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Antimony(V) Cations

Establishing the Coordination Chemistry of Antimony(V) Cations: Systematic Assessment of $Ph_4Sb(OTf)$ and $Ph_3Sb(OTf)_2$ as Lewis Acceptors

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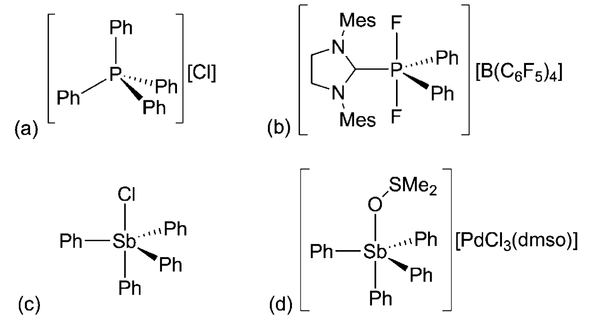
Abstract: The coordination chemistry of the stiboranes $Ph_4Sb(OTf)$ (**1a**, OTf = OSO_2CF_3) and $Ph_3Sb(OTf)_2$ (**3**) with Lewis bases has been investigated. The significant steric encumbrance of the Sb center in **1a** precludes interaction with most ligands, but the relatively low steric demands of 4-methylpyridine-*N*-oxide (OPyrMe) and $OPMe_3$ enabled the characterization of $[Ph_4Sb(OPyrMe)][OTf]$ (**2a**) and $[Ph_4Sb(OPMe_3)][OTf]$ (**2b**), rare examples of structurally characterized complexes of stibonium acceptors. In contrast, **3** was found to engage a variety of Lewis bases, forming stable isolable complexes of the form $[Ph_3Sb(donor)_2][OTf]_2$ [donor = $OPMe_3$ (**6a**), $OPCy_3$ (**6b**, Cy = cyclohexyl), $OPPh_3$ (**6c**), OPyrMe (**6d**)], $[Ph_3Sb(dmap)_2(OTf)][OTf]$ (**6e**, dmap = 4-(dimethylamino)pyridine) and $[Ph_3Sb(donor)(OTf)][OTf]$ [donor = 1,10-phenanthroline (**7a**) or 2,2′-bipy (**7b**, bipy = bipyridine)]. These compounds exhibit significant structural diversity in the solid-state, and undergo ligand exchange reactions in line with their assignment as coordination complexes. Compound **3** did not form stable complexes with phosphine donors, with reactions instead leading to redox processes yielding $SbPh_3$ and products of phosphine oxidation.

Introduction

Coordination chemistry of transition-metal and Group 13 acceptors has been extensively developed and describes important features of structure, bonding, and reactivity in compounds of these elements. Lewis acceptor behavior is also observed for many of the other p-block elements,[1] but examples are generally limited by the comparatively small covalent radii and/or the limited availability of energetically appropriate acceptor orbitals. The replacement of substituents on an acceptor center by weakly coordinating anions (e.g., OSO_2CF_3 (OTf), AlX_4, $B(C_6F_5)_4$, PF_6) can, however, enhance the Lewis acidity of a p-block center and creates one or more vacant coordination sites, facilitating coordination chemistry.[2–4]

Antimony(III) and antimony(V) acceptors have been shown to engage a broad array of ligands,[5,6] and a number of structurally characterized complexes of cationic Sb^{III} acceptors have also been reported[2] along with one example of a cationic Sb^{I} acceptor.[7] Structurally characterized complexes featuring cationic Sb^{V} acceptors, however, are rare,[8,9] although spectroscopic characterization has been presented in some cases.[10–15] Furthermore, structurally characterized complexes involving prototypical pnictonium cations, that is, $[R_4Pn]^+$ (Pn = N, P, As, Sb, or Bi), as acceptors are rare,[8,14,16,17] likely a consequence of steric encumbrance at the pnictogen acceptor, an effect illustrated by the solid-state structures of $[Ph_4P][X]$ (X = Cl or Br) (Scheme 1 a).[18,19] Both compounds present ionic formulations, in which the phosphorus center is tetrahedral in geometry, and the shortest phosphorus–halide contact is greater than the sum of the P–X van der Waals radii (Σ_{vdW}). The only structurally characterized complex of a prototypical $[R_4P]^+$ acceptor, $[SIMesPF_2Ph_2][B(C_6F_5)_4]$ (SIMes = 1,3-dimesitylimidazolidin-2-yli-



Scheme 1. Solid-state structures observed for a) $[Ph_4P][Cl]$,[18] b) $[SIMesPF_2Ph_2][B(C_6F_5)_4]$,[16] c) Ph_4SbCl,[20] and d) $[Ph_4Sb(dmso)][PdCl_3(dmso)]$.[8]

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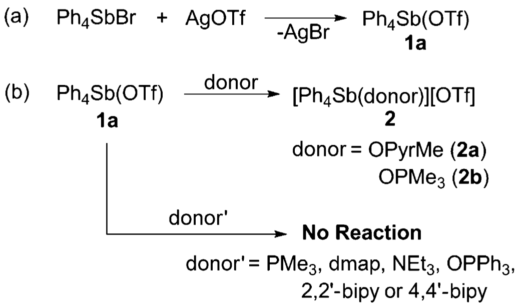
dene) (Scheme 1 b),[16] contains two fluoride substituents, which impart a significant Lewis acidity at the phosphorus atom with minimal steric imposition.

The greater atomic radii of the heavier pnictogen centers facilitates increasingly high coordination numbers, such that derivatives of Ph_4SbX (X = halide) are molecular in the solid state and contain penta-coordinate, trigonal-bipyramidal Sb centers (Scheme 1 c).[20–22] Nevertheless, only one complex $[Ph_4Sb(dmso)][PdCl_3(dmso)]$ (Scheme 1 d),[8] containing a prototypical stibonium acceptor has been structurally characterized, along with the recent spectroscopic characterization of $[(C_6F_5)_4Sb(OPEt_3)][B(C_6F_5)_4]$.[14] We now report, therefore, the preparation and characterization of $Ph_4Sb(OTf)$ (**1 a**) and $Ph_3Sb(OTf)_2$ (**3**), and the systematic exploration of their interaction with classical ligands, evolving our preliminary results for compound **3**,[3] and establishing a potentially diverse and extensive coordination chemistry for cationic Sb^V centers with implications for other heavy elements of the p block.

Results and Discussion

Preparation and coordination chemistry of compound 1 a

Treatment of a CH_2Cl_2 solution of Ph_4SbBr with AgOTf yields a colorless solid, which was spectroscopically characterized as $Ph_4Sb(OTf)$ (**1 a**) (Scheme 2 a), as previously reported through an alternative synthetic methodology.[23] We postulate that **1 a** adopts a trigonal-bipyramidal geometry in the solid-state as reported for Ph_4SbX (X = halide[21,22] or OSO_2Ph[23]) and $(C_6F_5)_4Sb(OTf)$,[14] but note that in solution the complex may be ionic, that is, $[Ph_4Sb][OTf]$, as reported for Ph_4SbI in CD_3CN.[21] Consistently the ^{121}Sb NMR spectrum of **1 a** in CD_3CN displays a broad singlet at $\delta = 673$ ppm (compare $\delta = 685$ ppm for Ph_4SbI),[21] the observation of which is in-line with a highly symmetric, tetrahedral Sb center. Interestingly the ^{121}Sb NMR spectrum of **1 a** in CD_2Cl_2 displays no such peak at ambient temperature suggesting that in this solvent the OTf anion may remain bound to the Sb center imposing a less symmetric trigonal-bipyramidal geometry at the Sb, leading to rapid quadrupolar relaxation of the Sb center.



Scheme 2. a) Synthesis of $Ph_4Sb(OTf)$ (**1 a**) and b) reactions of **1 a** with Lewis bases. OPyrMe = 4-methylpyridine-*N*-oxide, dmap = 4-(dimethylamino)pyridine, bipy = bipyridine.

The Lewis acceptor potential of **1 a** was subsequently explored by spectroscopic screening of the reactivity with an equimolar quantity of a range of Lewis bases (Scheme 2 b). There was no evidence of reaction with PMe_3, $OPPh_3$, NEt_3, 2,2′-bipy or 4,4′-bipy in CH_2Cl_2 over 2 h; and although reaction mixtures of **1 a** with dmap indicated a shift in the resonances associated with the ligand in the ^1H NMR spectrum, only **1 a** was isolated upon recrystallization of the reaction products. In contrast, treatment of **1 a** with a stoichiometric quantity of 4-methylpyridine-*N*-oxide (OPyrMe) or $OPMe_3$ yielded colorless solids, which were spectroscopically characterized as the 1:1 complexes $[Ph_4Sb(donor)][OTf]$ [donor = OPyrMe (**2 a**), $OPMe_3$ (**2 b**)]. In both cases the ^1H NMR resonances associated with the ligand are deshielded relative to those for the corresponding free species, and for compound **2 b** the $^{31}P\{^1H\}$ NMR spectrum illustrates the expected downfield shifted singlet ($\delta_P = 42.6$ ppm) (see also Table SI-1 in the Supporting Information), consistent with coordination of the ligand to the Lewis acidic Sb center of **1 a**. The possibility of a dissociative equilibrium in solution for compounds **2 a** and **2 b** was also, however, probed in the ^{31}P NMR spectra of **2 b** in CD_2Cl_2 at various concentrations. At concentrations below approximately 0.15 M, the chemical shift observed for solutions containing compound **2 b** approaches that of free $OPMe_3$ ($\delta_P = 36.3$ ppm) (see also Figure SI-6 in the Supporting Information), suggesting that association of **1 a** and $OPMe_3$ may be reversible in solution, with the kinetics of re-association increasingly unfavorable at lower concentrations.

