New synthetic opportunities using Lewis acidic phosphines

Neil Burford* and Paul J. Ragogna

*Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3.
E-mail: Neil.Burford@dal.ca*

Phosphines are traditional Lewis bases or ligands in transition metal complexes. In spite of their electron-rich (lone pair bearing) nature, an extensive coordination chemistry is developing for Lewis acidic phosphines, which highlights a new synthetic methodology leading to new structure and bonding.

Introduction

The developing chemistry of phosphorus is renowned for 'breaking the rules'[1] that are well established in organic chemistry. As the renaissance associated with stable carbenes defines new directions in carbon chemistry,[2,3] each novel bonding

Neil Burford is a native of Liverpool, England. He obtained a BSc honours degree in 1979 from Cardiff University and a PhD at the University of Calgary under the supervision of Professor Tristram Chivers. He worked with Professor Ronald Cavell at the University of Alberta as a Postdoctoral Fellow and with Professor Jack Passmore at the University of New Brunswick as a Research Associateship. In 1987, Neil was appointed Assistant Professor at Dalhousie University and was promoted to Professor in 1995. An Alexander von Humboldt Fellowship was awarded in 1996, enabling him to collaborate with Professor Peter Jutzi at the University of Bielefeld. Neil was selected as a Killam Professor at Dalhousie University in 1998, appointed Harry Shirreff Professor of Chemical Research in 2000 and became a Canada Research Chair (Tier 1) in 2001. His research is generally classified as synthetic chemistry involving the heavy elements of Group 15 with a focus on the discovery of new structure and bonding.

Paul Ragogna was born in 1974 and is a native of St. Catharines, Ontario, Canada. He joined the army in 1992 and from 1994–1995 served on a United Nations Peacekeeping mission in Croatia with the 1st Battalion of the Royal Canadian Regiment. He graduated from Brock University in 2000 with a BSc honours degree in chemistry gaining experience in synthetic inorganic chemistry of cationic boron compounds under the supervision of Professor J. Stephen Hartman and in EPR spectroscopy from Professor Art van der Est. Currently Paul is in his third year of doctoral studies under the supervision of Professor Neil Burford where he holds a Natural Sciences and Engineering Research Council Postgraduate Scholarship, a Walter C. Sumner Fellowship and was awarded a Douglas E. Ryan Prize. He is a synthetic inorganic chemist and is currently focused on the synthesis and characterisation of low coordinate phosphorus cations, leading to new structure, bonding and reactivity.


Neil Burford   Paul Ragogna

arrangement for phosphorus opens a new chapter in terms of structure, bonding and reactivity in the chemistry of this diverse element. This article highlights the emerging coordination chemistry of phosphines as acceptors that is challenging conventional Lewis acid–base chemistry.

'Coordination chemistry' usually refers to bonding interactions involving donation from electron-rich (lone pair bearing) non-metals (Lewis bases or ligands) to electron deficient metals (Lewis acids or acceptors). As such, this bonding model is restricted to the acceptor chemistry of transition metals and the elements of Groups 1, 2 and 13.

Reports of metal complexes behaving as ligands towards other metals[4] introduce new synthetic opportunities and novel bonding possibilities. In a similar context, electron-rich phosphine centres are observed to behave as Lewis acceptors exhibiting structural diversity that requires evolution of the simple bonding models for more general applicability.

PBr_4^- represents the simplest example of a phosphine (PBr_3) behaving as an acceptor (for bromide).[5] The disphenoidal structure of this complex anion is consistent with retention of a lone pair on phosphorus **1a**, but can be considered in the context of coordination chemistry **1b**.

A wide range of compounds representing complexes of phosphine centres involved in multiple bonding (**2b** and **3b**) have now been reported that demonstrate the versatile Lewis acidity of phosphines. Compounds described in this article can be drawn using Lewis conventions (**1a**, **2a**, **3a**), but in most cases coordinate interactions are symbolised with arrows (**1b**, **2b**, **3b**), as for transition metal complexes. Nevertheless, the reader should not misinterpret or over-interpret molecular line drawings, keeping in mind that the novel bonding in effect in most of these compounds requires a more sophisticated model to understand some structural features.

1a   **2a**   **3a**

1b   **2b**   **3b**
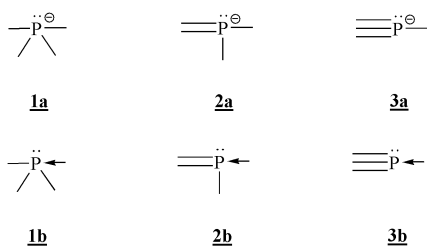
As a foundation for discussion, we first overview the bonding versatility accessible by phosphorus and the energetic factors that govern the Lewis acceptor capabilities of phosphines. Discussions of specific examples are categorised according to the type of ligand and deal primarily with molecular structure, but extensive spectroscopic data is available for all compounds and Table 1 provides a catalogue of representative examples with their ³¹P NMR chemical shift values.

Bonding environments for phosphorus

To appreciate the potential diversity of structure and bonding for phosphorus, Fig. 1 presents classic Lewis representations for each possible coordination number (1–6). Many of these 'bonding environments' have been observed in stable compounds, including those involving pπ-bonding with phosphorus.

