ELSEVIER

Coordination Chemistry Reviews
145 (1995) 27–54

COORDINATION CHEMISTRY REVIEWS

Phosphine complexes of the heavier p-block elements: aspects of structure and bonding

Nicholas C. Norman *, Nigel L. Pickett

Department of Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

Received 11 October 1994; accepted 17 October 1994

Contents

Abstract

This review deals with structural aspects of phosphine complexes of the heavier p-block elements, specifically aluminium, gallium, indium, germanium, tin, arsenic, antimony, bismuth, tellurium, bromine and iodine. In addition to a description of the structures themselves,

---

* Corresponding author.

SSDI 0010-8545(95)09104-1

consideration is also given to the bonding of the p-block element to phosphine and some general points are made concerning the observed stereochemistries ot some of the complexes.

Keywords: Phosphine complexes; p-Block elements; Structure

---

1. Introduction

Complexes containing phosphines as ligands are extremely numerous in d-block chemistry [1] but feature much less prominently in the chemistry of the s-, f- and p-block elements. Some insight into the reasons for this observation comes from the fact that, in general, phosphines are considered to be soft bases, so it is not surprising that they are generally found in association with soft acid centres such as those of low oxidation state d-block metals. Thus, the harder acid nature of s-block and lanthanide cations is a likely reason for the small number of phosphine coordination compounds encountered for these groups. The softer character of the heavier p-block and some actinide elements (particularly for lower oxidation states of the actinide elements), however, affords the opportunity of a reasonably extensive complex chemistry associated with this part of the periodic table. Despite these expectations, the coordination chemistry of the heavier p-block and actinide elements remains fairly undeveloped.

In this review, we will not consider the actinide elements but will concentrate on the heavier p-block elements. A comprehensive reivew of p-block phosphine complexes was published in 1976 by Levason and McAuliffe [2] and we will only cover the literature since that time. Moreover, it is evident from Ref. [2] that, while a considerable amount of spectroscopic work has been carried out on phosphine complexes of aluminium(III), gallium(III), indium(III) and tin(IV) halides, very few X-ray structural data are available. Quite a number of crystal structures have been determined and published since that time and this review will concentrate largely on aspects of structure and bonding.

2. Group 13

2.1. Hydrides

The hydrides of the heavier group 13 elements is currently an area of renewed interest [3,4] and some examples of phosphine complexes of AlH_3 and GaH_3 have recently been reported. The reaction between either $[GaH_3(NMe_3)]$ or $Li[GaH_4]$ and PCy_3 (Cy, cyclohexyl) affords the complex $[GaH_3(PCy_3)]$ (**1**) [5], which has been characterized by X-ray crystallography and shown to be monomeric, as illustrated in Fig. 1. The coordination geometry around the gallium atom is tetrahedral with a Ga—P bond length of 2.460(2) Å (see Table 1 for a listing of E—P bond lengths; E = Al, Ga, In). A similar reaction but using [1,2-bis(dimethylphos-

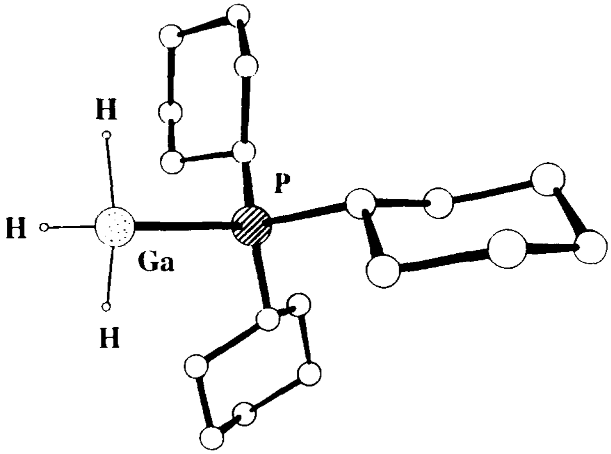


Fig. 1. Molecular structure of [$GaH_3(PCy_3)$] (**1**).

phino)ethane] (DMPE) resulted in the complex [$GaH_3\{P(Me)_2CH_2CH_2(Me)_2P\}$-$GaH_3$] (**2**), in which each phosphorus atom is bonded to a GaH_3 unit in the same manner as in **1** [5,6].

The aluminium analogue of **1**, i.e. [$AlH_3(PCy_3)$] (**3**), was prepared similarly using Li[AlH_4] and PCy_3, although this time in the presence of HCl [7], and an aluminium complex analogous to **2** but employing the diphosphine $(Cy)_2PCH_2CH_2P(Cy)_2$, i.e. [$AlH_3\{P(Cy)_2CH_2CH_2(Cy)_2P\}AlH_3$] (**4**), has also been prepared by this method [7]; in both cases, a single phosphorus atom is bonded to the aluminium centre. If the reaction is carried out with the diphosphine $(Pr^i)_2PCH_2CH_2P(Pr^i)_2$, however, a polymeric compound [$(AlH_3\{P(Pr^i)_2CH_2CH_2(Pr^i)_2P\})_x$] (**5**) is formed in which the aluminium atoms are five coordinate with a trigonal bipyramidal geometry, and with the two phosphorus atoms in the axial sites, as shown in Form 1.

The coordination geometries of **1**–**4** are unexceptional and, in **5**, the axial positions of the dative P → Al bonds are those expected for an [$EX_3(L)_2$] complex, where X is a formally uninegative group and L is a neutral two-electron donor [8]. It is interesting to note, however, that the Ga—P bond lengths are shorter than the Al—P bond lengths in related compounds and, in view of the fact that the covalent radii of aluminium(III) and gallium(III) are the same (or at least very similar), this implies that phosphine ligands tend to be more strongly bound to gallium than to aluminium. This probably reflects the fact that aluminium(III) is a slightly harder acid centre than gallium(III), as a result of the greater electronegativity of the gallium(III).

2.2. Alkyls and aryls

One of the first mononuclear compounds to have been structurally characterized was [$GaMe_3(PMe_3)$] (**6**), the structure of which was determined by gas-phase electron diffraction [9]. The structure is tetrahedral, as expected for a compound of

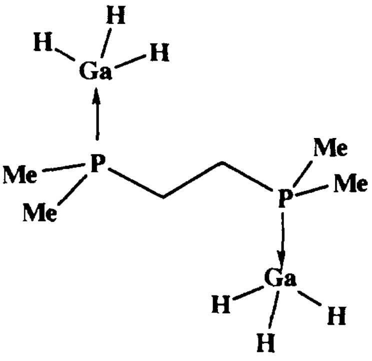
Table 1
E−P bond lengths and X−E−X and X−E−P bond angles (angles only for four-coordinate compounds), where E = Al, Ga, In and X = H, C, halide

Compound	Bond length (Å)	Average X−E−X, X−E−P and (X−E−X)-(X−E−P) diff. (Δ) (deg)	Ref.
1	Ga−P 2.460(2)		[5]
2	Ga−P 2.399(4)		[5]
2	Ga−P 2.403(1)		[6]
3	Al−P 2.467(1)	115, 103.2, $\Delta = 11.8$	[7]
4	Al−P 2.460(2)	115.7, 102.0, $\Delta = 13.7$	[7]
5	Al−P 2.755(3), 2.708(3)		[7]
6	Ga−P 2.52(2)^{a}	117.9, 101.1, $\Delta = 16.8$	[9]
7	Al−P 2.53(4)^{a}	115.0, 100.0, $\Delta = 15.0$	[10]
8	Al−P 2.535(1)	116.6, 100.6, $\Delta = 16.0$	[11]
9	Al−P 2.584(2)	113.9, 104.5, $\Delta = 9.4$	[11]
10	Ga−P 2.683(5)	118.0, 98.1, $\Delta = 19.9$	[12]
11	Ga−P 2.459(2)		[13]
12	Ga−P 2.539(6), 2.541(6)^{b}	113.5, 113.3, 105.0, 105.3, $\Delta = 8.5$, 8.0	[13]
13	Al−P 2.544(4)	115.8, 102.0, $\Delta = 13.8$	[14]
14	Ga−P 2.546(4)	116.1, 101.5, $\Delta = 14.6$	[14]
14	Ga−P 2.563(3)	116.3, 101.3, $\Delta = 15.0$	[15]
15	In−P 2.755(4)	117.3, 99.5, $\Delta = 17.8$	[14]
16	Ga−P 2.535(2)		[16]
17	Al−P 2.535(7), 2.504(6), 2.531(7)		[14]
18	Ga−P 2.353(2), 2.347(5)^{c}	109.3, 109.7	[17]
19	In−P 2.605(9), 2.592(9)^{b}	113.9, 110.1, 104.6, 104.9^{b}	[18]
20	In−P 2.586(6)	107.5, 111.4	[18]
23	In−P 2.701, 2.723		[20]
24	In−P 2.575(3), 2.576(3)		[21]
25	In−P 2.614(3), 2.622(3)		[22]
26	In−P 2.712(3), 2.719(3)		[22]
27	In−P 2.798(3), 2.819(2)		[21]
28	Al−P 2.499(3)		[23]
29	In−P 2.647(8), 2.650(8)		[24]
30	Al−P 2.554(2), 2.567(2)		[25]
31	In−P 2.607(5), 2.611(5)^{b}		[26]
32	In−P 2.739(2)		[27]

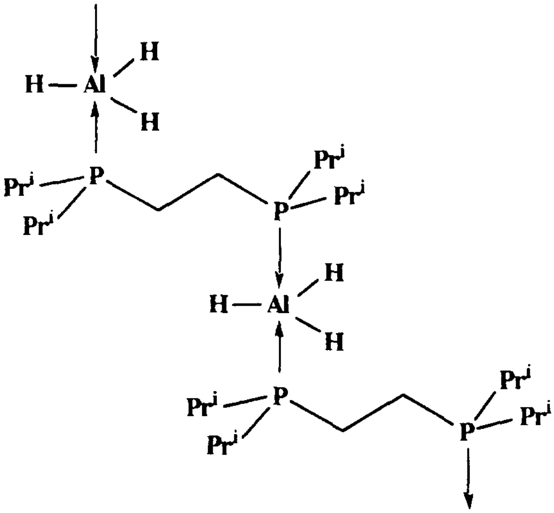
[a] Determined by gas-phase electron diffraction.
[b] Two independent molecules in the crystallographic asymmetric unit.
[c] The two different bond lengths are for data sets collected at 223 and 297 K.

this formula, but the bond angles deviate somewhat from idealized tetrahedral values, such that the C−Ga−C angles are larger (117.9°) and the P−Ga−C angles are smaller (101.1°). A similar study was carried out on the aluminium derivative [AlMe$_3$(PMe$_3$)] (**7**) [10], which revealed bond angles with very similar values; in this case, the Al−P and Ga−P bond lengths are the same, within experimental error.