Recrystallization from CH_2Cl_2/Et_2O or $MeCN/Et_2O$ for **2 a** and **2 b**, respectively, furnished the complexes in analytical purity, and crystals appropriate for analysis by single-crystal X-ray diffraction. Compound **2 a** crystallized in the space group $P2_1/c$, with a single formula unit in the asymmetric unit, exhibiting a trigonal-bipyramidal geometry at the Sb center (Figure 1 a). The OPyrMe ligand adopts an axial position, with a relatively long Sb–O bond (2.449(1) Å; compare the sum of the covalent radii (Σ_{CR}) = 2.03 Å),[24] which lies within the range defined by other examples of Sb^V–O coordinate bonds (1.94–2.57 Å).[8,25–27] The three equatorial phenyl substituents adopt a propeller conformation and are distorted towards the OPyrMe ligand with the angles between their *ipso* carbon atoms and that of

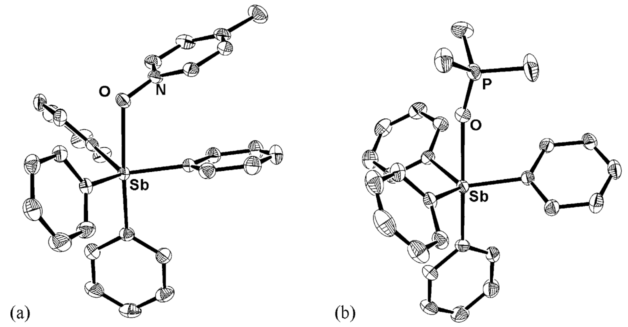


Figure 1. Solid-state structure of the cations in a) **2 a** and b) **2 b**. All hydrogen atoms are omitted for clarity.

the axial Ph substituent in the range 97.2–100.6°. The shortest Sb–O inter-ion contact (5.185(2) Å) is significantly greater than the sum of the Sb–O van der Waals radii (Σ_{vdW} = 3.58 Å),[28] and as such we assign an ionic formulation for **2a**, wherein the OPyrMe ligand has nucleophilically displaced the OTf anion from **1a**. The solid-state structure of compound **2b** is similar, again illustrating a trigonal-bipyramidal geometry at the Sb center, with the phosphine oxide ligand in an axial position (Figure 1b). The Sb–O bond (2.406(2) Å) is shorter than that in **2a**, but is significantly longer than those in examples of neutral Sb^V–OPR_3 adducts (range: 1.94–2.15 Å).[25–27] The P–O bond (1.499(2) Å) is slightly longer than that reported for $OPMe_3$ (1.488(5) Å),[29] which is consistent with coordination to the Lewis acidic Ph_4Sb^+ center. As for **2a**, the three *ipso* carbon atoms of the equatorial Ph substituents are bent out of the equatorial plane towards the $OPMe_3$ ligand, presumably alleviating the steric pressure imposed by interaction with the axial Ph substituent. The shortest Sb–OTf contact is an Sb–F interaction (4.312(7) Å; Σ_{vdW} = 3.53 Å),[28] the magnitude of which is consistent with an ionic formulation as for **2a** (Table 1).

Table 1. Selected solid-state metrical parameters for complexes **2a** and **2b**.

	Sb–ligand (Sb–O) bond length [Å]	Shortest Sb–OTf contact [Å]	O-Sb-Pn angle [°]
2a	2.449(1)	5.185(2) (Sb–O)	113.73(9)
2b	2.406(2)	4.312(7) (Sb–F)	164.8(1)

As cationic complexes of stibonium acceptors are rare,[8,30] compounds **2a** and **2b** represent important new examples. The cations in both are structurally similar to that in the closely related $[Ph_4Sb(dmso)][PdCl_3(dmso)]$,[8] which contains a trigonal-bipyramidal Sb center in which the ligand occupies an axial position, and exhibits a long Sb–ligand interaction (2.567(2) Å; Σ_{CR} = 2.03 Å). Steric congestion at the Sb center of **1a** precludes coordination of the prototypical Lewis bases PMe_3 and dmap, but the lower steric demands of the comparatively weak bases OPyrMe and $OPMe_3$, resulting from an "oxygen spacer" between the Sb center and the sterically demanding component of the ligand, permits formation of **2a**/**2b**, albeit with particularly long Sb–ligand bonds. The steric constraints illustrated in **1a** are apparently greater in its phosphonium analogue $[Ph_4P][OTf]$ (**1b**), for which no evidence of reaction with PMe_3, dmap, OPyrMe, or $OPMe_3$ was detected after stirring over 2 h at ambient temperature in CH_2Cl_2.

Preparation and coordination chemistry of compound 3

Compound **3** was prepared analogously to compound **1a**, through treatment of Ph_3SbCl_2 with two equivalents of AgOTf in CH_2Cl_2, and was isolated as a colorless crystalline solid with spectroscopic parameters in-line with a previous synthesis through an alternate synthetic method.[31]

Study of crystals of **3** (space group $P2_1/n$), attained by recrystallization from CH_2Cl_2/pentane at −30 °C, by X-ray diffraction revealed a penta-coordinate trigonal-bipyramidal Sb center, as for the As[32] and Bi[3] analogues, with two axially bound triflate substituents (O-Sb-O = 173.21(5)°), and three equatorial phenyl substituents in which the *ipso* carbon atoms are coplanar with the Sb center (Figure 2). The two Sb–O bonds (average 2.172(2) Å; Σ_{CR} = 2.03 Å),[24] are consistent in length with other examples of short Sb–OTf interactions,[33,34] and are representative of "fully coordinated" triflate substituents at Sb.

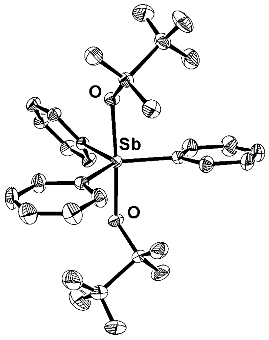


Figure 2. Solid-state structure of **3**. All hydrogen atoms are omitted for clarity.

Reaction of **3** with two equivalents of the prototypical phosphine PMe_3 in CH_2Cl_2 did not lead to the anticipated bis-phosphine complex $[Ph_3Sb(PMe_3)_2][OTf]_2$, but instead resulted in the immediate precipitation of a colorless solid, spectroscopically identified as the diphosphonium salt $[Me_3P–PMe_3][OTf]_2$ (**4a**) (Scheme 3).[7,35] The concomitant formation of $SbPh_3$ was confirmed by the ^1H and ^{13}C NMR spectra of the CH_2Cl_2-soluble reaction products, indicating a two-electron reduction of the Sb center and an oxidation of each P center. The products of the reaction are independent of stoichiometry, and attempts to observe the perceived intermediate bis-phosphine complex $[Ph_3Sb(PMe_3)_2][OTf]_2$ by low-temperature NMR spectroscopy were unsuccessful (see the Supporting Information).

$$\underset{\mathbf{3}}{Ph_3Sb(OTf)_2} \xrightarrow{2\ PR_3} \underset{\mathbf{4}}{[R_3P\text{-}PR_3][OTf]_2} + SbPh_3$$

R = Me (**4a**)
*n*Pr (**4b**)

Scheme 3. Reaction of **3** with PR_3 (R = Me or *n*Pr) to yield **4** and $SbPh_3$.

Analogous redox reactions were observed upon treatment of **3** with two equivalents of $PnPr_3$, yielding the previously unreported $[nPr_3P–PnPr_3][OTf]_2$ (**4b**) and $SbPh_3$. Compound **4b** represents a new derivative in the small library of known acyclic diphosphonium salts,[35] and was isolated in analytic purity following recrystallization from MeCN/Et_2O. The compound exhibits a singlet at δ = 31.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum in CD_3CN (compare δ = 28 ppm for **4a**), and the ^1H and ^{13}C NMR spectra were consistent with mutually equivalent *n*Pr groups.

Study of single crystals of **4b** by X-ray diffraction confirmed the expected atomic connectivity, with the compound crystal-

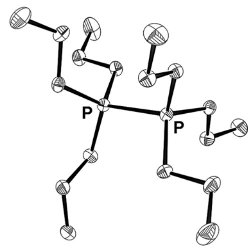
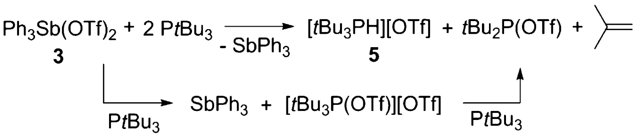


Figure 3. Solid-state structure of the dication in [nPr_3P–$PnPr_3$][OTf]$_2$ (**4b**). All hydrogen atoms are omitted for clarity.

lizing from MeCN/Et_2O at $-30\,^{\circ}C$ in the space group $P2_1/n$ with a single formula unit in the asymmetric unit (Figure 3). The P–P bond (2.2390(9) Å; $\Sigma_{CR} = 2.22$ Å) in **4b** is slightly longer than that reported in **4a** (2.198(2) Å), which is in line with the greater steric encumbrance of the substituents. The two phosphorus centers are tetrahedral in geometry (average X-P-X = 109.5°), with minimal distortion through triflate interaction, consistent with inter-ion P–O contacts (3.624(2) and 3.827(2) Å; $\Sigma_{vdW} = 3.32$ Å) which are greater than the Σ_{vdW} for the two elements. The cation exhibits a pseudo-staggered conformation down the P–P bond, with narrow C-P-P-C torsions in the range 31.9(1)–34.8(1)°. In comparison, **4a** has previously been shown to crystallize in a fully staggered conformation (average torsion angle: 60.1°),[35] but also to co-crystallize with [Sb(PMe_3)$_3$][OTf]$_3$ in an eclipsed conformation (torsion angles: 0.4(2)–0.7(2)°)[7] inferring minor thermodynamic preference for the staggered conformation. As such, we assign the counterintuitive narrow torsions observed in **4b** simply to packing effects in the solid state.

In contrast to reactions with PR_3 (R = Me or *n*Pr), the reaction of **3** with two equivalents of the highly sterically encumbered phosphine P*t*Bu$_3$ (cone angle 182°, compare $PMe_3 = 118°$ and P*n*Pr$_3$ = 132°)[36] led to two major products, evident in the ^{31}P NMR spectrum as singlet resonances at $\delta = 219$ and 52 ppm. The latter resonance appears as a doublet (^1J(P,H) = 460 Hz) of multiplets in the corresponding proton-coupled spectrum, which is in-line with the presence of a P–H bond. Following removal of all volatiles under vacuum, the resulting oily solid products were analyzed by ^1H NMR spectroscopy in CD_2Cl_2 indicating complete reduction of **3** to $SbPh_3$. Crystallization of the products from CH_2Cl_2/Et_2O at $-30\,^{\circ}C$ furnished well-formed colorless crystals, which were identified by X-ray diffraction and multinuclear NMR spectroscopy as [*t*Bu$_3$PH][OTf] (**5**) (see Figure SI-1 in the Supporting Information), correlating with the resonance at $\delta = 52$ ppm in the ^{31}P NMR spectrum of the reaction mixture. We postulate that the formation of **5** occurs through an initial redox process between **3** and one equivalent of P*t*Bu$_3$ to yield $SbPh_3$ and [*t*Bu$_3$P(OTf)][OTf], with the ligation of the latter by a second equivalent of P*t*Bu$_3$ to form [*t*Bu$_3$P–P*t*Bu$_3$][OTf]$_2$ precluded by the steric encumbrance of the phosphine. Instead, P*t*Bu$_3$ deprotonates a *t*Bu group of [*t*Bu$_3$P(OTf)]$^+$ furnishing **5**, and a zwitterionic salt, which eliminates isobutylene to produce *t*Bu$_2$P(OTf) (Scheme 4), assigned to the highly deshielded ^{31}P NMR resonance at $\delta = 219$ ppm of the crude reaction mixture. Consistently, the reaction of **3** with one equivalent of P*t*Bu$_3$ leads to an essentially identical ^{31}P NMR spectrum, and only approximately 50 % reduction of **3** to $SbPh_3$ is apparent in the ^1H NMR spectrum. Furthermore, upon repeating the reaction in CD_2Cl_2, analysis of the reaction mixture by ^1H NMR spectroscopy after 4 h at ambient temperature reveals resonances consistent with isobutylene ($\delta_H = 4.66$ and 1.67 ppm)[37,38] (Scheme 4). The assignment of the resonance at $\delta = 219$ ppm in the ^{31}P NMR spectrum to *t*Bu$_2$P(OTf) was also supported by treatment of the Et_2O-soluble reaction products (**5** is insoluble in Et_2O) with one equivalent of PMe_3. This reaction led to the appearance of two mutually coupled doublet resonances at $\delta = 42.6$ and 10.8 ppm (^1J(P,P) = 384 Hz) in the $^{31}P\{^1H\}$ NMR spectrum, which were assigned to the previously reported phosphino-phosphonium salt [Me_3P–P*t*Bu$_2$][OTf], with the remainder of the spectroscopic data in-line with this assignment.[35]

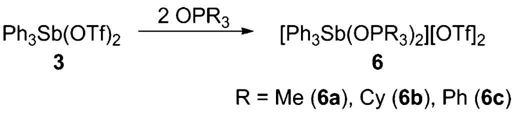


Scheme 4. Reaction of **3** with two equivalents of P*t*Bu$_3$.

