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# Phosphine Complexes of Lone Pair Bearing Lewis Acceptors

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## Abstract

An overview of the synthesis, structures and reaction chemistry of coordination complexes featuring an acceptor with at least one lone pair and at least one phosphine donor is presented. One or more examples of complexes have been structurally-characterized for the majority of *p*-block elements but few are known for most elements. The unusual condition of a *p*-block element centre accommodating a lone pair of electrons and offering a low energy LUMO gives the element centre the potential to behave as both a Lewis acid and a Lewis Base. The structural diversity and reactivity of the phosphine complexes highlights new directions in main group chemistry and by comparison with transition metal coordination chemistry, the featured complexes demonstrate significant configurational and stereochemical flexibility. Ligand exchange, oxidation and reduction chemistry at the lone pair acceptor centre reveals unusual reactivity and an interesting class of ligands and inorganic reagents, with new possibilities for catalysis or small molecule activation.

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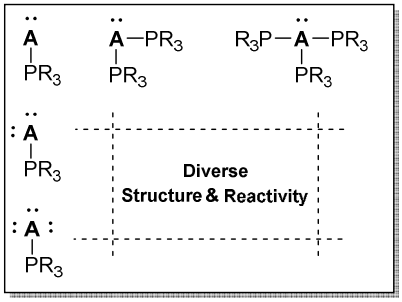



Text: *The unique structural outcomes and reactivity modes for phosphine complexes featuring lone-pair bearing acceptors are considered.*

**Author Bios**

Saurabh S. Chitnis obtained his B. Art. Sc. (*summa cum laude*) in 2010 from McMaster University, Hamilton with an Honours thesis project in the lab of Prof. Gary J. Schrobilgen. He joined the Burford group in 2010 at Dalhousie University, Halifax and subsequently at the University of Victoria as a Ph.D. student. He was a visiting researcher in the group of Prof. Jan J. Weigand at the Technische Universität Dresden in 2013. He is a Vanier Canada Graduate Scholar and the most recent recipient of the Julius F. Schleicher Graduate Scholarship from the University of Victoria.

Neil Burford obtained a BSc Honours from the University of Wales, Cardiff and a Ph.D from the University of Calgary. Following post-doctoral studies at the University of Alberta and at the University of New Brunswick, he was appointed Assistant Professor at Dalhousie University in 1987, Harry Shirreff Professor of Chemical Research in 2000 and Canada Research Chair Tier I in 2001. He was appointed Chair of the Department of Chemistry at Dalhousie University in 2008 and in 2011, he moved to the University of Victoria as Professor and Chair of the Department of Chemistry.

## 1.0 Introduction

Phosphines represent prototypical ligands in the broad array of established coordination complexes of *d*- and *f*-block metals. Bonding in such complexes is understood in terms of the donor-acceptor model and is described in terms of a frontier orbital interaction between the highest occupied molecular orbital (HOMO) of the phosphine (a non-bonding electron pair or 'lone pair') and the lowest unoccupied molecular orbital (LUMO) of the metal centre. The interaction is enhanced for metal centres with relatively low energy *d*-orbital(s) LUMO, often imposed by a cationic charge on the complex. Many *p*-block element centres also behave as Lewis acceptors for phosphine donors but the bonding is less well defined than for transition metal complexes and has been described by invoking vacant *p*- or $\sigma^*$-orbitals, as the *d*-orbitals of *p*-block elements are of higher energy than those in transition metals. As for *d*-block metals, introduction of a cationic charge at a lone pair bearing *p*-block acceptor centre enhances the Lewis acidity and usually creates a vacant coordination site, further augmenting the coordination chemistry. A more unusual condition occurs when a *p*-block element centre accommodates a lone pair of electrons and also a low energy LUMO, so that the element centre has the potential to behave as both a Lewis acid and a Lewis base. The structural, stereochemical and bonding consequences of such interactions have recently been highlighted and define new parameters to consider for this new direction in coordination chemistry. Moreover, coordination complexes of *p*-block element acceptors offer new possibilities for catalysis or small molecule activation.

## 2.0 Scope

This perspective highlights the synthesis, structures and reaction chemistry of coordination complexes featuring an acceptor with at least one lone pair and at least one phosphine donor. The term 'coordination complex' is applied most routinely to compounds of the transition metals, but can be generally applied across the periodic table.[1] In a recent review of cationic compounds containing Pn-Pn bonds (Pn = N, P, As, Sb or Bi),[2] we described the foundational concepts, structural definitions, bonding notations and abbreviations[3] that have been applied to compounds of this type. The recent updating of definitions such as 'valence', 'oxidation state' and 'coordination'[4,5,6,7] augment the longstanding applications of the Lewis bonding and VSEPR[8] structural models to provide evolving insights into the structure and bonding illustrated by these compounds. Two recent reviews[9,2] have catalogued reports of most of the complexes discussed here.

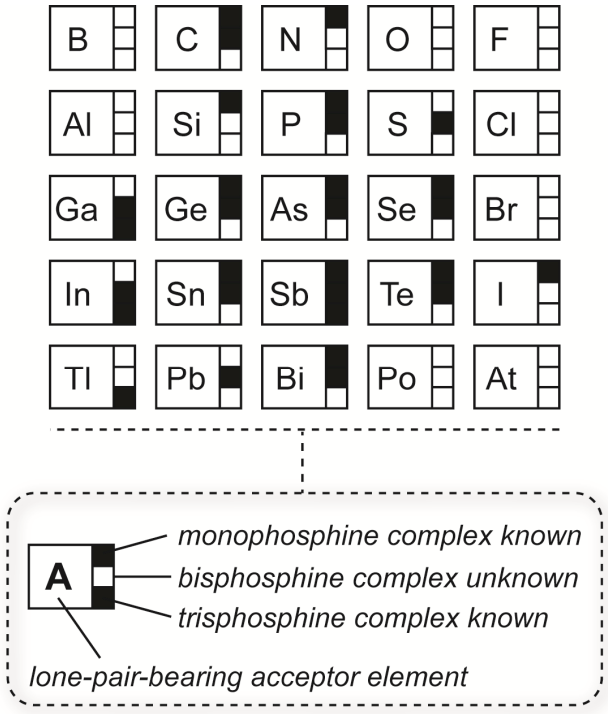



**Figure 1.** The *p*-block elements with markers indicating those elements for which complexes with one, two or three phosphine ligands have been structurally characterized and for which the acceptor site contains at least one lone-pair.

Phosphine complexes of lone pair-bearing acceptors have been structurally-characterized for the majority of *p*-block elements (summarized in Figure 1), but remain rare as few examples are known for most elements. A limited number of elements adopt *bis*-phosphine complexes and *tris*-phosphine complexes have only been reported for gallium,[31] indium,[31] thallium[10] and antimony.[11] Phosphine complexes of boron(I) or aluminium(I) are not known even though complexes of these centres with carbene or diketiminate ligands have been reported as stable compounds or trapped intermediates.[12]

Description of a compound as a complex depends on the perceived nature of the bonds. A coordinate bond usually has the facility to dissociate heterolytically,[13] but this feature by itself does not definitively characterize a molecule as a complex, especially for some examples of *p*-block compounds that are better described using Lewis and Valence Bond models.[7,14] Compounds such as phosphorus ylides, carbodiphosphoranes (carbones), $[(PPh_3)N_2(PPh_3)]$,[15] derivatives of $[(R_3P)I_2]$,[16,17] and $[(Ph_2(MeCarb)P)I_2(PPh_2(MeCarb))]$[18] (*MeCarb* = 1-(2-Me-1,2-$C_2B_{10}H_{10}$)) can be described using a coordinate model or a Lewis model and are included in this discussion. However, phosphine chalcogenides $R_3PE$ (E = O, S, Se, Te), derivatives of Hendrickson's reagent ($[R_3POPR_3]^{2+}$),[19] and halophosphonium cations $[R_3PX]^{1+}$ (X = F, Cl, Br) are not discussed as the conventional Lewis models

adequately describe the structure and bonding, and the donor/acceptor model does not add to the description.