Phosphines provide the most familiar three coordinate bonding environment (**K**) for phosphorus, but the chemistry of **L**[6] and **M**[7] are being actively developed. Phosphonium (**O**), phosphorane (**P**, **T**) and phosphate environments (**Q**, **R**, **S**, **U**) are also typical representatives in the chemistry of phosphorus. Representations **A–J** can be described as coordinatively unsaturated (less than a full or typical complement of ligands or substituents) with the potential for pπ-bonding. Examples of mono-coordinate phosphorus centres **A**, **B** and **D** are evident in phosphaalkynes,[8] phosphadiazonium (iminophosphenium)

Table 1 ³¹P NMR chemical shifts for representative complexes of Lewis acidic phosphines

	δ ³¹P/ppm	Ref.
Mes*NP(carbene)Cl	172	7
[Mes*NP(carbene)]OTf	339	7
[Ph₂P(carbene)]AlCl₄	−27	26
[Mes*NP(benzene)]Ga₂Cl₇	93	16
[Me₂NCH₂CH₂N(Me)PCl]Cl	165	34
[{Me₂NCH₂CH(Bu)O}₂P]Cl	103	35
[Mes*NP(quinuclidine)]OTf	144	37
[Mes*NP(dipyridine)]OTf	54	37
[Ph₂P(DMAP)]OTf	88	^{a}
[(ⁱPr₂N)₂P(DBN)]PF₆	108	38
{Cl₂Al(NSiMe₃)₂P}(quinuclidine)	208	41
[Ph₂P(Ph₂PCl)]GaCl₄	78, 3	48
[P(PPh₃)₂]AlCl₄	−174	21
[Mes*NP(PPh₃)]OTf	53, −5	52
[(Me₃Si)₂CP(PPh₃)]AlCl₄	300, 20	54
Ph₂P(gallane)OTf	−57	59

Carbene = **4**; gallane = {DippNC(Me)CH₂C(Me)N(Dipp)}Ga; Dipp = 2,6-diisopropylphenyl. ^{a} N. Burford, P. Losier, A. D. Phillips, P. J. Ragogna and T. S. Cameron, *Inorg. Chem.*, submitted.
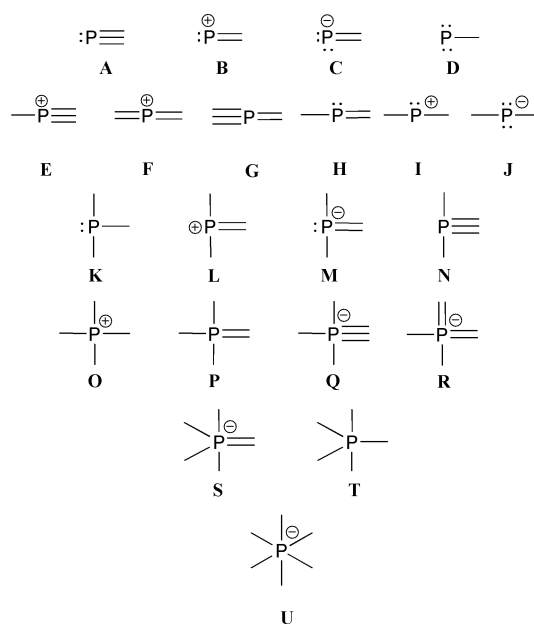

Fig. 1 Potential bonding environments for phosphorus.

cations[9] (**A** or **B**) and phosphinidines,[10] respectively. Examples of isolated compounds containing **C**, **E**, **F** or **G** have not been reported. While **H** is representative of the bonding in many examples of phosphaalkenes[11] and iminophosphines,[12] the distinction with **I** is subtle in that spectroscopic and structural data for phosphenium cations (**I**) also indicate π-delocalisation onto phosphorus.[13,14] The structural possibilities that have not yet been exploited represent key synthetic targets in the systematic and rational development for the chemistry of phosphorus.

The coordinatively unsaturated phosphine bonding environments **A–J** are most suited for coordination chemistry as Lewis acceptors in terms of steric considerations. The cationic species **B**, **E**, **F** and **I** are likely to exhibit the greatest Lewis acidity by virtue of the molecular charge, and most of the examples described below are representative of complexes involving **B** and **I**.

Phosphadiazonium derivatives [RNP]X (R = Mes* = 2,4,6-tri-*tert*-butylphenyl; X = Cl,[9] Br,[12] I,[12] OTf,[15] AlCl₄,[9] GaCl₄,[16] Ga₂Cl₇ [16]), analogues of diazonium salts, contain a cationic representative of **A** and are isoelectronic with phosphaalkynes (RCP).[8] Consistently, the solid state structures reveal very short NP distances (<1.50 Å), a C–N–P angle of close to 180°, and

the data from vibrational sprectra are interpreted in terms of a multiple NP bond order.[17] The P–X distances in these compounds vary considerably indicating different degrees of P–X heterolytic dissociation or ionicity. For example, RNPCl [P–Cl 2.142(4) Å][9] is essentially covalent (representing **H**), while [RNP]AlCl₄ (shortest P–Cl 3.16 Å)[9] is interpreted as an ionic compound (representing **A** or **B**).

Phosphenium cations[13,18,19] have been most extensively developed as compounds containing a dicoordinate phosphine (**H**) environment. The ability of phosphorus to access a diverse range of bonding options is demonstrated by the variety of bonding models (Fig. 2) that are required to rationalise the
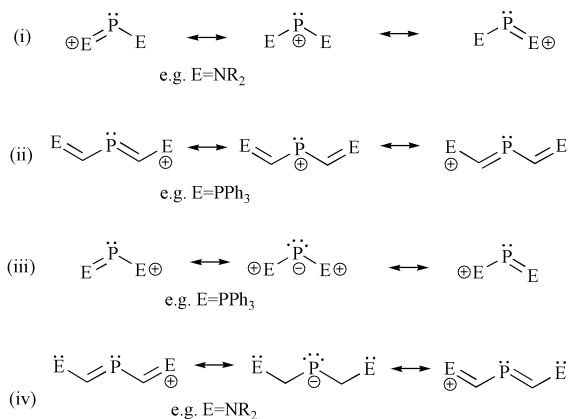
Fig. 2 Bonding models for phosphenium cations.

examples of isolated 'phosphenium' salts. All examples involve the phosphorus centre on an allylic manifold, which is mediated by the electronic structure of the peripheral components. Aminophosphine derivatives [represented by (i)] are classical 3-centre 4π-electron frameworks[13] and are related to phosphaallylphosphines[14,20] [represented by (ii)] by virtue of the extended conjugation through d orbital availability at the phosphorane units. Models (i) and (ii) are distinct from the 3-centre 2π-electron framework of triphosphenium cations[21,22] [represented by (iii)] and the 5-centre 6π-electron phosphamethine cyanines[19,23] [represented by (iv)], which both involve a phosphide resonance contributor. Therefore, only (i) and (ii) have access to the non-octet (6-valence electron phosphorus centre) resonance contributor that illustrates the carbene analogy responsible for the common 'phosphenium' nomenclature, and which is typically used to rationalise the reactivity of these compounds.[13]

Observation of short P–N or P–C bond lengths and planar environments for N and C provide evidence of π-resonance for derivatives of (i), (ii) and (iv), however, P–P bonds in triphosphenium cations (iii) are typical of single bonds and an alternative bonding model is more appropriate involving P→P coordinate bonds (see below). Resonance models (i), (ii), (iii) and (iv) should not be overinterpreted in terms of molecular positive charge distribution.

