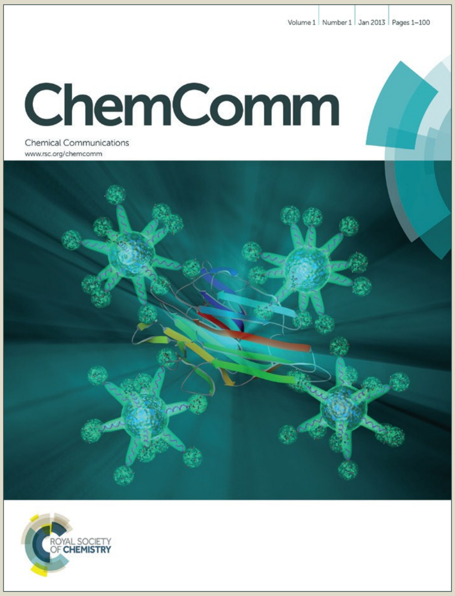
Volume 1 | Number 1 | Jan 2013 | Pages 1–100
ChemComm
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Journal Name

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Distinction between coordination and phosphine ligand oxidation: interactions of di- and triphosphines with Pn^{3+} (Pn = P, As, Sb, Bi)

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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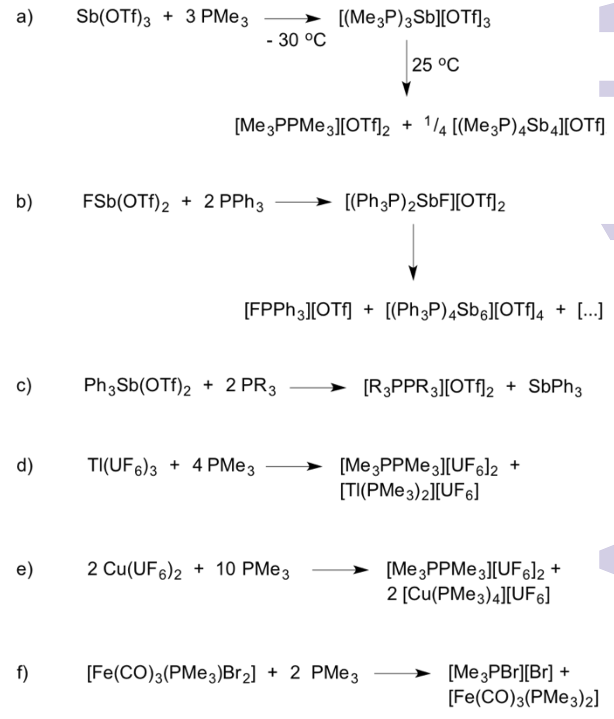
Reactions of polydentate phosphines with sources of Pn^{3+} (Pn = P, As, Sb, Bi) yield complexes of Pn^{1+} (Pn = P, As) or Pn^{3+} (Pn = Sb, Bi) acceptors. The distinction between coordination of a phosphine center to Pn and oxidation of a phosphine ligand is dependent on Pn. The first structurally verified triphosphine complexes of Sb(III) and Bi(III) acceptors are reported.

The diphosphines 1,1-bis(diphenylphosphino)methane (*dppm*), and 1,2-bis(diphenylphosphino)ethane (*dppe*), and the triphosphine 1,1-bis(diphenylphosphinoethyl)phenylphosphine (*triphos*) are important ligands that influence a wide array of coordination chemistry for the *d*- and *f*-block elements by offering the opportunity for multidentate interaction.[1-4] Many *p*-block element centres also behave as Lewis acceptors for multidentate phosphine donors,[5] but examples are comparatively sparse, particularly with di- and triphosphine ligands.[6] The Lewis acidity of an acceptor site can be enhanced by introduction of one or more cationic charges, facilitating coordination by multiple ligands. However, the enhanced electrophilicity and Lewis acidity concomitantly increase the oxidative strength of the acceptor, limiting the use of redox-susceptible phosphines as ligands. For example it has been reported that polyphosphine adducts of electrophilic antimony,[7-10] thallium,[11] copper,[11] and iron[12] acceptors undergo spontaneous reductive elimination of either halophosphonium, $[R_3PX]^{1+}$ or diphosphonium cations$[R_3PPR_3]^{2+}$, demonstrating versatile modes of phosphine ligand activation within the coordination sphere of strong Lewis acids (Scheme 1a-f). Nevertheless, as shown in Chart 1, several complexes of *p*-block element acceptors with diphosphine ligands have been isolated.[8,13-15]



Scheme 1. Oxidation of phosphines in complexes of highly Lewis acidic acceptors. See text for references.