### 3. Structural Features for Phosphine Complexes of Lone Pair Bearing Lewis Acceptors

Figure 2 gives an overview of the formulae that are possible for *mono*-, *bis*-, and *tris*-phosphine complexes of lone-pair bearing *p*-block acceptors. Based on the limited data available, the observed geometries at the acceptor centres are dictated primarily by the balance between the stereochemical presence of the lone pair and the covalent radius of the element. For example, complexes of the form $[(PPh_3)_2EPh_2]^{1+}$ (E = Sb, Bi) are prepared in high yields,[20] whereas the analogous phosphorus complexes of the form $[(PR_3)_2PR'_2]^{1+}$ have not been reported. Attempts to prepare diphosphine chelate complexes of $[PR'_2]^{1+}$ result in the diphosphine ligand bridging two phosphorus acceptors as in the example of $[Ph_2P\text{-}(dppe)\text{-}PPh_2]^{2+}$.[21] Further distinction between the coordination chemistry of phosphorus and antimony is evidenced by the reactions of excess trialkylphosphines with $PCl_3$ and $SbCl_3$. While $PCl_3$ is observed to undergo a redox process resulting in 'triphosphenium' cations, $[(PR_3)_2P]^{1+}$,[22,23,24] interpreted as a phosphide centre bridging two phosphonium centres or a bis-phosphine complex of $[P]^{1+}$, $SbCl_3$ is redox resistant and derivatives of $[(PR_3)_2SbCl_3]$ are isolated in which the larger coordination sphere of antimony can accommodate five bond pairs and a lone pair.[26] In general, halides of the heavier *p*-block elements behave as classical transition metal acceptors, and interion- as well as nearest-neighbour contacts participate in the coordination geometry of the acceptor, usually imposing a hypervalent environment.

| | *Mono-P* | *Bis-P* | *Tris-P* |
|---|---|---|---|
| *One lone pair at A* | $AP_1B_0E_1$ | $AP_2B_0E_1$ | $AP_3B_0E_1$ |
| | $AP_1B_1E_1$ | $AP_2B_1E_1$ | $AP_3B_1E_1$ |
| | $AP_1B_2E_1$ | $AP_2B_2E_1$ | $AP_3B_2E_1$ |
| | $AP_1B_3E_1$ | $AP_2B_3E_1$ | |
| | $AP_1B_4E_1$ | | |
| *Two lone pairs at A* | $AP_1B_0E_2$ | $AP_2B_0E_2$ | $AP_3B_0E_2$ |
| | $AP_1B_1E_2$ | $AP_2B_1E_2$ | $AP_3B_1E_2$ |
| | $AP_1B_2E_2$ | $AP_2B_2E_2$ | |
| | $AP_1B_3E_2$ | | |
| *Three lone pairs at A* | $AP_1B_0E_3$ | $AP_2B_0E_3$ | |
| | $AP_1B_1E_3$ | $AP_2B_1E_3$ | |
| | $AP_1B_2E_3$ | | |

**Figure 2.** Generic formulae for the 26 possible *mono*-, *bis*- and *tris*-phosphine complexes of a lone pair-bearing acceptor A, organized according to the type of electron pairs around the acceptor. Assuming a maximum of six electron pairs around A, P = phosphine donor electron pair, B = substituent electron pair (e.g. alkyl, aryl, halogen, etc.), and E = non-bonding lone pair.

**3.1 Lone Pair Stereochemistry and VSEPR Configurational Diversity.** Lone pair stereochemical activity is a feature of *p*-block coordination chemistry that is not apparent in the structures of *d*-block coordination complexes. Due to large promotion energies in heavy elements, *sp*, $sp^2$ and $sp^3$ hybridisation are less favourable,[25] and lone pairs are accommodated primarily in *s*-type orbitals while bonding occurs primarily through the *p*-orbitals. As a result, bond angles to directly-bonded substituents are close to 90° for three-coordinate geometries and when inter-ion contacts are considered, distorted square-planar or octahedral arrangements are observed for five- and six-coordinate geometries, respectively, as shown in the examples presented in Figure 3. The P-Sb-Cl angles in the pyramidal $[(PMe_3)SbCl_2]^{1+}$ cation[26] (Figure 3a) are 90.71(3)° and 90.62(3)° and the Cl-Sb-Cl angle is 92.78(3)°. A six-coordinate geometry is imposed at antimony by considering the interion contacts, and the average O1-Sb-O3 and O2-Sb-O3 angles of 115.4°, implicate the presence of a stereochemically active lone pair. Similarly, the average Cl-Sb-Cl angle in the $[(PMe_3)_2SbCl_4]^{1-}$ anion (Figure 3b) is 89.47°, but the average P-Sb-Cl angle is compressed to 84.39°, indicating steric pressure from the presence of a lone pair *trans* to the phosphine interaction. Consistently, the calculated (MP2/Def2-TZVPP) electronic structure shows significant accumulation of electron density at the Sb atom in the HOMO (Figure 3c) of the $[(PMe_3)SbCl_4]^{1-}$ anion.[26]

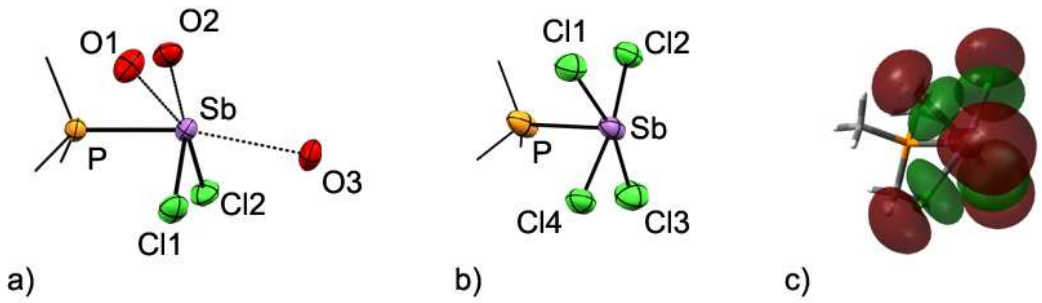



**Figure 3.** Molecular structure of a) $[(PMe_3)SbCl_2]^{1+}$ with three weak inter-ion contacts, b) $[(PMe_3)_2SbCl_4]^{1-}$, and c) HOMO of $[(PMe_3)SbCl_4]^{1-}$ as calculated at the MP2/Def2-TZVPP level.[26]

The potential configurational diversity within a VSEPR geometry for phosphine complexes of antimony trihalides is illustrated in Chart 1, and trends in structural configurations have been assessed,[26] to derive the following *trans*-labilizing influence of substituents and ligands: lone-pair < $PPh_3$ < halide < $PCy_3$ ≈ $PMe_3$ < Ph. Consequently,

$[(PMe_3)SbPhCl_2]$ is observed to adopt a configuration in which the phenyl group and $PMe_3$ are *cis* to each other, with the two chlorine substituents *trans* to each other (Figure 4). Similarly in the anion $[(PMe_3)SbCl_4]^{1-}$, the phosphine ligand adopts the apical site (Figure 3(b)).

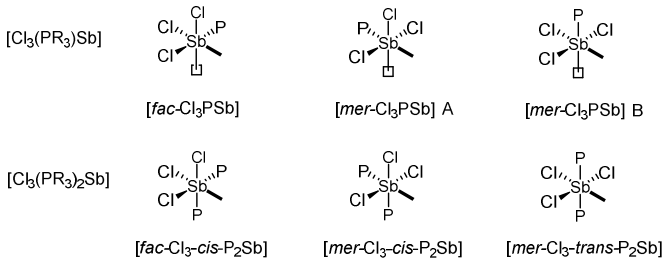



**Chart 1.** Potential configurational variety (VSEPR-inconsistent structures are not considered) in an octahedral frame for chloroantimony complexes composed of three chloride substituents and one or two phosphine ligands (P = $PR_3$). Bold line = lone pair, Square = vacant coordination site. Adapted from ref 26.