## Energetic factors governing phosphine acceptors

The acceptor capability of a Lewis acid is governed by the thermodynamic factors associated with the formation of the adduct bond(s) and consequential structural adjustments of the donor and the acceptor. For neutral adducts of neutral phosphine acceptors, structural adjustments are minimal (see below), so that the adduct bond energy is essentially determined by the HOMO (donor)–LUMO (acceptor) interaction. The LUMO energies of phosphine cations are naturally lower than those of corresponding neutral phosphines, highlighting cations as superior acceptors. The π*-LUMO of coordinatively unsaturated phosphines are localised at the more electropositive phosphorus centre,[13] so that both kinetic and thermodynamic

factors direct donor activity to phosphorus. More specifically, the LUMO is orthogonal to the bond axes and the non-bonding electron pair (usually designated as the 'lone pair'). In this context, the coordinate interaction(s) are modeled to be perpendicular to the plane of the Lewis acceptor.[24] In addition, the solid state structures consistently show a distinctively pyramidal environment illustrated by the largest angles at the acceptor phosphorus centre listed in Tables 2 and 3.

Phosphines bearing good leaving groups are prone to anion displacement on interaction with a neutral ligand. The energetics of the resulting ionic system benefits from the introduction of an additional electrostatic component, that may be principally responsible for the thermodynamic preference for the observed product.

Complexes of phosphines with carbene ligands

The strong Lewis basic character of the Arduengo carbene **4**[25] highlights it as an ideal ligand for phosphines. Complexes have been isolated from reactions of **4** with Mes*NPCl,[7] Mes*NPOTf[7] and Ph₂PCl.[26] The solid state structures of the complexes reveal varying degrees of anion displacement.
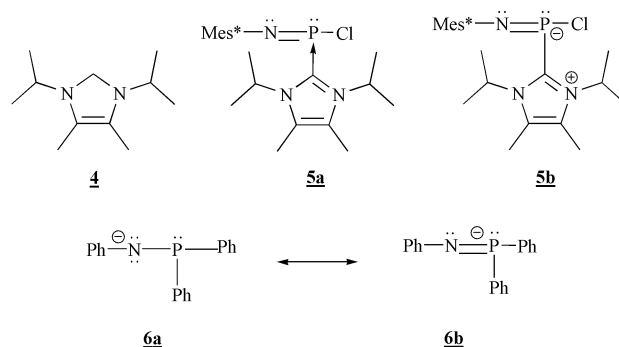
A primarily covalent arrangement is observed for the chloride complex (Fig. 3), which involves a tricoordinate pyramidal phosphine centre with two interactions [P–Cl 2.471(2); P–C 1.886(5) Å] that are typical of single bonds and one N–P bond [1.585(5) Å] that is comparable in length with the multple bond assigned for the free acid [Mes*NPCl, N–P 1.509(2) Å].[9] As such, the structure is best described by **5a** and represents a unique example of an iminophosphide bonding environment **5b**. Salts of anions assigned as iminophosphides **6b**[27] (also referred to as iminophosphoranides)[28] have solid state structures best described as the corresponding phosphinoamides **6a**,[29,30] the relative stability of which has been theoretically modeled.[31] Therefore, the coordination chemistry of the unsaturated phosphine Mes*NPCl (**H**) provides a new synthetic approach to access new structure and bonding for phosphorus.

The structure of [Mes*NP(carbene)]OTf[7] is more ionic than Mes*NP(carbene)Cl, with the cation (Fig. 4) complex **7** essentially dissociated from the anion [P–O 2.951(5) Å; cf. Mes*-NPOTf, P–O 1.923(3) Å].[15] Nevertheless, the NPC fragment
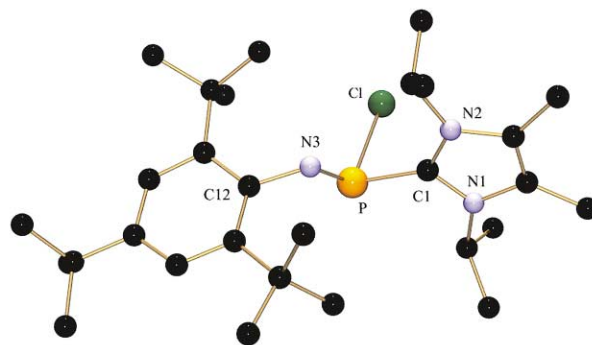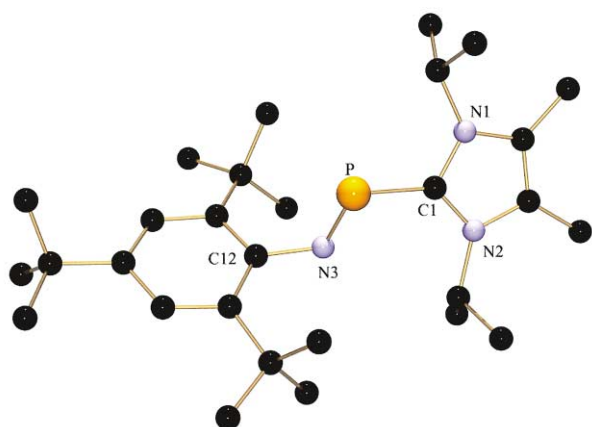