Crystal structures have also been reported for the triaryl phosphine complexes [AlMe$_3$(PPh$_3$)] (**8**) and [AlMe$_3${P(*o*-tolyl)$_3$}] (**9**) [11], which also show significantly



2

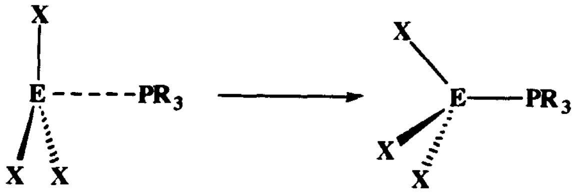


5

larger C—Al—C and smaller P—Al—C bond angles (116.6(1)° and 100.6(1)° for **8** and 113.9(1)° and 104.5(1)° for **9**) compared with those of a regular tetrahedron. These variations in bond angle are associated with a T_d to C_{3v} type of distortion — specifically, a trigonal pyramidal flattening of the tetrahedron — and would appear to be quite general for these types of complex, although for reasons which are well understood and have been discussed in Ref. [8]. Briefly, and in line with simple valence shell electron pair repulsion (VSEPR) considerations, donor or dative bonds ($D \rightarrow E$) occupy less space around the central element centre with respect to normal two-centre, two-electron bonds (E—X), which allows for an expansion of the X—E—X angles at the expense of the X—E—D angles.

Another example of a trialkyl gallium compound is $[Ga(CH_2Bu^t)_3(PHPh_2)]$ (**10**) [12], which shows a very marked pyramidal flattening, with C—Ga—C angles averaging 118.0° and C—Ga—P angles averaging 98.1°; in this case, the $Ga(CH_2Bu^t)_3$ unit is only slightly distorted from that expected for the uncomplexed molecule and the overall structure of **10** is perhaps best described as a trigonal-based pyramid. This geometry is also associated with a long Ga—P bond (Table 1) and there is a clear trend in many of the structures towards more tetrahedral geometries as the E—P bond length decreases. This geometric change, shown in Scheme 1, is associated with the formation of the E—P bond and consequent structural change or rehybridization at the E centre. For structures such as **10**, we may assume that the E centre is sp^2 hybridized, forming three E—X bonds, with the phosphine ligand interacting weakly with the vacant unhybridised p orbital.

Examples of aryl gallium compounds are $[GaClPh_2\{P(SiMe_3)_3\}]$ (**11**) and $[GaPh_3\{P(SiMe_3)_3\}]$ (**12**) [13], with the structure of **12** being shown in Fig. 2. Some examples of EMe_3 (E = Al, Ga, In) in coordinated to diphosphines are also known and these generally have structures analogous to those of **2** and **4**. Structurally



Scheme 1.

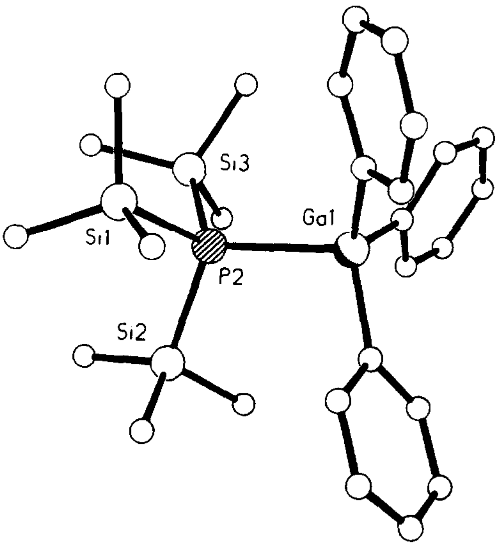


Fig. 2. Molecular structure of $[GaPh_3\{P(SiMe_3)_3\}]$ (**12**).

characterized compounds are $[EMe_3\{P(Ph)_2CH_2CH_2(Ph)_2P\}EMe_3]$ (**13**, E = Al; **14**, E = Ga; **15**, E = In) [14,15]; a view of **14** is shown in Fig. 3. Structures of $[GaClMe_2\{P(Ph)_2CH_2(Ph)_2P\}]$ (**16**) [16] and of $[(AlMe_3)_3\{(Ph_2PCH_2CH_2)_2PPh\}$ (**17**) [14], which contain the triphos ligand in which each phosphorus atom is bonded to a $AlMe_3$ group, have also been determined.

2.3. Halides

A large number of phosphine complexes of group 13 trihalides have been described [2] but those which have been structurally characterized fall into two types, i.e. monophosphine and bisphosphine complexes. Examples of monophosphine derivatives analogous to the alkyl and aryl complexes described in Section 2.2 are $[GaCl_3(PMe_3)]$ (**18**) [17], $[InI_3(PHPh_2)]$ (**19**) [18] and $[InI_3(PHBu^t_2)]$ (**20**) [18], while examples of bisphosphine complexes are $[AlCl_3(PMe_3)_2]$ (**21**) [19], $[InCl_3(PMe_3)_2]$ (**22**) [19], $[InCl_3(PPh_3)_2]$ (**23**) [20], $[InCl_3(PMe_3)_2]$ (**24**) [21], $[InBr_3(PMe_2Ph)_2]$ (**25**) [22] and $[InI_3(PMePh_2)_2]$ (**26**) [22]. In all the bisphos-

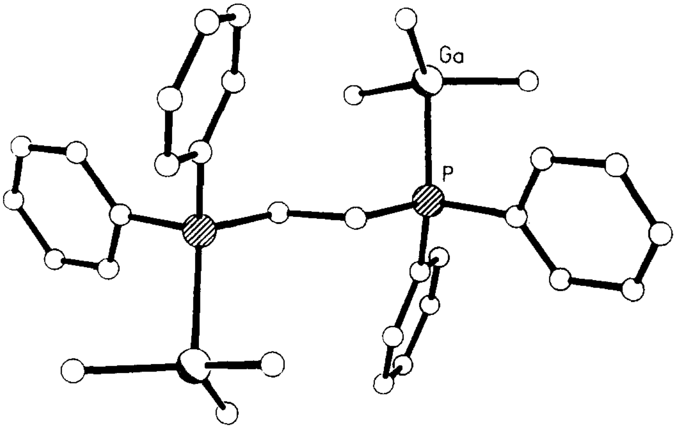
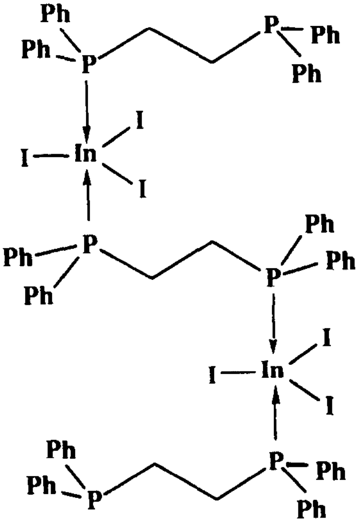


Fig. 3. Molecular structure of [$GaMe_3(PPh_2CH_2CH_2Ph_2P)GaMe_3$] (**14**).

phine complexes, the geometry around the group 13 element centre is trigonal bipyramidal, with the phosphine ligands in axial sites (for **21** and **22**, this is based on the fact that the X-ray powder patterns show that these compounds are isomorphous with the known structure of [$CrCl_3(NMe_3)_2$]). One final compound is [$(InI_3)_2\{P(Ph)_2CH_2CH_2(Ph)_2P\}_3$] (**27**) [21], the structure of which is shown in



27

Form 2, and which incorporates both monodentate and bridging bidentate $Ph_2PCH_2CH_2PPh_2$ ligands; a view of **25** is shown in Fig. 4.

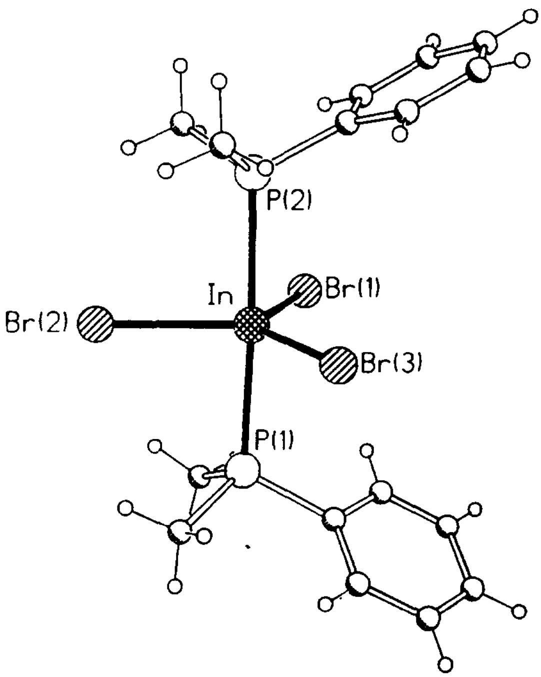


Fig. 4. Molecular structure of [$InBr_3(PMe_2Ph)_2$] (**25**).

2.4. *Miscellaneous*

Miscellaneous compounds for which structural data are available include the four-coordinate aluminium phenoxide complex [$AlMe_2(O$-2,6-Bu^t_2-4-$MeC_6H_2)(PMe_3)$] (**28**) [23], the six-coordinate triazene compound [$InCl_2(DPT)(PEt_3)_2$] (DPT, 1,3-diphenyltriazene) (**29**) [24], the carboranyl derivative [endo-10-{$AlEt(PEt_3)_2$}-7,8-$C_2B_9H_{11}$] (**30**) [25] and the four-coordinate organo-transition metal species [$InCl_2\{Co(CO)_4\}(PPh_3)$] (**31**) [26] and [$InI\{Fe(CO)_2(\eta$-$C_5H_5)\}_2(PMe_2Ph)$] [**32**) [27].