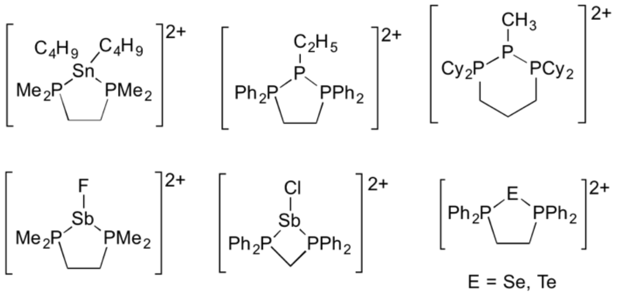


Chart 1. Select examples of isolable dicationic complexes featuring diphosphine ligands. See text for references.

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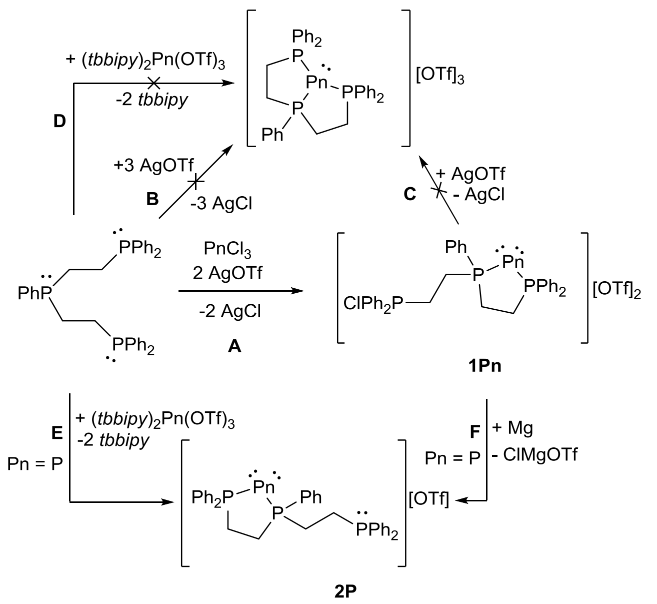
† We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Vanier Canada Graduate Scholarships program (S.S.C.) for funding.

Electronic Supplementary Information (ESI) available: Syntheses and characterization data, crystallographic details. See DOI: 10.1039/x0xx00000x



Scheme 2. Reactions of *triphos* with sources of Pn^{3+} to give **1Pn** and **2P**. Pn = P, As.

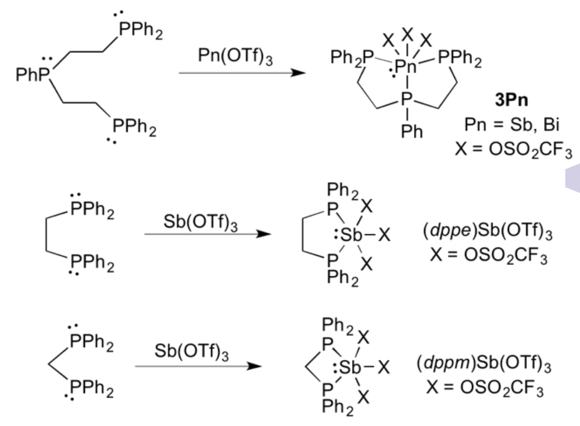
We now report studies of the interactions of *dppm*, *dppe* or *triphos* with $Pn(OTf)_3$ for Pn = P, As, Sb and Bi, revealing new phosphine complexes of Pn^{1+} for Pn = P or As and Pn^{3+} for Pn = Sb and Bi.[24] The results distinguish between phosphine coordination in which the phosphine centers act as classical ligands, and redox chemistry for P^{3+} or As^{3+}, where a phosphine center formally transfers two electrons to the acceptor.