Reaction of **3** with one or two equivalents of PPh_3 gave intractable mixtures with more than four products apparent by $^{31}P\{^1H\}$ NMR spectroscopy ($\delta_P = 40$ to 70 ppm), and complete consumption of PPh_3 in both cases. A redox reaction was, nonetheless, again illustrated by the formation of $SbPh_3$, which was isolated as the only Et_2O-soluble reaction product.

Although it has not been possible to isolate phosphine complexes of compound **3**, the unexpected redox processes leading to P–P coupling may have synthetic utility, as illustrated by the recent report of the synthesis of [$P_7(AsPh_3)_3$][OTf]$_3$ through reaction of PCl_3 with $Ph_3As(OTf)_2$, the As analogue of compound **3**.[32] Furthermore, mild methods of oxidizing phosphorus centers while at the same time installing weakly coordinating anions are also synthetically significant in the ongoing exploration of the cationic coordination chemistry of this element, with the ready solubility of $SbPh_3$ in most common organic solvents facilitating removal from the primary reaction products, and enhancing its reagent potential.

The redox reactivity observed between **3** and phosphines is, however, precluded in reactions of **3** with two equivalents of OPR_3 (R = Me, cyclohexyl (Cy), or Ph) in CH_2Cl_2 at ambient temperature, which quantitatively yield complexes of the generic formula [$Ph_3Sb(OPR_3)_2$][OTf]$_2$ (R = Me (**6a**), Cy (**6b**), and Ph (**6c**)) (Scheme 5). The respective $^{31}P\{^1H\}$ NMR spectra for the three compounds show an upfield-shifted singlet ($\delta_P = 73$ (**6a**), 79 (**6b**), and 48 ppm (**6c**)) relative to the values for the corresponding free ligands, and the ^1H and ^{13}C NMR spectra are consistent with a single ligand environment and the proposed formulations (see Table SI-2 in the Supporting Information), with analytic purity also confirmed by elemental microanalysis.



Scheme 5. Reaction of **3** with phosphine oxides to yield **6a**–**6c**.

The significant chemical shifts relative to those of the starting materials observed in all cases are consistent with the complexes remaining intact in solution. Consistently, for the representative example of complex **6c**, which contains the most weakly basic ligands, no change was observed in the ^{31}P NMR chemical shift over a range of concentrations, in contrast to derivatives of **2**. Nevertheless, the presence of a small dissociative equilibrium cannot be discounted. The ^{31}P NMR shift of **6a** (73.2 ppm) is significantly more downfield than that observed for **2b** (42.6 ppm), which reflects the anticipated increased Lewis acidity of the Ph_3Sb^{2+} acceptor relative to Ph_4Sb^+.

The atomic connectivity of **6a** and **6c** has also been confirmed by X-ray diffraction studies of crystals obtained from CH_2Cl_2/Et_2O at −30 °C. Complex **6a** crystallized in the space group $P\bar{1}$ with a single formula unit and a CH_2Cl_2 molecule in the asymmetric unit. The Sb center adopts a slightly distorted trigonal-bipyramidal geometry, in which the oxygen atoms of the two $OPMe_3$ ligands occupy axial positions (O-Sb-O = 179.9(1)°), and the three propeller-configured phenyl rings occupy equatorial positions (C_{ipso}-Sb-C_{ipso} = 117–124°) (Figure 4a). The Sb–O bonds average 2.089(3) Å (Σ_{CR} = 2.03 Å),[24] and the P–O bonds (1.528(3) Å) are longer than the corresponding P–O bonds in the free ligand (1.488(5) Å),[29] which is consistent with the coordination of $OPMe_3$ to a highly Lewis acidic center. The Sb–O bonds are also markedly shorter than those in **2b** (2.406(2) Å), which is in-line with the lesser steric encumbrance of the Sb center in **3** relative to that of **1a**, and the enhanced Lewis acidity implied by respective ^{31}P NMR chemical shifts. The shortest Sb–OTf inter-ion interaction (4.68(3) Å; Σ_{vdW} = 3.58 Å) is significantly greater than the sum of the van der Waals radii of Sb and O, illustrating the displacement of the triflate anions by the $OPMe_3$ donors (compare Sb–OTf in compound **3**: 2.172(2) Å). As such **6a** represents an ionic formulation, and is interpreted as a bis-trimethylphosphine oxide complex of a Ph_3Sb^{2+} acceptor. The solid-state structure of **6c** (Figure 4b) is similar to that of **6a**, again illustrating a trigonal-bipyramidal geometry at Sb, and key metrical parameters are detailed in Table 2. The Sb-O-P angles, however, which for **6a** are similar (150.0(2) and 148.8(2)°), are larger for **6c** and have a wider range (151.6(1) and 161.1(1)°), which is consistent with the greater steric bulk of the $OPPh_3$ ligands. Despite the different angles of binding of the two $OPPh_3$ moieties in **6c**, the two Sb–$OPPh_3$ bond lengths are statistically identical (2.100(2) Å).

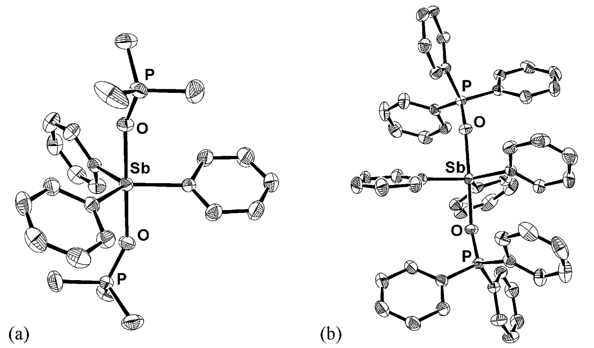
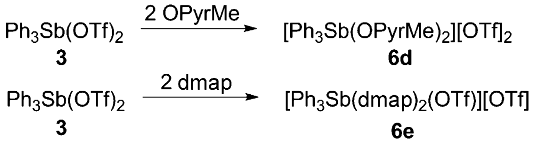


Figure 4. Solid-state structures of the cations in a) **6a** and b) **6c**. All hydrogen atoms and solvent molecules are omitted for clarity.

Table 2. Selected solid-state parameters for complexes **6a** and **6c**.

	Sb–OPR_3 bond lengths [Å]	Shortest Sb–OTf contact [Å]	O-Sb-O angle [°]	P–O bond lengths [Å]
6a	2.104(3) 2.074(3)	4.68(3) (Sb–O)	179.9(1)	1.526(3) 1.530(3)
6c	2.103(2) 2.100(2)	4.998(3) (Sb–O)	178.44(8)	1.529(2) 1.524(2)

Reactions of **3** with two equivalents of the oxidation resistant ligands OPyrMe or dmap also produce stable complexes of analogous formulae $Ph_3Sb(donor)_2(OTf)_2$ [donor = OPyrMe (**6d**) or dmap (**6e**)] (Scheme 6). Following recrystallization from CH_2Cl_2/Et_2O at −30 °C, spectroscopic and elemental microanalysis data for **6d** and **6e** were consistent with the assigned formulae, with the solution stability of the adducts inferred by significant shifts in the NMR resonances of the respective components, particularly the ligands, relative to the starting materials (see Table SI-3 in the Supporting Information).



$$\underset{\mathbf{3}}{Ph_3Sb(OTf)_2} \xrightarrow{\text{2 OPyrMe}} \underset{\mathbf{6d}}{[Ph_3Sb(OPyrMe)_2][OTf]_2}$$

$$\underset{\mathbf{3}}{Ph_3Sb(OTf)_2} \xrightarrow{\text{2 dmap}} \underset{\mathbf{6e}}{[Ph_3Sb(dmap)_2(OTf)][OTf]}$$

Scheme 6. Reactions of **3** with OPyrMe or dmap to yield **6d** and **6e**.

In both cases the solid-state structures were also confirmed by single-crystal X-ray diffraction. Compound **6d** crystallized in the space group $P2_1/n$ with a single formula unit in the asymmetric unit, and the Sb center adopts a trigonal-bipyramidal geometry similar to those in **6a** and **6c**, with two oxygen-bound OPyrMe ligands in axial positions (O-Sb-O = 176.44(6)°), and three equatorial phenyl groups (C_{ispo}-Sb-C_{ipso} = 118–121°) (Figure 5a). The two very similar Sb–OPyrMe (Sb–O) bonds (average 2.139(1) Å; Σ_{CR} = 2.03 Å)[24] are slightly longer than those observed in **6a** and **6c**, perhaps as a consequence of a lower basicity of OPyrMe. The Sb–OPyrMe interactions are, however, significantly shorter than that observed in the related **2a** (2.449(1) Å), reflecting the lesser steric constraints and greater Lewis acidity of the Sb site in **3** relative to that in **1a**. The two OPyrMe ligands in **6d** bind in a bent fashion (average Sb-O-N angle = 117.5(1)°) to a much greater extent than observed in the corresponding phosphine oxide complexes **6a** and **6c** (Sb-O-P > 150°), presumably facilitated by the planarity of the OPyrMe ligand. The shortest inter-ion Sb–OTf interactions in **6d** (4.656(2) and 4.820(2) Å; Σ_{vdW} = 3.58 Å) are well beyond the Σ_{vdW} for Sb and O, which is consistent with an ionic formulation, and the nucleophilic displacement of the triflate anions in **3** by two OPyrMe ligands.

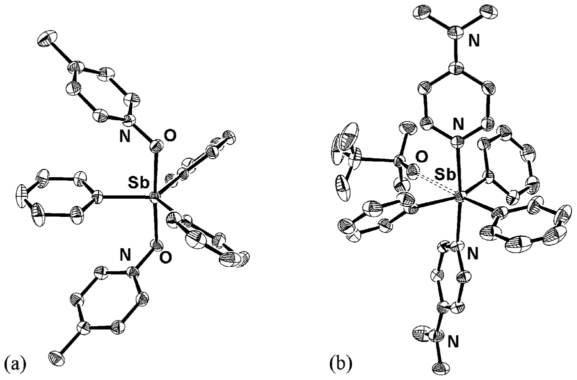


Figure 5. Solid-state structures of the cations in a) **6d** and b) **6e**. All hydrogen atoms and solvent molecules are omitted for clarity.

