Coordination Chemistry Reviews, 60 (1984) 67–105
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE COORDINATION CHEMISTRY OF SECONDARY PHOSPHINE CHALCOGENIDES AND THEIR CONJUGATE BASES

BERNHARD WALTHER

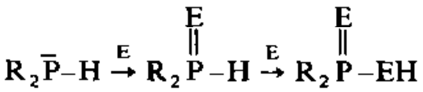
Department of Chemistry, Martin Luther University Halle-Wittenberg, GDR-4020 Halle (S.), Weinbergweg 16 (German Democratic Republic)

(Received 24 October 1983)

CONTENTS

A. INTRODUCTION

Secondary phosphines, R_2PH (R = alkyl, aryl), can easily be oxidized with oxygen, sulphur or selenium to form, initially, secondary phosphine chalcogenides, $R_2P(E)H$ (E = O, S, Se). These are sensitive to further oxidation, resulting in the chalcogenophosphinic acids, $R_2P(E)EH$ (eqn. (1)). The oxidation numbers of the phosphorus atom in these compounds are +1, +3 and +5, respectively.



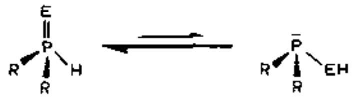
$$R_2\overline{P}{-}H \xrightarrow{E} R_2\overset{\overset{\displaystyle E}{\|}}{P}{-}H \xrightarrow{E} R_2\overset{\overset{\displaystyle E}{\|}}{P}{-}EH \tag{1}$$

Besides the synthesis of secondary phosphine chalcogenides by direct oxidation of secondary phosphines, a variety of other synthetic procedures has been developed [1].

0010-8545/84/$11.70

The secondary phosphine chalcogenides, which may be regarded as one of the basic groups in organic phosphorus chemistry, were made accessible comparatively recently, as illustrated by the years of their first synthesis: $R_2P(O)H$ in 1952 [2], $R_2P(S)H$ in 1960 [3], and $R_2P(Se)H$ in 1966 [4]. This was, in part, due to the widely accepted view that they would have low stability with respect to their disproportionation into phosphines and phosphinic acids. In 1960, Sander [5] demonstrated the stability of secondary phosphine oxides by showing that the disproportionation of $Bu^n_2P(O)H$ proceeds slowly only above 150°.

In recent years, the chemistry of secondary phosphine chalcogenides, particularly their coordination chemistry, has attracted increasing interest, one reason being the manifold reactivity of these ambivalent compounds. Simple dialkyl and diaryl phosphine chalcogenides, being tetracoordinated about the pentavalent phosphorus atom, do exist in solution in tautomeric equilibrium with the appropriate chalcogenophosphinous acids (alternatively named as hydrogenchalgogenide substituted phosphines) containing a tricoordinated phosphorus atom, thus



(2)

Surprisingly, no systematic studies of this equilibrium have been described so far for secondary phosphine chalcogenides, although there are some papers dealing with the analogous equilibrium for secondary phosphites, $(RO)_2P(O)H$ [6]. Howevever, it is obvious that eqn. (2) favours the secondary phosphine chalcogenide tautomer for all but CF_3-substituted compounds to such an extent that the chalcogenophosphinous tautomers cannot be detected by IR and NMR spectroscopy. Those compounds with $R = CF_3$ do exist as the chalcogenophosphinous acid tautomers ($E = O$ [7], S [8]), owing to the strong electron-withdrawing power of the trifluoromethyl group, which lowers the basicity of the phosphorus atom so that the chalcogen atom becomes more basic and binds the proton.

The tautomeric equilibrium (2) has often been invoked as a necessary step of reaction mechanisms. For example, the slow formation of poorly soluble $AgOPPh_2$ from $Ph_2P(O)H$ and $AgNO_3$ in water has been attributed to the slow pre-equilibrium (2) [9]. Quin and co-workers [10,11] used the same explanation for the reation of $Ph_2P(O)H$ with PCl_3 or $Ph_2P(O)Cl$ to form Ph_2PCl and $Ph_2P(O)OPPh_2$, respectively. Grayson et al. [12] proposed a mechanism, on the basis of kinetic experiments, for the reaction of secondary phosphine oxides with phenyldisulphide which also involves the phosphinous acid tautomer as an intermediate.

Secondary phosphine chalcogenides are weak acids and thus can react with strong bases like alkaline organic compounds or alkali metals to give the corresponding conjugate bases [1]. Earlier, ^{31}P NMR measurements [13] showed the alkaline derivatives of secondary phosphine oxides to be described best by canonical structures with a tricoordinated phosphorus atom, $R_2\overline{P}\text{-}\underline{\overline{O}}\text{-}M \leftrightarrow [R_2\overline{P}\text{-}\underline{\overline{O}}|]^- M^+$, requiring that the negative charge is essentially located on oxygen. Other canonical structures, $[R_2\overline{P}{=}\underline{\overline{O}}]^- M^+ \leftrightarrow R_2\underset{\underset{O}{\|}}{P}-M$, are likely to contribute only to a minor extent, if at all.

The aim of the present review is to summarize the chemistry of transition metal complexes containing secondary phosphine chalcogenides and their conjugate bases as ligands. The review article in 1978 by Roundhill et al. [14] on the metal complexes of substituted phosphinites and secondary phosphites includes part of this account but an account of the metal complexes of secondary phosphine sulphides and selenides has never been compiled. Furthermore, since 1978 many papers have appeared which are concerned with such complexes. It is hoped that this account will promote further studies of the coordination chemistry of this type of ligand.

B. COORDINATION MODES OF SECONDARY PHOSPHINE CHALCOGENIDES TABULAR SURVEY

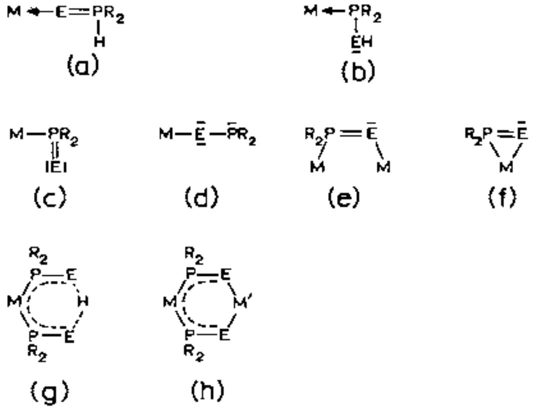
Secondary phosphine chalcogenides and their chalcogenophosphinous acid tautomers, as well as their conjugate bases, can act as ligands towards transition metals. Scheme 1 shows the various types of coordination that have been observed to date. It is always important in this chemistry to ascertain the actual coordination mode adopted by these ligands.

The coordination modes of the neutral ligands are represented by (a) and (b). These differ in the nature of the donor atom, which can either be the chalcogen atom E (a) or the phosphorus atom (b), the latter mode implying stabilization of the chalcogenophosphinous acid by fixation on the metal. Mode-(a) complexes have only been described with the central atoms Cr, Mo, W, Mn and Re, whereas mode (b) complexes have been found with Fe, Ir, Pd, and Pt, in addition.

Lindner and Schilling [15] have compared the relative stability of complexes in these two modes. The stability of mode-(a) complexes, with respect to their isomerization into mode-(b) complexes, depends on E, given M, and on M, given E, as follows: O < S ≪ Se; Cr < Mo < W; Mn < Re. Thus, O-bonded Mn complexes are unknown, and the Re complexes could only be detected spectroscopically. S-bonded complexes of all metals so far investigated are known, but the P-bonded isomers are thermodynamically preferred. P-bonded complexes of the secondary phosphine selenides are unstable owing to the ready separation of elemental selenium.

The spectroscopic behaviour of the E and P isomers are significantly different. Generally, whereas the ligand parts of the spectra of mode-(a) complexes are similar to the spectra of the respective non-coordinated secondary phosphine chalcogenides, those of mode-(b) complexes differ in this respect [1,16–18]. The π-acceptor ability of the S-coordinated ligands has been found to be lower than that of phosphine ligands, and comparable to that of tertiary phosphine sulphide ligands [17]. The isomeric P-coordinated ligands are significantly stronger π-acceptors [16–18].

The anionic ligands R_2PE^- can be coordinated on the metal in the terminal fashion, either through the phosphorus atom (mode (c)), which has been observed most frequently so far (Mo, W, Mn, Re, Fe, Pt and Au complexes), or through the chalcogen atom (mode (d)), found in Fe, Rh, Ir, and Ag complexes. Complexes containing the R_2PE^- ligand in the bridging mode (e) are known with Cr, Mn, Re, Fe, Co, Ni, Ir, Pd, Pt, and Au. In the majority of complexes described, two metal atoms are bridged by two ligands, thus generating six-membered ring units $[M_2(\mu\text{-}EPR_2)_2]$. X-ray molecular structure determination [19–24] reveals that these rings adopt different conformations. Only one family of complexes $[\{ML(\mu\text{-}EPR_2)\}_2]$ (M = Pd, Pt) [25,26] has been found to exist to date, in which both metal atoms are linked by two bridging R_2PE ligands and an adjacent metal–metal bond. Dinuclear complexes of the bridging mode (e) may exist in equilibrium with their monomeric units, $[L_nM(\eta^2\text{-}EPR_2)]$, in which the ligand R_2PE^- probably coordinates in the dihapto fashion (f) in order to obey the EAN rule. These highly reactive three-membered ring complexes have been found to be intrinsic intermediates of the reactions of the six-membered ring complexes [22,27–30]. The dihapto mode (f), described for Mo, W, Rh, and Ir complexes, has been verified very recently by X-ray analysis [31]. The



Scheme 1. Coordination modes of secondary phosphine chalcogenides and their conjugate bases.

ligand is considered to be a four-electron donor [31]. The spectroscopic behaviour of complexes containing the R_2PE^- ligand is quite different and depends not only on the actual coordination mode but also on the central atom and on the other ligands that are attached to it.

Mode (g), containing the anionic $R_2PO \cdots H \cdots OPR_2^-$ ligand, results from a *cis* arrangement of an anionic ligand of mode (c) and a neutral ligand of type (b), so (g) is not basically a new coordination mode. However, the special features and the great number of complexes known of this type justify separate treatment of these complexes. This coordination mode has been described with the metals Cr, Mo, W, Ru, Rh, Ir, Pd, and Pt. The driving force for the preferred formation of this mode is obviously the formation of the strong and often symmetric hydrogen bridge between the oxygen atoms. The first compounds of this mode containing a hydrogen bridge between oxygen and sulphur have been described only recently [23,32,33]. X-ray analysis has consistently shown the distance between the oxygen atoms to be around 240 pm [34–36]. Oxygen–oxygen distances of $\leqslant 250$ pm are regarded as evidence of strong hydrogen bridges [37]. No IR band appears in the normal ν (OH) region because the $O \cdots H \cdots O$ vibrations occur below 2000 cm^{-1} [37]. Vibrations of the $Ph_2PO \cdots H \cdots OPPh_2^-$ ligand are found at 1040 cm^{-1}, which is assigned to $\nu(PO)$, and at 1330, 1236 and 773 cm^{-1}, which were tentatively assigned to $\delta(O \cdots H \cdots O)$, $\gamma(O \cdots H \cdots O)$ and $\nu_{as}(O \cdots H \cdots O)$, respectively, on the basis of deuteration experiments [35]. Other authors have assigned a band at ca. 1000 cm^{-1} to $\nu(PO)$, and very broad absorptions in the 1200–1600 and 700–800 cm^{-1} regions, as well as a strong absorption at 330 cm^{-1}, to the $M\{(Ph_2PO)_2H\}$ system [38].

The preference for type-(g) complexes could be demonstrated by the *trans* → *cis* rearrangements occurring during their synthesis from *trans*-configuration starting compounds [39]. The bridging hydrogen atom of type-(g) complexes is acidic and therefore can be titrated [40]. Replacement of the hydrogen atom by a metal atom M′ leads to complexes of type (h) which contain the chelating ligand $M(R_2PO)_2^-$ attached to M′. An extension of coordination mode (g) generates complexes containing the tridentate, anionic, doubly hydrogen-bridged ligand $(R_2PO)_3(H)_2^-$ [41–46]. One example has been reported to contain the $(R_2PO)_2H^-$ ligand, bridging two metal atoms, $[L_nM{-}P(R)_2O \cdots H \cdots O(R)_2P{-}ML_n]^+$ [47]. This is not really a type-(g) complex, but the similarities are obvious.

A large body of coordination chemistry has appeared which uses secondary phosphites, $(RO)_2P(O)H$, and their anions, $(RO)_2PO^-$, as ligands. The coordination modes adopted by these ligands are essentially the same as (a)–(h). Such complexes are described in the account by Roundhill et al. [14]. As far as the author is aware, the coordination chemistry of the sulphur

TABLE 1

Type of complex	M	E	No. in text	Ref.
Mode (a): $M\{EP(H)R_2\}$				
$M(CO)_5SP(H)R_2$	Cr, Mo, W	S	**1a–1q**	[17]
$M(CO)_4XEP(H)R_2$	Mn, Re	O, S, Se	**13a–13o**	[15,16,18]
Mode (b): $M\{P(EH)R_2\}$				
$[M(CO)_5\{P(EH)R_2\}]$	Cr, Mo, W	O, S	**2a–2j**	[17,48–52]
$[M(CO)_4L\{P(OH)Ph_2\}]$	Mo, W	O	**4a–4c**	[32,55,56]
$[M(CO)_4X\{P(EH)R_2\}]$	Mn, Re	O, S, Se	**14a–14q**	[15,16,18]
$[Mn(CO)_2(\eta^5\text{-Cp})\{P(SH)Me_2\}]$	Mn	S	**15**	[61]
$Na_2[\{M(CO)_4[P(E)R_2]\}_2](M{-}M)$	Mn, Re	O, S	**16a–16q**	[65–71]
$Na_2[Mn(CO)_4\{P(E)R_2\}]$	Mn	O, S	**17a–17c**	[65–71]
$[Fe(CO)_2(\eta^5\text{-Cp})\{P(OH)PhR\}]^+ Br^-$	Fe	O	**26a, 26b**	[47]
$[Fe(CO)_2(\eta^5\text{-Cp})(PhBu^tPO \cdots HNEt_3)]^+ PF_6^-$	Fe	O	**27**	[47]
$[Ir(Cl)H(L_2)\{P(OH)Ph_2\}]^+ BF_4^-$	Ir	O	**37**	[84]
$[(Et_2NCS_2)Pt(\mu\text{-}SPPh_2)_2IrCl(H)\{P(OH)Ph_2\}_2]$	Pt/Ir	S	**39**	[84]
cis-$[PtX_2\{P(OH)R_2\}(PR'_3)]$	Pt	O	**42a–42h**	[85]
cis-$[PdCl_2\{P(OH)Ph_2\}\{PCH_2C(O)CF_3\}]$	Pd	O	**53**	[35]
$[PdCl\{P(OH)Ph_2\}\{Ph_2PCH=C(CF_3)O\}]$	Pd	O	**54**	[35]
Mode (c): $M\{P(E)R_2\}$				
trans-$[M(CO)_2L(\eta^5\text{-Cp})\{P(E)Ph_2\}]$	Mo, W	O, S, Se	**5a–5e**	[57,58]
cis-$[Re(CO)_4(NH_3)\{P(S)[Me_2\}]$	Re	S	**18**	[72]
cis-$[Mn(CO)_4(PMe_3)\{P(S)Me_2\}]$	Mn	S	**20**	[74]
$[Fe(CO)_2(\eta^5\text{-Cp})\{P(E)R_2\}]$	Fe	O, S, Se	**21a–21g**	[47,75–78]
$[Fe(CO)L(\eta^5\text{-Cp})\{P(E)R_2\}]$	Fe	S, Se	**23a–23e**	[77,78]
$[\{Pt[P(O)R_2](PR'_3)(\mu\text{-}SEt)\}_2]$	Pt	0	**45a, 45b**	[85]
$[PtCl\{P(O)Ph_2\}(PEt_3)(p\text{-tol})]$	Pt	O	**46**	[85]
$[PtPh\{P(O)Ph_2\}(PPh_3)(RCN)]$	Pt	O	**47a–47d**	[86]
trans-$[PtH\{P(S)R_2\}(PR'_3)_2]$	Pt	S	**50**	[24]
$[Pt(S_2CNEt_2)\{P(O)Ph_2\}(Ph_2POMe)]$	Pt	O	**62**	[36]
$cat^+ [Pt(S_2CNR_2)\{P(S)Ph_2\}_2]^-$	Pt	S	**64a, 64b**	[23,33]