**Fig. 3** Structure of Mes*NP(carbene)Cl.

Table 2 N(ligand)–P distances (Å) and the largest bond angle (°) at phosphorus in amine and imine complexes of Lewis acidic phosphines

	N–P	Largest P angle	Ref.
[Me$_2$NCH$_2$CH$_2$N(Me)PCl]Cl	1.84	1.62	34
[{Me$_2$NCH$_2$CH(Bu)O}$_2$P]Cl	2.05, 2.06		35
[Mes*NP(quinuclidine)]OTf	1.933(2)	103.7(1)	37
[Mes*NP(pyridine)]OTf	1.958(8)	107.8(4)	7
[Mes*NP(dipyridine)]OTf	2.066(4), 2.065(4)	113.0(2)	37
[Ph$_2$P(DMAP)]OTf	1.78(1)	104.4(7)	a
[(^{i}Pr$_2$N)$_2$P(DBN)]PF$_6$	1.796(3)	101.6(2)	38
{Cl$_2$Al(NSiMe$_3$)$_2$P}(quinuclidine)	2.038(9)	103.7(1)	41
{Cl$_2$Al(NSiMe$_3$)$_2$P}$_2$(TMEDA)	2.110(6)	100.7(3)	41

a N. Burford, P. Losier, A. D. Phillips, P. J. Ragogna and T. S. Cameron, *Inorg. Chem.*, submitted.

Table 3 P(ligand)–P distances (Å) and the largest bond angle (°) at the phosphorus acceptor in phosphine complexes of Lewis acidic phosphines

	P–P	Largest P angle	Ref.
[Ph$_2$P(Ph$_2$PCl)]GaCl$_4$	2.205(4)	106.8(6)	48
[Ph$_2$P(Ph$_3$P)]OTf	2.230(1)	104.2(1)	48
[N(R)CH$_2$CH$_2$N(R)P(Me$_3$P)]OTf	2.3065(9)	109.13(8)	50
[{GaCl$_3$}Me$_2$P(Me$_2$PCl)]GaCl$_4$	2.138(7)	110.5(3)	47
[P(Ph$_3$P)$_2$]AlCl$_4$	2.137(6), 2.128(6)	103.0(3)	21
[Mes*NP(PPh$_3$)]OTf	2.625(2)	109.8(2)	52
[(Me$_3$Si)$_2$CP(PPh$_3$)]AlCl$_4$	2.267(2)	101.6(2)	54
[Mes*PP(PPh$_3$)]BPh$_4$	2.206(1)	98.8	53

Fig. 4 Structure of the cation in [Mes*NP(carbene)]OTf.

[N–P 1.574(4) Å] is structurally similar to that in the covalent chloride Mes*NP(carbene)Cl [N–P 1.585(5) Å].

Carbene **4** effects more complete anionic displacement from the tricoordinate phosphine Ph$_2$PCl in halide abstraction conditions (with AlCl$_3$) to give [Ph$_2$P(carbene)]AlCl$_4$.[26] The cation (Fig. 5) is an imidazolium derivative of a pyramidal phosphine **8b** and can only be accessed *via* coordination chemistry **8a** of a diphenylphosphenium cation.
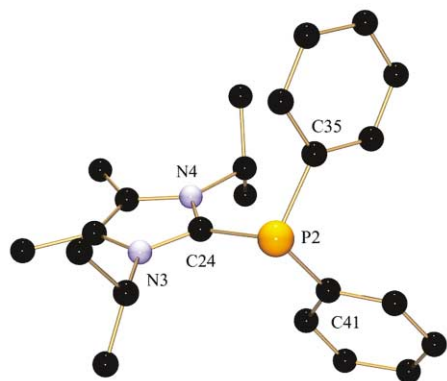
Fig. 5 Structure of the cation in [Ph$_2$P(carbene)]AlCl$_4$.

| **7** | **8a** | **8b** |
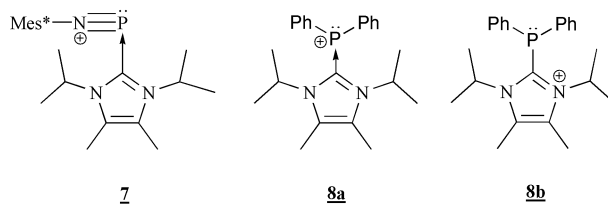
Complexes of phosphines with arene ligands

Tetrachloroaluminate,[9] tetrachlorogallate[16] and heptachloro-digallate[16,32] salts of the phosphadiazonium cation [Mes*NP]$^+$ are readily isolated from benzene, toluene or mesitylene solvents. Structural (Fig. 6) and spectroscopic data show that an
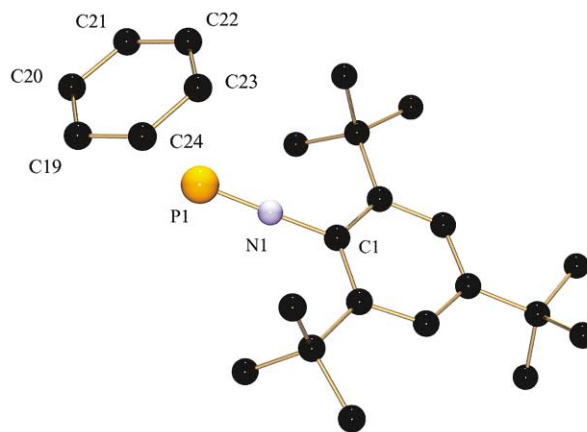
Fig. 6 Structure of the cation in [Mes*NP(benzene)]Ga$_2$Cl$_7$.

arene molecule is η^6 π-coordinated to the phosphorus centre.[16] The P–C(arene centroid) distances in the digallate salts correlate with the π-donor strength of the arene, decreasing in the order, benzene [2.820(4) Å] > toluene [2.767(7) Å] > mesitylene [2.687(7) Å]. Phosphorus-31 NMR spectra show that the complexes are resilient in solution, but under dynamic vacuum crystals of the tetrachloroaluminate and tetrachlorogallate salts release the arene and lose their integrity.[33] The complexes represent experimental models of the π-coordination complex

intermediates that are postulated to form during electrophilic aromatic substitution reactions.[16]

Complexes of phosphines with amine or imine ligands

Amines and imines have been used to effect halide displacement from halophosphines to give a wide variety of cationic products that are best described as complexes of phosphenium or phosphadiazonium acceptors. Structural features ($N_{(ligand)}$–P distances and the largest angle at phosphorus) that are demonstrative of the bonding in these complexes are compared in Table 2.