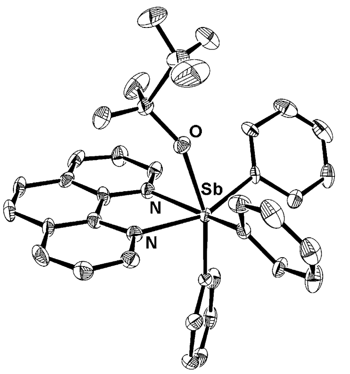
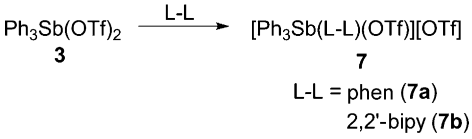


Figure 6. Solid-state structure of one of the two cations in the asymmetric unit of **7a**. All hydrogen atoms and solvent molecules are omitted for clarity.

The dmap derivative **6e** crystallized in the space group $P\bar{1}$ with a single formula unit and three molecules CH_2Cl_2 in the asymmetric unit. In contrast to the structures of **6a** and **6c**/**6d**, the Sb center of **6e** adopts a pseudooctahedral geometry by virtue of a short contact with a triflate anion, along with bonds to two dmap ligands and three phenyl substituents, and is best represented as $[Ph_3Sb(dmap)_2(OTf)][OTf]$ (Figure 5b). The two dmap ligands are *trans* configured (N-Sb-N = 170.69(7)°) as for the ligands in **6a** and **6c**/**6d**, with the *ipso* carbon atoms of the phenyl substituents and an oxygen atom of a triflate anion occupying the remaining four coordination sites all of which are essentially coplanar. The two similar Sb–N bonds (average 2.222(2) Å; $\Sigma_{CR} = 2.11$ Å)[24] are relatively short, but consistent with other examples of coordinate N–Sb bonds (range = 2.27–2.81 Å).[2] Although a short Sb–OTf inter-ion contact clearly prevails in **6e** (Sb–O = 2.714(2) Å), the Sb–O distance is significantly longer than those observed in **3** (average 2.172(2) Å; Σ_{vdW} 3.58 Å), which is consistent with the coordination of two donor atoms at Sb. The second triflate anion, for which Sb–OTf = 5.248(2) Å, is considered non-interacting, and as such **6e** is ionic, but contains a monocation. The short Sb–OTf contact in **6e** contrasts the observations for the otherwise closely related cations in **6a** and **6c**/**6d**, and is likely a consequence of the end-on binding and planarity of dmap, which minimize the steric pressure at the Sb center.

Reactions of **3** with one equivalent of the chelating nitrogen donors 1,10-phenanthroline (phen) or 2,2′-bipyridine (2,2′-bipy) in CH_2Cl_2 furnished compounds of the form $[Ph_3Sb(L\text{-}L)(OTf)][OTf]$ (L-L = phen (**7a**), 2,2′-bipy (**7b**)) (Scheme 7). The colorless solid products were recrystallized from $MeCN/Et_2O$ (**7a**) or CH_2Cl_2/Et_2O (**7b**) at −30 °C, and were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopies (see also Table SI-3 in the Supporting Information), elemental microanalysis, and single-crystal X-ray diffraction. The solid-state structure of **7a** (Figure 6), which crystallized in the space group C_c, with two formula units and three molecules of MeCN in the asymmetric unit, reveals a pseudooctahedral geometry at the Sb in the two closely related cations, analogous to that observed in **6e**, with the *cis* nitrogen atoms of the phen ligand *trans* to the phenyl substituents. The *ipso* carbon centers of these phenyl rings are above the plane defined by the phen ligand and the Sb center, and the phenyl rings are twisted from this plane by 51–65°. The other coordination sites are occupied by the third phenyl substituent and a triflate anion, which are *trans* configured with respect to each other. The Sb–OTf bond (average 2.25(1) Å) is significantly shorter than that in **6e** (2.714(2) Å), and is similar to those observed in **3** (2.172(2) Å). The proximity of the oxygen atom of the triflate anion to the Sb center in compound **7a** is likely facilitated by the planarity of the phen ligand, which contrasts the observed separate planes occupied by the two dmap rings in **6e**. The Sb–N bonds average 2.262(7) Å, and are similar in magnitude to those in **6e**. Attempts to elucidate the solid-state structure of the corresponding 2,2′-bipy complex **7b** were repeatedly hampered by desolvation of single crystals following recrystallization from various solvent mixtures. A rough structure, appropriate for determination of atomic connectivity only, nonetheless revealed a structure analogous to that of **7a** (see Figure SI-2 in the Supporting Information).

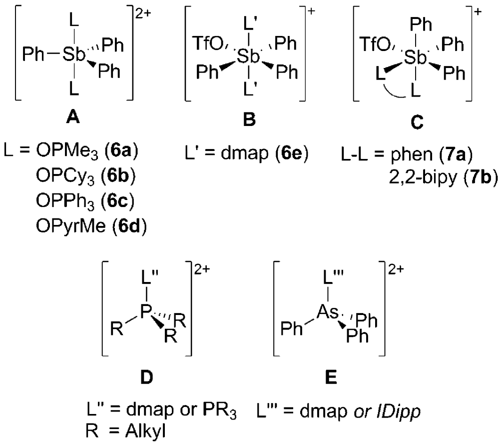


$$\underset{\mathbf{3}}{Ph_3Sb(OTf)_2} \xrightarrow{\text{L-L}} \underset{\mathbf{7}}{[Ph_3Sb(L\text{-}L)(OTf)][OTf]}$$

L-L = phen (**7a**)
2,2′-bipy (**7b**)

Scheme 7. Reaction of **3** with chelating nitrogen donors to yield **7a/b**.

Although the extent of interaction between the Sb center and the triflate anions varies for compounds **6a**–**6e** and **7a**/**7b**, all seven can be considered to be derived from Ph_3Sb^{2+} acceptors, and represent the first such structurally characterized complexes. The bis-ligand complexes **6a**–**6e** (Scheme 8, structures A and B) contrast the previous reports of mono-ligand complexes of R_3Pn^{2+} for Pn = P or As (Scheme 8, structures D and E).[35,39] Attempts to obtain analogous 1:1 complexes of compound **3** with $OPMe_3$ and dmap from equimolar mixtures gave NMR spectra that are interpreted as mixtures of the previously described 2:1 adducts **6a** or **6e** and new species tentatively assigned as $Ph_3Sb(OPMe_3)(OTf)_2$ (**8a**) or $Ph_3Sb(dmap)(OTf)_2$ (**8b**), respectively, with the latter proving impossible to isolate through recrystallization. Furthermore, complexes of R_3Pn^{2+} (Pn = P or As) with chelating ligands have



Scheme 8. Observed solid-state structural motifs for cationic complexes derived from $R_3Pn(OTf)_2$ [Pn = P or Sb (**3**)]. A–C represent structures observed in this study, and D and E represent previously reported structures for phosphorus[35,39] and arsenic,[32] respectively.

yet to be reported, and as such complexes **7a**/**7b** (Scheme 8, structure C) represent a unique class of complexes of Pn^V Lewis acceptors. The differing coordination preferences of R_3Pn^{2+} (Pn = P or As) and R_3Sb^{2+} acceptors is attributed to the radii of the respective pnictogen elements, with the smaller phosphorus center unable to accommodate a second donor atom, that is, adopt a penta-coordinate geometry, consistent with the previously described ionic nature of $[Ph_4P][Cl]$ and molecular nature of Ph_4SbCl. We note that attempts to prepare the phosphorus analogue of **3**, $Ph_3P(OTf)_2$, for comparative purposes through reactions of Ph_3PX_2 (X = Cl or I) with AgOTf or Me_3SiOTf, or reactions of $OPPh_3$ with triflic anhydride were unsuccessful.

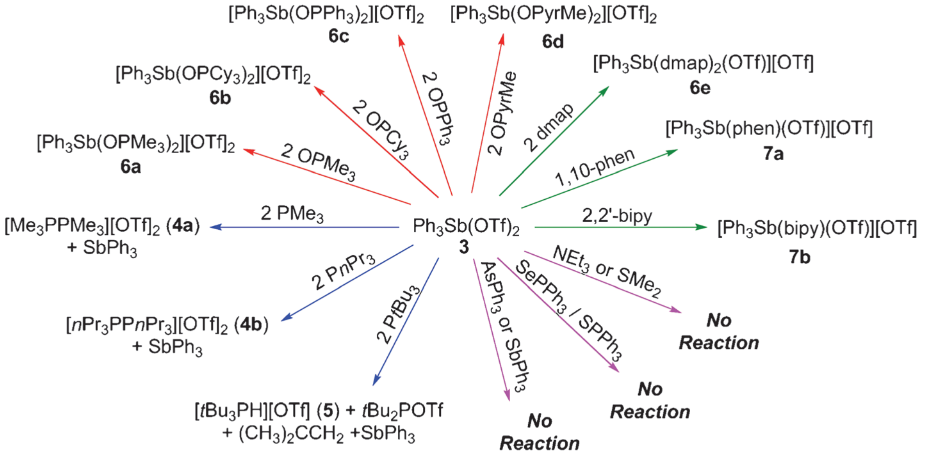
Mixtures of **3** with $PnPh_3$ (Pn = As or Sb), $ChPPh_3$ (Ch = S or Se), NEt_3, or SMe_2 show no evidence of reaction at ambient temperature in CH_2Cl_2, and unreacted **3** was recovered in all cases. These observations reflect the relatively low Lewis basicities of these ligands compared to those discussed above. The reactivity of **3** with p-block Lewis bases is summarized in Scheme 9.

The Sb–ligand bonding in complexes of **3** was also probed through representative ligand exchange reactions of each class of complex. Treatment of solutions of **6a**, **6d**, **6e**, or **7b** in CH_2Cl_2 with two equivalents of $OPMe_3$, OPyrMe, dmap, or 2,2′-bipy were studied by NMR spectroscopy after stirring over 18 h at ambient temperature. In all cases evidence of exchange was apparent, which is consistent with the description of the reported derivatives of **6** and **7** as coordination complexes. Incomplete ligand exchange is observed in most reactions, with the two ligand classes presumably competitively binding the Sb center and reaching equilibrium. Notably, however, the addition of two equivalents of dmap, OPyrMe, or $OPMe_3$ to **7b** led to quantitative displacement of the bipy ligand, and clean formation of complexes **6a**, **6d**, and **6e**, respectively, based on analysis by ^1H NMR spectroscopy. The representative reaction of **6e** with two equivalents of PMe_3 was also explored and led to the quantitative formation of **4a** and liberation of dmap and $SbPh_3$, although this reaction cannot be directly compared to the other equilibrium processes as the formation and precipitation of **4a** are presumably irreversible.