$[Pt(S_2CNPr^i_2)\{P(S)Ph_2\}(Ph_2POMe)]$	Pt	S	**65**	[23,33]
$Cs^+[Pt(S_2CNPr^i_2)\{P(O)Ph_2\}\{P(S)Ph_2\}]^- \cdot 2H_2O$	Pt	O/S	**67**	[23,33]
$[Pt(Y_2CNR_2)\{P(Se)Ph_2\}(Ph_2PH)]$	Pt	Se	**69a–69c**	[23]
$HNEt_3^+[AuCl\{P(O)R_2\}]^-$	Au	O	**77a, 77b**	[96]
$[Au\{P(O)Bu^t_2\}(PBu^t_3)]$	Au	O	**79**	[96]
Mode (d): M{(EPR₂)}				
$[Fe(CO)_2(\eta^5\text{-}Cp)\{EP(CF_3)_2\}]$	Fe	O, S, Se	**22a–22c**	[75]
$[Ir(CO)Cl(H)(PPh_3)_2(SPPh_2)]$	Ir	S	**31**	[82]
$[Rh(CO)(PPh_3)_2(SPPh_2)]$	Rh	S	**34**	[83]
$[AgOPPh_2]$	Ag	O	**76**	[9,95]
Mode (e): M₂(μ-EPR₂)				
$HNEt_3^+[\{Cr(CO)_5\}_2(\mu\text{-}SPMe_2)]^-$	Cr	S	**3**	[49]
$[\{M(CO)_4(\mu\text{-}EPR_2)\}_2]$	Mn, Re	O, S, Se	**19a–19j**	[19,20,22,27,28,29,73,74]
$[\{Fe(CO)_3\}_2\{\mu\text{-}P(CF_3)_2\}\{\mu\text{-}SeP(CF_3)_2\}]$	Fe	Se	**24**	[76]
$[(\eta^5\text{-}Cp)Co(\mu\text{-}Et_2PO)_3Co(\mu\text{-}OPEt_2)_3Co$ $(\eta^5\text{-}Cp)]^+$ anion$^-$	Co, Co	O	**30**	[81]
$[\{Ni(\eta^5\text{-}Cp)(\mu\text{-}SPR_2)\}_2]$	Ni	S	**41a, 41b**	[21,30]
$[(Et_2NCS_2)Pt(\mu\text{-}SPPh_2)_2IrCl(H)\{P(OH)Ph_2\}_2]$	Pt/Ir	S	**39**	[84]
$[\{PtX(\mu\text{-}OPR_2)(PR'_3)\}_2]$	Pt	O	**43a–43g**	[85]
$[\{Pt(OH)(\mu\text{-}OPR_2)(PR'_3)\}_2]$	Pt	O	**44a, 44s**	[85]
$[\{M(PR'_3)(\mu\text{-}EPR_2)\}_2](M\text{–}M)$	Pd, Pt	S, Se	**48a–48p**	[25,26]
$[\{ML(\mu\text{-}EPR_2)\}_2](M\text{–}M)$	Pd, Pt	S	**49a–49n**	[25,87,88]
$[\{PtH(PBu^t_3)(\mu\text{-}SPPh_2)\}_2]$	Pt	S	**51**	[24]
$[\{M(Ph_2PO)_2\}_n]$	Pd, Pt	O	**56a, 56b**	[39,41]
$[\{Pt(\mu\text{-}OPPh_2)[(Ph_2PO)_2H]\}_2]$	Pt	O	**59**	[41]
$[\{Pt(S_2CNR_2)(\mu\text{-}SPPh_2)\}_2]$	Pt	S	**68a–68c**	[23,33]
$[\{Au(\mu\text{-}OPBu^t_2)\}_3]$	Au	O	**78**	[97]
Mode (f): M(η²-EPR₂)				
$[M(CO)_2(\eta^5\text{-}Cp)(\eta^2\text{-}EPPh_2)]$	Mo, W	S, Se	**6a–6c**	[31,58]
$[M(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2]$	Mo, W	S	**7a, 7b**	[31]
$[Rh(PPh_3)_2(\eta^2\text{-}SPPh_2)]$	Rh	S	**32**	[83]
$[MCl(H)(PPh_3)_2(\eta^2\text{-}SPPh_2)]$	Rh, Ir	S	**33a, 33b**	[83]

TABLE 1 (continued)

Type of complex	M	E	No. in text	Ref.
Mode (g): $M\{(R_2PE)_2H\}$ and related complexes				
$[HNEt_3]^+$*cis*-$[M(CO)_4\{(Ph_2PO)_2H\}]^{-1}$	Cr, Mo, W	O	**8a–8c**	[39,53,54,59]
cis-$[Mo(CO)_4\{(Ph_2PO)(Ph_2PS)H\}]$	Mo	O/S	**12**	[32]
$[\{Fe(CO)_2(\eta^5\text{-}Cp)[P(Ph)(R)O]\}_2H]^+$ anion$^-$	Fe	O	**25a, 25b**	[47]
$[Ph_2P(OR)_2(PH_2POH)Ru(\mu\text{-}Cl)_3Ru(Ph_2PO)(Ph_2POH)_2]$	Ru	O	**28a, 28b**	[45]
$[Ru(Me_2PS_2)\{(Ph_2PO)_3(H)_2\}]$	Ru	O	**29**	[46]
$[Ir(COD)(Cl)H\{(Ph_2PO)_2H\}]$	Ir	O	**35**	[84]
$[Ir(Cl)H(L_2)\{(Ph_2PO)_2H\}]$	Ir	O	**36a–36c**	[84]
cat$^+$ $[\{RhCl[(Ph_2PO)_2H]\}_2(\mu\text{-}Cl)_3]$	Rh	O	**40**	[84]
$[\{M(\mu\text{-}X)[(Ph_2PO)_2H]\}_2]$	Pd, Pt	O	**52a–52d**	[34,35,39,41]
$[MX\{(Ph_2PO)_3(H)_2\}]$	Pd, Pt	O	**55a–55c**	[41,43,44]
$[MX(L)\{(Ph_2PO)_2H\}]$	Pd, Pt	0	**57a–57g**	[41,43,44]
$[Pt\{(Ph_2PO)_2H\}_2]$	Pt	0	**58**	[41,42,44]
$[\{M(\mu\text{-}OPPh_2)[(Ph_2PO)_2H]\}_2]$	Pd, Pt	0	**59a, 59b**	[41,43]
$[Pt\{(Ph_2PO)_2[(PhO)_2PO]_2(H)_2\}]$	Pt	O	**60**	[42]
$[M(\overset{\frown}{S\ S})\{(Ph_2PO)_2H\}]$	Pd, Pt	O	**61a–61g**	[36]
$[Pt(S_2CNR_2)(Ph_2POH\cdots SPPh_2)]$	Pt	O/S	**66a, 66b**	[23,33]
Mode (h): $M\{(R_2PO)_2M'\}$				
$[HNEt_3]^+$*cis*-$[Mo(CO)_4\{(Ph_2PO)_2BF_2\}]$	Mo	O	**9**	[59]
cis-$[Mo(CO)_4\{(Ph_2PO)_2SiMeR\}]$	Mo	O	**10a, 10b**	[59]
$[\{Mo(CO)_4(Ph_2PO)_2\}_2Si]$	Mo	O	**11**	[59]
$[Ir(Cl)H(L_2)\{(Ph_2PO)_2BF_2\}]$	Ir	O	**38**	[84]
$[Pt(S_2NCEt_2)\{(Ph_2PO)_2M'\}]$	Pt	O	**63a–63c**	[46]
$[MLL'\{(Ph_2PO)_2BF_2\}]$	Pd, Pt	O	**70a–70f**	[38,44,94]
$[Pt\{(Ph_2PO)_2BF_2\}_2]$	Pt	O	**71**	[38,44]
$[\{Pt(\mu\text{-}OPPh_2)[(Ph_2PO)_2BF_2]\}_2]$	Pt	O	**72**	[38]
$[\{Pd(\mu\text{-}X)[(Ph_2PO)_2BF_2]\}_2]$	Pd	O	**73a–73b**	[38]
$[PtCl(PEt_3)\{(Ph_2PO)_2SiMe_3\}]$	Pt	O	**74**	[38]
$[\{PtCl(PEt_3)(Ph_2PO)_2\}_2VO]$	Pt	O	**75**	[38]

analogues, $(RO)_2P(S)H$ and $(RO)_2PS^-$, remains little explored.

In Table 1 are collected the general types of complex so far established, according to their coordination mode: the numbering of the individual complexes used in the text is also indicated. This numbering is intended as a guide to individual complexes described in the text.

C. TRANSITION METAL COMPLEXES OF SECONDARY PHOSPHINE CHALCOGENIDES AND THEIR CONJUGATE BASES

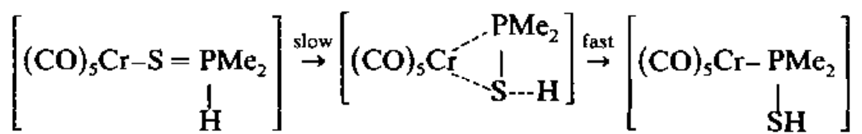
(i) Cr, Mo, W

Type-(a) complexes $[M(CO)_5\{SP(H)R_2\}]$ (**1**) (M = Cr, Mo, W) have been obtained by treating photochemically produced $[M(CO)_5(THF)]$ with the appropriate secondary phosphine sulphide at low temperature [17]. Slightly raising the temperature irreversibly rearranges **1** into the P-isomers **2** (type (b)), as shown in eqn. (3) [17]

$$[M(CO)_5(THF)] + R_2P(S)H \xrightarrow[10^\circ]{THF} \underset{(\mathbf{1})}{[M(CO)_5\{SP(H)R_2\}]} \xrightarrow[25\text{–}60^\circ]{THF} \underset{(\mathbf{2})}{[M(CO)_5\{P(SH)R_2\}]} \quad (3)$$

1	**a**	**b**	**c**	**d**	–	**e**	**f**	**g**
2	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**
M	Cr	Cr	Cr	Mo	Mo	Mo	W	W
R	Me	Et	Ph	Me	Et	Ph	Me	Ph

This isomerization reaction has been studied kinetically for the example of **1a** → **2a** and was found to be of first order, with the rate law $\mathrm{d}c[\mathbf{1a}]/\mathrm{d}t = -kc[\mathbf{1a}]$, $\Delta H^{\#} = 25.5$ kcal mol^{-1} and $\Delta S^{\#} = 9.4$ cal mol^{-1}, [17]. On this basis, an intramolecular mechanism without solvent participation has been proposed. The coordination of the $Me_2P(S)H$ ligand on the metal activates the hydrogen atom, which migrates from phosphorus to sulphur with a concerted cleavage of the metal–sulphur bond. The subsequent fast step coordinates the ligand via the P atom, as shown in eqn. (4)



$$\left[(CO)_5Cr{-}S{=}\underset{\displaystyle H}{\underset{|}{PMe_2}}\right] \xrightarrow{\text{slow}} \left[(CO)_5Cr\begin{smallmatrix}\cdot\cdot PMe_2\\ |\\ \cdot\cdot S{-}{-}H\end{smallmatrix}\right] \xrightarrow{\text{fast}} \left[(CO)_5Cr{-}\underset{\displaystyle SH}{\underset{|}{PMe_2}}\right] \quad (4)$$

(**1**) (**2**)

The weak metal–sulphur bond of **1** is also indicated by the easily occurring substitution reactions shown in eqn. (5) [17]

$$[\mathrm{M(CO)_5\{SP(H)R_2\}}] + \mathrm{L} \xrightarrow[10-20\,°\mathrm{C}]{\mathrm{THF}} [\mathrm{M(CO)_5L}] + \mathrm{R_2P(S)H} \qquad (5)$$

$$\mathrm{L = CO, PPh_3, AsPh_3}$$

The molecular structure of **2a** has been determined by X-ray analysis [48]. The chromium atom is pseudooctahedrally coordinated by five CO groups and the thiophosphinous acid ligand. The Cr–P distance of 234.4 pm appears to be shortened by d_π–d_π back-bonding. The *trans*-Cr–C distance has been found to be smaller than the *cis*-Cr–C distance, probably because of the lower π-acceptor capacity of the phosphorus ligand compared with that of the CO ligand.

The acidic SH group of **2a** can be methylated by CH_2N_2 [49]. Sodium or NEt_3 convert **2a** into its anion, which reacts with $[Cr(CO)_5THF]$ to make the dinuclear complex $[HNEt_3]^+[\{Cr(CO)_5\}_2(\mu\text{-}SPMe_2)]-$ (**3**) [49]. $[Mo(CO)_5\{P(OH)Ph_2\}]$ (**2i**) results as a yellow oil, either by thermal reaction of $[Mo(CO)_6]$ and $Ph_2P(O)H$, or, contaminated with $[\{Mo(CO)_5\}_2(\mu\text{-}Ph_2POPPh_2)]$, by treating $[Mo(CO)_5(Ph_2PCl)]$ first with KOH and subsequently with HCl [50]. Hydrolysis or thiolysis of diorganochlorophosphine complexes in the presence of equimolar amounts or excess of triethanolamine leads, as expected to type-(b) complexes **2** or their ammonium salts, as in eqn. (6) [17,50–52]

$$[\mathrm{M(CO)_5(Ph_2PCl)}] + \mathrm{H_2E} \xrightarrow[-\mathrm{NEt_3 \cdot HCl}]{\mathrm{NEt_3}} [\mathrm{M(CO)_5\{P(EH)R_2\}}] \qquad (6)$$

$$\text{or}$$

$$[\mathrm{M(CO)_5\{P(EH \cdot NEt_3)R_2\}}]$$

2	a	e	j	i*	d	e*	g*
M	Cr	Cr	Mo	Mo	Mo	Mo	W
E	S	S	O	O	S	S	S
R	Me	Ph	Me	Ph	Me	Ph	Me

* $[HNEt_3]^+$ instead of H^+

On the contrary, Vahrenkamp [52] obtained dinuclear complexes with the bridging R_2PEPR_2 ligand upon hydrolysis or thiolysis of $[W(CO)_5(Me_2PCl)]$ in the presence of two equivalents of NEt_3, thus

$$2[\mathrm{W(CO)_5(Me_2PCl)}] + \mathrm{H_2E} \xrightarrow[-2\mathrm{NEt_3 \cdot HCl}]{2\mathrm{NEt_3}} [\{\mathrm{W(CO)_5}\}_2(\mu\text{-}\mathrm{Me_2PEPMe_2})] \qquad (7)$$

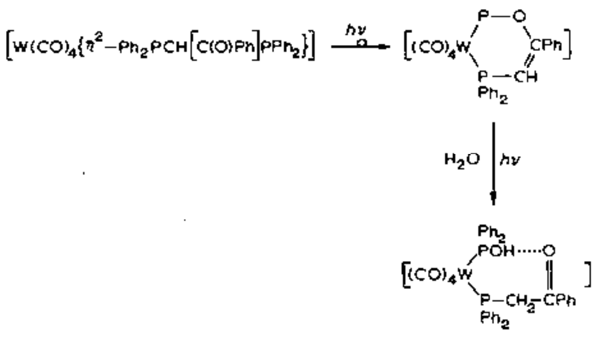
$$\mathrm{E = O,S}$$

Earlier, Kraihanzel and Bartish [50] had already demonstrated the possibility of stabilizing phosphinous acid anhydrides (tetraorganophosphoxanes), which are unstable with respect to tetraorganobiphosphine monoxides, by preparing $[\{Mo(CO)_5\}_2(\mu\text{-}R_2POPR_2)]$ from **2j** and $[Mo(CO)_5(Me_2PCl)]$ in the presence of NEt_3 or from **2i** and $[Mo(CO)_5(Ph_2PCl)]$.