The extensive series of complexes involving intramolecular coordinate interactions observed for halophosphines possessing tethered amines has been reviewed.[34] The structure of $[Me_2NCH_2CH_2N(Me)PCl]^+$ shown in Fig. 7 is representative
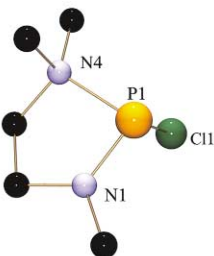
Fig. 7 Structure of the cation in $[Me_2NCH_2CH_2N(Me)PCl]Cl$.

and rationalises the heterolytic dissociation of one P–Cl bond in terms of nucleophilic displacement by the coordinate interaction of the pendant amine (N4).

A second tethered amine can be introduced to give cationic spirocyclic phosphines.[34–36] The 'see-saw' geometry observed at phosphorus in the solid state structure of the cation (Fig. 8)
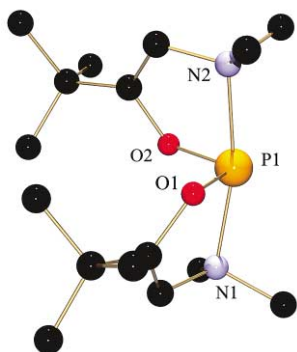
Fig. 8 Structure of the cation in $[\{Me_2NCH_2CH(Bu)O\}_2P]Cl$.

implies retention of a stereochemically active lone pair. Variable temperature NMR experiments have shown dynamic behaviour of these complexes in solution that are interpreted in terms of the dissociation of the amine coordinate bond.[34]

Intermolecular coordination complexes are evident in the cations of $[Mes*NP(quinuclidine)]OTf$[37] (Fig. 9) and [Mes*NP-
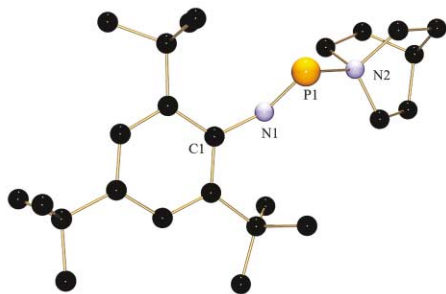
Fig. 9 Structure of the cation in $[Mes*NP(quinuclidine)]OTf$.
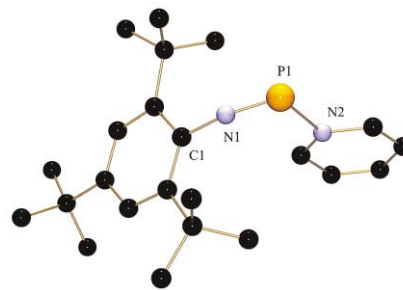
Fig. 10 Structure of the cation in $[Mes*NP(pyridine)]OTf$.

(pyridine)]OTf[7] (Fig. 10). They are analogous to the carbene complex cation of $[Mes*NP(carbene)]OTf$,[7] with retention of a short (Mes*)NP distance and effective displacement of the triflate anion.

Interesting comparisons can be made with the dipyridine complex $[Mes*NP(dipyridine)]OTf$ (Fig. 11), which represents a
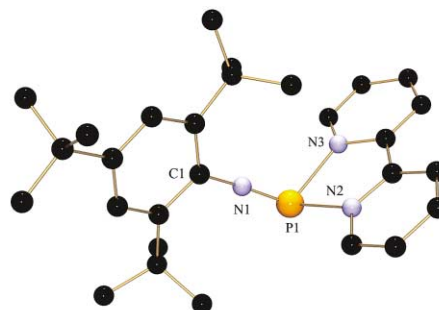

Fig. 11 Structure of the cation in $[Mes*NP(dipyridine)]OTf$.

unique example of an intermolecular chelate complex of a phosphine.[37] As expected, the two chelate N_{ligand}–P distances [2.066(4), 2.065(4) Å] are identical and slightly longer than those in the pyridine [1.958(8) Å] and quinuclidine [N–P 1.933(2) Å] complexes. The multiple bonding character of the NP bond is retained [N–P 1.497(4) Å], as is the pyramidal geometry of the phosphorus centre.

Complexes of amine and imine ligands have also been isolated for dicoordinate phosphine (phosphenium) acceptors. The DMAP (4-dimethylaminopyridine) complex of diphenylphosphenium (Fig. 12) is formed by phosphine ligand dis-
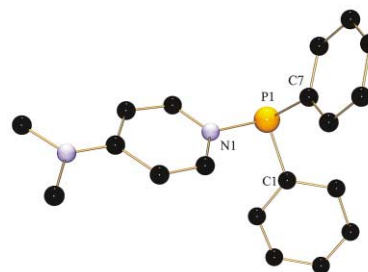

Fig. 12 Structure of the cation in $[Ph_2P(DMAP)]OTf$.

placement from a phosphine-phosphenium salt (see below) and (tetraisopropyldiamino)chlorophosphine reacts with DBN (1,5-diazabicyclo[4.3.0]non-5-ene) with more familiar chloride ion displacement to give a trisaminophosphine cation **9** shown in Fig. 13.[38] Similar reactions of DBN with (diisopropylamino)-dichlorophosphine and trichlorophosphine give the corresponding dication **10** and trication **11**, which have been spectroscopically characterised.[39]