3. Group 14

3.1. *Halides*

In contrast to the structural data for phosphine adducts of group 13 element compounds described in Section 2, much less information is available for the group 14 elements, despite the fact that a considerable amount of spectroscopic data have been reported for phosphine complexes of tin(IV) halides [1]. Indeed, the only phosphine complexes of group 14 element halides to have been structurally characterized are the germanium(II) complexes [$GeI_2(PPh_3)$] (**33**) [28] and

$[GeCl_2(PPh_3)]$ (**34**) [29], and the tin(IV) complexes $[SnCl_4(PEt_3)_2]$ (**35**) [30] and $[SnCl_3Bu^n(PPh_3)]$ (**36**) [31]. Complexes **33** and **34** are monomeric with a trigonal pyramidal germanium centre, and Ge—P bond lengths of 2.503(4) and 2.510(5) Å for **33** (for two crystallographically independent molecules) and 2.511 Å for **34**. An examination of the bond angles is also interesting, in that, for **33**, the average I—Ge—I angle is 99.0°, whereas the P—Ge—I angles average 92.9°, i.e. some 6° smaller. For **34**, the corresponding average angles are 97.7° and 91.9°. This is contrary to what might be expected on steric grounds, as a result of the size of the PPh_3 ligands, and suggests a possible electronic explanation in which the PPh_3 ligand is essentially bonded to the GeX_2 unit through the formally vacant p-orbital (orthogonal to the GeX_2 plane) associated with the germanium(II) centre. Similar arguments were advanced for the trigonal-based pyramidal nature of many $[EX_3(L)]$ complexes, where E is a group 13 element. A view of **33** is shown in Fig. 5.

The structure of the tin(IV) complex **35** is octahedral about the tin(IV) centre, with the two phosphine ligands mutually *trans*. None of the interbond angles deviates significantly from idealized values and the Sn—P bond lengths are both 2.615(5) Å. Compound **36** contains only one phosphine ligand and the geometry around the tin centre is trigonal bipyramidal, with the phosphine ligand and one chlorine in the axial sites; the Sn—P bond length is 2.862 Å. The fact that **36** contains only one phosphine rather than the two found in **35** is probably the result of PPh_3 being significantly larger than PEt_3; this is also reflected in the much longer Sn—P bond length in **36**.

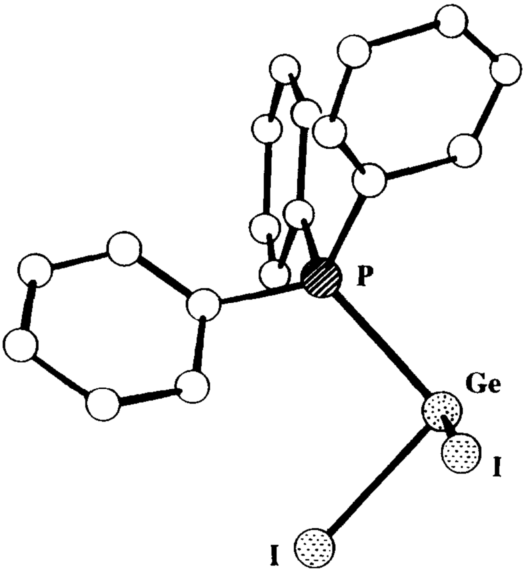
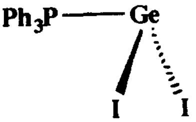


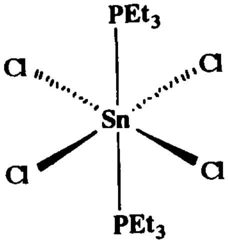
Fig. 5. Molecular structure of $[GeI_2(PPh_3)]$ (**33**).

3.2. Miscellaneous

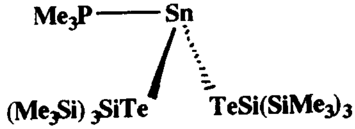
One structure is known which falls under this heading, i.e. that of a PMe_3 adduct of a tin(II) tellurolate complex — $[Sn\{TeSi(SiMe_3)_3\}_2(PMe_3)]$ (**37**) [32]. The structure is similar to that of the Ge(II) complexes **33** and **34**, in being monomeric



33



35



37

and having a trigonal pyramidal element(II) centre (see Form 3). The Sn—P bond length of 2.663(2) Å is significantly longer than the Sn—P bonds in **35**, which is at first surprising, in view of the lower coordination number of **37** (three) vs. **35** (six) and the fact that PMe_3 and PEt_3 are of similar size; however, since the ionic radius of tin(II) is considerably larger than that of tin(IV), the observation is less unexpected. The variations in bond angle seen in **33** and **34** are also present in **37**; thus, the Te—Sn—Te angle is 98.86(2)°, whereas the two Te—Sn—P angles are several degrees smaller (90.24(4)° and 84.83(4)°).

4. Group 15

4.1. Halides

Phosphine complexes of antimony and bismuth halides have only recently been structurally characterized and there are now several examples comprising various structural types. For neutral compounds with the empirical formula $[EX_3(PR_3)]$ ($E = Sb, Bi$), two forms have been characterized. The complex $[Bi_4Br_{12}(PEt_3)_4]$ (**38**) [33] is a tetramer, as shown in Fig. 6, in which each bismuth centre is octahedrally coordinated, being bonded to one PEt_3 ligand and five bromines; none of the bond

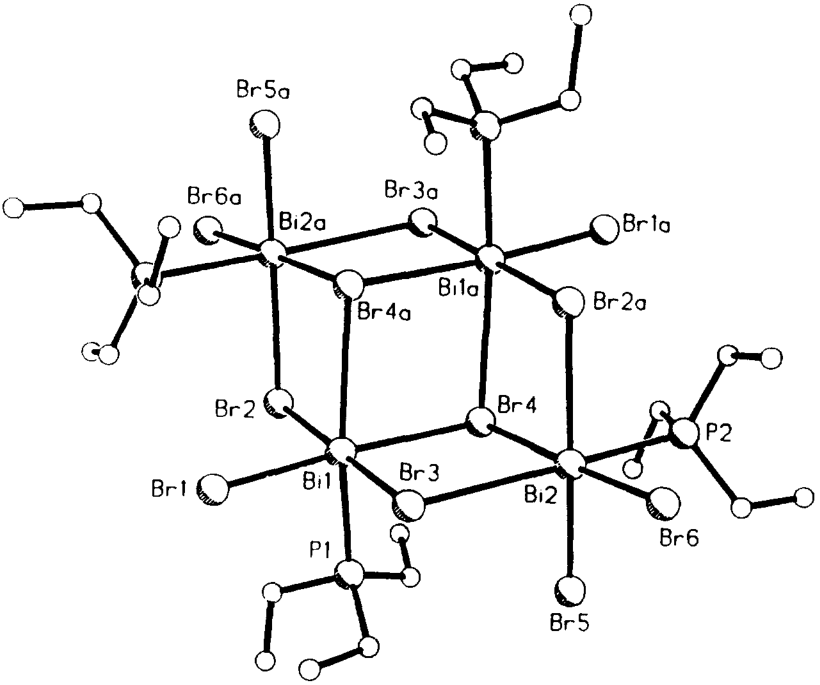


Fig. 6. Molecular structure of $[Bi_4Br_{12}(PEt_3)_4]$ (**38**).

angles deviates significantly from idealized octahedral values, and the Bi—P bond lengths are 2.733(6) and 2.747(7) Å (Table 2). A particular point of interest is that the Bi—Br bonds *trans* to the phosphine ligands are significantly longer than similar bonds where a *trans* phosphine is absent. Thus, referring to the numbering scheme

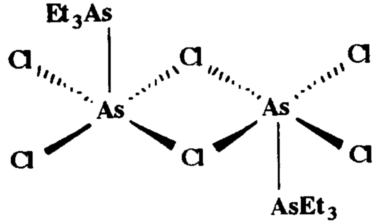
Table 2
Sb—P and Bi—P bond lengths

Compound	Bond length (Å)	Ref.
38	2.733(6), 2.747(7)	[33]
39	2.627(5), 2.633(6)	[33]
41	2.716(3), 2.865(3)	[33]
42	2.725(2)	[35]
43	2.678(8), 2.791(7)	[33]
44	2.575(2), 2.659(3)	[33]
45	2.584(3), 2.662(3), 2.498(6), 2.656(4)	[33]
46	2.762(3)	[36]
47	2.637(5), 2.637(5)	[37]
48	2.666(2), 2.644(2)	[38]
49	2.981(2), 3.005(2)	[37]
50	2.596(4)	[39]
51	2.594(6)	[40]

in Fig. 6, the Bi(1)—Br(4a) and Bi(2)—Br(3) bonds *trans* to P(1) and P(2), respectively, are about 0.2 Å longer than the other Bi to bridging bromine bonds. This observation implies a large phosphine *trans* influence — a feature which is also present in many of the examples described below.

An alternative structural form to **38** is encountered in the antimony complex $[Sb_2I_6(PMe_3)_2]\cdot THF$ (**39**) [33] (THF, tetrahydrofuran), which is polymeric, as shown in Fig. 7. What is notable about this structure is that the two crystallographically independent pairs of $Sb_2(\mu\text{-}I)_2$ units have markedly different μ-I bridge asymmetries — the longer bonds in the most asymmetric units are *trans* to the PMe_3 ligands, again revealing the presence of a large phosphine *trans* influence. Indeed, the long Sb(2)—I(4a) and Sb(1)—I(6a) bonds (3.547(2) and 3.698(2) Å respectively) are 0.5–0.6 Å longer than the Sb(1)—I(4) and Sb(2)—I(6) bonds (2.970(2) and 2.894(2) Å), which is consistent with a description of the overall solid-state structure as a loosely bound polymer of strongly bound dimers.