Treatment of $Na^+[Mo(CO)_5(Ph_2PO)]^-$ with either Ph_2PCl or $PhPCl_2$ permitted the preparation of $[Mo(CO)_5(\eta^1\text{-}Ph_2POPPh_2)]$ [53] and $[\{Mo(CO)_5(Ph_2PO)\}_2PPh]$ [54], respectively, the latter containing the new ligand $Ph_2POP(Ph)OPPh_2$ in a bridging fashion.

cis-$[Mo(CO)_4(Ph_2PCl)_2]$ reacts with *N,N*-dimethylethanolamine [55] or sodium ethoxide [32] to yield *cis*-$[M(CO)_4L\{P(OH)Ph_2\}]$ (**4**) (M = Mo, L = $Ph_2POCH_2CH_2NMe_2$ (**4a**), Ph_2POEt (**4b**). The mechanism of formation of these complexes is unknown.

Al-Jibori et al. [56] have recently shown that $[W(CO)_4\{\eta^2\text{-}Ph_2PCH[C(O)Ph]PPh_2\}]$ can be transformed into an isomeric six-membered ring chelate which, in the presence of water, undergoes hydrolysis to give the type-(b) complex **4c**, as in eqn. (8). Both reactions require exposure to light. X-ray analysis has revealed that **4c** adopts a distorted octahedral structure with both phosphorus ligands in a *cis* position (bond angle PWP = 96.1°). The intramolecular oxygen–oxygen distance P–O ··· O=C of 257 pm is consistent with a strong hydrogen bond, although the H atom has not been located. In line with this result, no ν(OH) could be found, but a broad IR band at 3070 cm^{-1} may be due to this hydrogen bond.



(4c)

(8)

Treatment of $[\{Mo(CO)_3(\eta^5\text{-}Cp)\}_2]$ with excess Ph_2PO–allyl gives mainly the type-(c) complex *trans*-$[M(CO)_2L(\eta^5\text{-}Cp)\{P(E)Ph_2\}]$ (**5**) (M = Mo, E = O, L = Ph_2PO–allyl (**5a**)). The ionic complex $[Mo(CO)_2(\eta^5\text{-}Cp)(Ph_2PO\text{–allyl})]^+[Mo(CO)_3(\eta^5\text{-}Cp)]^-$, considered to be an intermediate in the formation of **5a**, was also isolated [57].

$Ph_2P(S)H$ is reported to react with $[M(CO)_3(\eta^5\text{-}Cp)Cl]$ or $[M(CO)_3(Cl)_2(PPh_3)_2]$ to give the molybdenum and tungsten complexes **6** and **7**, respectively, with side-on coordinated Ph_2PS^- ligands (type-(f)), according to eqns. (9) and (10) [31]

$$[M(CO)_3(\eta^5\text{-Cp})Cl] + Ph_2P(S)H \xrightarrow[-HCl,\,-CO]{NEt_3} [M(CO)_2(\eta^5\text{-Cp})(\eta^2\text{-SPPh}_2)] \tag{9}$$

6	**a**	**b**
M	Mo	W

$$[M(CO)_3(Cl)_2(PPh_3)_2] + Ph_2P(S)H \xrightarrow[-HCl,\,-CO,\,-PPh_3]{NEt_3} [M(CO)_2(PPh_3)(\eta^2\text{-SPPh}_2)_2] \tag{10}$$

7	**a**	**b**
M	Mo	W

As shown by X-ray analysis [31], **7a** adopts a pentagonal bipyramidal structure with a seven-coordinated Mo atom. Both CO groups are axial, the other ligands being equatorially positioned. The central Mo(II) atom obeys the EAN rule if each uninegative bidentate $SPPh_2$ ligand provides four electrons. Selected bond distances and angles (average) are: Mo–S, 262.2 pm, Mo–P, 239.2 pm, P–S, 201.1 pm; P–Mo–S, 47.0°, Mo–S–P, 60.5°, S–P–Mo, 72.5°. ν(PS) appears in the IR spectra of **6** and **7** about 100 wavenumbers lower than is found for $Ph_2P(S)H$. The ^{31}P chemical shift of the (η^2-$SPPH_2$) ligand shows considerable sensitivity to changes of the other ligands around the central metal atoms.

Phosphido complexes of molybdenum and tungsten are easily oxidized by sulphur or selenium to yield the corresponding chalcogenophosphinito complexes **5** (eqn. (11)) [58]. Thermal or photochemical treatment of tungsten complexes thus obtained causes CO elimination and conversion of the terminal bonded chalcogenophosphinito ligand to side-on bonded (eqn. (12)) [58]. These complexes do not show any reaction with PMe_3, proving the stability of the WEP cycle [58].

$$[M(CO)_2L(\eta^5\text{-Cp})(PPh_2)] \xrightarrow{E_8} \underset{(\mathbf{5})}{[M(CO)_2L(\eta^5\text{-Cp})\{P(E)Ph_2\}]} \tag{11}$$

5	**b**	**c**	**d**	**e**
M	Mo	W	W	W
L	PMe_3	CO	CO	PMe_3
E	S	S	Se	S

$$\mathbf{5c},\ \mathbf{5d} \xrightarrow[-CO]{\Delta \text{ or } h\nu} [W(CO)_2(\eta^5\text{-Cp})(\eta^2\text{-EPPh}_2)] \tag{12}$$

6	**b**	**c**
E	S	Se

Gray and Kraihanzel [59] studied the reaction of *cis*-$[Mo(CO)_4(Ph_2PCl)_2]$

with a variety of nucleophiles, including H_2O/NEt_3 which forms $[HNEt_3]^+$*cis*-$[M(CO)_4\{(Ph_2PO)_2H\}]^-$ (**8**), (M = Mo (**8b**)); eqn. (13). Analogous Cr and W complexes (**8a** and **8c**, respectively) have been prepared by Wong et al. [53,54]. Compound **8b** is proposed to contain a symmetrical hydrogen bridge between the two oxygen atoms at the P atoms, with the coordination mode (g). Interestingly, Wong and Bradley [39[showed that **8b** also results from hydrolysis of *trans*-$[Mo(CO)_4(Ph_2PCl)_2]$ under identical conditions (eqn. (13)). This *trans* → *cis* rearrangement during hydrolysis, which is contrary to the slight thermodynamic preference of the *trans* isomers of $[Mo(CO)_4(\text{phosphine})_2]$ complexes [60] is obviously due to the favourable intramolecular hydrogen bridge in type-(g) complexes.

$$\textit{cis}\text{-or }\textit{trans}\text{-}[Mo(CO)_4(Ph_2PCl)_2] + 2H_2O \xrightarrow[-2NEt_3\cdot HCl]{3NEt_3} \underset{(\mathbf{8b})}{[HNEt_3]^+\textit{cis}\text{-}[Mo(CO)_4\{(Ph_2PO)_2H\}]^-} \qquad (13)$$

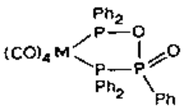
The observed lower $\nu(CO)$ values of **8b** are indicative of the negative charge being delocalized onto the metal, thereby increasing the $(d \rightarrow \pi^*)$ back-bonding [59].

Several reactions have been carried out to confirm the proposed structure of **8b** by converting this type-(g) complex into a type-(h) complex [59]. Thus, reaction with $F_3B \cdot OEt_2$ yields $[HNEt_3]^+$*cis*-$[Mo(CO)_4\{(Ph_2PO)_2BF_2\}]^-$ (**9**). Cl_2SiMeR gives *cis*-$[Mo(CO)_4\{(Ph_2PO)_2SiMeR\}]$ (R = Me (**10a**), Ph(**10b**)) and $SiCl_4$ yields the unique spiro-complex $[\{Mo(CO)_4(Ph_2PO)_2\}_2Si]$ (**11**). Treatment of **8b** with $NaOH/NEt_4Cl$, originally reported to yield $[NEt_4]^+$*cis*-$[Mo(CO)_4\{(Ph_2PO)_2Na\}]^-$ [59], was later revised to maintain **8b** unchanged [32].

Conversion of **8** into the chelate complexes *cis*-$[M(CO)_4(\eta^2\text{-}Ph_2POPPh_2)]$ can be achieved by treatment either with trifluoroacetic acid in trifluoroacetic anhydride [53] or with acid chloride/NEt_3 (acid chloride = $2CH_3C(O)Cl$, PCl_3, $MeOP(O)Cl_2$ or $[Mo(CO)_5\{P(Cl)_2Me\}]$) [32]. This reaction can be reversed by rapid hydrolysis in aqueous THF under basic conditions, as shown in eqn. (14)

$$\mathbf{8} \underset{\substack{H_2O/THF/OH^- \\ -H_2O}}{\overset{\substack{CF_3COOH/(CF_3CO)_2O \\ \text{or acid chloride}/NEt_3}}{\rightleftharpoons}} [Mo(CO)_4(\eta^2\text{-}Ph_2POPPh_2)] \qquad (14)$$

The reaction of **8** with $PhPCl_2$ does not lead to the expected symmetrical six-membered chelate complexes, *cis*-$[M(CO)_4\{Ph_2POP(Ph)OPPh_2\}]$, but results in a product shown by ^{31}P NMR spectroscopy and X-ray structure analysis (M = Mo) to contain a five-membered chelate ring [54]



Only in the case of the reaction of **8c** could the transient six-membered chelate species be detected by ^{31}P NMR, but it readily isomerizes into the five-membered complex.

In an attempt to prepare the sulphur analogue of **8b**, $[HNEt_3]^+$ $[Mo(CO)_4\{(Ph_2PS)_2H\}]^-$, by treatment of *cis*-$[Mo(CO)_4\{P(Cl)Ph_2\}_2]$ with H_2S/NEt_3, Gray and Kraihanzel [32] obtained instead *cis*-$[Mo(CO)_4(Ph_2PSPPh_2)]$ which, as shown in eqn. (15), undergoes hydrolysis to form *cis*-$[Mo(CO)_4\{(Ph_2PO)(Ph_2PS)H\}]$ (**12**).

$$\begin{tikzcd} cis\text{-}[Mo(CO)_4\{P(Cl)Ph_2\}_2] \arrow[r, "H_2S/NEt_3"] & cis\text{-}[Mo(CO)_4(Ph_2PSPPh_2)] \arrow[d, "\begin{array}{l}NH_4Cl\\ NaOH{,}H_2O\end{array}"] \\ & [HNEt_3]^+ cis\text{-}[Mo(CO)_4\{(Ph_2PO)(Ph_2PS)H\}]^- \\ & \mathbf{(12)} \end{tikzcd} \qquad (15)$$

(ii) Mn, Re

Dialkyl- and diarylphosphine sulphide, as well as diphenylphospine selenide, readily react with pentacarbonyl(halide)manganese and rhenium complexes to yield type-(a) complexes **13**, as in eqn. (16) [15,16]. The analogous oxygen-linked complexes of the secondary phosphine oxides (**13n**, **13o**) can only be prepared by reacting $[\{Re(CO)_4(\mu\text{-}X)\}_2]$ with diphenylphosphine oxide (eqn. (16)) [18]. These last two complexes could undoubtedly be identified in solution, but they are too unstable to be isolated in pure form. O-linked manganese complexes could not be obtained owing to their low stability. **13a** and **13b** readily isomerize about 5° above their formation temperature, yielding the appropriate P-coordinated complexes **14a** and **14b**. The type-(b) rhenium complexes **14c**–**14g** are more conveniently obtainable by direct reaction of the starting materials in a sealed tube than by the isomerization reaction, owing to the partial decomposition accompanying this process [15,18]. P-coordinated complexes of $Ph_2P(Se)H$ are unknown [15].

The reactivity of the Se-coordinated manganese and rhenium complexes **13c** and **13m** distinctly distinguish their O- and S- analogues [15]. Thus, KOH causes elimination of selenium, and heating them in n-heptane causes evolution of H_2Se and formation of the diphenylphosphine complexes $[M(CO)_4Br(PHPh_2)]$ (M = Mn, Re). Also, the ring closure reaction (20) outlined below does not occur with these complexes.

$$\begin{tikzcd}
{[M(CO)_5X] + R_2P(E)H} & & {[M(CO)_4X\{P(EH)R_2\}]\ \mathbf{(14)}} \arrow[ll, "{\substack{M=Mn,\ E=S,\ \sim 50\,°C \\ M=Re,\ E=O,\ S;\ \text{sealed tube}}}"'] \\
& {[M(CO)_4X\{EP(H)R_2\}]\ \mathbf{(13)}} \arrow[ul, "{\substack{M=Mn,\ E=S,\ -40\,°C \\ M=Re,\ E=S,\ 85\,°C}}"] \arrow[ur, "\Delta"'] & \\
& {0.5[\{Re(CO)_4(\mu\text{-}X)\}_2] + Ph_2(O)H} \arrow[u] &
\end{tikzcd} \qquad (16)$$

13	14	M	E	X	R
a	**a**	Mn	S	Cl	Me
b	**b**	Mn	S	Br	Me
c	–	Mn	Se	Br	Ph
d	**c**	Re	S	Cl	Me
e	**d**	Re	S	Br	Me
f	**e**	Re	S	I	Me
g	**f**	Re	S	Cl	Et
h	**g**	Re	S	Br	Et
i	**h**	Re	S	I	Et
j	**i**	Re	S	Cl	Ph
k	**j**	Re	S	Br	Ph
l	**k**	Re	S	I	Ph
m	–	Re	Se	Br	Ph
n	**l**	Re	O	Br	Ph
o	–	Re	O	I	Ph
–	**m**	Mn	O	Br	Me
–	**n**	Mn	O	Br	Ph
–	**o**	Re	O	Cl	Me
–	**p**	Re	O	Br	Me
–	**q**	Re	O	I	Me

According to eqn. (17), $[Mn(CO)_2(\eta^5\text{-}Cp)(THF)]$ and $Me_2P(S)H$ yield the type-(b) complex **15** [61]. The corresponding S isomer could not be isolated, even at low temperature.

$$[Mn(CO)_2(\eta^5\text{-}Cp)(THF)] + Me_2P(S)H \xrightarrow[-THF]{60\,°C} [Mn(CO)_2(\eta^5\text{-}Cp)\{P(SH)Me_2\}] \quad (17)$$

(15)

The P isomers **14** and **15** contain reactive EH groups which makes them accessible to various reactions. Thus, reaction with CH_2N_2 easily leads to the methyl esters $[L_nM{-}P(EMe)R_2]$ [16,61,62]. Sodium or triethylamine react to form the respective salts, $cat^+[L_nM{-}P(E)R_2]^-$ [61]. Acylation of these salts yields acyl derivatives $[L_nMP(SCOR')R_2]$ which on warming may eliminate CO to form the alkyl compounds $[L_nMP(SR')R_2]$ [61]. Metathesis with $Me_{4-n}Y\,Cl_n$ (Y = Si, Ge, Sn) has been reported to give complexes containing the ligands $(Me_2P{-}S)_nYMe_{4-n}$ [63]. Compound **15** can be oxidized by oxygen to give the complex $[\{(CO)_2(\eta^5\text{-}Cp)MnP(Me)_2S\}_2]$, containing the ligand $Me_2P{-}S{-}S{-}PMe_2$ which is unstable as a non-coordinated compound [61]. Metathetic reaction between a salt of **15** and $[Mn(CO)_2(\eta^5\text{-}Cp)(Me_2PCl)]$ allows one to obtain $[\{Mn(CO)_2(\eta^5\text{-}Cp)\}_2(\mu\text{-}Me_2PSMe_2)]$ [61]. The solid-state structure of the last two complexes has been established by X-ray analysis [64]. The ring closure reactions of **14** will be discussed later. The chalcogenophosphinous acid complexes **14** can be reduced with Na/Hg in dimethoxyethane to form dinuclear anionic complexes **16** containing a metal–metal single bond (eqn. (18)). Further reduction with sodium in THF is restricted to the manganese complexes and leads, by cleavage of the metal–metal bond, to the doubly charged anions **17** (eqn. (18)) [65,66]. Complexes **16** and **17** may formally be considered as the sodium compounds of dinuclear and mononuclear type-(b) complexes, respectively. These highly reactive species offer a variety of interesting reactions [65–71].