The novel cyclic iminophosphine **12**[40] forms adducts with quinuclidine[41] (Fig. 14) and the bifunctional amine TMEDA (Fig. 15).[41] Although the N_{ligand}–P distances are relatively long
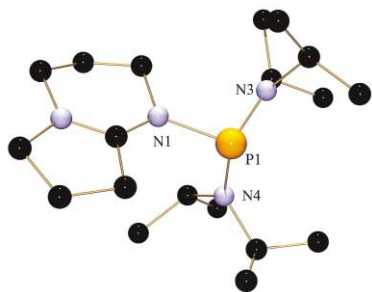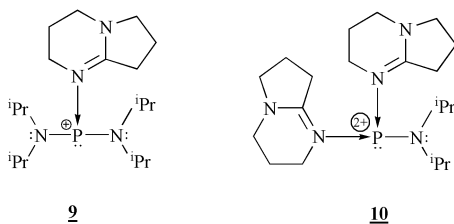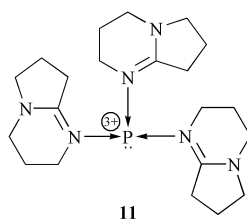
Fig. 13 Structure of the cation in [(iPr₂N)₂P(DBN)]PF₆.

9   **10**

11
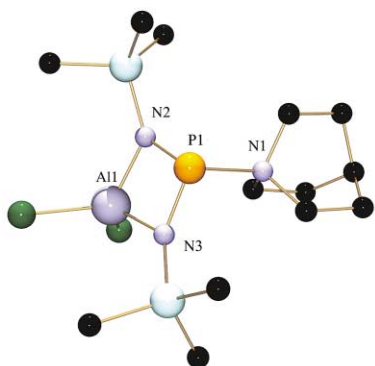
Fig. 14 Structure of {Cl₂Al(NSiMe₃)₂P}(quinuclidine).
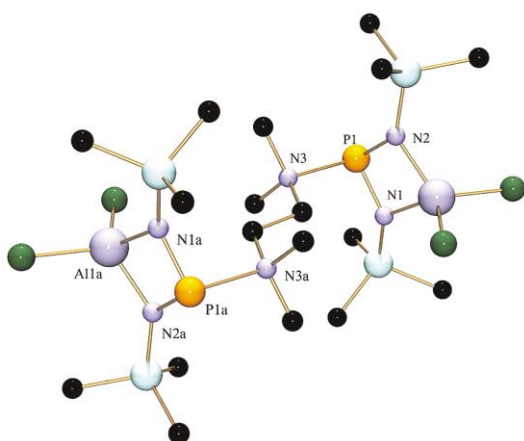
Fig. 15 Structure of {Cl₂Al(NSiMe₃)₂P}₂(TMEDA).

(Table 2), the structural features of neutral dicoordinate phosphine acceptor site are analogous to those in the cation of [Ph₂P(DMAP)]OTf, and the compounds represent inter-molecular amine–phosphine coordination.
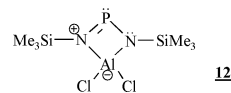
12

All N_ligand–P distances listed in Table 2 are substantially longer than a documented NP single bond [1.800(4) Å],[42] except for those in [Ph₂P(DMAP)]OTf and [(iPr₂N)₂P(DBN)]PF₆. We speculatively interpret the distinct differences with similar complexes of the neutral acceptor {Cl₂Al(NSiMe₃)₂P} in terms of the energy of the LUMOs, which are relatively stabilised by the molecular charge in the cations allowing for a more effective interaction with the HOMO of the donor.

Complexes of phosphines with phosphine ligands

Parry first recognised the interaction between haloamino-phosphines upon reaction with aluminium chloride by virtue of the characteristic $^1J_{P–P}$ (>200 Hz) coupling in the ^{31}P NMR spectra.[43–45] The compounds were appropriately assigned the phosphine–phosphenium complex formalism **13a**, represent-ing a coordination complex of a phosphine ligand on a phosphenium cation, as well as the phosphinophosphonium bonding model **13b**. Lability and dynamic behaviour in solution renders these salts difficult to isolate, but corresponding reactions of dialkyl- and diaryl-halophosphines give similar ^{31}P NMR spectroscopic features.[46,47] These complexes are more resilient than amino derivatives enabling isolation and comprehensive characterisation.[47,48] Structural features for selected examples of complexes interpreted in terms of (phosphine)P⟶P(phosphine) coordinate bonding are summar-ised in Table 3.
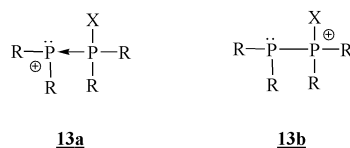
13a   **13b**

The structure of the cation in [Ph₂P(Ph₂PCl)]GaCl₄ (Fig. 16) confirms the P–P interaction, which is similar in length [2.205(4) Å][48] to that in Ph₂P–PPh₂ [2.217(1) Å].[49] The dis-tinct ^{31}P NMR chemical shifts observed for phosphine–phosphenium cations indicate that chlorine cation exchange is restricted. Moreover, the coordinate P⟶P nature of the inter-action is demonstrated by the ligand exchange behaviour. Phosphorus-31 NMR spectra of a reaction mixture containing [Ph₂P(Ph₂PCl)]GaCl₄ and PPh₃ shows quantitative release of Ph₂PCl and formation of a new P–P compound that has been comprehensively characterised as [Ph₂P(PPh₃)]GaCl₄. The pentaphenylphosphinophosphonium cation is also formed in the reaction of Ph₂PCl, Ph₃P and Me₃SiOTf and the structure is shown in Fig. 17.
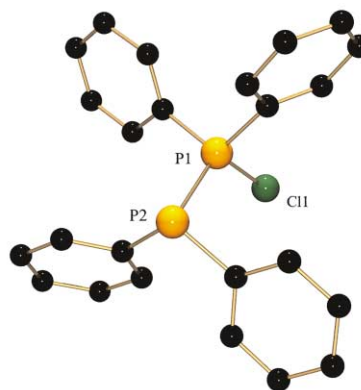

Fig. 16 Structure of the cation in [Ph₂P(Ph₂PCl)]GaCl₄.
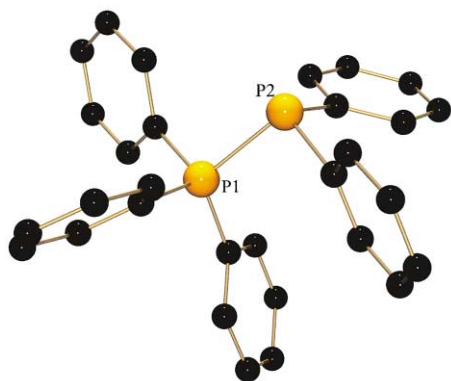
Fig. 17 Structure of the cation in [Ph₂P(PPh₃)]OTf.

