Et, Ph) have been prepared as the perchlorate salts, and the X-ray photoelectron spectra recorded [271]. The sulfur 2*p* binding energies are typical for neutral or nearly neutral sulfur centres: the change in binding energy on coordination ($\Delta E = 20(20)$ kJ mol^{-1}) is significantly lower than that observed for dithiocarbamate (ΔE = ca. 70–100 kJ mol^{-1}) [272] or thiourea (ΔE = ca. 100 kJ mol^{-1}) [273] ligands.

Turpin et al. have prepared the copper(I) complex $[\{CuCl(e\text{PSMe})\}_2]$ and postulated a chloride-bridged dimeric structure with (*P*)-monodentate coordination of the phosphino–thiolate ligand on the basis of NMR and mass spectroscopic evidence [274].

The formation of silver(I) complexes of *m*PSR (R = Me, Ph) and *e*PSR (R = Me, Et, Ph) has been studied by pontentiometry and calorimetry in DMSO solution [275] and in propylene carbonate solution [276]. In DMSO solution, only mononuclear (*P*)-coordinated complexes appear to be formed. In the less coordinating solvent, propylene carbonate, with *e*PSR as the ligand, the more negative values of ΔH and of ΔS indicate the formation of chelate complexes. The X-ray structure of a co-crystal of $[\{Ag(\eta^1\text{-}ClO_4)(\mu\text{-}e\text{PSEt})\}_2]$ and *catena*-$[\{Ag(\eta^1\text{-}ClO_4)(\mu\text{-}e\text{PSEt})\}_n]$ has been determined [276].

The halide-bridged silver(I) complexes $[\{AgX[(Ph_2PCH_2CH_2)_2S]\}_2]$ (X = Cl, I) [277,278] and the monomeric gold(I) complex $[AuCl(e\text{PSMe–}P)]$ [274] have been crystallographically characterised.

5.2.7. Group 12: mercury

Mercury(II) halides react with the phosphino–thioether ligands *m*PSPh and *e*PSPh to give 1:1 complexes $[HgX_2(PSPh)]$ (X = Cl, I) [225].

The X-ray crystal structure of the mercury(II) complex $[HgI_2\{(Ph_2PCH_2CH_2)_2S\}]$ has been determined, and the phosphino–thioether ligand shown to be bound only through the terminal phosphorus centres, with the mercury being tetrahedrally coordinated [279].

Mercury(II) chloride also reacts with phosphino–thioether complexes of rhodium, palladium and platinum to form addition products (Rh) or adducts (Pd, Pt) (see Sections 5.2.4 and 5.2.5).

5.2.8. Catalytic applications of phosphino–thioethers

Phenylene-bridged phosphino–thioethers *ph*PSR (R = Me, Pr^i, Bu^t, CMe_2Et) are reported to be relatively poor catalyst modifiers in the rhodium-catalysed hydrogenation of 1-hexene, but no details of complex characterisation were given [280].

Phosphino–thioether complexes of palladium(II) formed in situ from the reaction of $[Pd(MeCN)_4]^{2+}$ with one equivalent of ligand (*e*PSR, *m*PSPh; R = Me, Et, Cy, Ph), are catalysts for the carbonylation of styrene to diphenylpentenones [281]. The use of *e*PSEt leads to a high selectivity for the branched-chain ketone (*E*)-1,4-diphenylpent-1-en-3-one, in contrast to the use of dppp as a catalyst modifier which leads to selectivity for the straight-chain isomer (*E*)-1,5-diphenylpent-1-en-3-one [282].

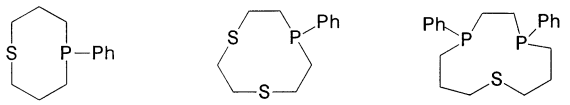
Palladium(II) phosphino–thioether complexes $[PdCl_2(R_2PCH_2CH_2SR')]$ are catalysts for the photochemical carbonylation of benzene if R = alkyl or R = R′ = Ph. The inactivity of $[PdCl_2(ePSR')]$ (R′ = Me, Et) is thought to be due both to the relatively low electron density on the palladium centre and to the strength of the palladium–sulfur bond. The analogous platinum complexes are also active catalysts [247].

Phosphino–thioether and related ligands *pr*PSR, *pr*AsSR and *pr*PSeR (R = Me, Ph, C_6H_4OMe-*o*) have been used as catalyst modifiers in the palladium-catalysed copolymerisation of alkenes with carbon monoxide, where they are more efficient than simple tertiary phosphines: no details of complex characterisation were given [93].

Rhodium and iridium phosphino–thioether complexes $[M(O_2)(ePSR)]$ (R = Me, Et, Ph) are catalysts for the oxidation of alkenes to methyl ketones [218,219]. Nickel hydrido phosphino–thioether complexes are catalysts for the isomerisation of terminal alkenes [244].