$$2[M(CO)_4\{P(EH)R_2\}Br] \xrightarrow{Na/Hg} \begin{array}{c} Na_2[\{M(CO)_4[P(E)R_2]\}_2](M{-}M) \\ \mathbf{(16)} \\ \downarrow Na \\ 2Na_2[Mn(CO)_4\{P(E)R_2\}] \\ \mathbf{(17)} \end{array} \qquad (18)$$

16	a	b	c	d	e	f	g
M	Mn	Mn	Mn	Re	Re	Re	Re
E	O	O	S	O	O	S	S
R	Me	Ph	Me	Me	Ph	Me	Ph

17	a	b	c
E	O	O	S
R	Me	Ph	Me

The type-(c) complex *cis*-$[Re(CO)_4(NH_3)\{P(S)Me_2\}]$ (**18**) can be synthesized from **14d** by treatment with NH_3 in a sealed tube [27]. The reaction proceeds via the type-(e) dimer (eqn. 19).

$$\mathbf{14d} \xrightarrow[-NH_4Br]{2NH_3} [\{Re(CO)_4(\mu\text{-}SPMe_2)\}_2] \xrightarrow{2NH_3} 2\,cis\text{-}\underset{\mathbf{(18)}}{[Re(CO)_4(NH_3)\{P(S)Me_2\}]} \qquad (19)$$

The single-crystal X-ray structure determination of **18** [72] shows the NH_3 and the $P(S)Me_2^-$ ligand in mutual *cis* positions. Six-membered ring systems, $[\{M(CO)_4(\mu\text{-}EPR_2)\}_2]$ (**19**) (type (e)), have been synthesized either by dehydrobromination of type-(b) complexes **14** [73] or, starting with the reactive $[\{M(CO)_4(\mu\text{-}ESnMe_3)\}_2]$ complexes, by substitution of Me_3Sn for Me_2P, [74] thus

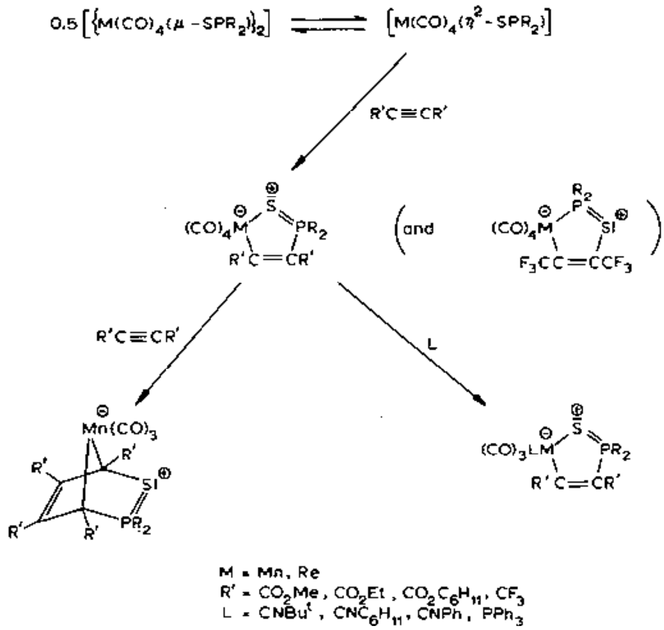
$$\begin{tikzcd}
2[M(CO)_4\{P(EH)R_2\}Br] \arrow[dr, "base", "-2HBr"'] & \\
 & {[\{M(CO)_4(\mu\text{-}EPR_2)\}_2]} \quad \textbf{(19)} \\
{[\{M(CO)_4(\mu\text{-}ESnMe_3)\}_2]} \arrow[ur, "2Me_2PCl", "-2Me_3SnCl"'] &
\end{tikzcd} \tag{20}$$

19	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**
M	Mn	Mn	Mn	Mn	Mn	Re	Re	Re	Re	Re
E	O	O	S	S	Se	O	O	S	S	Se
R	Me	Ph	Me	Ph	Me	Me	Ph	Me	Ph	Me

The molecular structures of **19b** [20], **19c** [22] and **19f** [19] have been established by X-ray structure determination. Their ring conformations are revealed to be quite different: twisted boat (**19b**), ideal chair (**19c**) and distorted chair (**19f**). The PE bond distances (av.), found to be 154, 207 and 153 pm, respectively, may reasonably be interpreted to have an appreciable π-bond character. The X-ray structures suggest a fairly weak metal–chalcogen bond in these compounds, which may thus readily be cleaved by Lewis bases, as demonstrated by the following reaction [74]

$$\mathbf{19c} + 2Me_3P \rightarrow 2\,cis\text{-}[Mn(CO)_4(PMe_3)\{P(S)Me_2\}] \quad \mathbf{(20)} \tag{21}$$

The metalacyclic complexes **19** are assumed to exist in solution in equilibrium with their monomeric units, which would contain the chalgogenophosphinito ligand in a η^2 fashion (**18e**) (type (f)) rather than in the exclusively P- or S-bonded fashion (c) or (d) (**16e**). These highly reactive intermediates can be trapped with electron-deficient alkynes to give isolable P=S-containing metalacyclopentadienes (eqn. (22)) [22,27–29]. Usually, those metalacyclopentadienes containing a M–S bond are formed, but in the case of $F_3CC{\equiv}CCF_3$, a mixture of the M–S and M–P isomers is observed. This result is considered to be indicative of an intermediate bearing the η^2-SPR_2 bonded ligand. The metalacyclopentadienes are accessible to further reactions, e.g. with excess alkynes, isonitriles or phosphines, as shown in eqn. (22) [22,27–29].



(22)

(iii) Fe, Ru

[{Fe(CO)$_2$(η^5-Cp)}$_2$] reacts with (F$_3$C)$_2$P–P(CF$_3$)$_2$ to give [Fe(CO)$_2$(η^5-Cp){(P(CF)$_3$)$_2$}]. Oxidation of this phosphido complex with NO, S$_8$ or Se$_8$ leads to complexes of the type [Fe(CO)$_2$(η^5-Cp){P(E)R$_2$}] (**21**) (type (c)) which upon irradiation rearrange into the isomeric type-(d) complexes **22** [75], thus

$$\left[Fe(CO)_2(\eta^5\text{-}Cp)\{P(CF_3)_2\}\right] \xrightarrow[-N_2O]{2NO \text{ or } E_8} \left[Fe(CO)_2(\eta^5\text{-}Cp)\{P(E)(CF_3)_2\}\right] \quad (23)$$

$$\begin{array}{c} (\mathbf{21}) \\ \downarrow h\nu \\ \left[Fe(CO)_2(\eta^5\text{-}Cp)\{EP(CF_3)_2\}\right] \\ (\mathbf{22}) \end{array}$$

21	a	b	c
22	a	b	c
E	O	S	Se

Complex **21b** is generated in the course of an anti-Arbusov reaction from [FeCl(CO)$_2$(η^5-Cp)] and (CF$_3$)$_2$PSH [75]. The superior stability of these type-(c) complexes compared with the type-(d) complexes can be seen by the reaction of [{Fe(CO)$_2$(η^5-Cp)}$_2$] with (CF$_3$)$_2$PEP(CF$_3$)$_2$ (E = S, Se) leading to an equimolar mixture of **21b** and **21c**, respectively, and [Fe(CO)$_2$(η^5-Cp){P(CF$_3$)$_2$}] [76]. Complexes **21** (E = S, R = Me (**21d**), E = Se, R = Ph (**21e**)) have also been synthesized by metathetic reactions of Na[Fe(CO)$_2$(η^5-Cp)] with Me$_2$P(S)Br and Ph$_2$P(Se)Cl, respectively. Treating **21d** and **21e** with PPh_3 or Me_2PhP leads to complexes $[Fe(CO)L(\eta^5\text{-}Cp)\{P(E)R_2\}]$ **(23)** ($E = S$, $R = Me$; $L = PPh_3$ **(23a)**, Me_2PhP **(23b)**; $E = Se$, $R = Ph$; $L = PPh_3$ **(23c)**, Me_2PhP **(23d)** [77]. Complexes **21d** and **21e** are reported to react with $[Me_3O]^+[BF_4]^-$ or MeI under S or Se methylation, resulting in the cationic complexes $[Fe(CO)_2(\eta^5\text{-}Cp)\{P(EMe)(CF_3)_2\}]^+$ ($E = S$, Se) [77]. Treatment of $[Fe(CO)_2(\eta^5\text{-}Cp)Cl]$ with excess $Ph_2P{-}OPr^i$ in benzene under reflux affords, besides a low yield of $[Fe(CO)(\eta^5\text{-}Cp)Cl(Ph_2OPr^i)]$, the products $[Fe(CO)_2(\eta^5\text{-}Cp)\{P(O)Ph_2\}]$ **(21f)** and $[Fe(CO)(\eta^5\text{-}Cp)(Ph_2POPr^i)\{P(O)Ph_3\}]$ **(23e)**. The formation of these complexes occurs via $[Fe(CO)_2(\eta^5\text{-}Cp)(Ph_2POPr^i)Cl]$ as intermediate, followed by an Arbusov rearrangement [78]. The extent of the Fe → P π-back-bonding in **21a**–**21c** has been discussed on the basis of spectroscopic data [79,80], and for **21a** on the basis of the Fe–P bond distance as determined by X-ray crystallography [80]. The Fe–P bond length decreases from 226.5 pm in $[Fe(CO)_2(\eta^5\text{-}Cp)\{P(CF_3)_2\}]$ to 219.1 pm found for **21a**.

$(CF_3)_2PSeP(CF_3)_2$ reacts with $[Fe_2(CO)_9]$ to give a complex suggested to be $[\{Fe(CO)_3\}_2\{\mu\text{-}P(CF_3)_2\}\{\mu\text{-}SeP(CF_3)_2\}]$ **(24)** on the basis of the ^{19}F NMR resonance and the mass spectrum [76].

Hydrolysis of $[Fe(CO)_2(\eta^5\text{-}Cp)(PhRPCl)]^+X^-$ ($X = PF_6$, BF_4, BPh_4) in acetone in the presence of triethylamine affords the hydrogen-bridged dinuclear cationic complexes **25** [47] thus

$$2[Fe(CO)_2(\eta^5\text{-}Cp)(PhRPCl)]^+ \xrightarrow[-2HNEt_3^+]{\substack{2H_2O\\3NEt_3}} [\{Fe(CO)_2(\eta^5\text{-}Cp)[P(Ph)(R)O]\}_2H]^+ \qquad (24)$$

(25)

R	Bu^t	Ph
25	**a**	**b**

It is argued that these dinuclear hydrogen-bridged complexes probably arise from the reaction of an acid HA with its anion A^- to form an $[AHA]^-$ species, i.e. its isolation may be the consequence of the solvent used in the synthesis. Titration against a standard base in aqueous acetone solution revealed these complexes to be of moderate acid strength with K_a in the range 10^{-2}–10^{-3}, and to be substantially dissociated according to the following equilibrium

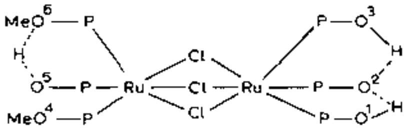
$$\mathbf{25a}, \mathbf{25b} \rightleftharpoons [Fe(CO)_2(\eta^5\text{-}Cp)\{P(OH)PhR\}]^+ + [Fe(CO)_2(\eta^5\text{-}Cp)\{P(O)PhR\}] \qquad (25)$$

A single-crystal X-ray diffraction study has been carried out on **25a** (anion

BF_4^-) [47]. The oxygen atoms of the $PhBu^tP(O)^-$ ligands are the only atoms which are at a distance appropriate for linking the halves of the molecule. The oxygen–oxygen distance of only 240.3 pm implies a strong and probably symmetrical hydrogen bond.

Gaseous HBr converts the dinuclear cations **25** into the mononuclear type-(b) complexes $[Fe(CO)_2(\eta^5\text{-}Cp)\{P(OH)PhR\}]^+Br^-$ (R = Bu^t (**26a**), Ph (**26b**)). Deprotonation of **25b** occurs with NEt_3 and results in the type-(c) complex **21f**. On the contrary, **25a** gives a mixture of $[Fe(CO)_2(\eta^5\text{-}Cp)(PhBu^tP=O\cdots HNEt_3)]^+PF_6^-$ (**27**) and $[Fe(CO)_2(\eta^5\text{-}Cp)\{P(O)PhBu^t\}]$ (**21g**) [47].

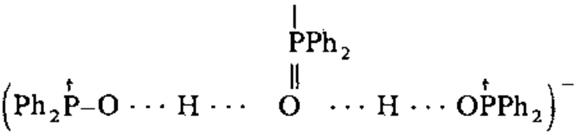
Diamagnetic Ru(II) complexes $[(Ph_2POR)_2(Ph_2POH)Ru(\mu\text{-}Cl)_3Ru(Ph_2PO)(Ph_2POH)_2]$ (R = Me (**28a**), Et (**28b**)) have been prepared by pyrolysis of $[\{Ru(Ph_2POMe)_3\}_2(\mu\text{-}Cl)_3]^+Cl^-$ at 120° in a sealed tube. Complex **28a** was characterized by X-ray structure analysis [45]. Hydrogen bonds of different strength appear to be an important feature of the structure, as deduced from the oxygen–oxygen distances.



(28a) (Ph groups omitted)

distances (pm)	
O^1O^2	254
O^2O^3	277
O^1O^3	297
O^4O^5	292
O^5O^6	266

One Ru atom bears two diphenylphosphinous acid ligands of type (b) together with one diphenylphosphinoyl ligand of type (c) in an arrangement favouring the formation of two hydrogen bridges. In other words, these complexes contain the tridentate anionic ligand



$$\left(Ph_2\overset{+}{P}\text{–}O\cdots H\cdots \overset{\overset{|}{PPh_2}}{\overset{\|}{O}}\cdots H\cdots O\overset{+}{P}Ph_2\right)^-$$

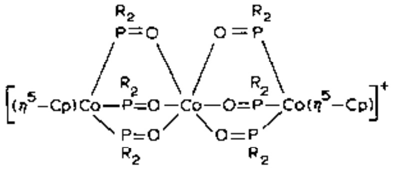
in a bichelating mode.

This ligand has also been observed in $[Ru(Me_2PS_2)\{(Ph_2PO)_3(H)_2\}]$ (**29**) prepared by the reaction of *cis*-$[Ru(Me_2PS_2)_2(PPh_3)_2]$ with excess Ph_2PCl in aqueous acetone [46]. The reaction of the initial ruthenium complex with $Ph_2P(O)H$ did not give **29**, showing that the HCl released in situ by hydrolysis of the Ph_2PCl is necessary to protonate and subsequently remove one of the two $Me_2PS_2^-$ ligands.

Reactions of **29** with $F_3B\cdot OEt_2$, $VO(acac)_2$, $Co(acac)_2$ and CO have been briefly mentioned [46].