An interesting structure for comparison with **39** is the arsenic species $[As_2Cl_6(AsEt_3)_2]$ (**40**) [34], which is essentially a triethylarsine complex of arsenic trichloride (see Form 4). The structure of **40** resembles that of the strongly bound dimeric unit in **39**, but there are no longer As ··· Cl interactions to complete an octahedral coordination around the central arsenic atoms; therefore, there is no



40

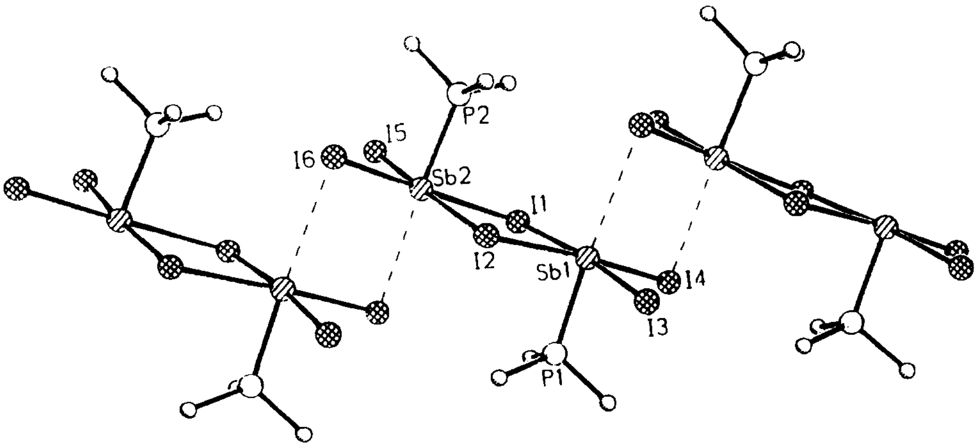
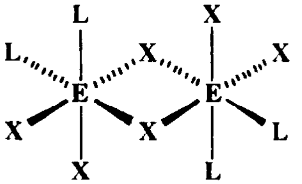


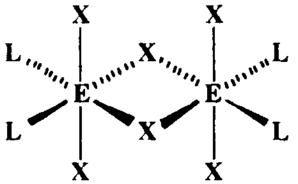
Fig. 7. Part of the solid state structure of $[Sb_2I_6(PMe_3)_2]\cdot THF$ (**39**).

polymeric structure, presumably as a result of the slightly lower Lewis acidity of the arsenic chloride centres.

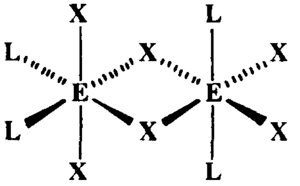
Examples of compounds of the general formula $[EX_3(PR_3)_2]$, in which two phosphine ligands are present for each antimony or bismuth centre, are $[Bi_2Br_6(PMe_3)_4]$ (**41**) [33,35], $[Bi_2Br_6(PMe_2Ph)_2(OPMe_2Ph)_2]$ (**42**) [35], $[Bi_2Br_6(DMPE)_2]$ (**43**) [33] and $[Sb_2Br_6(DMPE)_2]$ (**44**) [33], all of which adopt an edge-shared, bioctahedral structure with the particular isomeric form shown in A



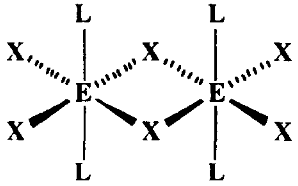
A



B



C



D

in Form 5 and in Fig. 8 for **41** (for **42**, L = PMe_2Ph, $OPMe_2Ph$, with the PMe_2Ph lying in the plane of the $Bi_2(\mu\text{-}Br)_2$ unit). The *trans* influence of the phosphine ligands is again evident in all these structures, particularly in the lengthening of the μ-Br bonds *trans* to phosphorus (Fig. 8).

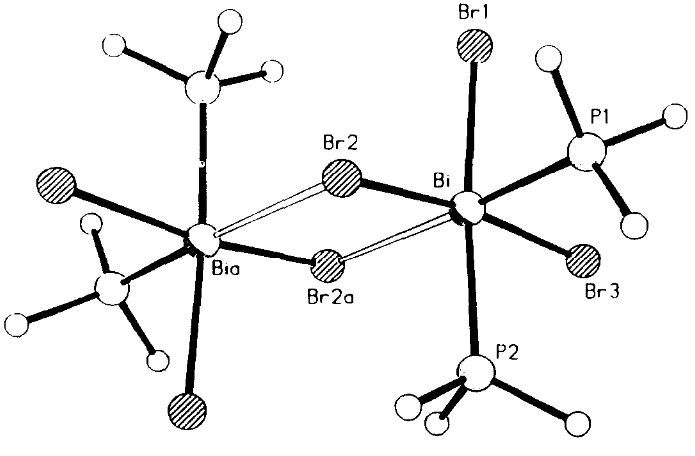
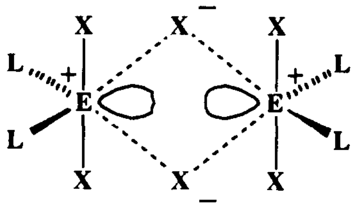


Fig. 8. Molecular structure of $[Bi_2Br_6(PMe_3)_4]$ (**41**).

The reason for the particular structural form adopted, i.e. **A**, is interesting in connection with other possible isomers, such as those shown in **B**—**D**, these being commonly encountered in analogous transition metal(III) halide complexes. Examples of transition metal complexes and the factors that affect which isomeric form is adopted have been discussed in Ref. [33] and references therein, and will not be repeated in detail here. Briefly, however, for monodentate ligands, type **C** is preferred largely on steric grounds, because the ligands are furthest apart from each other in this configuration, so unfavourable steric interactions are minimized (in general, L is larger than X). Examples of type **D** are not especially common, although they are found for some small ligands such as THF. Type **B** is found most often where the metal centres have a d^1 electron count, for electronic reasons that have been traced to favourable M—X π-interactions for this particular electron configuration.

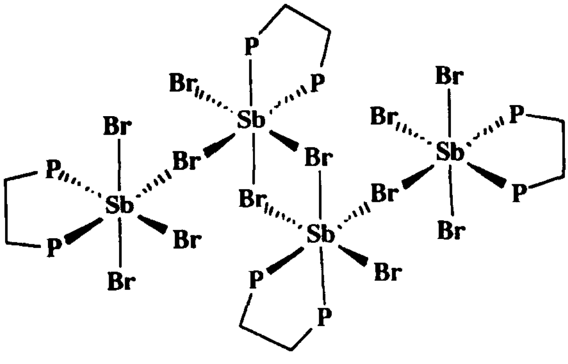
The reasons for the preference for the type **A** structure found in the group 15 examples are not entirely clear, although it is obviously not a structure which minimizes steric interactions between the ligands, based on the discussion given above (for complexes containing DMPE, a *cis* arrangement is obviously constrained by the chelating nature of the ligand but this can be accommodated in either **A** or **B**). Indeed, sterically, the type **A** structure is similar to type **B**, so an electronic origin is also likely and a possible reason for an electronic preference is associated with the observed large *trans* influence of the phosphine ligands (any *trans* influence of phosphine ligands in the analogous d-block complexes is much less, with particular M—X bonds being more nearly the same length such that, for bridging X groups, the M—X—M bridges are fairly symmetric, regardless of whether a particular M—μ-X bond is *trans* to P or X).

Thus, in a type-**B** structure, a large phosphine *trans* influence would tend to weaken and lengthen all the bridging E—X bonds, as shown in **E** in Form 6. While this may not be important in itself, the effect of creating what is essentially a pair of $[EX_2(L)_2]^+$ cations (and a pair of X^- anions) in close proximity may not be energetically favoured, since the stereochemically active lone pairs of these cations (shown in **E**) would be pointing directly towards each other, resulting in a repulsive interaction. In most of the complexes described so far, the fairly regular six-coordinate octahedral geometry implies the presence of lone pairs with little or no stereochemical activity; however, for a four-coordinate $[EX_2(L)_2]^+$ complex, a disphenoidal geometry with stereochemically active lone pairs localized as indicated would be expected.



E

An alternative structural form of **44** which has been crystallographically characterized is the tetrameric compound $[Sb_4Br_{12}(DMPE)_4]$ (**45**) [33], which is shown in Form 7. This may be viewed as containing a central $[Sb_2Br_6(DMPE)_2]$ unit similar to that in **44**, to which two additional $SbBr_3(DMPE)$ groups are attached via approximately linear, single Sb—Br—Sb bridges. Both these Sb—Br bonds are long, because they are both *trans* to a coordinated phosphine. A linear or near linear P—E—X—E—P (E = Sb, Bi; X = halide) arrangement presents a situation which is not dissimilar to the problem of two phosphines *trans* to the same bridging halide, as described above and this might also be expected to be unfavourable. The fact that such an arrangement is observed, however, may result from the greater E ··· E distance for a linear system mitigating any destabilizing effects due to localised lone pairs in close proximity.



45

In addition to the neutral compounds described above, a number of monoanionic complexes have also been structurally characterized, these being $[PMe_3H][Bi_2Br_7(PMe_3)_2]$ (**46**) [36] (Fig. 9), $[PEt_3H][Sb_2Br_7(PEt_3)_2]$ (**47**) [37] (Fig. 10), $[H(pyridine)_2][SbI_4(DMPE)]$ (**48**) [38] and $[PPh_4][BiI_4(PMe_2Ph)_2]$ (**49**) [37] (Fig. 11). The anion in **46** is polymeric, a section of which is shown in Fig. 9. The repeat unit is of an edge-shared, bioctahedral form, in which the two phosphine ligands are in axial sites (taking the $Bi_2(\mu\text{-}Br)_2$ plane as the equatorial plane) with a relative *anti* configuration. These units are linked via linear bromine bridges, with both Bi—Br bonds being *trans* to a PMe_3 and, hence, long (somewhat similar to the situation in **45**).