5.3. Macrocyclic phosphino–thioethers and arsino–thioethers

The chemistry of macrocyclic phosphino–thioethers and arsino–thioethers [283] has more in common with that of other macrocyclic ligands than with than of their acyclic analogues, but a brief description is included here for completeness.



8PS 9PS2 11P2S

Fig. 13. Mesocyclic phosphino-thioethers.

5.3.1. Small-ring macrocycles ('mesocycles')

The somewhat antimoronic term 'small ring macrocycle' (alternatively 'mesocycle') refers to cyclic ligands which have a ring too small to fit completely around a metal atom, that is a ring of less than about 14 atoms. These ligands have properties intermediate between those of true macrocycles and those of acyclic multidentate ligands. The chemistry of phosphorus-containing heterocycles of this nature has recently been reviewed [284].

A series of platinum(II) complexes of the eight-membered cyclic phosphino–thioether 5-phenyl-1-thia-5-phosphacyclooctane (8PS, see Fig. 13) have been prepared and crystallographically characterised: [PtXY(8PS)] (X = Y = Cl, I: X = Cl; Y = Me) and $[Pt(8PS)_2]^{2+}$. The chloride ligand of [PtClMe(8PS)] can be displaced by triphenylphosphine, while the thioether group of 8PS is displaced by the phosphine centre of dppp forming the dimeric complex $[\{PtClMe(8PS\text{-}P)\}_2(\mu\text{-dppp})]$ [285].

The nine-membered mesocycle 7-phenyl-1,4-dithia-7-phosphacyclononane (9PS2, see Fig. 13) has been prepared by high-dilution methods in 44% yield from ePS_2^{2-} and 1,2-dibromoethane [286]. Although it can be prepared by template methods (from $[Mo(ePS_2)(CO)_3]^{2-}$), as can its dibenzo[*e*,*h*] analogue (from $[Mo(phPS_2)(CO)_3]^{2-}$), it is impossible to remove the mesocycle from the molybdenum centre.

Iron(II), nickel(II) and mercury(II) complexes $[M(9PS2)_2]^{2+}$, and copper(I) and silver(I) complexes $[M(9PS2)_2]^{+}$, have been prepared [286]. Cyclic voltammetric experiments with $[Ni(9PS2)_2]^{2+}$ show a reversible one-electron oxidation at $E_{1/2} = +0.81$ V (c.f. $E_{1/2} = +1.51$ V for $[Ni(9S3)_2]^{2+/3+}$ [287], +1.43 V for $[Ni(9NS2)_2]^{2+/3+}$ [288]) and a reversible one-electron reduction at $E_{1/2} = -0.44$ V (c.f. irreversible reduction, $E = -0.6$ V for $[Ni(9S3)_2]^{2+}$). Hence the substitution of phosphorus for sulfur in the mesocyclic ligand makes the complex both easier to oxidise (as a consequence of the greater σ-donation) and easier to reduce (due to the greater π-acidity). The copper(I) complex, $[Cu(9PS2\text{-}P,S,S')(9PS2\text{-}P)]^{+}$ has been crystallographically characterised [286] (see Fig. 14).

The eleven-membered mesocycles 1,4-dithia-8-phosphabenzo[*b*]cycloundecane and 1-thia-5,8-diphosphabenzo[*f*]cycloundecane have been prepared by high-dilution methods [289,290], and the crystal structure of the latter compound [290] and its copper(I) complex [CuClL] [291] determined.

Chromium, molybdenum and tungsten complexes of 5,8-diphenyl-1-thia-5,8-diphosphabenzo[*f*]cycloundecane (11P2S see Fig. 13), $[M(CO)_4L]$, and a molybde-

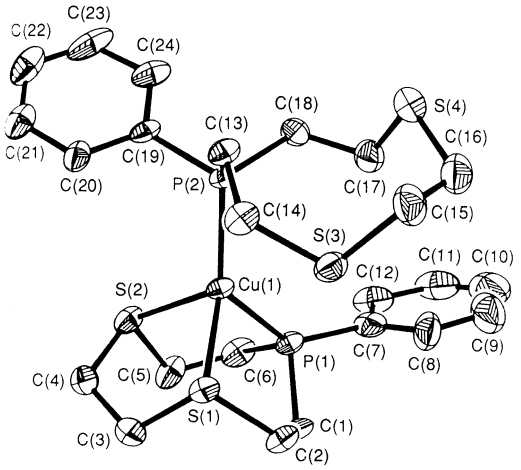


Fig. 14. The solid-state structure of $[Cu(9PS2)_2]^+$. Reproduced with permission from Ref. [286]: © Royal Society of Chemistry 1993.

num complex of the diarsa analogue, have been prepared and their electrochemistry studied: in general, the complexes display one or two broad oxidation waves which are not fully reversible [292].