(iv) Co, Rh, Ir

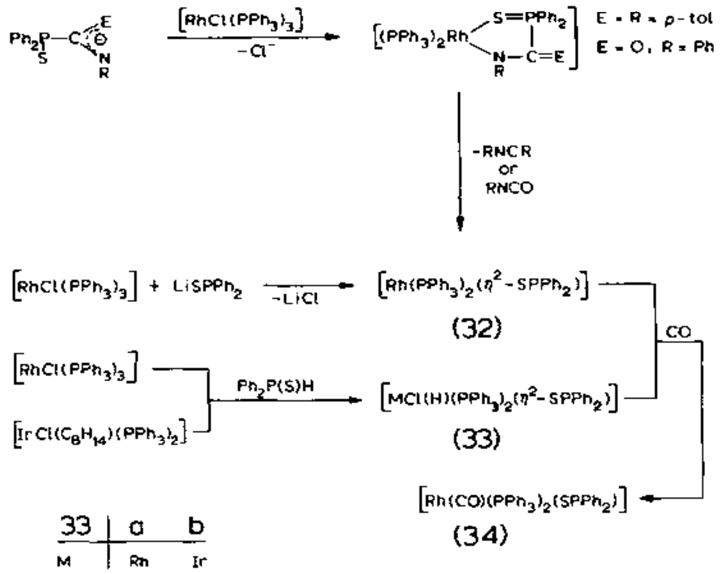
Ebersach et al. [81] described octahedral Co^{3+} d^6 complexes of the type



with R = Et (**30**) or O-alkyl. Whereas those complexes with R = O-alkyl exhibit a temperature-dependent high spin–low spin equilibrium due to the weak and hard tripod ligand $[Co(\eta^5\text{-}Cp)\{P(O)R_2\}_3]^-$ which can be controlled by the steric requirements of the alkoxy groups, complex **30** is found to exist exclusively in the diamagnetic low-spin configuration, reflecting the comparatively stronger field of this ligand.

Yellow $[Ir(CO)Cl(H)(PPh_3)_2(SPPh_2)]$ (**31**) (type (3)) has been obtained by an oxidative addition reaction of $[Ir(CO)Cl(PPh_3)_2]$ and $Ph_2P(S)H$ [82]. Spectroscopic data indicate that this complex adopts a pseudooctahedral structure with both PPh_3 ligands *trans* to one another and the S-linked thiophosphinito ligand *trans* to the CO group. Analogous attempts with $[Rh(CO)Cl(PPh_3)_2]$ did not give a Rh(III) complex but, in the absence of any evidence, are presumed to result in $[Rh(CO)(PPh_3)_2(SPPh_2)]$ [82]. Complex **31** reacts with alkyl iodides to form $[Ir(CO)Cl(H)I(PPh_3)]$. This reaction probably involves initial S-alkylation and the formation of a cationic complex, followed by coordination of the iodide ligand and release of the alkylated thiophosphinito group [82]. Thewissen [83] was the first to report complexes in which the R_2PS^- ligand coordinates in the η^2-mode (f). Thus, $[RhCl(PPh_3)_3]$ was treated with $Ph_2P(S)C(Np\text{-tol})(NHp\text{-tol})$ and an equimolar quantity of $LiBu^n$, or with $Ph_2P(S)C(O)NHPh$ in the presence of a small excess of NEt_3, to form isolable intermediates in which the respective heteroallylic systems coordinate through both the P-bonded sulphur atom and the nitrogen atom. These intermediates eliminate fairly rapidly the heteroallenes p-tolN = C=Ntol-p and PhN=C=O, respectively, resulting in the compound $[Rh(PPh_3)_2(\eta^2\text{-}SPPh_2)]$ (**32**).

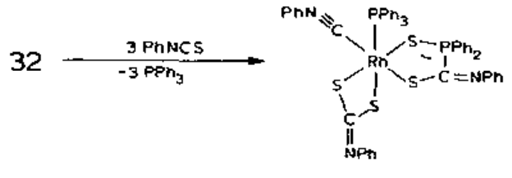
The same complex was obtained by reaction of $[RhCl(PPh_3)_3]$ with $LiSPPh_2$. From the direct interaction of $[RhCl(PPh_3)_3]$ or $[IrCl(C_8H_{14})(PPh_3)_2]$ and $Ph_2P(S)H$, complexes $[MCl(H)(PPh_3)_2(\eta^2\text{-}SPPh_2)]$ (**33**) (M = Rh (**33a**), Ir (**33b**)) were obtained by an oxidative elimination reaction. Upon standing for a few days, **33a** loses HCl and converts into **32**. Complexes **32** and **33a** can be transformed into (probably *trans*-) $[Rh(CO)(PPh_3)_2(SPPh_2)]$ (**34**) by bubbling CO into the benzene solutions. The three-membered RhSP ring is opened during this reaction and the Ph_2PS^- ligand becomes S-bonded. The reactions are summarized in eqn. (26).



(26)

The IR bands of **32**, **33a** and ^{33}**b** at 513, 512 and 511 cm^{-1}, respectively, are assigned to the PS vibrations, and are interpreted as showing the involvement of the sulphur atom in the coordination sphere of the central metals [83]. The ^{31}P NMR spectra of these compounds indicate three inequivalent phosphorus atoms. The small ^1J(RhP) coupling of 119 (**32**) and 82 Hz (**33a**), respectively, found for the Ph_2PS^- ligand, are considered to be of diagnostic value for the Rh(η^2-$SPPh_2$) coordination mode [83].

Refluxing **32** with a large excess of PhNCS yields a main product which has formally incorporated three molecules of PhNCS. In more detail, this product follows from the insertion of one molecule into the Rh(η^2-$SPPh_2$) bond and from the disproportionation of two PhNCS molecules forming the ligands PhNC and $PhNCS_2^{2-}$ [83], thus



(27)

[{IrCl(COD)}$_2$] (COD = 1,5-cyclooctadiene) reacts with excess Ph_2PCl in aqueous methanol (which means with $Ph_2P(O)H$ and HCl) to yield the Ir(III) complex **35** which in solution loses COD and incorporates the chelate ligands L_2 as follows [84]

$$[\{IrCl(COD)\}_2] \xrightarrow{\overset{Ph_2PCl}{H_2O, MeOH}} [Ir(COD)(Cl)H\{(Ph_2PO)_2H\}]\ (\mathbf{35}) \qquad (28)$$

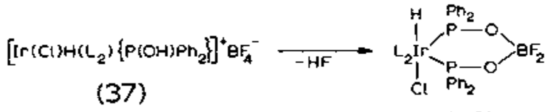
$$\downarrow L_2$$

$$[Ir(Cl)H(L_2)\{(Ph_2PO)_2H\}]$$

$$(\mathbf{36})$$

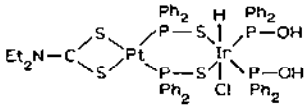
36	L_2
a	$Ph_2P(CH_2)_2PPh_2$
b	$Ph_2As(CH_2)_2AsPh_2$
c	$PhS(CH_2)_2SPh$

Complex **36b** can be protonated with HBF_4 to form the cationic complex **37**, which in $CHCl_3$ gives **38**, [84], thus



(37) (38) (29)

A note is given that **35** and $[H_2NEt_2]^+[Pt(S_2CNEt_2)\{P(S)Ph_2\}_2]^-$ results in the heterodinuclear complex **39** with the ligands considered to be of types (b) and (e) [84]

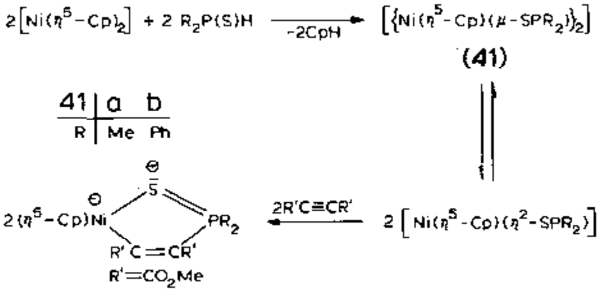


(39)

The reaction of $[\{RhCl(COD)\}_2]$ and Ph_2PCl in aqueous methanol depends critically on the $H_2O/MeOH$ ratio. Under certain conditions the dinuclear anionic complexes $cat^+[\{RhCl[(Ph_2PO)_2H]\}_2(\mu\text{-}Cl)_2]$ (**40**) (cat = $AsPh_4$, Cs, Ph_3PCH_2Ph) could be obtained [84]. Preliminary X-ray results show the O ··· O distance to be 240 pm [84].

(v) Ni, Pd, Pt

$[Ni(\eta^5\text{-}Cp)_2]$ and $R_2P(S)H$ react to give $[\{Ni(\eta^5\text{-}Cp)(\mu\text{-}SPR_2)\}_2]$ (**41**) (R = Me (**41a**), Ph (**41b**)), which has been characterized spectroscopically and by single-crystal X-ray structure determination of **41a** [21,30]. Complex **41a**, like **19c**, adopts an ideal chair conformation. Analogous to the six-membered Mn and Re complexes **19**, **41** are supposed to exist in a dissociation equilibrium with their monomeric units [Ni(η^5-Cp)(η^2-SPR$_2$)], which can be trapped with electron-deficient acetylenes [30]. The reactions are outlined in eqn. (30).

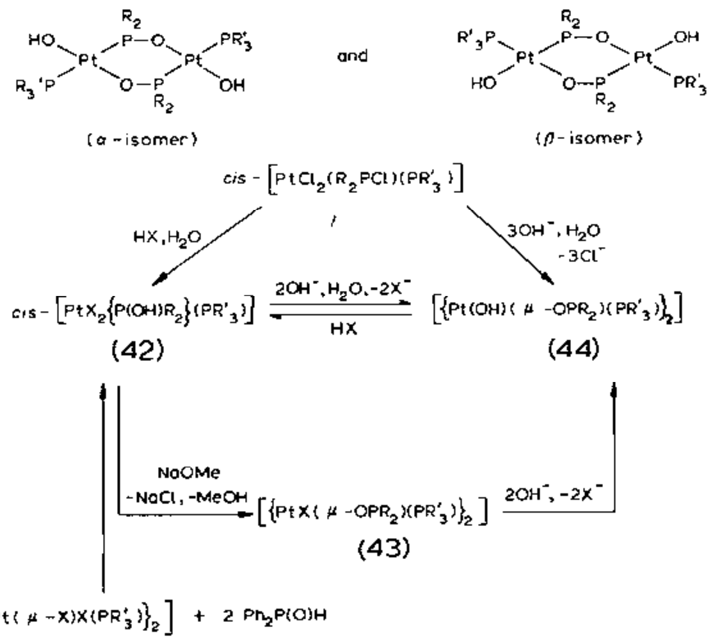


(30)

Chatt and Heaton [85] described complexes obtained by stepwise hydrolysis of *cis*-[PtX$_2$(R$_2$PCl)(PR'$_3$)] (eqn. (31)). The first hydrolysis products of type (b), *cis*-[PtX$_2${P(OH)R$_2$}(PR'$_3$)] (**42**), were obtained by (a) acidic hydrolysis of *cis*-[PtCl$_2$(Ph$_2$PCl)(PR'$_3$)], (b) reaction of Ph$_2$P(O)H with [{Pt(μ-X)X(PR'$_3$)}$_2$] or (c) treatment of the third hydrolysis product [{Pt(OH)(μ-OPR$_2$)(PR'$_3$)}$_2$] with excess HX. Selective hydrolysis of the second chloride ligand is readily performed with one equivalent of sodium methoxide, resulting in dinuclear complexes with bridging R$_2$PO$^-$ ligands (**43**), as in eqn. (31). The structure of these complexes, based on the IR and NMR spectra, seems to be centrosymmetric except that **43a** and **43b** are supposed to have a *cis* arrangement of the X$^-$ ligands, each linked to one platinum atom. Interestingly, complexes **43** have a structure with the halides *trans* to the oxygen atoms of the bridging R$_2$PO$^-$ ligands, and the ν(PtX) values indicate that both the phosphorus and the oxygen atoms exert a high *trans* influence [85]. All three chloride ligands of the starting complex are hydrolysed either by reacting the starting complex with three equivalents of sodium hydroxide, or by treating **42** or **43** with two equivalents of NaOH (eqn. (31)). The products **44** (R = Ph, R' = Me (**44a**); R = Ph, R' = Et, (**44b**)) were isolated as the α-isomers. By shaking the benzene solution with excess NaOH, these are converted into the β-isomers. These isomers are tentatively assigned the following structures [85] .

42	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**
43	**a**	**b**	**c**	**d**	**e**	**f**	–	**g**
X	Cl	Br	Cl	Br	I	Cl	Cl	Cl
R	Ph	Ph	Ph	Ph	Ph	Et	Ph	Ph
R'	Me	Me	Et	Et	Et	Et	Bu	AsEt$_3^*$

(*instead of PR'$_3$)



(31)

Complexes containing P-bonded $R_2P(O)^-$ ligands were prepared from **43c** and **43f** by treatment with NaSEt, which substitutes the halogenide ligand and adopts the bridging positions, thereby moving the μ-OPR_2 ligand into the terminal mode (c), as follows [85]

$$\mathbf{43c},\ \mathbf{43f}\ \underset{-2NaCl}{\overset{2NaSEt}{\rightarrow}}\ \underset{\mathbf{(45)}}{\left[\{Pt\{P(O)R_2\}(PR'_3)(\mu\text{-}SEt)\}_2\right]} \tag{32}$$

45	a	b
R	Ph	Et
R′	Et	Et

Reaction of **43c** with two equivalents of p-toluidine generates the simple bridge-splitting product $[PtCl\{P(O)Ph_2\}(PEt_3)(p\text{-}tol)]$ **(46)** [85].

On treatment with stable nitrile oxides, triphenylphosphine platinum (0) complexes $[PtL(PPh_3)_2]$ ($L = PPh_3$, C_2H_4) yield products **47**, which, as shown by single-crystal X-ray structure determination of **47a** and **47b**, have resulted from transferring the oxygen atom of the nitrile oxide to one PPh_3 ligand. Moreover, in a concerted fashion there is the migration of one phenyl group from the phosphorus to the platinum atom (eqn. (33)) [86]. The P-bonded $R_2P(O)^-$ ligand is found in the *cis* position to the phenyl group, as well as to the nitrile ligand. The lengthening of the *trans* Pt–P bond compared with *trans*-$[Pt^{II}(PPh_3)_2]$complexes has been attributed to a greater *trans* influence of the $R_2P(O)^-$ ligand than the PPh_3 ligand. The P–O bond length is 151 pm, corresponding to a ν(PO) of 1120–1125 cm^{-1}.

$$\begin{tikzcd}[column sep=large] [Pt(PPh_3)_3] \arrow[dr, "2RCNO", "-RCN,\,-OPPh_3"'] & \\ & [PtPh\{P(O)Ph_2\}(PPh_3)(RCN)] \\ [Pt(C_2H_4)(PPh_3)_2] \arrow[ur, "RCNO", "-C_2H_4"'] & \end{tikzcd} \qquad (33)$$

(47)

47	R
a	3,5-dichloro-2,4,6-trimethylphenyl
b	9-anthracenyl
c	2,4,6-trimethoxyphenyl
d	2,4,6-trimethylphenyl

The reaction of tetraorganodiphospine disulphides with phosphine platinum(0) complexes yields diplatinum(I) complexes **48**, containing two bridging SPR_2 ligands accompanied by a metal–metal bond (eqn. (34)) [25]. The same type of complex, including palladium as the central atom and $SePPh_2^-$ as the bridging ligand, has more conveniently been prepared by treatment of the phosphine platinum(0) complexes with the appropriate secondary phosphine chalcogenides (eqn. (34)) [26]. It should be noted that this latter reaction can be contrasted with the $[Pt(PR_3)_4]/(Ph_2PO)H$ reaction [44] outlined below. The range of available complexes could be extended by terminal substitution reactions (eqn. (34)) [25,87,88]. Noteworthy is the reaction of **48o** with bis(diphenylphosphino)methane (dppm) which leads to **49l**, containing the dppm ligands in a monodentate fashion, and does not as would be expected, give the complex $[\{Pt(\mu\text{-dppm})(SPPh_2)\}_2]$. This observation, as well as the failure to achieve insertion reactions of the metal–metal bond by treatment of those complexes with CNR, CO, S_8, and SO_2, respectively, demonstrates the high stability of the $[\{Pt(\mu\text{-}SPR_2)\}_2](M\text{–}M)$ core, which in turn is based upon the restricted flexibility of this unit by the strong μ-SPR_2 ligands [87].