The same basic formula unit is also present in the anion in **47** (see Fig. 10), although this time the structure exists as a discrete dimeric form, with a different structure which can be described as a face-shared, bioctahedral structure. Two points should be noted. First, the *trans* influence of the phosphine ligands is again evident, in that, while Br(4) bridges fairly symmetrically between the two antimony centres, the bromines Br(3) and Br(5) are much more asymmetrically bound, with the longer Sb—Br bonds being *trans* to the phosphine ligands. Secondly, the configuration with regard to the phosphine ligands may be described as *gauche*, as illustrated in **F** in Form 8, in contrast to the *syn* form shown in **G**. Transition metal complexes of both types are known [39] but, in both cases, the M—X—M bridges for the transition

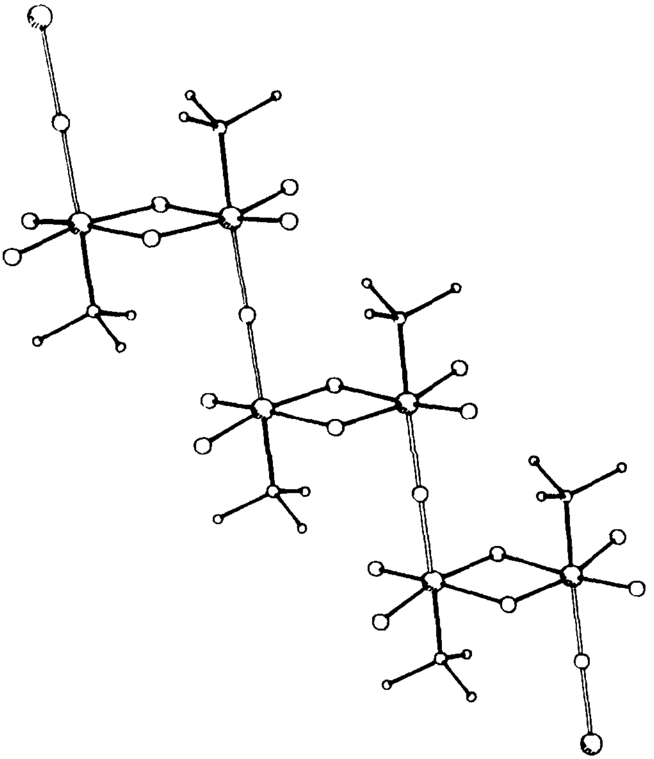


Fig. 9. View of part of the polymeric structure of the $[Bi_2Br_7(PMe_3)_2]^-$ anion in **46**.

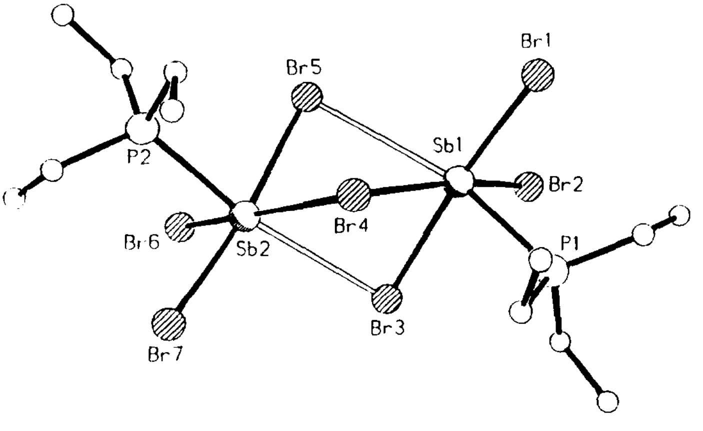


Fig. 10. Molecular structure of the anion $[Sb_2Br_7(PEt_3)_2]^-$ in **47**.

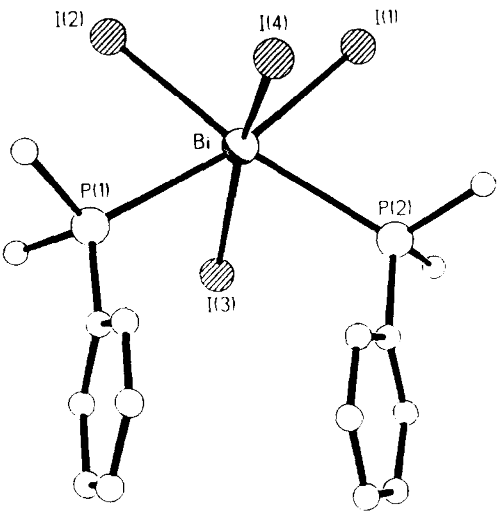
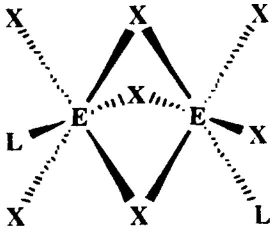
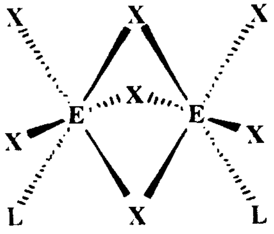


Fig. 11. Molecular structure of the $[BiI_4(PMe_2Ph)_2]^-$ anion in **49**.



F

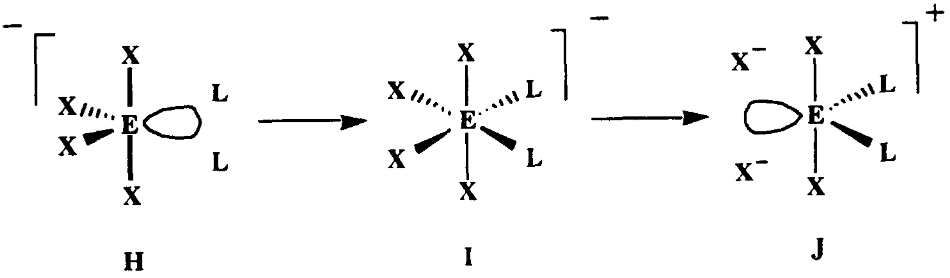


G

metal complexes are much more symmetric, regardless of the nature of the *trans* group, as is also found in the neutral transition metal $[M_2X_6(L)_4]$ dimers.

In line with the discussion presented above for the absence of type-**B** structures for complexes of the form $[E_2X_6(L)_4]$, the absence of a type-**G** structure may also be traced to the fact that, in this configuration, both phosphine ligands would be *trans* to the same bridging halide.

The structures of the anions in **48** and **49** are similar, in that they are monomeric and the coordination geometry around the E centre is close to being octahedral; a view of the anion in **49** is shown in Fig. 11. In both cases, the phosphine ligands are *cis* (constrained to be so, in the case of **48**, by the chelating nature of the DMPE ligand) but more notable are the distortions from a regular octahedral geometry, in terms of the bond angles at the E centres. Thus, in **48**, the angle between the two iodines *trans* to the phosphorus atoms is 123.92(2)°, where the angle in **49** between the two phosphines is 112.33(6)°. These distortions have been discussed in terms of the localization of the E(III) lone pair in the region between the expanded (and



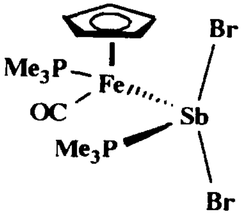
Scheme 2.

lengthened) pair of *cis* bonds, i.e. towards the edge of the octahedron defined by the vector between two *cis* atoms (I···I for **48** and P···P for **49** [37]), and also in terms of a reaction coordinate analysis, as shown in Scheme 2. The point about localization of the E(III) lone pair is relevant to the discussion presented earlier regarding structure **E**, in which a lengthening of two *cis* E—X bonds and/or an increase in the interbond angle is associated with lone pair localization in this region.

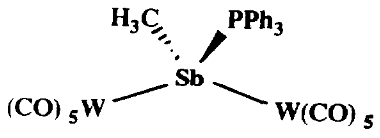
In terms of a reaction coordinate analysis, a regular octahedral geometry (as represented in **I**) implies a stereochemically inactive lone pair. This can be viewed as an intermediate along a reaction coordinate, where two ligands (L) displace two halides (X^-); for this, the extremes are the four-coordinate anion **H** before the ligands have encountered the element centre E, and the four-coordinate cation **J** in which the two halides *trans* to the approaching ligands have been displaced or substituted by the ligands L. In both **H** and **J**, the lone pairs would be expected to be localized in the regions indicated. Thus, on this basis, we may view **48** as lying towards **J** and **49** as lying more towards **H**, with both structures being thought of as arrested transition states along this double-nucleophilic substitution reaction coordinate.

4.2. *Miscellaneous*

Two compounds containing Sb—P bonds are known which fall into this category, i.e. the PMe_3 adduct of the dibromostibido complex $[SbBr_2\{Fe(CO)(PMe_3)(\eta\text{-}C_5H_5)\}(PMe_3)]$ (**50**) [40] and the PPh_3 adduct of the stibinidene complex $[SbMe(PPh_3)\{W(CO)_5\}_2]$ (**51**) [41] (see Form 9). In compound **50**, the antimony



50



51

centre is four coordinate, being bonded to two bromines, the iron atom of an $Fe(CO)(PMe_3)(\eta\text{-}C_5H_5)$ fragment and a PMe_3 ligand. The coordination geometry is based on a trigonal bipyramid, with the bromines in the axial sites and the Sb(III) lone pair stereochemically active in one of the equatorial sites. The most marked deviations from an idealized geometry are the Br—Sb—Br angle (149.1(1)° and the Fe—Sb—P angle (104.6(1)°).

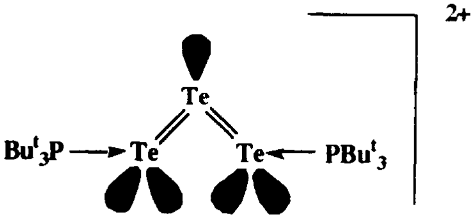
In **51**, the antimony lone pair is involved in multiple bonding interactions with the $W(CO)_5$ groups and the geometry around the antimony centre is closer to being tetrahedral, with the only angles deviating significantly from 109.5° being W—Sb—W (127.4(1)°) and P—Sb—C (92.0(5)°) — such angles are generally encountered in a range of stibinidene complexes.

5. Group 16

5.1. Tellurium complexes

Phosphine complexes of heavier group 16 element compounds are not particularly common, although it is worth noting the example of the phosphine telluride Bu^t_3PTe (**52**) [42], which can be viewed as a phosphine complex of a tellurium atom. We will not discuss this type of complex in any detail, except to mention the P—Te bond length of 2.368 Å, which is estimated to have a bond order of about 1.5. Nevertheless, it should be noted that phosphine tellurides are useful reagents as sources of tellurium atoms.