Conclusion

The stiboranes $Ph_4Sb(OTf)$ (**1a**) and $Ph_3Sb(OTf)_2$ (**3**) have been prepared and characterized as synthons for the coordination chemistry of cationic antimony(V). Complexes with classical nitrogen, oxygen, phosphorus, sulfur, arsenic, and antimony donors have been investigated, and two series of derivatives have been isolated and comprehensively characterized. Compound **3** was also shown to undergo redox reactions with phosphines to give phosphonium and diphosphonium cations.

The significant steric encumbrance of the Sb center in **1a** limits its coordination chemistry, and no reaction is observed between **1a** and prototypical phosphine or amine donors. Nevertheless, compounds with the generic formula $[Ph_4Sb(donor)][OTf]$ [donor = OPyrMe (**2a**) and $OPMe_3$ (**2b**)] are feasible due to the "oxygen spacer" between the donor and the sterically restricted core of the acceptor. The steric pressures impose comparatively long bonds between the Sb center and the ligand in the solid-state structures of derivatives of **2**. These compounds expand the small library of structurally characterized complexes of stibonium acceptors, and adopt a trigonal-bipyramidal geometry at the Sb center with the ligands occupying axial positions. Corresponding mixtures of the analogous phosphonium salt, $[Ph_4P]$



Scheme 9. Overview of the reactivity of **3** with p-block donor ligands. Blue = phosphorus donors, red = oxygen donors, green = nitrogen donors, pink = no reaction.

[OTf] (**1 b**) with the ligand library employed for compound **1 a** show no evidence of reaction.

Compound **3** forms complexes of the generic formulae $[Ph_3Sb(donor)_2][OTf]_2$ [donor = $OPMe_3$ (**6 a**), $OPCy_3$ (**6 b**), $OPPh_3$ (**6 c**), OPyrMe (**6 d**)], $[Ph_3Sb(donor)_2(OTf)][OTf]$ [donor = dmap (**6 e**)], and $[Ph_3Sb(donor)(OTf)][OTf]$ [donor = 1,10-phen (**7 a**) or 2,2′-bipy (**7 b**)]. The solid-state structures of the compounds containing oxygen donors (**6 a**–**6 d**) involve a trigonal-bipyramidal Sb center around which the ligands occupy both axial positions, and represent dicationic complexes of the Ph_3Sb^{2+} acceptor. The corresponding compounds containing nitrogen donors (**6 e** and **7 a**/**7 b**) adopt octahedral geometries at the Sb center by virtue of a short contact to a triflate anion, an interaction presumably facilitated by the lower steric pressures of the planar nitrogen donors relative to the conical OPR_3, and side-on binding OPyrMe. In **6 e**, the dmap ligands are *trans* configured, analogous to the ligand configurations in **6 a**–**6 d**, with the chelating donors present in **7 a**/**7 b** enforcing a *cis* configuration of the donors. Compound **3** does not form stable adducts with the weaker Lewis bases $SPPh_3$, $SePPh_3$, $AsPh_3$, $SbPh_3$, SMe_2, or NEt_3 under ambient conditions.

Derivatives of **2**, **6**, and **7** highlight a potentially diverse and extensive coordination chemistry for cationic Sb^V, which evolves from the coordination chemistry of transition metals, but offers the unusual feature of reductive elimination of phosphine ligands. Together with the demonstrated ligand exchange reactivity, this new avenue of coordination chemistry has interesting possibilities for catalysis.

Experimental Section

All reactions and manipulations were performed under an atmosphere of nitrogen by using either standard Schlenk techniques, or within an MBraun or Innovative Technology glovebox. All non-deuterated solvents were initially dried using a Grubbs-type solvent purification system, and subsequently distilled from CaH_2. Deuterated solvents were purchased from Sigma Aldrich Ltd. and dried over 3 Å (CD_3CN) or 4 Å (CD_2Cl_2) molecular sieves. Unless otherwise stated, all chemicals were purchased from Sigma Aldrich Ltd. and purified according to the following regimes. Ph_4SbBr, $OPPh_3$, $OPCy_3$, $OPMe_3$, 4-methylpyridine-*N*-oxide (OPyrMe), $SPPh_3$, $SePPh_3$, and PPh_3 were dried under high vacuum overnight. NEt_3 was distilled from CaH_2. 4-(Dimethylamino)pyridine (dmap) and 1,10-phenanthroline (phen) were sublimed under reduced pressure. 2,2′-Bipyridine (2,2′-bipy) was recrystallized from CH_2Cl_2. PMe_3 and AgOTf were purchased from Strem Chemicals, and the former was distilled prior to use.

NMR spectra were recorded using either Bruker Avance 500, 360, or 300 MHz spectrometers. Chemical shifts are reported relative to residual protonated solvent peaks (^1H, ^{13}C), or to external H_3PO_4 (^{31}P), $CFCl_3$ (^{19}F), and Me_2Se (^{77}Se). IR spectra were recorded on a Perkin–Elmer Spectrum 1000 FTIR spectrometer as Nujol mulls on KBr plates, and elemental analyses were performed by Canadian Microanalytical Service Ltd, Delta British Columbia, Canada. Melting point data was collected on a Gallenkamp melting point apparatus in sealed capillaries.

X-ray crystallographic data were collected at the MAX Diffraction Facility at McMaster University or at the University of Alberta X-Ray Facility. In the former case, suitable crystals were selected and mounted in paratone oil on a MiTeGen loop, then placed in the cold stream of the diffractometer (173 K). Data were collected by using 0.5 degree ω and ϕ scans on a Bruker Apex2 diffractometer by using $Mo_{K\alpha}$ radiation. Unit cell parameters were determined from three consecutive scans at different orientations. The data were integrated by using SAINT[40] and then corrected for absorption with SADABS,[41] solved with SHELXT[42] and refined against F_o^2 data with SHELXL-97.[42] Software: Bruker APEX2 v2014.9–0: Bruker AXS Inc., Madison, WI. In the case of samples analyzed at the University of Alberta, crystallographic analysis was carried at 173 K, on a Bruker D8/APEX II CCD by using graphite-monochromated $Mo_{K\alpha}$ radiation. Structures were solved by using SHELXT and refined against all Fo2 data with using SHELXL-97. For full crystallographic details, see the Supporting Information. Molecular structures presented in the manuscript were plotted by using ORTEP-3V2.02, with thermal ellipsoids at the 50 % probability level. CCDC 975311 (**6 c**), 975313 (**6 e**), 975315 (**3**), 1037803 (**4 b**), 1037804 (**6 a**), 1037805 (**7 a**), 1037806 (**2 b**), 1037807 (**2 a**), 1037808 (**6 d**) and 1037809 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Experimental procedures

Synthesis of Ph_4SbOTf *(**1 a**)*: To a solution of Ph_4SbBr (0.5 g, 0.98 mmol) was added solid AgOTf (0.25 g, 0.98 mmol) leading to the precipitation of a yellow solid over 2 h at ambient temperature in the dark. The mixture was then filtered and all volatiles were removed under high vacuum to furnish the product as a colorless solid. Yield: 0.52 g, 92 %; ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 7.82–7.71$ (m, 4 H; Ph), 7.71 ppm (apparent doublet, $J(H,H) = 5$ Hz, 16 H; Ph); $^{13}C\{^1H\}$ NMR (76 MHz, CD_2Cl_2): $\delta_C = 136.0$ (s, Ph), 134.6 (s, Ph), 131.9 (s, Ph), 122.5 ppm (s, Ph); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.9$ ppm (s, CF_3); ^{121}Sb NMR (86 MHz, CD_3CN): $\delta_{Sb} = 673$ ppm (br s, $[Ph_4Sb]$).

Synthesis of complexes of $Ph_4Sb(OTf)$ **(1 a)**: The syntheses of both complexes of **1 a** were carried out by analogous method, with the synthesis of $[Ph_4Sb(OPyrMe)][OTf]$ (**2 a**) described in full as a representative example.

*$[Ph_4Sb(OPyrMe)][OTf]$ (**2 a**)*: To a solution of **1 a** (100 mg, 0.17 mmol) in CH_2Cl_2 (3 mL) at ambient temperature was added solid OPyrMe (18.8 mg, 0.17 mmol), and the resulting clear, colorless solution was stirred for 2 h. All volatiles were then removed under high vacuum to quantitatively furnish the product as a colorless solid. Yield: 100 mg, 84 %; m.p. 115–117 °C; ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 7.74–7.56$ (m, 20 H; $SbPh_4$), 7.25 (dm, $J(H,H) = 7$ Hz, 2 H; Ar-H [OPyrMe]), 6.91 (dm, $J(H,H) = 7$ Hz, 2 H; Ar-H [OPyrMe]), 2.26 ppm (s, 3 H; CH_3); $^{13}C\{^1H\}$ NMR (76 MHz, CD_2Cl_2): $\delta_C = 142.7$ (s), 138.8 (s), 135.7 (s), 133.3 (s), 131.2 (s), 127.5 (s), 127.4 (s), 20.6 ppm (s, Me); ^{19}F NMR (276 MHz, CD_2Cl_2): $\delta_F = -78.7$ ppm (s, CF_3); FTIR (Nujol mull, ranked intensities): $\tilde{\nu} = 1264$ (1), 1225 (6), 1179 (7), 1158 (4), 1031 (2), 1068 (10), 995 (9), 736 (5), 693 (8), 637 cm^{-1} (3); elemental analysis calcd (%): C 54.09, H 3.95, N 2.03; found: C 54.23, H 3.83, N 2.04.

*$[Ph_4Sb(OPMe_3)][OTf]$ (**2 b**)*: Colorless solid; yield: 98 mg, 85 %; m.p. 141–143 °C; ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 7.74–7.58$ (m, 20 H; $SbPh_4$), 1.09 ppm (d, $J(H,P) = 13$ Hz, 9 H; $OP(CH_3)_3$); $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2): $\delta_P = 42.6$ ppm (s); $^{13}C\{^1H\}$ NMR (76 MHz, CD_2Cl_2): $\delta_C = 135.7$ (s, Ph), 133.4 (s, Ph), 131.2 (s, Ph), 128.5 (s, Ph), 17.2 ppm (d, $J(C,P) = 70$ Hz, $P(CH_3)_3$); ^{19}F NMR (276 MHz, CD_2Cl_2): $\delta_F = -78.8$ ppm (s, CF_3); FTIR (Nujol mull, ranked intensities): $\tilde{\nu} = 1300$ (3), 1264 (1), 1224 (6), 1133 (4), 1071 (10), 1030 (2), 949 (8), 737 (7), 693 (9), 637 cm^{-1} (5); elemental analysis calcd (%): C 55.10, H 4.35; found: C 55.32, H 4.29.