$$\begin{tikzcd}[column sep=large] 2[Pt(PR'_3)_4] + R_2P(S)P(S)R_2 \arrow[dr, "-6PR'_3"'] & \\ & [\{M(PR'_3)(\mu\text{-}EPR_2)\}_2] \ \mathbf{(48)} \arrow[d, "2L", "-2PR'_3"'] \\ 2[M(PR'_3)_4] + 2R_2P(E)H \arrow[ur, "-H_2,\,-6PR'_3"'] & [\{ML(\mu\text{-}EPR_2)\}_2] \ \mathbf{(49)} \end{tikzcd} \qquad (34)$$

48	a	b	c	d	e	f	g	h	i	j	k	l
M	Pd	Pd	Pd	Pd	Pd	Pd	Pt	Pt	Pt	Pt	Pt	Pt
E	S	S	S	S	S	Se	S	S	S	S	S	S
R_2	Me_2	Et_2	Cy_2	Ph_2	Ph_2	Ph_2	Me_2	Me_2	Et_2	Et_2	MePH	Et_2
R'_3	Ph_3	Ph_3	$MePh_2$	Ph_3	Cy_3	Ph_3	$MePh_2$	Ph_3	$MePh_2$	Ph_3	Ph_3	Me_2Ph

48	m	n	o	p
M	Pt	Pt	Pt	Pt
E	S	S	S	Se
R_3	Cy_2	Ph_2	Ph_2	Ph_2
R'_3	Ph_3	$MePh_2$	Ph_3	Ph_3

49	a	b	c	d	e	f	g
M	Pd	Pd	Pd	Pd	Pd	Pt	Pt
E	S	S	S	S	S	S	S
R_2	Et_2	Et_2	Ph_2	Ph_2	Ph_2	Me_2	Et_2
L	$PPh(OPh)_2$	$P(OPh)_3$	$P(OPh)_3$	CNMe	$CNBu^t$	$P(OPh)_3$	$P(OPh)_3$

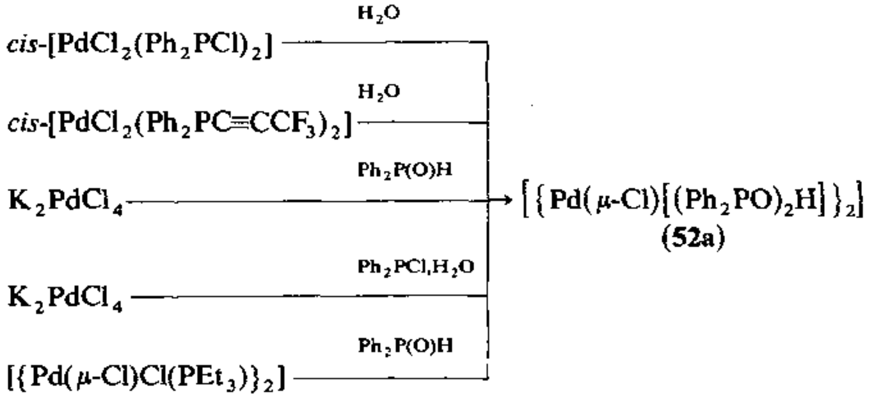
49	h [88]	i	j	k	l	m	n
M	Pt	Pt	Pt	Pt	Pt	Pt	Pt
E	S	S	S	S	S	S	S
R_2	Me_2	Et_2	Cy_2	Ph_2	Ph_2	Et_2	Ph_2
L	$P(OMe)_3$	$PPh(OPh)_2$	$P(OPh)_3$	$PPh(OPh)_2$	η^1-dppm	CNMe	$CNBu^t$

Single-crystal X-ray structures, available for **49d** [87] and **49g** [25] show these complexes to be essentially planar and centrosymmetric. The M–M distances of 264 and 262.8 pm, respectively, are in accord with a M–M single bond, which is expected for such dimetal(I) complexes. An oxidation state of +1 is supported by ESCA data [89]. The P–S bond lengths of 202.8 and 204.6 pm, respectively, suggest the bond order to be close to 1.5, in agreement with the IR frequencies [26] and ESCA measurements [89]. It has been deduced from the ^{31}P NMR spectra of a series of complexes **48** and **49** (including those with R = OEt) that (a) the π-acceptor ability of the terminal ligands strongly influence the chemical shift of these ligands as well as various coupling constants, (b) $J(^{195}Pt^{195}Pt)$ changes sign among the range of complexes investigated, and (c) thermal singlet triplet excitation causes paramagnetism of these complexes. EPR measurements and EHT calculations have been carried out in order to support these observations [90].

The $[Pt(PR'_3)_4]/R_2(E)H$ reaction, eqn. (34), involves an oxidative addition to form the intermediate *trans*-$[PtH\{P(S)R_2\}(PR'_3)_2]$ (**50**), which could be isolated and spectroscopically characterized at low temperatures in the case of R = Ph and $PR'_3 = PMePh_2$ [24]. Above $-15\,°C$, **50** slowly eliminates H_2 to yield the final dinuclear complex **48n**. In an attempt to stabilize the transient platinum(II) hydrides **50**, $Ph_2P(S)H$ was reacted with $[Pt(PBu^t_3)_2]$.

Surprisingly, the dinuclear dihydrido complex$[\{PtH(PBu^t_3)(\mu\text{-}SPPh_2)\}_2]$ **(51)** was formed. According to a single-crystal X-ray structure determination [24] the six-membered $Pt_2(\mu\text{-}SPPh_2)_2$ ring adopts a boat-shaped arrangement with a non-bonding Pt–Pt distance of 362 pm. Both Pt atoms have square planar geometry, with the bridging and terminal phosphorus atoms in a mutual *trans* position. The Pt–H distance is 142.2 and the Pt–S distance 245.1 pm, the latter being rather long. ^1H and ^{31}P NMR measurements reveal the dimeric structure to be maintained in solution and stable up to at least 100 °C [24].

The complexes of type $[\{M(\mu\text{-}X)[(Ph_2PO)_2H]\}_2]$ **(52)** with M = Pd and X = Cl **(52a)** have been described by several authors (eqn. (35)) [34,35,39,41,43].

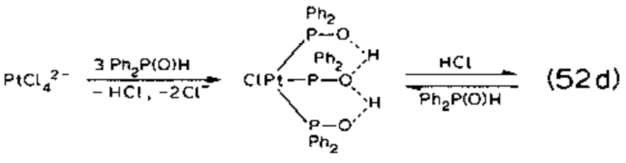


(35)

The hydrolysis of $cis\text{-}[PdCl_2(Ph_2PCl)_2]$ has earlier been described to yield $cis\text{-}[PdCl_2(Ph_2POH)_2]$ [91] but this statement has now been questioned convincingly by Wong and Bradley [39]. Austin [91] further reported the reaction of a complex considered to be $cis\text{-}[PtCl_2(Ph_2POH)_2]$ with BF_3, but the structure of the product was not definitely established.

Complex **52a** can be transformed into the bromo **(52b)** and the thiocyanato **(52c)** derivatives by metathetic reactions [34,35]. Hydrolysis of $cis\text{-}[PdCl_2(Ph_2PC{\equiv}CCF_3)_2]$ at room temperature results in a mixture of different complexes, among them also the type-(b) complexes $cis\text{-}[PdCl_2\{P(OH)Ph_2\}\{Ph_2PCH_2C(O)CF_3\}]$ **(53)** and $[PdCl\{P(OH)Ph_2\}\text{-}\{Ph_2PCH{=}C(CF_3)O\}]$ **(54)**. Their formation follows through nucleophilic attack on both the coordinated phosphorus atom and the non-coordinated C–C triple bond [35].

Treatment of K_2PtCl_4 with $Ph_2P(O)H$ yields primarily the complex $[MX\{(Ph_2PO)_3(H)_2\}]$ **(55)** (M = Pt, X = Cl **(55a)**), contrary to the reaction of K_2PdCl_4 outlined in eqn. (35). This difference was attributed to the greater stability of the chlorine bridges for the Pd complex and/or to the greater affinity of platinum for phosphorus ligands [41]. Complex **55a** can be converted into $[\{Pt(\mu\text{-}Cl)[(Ph_2PO)_2H]\}_2]$ (**52d**) by reaction with HCl as follows [41]



(55a)

(36)

The Pd complex $[PdCl\{(Ph_2PO)_3(H)_2\}]$ (**55b**), on the other hand, has been obtained from **52a** and $Ph_2P(O)H$ [41]. Several reactions, mostly similar for Pd and Pt complexes, have been described with **52a, 52d, 55a** and **55e** [41]. These include the preparation of the coordination polymeric complexes $[\{M(Ph_2PO)_2\}_n]$ (M = Pd (**56a**), Pt (**56b**)), the former also being described by Wong and Bradley [39], and the substitution products $[MX(L)\{(Ph_2PO)_2H\}]$ (**57**) (M = Pd, L = PEt_3, X = Cl (**57a**); M = Pt, L = PEt_3, X = Cl (**57b**), PPh_3 (**57c**)). Differences between Pd and Pt complexes were found, in that reactions of **55a** with $AgOPPh_2$ and NaOH, respectively, gave the complexes $[Pt\{(Ph_2PO)_2H\}_2]$ (**58**) and $[\{Pt(\mu\text{-}OPPh_2)[(Ph_2PO)_2H]\}_2]$ (**59a**) [41]. Analogous Pd complexes could not be obtained by these authors but $[\{Pd(\mu\text{-}OPPh_2)[(Ph_2PO)_2H]\}_2]$ (**59b**) was briefly mentioned by Kong et al. [43].

The molecular structure of **52c** was established by X-ray determination [34,35]. The molecule adopts a centrosymmetric structure with an O ··· O distance of 242.1 pm and two nearly equal P–O bonds of 154.9 and 153.6 pm, respectively, despite having different *trans* donor atoms (N or S). This result supports the assumption of a strong symmetric O ··· H ··· O hydrogen bridge. Roundhill and co-workers [42–44] showed that hydrolysis of complexes $[Pt(Ph_2POR)_4]$ can afford three types of complex, $[PtH(Ph_2POR)\{(Ph_2PO)_2H\}]$ (**57**) (R = Pr^i (**57d**), Bu^n (**57e**)), $[PtH\{(Ph_2PO)_3(H)_2\}]$ (**55c**) and **58**, depending on both the reaction time and R (eqn. (37)). Thus, if R = Me the product is **55c**. If R = Pr^i or Bu^n the products are either **57d** and **57e** or **58**. These products can be rationalized on the basis of dissociation equilibrium of the starting Pt(0) complexes which allows the free alkyl diphenylphosphinite to undergo hydrolysis readily. The reaction of $Ph_2P(O)H$ thus formed with the Pt(0) complex would explain the formation of **57d** and **57e**. The subsequent hydrolysis of the Ph_2POR ligand of **57d** and **57e**, respectively, leads to **55c**, which reacts with $Ph_2P(O)H$ with evolution of H_2 to yield **58**, as in eqn. (37). These reactions were both confirmed in separate runs [44].

$$\begin{tikzcd}
{[Pt(Ph_2POR)_4]} \arrow[ddd, "\begin{array}{c}Ph_2P(O)H\\(excess)\end{array}"] & \rightleftharpoons & 2Ph_2POR + \arrow[d, dash, "\begin{array}{l}2H_2O\\-2ROH\end{array}"] & {[Pt(Ph_2POR)_2]} \arrow[dl] \\
 & & 2Ph_2P(O)H \arrow[d] & \\
 & & {[PtH(Ph_2POR)\{(Ph_2PO)_2H\}]} \arrow[d, "H_2O"] & \\
{[Pt\{(Ph_2PO)_2H\}_2]} & & {[PtH\{(Ph_2PO)_3H_2\}]} \arrow[ll, "Ph_2P(O)H"'] &
\end{tikzcd} \qquad (37)$$

(57d, 57e)

(58) **(55c)**

The following reaction (eqn. (38)) verifies the possibility of the protonation step occurring with Pt(0) complexes by $Ph_2P(O)H$ in reactions according to eqn. (37) [44].

$$[Pt(PPh_2R)_4] + 2Ph_2P(O)H \rightarrow [PtH(PPh_2R)\{(Ph_2PO)_2H\}] \qquad (38)$$

(57)

57	**f**	**g**
R	Ph	Me

This straightforward reaction involves both an oxidative addition and a ligand substitution step, and the formation of the coordination mode (g) may be considered to be the driving force.

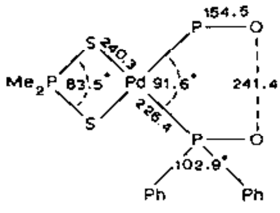
The ^1H NMR spectra of **57e** and **57g** show the PtH resonance in the high-field region at $\delta = -4.14$ and -3.91 ppm, respectively ($J(PtH) = 880$ and 884 Hz). The proton signal of the hydrogen-bridge is broad and centered at $\delta = 13.43$ ppm [44]. The type-(g) complex **57g** shows a concentration-dependent ^{31}P NMR spectrum with a reversible broadening of the signals of the Ph_2MeP ligand and its *trans*-phosphinito ligand only at high solute concentration. As proposed, this may be due to a monomer–dimer equilibrium [92]. Complexes of type (g) are acids and can be titrated in MeOH against a standard solution of NaOMe, as shown by Sperline and Roundhill [40]. The diprotic complex **58** behaves as a dibasic acid but shows only one break in the titration curve [93]. T_1 measurements of some type-(g) complexes were reported [92]. An interesting substitution reaction of **58** occurs with triphenyl phosphite [42]. The product $[Pt(Ph_2PO)_2\{(PhO)_2PO\}_2(H)_2]$ **(60)** reveals that only two phosphinito ligands are substituted by the phosphite.

Cornock et al. [36] studied the reaction of $[M(\overset{\frown}{S\ S})_2]$ with Ph_2POR (R = Me, Et) and obtained complexes of the type $[M(\overset{\frown}{S\ S})\{(Ph_2PO)_2H\}]$

(**61**), (M = Pd, $\widehat{S\,S}$ = $Me_2PS_2^-$ (**61a**), $Ph_2PS_2^-$ (**61b**), $Et_2NCS_2^-$ (**61c**); M = Pt, $\widehat{S\,S}$ = $Me_2PS_2^-$ (**61d**), $Et_2NCS_2^-$ (**61e**)).

The intermediates $[Pt(S_2CNEt_2)(Ph_2POMe)_2]^+X^-$ and $[Pt(S_2CNEt_2)\{P(O)Ph_2\}(Ph_2POMe)]$ (**62**) could be isolated in the $[Pt(S_2CNEt_2)_2]/Ph_2POMe$ reaction. Complex **62** is transformed into the final complex by substitution of Ph_2POMe for $Ph_2P(O)H$ (from Ph_2POMe), indicating the preference for type (g)). Derivatives **61a**–**61c** were also obtained from **52a** with either $NaS_2PMe_2 \cdot 2H_2O$, $NH_4S_2PPh_2$ or $NaS_2CNEt_2 \cdot 3H_2O$ [36]. This metathetic reaction also occurs with KS_2COPr^i to produce $[Pd(S_2COPr^i)\{(Ph_2PO)_2H\}]$ (**61f**), whereas $[Pd(S_2COPr^i)_2]$ and Ph_2POEt only yields $[Pd(S_2COPr^i)(Ph_2POEt)_2]$. Recently, the same group [23] has prepared **61e** as well as the analogous *N,N*-diisopropyldithiocarbamato complex **61g** by treatment of $[Pt(S_2CNR_2)_2]$ with either $Ph_2P(O)H$ or Ph_2PCl in wet MeOH. Some derivatives of coordination type (h), $[Pt(S_2NCEt_2)\{(Ph_2PO)_2M\}]$ (**63**) (M = BF_2 (**63a**), VO/2 (**63b**), Co/2 (**63c**)) have also been prepared from **61e** by treatment with $BF_3 \cdot OEt_2$, $VOacac_2$ and $Coacac_2$, respectively [46].