However, the oxiation of **52** with ferricenium salts affords complexes which may be described as phosphine complexes of the Te_3^{2+} cation, a structurally characterized example of which is $[Bu^t_3PTe_3PBu^t_3][SbF_6]_2$ (**53**) [43] (see Form 10), the cation of which is shown in Fig. 12. The P—Te bond lengths are 2.492(3) and 2.505(4) Å, i.e. somewhat longer than the corresponding bond in **52**, so in line with the single bond character, while the Te—Te bond lengths of 2.713(1) and 2.715(2) Å are consistent with some degree of Te—Te multiple bonding. The three angles at the tellurium atoms are Te(1)—Te(3)—Te(2) (109.0(1)°), P(1)—Te(1)—Te(3) (108.4(1)°) and P(2)—Te(2)—Te(3) (108.8(1)°), and these data, together with the bond distances, are consistent with a canonical form (illustrated in Form 10), although others can also be drawn.



53

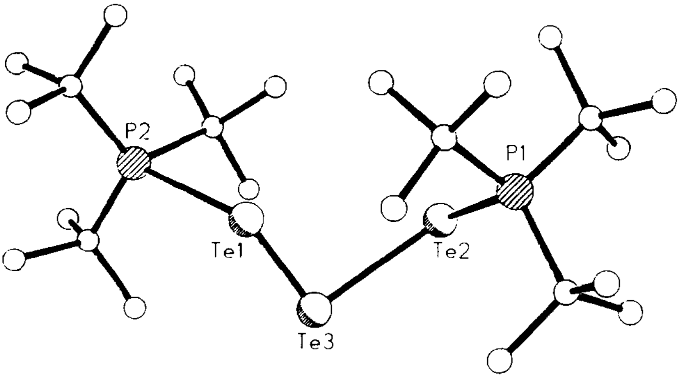
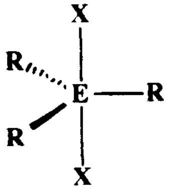


Fig. 12. Molecular structure of the cation $[\mathrm{Bu^t_3PTe_3PBu^t_3}]^{2+}$ in **53**.

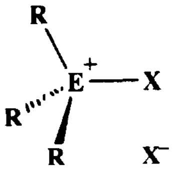
6. Group 17

6.1. Dihalogen compounds

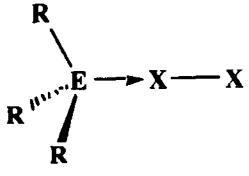
The study of the reaction between phosphines PR_3 (R = alkyl, aryl), and some of their heavier congeners, and the dihalogens Cl_2, Br_2 and I_2 has a long history. Indeed, there is now a considerable body of spectroscopic and analytical data concerning the nature of the products both in solution and in the solid-state. Most of the data have been interpreted in terms of the formation of either of one of two types of compound, i.e. a molecular five-coordinate species (R_3EX_2 (**K**) (E = P, As, Sb; X = halide)) or an ionic form involving a four-coordinate phosphonium cation ($[R_3EX]^+X^-$ (**L**)) (see Form 11).



K



L



M

Recent structural data, however, have established the existence of a third type **M**, in which the phosphorus centre is also four coordinate, as in **L**, but in which an X—X bond is still present, resulting in a species which can be described as a molecular phosphine adduct of a dihalogen (a type of complex sometimes referred to as a charge transfer complex). Thus, crystallization of the product of the reaction between PPh_3 and I_2 in Et_2O afforded crystals of the complex $[Ph_3P—I—I]$ (**54**) [44], the X-ray structure of which is shown in Fig. 13. The P—I bond length in **54** is 2.481(4) Å but, of more interest is the I—I distance of 3.161(2) Å. This may be compared with the slightly shorter I—I distance in the isomorphous arsine complex

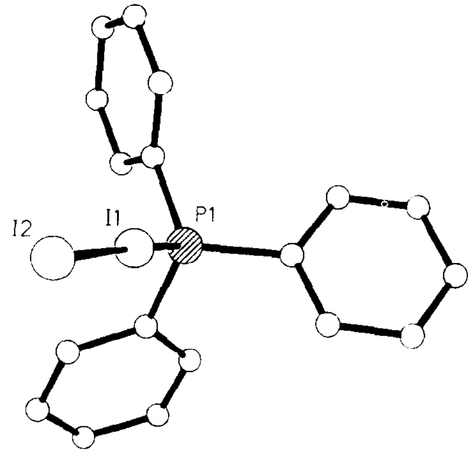


Fig. 13. Molecular structure of $[Ph_3P{-}I{-}I]$ (**54**).

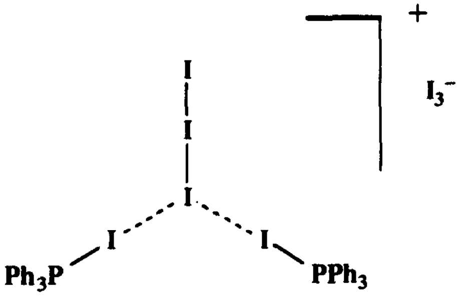
$[Ph_3As{-}I{-}I]$ (**55**) (3.005(1) Å) [45] and with the I—I distance in crystalline I_2 of 2.715 Å (2.666 Å for gaseous I_2). The lengthening of the I—I bond in both **54** and **55**, and the linear nature of the P—I—I unit in **54** (178.22(7)°; 174.8° for the As—I—I angle in **55**) are consistent with a molecular complex in which the phosphine (or arsine) lone pair is interacting with the I—I σ^* oribtal.

Another example of a phosphine complex of diiodine is $[Bu^t_3P{-}I{-}I]$ (**56**) [46], which has a solid state structure similar to that of **54**, in that the P—I—I angle is 177.6(1)°. The I—I bond length, however, is considerably longer (3.326(1) Å) than that in **54**, whereas the P—I bond distance is somewhat shorter (2.461(2) Å). In terms of a phosphine complex of I_2 as described above, the data for **56** are consistent with a stronger P—I interaction, which leads to a greater population of the I—I σ^* orbital and a concomitant lengthening of the I—I bond. Clearly, at some point, cleavage of the I—I bond will result and a description as an ionic compound $[R_3PI]^+I^-$ will then be more appropriate. To some extent, which description is used for **56** is a matter of choice, but the I—I distance is well within the sum of the van der Waals radii for iodine (4.30 Å).

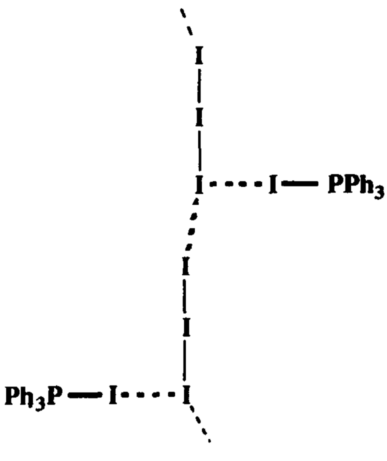
The dibromine analogue of **54**, i.e. $[Ph_3P{-}Br{-}Br]$ (**57**) [47], has also been described, with the crystal structure being isomorphous with those of **54** and **55**. Relevant metric parameters for **57** are the bond distances P—Br (2.181(3) Å) and Br—Br (3.123(2) Å), and the angle P—Br—Br (177.16(8)°). In this case, the Br—Br distance is quite long relative to that in solid Br_2 (2.27 Å), with the difference between the Br—Br bond lengths in **57** and Br_2 being 0.85 Å, whereas the corresponding difference in the I—I distances in **54** and I_2 is only 0.45 Å. This long Br—Br bond in **57** has led to the suggestion [48] that the structure of **57** is adequately described as ionic (as in **L**), rather than as a neutral coordination complex **M** — such a description is consistent with previous nuclear magnetic resonance (NMR), conductivity and Raman studies, which point to an ionic structure. Care must be exercized in these comparisons, however, since the NMR and conductivity studies have been carried out in solution and a Raman spectrum may not reveal a signal that results from a weak Br—Br bond. The facts remain that, in the crystal structure of **57**, a significant interaction (considerably less than the sum of the van der Waals radii) exists between the two bromine atoms and, more significantly, the P—Br—Br geometry is linear. The linear geometry is a consequence of the bonding in a covalent structure of type **M**, but it is not clear why such an arrangement would necessarily be found for an ionic compound, except perhaps accidentally. Clearly, a continuum of structures exists, with forms **L** and **M** as extremes of this continuum, and any discussion of intermediate cases as either one or the other must be considered with caution.

6.2. Polyhalogen compounds

In addition to phosphine complexes of the dihalogens, a number of phosphine and arsine complexes of polyhalogen species are also known. As mentioned in Section 6.1, the reaction between PPh_3 and I_2 in Et_2O affords the complex **54**. However, earlier work by Cotton and Kibala established that the reaction in dichloroethane afforded the complex $[(Ph_3PI)_2I_3][I_3]$ (**58**) [49], whereas the same reaction carried out in toluene afforded the complex $[Ph_3PI][I_3]$ (**59**) [49]. Compound **59** is best considered as an ionic material with $[Ph_3PI]^+$ cations and I_3^- anions, although there are a number of close contacts between the iodine atoms in the cations and anions. In **58**, the anion is the same but the cation is more complex



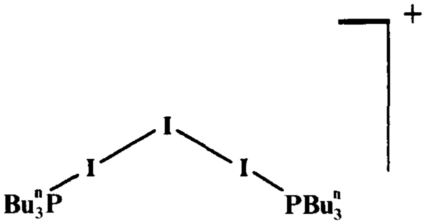
58



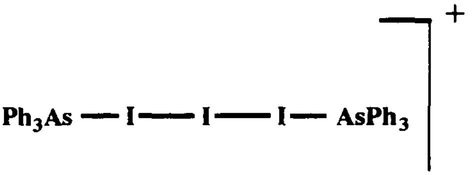
59

(see Form 12), although this also can be thought of as two $[Ph_3PI]^+$ cations and one I_3^- anion.