*Mixtures of **1a** with PMe_3 or NEt_3*: To a solution of **1a** (50 mg, 0.086 mmol) in CH_2Cl_2 (2.5 mL) was added neat PMe_3 or NEt_3 (0.17 mmol) at ambient temperature, and the resulting mixture was stirred for 2 h before removing all volatiles under high vacuum to furnish a colorless solid. Analysis by ^1H NMR spectroscopy in CD_2Cl_2 showed only unreacted **1a**, with unreacted PMe_3/NEt_3 presumably removed under vacuum.

*Mixtures of **1a** with 2,2′-bipy or 4,4′-bipy*: To a solution of **1a** (50.0 mg, 0.086 mmol) in CH_2Cl_2 (2.5 mL) was added solid 2,2′-bipy (13.5 mg, 0.086 mmol) or 4,4′-bipy (6.7 mg, 0.043 mmol) at ambient temperature, and the resulting mixture was stirred for 2 h before removing all volatiles under high vacuum to furnish a colorless solid in both cases. Analysis of the solids by ^1H NMR spectroscopy in CD_2Cl_2 showed only unreacted compound **1a** and bipy, with recrystallization of the solid from CH_2Cl_2/Et_2O at $-30\,^\circ C$ in the latter case yielding crystals identified as pure **1a** by ^1H NMR spectroscopy.

*Mixtures of **1a** with dmap*: To a solution of **1a** (50.0 mg, 0.086 mmol) in CH_2Cl_2 (2.5 mL) was added solid dmap (10.5 mg, 0.17 mmol) at ambient temperature, and the resulting mixture was stirred for 2 h before removing all volatiles under high vacuum to furnish a colorless solid. Analysis of the solids by ^1H NMR spectroscopy in CD_2Cl_2 indicated a shift in the resonances of the dmap ligand [$\delta_H = 7.88$ (2 H), 6.42 (2 H), 2.95 ppm (6 H)] from that of the free ligand in the same solvent, along with resonances consistent with compound **1a**. Recrystallization the crude reaction products from CH_2Cl_2/Et_2O at $-30\,^\circ C$, however, repeatedly yielded crystals only of **1a**.

*Synthesis of $[Ph_4P][OTf]$ (**1b**)*: To a solution of $[Ph_4P][Cl]$ (0.4 g, 1.07 mmol) in CH_2Cl_2 (7 mL) was added solid AgOTf (0.27 g, 1.07 mmol) and the mixture stirred at ambient temperature in the dark for 2 h; before filtering, and removing all volatiles under high vacuum to furnish **1b** as a colorless solid. Yield: 0.47 g, 90%; ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 7.95–7.88$ (m, 4 H; Ph), 7.80–7.72 (m, 8 H; Ph), 7.67–7.58 ppm (m, 8 H; Ph); $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2): $\delta_P = 23.3$ ppm (s); $^{13}C\{^1H\}$ NMR (76 MHz, CD_2Cl_2): $\delta_C = 136.1$ (d, $J(C,P) = 2$ Hz, Ph), 134.8 (d, $J(C,P) = 11$ Hz, Ph), 131.0 (d, $J(C,P) = 13$ Hz, Ph), 118.0 ppm (d, $J(C,P) = 90$ Hz, Ph); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.8$ ppm (s, CF_3).

*Mixtures of **1b** and Me_3P, dmap, $OPMe_3$, or OPyrMe*: To a solution of **1b** (40 mg, 0.08 mmol) in CH_2Cl_2 (2 mL) was added neat Me_3P or solid dmap, $OPMe_3$, or OPyrMe (0.08 mmol), respectively, and the resulting clear colorless mixtures were stirred at ambient temperature for 2 h before removing all volatiles under high vacuum. Analysis of the resulting solids by NMR spectroscopy in CD_2Cl_2 in all cases indicated the presence of only **1b** and free ligand, with the exception of the reaction with Me_3P (b.p. = 40 °C), which indicated the presence of only **1b**.

Synthesis of Ph_3SbCl_2: To a solution of Ph_3Sb (5.0 g, 8.5 mmol) in CH_2Cl_2 (50 mL) was added a 1 M solution of SO_2Cl_2 in CH_2Cl_2 (9.3 mL, 9.4 mmol) at $-78\,^\circ C$, and the mixture was stirred for 15 min before warming to ambient temperature and stirring for a further 1 h. All volatiles were then removed under high vacuum to leave an off-white solid, which was recrystallized from CH_2Cl_2/Et_2O at $-30\,^\circ C$. Yield: 5.5 g, 91%; ^1H NMR (300 MHz, $CDCl_3$): $\delta_H = 8.33–8.25$ (m, 6 H; Ph), 7.63–7.54 ppm (m, 9 H; Ph).

*Synthesis of $Ph_3Sb(OTf)_2$ (**3**)*: To a solution of Ph_3SbCl_2 (0.10 g, 0.28 mmol) in CH_2Cl_2 (3 mL) was added solid AgOTf (0.12 g, 0.47 mmol) at ambient temperature and the mixture was stirred for 2 h in the dark before filtering to yield a clear, colorless solution. All volatiles were then removed under high vacuum and the resulting solid was recrystallized at $-30\,^\circ C$ from CH_2Cl_2/pentane. ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 8.08–8.02$ (m, 6 H; Ph), 7.85–7.73 ppm (m, 9 H; Ph); $^{13}C\{^1H\}$ NMR (76 MHz, CD_2Cl_2): $\delta_C = 135.0$ (s), 134.7 (s), 131.6 (s), 131.5 ppm (s); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.0$ ppm (s, CF_3).

Reactions of 3 with phosphines

*Reaction of **3** with two equivalents of PMe_3*: To a solution of Ph_3SbCl_2 (100 mg, 0.24 mmol) in CH_2Cl_2 (3 mL) was added solid AgOTf (121 mg, 0.47 mmol) at ambient temperature and the mixture was stirred in the dark for 2 h before filtering through glass fibre paper. To the resulting clear, colorless solution was then added neat PMe_3 (48.8 μL, 0.47 mmol), leading to the immediate precipitation of a colorless solid, and the mixture was then stirred for a further 1 h. All volatiles were then removed under high vacuum to yield a colorless solid, which was dissolved in CD_3CN for analysis by multinuclear NMR spectroscopy, indicating the formation of $[Me_3P{-}PMe_3][OTf]_2$ (**4a**) and Ph_3Sb. The products were separated by removing all volatiles under high vacuum and washing the resulting solids with CH_2Cl_2. The residue was then re-dissolved in CD_3CN and analyzed by NMR spectroscopy, confirming this component as compound **4a**. ^1H NMR (300 MHz, CD_3CN): $\delta_H = 2.45–2.28$ ppm (m, 18 H); $^{31}P\{^1H\}$ NMR (122 MHz, CD_3CN): $\delta_P = 28.4$ ppm (s, $[Me_3P\text{-}PMe_3]$); $^{13}C\{^1H\}$ NMR (76 MHz, CD_3CN): $\delta_C = 8.83–7.99$ ppm (m, CH_3); ^{19}F NMR (283 MHz, CD_3CN): $\delta_F = -79.4$ ppm (s, CF_3). The CH_2Cl_2 washings were combined and the solvent removed under high vacuum before re-solvating in CD_2Cl_2 for multinuclear NMR analysis, which confirmed the second product to be $SbPh_3$. ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 7.49–7.42$ (m, 6 H; Ph), 7.37–7.32 ppm (m, 9 H; Ph); $^{13}C\{^1H\}$ NMR (76 MHz, CD_2Cl_2): $\delta_C = 138.8$ (s, Ph), 136.8 (s, Ph), 129.5 (s, Ph), 129.3 ppm (s, Ph).

To investigate the intermediate presence of $[Ph_3Sb(PMe_3)_2][OTf]_2$, the reaction was monitored at low temperature. Neat PMe_3 was vacuum transferred onto a frozen ($-196\,^\circ C$) CD_2Cl_2 solution of compound **3** in a J. Young NMR tube and warmed to $-80\,^\circ C$ in the NMR spectrometer. Analysis of the mixture suggested no ^{31}P-containing species in solution, similarly at $-60\,^\circ C$ and at ambient temperature. Consistently, upon removing the sample from the spectrometer a colorless solid was apparent in solution, identified as **4a** by subsequent isolation and analysis by ^{31}P NMR spectroscopy in CD_3CN. $^{31}P\{^1H\}$ NMR (122 MHz, CD_3CN): $\delta_P = 28.4$ ppm (s, $[Me_3P{-}PMe_3]$).

*Reaction of **3** with one equivalent of PMe_3*: To a solution of Ph_3SbCl_2 (100 mg, 0.24 mmol) in CH_2Cl_2 (4 mL) at ambient temperature was added solid AgOTf (121 mg, 0.47 mmol) and the mixture then stirred at ambient temperature in the dark for 2 h before filtering. To the resulting clear, colorless solution was added neat PMe_3 (18.0 mg, 0.24 mmol) leading to immediate precipitation of a colorless solid, and the mixture was stirred for 1 h before removing all volatiles under high vacuum. The solid products were then dissolved in CD_3CN for analysis by multinuclear NMR spectroscopy. ^1H NMR (360 MHz, CD_3CN): $\delta_H = 8.07–8.02$ (m, $Ph_3Sb(OTf)_2$), 7.85–7.75 (m, $Ph_3Sb(OTf)_2$), 7.43–7.39 (m, $SbPh_3$), 7.35–7.30 (m, $SbPh_3$), 2.39–2.24 ppm (m, $[Me_3P\text{-}PMe_3]$); $^{31}P\{^1H\}$ NMR (146 MHz, CD_3CN): $\delta_P = 28.6$ ppm (s, $[Me_3P{-}PMe_3]$).

*Reaction of **3** with two equivalents of $PnPr_3$*: To a solution of Ph_3SbCl_2 (200 mg, 0.47 mmol) in CH_2Cl_2 (6 mL) was added solid AgOTf (242 mg, 0.94 mmol) and the mixture then stirred at ambient temperature in the dark for 2 h before filtering to furnish a clear, colorless solution. Neat $PnPr_3$ (188.8 μL, 0.94 mmol) was then added dropwise leading to the immediate precipitation of a colorless solid. The mixture was stirred subsequently for 1 h at ambient temperature before filtering through glass fibre filter paper. All volatiles were removed from the filtrate to furnish an oily white solid, which was analyzed by multinuclear NMR spectroscopy in CD_2Cl_2 indicating the formation of Ph_3Sb. ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 7.55–7.48$ (m, 6H; $SbPh_3$), 7.40–7.34 (m, 9H; $SbPh_3$), and various minor aliphatic resonances between 3 and 1 ppm. The residue of the filtration was collected by dissolution in MeCN (4 mL), and recrystallized by layering with Et_2O and storing at −30 °C overnight. Large colorless crystals of the product, characterized as $[nPr_3P\text{-}PnPr_3][OTf]_2$ (**4b**), were collected and dried under high vacuum before analyzing by multinuclear NMR spectroscopy. Yield: 0.15 g, 33 %; m.p. > 220 °C (decomposed); ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 2.72–2.60$ (m, 4H; PCH_2), 1.82–1.65 (m, 4H; CH_2CH_3), 1.12 ppm (tt, J(H,H) = 7, J(H,P) = 1 Hz, 9H; CH_3); $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2): $\delta_P = 31.2$ ppm (s); $^{13}C\{^1H\}$ NMR (91 MHz, CD_2Cl_2): $\delta_C = 21.3$ (apparent triplet, J(C,P) = 16 Hz), 17.8 (s), 15.5 ppm (apparent triplet, J(C,P) = 10 Hz); ^{19}F NMR (276 MHz, CD_2Cl_2): $\delta_F = -79.2$ ppm (s, CF_3); FTIR (Nujol mull, ranked intensities): $\tilde{\nu} = 1418$ (7), 1257 (1), 1224 (5), 1156 (4), 1072 (6), 1030 (2), 757 (1), 638 (3), 573 (9), 517 cm^{-1} (8); elemental analysis calcd (%): C 38.83, H 6.84; found: C 38.95, H 7.18.

