Tris(benzoimidazol)amine (L) complexes of pnictogen(III) and pnictogen(v) cations and assessment of the [LP]\(^{3+}/[LPF_2]^{3+}\) redox couple†

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A series of cationic complexes involving a pnictogen(III) (Pn = P, As, Sb) centre and the tetradeinate ligand tris(1-ethyl-benzoimidazol-2-yl)methylamine (BIMEt\(^3\)) have been synthesized and comprehensively characterized. Oxidation of [P(BIMEt3)]\(^3+\) with XeF\(_2\) provides access to [PF\(_2\)(BIMEt3)]\(^3+\) representing the first structurally characterized example of a phosphorus(v) centred trication.

**Introduction**

Phosphorus(III) centers can undergo reversible oxidative addition of N–H and O–H bonds and have potential application as catalysts in organic transformations. This traditional Lewis basic reactivity extends to pnictogen(III) centers in general, but has been challenged by the realization of the Lewis acid umpolung made possible by the introduction of a cationic charge. A variety of pnictogen(III) based cations have been synthesized by halide abstraction from PnX\(_3\) derivatives in the presence of various ligands and weakly coordinating anions. The cationic charge of such complexes not only lowers the energy of the pnictogen based LUMO but also lowers the energy of the HOMO, so that oxidation is impeded. Consequently, examples of redox couples of the type [Pn(III)L]\(^{3+}/[Pn(V)R_2L]\(^{3+}\) have not yet been reported. The fluorophilicity of ligand stabilized phosphonium cations and dications is well established and has led to the discovery of effective catalysts for hydrofluorination reactions. The Lewis acidity of [PRL]\(^{3+}\) with L = terpyridine renders it an active catalyst for dehydrofluorination of fluoroalkanes, and suggests it has a substantial fluoride ion affinity. We have recently shown that the multidentate tris(benzoimidazol)amine ligand (BIMEt\(^3\)) encapsulates a germanium dication that is readily oxidized to [GeF\(_2\)BIMEt\(^3\)][OTf\(_2\)]\(^+\), and we have now exploited the versatility of this ligand to synthesize derivatives of [Pn[BIMEt\(^3\)][OTf\(_2\)]\(^+\) for Pn = P, As and Sb. As an analogue of the Verkade superbases [P(PRZ)]\(^+\) [P(BIMEt\(^3\))]\(^+\), adopts a proazaphosphatrane type cage structure. Oxidation of [P(BIMEt\(^3\))][OTf\(_3\)] by XeF\(_2\) gives [PF\(_2\)(BIMEt\(^3\)][OTf\(_3\), containing a rare example of a cationic complex of the high oxidation state Pn(v) center. Previous examples include derivatives of [PnPh\(_2\)L][OTf\(_3\) (L = pyridine N-oxide and Pn = As, Sb, Bi\(^{13}\)) and [SbPh\(_2\)L][OTf\(_3\) (L = pyridine N-oxide\(^{13}\)).

**Results**

The reaction of BIMH\(_3\) and PCl\(_3\) in the presence of a slight excess of NaH in THF at room temperature gives P(BIM). Quantitative formation of P(BIM) is evidenced by a single peak in the \(^{31}\)P NMR spectrum (\(^{31}\)P \(\delta = 44.7\) ppm). Crystals of P(BIM) were obtained by slow evaporation of the solvent from a DCM/MeCN solution. In the solid-state structure (Fig. 1a), two enantiomers are present in the unit cell, with the benzoimidazole groups arranged either in an S or R configuration. The geometry at N1 is essentially planar (353.77 and 355.85°, respectively) and features a pre-ordered N1…P bond with an average distance of 2.925 Å. The P–N3 bonds (1.721 Å) are significantly longer than those observed in P(PZ) (e.g. 1.694 Å for N(CH\(_2\)-CH\(_2\)-NR\(_2\))P with R = CH(Me)Ph\(^{13}\)).

The nucleophilic behaviour of P(BIM) was explored through reactions involving a variety of stoichiometric ratios of methyltriflate. In each case the \(^{31}\)P-NMR spectrum of the reaction mixture indicated the formation of several products that we speculate to result from simultaneous methylation of the nitrogen and phosphorus atoms. We have modelled the...