Other interesting compounds have also been isolated from reactions between either metal powders or metal carbonyls and complexes of the type R_3EX_2 analogous to **54–56**. Thus, in the reaction between $Bu^n_3PI_2$ and cobalt powder, the isolated complex was the ionic material $[\mathrm{Bu}^n_3\mathrm{PI}_3\mathrm{PBu}^n_3][\mathrm{CoI}_4(\mathrm{IPBu}^n_3)]$ (**60**) [50]. The anion in **60** may be viewed as comprising a $[\mathrm{CoI}_4]^{2-}$ dianion and a $[\mathrm{Bu}^n_3\mathrm{PI}]^+$ cation, but of more interest is the cation $[\mathrm{Bu}^n_3\mathrm{PI}_3\mathrm{PBu}^n_3]^+$ illustrated in Form 13. Key features of the cation in **60** are the geometries at the iodine atoms, which are bent at the central iodine and close to linear at the two terminal iodines. The simplest description of the bonding in the cation in **60** is as a bisphosphine adduct of the I_3^+ cation, for which a bent geometry at the central iodine is expected, with the phosphine interacting with the σ* orbital of each I—I bond, leading to a linear I—I—P arrangement in both cases.



60



61

In this regard, it is interesting to compare the structure of the cation in **60** with that of the cationic tellurium complex in **53**. The electron count for the cation in **60** is four electrons greater than for the cationic tellurium complex in **53**. Therefore, if these extra electrons in **60** are associated with the terminal iodines, then the resulting linear geometry at iodine — as opposed to the bent geometry at the terminal tellurium atoms in **53** — is readily accounted for in terms of VSEPR arguments.

A somewhat similar compound is obtained from the reaction between $[\mathrm{Co}_2(\mathrm{CO})_8]$ and **55**, which is described as $[\mathrm{Ph}_3\mathrm{AsI}_3\mathrm{AsPh}_3][\mathrm{CoI}_3\mathrm{AsPh}_3]$ (**61**) [51], i.e. containing the valence isoelectronic $[\mathrm{Ph}_3\mathrm{AsI}_3\mathrm{AsPh}_3]^+$ cation similar to that found in **60** (see Form 13). A major difference between the cations in **60** and **61**, however, is that the cation in **61** contains a linear I_3 geometry (in fact, a linear $\mathrm{AsI}_3\mathrm{As}$ geometry), which is difficult to rationalize in terms of a cation as formulated. Nevertheless, it is that expected for a bisarsine adduct of the I_3^- anion, so it is possible that **61** should be formulated as $[\mathrm{CoI}_3\mathrm{AsPh}_3]^+[\mathrm{Ph}_3\mathrm{AsI}_3\mathrm{AsPh}_3]^-$; this would involve a complex of cobalt(IV) rather than cobalt(II). Alternatively, however, a loose ion trio-type interaction of the form $[\mathrm{Ph}_3\mathrm{AsI}]^+\cdots[\mathrm{I}]^-\cdots{}^+[\mathrm{IAsPh}_3]$ is also possible, in which the expected bent geometry at the central iodine is not observed, as a result of the predominance of ionic bonding and the weakness of any covalent bonding.

7. General considerations

Finally, it is useful to consider some aspects of the bonding in p-block phosphine complexes, particularly in relation to the range of observed structures. In complexes of the types $[\mathrm{EX}_3(\mathrm{L})]$ and $[\mathrm{EX}_2(\mathrm{L})]$, where E is a group 13 element(III) centre and a group 14 element(II) centre, respectively, the situation is relatively straightforward, in that the element centres have an octet of electrons, with the L→E donor bond being one of the bonding electron pairs. The complexes are tetrahedral and trigonal pyramidal, respectively, though are slightly distorted in some cases. Of all the complexes described here, however, these are the only complexes which obey the octet rule (formally at least) and, for the other complexes, we must consider bonding models which involve multicentre interactions. (A somewhat more traditional approach that involves d orbital participation and localized two-centre, two-electron bonds is also available but current thinking is tending to stress the relative unimportance of d orbitals in the bonding in p-block element complexes [52].)

In group 13 complexes of the type $[EX_3(L)_2]$, a trigonal bipyramidal geometry is always observed in which the phosphines are *trans* to each other in axial sites. Here, we may assume that the E centre is sp^2 hybridized and that the two phosphines interact with the remaining and vacant p orbital, resulting in a three-centre, four-electron interaction. A similar bonding model may be employed for the tin(IV) complex **36**, for which the three-centre, four-electron interaction involves the axial chlorine and phosphorus atoms (treating Cl as Cl^-). Likewise, in the octahedral tin(IV) complex **35**, we may view the planar $SnCl_4$ unit as involving two of the tin p orbitals, together with the s orbital, with the *trans* phosphines sharing the remaining p orbitals (perhaps somewhat arbitrarily). Regardless of the details of the bonding, however, it is clear from the examples known that the *trans*-axial phosphines configuration is favoured for the $[EX_3(L)_2]$ compounds, and perhaps also for the $[EX_4(L)_2]$ group 14 analogues, although there is only one structurally characterized example of such a compound.

In structurally characterized tin(IV) $[SnX_4(L)_2]$ complexes with other types of donor ligand, both *cis* and *trans* geometries are observed, indicating that the two configurations have similar energies [53]. Nevertheless, for the group 13 examples, it is interesting to note that the observed configuration places the sterically bulky ligands in the sterically more congested axial sites (according to VSEPR), which is suggestive of an electronic origin for this geometric preference. We must be careful with this argument, however, since the effective difference in size between normal two-centre, two-electron bonds and dative bonds at the central element centre is also important, as discussed by Haaland [8].

In none of these complexes is a lone pair of electrons present at the central element, except in the germanium(II) and tin(II) complexes, where it is part of the valence octet. In the group 15 complexes, however, the element oxidation state is three and a lone pair is present in all of the examples; thus, its potential stereochemical activity is an important consideration. If we consider the complexes of general formula $[EX_3(L)]$, it is immediately apparent that the structures are quite different from those of the corresponding group 13 complexes. Therefore, while the group 13 examples are all monomeric and tetrahedral, the group 15 derivatives are oligomeric, as a result of bridging X interactions, such that the coordination geometry around the group 15 element centre is six and octahedral. Furthermore, the only significant deviations from a regular geometry are associated with the lengthening of E—X bonds *trans* to the phosphine, i.e. the large phosphine *trans* influence previously mentioned.

Group 15 element complexes of the type $[EX_3(L)_2]$ also differ from the group 13 examples of the same formula, in that, while the group 13 examples are invariably monomeric, the group 15 complexes are dimeric (tetrameric in the case of **45**), as a result also of halide bridging. The phosphine *trans* effect on the E—X bonds is again evident and it is also observed that the phosphine ligands on a particular element centre are *cis* rather than *trans* to each other. For large phosphines, a *cis* arrangement is sterically unfavourable, which also suggests a possible electronic origin for this geometry.

Considering both the neutral group 15 $[EX_3(L)]$ and $[EX_3(L)_2]$ complexes, and the anions of general formula $[EX_4(L)_2]^-$ and $[E_2X_7(L)_2]^-$, it is actually a general feature that, despite the differences in gross structure, the local structure around the E centre is octahedral and that, where two phosphine ligands are present, they are always *cis*. Bond length and angle distortions are observed to a greater or lesser extent, these being generally associated with the large phosphine *trans* influence. This *trans* influence affects one bond or two *cis* bonds *trans* to two *cis* phosphines with a concomitant distortion in the *cis* bond angles may also be stated in terms of the localization of the element(III) lone pair, i.e. the onset of lone pair stereochemical activity, the importance of which was mentioned above. Thus, complete removal of one X group *trans* to a phosphine would lead to a five-coordinate square-based pyramidal structure in which the lone pair is stereochemically active in the vacant sixth coordination site. In structures where bridging halides are present, phosphines may be observed *trans* to both E—X bonds in linear E—X—E systems, with one μ-X bridge; however, for systems with two or three μ-X groups, i.e. $E_2(\mu\text{-}X)_2$ and $E_2(\mu\text{-}X)_3$, no examples are known in which both E—X bonds for a given X are *trans* to a phosphine.

Clearly, there are a number of factors which require explanation. First, the monomeric nature of the group 13 complexes of formulae $[EX_3(L)]$ and $[EX_3(L)_2]$ is in sharp contrast to the dimeric or oligomeric nature of the group 15 analogues. At first sight, this observation is counter-intuitive, since, if we compare indium and antimony, for example, indium(III) has a larger covalent radius than that of antimony(III), so is presumably more able to support a larger coordination number. Moreover, the lesser electronegativity of indium would mean a greater electronegativity difference for the In—X or In—P bonds, so generating a larger δ^+ charge at the indium centre. Clearly, neither of these factors is especially important and it is perhaps more the case that the greater covalency of the antimony compounds (associated with the aforementioned electronegativity differences) is reflected in the maximizing of the number of covalent bonding interactions.

A possible reason for the observations concerning phosphines *trans* to bridging halides and the effect this might have on the observed geometries of $[E_2X_6(L)_4]$ and $[E_2X_7(L)_2]^-$ compounds has been discussed in the text, but the reason why *cis* bisphospine geometries are observed in group 15 in contrast to the more general *trans* arrangement in groups 13 and 14 still requires an explanation; a comparison here might be made between the tin complex **35** and the bismuth complex **49**.

The fundamental difference between group 14 $[EX_4(L)_2]$ and group 15 $[EX_4(L)_2]^-$ compounds is two valence electrons, i.e. the lone pair of electrons for the group 15 complex. Whether or not the electron count is a decisive factor here will require a future study involving detailed molecular orbital calculations. A very approximate (perhaps too approximate) explanation can be obtained, however, if we consider an $[EX_n(L)_2]$ compound to consist of the ions $[E(L)_2]^{n+}$ and nX^-. Thus, a tin(IV) system would have four valence electrons, so should be linear, whereas an anionic bismuth system would have six electrons, so should be bent.