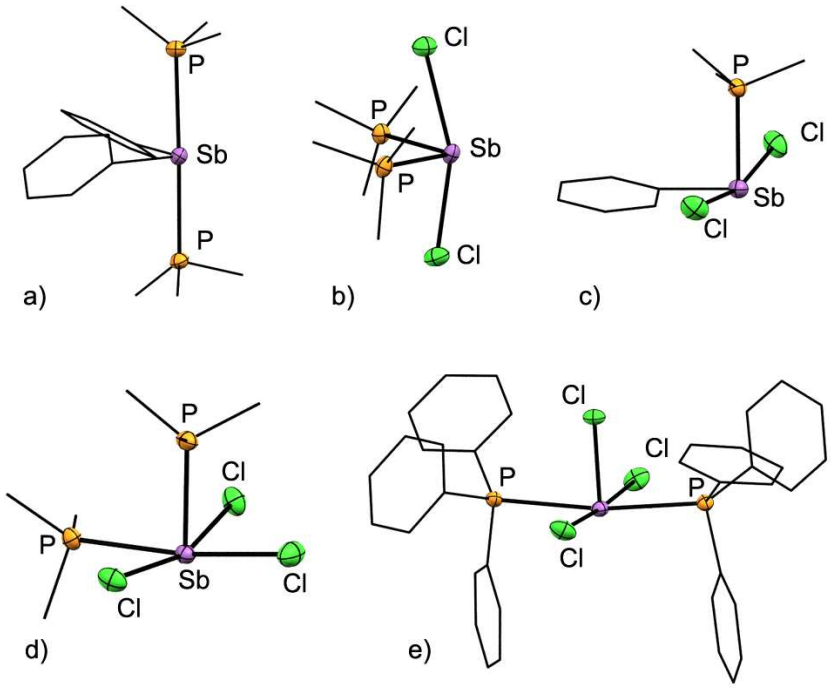



**Figure 4.** Structural diversity for four- and five-coordinate phosphine complexes of antimony acceptors: a) $[(PMe_3)_2SbPh_2]^{1+}$, b) $[(PMe_3)_2SbCl_2]^{1+}$, c) $[(PMe_3)SbPhCl_2]$, d) $[(PMe_3)_2SbCl_3]$, and e) $[(PPh_3)_2SbCl_3]$.[26]

The relative *trans*-labilizing influence of phosphines and substituents derived for antimony acceptors applies generally for observed structures of other group 15 acceptors. For

example, all N-heterocyclic or cyclic-alkylamino carbene adducts of $ECl_3$ (E = P, As, Sb, Bi)[27] adopt structures in which the ligand is *cis*-configured with respect to all halides. The relative *trans*-labilizing influence of phosphines and substituents described above is a feature unique to complexes involving lone pair bearing acceptors. As illustrated in Chart 2, $[(PMe_3)_2InCl_3]$[28] and $[(PMe_3)_2SnCl_4]$[29] exhibit *trans*-configured $PMe_3$ ligands in contrast to the *cis*-configured $[(PMe_3)_2SbCl_3]$.[26]

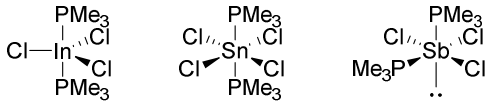



**Chart 2.** Observed solid-state geometries for *bis*-$PMe_3$ complexes of $InCl_3$, $SnCl_4$, and $SbCl_3$.

**3.2 Electronic Structure from Molecular Structure.** Beyond highlighting the configurational ambiguity of VSEPR structures, consideration of lone-pair stereochemical activity at the acceptor sites in phosphine complexes has also provided important insights into the electronic structure of such complexes. The most significant example of this relationship between electronic and molecular structure comes from compounds of the formula $(PR_3)_2C$, which have been described as *bis*-phosphine complexes of carbon on the basis of quantum-chemical calculations[30] and reactivity studies (*vide infra*). Foreshadowing their ability to behave as double-bases (*i.e.* engage two Lewis acids simultaneously), the structures of several derivatives adopt a bent geometry at the carbon atom with a P-C-P angle of *ca.* 140°, consistent with two stereochemically active lone pairs at the acceptor site. Importantly, the observed geometry refutes the alternative allenic electronic structure, which is expected to yield a linear geometry around carbon.

Another example is furnished by the phosphine coordination chemistry of M(I), where M = In or Ga.[31] The *tris*-phosphine complexes $[M(PPh_3)_3]^{1+}$ have pyramidal geometries, as expected for $AX_3E$ compounds, with P-M-P angles around 95°, consistent with occupation of the three *p*-orbitals by the ligands and a residual lone pair on the metal (Figure 5). When *tri*-$^t$butylphosphine was employed as a ligand, due to steric factors, only two of the phosphines bind the metal centres, giving a bent geometry (P-M-P angles of *ca.* 117°). Quantum-chemical analysis of model pyramidal and bent structures showed that the former geometry yields an essentially *s*-type lone-pair, while the latter results in a $sp^2$-type lone pair (in the P-M-P plane) and a vacant *p*-orbital as the lowest-unoccupied-molecular-orbital (LUMO). Consequently, the *tris*-phosphine complexes have the potential to behave as $\sigma$-donors via the

metal, while the *bis*-phosphine complexes are simultaneously σ-donors and π-acceptors. Experimental evidence distinguishing these two modes of reactivity has not yet been reported, nevertheless, the structural diversity clearly suggests a mechanism by which the coordination chemistry of an acceptor-centred lone pair might be tuned by the choice of phosphine ligand in a complex.

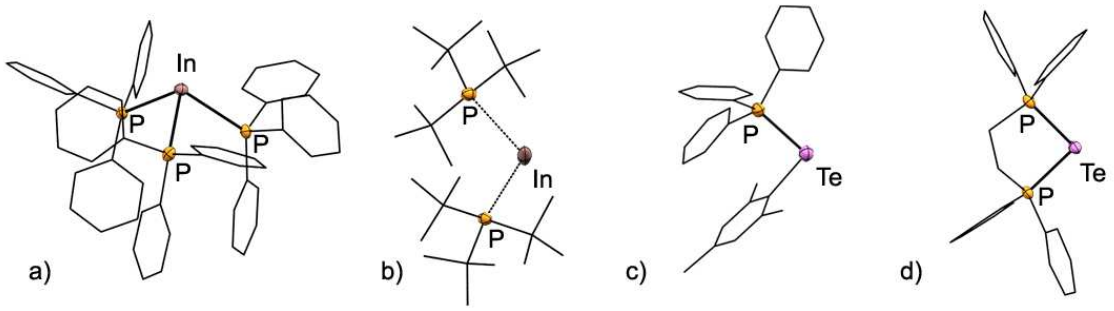



**Figure 5.** Molecular structures of a) $[(PPh_3)_3In]^{1+}$,[31] b) $[(P^tBu_3)_2In]^{1+}$,[31] c) $[(PPh_3)TeMes]^{1+}$,[32] and d) $[(dppe)Te]^{2+}$ in the solid state.[37]