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energetic profile of the reactions using DFT calculations at the PBEPBE/6-311+G(d,p) level of theory.\textsuperscript{46}

Geometry optimizations for each complex suggest that methylation is favoured at the imino nitrogen atoms (Table 1). In the gas phase each methylation of an imino centre is exergonic. Similar results were obtained with MeCN as a solvent model but an energetic minimum was not evident for \([\text{PMe(BIMMe}_3]\)\(^+\) (Table 1 and ES\textsuperscript{†}), and consistently, complicated reaction mixtures are observed for MeOTf and P(BIM).

Nevertheless, addition of excess MeOTf resulted in a colourless precipitate (insoluble in common organic solvents) which suggests the potential formation of \([\text{PMe(BIMMe}_3]\)\(^+\). We have modelled the bonding in the potentially stable tricationic complex \([\text{BIMMe}_3\text{P}]^{1+}\) (at the PBEPBE/6-311+G(d,p) level of theory). NBO analysis on the optimized structure reveals a natural charge of +1.5 at phosphorus, and +0.5 on each benzoimidazole group, consistent with relatively strong P–N bonds (Wiberg bond index of 0.73).

Based on the modelled stability of \([\text{P(BIMMe}_3]\)\(^1\), we examined the reaction of BIME\(_t_3\) (ref. 17) with “P\(\text{OTf}_2\)” by mixing PCl\(_3\) and AgOTf acetonitrile in the presence of BIME\(_t_3\) (Scheme 1a). A singlet at \(\delta = 56.1\) ppm in the \(^31P\) NMR spectrum indicates the quantitative formation of \([\text{P(BIME}_t_3]\)\(\text{OTf}_2\], which has been separated from the AgCl by filtration, and crystallized by layering the reaction mixture with diethyl ether. The analogous reactions of AsCl\(_3\) or SbCl\(_3\) provided \([\text{As(BIME}_t_3]\)\(\text{OTf}_3\] and \([\text{Sb(BIME}_t_3]\)\(\text{OTf}_3\], respectively. In contrast, reaction of AsCl\(_3\) with BIME\(_t_3\) and excess TMSOTf formed \([\text{AsCl(BIME}_t_3]\)\(\text{OTf}_3\], as a primary product (Scheme 1b), which has been isolated in small quantities. The antimony fluoride derivative \([\text{SbF(BIME}_t_3]\)\(\text{OTf}_2\] is formed quantitatively in the reaction of SbF\(_3\) with BIME\(_t_3\) and two equivalents of TMSOTf (Scheme 1c).

The derivatives of \([\text{MX(BIME}_t_3]\)\(\text{OTf}_2\]) exhibit one set of signals for the benzoimidazole groups in the \(^1\)H-NMR spectrum, consistent with the trilate being labile in solution, as observed for analogous germanium complexes.\textsuperscript{8}

\([\text{P(BIME}_t_3]\)\(\text{OTf}_2\])\(\text{OTf}_2\]–(MeCN)\(_2\) crystallizes in the space group \(P\overline{1}\) (see Fig. 1b). The three trilate anions are remote from the phosphorus centre (3.58–3.92 Å). The unique apex nitrogen atom (\(\Sigma_{N1} = 350.5\)) is significantly bent out of plane towards the phosphorus centre consistent with a cross-ring bonding interaction. Nevertheless, N1···P(2.866(2) Å) is only slightly shorter than those in \(\text{P(BIM)}\) (2.912(2) and 2.938(2) Å). In the solid state \([\text{As(BIME}_t_3]\)\(\text{OTf}_3\] and \([\text{Sb(BIME}_t_3]\)\(\text{OTf}_3\] (Fig. 2c and d) exhibit a significantly different geometry around the pnicotene centre. The polygon described by the ligands is best described as a pentagonal bipyramid with three nitrogen atoms (N1, N2 and N3), one trilate oxygen atom and the lone pair in the plane. A second trilate oxygen atom and one nitrogen (N4) atom occupy the axial positions. This geometry enables significantly shorter Ph–N1 bond (As–N1 2.104(4) and Sb–N1 2.389(2)