Ligand exchange is observed generally for phosphenium salts [22,44,47] and represents a versatile new synthetic methodology in phosphorus chemistry (see above and below) that is potentially applicable across the electron-rich elements of the p block.

The Lewis acidity and electrophilicity of the aminophosphenium acceptor is mediated by the π-delocalisation of the nitrogen lone pairs into the formally empty p-orbital at phosphorus, which lowers the energy of the LUMO relative to that of the alkyl- and aryl-phosphenium cations. Nevertheless, the labile complex of trimethylphosphine on diazaphosphenium (Fig. 18) has been crystallographically characterised.[50]
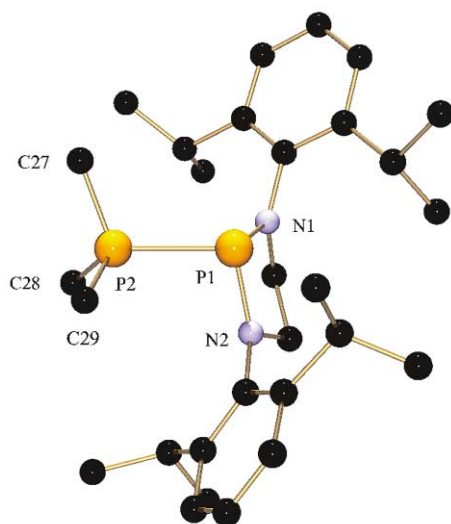

Fig. 18 Structure of the cation in [{N(Dipp)CH₂CH₂N(Dipp)}-P(Me₃P)]OTf.

A fascinating aspect of all ligand→P(phosphine) interactions is the retention of the stereochemically active lone pair at the acceptor site. The Lewis donor opportunity for this lone pair has been realised in one instance with the isolation and structural characterisation (Fig. 19) of [{GaCl₃}Me₂P(Me₂-PCl)]GaCl₄,[47] showing a phosphine ligand on a phosphenium acceptor, which is itself a ligand on gallium chloride. The cation is referred to as an 'in-series' coordination complex **14**, recognising that dimethylphosphenium cation is behaving as both a Lewis acid and a Lewis base simultaneously, demonstrating the Lewis amphoteric nature of phosphenium cations.

Although PCl₃ does not react with amino-, alkyl- or aryl-phosphines, the introduction of AlCl₃ effects chloride exchange and the formation of triphosphenium cations.[19,21,22] In contrast to the nitrogen centred analogue [N(PPh₃)₂]⁺, which adopts angles of 135–180° at nitrogen and is viewed as a multiply bonded 'allene-like' framework, the P–P distances in [P(PPh₃)₂]AlCl₄ [2.137(6) and 2.128(6) Å] are typical of single bonds and the acute angle at the central phosphorus [102.2(2)

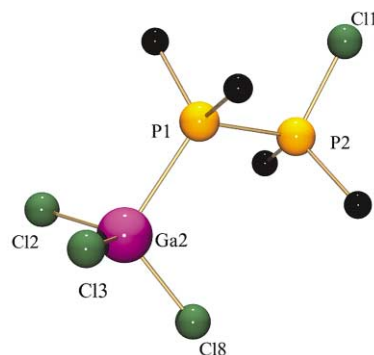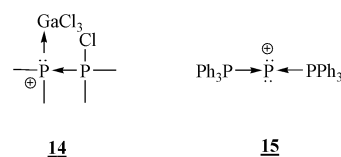**Fig. 19** Structure of the cation in [{GaCl₃}Me₂P(Me₂PCl)]GaCl₄.

and 103.0(3)°][21] implicates a bonding model that involves a P⁺ acceptor with two phosphine ligands **15**.

14   **15**

Solution ³¹P NMR spectroscopy of the reaction between [Mes*NP]AlCl₄ and PPh₃ first revealed the potential formation of a coordination complex of the type [Mes*NP(PPh₃)]⁺.[51] The structure was confirmed for the triflate salt [Mes*NP]OTf[52] (Fig. 20) and shows an extension of the P–OTf interaction

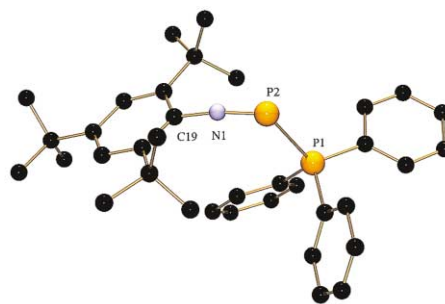**Fig. 20** Structure of the cation in [Mes*NP(PPh₃)]OTf.

[2.298(4) Å] relative to that observed for Mes*NPOTf [1.923(3) Å],[15] implicating displacement of the OTf anion from [Mes*NP]⁺. The P–P coordinate interaction in [Mes*NP-(PPh₃)]⁺ is best modeled by **16**, as the P–P bond is unusually long [2.625(2) Å], the nitrogen centre retains a nearly linear geometry [169.5(4)°] and the NP bond [1.486(4) Å] remains very short, consistent with carbene,[7] amine[37] and imine[37] complexes of [Mes*NP]⁺.