In complexes where the acceptor site has more than one lone pair, the structural outcomes are somewhat trivial as a limited number of symmetric VSEPR-consistent geometries are observed. Therefore phosphine complexes of group 16 acceptors yield bent or T-shaped geometries (Figure 5 c,d).[32,33,34,35,36,37] In the sole element of group 17 that is relevant to this perspective, the presence of three lone pairs and two bonding pairs at the acceptor iodine necessitates a linear geometry. The acceptor chemistry of molecular $I_2$ is not widely recognized and may appear unusual. A comprehensive discussion, including a detailed analysis of steric effects has been presented.[16,17] As shown in Table 1, complexes of $I_2$ with strongly donating phosphines lead to shorter P-I bond distances and longer I-I distances, indicating that the acceptor orbital is the I-I $\sigma^*$ orbital. Consistently, with trialkylphosphines, solid- and solution-phase species described as $[IPR_3][I]$ are formed due to complete displacement of an iodide by phosphine from molecular $I_2$. Thus the arrested-displacement embodied in the so-called "spoke" complexes (Figure 6a) of the form $[(R_3P)XX]$ is a snapshot of the familiar hypervalent transition state for $S_N2$ nucleophilic displacement in an alkyl halide. On the basis of their established ligand-exchange chemistry, these complexes have been described as phosphine adducts of $I_2$ or as iodide adducts of iodophosphonium cations, the latter description emphasizing the preference for soft/soft iodide/iodine interactions over soft/hard iodide/phosphonium interactions.[16]

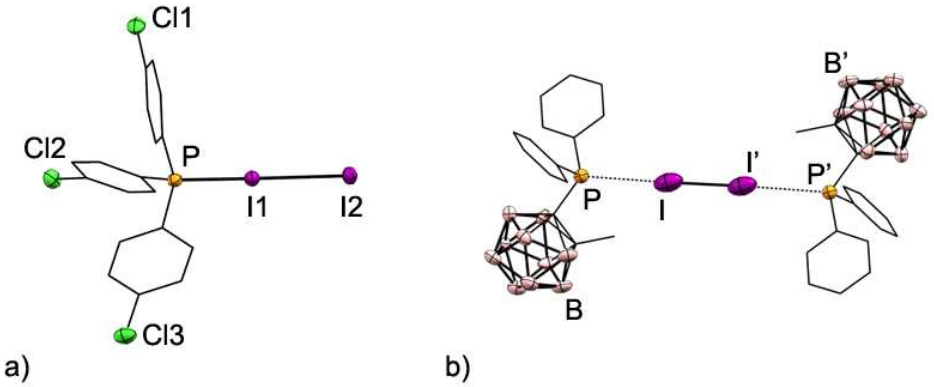



**Figure 6.** Molecular structures of a) a spoke complex $[(p\text{-ClPh})_3PI_2]$[17] and b) $[(MecarbPh_2P)I_2(PPh_2MeCarb)]$[18] in the solid state. Hydrogen atoms omitted for clarity.

Remarkably, molecular $I_2$ can even accept two phosphine ligands and the linear P-I-I-P framework (Figure 6b) has been reported[18] using the very weakly-coordinating carboranyl phosphine $PPh_2$(*MeCarb*). The P-I-I-P framework is apparently retained in halocarbon solutions, and this may be due to kinetic factors or additional intramolecular stabiliziation *via* weak contacts. With more strongly donating phosphines, spoke complexes or phosphonium salts are formed.[38] The phosphine coordination chemistry of molecular $I_2$ illustrates that very weakly-coordinating ligands have the ability to stabilize unusual *hypervalent* bonding motifs, complementing the ability of very strongly-coordinating ligands such as carbenes to stabilize unusual *hypovalent* bonding motifs.

**Table 1.** Key structural parameters in selected phosphine-diiodine adducts, $[(PR_3)I_2]$. All data taken from reference[33] and references within.

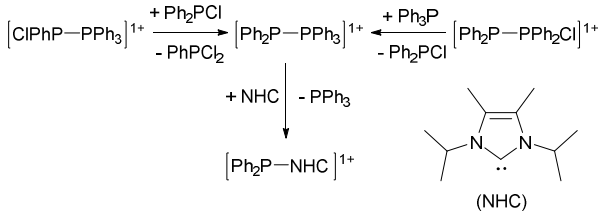
| Complex | d(P-I) | d(I-I) |
|---|---|---|
| $[(p\text{-}FC_6H_4)_3PI_2]$ | 2.507(3)<br>2.461(3) | 3.0807(12)<br>3.1529(11) |
| $[(p\text{-}ClC_6H_4)_3PI_2]$ | 2.488(2) | 3.1332(9) |
| $[(C_6H_5)_3PI_2]$ | 2.481(4) | 3.161(2) |
| $[(p\text{-}CH_3C_6H_4)_3PI_2]$ | 2.472(5) | 3.1815(13) |
| $[(p\text{-}(SCH_3)C_6H_4)_3PI_2]$ | 2.468(2) | 3.1946(8) |
| $[(p\text{-}(OCH_3)C_6H_4)_3PI_2]$ | 2.448(4) | 3.2123(7) |

## 4. Acceptor-centred reactivity in Phosphine Complexes of Lone Pair Bearing Lewis Acceptors

Complexes of *p*-block element centres that accommodate a lone pair offer reaction options that are not possible for transition metal centres. By analogy with transition metal coordination chemistry and organometallic chemistry, coordination complexes of *p*-block

element acceptors offer new possibilities for catalysis or small molecule activation. The established reactivity of the featured complexes is discussed here in three broad categories i) ligand exchange, ii) coordination and oxidation of lone pair bearing acceptor centres, and iii) reductive coupling.

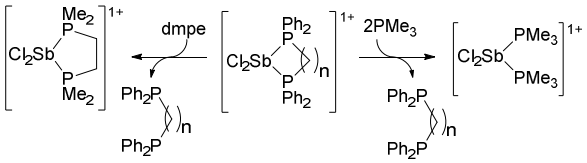
**4.1 Ligand Exchange.** The capacity to engage in ligand exchange chemistry is suggested by the description of a compound as a coordination complex. While ligand exchange should be broadly applicable in phosphine complexes of lone pair bearing acceptors, experimental efforts in our labs have focused on P-Pn complexes (Pn = P, As, and Sb), supporting the classification of these complexes as phosphine coordination compounds. For example, reaction of $[(PPh_2Cl)PPh_2]^{1+}$ with $PPh_3$ or NHC results in displacement of the weaker base by the stronger one to give $[(PPh_3)PPh_2]^{1+}$ or $[(NHC)PPh_2]^{1+}$, respectively (Scheme 1).[39] The non-trivial equilibrium between bound phosphinophosphonium complexes and their unbound constituents also enables acceptor exchange. Addition of $Ph_2PCl$ to a solution of $[(PPh_3)PPhCl]^{1+}$, liberates $PhPCl_2$ and yields the $[(PPh_3)PPh_2]^{1+}$.[40] This observation is interpreted as abstraction of chloride from $Ph_2PCl$ by $[PhClP]^{1+}$, since the latter is a more Lewis acidic phosphenium cation than $[Ph_2P]^{1+}$ due to the presence of an electronegative chlorine substituent at the phosphorus centre. The enhancement of Lewis acidity in phosphenium cations with very electronegative substituents was also noted in a computational study.[41]




**Scheme 1.** Formation of $[(PPh_3)PPh_2]^{1+}$ *via* i) acceptor exchange from $[(PPh_3)PPhCl]^{1+}$ or ii) ligand exchange from $[(PPh_2Cl)PPh_2]^{1+}$, and iii) formation of $[(NHC)PPh_2]^{1+}$ *via* ligand exchange from $[(PPh_3)PPh_2]^{1+}$.