The cyclic arsino–thioethers 5,9-diphenyl-1-thia-5,9-diarsacyclododecane and 9-phenyl-1,5-dithia-9-arsacyclododecane [293], and the functionalised macrocycle 10-(3-chloropropyl)-9-phenyl-1,5-dithia-9-arsacyclododecane [294], have been prepared by high-dilution methods, but their coordination chemistry does not appear to have been studied.

5.3.2. Large-ring macrocycles

Fourteen ring atoms is about the lower size limit for a macrocyclic to accomodate a transition metal atom completely within the ring. The three possible arrangements of an E_2S_2-donor set within the normal synthetic constraints of a 14-membered macrocycle are shown in Fig. 15.

The first of these to be prepared were the type I systems 8,11-diphenyl-1,4-dithia-8,11-diphosphadibenzo[*b*,*i*]cyclotetradecane (E = PhP) [295] and 8,11-dimethyl-1,4-dithia-8,11-diarsadibenzo[*b*,*i*]cyclotetradecane (E = MeAs) [296]: both macrocycles are prepared exclusively as the *cis*,*meso*-diastereomer, with substituents on both the

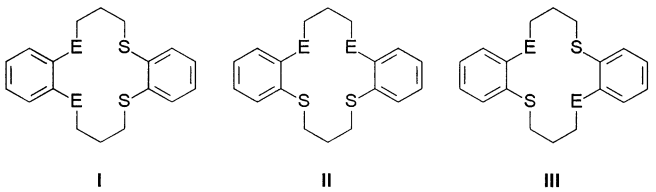


Fig. 15. Three types of 14-membered macrocyclic phosphino–thioethers and arsino–thioethers.

pnictogen centres towards the same face of the phenylene bridge. The crystal structure of the former macrocycle has been determined: the favoured solid-state conformation has the benzene rings almost perpendicular to the plane of the donor atoms. The crystal structure of the iron(II) complex $[FeCl_2L_2]$ shows the former ligand to coordinate only through the phosphorus atoms, and this is thought to be its preferred mode of coordination [297]. However, the platinum(II) complex $[PtL]^{2+}$ has also been prepared [298].

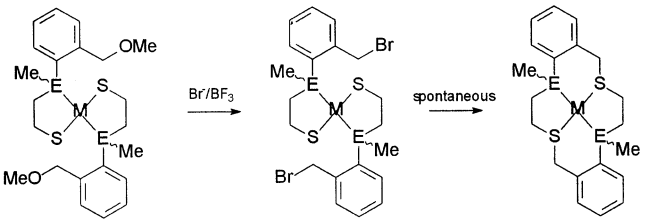
The alternative *cis*-P_2S_2 donor set is a type II macrocycle, and 4,8-diphenyl-1,11-dithia-4,8-diphosphadibenzo[*b*,*i*]cyclotetradecane has been prepared as its *cis*- and *trans*-isomers (*rac*- and *meso*-, respectively), which can be separated by chromatography [299]. The nickel(II) complex $[NiClL]^+$ of the *trans*-isomer and the complexes $[ML]^{2+}$ (M = Ni, Pd) of both isomers have been prepared [298]. The *meso*(*trans*)-isomer of the monocyclic ligand 4,8-diphenyl-1,11-dithia-4,8-diphosphacyclotetradecane has been prepared, as have its palladium and platinum complexes, $[ML]^{2+}$ (M = Pd, Pt), and its rhodium(III) complex $[RhCl_2L]^+$. $[PtL]^{2+}$ and $[RhCl_2L]^+$ have been crystallographically characterised [300].

Template methods have been used to prepare the *trans*-E_2S_2 macrocycles shown in Scheme 7 [301–303]: coupled with the procedure for resolving chiral phosphino–thiols and arsino–thiols described in Section 2.1.7 (see Scheme 3) [32,301], this allows the production of enatiomerically pure macrocycles, as has been achieved for E = As. The nickel(II) complex of (*R**,*R**)-4,11-dimethyl-1,8-dithia-4,11-diphosphadibenzo[*e*,*l*]cyclotetradecane, $[NiL]^{2+}$, has been crystallographically characterised, as has the *rac*-diastereomer of the analogous arsino-thioether macrocycle (*R**,*R**)-4,11-dimethyl-1,8-dithia-4,11-diarsadibenzo[*e*,*l*]cyclotetradecane and the *rac*- and *meso*-diasteromers of its palladium(II) complex, $[PdL]^{2+}$ [304].