Complexes **61** were characterized spectroscopically and by X-ray analysis of **61a** [36]. The Pd atom is almost planar coordinated, and the plane defined by the symmetry-related phosphorus and oxygen atoms is tilted by 26.1° with respect to the coordination plane.

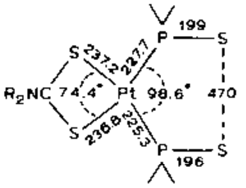


(61a)

(bond distances [pm])

This complex shows $\nu(PO)$ at 1010 cm^{-1} and ^{31}P resonances at $\delta = 84.29$ ($Me_2PS_2^-$) and 83.2 ppm ($Ph_2POHOPPh_2^-$) [36].

In an attempt to synthesize complexes of coordination type (g) with E = S, Stephenson and co-workers [23,33] have examined reactions of $[M(S_2CNR_2)_2]$ (M = Pt, R = Et, Pr^i; M = Pd, R = Et) with diphenylphosphine sulphide and found that, contrary to reaction with $Ph_2(O)H$, the sulphide species produces a variety of products, depending upon the amount of sulphide used, the amount of water present and the duration of the reaction. Thus, the $[Pt(S_2CNR_2)_2]/Ph_2P(S)H$ (excess) reaction, under reflux conditions in dry methanol, produces $cat^+[Pt(S_2CNR_2)\{P(S)Ph_2\}_2]^-$ (**64**) ($cat^+ = H_2NEt_2^+$, R = Et (**64a**), R = Pr^i(**64b**)). The ammonium cation may be exchanged by cations Cs^+ (**64c**) or $P(CH_2Ph)Ph_3^+$ (**64d**). Refluxing the same mixture for a long time results in a complex formulated as $[Pt(S_2CNPr^i_2)(Ph_2PS)(Ph_2POMe)]$ (**65**), which may be generated from the reaction of **64a** with Ph_2POMe (formed from $Ph_2P(S)H$ and MeOH in a prolonged reaction). The molecular structure of **64a** has been established by X-ray structure analysis [23,33]. The ammonium ion lies fairly close to the complex anion, and this ion pair is maintained in CH_2Cl_2/acetone solution, but not in MeOH, as shown by conductivity measurements. The platinum atom is square planar coordinated and the plane defined by the two PS bonds is tilted 70° from this coordination plane.



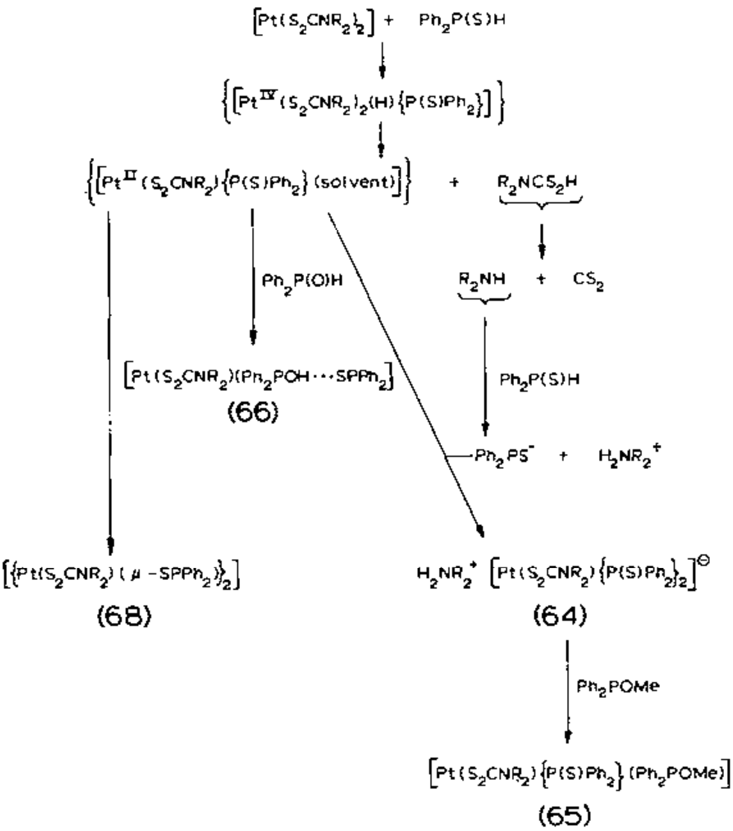
(64a)

(bond distances [pm])

Complexes **64a** and **64b** have been characterized further by ^1H, ^{13}C, ^{195}Pt, ^{31}P and IR spectroscopy [23,33].

If $[Pt(S_2CNR_2)_2]/Ph_2P(S)H$ (excess) are refluxed in technical grade MeOH, the interesting complexes of type (g) $[Pt(S_2CNR_2)(Ph_2POH\cdots SPPh_2)]$ (R = Et (**66a**), Pr^i (**66b**)) are formed [23]. On the basis of NMR and IR spectroscopy, these are proposed to contain a proton, strongly bonded to the oxygen atom, but also interacting with the sulphur atom. Addition of CsCl to the solution of **66b** precipitates $Cs[Pt(S_2CNPr^i_2)\{P(O)Ph_2\}\{P(S)Ph_2\}]\cdot 2H_2O$ (**67**).

Dinuclear complexes of type $[\{Pt(S_2CNR_2)(\mu\text{-}SPPh_2)\}_2]$ (**68**) (R = Et (**68a**), Pr^i (**68b**)) result either from the reaction of $[Pt(S_2CNR_2)_2]$ with equimolar amounts of $Ph_2P(S)H$ or from treatment of **64a** with HCl gas. The ^{31}P NMR spectrum of **68a** shows a signal centred at $\delta = 30.5$ ppm with $^1J(PtP) = 3656.4$, $^2J(PtP) = 80.5$, $^3J(PP) = 13.6$ and $^3J(PtPt) = 940$ Hz [33]. The molecular structure of **68b**, established by X-ray analysis, reveals this complex to have a centrosymmetric chair conformation with a square planar arrangement of the ligating atoms around the platinum atoms. The interplane angle between the coordination planes of the metal atoms and the plane defined by both the P–S bonds is found to be 54°. The analogous dinuclear palladium complex, $[\{Pd(S_2CNEt_2)(\mu\text{-}SPPh_2)\}_2]$ (**68c**), as well as $H_2NEt_2^+[Pd(S_2CNEt_2)\{P(S)Ph_2\}]^-$ (**64e**) have both been isolated from the $[Pd(S_2CNR_2)_2]/Ph_2P(S)H$ reaction in dry methanol [23,33]. The variety of products obtained from the $[Pt(S_2CNR_2)_2]/Ph_2P(S)H$ reaction may be generated via the same intermediate [Pt(S$_2$CNR$_2$){P(S)Ph$_2$}(solvent)] formed from the starting materials by oxidative addition and reductive elimination reactions, as illustrated in eqn. (39) [23,33]



(39)

The reaction of [Pt(y$_2$CNR$_2$)$_2$] (y = S, Se) with Ph$_2$P(Se)H results in only one type of complex, [Pt(y$_2$CNR$_2$){P(Se)Ph$_2$} (Ph$_2$PH)] **(69)** (y = S, R = Et **(69a)**, Pr^i **(69b)**; y = Se, R = Et **(69c)**) and is thus to be contrasted with the reactions of diphenylphosphine sulphide [23]. The reaction of type-(g) complexes with either F$_3$B · OEt$_2$ or HBF$_4$ to form derivatives containing the unit [M{(Ph$_2$PO)$_2$BF$_2$}] (named "BF$_2$-capped" [44]) has frequently been employed to characterize type-(g) complexes.

Typical vibrations of the Ph$_2$POBF$_2$OPPh$_2^-$ ligand were assigned at 1060, 1005 and 890 cm^{-1}, the latter especially being proposed to be of diagnostic value [38]. The following complexes of this type (h) have been described

{MLL′{(Ph$_2$PO)$_2$BF$_2$}]
(70)

70	**a** [44]	**b** [44,94]	**c** [38]	**d** [38]	**e** [38]	**f** [38]
M	Pt	Pt	Pt	Pd	Pt	Pt
L	H	H	Cl	Cl	Cl	Cl
L′	Ph_2POBu^n	$MePh_2P$	PEt_3	PEt_3	PPh_3	Ph_2PH

$[Pt\{(Ph_2PO)_2BF_2\}_2]$ (**71**) [38,44]

$[\{Pt(\mu\text{-}OPPh_2)[(Ph_2PO)_2BF_2]\}_2]$ (**72**) [38]

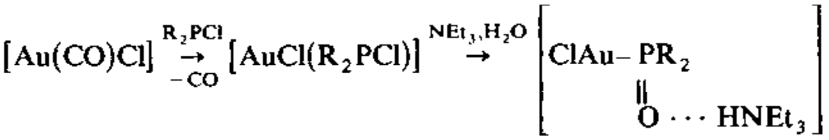
$[\{Pd(\mu\text{-}X)[(Ph_2PO)_2BF_2]\}_2]$ (**73**) (X = Cl (**73a**), Br (**73b**)) [38]

The reaction of $[PtCl(PEt_3)\{(Ph_2PO)_2H\}]$ (**57b**) with Me_3SiCl is complicated, and the product, assumed to be $[PtCl(PEt_3)\{(Ph_2PO)_2SiMe_3\}]$ (**74**) is ill-defined [38]. Species **57b** was also treated with $VOacac_2$ and the product isolated, $[\{PtCl(PEt_3)(Ph_2PO)_2\}_2VO]$ (**75**), was characterized by crystal field, IR and EPR spectra [38].

(vi) Ag, Au

Aqueous solutions of $Ph_2P(O)H$ react quantitatively with $AgNO_3$ to precipitate insoluble silver diphenylphosphinite (**76**) [9]. To complete the precipitation requires 3–4 h, and the authors argued that this is due to the tautomeric pre-equilibrium (2). Quin and Montgomery [95] questioned this argument. The structure of **76** is still uncertain, although type (d), $[AgOPPh_2]$, was favoured on the basis of IR spectroscopy [95]. The present author believes this compound to be coordination polymeric and hence to contain the Ph_2PO^- ligand in the bridging mode (e), $[\{AgOPPh_2\}_n]$.

Me_2PCl and Ph_2PCl react with [AuCl(CO)] to make $[AuCl(R_2PCl)]$ which can be hydrolyzed in the presence of NEt_3. The resulting anionic phosphinito complex **77**, believed to contain a hydrogen bridge with its ammonium cation, reacts with Me_3SiCl to afford the siloxyphosphinito gold complex $[AuCl(Ph_2POSiMe_3)]$ (eqn. (40)) [96]

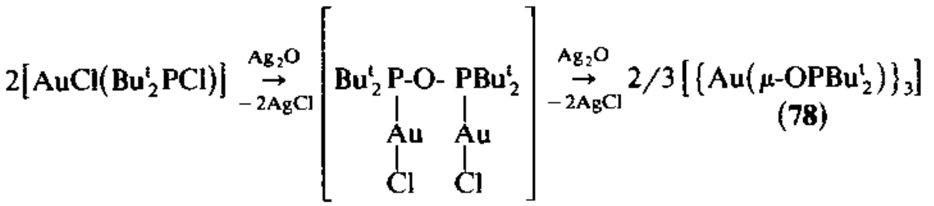


$$[Au(CO)Cl] \underset{-CO}{\overset{R_2PCl}{\rightarrow}} [AuCl(R_2PCl)] \overset{NEt_3,H_2O}{\rightarrow} \left[\begin{array}{l} ClAu-PR_2 \\ \qquad\;\; \| \\ \qquad\;\; O \cdots HNEt_3 \end{array}\right] \qquad (40)$$

(**77**)

77	**a**	**b**
R	Me	Ph

[AuCl(CO)] and Bu^t_2PCl likewise lead to $[AuCl(Bu^t_2PCl)]$ which, on treatment with Ag_2O, affords $[\{Au(\mu\text{-}OPBu^t_2)\}_3]$ **78** according to eqn. (41) [97]. The symmetric structure follows from six Bu^t groups, showing only one ^1H doublet signal at δ 0.6 ppm ($^3J(PH) = 15$ Hz).



$$2[\mathrm{AuCl(Bu^t_2PCl)}] \xrightarrow[-2\mathrm{AgCl}]{\mathrm{Ag_2O}} \left[\begin{array}{ccc}\mathrm{Bu^t_2P} & \text{-O-} & \mathrm{PBu^t_2}\\ | & & | \\ \mathrm{Au} & & \mathrm{Au}\\ | & & | \\ \mathrm{Cl} & & \mathrm{Cl}\end{array}\right] \xrightarrow[-2\mathrm{AgCl}]{\mathrm{Ag_2O}} \underset{\mathbf{(78)}}{2/3[\{\mathrm{Au}(\mu\text{-}\mathrm{OPBu^t_2})\}_3]} \qquad (41)$$

Monomeric $[\mathrm{Au(PBu^t_3)\{P(O)Bu^t_2\}}]$ **(79)** has been prepared by the following reaction (eqn. (42) and is found spectroscopically to contain a linear P–Au–P system [96]

$$[\mathrm{AuCl(PBu^t_3)}] \xrightarrow{\mathrm{LiMe}} [\mathrm{AuMe(PBu^t_3)}] \xrightarrow{\mathrm{Bu^t_2P(O)H}} \underset{\mathbf{(79)}}{[\mathrm{Au\{P(O)Bu^t_2\}(PBu^t_3)}]} \qquad (42)$$

D. CONCLUDING REMARKS

Although the chemistry of the complexes of secondary phoshine chalcogenides and their conjugate bases has grown rapidly over the last decade, the knowledge is still far from being comprehensive. Several well-established procedures exist for binding these ligands on the metal atom. The reaction of the secondary phosphine chalcogenide with an appropriate metal compound and the hydrolysis of a precoordinated R_2PX (X = any good leaving group) ligand has been most successfully employed. Other reactions, such as Arbusov-like ones, the oxidation of diorganophosphido complexes or metathetic reactions have also been used to prepare special complexes.

Most of the complexes so far described contain soft metals on the metal site and on that account prefer to coordinate either through the phosphorus atom only, or through both the phosphorus and the chalgogen atom. Complexes of the types (a) and (d), in which the ligands are attached to the metal only by the chalcogen atoms, are still small in number, and as shown in some cases, are thermodynamically unstable with respect to the P-linked isomers. It seems ingenious to extend the range of metals explored to the hard metal ions. New coordination modes may also be expected by using these ligands in metal cluster chemistry.

More systematic studies on the ligand site are necessary in order to compare the ligand properties of the secondary phosphine oxides, sulphides and selenides, as well as their corresponding anions. Differences between these ligands as a function of the chalcogen atom arise most obviously first, from the strong propensity of the neutral and anionic oxide ligands to form hydrogen bridges wherever the possibility exists, and secondly, from the lower thermal stability of the selenide ligands.

ACKNOWLEDGEMENT

The author is grateful to Professor Dr. D.M. Roundhill, Tulane University, New Orleans, U.S.A., for bringing several references to his attention.