Most of the tellurium and iodine compounds described in Sections 5 and 6 have structures which can be rationalized on the basis of the phosphine ligands interacting with either Te—Te or I—I σ^* orbitals, as mentioned above, and the overall geometry of the compounds can usually be accounted for by considering localized electron pairs arranged according to VSEPR rules (in particular, lone pairs in equatorial positions for situations where five electron pairs are formally present around any particular centre). Nevertheless, the situation with compounds **60** and **61** shows that complications may arise and that care must be exercized in applying simple structural or bonding models.

Note added in proof

Since the completion of this manuscript, the following papers have appeared describing X-ray structures of a number of phosphine complexes relevant to this article: $[AlCl_3\{P(SiMe_3)_3\}]$ and $[AlBr_3\{P(SiMe_3)_3\}]$ (R.L. Wells, A.T. McPhail, J.A. Laske and P.S. White, Polyhedron, 13 (1994) 2737); $[AlCl_{3-n}R_n\{P(SiMe_3)_3\}]$ ($R =$ Et, $n = 1$; $R = Bu^i$, $n = 2$) (R.L. Wells, A.T. McPhail, M.F. Self and J.A. Laske, Organometallics, 12 (1993) 3333); $[Ga(CH_2SiMe_3)_3\{P(SiMe_3)_3\}]$ and $[In(CH_2SiMe_3)\{P(SiMe_3)_3\}]$ (R.L. Wells, R.A. Baldwin and P.S. White, Organometallics, 14 (1995) 2123); $[In(CH_2Gu^t)_3\}P(SiMe_3)_3\}]$ and $[InMe(CH_2Bu^t)_2y\{P(SiMe_3)_3\}]$ (M.F. Self, A.T. McPhail, L.J. Jones and R.L. Wells, Polyhedron, 13 (1994) 625); $[AlMe_2(SePh)(PPh_3)]$ (R. Kumar, D.G. Dick, S.U. Ghazi, M. Taghiof, M.J. Heeg and J.P. Oliver, Organometallics, 14 (1995) 1601).

References

[1] C.A. McAuliffe (ed.), Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands, Macmillan, London, 1973.
[2] W. Levason and C.A. McAuliffe, Coord. Chem. Rev., 19 (1976) 173.
[3] A.J. Downs and C.R. Pulham, Chem. Soc. Rev., 23 (1994) 175.
[4] C. Jones, G.A. Koutsantonis and C.L. Raston, Polyhedron, 12 (1993) 1829.
[5] J.L. Atwood, K.D. Robinson, F.R. Bennett, F.M. Elms, G.A. Koutsantonis, C.L. Raston and D.J. Young, Inorg. Chem., 31 (1992) 2673.
[6] D. O'Hare, J.S. Foord, T.C.M. Page and T.J. Whitaker, J. Chem. Soc., Chem. Commun., (1991) 1445.
[7] F.R. Bennett, F.M. Elms, M.G. Gardiner, G.A. Koutsantonis, C.L. Raston and N.K. Roberts, Organometallics, 11 (1992) 1457.

[8] A. Haaland, Angew. Chem., Int. Ed. Engl., 28 (1989) 992.
[9] L.M. Golubinskaya, A.V. Golubinskii, V.S. Mastryukov, L.V. Vilkov and V.I. Bregadze, J. Organometall. Chem., 117 (1976) C4.
[10] A. Almenningen, L. Fernholt and A. Haaland, J. Organometall. Chem., 145 (1978) 109.
[11] D.A. Wierda and A.R. Barron, Polyhedron, 8 (1989) 831.
[12] M.A. Banks, O.T. Beachley, J.D. Maloney and R.D. Rogers, Polyhedron, 9 (1990) 335.
[13] R.L. Wells, S.R. Aubuchon, M.F. Self, J.P. Jasinski, R.C. Woudenberg and R.J. Butcher, Organometallics, 11 (1992) 3370.
[14] D.C. Bradley, H. Chudzynska, M.M. Faktor, D.M. Frigo, M.B. Hursthouse, B. Hussain and L.M. Smith, Polyhedron, 7 (1988) 1289.
[15] A. Boardman, R.W.H. Small and I.J. Worrall, Inorg. Chim. Acta, 119 (1986) L13.
[16] H. Scmidbaur, S. Lauteschläger and G. Müller, J. Organometall. Chem., 281 (1985) 25.
[17] J.C. Carter, G. Jugie, R. Enjalbert and J. Galy, Inorg. Chem., 17 (1978) 1248.
[18] N.W. Alcock, I.A. Degnan, O.W. Howarth and M.G.H. Wallbridge, J. Chem. Soc., Dalton Trans., (1992) 2775.
[19] I.R. Beattie, G.A. Ozin and H.E. Blayden, J. Chem. Soc. A, (1969) 2535.
[20] M.V. Veidis and G.J. Palenik, Chem. Commun., (1969) 586.
[21] I.A. Degnan, N.W. Alcock, S.M. Roe and M.G.H. Wallbridge, Acta Crystall., Sect. C, 48 (1992) 995.
[22] W. Clegg, N.C. Norman and N.L. Pickett, Acta Crystall., Sect. C, 50 (1994) 36.
[23] M.D. Healy, D.A. Wierda and A.R. Barron, Organometallics, 7 (1988) 2543.
[24] J.T. Leman, H.A. Roman and A.R. Barron, J. Chem. Soc., Dalton Trans., (1992) 2183.
[25] D.M. Schubert, A.A. Bandman, W.S. Rees, C.B. Knobler, P. Lu, W. Nam and M.F. Hawthorne, Organometallics, 9 (1990) 2046.
[26] L.M. Clarkson, K. McCrudden, N.C. Norman and L.J. Farrugia, Polyhedron, 9 (1990) 2533.
[27] L.M. Clarkson, N.C. Norman and L.J. Farrugia, Organometallics, 10 (1991) 1286.
[28] Y. Inoguchi, S. Okui, K. Mochida and A. Itai, Bull. Chem. Soc. Jpn., 58 (1985) 974.
[29] N.G. Bokii, Yu.T. Struchkov, S.P. Kolesnikov, I.S. Rogazhin and O.M. Neferov, Izv. Akad. Nauk. SSSR, Ser. Khim., (1975) 812.
[30] G.G. Mather, G.M. McLaughlin and A. Pidcock, J. Chem. Soc., Dalton Trans., (1973) 1823.
[31] A.I. Tursina, V.M. Ionov, L.A. Aslanov, S.V. Medvedev and I.B. Zastenker, Zh. Strukt. Khim., 24 (1983) 181.
[32] A.L. Seligson and J. Arnold, J. Am. Chem. Soc., 115 (1993) 8214.
[33] W. Clegg, M.R.J. Elsegood, V. Graham, N.C. Norman, N.L. Pickett and K. Tavakkoli, J. Chem. Soc., Dalton Trans., (1994) 1743.
[34] G. Baum, A. Greiling, W. Massa, B.C. Hui and J. Lorberth, Z. Naturforsch. B, 44 (1989) 560.
[35] W. Clegg, R.J. Errington, R.J. Flynn, M.E. Green, D.C.R. Hockless, N.C. Norman, V.C. Gibson and K. Tavakkoli, J. Chem. Soc., Dalton Trans., (1992) 1753.
[36] W. Clegg, R.J. Errington, G.A. Fisher, M.E. Green, D.C.R. Hockless and N.C. Norman, Chem. Ber., 124 (1991) 2475.
[37] W. Clegg, M.R.J. Elsegood, N.C. Norman and N.L. Pickett, J. Chem. Soc., Dalton Trans., (1994) 1753.
[38] W. Clegg, M.R.J. Elsegood, V. Graham, N.C. Norman and N.L. Pickett, J. Chem. Soc., Dalton Trans., (1993) 997.
[39] F.A. Cotton and W.A. Wojtczak, Inorg. Chim. Acta, 216 (1994) 9.
F.A. Cotton and R.L. Luck, Inorg. Chem., 28 (1989) 182.
F.A. Cotton and R. Poli, Inorg. Chem., 26 (1987) 3310.
[40] H.-A. Kaul, D. Greissinger, W. Malisch, H.-P. Klein and U. Thewalt, Angew. Chem., Int. Ed. Engl., 22 (1983) 60.
[41] B. Sigwarth, U. Weber, L. Zsolnai and G. Huttner, Chem. Ber., 118 (1985) 3114.
[42] N. Kuhn, H. Schumann and G. Wolmershauser, Z. Naturforsch. B, 42 (1987) 674.
[43] N. Kuhn, H. Schumann and R. Boese, J. Chem. Soc., Chem. Commun., (1987) 1257.
[44] S.M. Godfrey, D.G. Kelly, C.A. McAuliffe, A.G. Mackie, R.G. Pritchard and S.M. Watson, J. Chem. Soc., Chem. Commun., (1991) 1163.

[45] C.A. McAuliffe, B. Beagley, G.A. Gott, A.G. Mackie, P.P. MacRory and R.G. Pritchard, Angew. Chem., Int. Ed. Engl., 26 (1987) 264.
[46] W.-W. du Mont, M. Bätcher, S. Pohl and W. Saak, Angew. Chem., Int. Ed. Engl., 26 (1987) 912.
[47] N. Bricklebank, S.M. Godfrey, A.G. Mackie, C.A. McAuliffe and G.R. Pritchard, J. Chem. Soc., Chem. Commun., (1992) 355.
[48] M.A.H.A. Al-Juboori, P.N. Gates and A.S. Muir, J. Chem. Soc., Dalton Trans., (1994) 1441.
[49] F.A. Cotton and P.A. Kibala, J. Am. Chem. Soc., 109 (1987) 3308.
[50] C.A. McAuliffe, S.M. Godfrey, A.G. Mackie and R.G. Pritchard, Angew. Chem., Int. Ed. Engl., 31 (1992) 919.
[51] S.M. Godfrey, H.P. Lane, A.G. Mackie, C.A. McAuliffe and R.G. Pritchard, J. Chem. Soc., Chem. Commun., (1993) 1190.
[52] A.E. Reed and P. von R. Schleyer, J. Am. Chem. Soc., 112 (1990) 1434.
[53] C.J. Carmalt, W. Clegg, M.R.J. Elsegood, B.O. Kneisel and N.C. Norman, Acta Crystall., Sect. C, in press.