Detailed mechanistic investigation of ligand exchange has been done for the P-P case, where both $S_N1$ and $S_N2$ pathways are implicated depending upon the steric bulk of the donor and the stability of the acceptor in the absence of a donor. For instance, displacement of the $PPh_3$ ligand from the phospholophosphonium cation $[(PPh_3)PC_4Et_4]^{1+}$ shows second-order kinetics consistent with an $S_N2$-type mechanism.[42] The most likely transition state is calculated to be only 18 kJ $mol^{-1}$ above the starting materials, and features a tetracoordinate geometry at the acceptor centre, with two identical and mutually-*trans* $PPh_3$ interactions. In

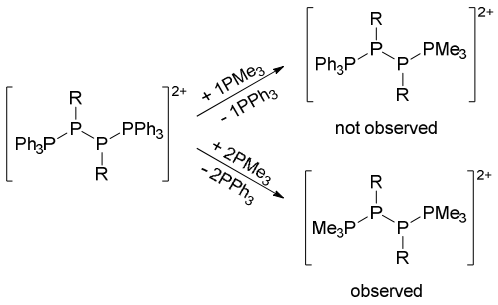
contrast, a dissociative pathway is evidenced in the reaction of $PMe_3$ with bis-(arylamino)phosphenium cations[43] and a computational analysis found no hypercoordinate transition state for these types of substitution reactions.[42] The enhanced steric bulk of the arylamino groups and the inherent stability of phosphenium cations attached to a π-donating heteroatom[44] results in the dominance of an $S_N1$ pathway in substitution reactions involving these acceptors.




**Scheme 2.** Ligand exchange in phosphine complexes of $[SbCl_2]^{1+}$ (n = 1 or 2).[74]

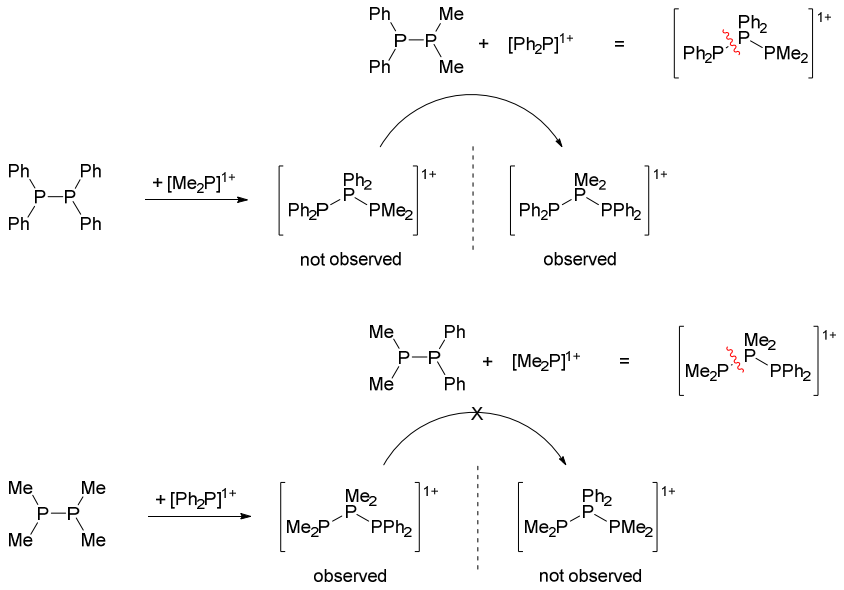
Ligand exchange at heavier main-group centres such as antimony and bismuth likely proceeds via associative mechanisms ($S_N2$ or AE), made possible by the larger covalent radii of these elements, which enables higher coordination numbers and stable hypervalent geometries. For example, while the reaction of $PMe_3$ with $PhPCl_2$ yields $[(PMe_3)_2PPh]^{2+}$,[24] the related reaction of $PMe_3$ with $PhSbCl_2$ yields the non-ionic, hypervalent neutral adduct $[(PMe_3)SbPhCl_2]$.[26] Displacement of a chloride ion is not observed even in the presence of excess phosphine. By comparison, ligand exchange occurs readily in cationic phosphine complexes of antimony (Scheme 2).[74]

An intriguing feature of some ligand exchange reactions is the strong preference for homoleptically substituted acceptor centres. As shown in Scheme 3, the mixed $PPh_3/PMe_3$ derivative is not observed when a one equivalent of $PMe_3$ is added to a solution of $[(PPh_3)RPPR(PPh_3)]^{2+}$. Instead a 1:1 mixture of the starting material and *bis*-$PMe_3$ substituted dication $[(PMe_3)RPPR(PMe_3)]^{2+}$ is obtained. When two equivalents of $PMe_3$ are added, clean conversion to $[(PMe_3)RPPR(PMe_3)]^{2+}$ is observed, together with quantitative liberation of $PPh_3$.[45] Analogous experiments targeting displacement of a single stibine ligand from $[(SbPh_3)RPPR(SbPh_3)]^{2+}$ by an equivalent of arsine or phosphine ligand consistently give only the homoleptic derivatives, $[(PnPh_3)RPPR(PnPh_3)]^{2+}$ (Pn = As, P) and unreacted starting material.[46] The reason for this preference is not yet understood.



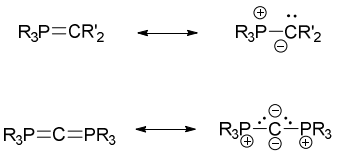

**Scheme 3.** Ligand exchange in 2,3-diphosphino-1,4-diphosphonium dications.

An intramolecular ligand exchange reaction is observed in 1,3-diphosphino-2-phosphonium monocations, $[R_2PP(R_2)PR_2]^{1+}$ (Scheme 4), further highlighting the lability of coordinate P-P bonds. These cations are readily generated by the reaction of diphosphines ($R_2PPR_2$) with chlorophosphines ($R'_2PCl$) in the presence of a halide abstractor. When R = Me and R' = Ph, the expected asymmetrically-substituted cation $[Me_2PP(Me_2)PPh_2]^{1+}$ is obtained. However when R = Ph and R' = Me, only the symmetrically substituted $[Ph_2PP(Me_2)PPh_2]^{1+}$ is observed. An intramolecular ligand exchange is proposed that involves dissociation of a $[Ph_2P]^{1+}$ fragment from the $[Ph_2PP(Ph_2)PMe_2]^{1+}$ cation and re-association at the more basic alkylphosphine site of the resulting neutral diphosphine, $Ph_2PPMe_2$. When R = Me and R' = Ph, this rearrangement is inhibited by the high Lewis acidity of $[Me_2P]^{1+}$ (calculated fluoride-ion-affinity of 960 kJ $mol^{-1}$),[41] which disfavours dissociation of $[Me_2PP(Me_2)PPh_2]^{1+}$ into $[Me_2P]^{1+}$ and neutral $Me_2PPPh_2$. Even if such dissociation occurs to a small extent, the subsequent re-association engages the more basic dimethylphosphine moiety of $Me_2PPPh_2$, giving the observed product.




**Scheme 4.** Insertion of phosphenium cations into P-P bonds.

**4.2 Coordination and Oxidation of Lone Pair Bearing Acceptor-Centres**. Unlike coordination complexes of transition metal acceptors, the complexes discussed here feature a distinct acceptor-centred lone pair, potentially capable of binding to another acceptor or oxidation. The term "push-pull" has been used to describe complexes that feature an element centre acting as both a Lewis acid and a Lewis base. Some remarkable examples of the application of this strategy have been the subject of a recent Perspective article, and most feature the use of N-heterocyclic carbene stabilized acceptors behaving as donors.[47]



**Scheme 5.** Resonance structures for phosphonium ylides (top) and double ylides (bottom).

Analogous Lewis-basic behaviour for phosphine stabilized complexes has only been reported for a few acceptor elements. In group 14, the most diverse examples are from the coordination chemistry of phosphonium ylides and double ylides (carbodiphosphoranes). Both species feature a highly-nucleophilic carbon acceptor with a maximum of one and two lone pairs, respectively, available for coordination (Scheme 5). Coordination of phosphorus ylides to transition metals is well-established and has been reviewed[48] but their use as ligands in main-group chemistry is rare. The structures of $[(Ph_3PCMe_2)BH_3]$,[49] $[(Ph_3PCHMe)SbCl_3]$,[50] and $[(Ph_3PCMe_2)GeCl_2]$[49] are shown in Figure 7 and represent complexes of ylides with prototypical neutral Lewis acids from groups 13, 14 and 15.