The 14-membered P_3S-donor macrocycle 4,8,11-triphenyl-1-thia-4,8,11-diphosphadibenzo[*b*,*i*]cyclotetradecane has been prepared as its *cis*- and *trans*-isomers by high-dilution methods. The Xray crystal structures of the nickel(II) complexes of its *trans*-isomer $[NiClL]^+$ and $[Ni(MeCN)L]^{2+}$, and of the platinum(II) complex of its *cis*-isomer $[PtL]^{2+}$, have been determined [299].

The platinum complex of a 16-membered macrocycle 5,13-diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane, $[PtL]^{2+}$, has been prepared and crystallographically characterised [285].

The first macrocyclic phosphino–thioether to be prepared was the 16-membered 9,13-diphenyl-1,6-dithia-9,13-diphosphabenzo[*c*]cyclohexadecane, as its nickel(II) complex $[NiBrL]^+$ [231].



Scheme 7. The template preparation of *trans*-E_2S_2 macrocycles.

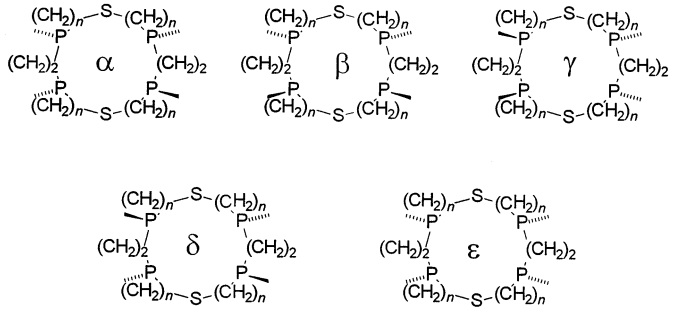


Fig. 16. The five diastereomers of 18- and 22-membered macrocycles: redrawn from Ref. [305].

5.3.3. Super-large ring macrocycles

If a large-ring macrocycle is one which is large enough to fit around the meridional plane of a metal centre, a super-large ring macrocycle is one which is large enough to wrap completely around the metal [305]: at least an 18-membered ring. Macrocycles having a P_4S_2 donor set within 18-membered [306] or 24-membered [307] rings have been prepared: because of the restricted inversion of the phosphorus(III) centres, they exist as five different diastereomers, labelled α–ε (see Fig. 16).

Cobalt(II) and nickel(II) complexes of all five diastereomers of the cyclooctadecane ($n = 2$) ligand have been prepared. The X-ray crystal structures of $[Ni(\beta\text{-L})]^{2+}$, $[Ni(\delta\text{-L})]^{2+}$ and $[Co(\varepsilon\text{-L})]^{2+}$ have been determined, while the coordination in the other complexes was determined by spectroscopic techniques [306,308,309]. Cobalt(II) and nickel(II) showed a remarkable similarity in their coordination behaviour with these ligands, as is summarised in Table 20.

The α-, β- and δ-diastereomers of the analogous cyclodocosane ($n = 3$) have been isolated in a pure form, and the cobalt(II) and nickel(II) complexes of the latter two have been prepared. $[Ni_2Br_2(\beta\text{-L})]^{2+}$ and $[Co(\delta\text{-L})]^{2+}$ have been crystallographically characterised [307,310].

A wide range of macrocyclic arsino–thioethers with ring sizes up to 28-membered has been prepared, but their coordination chemistry does not appear to have been studied [293,294].

Table 20
The different geometrical constraints of the different diastereomers of 4,7,13,16-tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclooctadecane lead to different coordination behaviour with cobalt(II) and nickel(II) centres

	Coordination geometry	Ref.
α	square-pyramidal P_4S	[306]
β	*trans*-octahedral P_4S_2 [elongated r(M–S) for Ni complex]	[306]
γ	square-pyramidal P_4X (Co), square-planar P_4 (Ni)	[309]
δ	trigonal-bipyramidal P_4S	[308]
ε	*cis*-octahedral P_4S_2	[309]

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[124] The change from a phosphorus(III) centre to a phosphorus(V) centre leads to a lengthening of the C–S distance and a shortening of the C–N distance; hence Ph$_2$P(=S)CSNHPh has r(C–N) = 1.316(7) Å and r(C–S) = 1.628(5) Å: G. Siasos, E.R.T. Tiekink, Z. Kristallogr. 200 (1992) 295.
[125] This is not an absolute requirement. One possible model for this system would view the coupling of the thioamide band as a splitting of the band due to ν(C=N): as the C–S bond lengthens the coupling would reduce and the two bands assigned as ν_1(NCS) and ν_2(NCS) would get closer in frequency and finally merge, while at the same time a band of greater ν(C–S) character would emerge at a lower wavenumber.
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