16

17

18
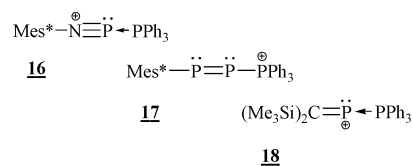
The structures observed for [Mes*PP(PPh₃)]BPh₄ Fig. 21[53] and [(Me₃Si)₂CP(PPh₃)]AlCl₄ Fig. 21[54] offer useful comparisons with that of [Mes*NP(PPh₃)]OTf. The P–PPh₃ bond [2.206(1) Å] in Fig. 22 [Mes*PP(PPh₃)]BPh₄ is typical of a single bond [cf. Ph₂P–PPh₂ 2.217(1) Å][49] and the small C_{ipso}PP bond angle at Mes*PP [98.8(2)°] highlights the molecule as a diphosphene–phosphonium cation **17** consistent with spectroscopic and theoretical evaluations. A slightly longer P–P bond [2.267(2) Å] is observed for [(Me₃Si)₂CP(PPh₃)]AlCl₄ and the molecule has been described in terms of a partial coordinate
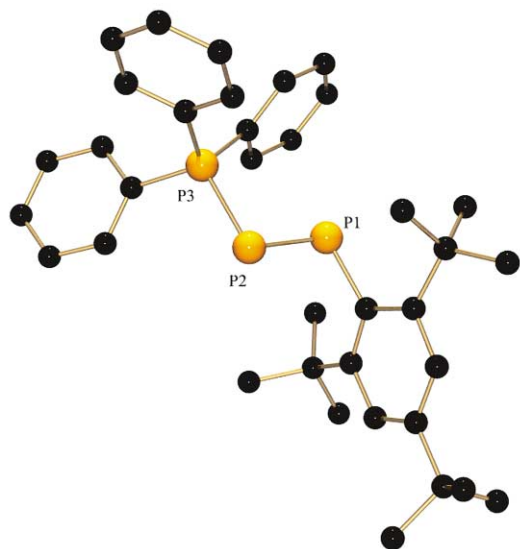
Fig. 21 Structure of the cation in [Mes*PP(PPh₃)]BPh₄.
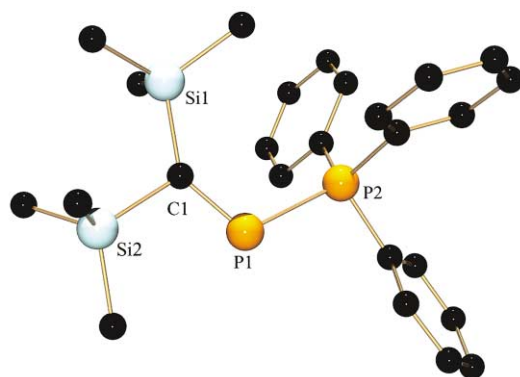
Fig. 22 Structure of the cation in [(Me₃Si)₂CP(PPh₃)]AlCl₄.

interaction **18**, recognizing the formal electron deficiency at the phosphorus site.

Intramolecular phosphine–phosphenium interactions have been recognised amongst the extensive series of cross-ring and cross-cage P–P interactions in bridgehead diphosphines,[55–57] represented by **19**. A more unexpected phosphiridine three-membered ring is imposed in **20**.[58]
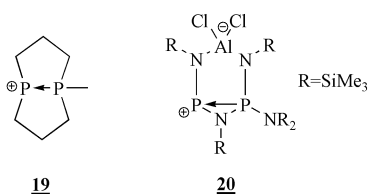
Complex of a phosphine with a gallane ligand: a coordination chemistry umpolung

Phosphine–phosphenium cations **13** have been described above as a synthetic source of phosphenium cations by virtue of their susceptibility to ligand exchange with stronger bases than the resident phosphine. The most profound application of the ligand exchange process has been the formation of the (gallane)Ga→P(phosphine) complex **21**.[59]
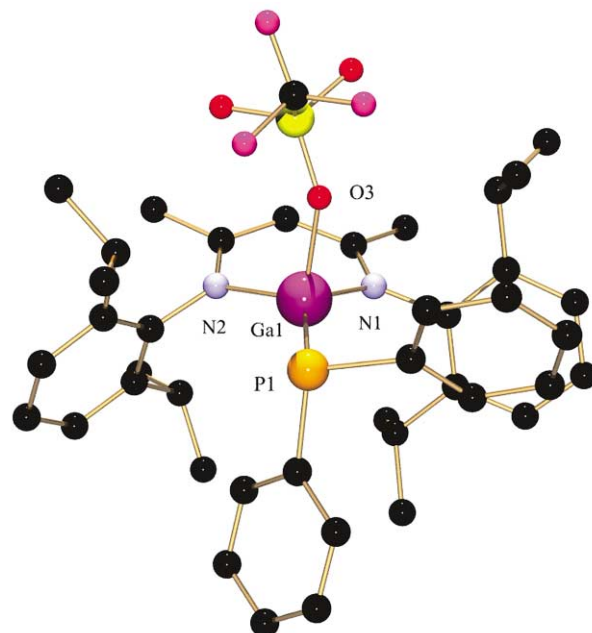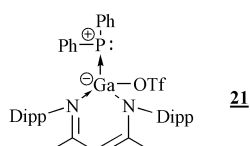

Fig. 23 Structure of Ph₂P(gallane)OTf.

The solid state structure (Fig. 23) confirms the Ga–P connectivity. The complex is conveniently modeled as a coordinatively unsaturated gallium(I) ligand[60] on a phosphenium cation, and can be considered an example of a 'coordination chemistry umpolung' (an inverse of the traditional coordinate bond) in that the metal centre (gallium) behaves as the Lewis donor (ligand) and the electron-rich non-metal centre (phosphorus) behaves as the Lewis acceptor.

Conclusions

Phosphine centres can behave as Lewis acids in spite of the presence of a lone pair. Comprehensive characterisation data is available for complexes of phosphines with carbene, arene, amine, imine, phosphine and gallane ligands. Cationic phosphines are naturally the most effective acceptors, but the coordination chemistry of neutral phosphines is developing. Phosphines bearing good leaving groups are prone to anion displacement on interaction with a ligand, due to the electrostatic thermodynamic benefits for the product. Complexes involving all electron-rich donors (elements of Groups 15, 16 and 17) will be accessible and the diversification of the coordination chemistry of phosphines offers opportunities for novel catalysis and the discovery of new structure and bonding.

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