*Reaction of **3** with two equivalents of $PtBu_3$*: To a solution of Ph_3SbCl_2 (100 mg, 0.24 mmol) in CH_2Cl_2 (3 mL) was added solid AgOTf (121 mg, 0.47 mmol) and the resulting mixture then stirred at ambient temperature in the dark for 2 h before filtering. A solution of $PtBu_3$ (95.4 mg, 0.47 mmol) in CH_2Cl_2 (0.85 mL) was then added, and the resulting clear, colorless solution was stirred for 18 h. All volatiles were then removed to furnish a colorless oily solid, which was dissolved in CD_2Cl_2 for analysis by NMR spectroscopy. $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2): $\delta_P = 219.1$ (s), 123.0 (minor singlet), 51.8 ppm (s); ^{31}P NMR (146 MHz, CD_2Cl_2): $\delta_P = 219.1$ (m), 123.0 (m), 51.8 ppm (dm, ^1J(H,P) = 460 Hz). ^1H NMR spectroscopy also indicated complete consumption of compound **3** to yield Ph_3Sb. Recrystallization of the crude products from CH_2Cl_2/Et_2O at −30 °C afforded well-formed single crystals, identified spectroscopically and crystallographically as $[tBu_3PH][OTf]$ (**5**): ^1H NMR (360 MHz, CD_2Cl_2): $\delta_H = 6.14$ (d, ^1J(H,P) = 460 Hz, 1H; $[HPtBu_3]^+$), 1.62 ppm (d, ^3J(H,P) = 15 Hz, 27H; tBu); $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2): $\delta_P = 52.0$ ppm (s, $[tBu_3PH]^+$); $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2): $\delta_P = 52.0$ ppm (dm, ^1J(H,P) = 460 Hz, $[tBu_3PH]^+$); $^{13}C\{^1H\}$ NMR (91 MHz, CD_2Cl_2): $\delta_C = 121.4$ (q, ^1J(C,P) = 321 Hz, CF_3), 37.6 (d, ^1J(C,P) = 29 Hz, $C(CH_3)_3$), 30.4 ppm (s, $C(CH_3)_3$); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.9$ (s, CF_3). Analysis of the reaction mixture in CD_2Cl_2 after 4 h, evidenced complete conversion to the products based on ^{31}P NMR spectroscopy, and the ^1H NMR spectrum illustrated two peaks consistent with isobutylene at $\delta_H = 4.66$ and 1.67 ppm, respectively, along with Ph_3Sb and "$tBuP$"-containing products.

*Reaction of **3** with two equivalents of $PtBu_3$, and subsequently one equivalent PMe_3*: To a solution of Ph_3SbCl_2 (100 mg, 0.24 mmol) in CH_2Cl_2 (2 mL) was added solid AgOTf (121 mg, 0.47 mmol) and the resulting mixture was stirred at ambient temperature in the dark for 2 h before filtering. A solution of $PtBu_3$ (95.4 mg, 0.47 mmol) in CH_2Cl_2 (0.85 mL) was then added, and the resulting clear, colorless solution was stirred for 18 h. The mixture was then precipitated into Et_2O (10 mL) and the solids (identified as compound **5** by NMR spectroscopy) were removed by filtration. Neat PMe_3 (17.9 mg, 0.24 mmol) was then added leading to the precipitation of a colorless solid, and the resulting mixture was stirred at ambient temperature for 1 h. The solids were then removed by filtration and analyzed by NMR spectroscopy in CD_2Cl_2, and the results were consistent with the formation of $[Me_3P{-}PtBu_2][OTf]$ as the primary product: ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 2.15$ (dd, ^2J(H,P) = 13, ^3J(H,P) = 2 Hz, 9H; PMe_3), 1.45 ppm (dd, ^3J(P,P) = 13, ^4J(P,P) = 1 Hz, 18H; $PtBu_2$); $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2): $\delta_P = 42.6$ (d, ^1J(P,P) = 384 Hz, PMe_3), 10.8 ppm (d, ^1J(P,P) = 384 Hz, $PtBu_2$); $^{13}C\{^1H\}$ NMR (91 MHz, CD_2Cl_2): $\delta_C = 121.4$ (q, ^1J(C,F) = 321 Hz, CF_3), 37.2 (dd, ^1J(C,P) = 31, ^2J(C,P) = 5 Hz, $P(C(CH_3)_3)_2$), 32.2 (dd, ^2J(C,P) = 13, ^3J(C,P) = 6 Hz, $P(C(CH_3)_3)_2$), 14.7 ppm (dd, ^1J(C,P) = 42, ^2J(C,P) = Hz, PMe_3); ^{19}F NMR (282 MHz, CD_2Cl_2): $\delta_F = -78.9$ ppm (s, CF_3).

*Reaction of **3** with PPh_3*: To a solution of Ph_3SbCl_2 (50 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) was added solid AgOTf (60.5 mg, 0.24 mmol) and the mixture was stirred at ambient temperature in the dark for 2 h, before filtering to furnish a clear, colorless solution. Solid PPh_3 (61.9 mg, 0.24 mmol) was then added initially leading to the precipitation of a colorless solid, which re-dissolved upon stirring at ambient temperature over 2 h. All volatiles were then removed under high vacuum to furnish a colorless solid, which was analyzed by NMR spectroscopy in CD_2Cl_2 indicating the complete consumption of PPh_3 and the formation of four new unidentified species. $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2): $\delta_P = 65.9$ (s) [3 %], 58.6 (br s) [57 %], 48.4 (s) [19 %], 44.2 ppm (s) [21 %]. The ^1H NMR spectrum of the products showed a complex series of over-lapping aryl resonances between 7.0 and 8.0 ppm. Purification of the individual components of the mixture proved not to be possible despite attempted recrystallization under various conditions. The reaction of **3** with a single equivalent of PPh_3 under the same conditions again led to a mixture of four unidentified products by ^{31}P NMR spectroscopy: $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2): $\delta_P = 74.8$ (s) [29 %], 50.0 (s) [30 %], 40.4 (s) [19 %], 44.2 ppm (s) [22 %].

Syntheses of complexes of 3: The syntheses of all complexes of **3** from Ph_3SbCl_2 were carried out through a similar method. The synthesis of $[Ph_3Sb(OPMe_3)_2][OTf]_2$ (**6a**) is described as a representative example, followed by characterization data for all compounds.

*$[Ph_3Sb(OPMe_3)_2][OTf]_2$ (**6a**)*: To a solution of Ph_3SbCl_2 (0.15 g, 0.35 mmol) in CH_2Cl_2 (4 mL) was added solid AgOTf (0.18 g, 0.71 mmol) and the mixture was then stirred for 2 h at ambient temperature in the dark. The mixture was then filtered through glass fibre filter paper leaving a clear, colorless solution. Solid $OPMe_3$ (65.1 mg, 0.71 mmol) was then added, and the mixture was stirred at ambient temperature for 1 h before removing all volatiles under high vacuum to furnish a colorless solid, which was recrystallized from CH_2Cl_2/Et_2O at −30 °C. Yield: 0.23 g, 78 %; m.p. 185–187 °C; ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 8.10–8.04$ (m, 6H; SbPh), 7.89–7.79 (m, 9H; SbPh), 1.48 ppm (d, J(H,P) = 13 Hz, 18H; PMe); $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2): $\delta_P = 73.2$ ppm (s); $^{13}C\{^1H\}$ NMR (91 MHz, CD_2Cl_2): $\delta_C = 134.9$ (s, Ar), 134.1 (s, Ar), 133.6 (s, Ar), 132.2 (s, Ar), 121.4 (q, J(C,F) = 321 Hz, CF_3), 15.9 ppm (d, J(C,P) = 68 Hz, Me); ^{19}F NMR (282 MHz, $CD_{32}Cl_2$): $\delta_F = -78.8$ ppm (s, CF_3); FTIR (Nujol mull, ranked intensities): $\tilde{\nu} = 1306$ (6), 1266 (2), 1226 (7), 1152 (5), 1043 (3), 1030 (1), 997 (8), 962 (9), 735 (10), 638 cm^{-1} (4); elemental analysis calcd (%): C 37.38, H 3.98; found C 37.07, H 4.07.

*$[Ph_3Sb(OPCy_3)_2][OTf]_2$ (**6b**)*: Colorless solid; yield: 0.45 g, 61 %; m.p. > 318 °C (decomposed with gas evolution); ^1H NMR (300 MHz, CD_3CN): $\delta_H = 8.12–8.03$ (m, 6H; Ph), 7.97–7.87 (m, 9H; Ph), 1.87–1.68 (m, 6H; Cy), 1.53 (br s, 18H; Cy), 1.36 (br s, 12H; Cy), 0.81–0.24 ppm (m, 30H; Cy); $^{31}P\{^1H\}$ NMR (203 MHz, CD_3CN): $\delta_P = 78.6$ ppm (s); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN): $\delta_C = 135.9$ (s, Ph), 135.1 (s, Ph), 134.6 (s, Ph), 133.3 (s, Ph), 35.7 (d, J(C,P) = 56 Hz, Cy), 27.1 (d, J(C,P) = 13 Hz, Cy), 26.6 (d, J(C,P) = 4 Hz, Cy), 26.3 ppm (s, Cy); ^{19}F NMR (282 MHz, CD_3CN): $\delta_F = -79.2$ ppm (s, CF_3); FTIR (Nujol mull, ranked intensities): $\tilde{\nu} = 1265$ (2), 1222 (6), 1146 (4), 1031 (1), 995 (5), 892 (10), 735 (7), 690 (9), 637 (3), 517 cm^{-1} (8); elemental analysis calcd (%): C 54.06, H 6.56; found C 54.22, H 6.98.