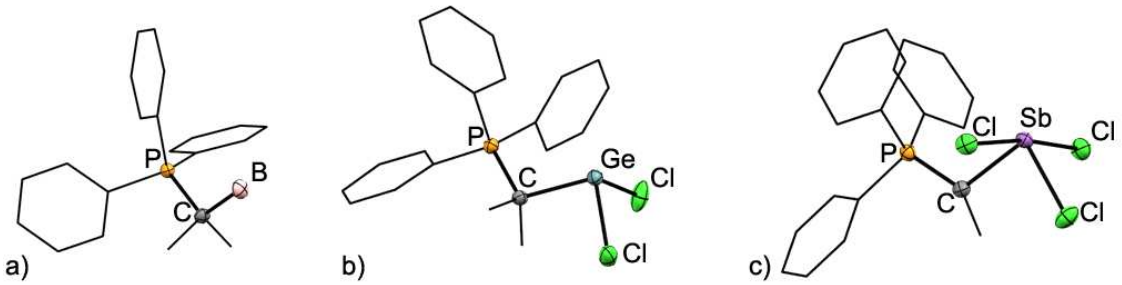



**Figure 7.** Molecular structures of a) $[(Ph_3PCMe_2)BH_3]$,[49] b) $[(Ph_3PCMe_2)GeCl_2]$,[49] and c) $[(Ph_3PCMeH)SbCl_3]$[50] in the solid state.

Investigations into the electronic structure of carbodiphosphoranes revealed them to be good $\sigma$- and $\pi$-donors (*c.f.* NHCs which are $\sigma$-donors and $\pi$-acceptors), capable of binding to one or two Lewis acids.[51] These predictions have been confirmed experimentally and prototypical structures of carbone complexes with one and two acceptors are shown in Figure 8(a-b).

The structures of an interesting set of complexes, $[(PR_3)_2Pb(Cr(CO)_5)_2]$ (R = Me, Et, and $^n$Bu) have been reported, showing P-Pb-P angles in the 86.93(5)-95.00(4)° range and Cr-Pb-Cr angles in the 127.73(5)-129.80(3)° range (Figure 8c).[52] While these complexes were made by displacement of halides from the Pb(II) precursors, $[X_2Pb(Cr(CO)_5)_2]^{2-}$ (X= Cl, Br, I), we interpret these compounds as chromium complexes of a dibasic Pb(0) donor, a plumbylone, as such complexes are predicted to be stable in theoretical studies.[53] An uncoordinated plumbylone has not been reported and ligand displacement from these chromium complexes may be one route to their discovery.

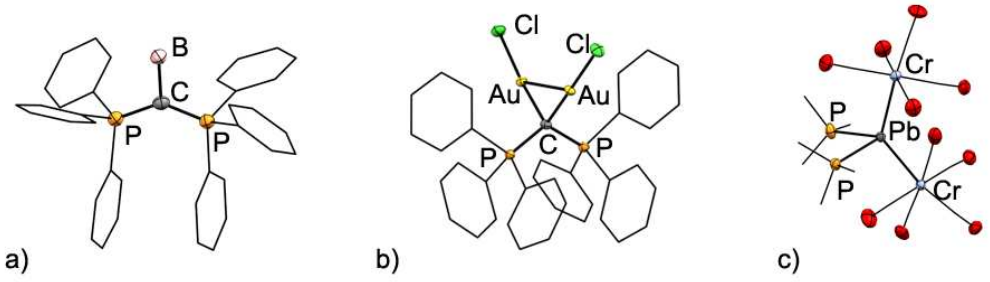
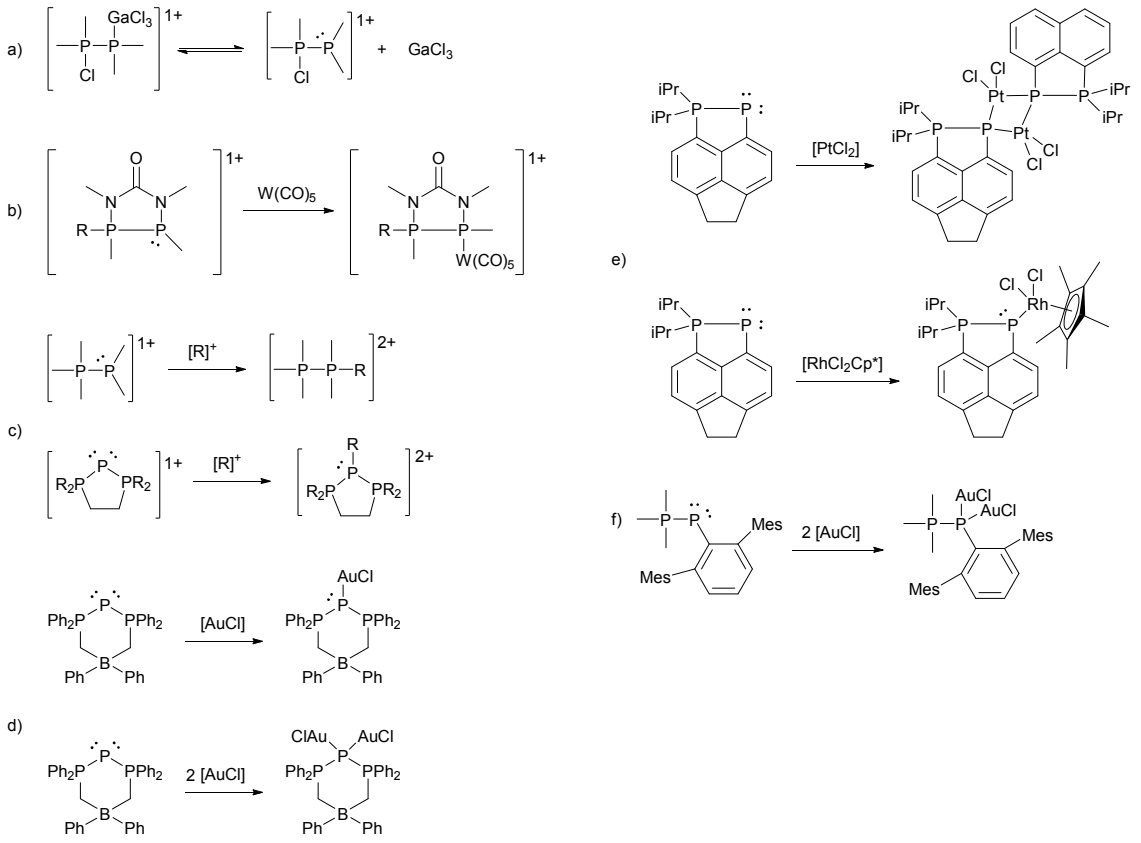



**Figure 8.** Molecular structures of a) $[(PPh_3)_2CBH_3]$,[54] b) $[(PPh_3)_2C(AuCl)_2]$[55], and c) $[(PMe_3)_2Pb(Cr(CO)_5)_2]$.[52]

The potential for the phosphine centre in phosphinophosphonium cations to behave as a donor is demonstrated (Scheme 6a) by the isolation of $[Me_2ClPP(Me_2)GaCl_3]^{1+}$,[56]

spectroscopic characterization of related $[RCl_2PP(R)(Cl)GaCl_3]^{1+}$ cations,[57] and isolation of transition metal complexes like the tungsten complex of a cyclic phosphinophosphonium (Scheme 6b).[58,59] The phosphine centre in $[(PMe_3)PMe_2]^{1+}$ can be alkylated to give $[P_2Me_6]^{2+}$, and $[(PMe_3)P(Me_2)(^tBu)]^{2+}$,[60] which is analogous to methylation of a triphosphenium cation (Scheme 6c).[61] Single and double coordination of transition metals at lone pairs of neutral P(I) centres has also been reported (Scheme 6d-f, Figure 9a and 9b).[62,63,64] The broad array of coordination chemistry that is now established for phosphine stabilized cationic and neutral P(I), and P(III) centres bodes well for the application of these species as an interesting family of ligands in the context of transition metal catalysis. The observation that other heavy acceptor centres such as antimony and bismuth show marked lone pair stereochemistry in their phosphine complexes suggests the possibility of engaging these centres in further coordination, as reported for phosphorus.[26, 65]




**Scheme 6.** Selected examples of phosphine complexes behaving as donors *via* phosphorus acceptor centred lone pairs. See text for references.