### Table 1

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<th>P-Methylation</th>
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<td>(-5.21)</td>
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![Fig. 1](image-url) Solid state structures of one of two independent molecules of P(BIM) (a), the cation in [P(BIME\(_t_3\)]\(\text{OTf}_2\]–(MeCN)\(_2\) (b), and cation in [PF\(_2\)(BIME\(_t_3\)]\(\text{OTf}_2\] MeCN (c). Thermal ellipsoids are shown at a 50% probability level. Hydrogen atoms, solvent molecules and trilate anions are omitted for clarity. Inter-atomic distances and angles are summarized in Table 2.
Table 2 Selected bond distances in Å, angles in ° and $^{31}$P NMR chemical shifts in ppm for P(BIM), [P(BIMEt$_3$)][OTf]$_3$ and [PF$_2$(BIMEt$_3$)][OTf]$_3$

| P–N1 | 2.912(2) | 2.866(2) | 1.893(13) |
| P–OTf | — | 3.591(2) | — |
| P–F | — | 3.922(2) | 3.584(2) |
| $^{31}$P δ | 44.7 (s) | 56.1 (s) | $-127.8$ (dd) |
| $^\circ$Σ$_P$ | 319.48 | 320.2 | — |
| $^\circ$Σ$_{N1}$ | 353.77 | 350.5 | 328.0 |

Fig. 2 Solid state structure of the cations in [AsCl(BIMEt$_3$)][OTf]$_3$ (a), [SbF(BIMEt$_3$)][OTf]$_3$ (b), [As(BIMEt$_3$)][OTf]$_3$ (c), and [Sb(BIMEt$_3$)][OTf]$_3$ (d). Thermal ellipsoids are shown at a 50% probability level. Oxygen atoms of the triflate anions that interact with the pnictogen centres are shown, but the other atoms of the anions are omitted for clarity as well as the hydrogen atoms and solvent molecules. Interatomic distances and angles are summarized in Table 3.

Scheme 1 Synthetic procedure for derivatives of [PnX(BIMEt$_3$)][OTf]$_3$, [Pn(BIMEt$_3$)][OTf]$_3$ and [PF$_2$(BIMEt$_3$)][OTf]$_3$.

and 2.370(2) Å, respectively) compared to that in [P(BIMEt$_3$)][OTf]$_3$ (P–N1 2.879 Å). Two of the three triflate anions have a weak interaction with the pnictogen centre (Table 3). The mono-halide derivatives [SbF(BIMEt$_3$)][OTf]$_3$ and [AsCl(BIMEt$_3$)][OTf]$_3$ crystallise as dimeric structures. The antimony fluoride is linked by two triflate anions and the arsenic chloride is linked by chlorine substituents (As–Cl 2.3342(7) and 3.913(2) Å). The antimony centre adopts a tetragonal pyramidal geometry with two oxygen atoms from the triflate anions (Sb–OTf 2.551(2) and 2.793(2) Å) and two nitrogen atoms (Sb–N 2.214(2) and 2.165(2) Å) with the antimony centre 0.486 Å above this plane.

Equimolar mixtures of PCl$_5$ and BIMEt$_3$ with three equivalents of AgOTf give a mixture of products as evidenced by the $^{31}$P NMR spectrum of the reaction mixture. Isolation of [P(BIMEt$_3$)][OTf]$_3$ from this mixture implicates formation of [PCl$_2$(BIMEt$_3$)][OTf]$_3$, which is subsequently reduced. In this context, we have studied the oxidation of [P(BIMEt$_3$)][OTf]$_3$ with the expectation that in the presence of iodine it will oxidise the phosphorus species. Rapid crystallization from a saturated acetonitrile solution at $35^\circ$C layered with diethyl ether yielded P(BIMEt$_3$)I$_3$. Two of the three triflate anions have a weak interaction with the pnictogen centre (Table 3).

The N1–P distance (1.893(13) Å) is significantly shorter than that in [P(BIMEt$_3$)][OTf]$_3$. The P–Fl bond trans to the tertiary amine is longer [1.577(9) Å] than P–F2 [1.604(9) Å]. Consequently, the pseudo $C_{3v}$-geometry of the cation in [P(BIMEt$_3$)]

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The phosphorus derivative \([\text{P(BIMEt}_3]\)[OTf]_3\) can be readily oxidized to form the \([\text{LPVF}_2]\)[OTf]_3^+\) species. A fundamental study for general use of such pnictogen salts in Lewis acid catalysis, small molecule activation or as catalytic fluorinating agents is ongoing.

**Conclusions**

We have presented a versatile and facile synthetic approach to a number of pnictogen cations in the BIMEt$_3$ ligand scaffold. The phosphorus derivative \([\text{P(BIMEt}_3]\)[OTf]_3\) can be readily oxidized to form the tricationic phosphorus(V) complex, \([\text{LPVF}_2]\)[OTf]_3^+. A fundamental study for general use of such pnictogen salts in Lewis acid catalysis, small molecule activation or as catalytic fluorinating agents is ongoing.

**Conflicts of interest**

The authors declare no conflict of interest.

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**Notes and references**