Note added in proof

Duncan et al. [98] have continued their work on $[\mathrm{Ir(COD)(Cl)H\{(Ph_2PO)_2H\}}]$ including heterobi- and tri-metallic compounds. This group also reported the triply chloride-bridged anionic complex $\mathrm{M^+[Rh_2Cl_5\{(Ph_2PO)_2H\}_2]^-}$ [99]. Heterobimetallic complexes of the type $[\mathrm{M\{(OPPh_2)_2Pt(S_2CNR_2)\}_n}]$ ($n = 2$: M = VO(IV), Co(II), Cu(II), Ni(II); $n = 3$: M = Mn(III)) have been described [100]. Cotton et al. [101] have reported an X-ray analysis of $\mathrm{Et_4N[Mo(CO)_4\{(Ph_2PO)_2H\}]\cdot 0.37\ CH_2Cl_2}$ and $[\mathrm{Mo(CO)_4(Ph_2POH)(Ph_2POCH_2CH_2NMe_2)\cdot H_2O}$. Wong et al. [102] have reacted $\mathrm{Na[Mo(CO)_5(Ph_2PO)]}$ with $\mathrm{PCl_3}$. Addition and insertion reactions of oxygen and sulfur into the $\mathrm{Rh_2P_2}$ unit of $[\mathrm{Rh_2(C_5Me_5)_2(\mu\text{-}PMe_2)_2}]$ have been studied [103]. Lindner et al. [104] found a new tricyclic compound by treatment of $[\{\mathrm{Mn(CO)_4(\mu\text{-}SPR_2)_2}\}_2]$ with R′NCS. This group has also reported complexes of type $[\mathrm{CpFe(CO)_2\{P(S)R_2\}}]$ [105]. $[\mathrm{Mn(CO)_4\{(Ph_2PO)_2H\}}]$ was obtained by reacting $\mathrm{Na_2[(CO)_4Mn=\bar{P}R_2]}$ with $\mathrm{SO_2Cl_2}$ [106]. Kläui et al. [107] describe reactions of $\mathrm{MCp_2}$ (M = Co, Ni) with $\mathrm{R_2P(E)H}$ (E = O, S). First attempts at using complexes containing $\mathrm{R_2PO^-}$ ligands as hydroformylation catalysts have been reported ($\mathrm{Rh/R_2PO}$ [108], $\mathrm{Pt/Ph_2PO}$ [109]). Finally, the stabilization of the parent phosphinous acid, $\mathrm{H_2P{-}OH}$, was achieved by P-complexation with tungsten pentacarbonyl [110].

REFERENCES

1 L.A. Hamilton and P.S. Landis, in G.M. Kosolapoff and L. Maier (Eds.), Organic Phosphorus Compounds, Vol. 4, Wiley, New York, NY, 1972, pp. 463 ff.
2 R.H. Williams and L.A. Hamilton, J. Am. Chem. Soc., 74 (1952) 5418.
3 G. Peters, J. Am. Chem. Soc., 82 (1960) 4751.
4 L. Maier, Helv. Chim. Acta, 49 (1966) 1000.
5 M. Sander, Chem. Ber., 93 (1960) 1220.
6 W.J. Pietro and W.J. Hehre, J. Am. Chem. Soc., 104 (1982) 3594 and references therein.
7 J.E. Griffiths and A.B. Burg, J. Am. Chem. Soc., 82 (1960) 1507.
8 A.B. Burg and K. Gosling, J. Am. Chem. Soc., 87 (1965) 2113.
9 B.B. Hunt and B.C. Saunders, J. Chem. Soc., (1957) 2413.
10 R.E. Montgomery and L.D. Quin, J. Org. Chem., 30 (1965) 2393.
11 L.D. Quin and H.G. Anderson, J. Org. Chem., 31 (1966) 1206.
12 M. Grayson, C.E. Farley and C.A. Streuli, Tetrahedron, 23 (1967) 1065.
13 K. Issleib, B. Walther and E. Fluck, Z. Chem., 8 (1968) 67.
14 D.M. Roundhill, R.P. Sperline and W.B. Beaulieu, Coord. Chem. Rev., 26 (1978) 263.

15 E. Lindner and B. Schilling, Chem. Ber., 110 (1977) 3725.
16 E. Lindner and H. Dreher, J. Organomet. Chem., 104 (1976) 331.
17 E. Lindner and W.P. Meier, J. Organomet. Chem., 114 (1976) 67.
18 E. Lindner and B. Shilling, Chem. Ber., 110 (1977) 3266.
19 G. Mundig, B. Schilling, M. Weishaupt, E. Lindner and J. Strähle, Z. Anorg. Allg. Chem., 437 (1977) 169.
20 S. Hoehne, E. Lindner and B. Schilling, J. Organomet. Chem., 139 (1977) 315.
21 E. Lindner, F. Bouachir and W. Hiller, J. Organomet. Chem., 210 (1981) C37.
22 E. Lindner, C.-P. Krieg, S. Hoehne and A. Rau, Z. Naturforsch, Teil B, 36 (1981) 1487.
23 D.M. Anderson, E.A.V. Ebsworth, T.A. Stephenson and M.D. Walkinshaw, J. Chem. Soc. Dalton Trans., (1982) 2343.
24 A.F.M. Magsudar Rahman, C.Ceccarelli, J.P. Oliver, B. Messbauer, H. Meyer and B. Walther, Inorg. Chem., (1984) submitted.
25 K.P. Wagner, R.W. Hess, P.M. Treichel and J.C. Calabrese, Inorg. Chem., 14 (1975) 1121.
26 B. Walther, B. Messbauer and H. Meyer, Inorg. Chim. Acta, 37 (1979) L525.
27 E. Lindner, A. Rau and S. Hoehne, Angew. Chem. Int. Ed. Engl. 20 (1981) 787.
28 E. Lindner, A. Rau and S. Hoehne, Chem. Ber., 144 (1981) 3281.
29 E. Lindner, A. Rau and S. Hoehne, J. Organomet. Chem., 218 (1981) 41.
30 E. Lindner, B. Bouachir and S. Hoehne, Chem. Ber., 116 (1983) 46.
31 H.P.M.M. Ambrosius, J.H. Noordik and G.J.A. Ariaans, J. Chem. Soc. Chem. Commun., (1980) 832.
32 G.M. Gray and C.S. Kraihanzel, J. Organomet. Chem., 238 (1982) 209.
33 D.M. Anderson, E.A.V. Ebsworth, T.A. Stephenson and M.D. Walkinshaw, Angew. Chem. Int. Ed. Engl., 20 (1982) 290.
34 D.V. Naik, G.J. Palenik S. Jacobson and A.J. Carty, J. Am. Chem. Soc., 96 (1974) 2286.
35 A.J. Carty, S.E. Jacobson, R.T. Simpson and N.J. Taylor, J. Am. Chem. Soc., 97 (1975) 7254.
36 M.C. Cornock, R.O. Gould, C.L. Jones and T.A. Stephenson, J. Chem. Soc. Dalton Trans., (1977) 1307.
37 W.C. Hamilton and J.A. Ibers, Hydrogen Bonding in Solids, W.A. Benjamin, New York, NY, 1968.
38 K.R. Dixon and A.D. Rattray, Inorg. Chem., 16 (1977) 209.
39 E.H. Wong and F.C. Bradley, Inorg. Chem., 20 (1981) 2333.
40 R.P. Sperline and D.M. Roundhill, Inorg. Chem., 16 (1977) 2612.
41 K.R. Dixon and A.D. Rattray, Can. J. Chem., 49 (1971) 3997.
42 Pi-Chang Kong and D.M. Roundhill, Inorg. Chem., 11 (1972) 749.
43 Pi-Chang Kong and D.M. Roundhill, J. Chem. Soc. Dalton Trans., (1974) 187.
44 W.B. Beaulieu, T.B. Rauchfuss and D.M. Roundhill, Inorg. Chem., 14 (1975) 1732.
45 R.O. Gould, C.L. Jones, W.J. Sime and T.A. Stephenson, J. Chem. Soc. Dalton Trans., (1977) 669.
46 I.W. Robertson and T.A. Stephenson, Inorg. Chim. Acta, 45 (1980) L215.
47 P.M. Treichel and L.D. Rosenhein, Inorg. Chem., 20 (1981) 1539.
48 W.P. Meier, J. Strähle and E. Lindner, Z. Anorg. Allg. Chem., 424 (1976) 154.
49 E. Lindner and W.P. Meier, Chem. Ber., 109 (1976) 3323.
50 C.S. Kraihanzel and C.M. Bartish, J. Am. Chem. Soc., 94 (1972) 3572.
51 C.S. Kraihanzel and C.M. Bartish, J. Organomet. Chem., 43 (1972) 343.
52 H. Vahrenkamp, Chem. Ber., 105 (1972) 3574.
53 E.H. Wong, L. Prasad, E.J. Gabe and F.C. Bradley, J. Organomet. Chem., 236 (1982) 321.

54 E.H. Wong, F.C. Bradley and E.J. Gabe, J. Organomet. Chem., 244 (1983) 235.

55 G.M. Gray and C.S. Kraihanzel, J. Organomet. Chem., 187 (1980) 51.

56 S.Al-Jibori, M. Hall, A.T. Hutton and B.L. Show, J. Chem. Soc. Chem. Commun., (1982) 1069.

57 R.J. Haines, A.L. Du Preez and I.L. Marais, J. Organomet. Chem., 28 (1971) 97.

58 W. Malisch, R. Maisch, I.J. Colquhoun and W. McFarlane, J. Organomet. Chem., 220 (1981) C1.

59 G.M. Gray and C.S. Kraihanzel, J. Organomet. Chem., 146 (1978) 23.

60 D.J. Darensbourg, Inorg. Chem., 18 (1979) 14.

61 E. Lindner, K.-W. Rodatz and J.-P. Gumz, Chem. Ber., 111 (1978) 125.

62 E. Lindner and H. Dreher, J. Organomet. Chem., 55 (1973) 347.

63 E. Lindner and K.-W. Rodatz, Z. Anorg. Allg. Chem., 437 (1977) 162.

64 S. Hoehne, E. Lindner and J.-P. Gumz, Chem. Ber., 111 (1978) 3818.

65 E. Lindner, G.v. Au and H.-J. Eberle, Z. Naturforsch., Teil B, 33 (1978) 1296.

66 E. Lindner, G.v. Au and H.-J. Eberle, J. Organomet. Chem., 204 (1981) 93.

67 E. Lindner and H.-J. Eberle, Angew. Chem. Int. Ed. Engl., 19 (1980) 73.

68 E. Lindner and H.J. Eberle, J. Organomet. Chem., 191 (1980) 143.

69 E. Lindner and G.v. Au, Z. Naturforsch., Teil B, 35 (1980) 1104.

70 E. Lindner and G.v. Au, J. Organometal. Chem., 202 (1980) 163.

71 E. Lindner, K.A. Starz, N. Pauls and W. Winter, Chem. Ber., 116 (1983) 1070.

72 E. Lindner, F. Bouachir, M. Weishaupt, S. Hoehne and B. Schilling, Z. Anorg. Allg. Chem., 456 (1979) 163.

73 E. Lindner and B. Schilling, Chem. Ber., 110 (1977) 3889.

74 V. Küllmer and H. Vahrenkamp, Chem. Ber., 110 (1977) 237.

75 R.C. Dobbie and P.R. Mason, J. Chem. Soc. Dalton Trans., (1973) 1124.

76 R.C. Dobbie and M.J. Hopkinson, J. Chem. Soc. Dalton Trans., (1974) 1290.

77 P. Piraino, F. Faraone and M.C. Aversa, J. Chem. Soc. Dalton Trans., (1976) 610.

78 R.J. Haines, A.L. Du Preez and I.L. Marais, J. Organomet. Chem., 28 (1971) 405.

79 M.J. Barrow and G.A. Sim, J. Chem. Soc. Dalton Trans., (1975) 291.

80 M.J. Barrow, G.A. Sim, R.C. Dobbie and P.R. Mason, J. Organomet. Chem., 69 (1974) C4.

81 W. Ebersbach, N. El-Murr and W. Kläui, Angew. Chem. Int. Ed. Engl., 21 (1982) 915.

82 V. Marsala, F. Faraone and P. Piraino, J. Organomet. Chem., 133 (1977) 301.

83 D.H.M.W. Thewissen, J. Organomet. Chem., 192 (1980) 115.

84 J.A.S. Duncan, D. Hedden, D.M. Roundhill, T.A. Stephenson and M.D. Walkinshaw, Angew. Chem. Int. Ed. Engl., 21 (1982) 452.

85 J. Chatt and B.T. Heaton, J. Chem. Soc. A, (1968) 2745.

86 W. Beck, M. Keubler, E. Leidl, U. Nagel, M. Schaal, S. Cenini, P. Del Buttero, E. Licandro and S. Maiorana, J. Chem. Soc. Chem. Commun., (1981) 445.

87 B. Messbauer, H. Meyer, B. Walther, M.J. Heeg, A.F.M. Maqsudar Rahman and J.P. Oliver, Inorg. Chem., 22 (1983) 272.

87 N.M. Boag, J. Browning, C. Crocker, P.L. Goggin, R.J. Goodfellow, M. Murray and J.L. Spencer, J. Chem. Res., S, (1978) 228; M (1978) 2962.

89 V.I. Nefedov, Ya.V. Salyn, B. Walther, B. Messbauer and R. Schöps, Inorg. Chim. Acta, 45 (1980) L103.

90 A. Zschunke, H. Meyer, I. Heidlas, B. Messbauer, B. Walther and H.D. Schädler, Z. Anorg. Allg. Chem., 504 (1983) 117.

91 T.E. Austin, Ph.D. Thesis, The University of North Carolina, Chapel Hill, NC, 1966, and ref. 1, p. 485.

92 D.M. Appel, A.S.F. Boyd, I.W. Robertson, D.M. Roundhill and T.A. Stephenson, Inorg. Chem., 21 (1982) 449.

93 R.P. Sperline, M.K. Dickson and D.M. Roundhill, J. Chem. Soc., Chem. Commun., (1977) 62.

94 R.P. Sperline, W.B. Beaulieu and D.M. Roundhill, Inorg. Chem., 17 (1978) 2032.

95 L.D. Quin and R.E. Montgomery, J. Inorg. Nucl. Chem., 28 (1966) 1750.

96 H. Schmidbaur and A.A.M. Aly, Angew. Chem. Int. Ed. Engl., 19 (1980) 71.

97 H. Schmidbaur, A.A.M. Aly and U. Schubert, Angew. Chem. Int. Ed. Engl., 17 (1978) 846.

98 J.A.S. Duncan, T.A. Stephenson, W.B. Beaulieu and D.M. Roundhill, J. Chem. Soc. Dalton Trans., (1983) 1755.

99 J.A.S. Duncan, T.A. Stephenson, D.M. Walkinshaw, D. Hedden and D.M. Roundhill, J. Chem. Soc. Dalton Trans., (1984) 801.

100 J.R. Allan, G.H.W. Milburn, T.A. Stephenson and P.M. Veitch, J. Chem. Res. S, (1983) 215; M, (1983) 2009.

101 F.A. Cotton, L.R. Falvello, M. Tomas, G.M. Gray and C.S. Kraihanzel, Inorg. Chim. Acta, 82 (1984) 129.

102 E.H. Wong, F.C. Bradley, L. Prasad and E.J. Gabe, J. Organomet. Chem., 263 (1984) 167.

103 B. Klingert and H. Werner, J. Organomet. Chem., 252 (1983) C47.

104 E. Lindner, C.-P. Krieg, W. Hiller and D. Hübner, Chem. Ber., 117 (1984) 489.

105 E. Lindner and C.-P. Krieg, J. Organomet. Chem., 269 (1984) 65.

106 R. Fawzi, W. Hiller, J.-P. Lorenz, J. Mohyla and C. Zeiher, J. Organomet. Chem., 262 (1984) C43.

107 W. Kläui, W. Ebersbach and W. Schwarz, J. Organomet. Chem., 252 (1983) 347.

108 M. Matsumoto and M. Tamura, J. Mol. Cat., 19 (1983) 365.

109 Eur. Pat. Appl. EP 82,576 to P.W.N.M. Leeuwen and C.F. Roobeck, Chem. Abstr., 99 (1983) 121813.

110 F. Mercier and F. Mathey, J. Chem. Soc., Chem. Commun., (1984) 782.