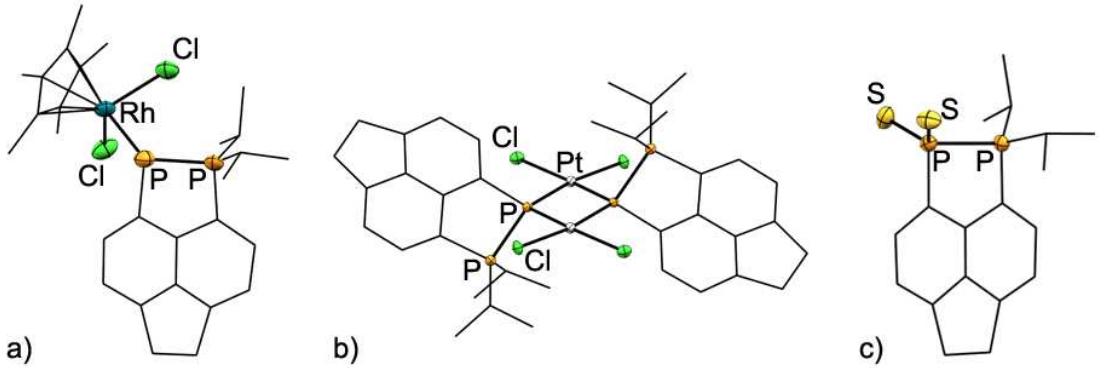
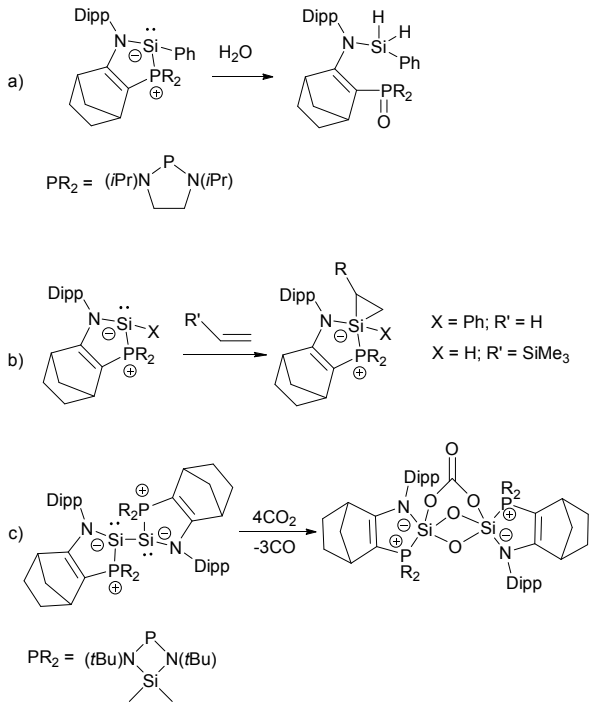


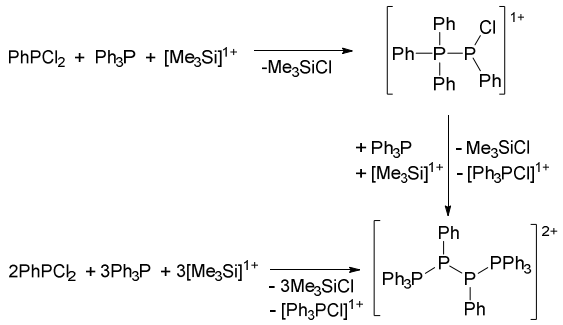

**Figure 9.** Acceptor centered a) single coordination, b) double coordination, and c) oxidation for a phosphine-stabilized phosphorus(I) acceptor.[63]

Examples of acceptor-centred two-electron oxidation are rare in main-group phosphine complexes as the phosphine ligand is itself susceptible to oxidation but some examples are known (Figure 9). Phosphonium sila-ylides, silicon analogues of phosphonium ylides, are transient species that can be isolated in rare instances using bulky substituents and intramolecular coordination.[66,67] For one family of complexes, a variety of two-electron oxidations have been demonstrated (Scheme 7).[67,68,69] In particular, the activation of small alkenes and $CO_2$ (Scheme 7 (b-c)) exemplifies the highly nucleophilic nature of the silicon atom in these systems.




**Scheme 7.** Silicon-centred two-electron oxidation in phosphonium sila-ylides.

**4.3 Reductive coupling**. Reductive coupling of phosphine-stabilized halo-element centres is analogous to reductive coupling of carbene-stabilized halo-element centres. However, unlike carbenes, phosphines are redox sensitive, acting as both a ligand and as a reducing agent. We first encountered such reactivity in the reaction of $PhPCl_2$ with excess halide abstracting agent TMSOTf and excess $PPh_3$, which we assumed would give the dicationic 2-phosphino-1,3-diphosphonium cation, $[(PPh_3)_2PPh]^{2+}$ as a triflate salt based on the previously reported synthesis of this cation as a tetrachloroaluminate salt several decades ago by Schmidpeter.[70] However, the $^{31}$P-NMR spectrum of the reaction mixture after 48 hours showed an AA'BB' pattern instead of the expected $AX_2$ pattern, corresponding to $[(PPh_3)PhPPPh(PPh_3)]^{2+}$, together with $[PPh_3Cl]^{1+}$.[71] The tetraphosphorus dication can be equivalently viewed as containing either two central P(I) phosphine centres bound to two terminal P(IV) phosphonium centres, or two central P(II) phosphenium centres bound to two terminal P(III) phosphine centres, depending upon the perceived localization of charge. The overall reaction is summarized in Scheme 8, and exemplifies the use of a phosphine as both a ligand and a reducing agent.




**Scheme 8.** Synthesis and reductive coupling of chlorophosphinophosphonium cations.

Reactions involving $Ph_3Sb$ instead of $PPh_3$ give the heteroleptically substituted $[(SbPh_3)RPPR(SbPh_3)]^{2+}$ dications together with the $[Ph_3SbCl]^{1+}$ cation as the oxidation product. These mixed P-Sb cations demonstrate a reversal of traditional donor (non-metal) and acceptor (metal) roles and undergo the expected displacement of the stibine ligands in the presence of more basic $AsPh_3$ or $PPh_3$ donors as discussed earlier in the context of ligand exchange reactivity.

The presence of a lone pair at the acceptor sites in $[(PnPh_3)PhPPPh(PnPh_3)]^{2+}$ (Pn = P, As, Sb) dications gives rise to unique stereochemical outcomes due to the high umbrella inversion barriers at tricoordinate phosphorus centres (Chart 3).[72] The distribution of *meso* or

*RR/SS* diastereomers depends on the substituent at the acceptor phosphorus centre. When R = Ph or Me and R' = Me, only the *RR/SS* enantiomers are observed, whereas when R = Me or Ph and R' = Ph, both the *meso* and *RR/SS* forms are observed (Figure 10).[45,46]