*$[Ph_3Sb(OPPh_3)_2][OTf]_2$ (**6c**)*: Colorless solid; yield: 0.51 g, 71 %; m.p. 196–198 °C; ^1H NMR (300 MHz, CD_2Cl_2): $\delta_H = 7.62–7.55$ (m, 15H; Ph), 7.49–7.42 (m, 6H; Ph), 7.38–7.30 (m, 12H; Ph), 7.10–6.91 ppm (m, 12H; Ph); $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2): $\delta_P = 48.4$ ppm (s, $Ph_3Sb(OPPh_3)_2$); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.6$ ppm (s, CF_3);

for details of the $^{13}C\{^{1}H\}$ NMR spectrum see the Supporting Information; FTIR (Nujol mull, ranked intensities): $\tilde{\nu} = 1262$ (1), 1150 (3), 1115 (4), 1030 (2), 1009 (6), 993 (5), 687 (7), 636 (8), 534 (9), 516 (10), 456 cm^{-1} (11); elemental analysis calcd (%): C 55.69, H 3.76; found: C 55.41, H 3.57.

*$[Ph_3Sb(OPyrMe)_2][OTf]_2$ (**6d**)*: Colorless solid; yield: 0.37 g, 72%; m.p. 181–183 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta_H = 8.14$–8.07 (m, 6H; SbPh), 7.98 (br d, 4H; $J(H,H) = 6$ Hz, C_6H_4N), 7.79–7.73 (m, 9H; SbPh), 7.26 (br d, 4H; $J(H,H) = 6$ Hz, C_6H_4N), 2.37 ppm (s, 6H; CH_3); $^{13}C\{^{1}H\}$ NMR (76 MHz, CD_2Cl_2): $\delta_C = 140.5$ (s), 135.7 (s), 135.1 (s), 132.3 (s), 129.3 (s), 127.4 (s), 121.5 ppm (q, $J(C,F) = 320$ Hz, CF_3); ^{19}F NMR (282 MHz, CD_2Cl_2): $\delta_F = -78.8$ ppm (s, CF_3); IR (Nujol mull, ranked intensities): $\tilde{\nu} = 1286$ (2), 1251 (1), 1221 (5), 1200 (7), 1152 (4), 1027 (3), 835 (10), 760 (9), 741 (8), 636 cm^{-1} (6); elemental analysis calcd (%): C 44.32, H 3.36, N 3.22; found C 44.57, H 3.48, N 3.28.

*$[Ph_3Sb(dmap)_2(OTf)][OTf]$ (**6e**)*: Colorless solid; yield: 0.38 g, 71%; m.p. 200–202 °C; ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta_H = 7.79$–7.69 (m, 15H; Ph), 7.59 (d, $J(H,H) = 8$ Hz, 4H; Ar-H [dmap]), 6.56 (d, $J(H,H) = 8$ Hz, 4H; Ar-H [dmap]), 3.09 ppm (s, 12H; NMe_2); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): $\delta_C = 156.8$ (s), 145.0 (s), 135.3 (s), 134.5 (s), 132.1 (s), 130.0 (s), 121.3 (q, $J(C,F) = 321$ Hz, CF_3), 108.7 (s), 40.2 ppm (s, $N(CH_3)_2$); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.8$ ppm (s, CF_3); FTIR (Nujol mull, ranked intensities): 1621 (7), 1258 (1), 1228 (4), 1150 (5), 1028 (2), 1008 (6), 995 (8), 739 (10), 725 (9), 635 cm^{-1} (3); elemental analysis calcd (%): C 45.60, H 3.94, N 6.26; found: C 45.32, H 3.97, N 6.22.

*$[Ph_3Sb(phen)(OTf)][OTf]$ (**7a**)*: In this case the product was found to precipitate from CH_2Cl_2 upon addition of the ligand, as a colorless solid. The solids were collected by decantation and washed with CH_2Cl_2 (3 mL) before drying under high vacuum, and subsequently recrystallizing from MeCN/Et_2O at −30 °C. Yield: 0.22 g, 55%; m.p. > 262 °C (decomposed); ^{1}H NMR (300 MHz, CD_3CN): $\delta_H = 9.18$ (dm, $J(H,H) = 8$ Hz, 2H; [phen]), 8.90 (dd, $J(H,H) = 6$, $J(H,H) = 1$ Hz, 2H; [phen]), 8.48 (s, 2H; [phen]), 8.26 (dd, $J(H,H) = 8$, $J(H,H) = 5$ Hz, 2H; [phen]), 7.85–7.79 (m, 6H; Ph), 7.68–7.55 ppm (m, 9H; Ph); $^{13}C\{^{1}H\}$ NMR (76 MHz, CD_3CN): $\delta_C = 147.1$ (s), 146.2 (s), 137.7 (s), 136.0 (s), 134.1 (s), 133.6 (s), 132.0 (s), 129.8 (s), 128.9 (s), 121.4 ppm (q, $J(C,F) = 320$ Hz, CF_3); ^{19}F NMR (283 MHz, CD_3CN): $\delta_F = -79.2$ ppm (s, CF_3); FTIR (Nujol mull, ranked intensities): $\tilde{\nu} = 1437$ (2), 1261 (1), 1235 (7), 1208 (6), 1157 (5), 1029 (3), 980 (4), 739 (9), 716 (10), 638 cm^{-1} (8); elemental analysis calcd (%): C 46.23, H 2.79, N 3.37; found: C 46.18, H 2.78, N 3.29.

*$[Ph_3Sb(bipy)(OTf)][OTf]$ (**7b**)*: Colorless solid; yield: 0.29 g, 61%; m.p. 180–182 °C; ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta_H = 9.12$ (d, $J(H,H) = 8$ Hz, 2H; Ar-H [bipy]), 8.65 (d, $J(H,H) = 6$ Hz, 2H; Ar-H [bipy]), 8.62 (t, $J(H,H) = 8.0$ Hz, 2H; Ar-H [bipy]), 7.93 (t, $J(H,H) = 7$ Hz, 2H; Ar-H [bipy]), 7.71 (d, $J(H,H) = 8$ Hz, 6H; Ph), 7.66–7.61 (m, 3H; Ph), 7.61–7.56 ppm (m, 6H; Ph); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): $\delta_C = 146.7$ (s), 144.1 (s), 141.8 (s), 136.3 (s), 135.1 (s), 133.4 (s), 131.4 (s), 130.1 (s), 126.5 (s), 120.5 ppm (q, $J(C,F) = 320$ Hz, CF_3); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.6$ ppm (s, CF_3); FTIR (Nujol mull, ranked intensities): $\tilde{\nu} = 1601$ (11), 1261 (1), 1232 (4), 1201 (5), 1157 (2), 1030 (3), 987 (7), 734 (8), 723 (9), 691 (10), 631 (6), 517 cm^{-1} (12); elemental analysis calcd: C 44.63, H 2.87 N 3.47; found: C 44.60, H 2.87, N 3.47.

*Attempted synthesis of $Ph_3Sb(OPMe_3)(OTf)_2$ (**8a**) and $Ph_3Sb(dmap)(OTf)_2$ (**8b**)*: To a solution of Ph_3SbCl_2 (150 mg, 0.35 mmol) in CH_2Cl_2 (4 mL) was added solid AgOTf (181.8 mg, 0.71 mmol), and the mixture was stirred for 2 h at ambient temperature in the dark before filtering. A solution of dmap or $OPMe_3$ (0.35 mmol) in CH_2Cl_2 (1 mL) was then added dropwise over approximately 15 min, and the resulting solutions were stirred at ambient temperature for 2 h. All volatiles were then removed, and the resulting colorless solid was analyzed by NMR spectroscopy in CD_2Cl_2. In the reaction with dmap, the ^{1}H NMR spectrum indicated conversion of dmap to two new products, consistent with compound **8b** and the previously assigned 1:2 adduct **6e** in a 7.5:1 ratio. In the reaction with $OPMe_3$ a similar mixture was apparent, but in this case compound **8a** and the 1:2 adduct **6a** were present in a 4:1 ratio. Separation of the 1:1 adducts from **6a** and **6e**, respectively, by recrystallization proved to be impossible.

*Mixtures of **3** with two equivalents of NEt_3 or SMe_2*: To a solution of Ph_3SbCl_2 (100 mg, 0.24 mmol) in CH_2Cl_2 (2 mL) was added solid AgOTf (121 mg, 0.47 mmol), and the mixture was stirred for 2 h at ambient temperature in the dark before filtering. Neat NEt_3 (65.6 μL, 0.47 mmol) or SMe_2 (34.6 μL, 0.47 mmol) was then added, and the mixtures were stirred for 1 h before removing all volatiles to furnish colorless solids in both cases. Analysis of the solids by ^{1}H NMR spectroscopy in CD_2Cl_2 showed only compound **3** in solution, with the unreacted volatile ligands presumably removed under vacuum.

*Mixtures of **3** with two equivalents of $ChPPh_3$ (Ch = S or Se)*: To a solution of Ph_3SbCl_2 (100 mg, 0.24 mmol) in CH_2Cl_2 (2 mL) was added solid AgOTf (121 mg, 0.47 mmol), and the mixture was stirred for 2 h at ambient temperature in the dark before filtering. Solid $ChPPh_3$ (Ch = S or Se) (0.47 mmol) was then added, and the mixtures were stirred for 1 h before removing all volatiles to furnish colorless solids. Analysis of the solids by ^{31}P NMR spectroscopy in CD_2Cl_2 showed signals consistent with the starting materials in both cases (Ch = S, $\delta_P = 43.1$ ppm; Ch = Se, $\delta_P = 34.8$ ppm (s, *with* ^{77}Se satellites $J(P,Se) = 348$ Hz). Recrystallization of both solids from CH_2Cl_2/Et_2O furnished only crystals identified as unreacted $ChPPh_3$ (S or Se) by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

*Mixtures of **3** with two equivalents of $PnPh_3$ (Pn = As or Sb)*: To a solution of Ph_3SbCl_2 (100 mg, 0.24 mmol) in CH_2Cl_2 (2 mL) was added solid AgOTf (121 mg, 0.47 mmol), and the mixture was stirred for 2 h at ambient temperature in the dark before filtering. Solid $AsPh_3$ or $SbPh_3$ (0.24 mmol) was then added, and the resulting mixtures were stirred at ambient temperature for 1 h before removing all volatiles under high vacuum to furnish colorless solids. Analysis of the products by ^{1}H NMR spectroscopy indicated that no reaction had occurred, showing signals consistent with both unreacted compound **3** and the free ligand.

Ligand exchange reactions of compounds 6a, 6d, 6e, and 7b: All exchange reactions were carried out according to analogous protocols, and the reaction of compound **7b** with $OPMe_3$ is therefore described in full as a representative example: To a solution of compound **7b** (40 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) was added solid $OPMe_3$ (9.1 mg, 0.1 mmol), and the resulting clear, colorless mixture was stirred at ambient temperature for 18 h. All volatiles were then removed under high vacuum, and the resulting solids were analyzed by ^{1}H NMR spectroscopy in CD_2Cl_2, illustrating the quantitative formation of compound **6a**, as previously assigned, and the presence of free 2,2-bipy in solution.

In cases where the ligand exchange was not quantitative, the degree of exchange was estimated through the relative integrals of resonances corresponding to each complex.

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