Reactions of *triphos* with $PnCl_3$ (Pn = P or As) in the presence of AgOTf proceed as per Scheme 2A. Formation of **1P** and **1As** was confirmed by ^{31}P NMR spectroscopy and elemental analysis. While formation of phosphine complexes of cationic Pn(I) centers generally requires a secondary reductant (*e.g.* added equivalent of PR_3, $SnCl_2$, or cyclohexene),[16] reduction of $PnCl_3$ to the Pn(I) centers in derivatives of **1Pn** is effected intramolecularly by one of the phosphine arms of *triphos*. Removal of three chloride anions from $PnCl_3$ or one chloride anion from **1Pn** is not observed even in the presence of excess AgOTf (Scheme 2B,C).

Reactions of *triphos* with $(tbbipy)_2P(OTf)_3$ (*tbbipy* = 4,4'-di-^{t}butyl-1,1'-bipyridine), a chloride-free source of $P(OTf)_3$,[17] give **2P** (Scheme 2E) rather than the tris-triflate comples, $(triphos)P(OTf)_3$ (Scheme 2D). Compound **2P** is also accessible by reduction of **1P** with elemental magnesium (Scheme 2F), presumably with formation of ClMg(OTf) as the oxidation product. Formation of **2P** was confirmed by the ^{31}P NMR spectra of the reaction mixture at -50 °C (Figure S1, ESI), which was consistent with previously reported ^{31}P NMR data for the cation.[18] The analogous reactions of **1As** with $(tbbipy)_2As(OTf)_3$ or Mg yielded a complex mixture of unidentified products. Formation of the redox products **1Pn** and **2P** illustrates the highly oxidizing nature of P^{3+} and As^{3+}.

In contrast to reactions involving sources of Pn^{3+} (Pn = P, As), reactions of *triphos* with $Pn(OTf)_3$ (Pn = Sb, Bi) give the corresponding Lewis complexes, $[(triphos)Pn(OTf)_3]$, **3Pn** (Scheme 3). The solid-state structures of **3Sb**•MeCN (Figure) and isostructural **3Bi** (Figure S2, ESI) have been determined to reveal a six-coordinate geometry at the antimony and bismuth centers due to a tridentate ligation by *triphos* and three interacting triflate anions. The Sb---O distances in **3Sb** [2.589(3)-2.808(3) Å] are longer than the sum of the covalent radii for O and Sb (2.03 Å),[19] but shorter than the sum of the van der Waals radii (3.58 Å).[20] The structural data for **3Bi** is unsuitable for detailed structural discussion due to twinning in the crystal, nevertheless the data unambiguously establishes the proposed connectivity.[25] Complexes **3Sb** and **3Bi** are the first structurally confirmed triphosphine complexes of Sb(III) and Bi(III), respectively.

The ^{31}P NMR spectra of **3Sb** (31.1 ppm, 53.4 ppm) and **3Bi** (81.3 ppm, 108.6 ppm) in CD_3CN show two phosphorus environments that are shifted significantly downfield compared to free *triphos* (-13.0 ppm, -17.1 ppm), consistent with strong deshielding of the phosphorus nuclei. The ^{19}F NMR resonances of **3Sb** (-79.1 ppm) and **3Bi** (-79.0 ppm) are indicative of dissociated triflate anions (*c.f.* -79.4 ppm for $[PPh_4][OTf]$). The ^{31}P and ^{19}F NMR resonances of these solutions do not vary over a broad concentration range, implying the absence of a bimolecular association process, as might be expected from an equilibrium between the anion-bound and anion-free cations. We therefore conclude that CD_3CN solutions of **3Sb** and **3Bi** contain solvated trications $[(triphos)Pn]^{3+}$ (Pn = Sb, Bi) and triflate anions. In line with implication of a high Lewis acidity, solutions of both compounds polymerize THF within hours of mixing.[21]



Scheme 3. Formation of **3Pn** (Pn = Sb, Bi), $(dppe)Sb(OTf)_3$ and $(dppm)Sb(OTf)_3$.