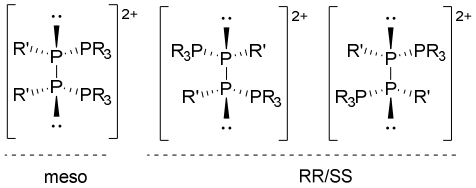



**Chart 3.** Stereochemical outcomes for 2,3-diphosphino-1,4-diphosphonium dications.

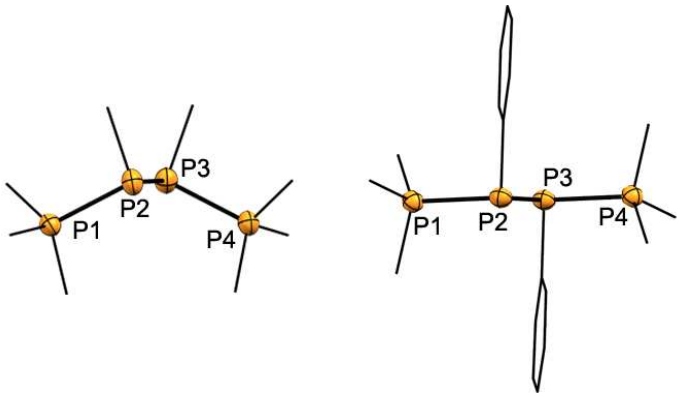
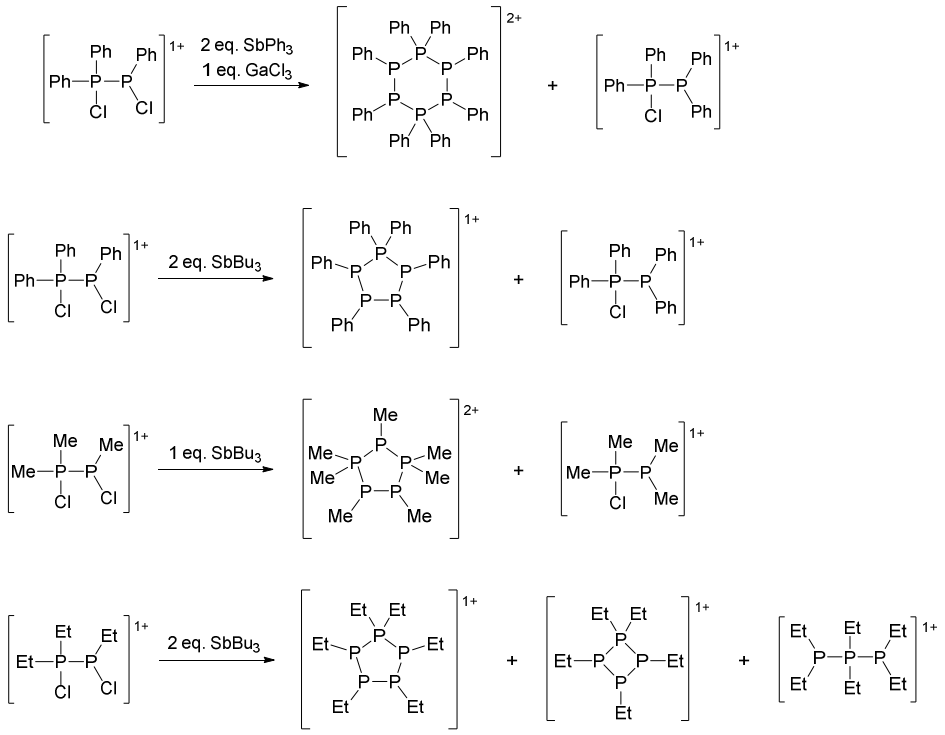


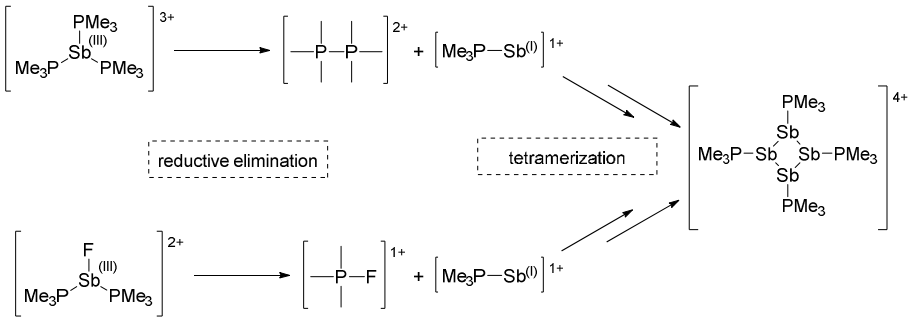

**Figure 10.** Molecular structures of the *S,S*-$[(PMe_3)(Me)PP(Me)(PMe_3)]^{2+}$ (left) and *meso*-$[(PMe_3)PhPPPh(PMe_3)]^{2+}$ (right) dications in the solid state. [45,46]

A seemingly trivial change from the use of $R_3P$ to $R_2PCl$ as the donor phosphine unlocks numerous secondary reductive coupling pathways yielding di-, tri-, tetra-, penta-, or hexa-phosphorus containing cations depending upon the choice of reducing agent and substituent at the phosphorus centres (Scheme 9). In each case, the oxidation product is $[R_3SbCl]^{1+}$. The moderate inversion barrier at the tricoordinate, lone-pair bearing phosphorus centres results in temperature-sensitive spin systems and diastereomeric mixtures at room temperature.[73]




**Scheme 9.** Formation of cyclic and linear *catena*-phosphorus cations by reductive coupling of chlorophosphinochlorophosphonium cations.[73]

The reductive coupling methodology has recently been extended to include phosphine complexes of lone-pair bearing Sb(III) centres. We have reported a series of compounds featuring anionic, neutral, monocationic and dicationic chloroantimony centres bound by one or two phosphine ligands.[26,74] The highly-electrophilic *tris*-phosphine cation, $[(PMe_3)_3Sb]^{3+}$, was isolated, but is unstable and undergoes reductive elimination of a diphosphonium dication, $[P_2Me_6]^{2+}$, at ambient temperatures and cyclizes to give the unique Sb(I) tetraphosphine complex, $[(PMe_3)_4Sb_4]^{4+}$ as a quantitative product (Scheme 10). This tetracation is also formed quantitatively via reductive elimination of a fluorophosphonium cation, $[PMe_3F]^{1+}$, from the fluoroantimony dication, $[(PMe_3)_2SbF]^{2+}$ with added phosphine.[11] Recently, we have also reported the reductive elimination of $[P_2Me_6]^{2+}$, from the reaction of $PMe_3$ with $Ph_3Pn(OTf)_2$ (Pn = Sb and Bi).[75]




**Scheme 10.** Assembly of a cyclic-tetrastibinotetraphosphonium tetracation by reductive elimination from highly charged phosphine-antimony complexes.

In each case, the distinction between coordination chemistry and redox chemistry is defined by the electrophilicity of the acceptor site. These examples further illustrate the key difference between carbenes and phosphines as ligands at low-valent main-group centres. Whereas the former are redox resistant ligands that behave as strong $\sigma$-donors and $\pi$-acceptors, the latter are best described as σ-donors that can simultaneously behave as reductants. The ready availability of a large array of sterically and electronically diverse phosphines inspires ongoing efforts in our laboratory to perform controlled reductive catenation at electrophilic main-group centres.

## 5. Conclusions and Outlook

Phosphine complexes of lone-pair bearing acceptors are now known for almost all elements in groups 13-17, except boron, aluminum, oxygen, and some halogens. However, few examples are known for most elements and, in particular, *tris*-phosphine complexes are only known for four elements. In some cases, such as the group 14 tetrylones, interpretation of compounds as phosphine coordination complexes has only recently been made, with important consequences for their reaction chemistry, and other analogous compounds may be reinterpreted as phosphine complexes in the future. The presence of a stereochemically active lone pair at the acceptor center offers unique structural and chemical outcomes that are not observed for phosphine complexes of transition metal elements, realising a new direction in coordination chemistry. Numerous configurational possibilities exist and many have been demonstrated for antimony as an acceptor. Complexes have been shown to undergo acceptor centered reactivity including ligand/acceptor exchange and coordination/oxidation and reductive coupling. In principle, each of these reaction modes can be modulated by appropriate choice of phosphine ligand and its steric and electronic properties, offering new

axes of investigation for studying the structures and reactivity of such complexes. The establishment of such structure-function relationships in main-group phosphine complexes may permit development of a wide array of useful applications in catalysis and small molecule activation.

**Acknowledgements**

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