The stability of **3Sb** and **3Bi** in the solid state and of $[(triphos)Sb]^{3+}$ and $[(triphos)Bi]^{3+}$ in solution is surprising in light of the previously reported oxidation of phosphines in the coordination sphere of highly Lewis acidic antimony and bismuth centers (Scheme 1).[7,8,9,22,23] To assess the significance of the tripodal ligation of *triphos* for the relative stability of **3Sb** in the solid state and in MeCN solutions, we prepared complexes of $Sb(OTf)_3$ featuring *dppm* and *dppe* as ligands. Equimolar solutions of $Sb(OTf)_3$ and *dppm* or *dppe* show quantitative formation of complexes $(dppm)Sb(OTf)_3$ (δ_P = 21.9 ppm) and $(dppe)Sb(OTf)_3$ (δ_P = 46.0 ppm) by ^{31}P NMR spectroscopy. The solid-state structures of both compounds have been determined (Figure 1) to confirm the presence of a single chelating ligand at antimony, with three triflate ion contacts, and, in the case of the *dppm* complex, a molecule of MeCN is coordinated to the antimony center.

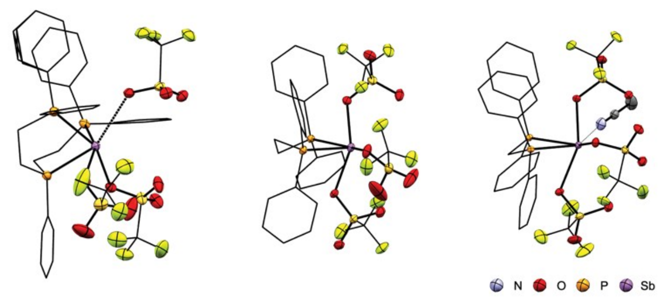
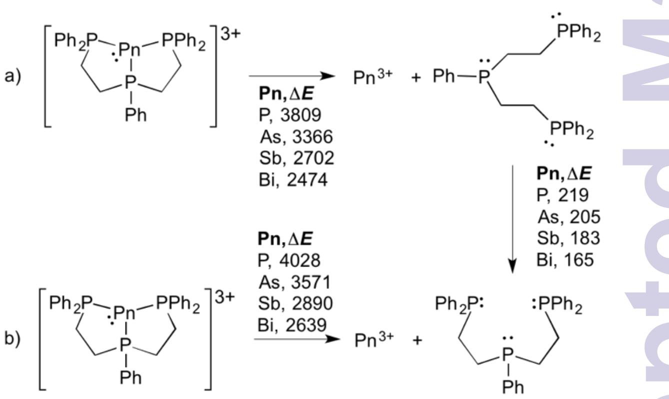


Figure 1. Molecular structure of (*triphos*)Sb(OTf)$_3$•MeCN (left), (*dppe*)Sb(OTf)$_3$ (middle), and (*dppm*)Sb(MeCN)(OTf)$_3$ (right). Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms and non-interacting solvent molecules have been omitted for clarity.

Isolation of *dppm* and *dppe* complexes with bidentate ligands discounts the tridenticity of *triphos* as a key determinant of the unexpected thermal stability of [(*triphos*)Pn]$^{3+}$ (Pn = Sb or Bi). Even upon heating to 82 °C in MeCN for an hour, solutions of **3Sb**, (*dppe*)Sb(OTf)$_3$ or (*dppm*)Sb(OTf)$_3$ show no evidence of degradation in the ^{31}P NMR spectrum. The analogous treatment of **3Bi** shows some deposition of elemental bismuth after 4 hours at 82 °C, but **3Bi** persists in solution (> 75 % by ^{31}P NMR). By comparison, reaction of three equivalents of PPh$_3$ with Sb(OTf)$_3$ shows a broad ^{31}P NMR resonance that is tentatively assigned to (Ph$_3$P)$_3$Sb(OTf)$_3$ (Figure S3, ESI). However, over 24 hours at room temperature this signal is replaced by a number of resonances, including those due to the *catena*-antimony compound [(Ph$_3$P)$_4$Sb$_6$][OTf]$_4$,[9] indicating a redox reaction. Analogously, we have previously shown that 2:1 or 3:1 reactions between Et$_3$P and Sb(OTf)$_3$ at room temperature give a mixture of [Et$_3$PPEt$_3$]$^{2+}$ and [(Et$_3$P)$_4$Sb$_4$]$^{4+}$ within minutes.[8] Equimolar solutions of *dppe* and (*tbbipy*)$_2$Pn(OTf)$_3$ (Pn = P, As) show only products due to redox chemistry, yielding Pn^{1+} containing species [(*dppe*)Pn]$^{1+}$. Collectively, these results indicate that in contrast to complexes of Pn(OTf)$_3$ (Pn = Sb, Bi) with monodentate phosphine ligands, those with bidentate and tridentate phosphine ligands are resilient towards ligand oxidation, and that complexes with Pn = Sb and Bi are more resilient towards oxidation than those with Pn = P or As.

To understand the steric and electronic consequences of tripodal ligation by *triphos* at Pn^{3+}, we have calculated the energy required for dissociation of *triphos* from the Pn^{3+} centres in hypothetical gas phase trications [(*triphos*)Pn]$^{3+}$ (Scheme 4). In Scheme 4a, the ligand is removed and allowed to relax to its minimum geometry while in Scheme 4b the ligand geometry following dissociation is constrained to that observed in complexes [(*triphos*)Pn]$^{3+}$. The difference between the energies of the two processes measures the strain resulting from the geometry required to bind a given acceptor. The values in Scheme 4 indicate the trend in Lewis acidity for gas phase Pn^{3+} to be P > As > Sb > Bi, with energies required for ligand dissociation in the range 2474-4809 kJ mol^{-1}. The strain energy values in Scheme 4 are relatively small, in the range 165-219 kJ mol^{-1} and exhibit the same trend P > As > Sb > Bi. As the variation in ligand dissociation energies is an order of magnitude greater than variation in ligand strain energies, we surmise that ring strain resulting from tripodal ligation cannot alone account for the redox instability of [(*triphos*)P]$^{3+}$ and [(*triphos*)As]$^{3+}$. On the other hand, the smaller P^{3+} and As^{3+} acceptors have substantially higher charge concentration ("hardness" according to Pearson's hard/soft acid base model)[24] than the larger Sb^{3+} and Bi^{3+} acceptors. Consistent with classification of phosphines as soft donors,[24] the hard/soft acceptor/donor mismatch in *triphos* complexes of P^{3+} and As^{3+} apparently favours ligand oxidation over coordination.



Scheme 4. a) Dissociation energies of the ligand from [(*triphos*)Pn]$^{3+}$, and b) dissociation of the ligand from [(*triphos*)Pn]$^{3+}$ with retention of the ligand geometry observed in [(*triphos*)Pn]$^{3+}$. All ΔE values are given in kJ/mol for gas phase processes.

In summary, we have investigated the reactions of the prototypical multidentate ligands *dppm*, *dppe*, and *triphos* towards sources of Pn(OTf)$_3$ (Pn = P, As, Sb, Bi) and discovered redox chemistry when E = P or As, and formation of stable coordination complexes when E = Sb or Bi. The observations indicate the following trend in oxidizing strength: P(OTf)$_3$ ≈ As(OTf)$_3$ > Sb(OTf)$_3$ ≈ Bi(OTf)$_3$. The possibility of di- or tri-denticity facilitates isolation of phosphine complexes with very electrophilic acceptors whereas nonchelating phosphine ligands are prone to oxidation giving diphosphonium cations. The first stable triphosphine complexes of Sb(III) and Bi(III) were isolated and structurally characterized. The range of reaction outcomes mapped here provides a guide for the development of phosphine coordination chemistry of strong Lewis acids across the periodic table by defining the conditions that lead to ligand non-innocence.

Notes and references

‡ Details of experimental procedures and characterization data for isolated compounds are given in the Electronic Supplementary Information. CCDC Numbers: (*triphos*)Sb(OTf)$_3$•MeCN (1417711), (*dppe*)Sb(OTf)$_3$ (1417713), and (*dppm*)Sb(OTf)$_3$ (1417712).

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25 Unit cell parameters for (*triphos*)Bi(OTf)$_3$•MeCN: a = 12.3334(4) Å, b = 16.8432(5) Å, c = 44.3167(13) Å, α = β = γ = 90°.