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Structural diversity for phosphine complexes of stibenium and stibinidenium cations[†]

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Reactions of trimethylphosphine or diphosphines with SbCl₃ in the presence of AlCl₃ or Me₃SiSO₃CF₃ give ligand stabilized stibenium and stibinidenium cations. The geometry at each antimony center reveals a variety of environments for antimony that describes new bonding and highlights new directions in the chemistry of the pnictogen elements.

Electron-rich pnictogen centers can behave as Lewis acceptor sites despite the presence of a lone pair of electrons, and coordination chemistry involving non-metal donor sites provides a versatile synthetic approach to bonds between nonmetal elements, as extensively demonstrated for phosphorus.¹ Cationic centers are the most effective acceptors, and have been recently applied to obtain a variety of rare bonds including P–As,^{2–4} P–Sb,^{3–6} P–Bi,⁴ As–Sb,⁷ As–Bi^{7,8} and Sb–Bi.⁸ We have now exploited this approach to obtain a series of new P–Sb bonded compounds that illustrate a variety of structural arrangements for antimony and highlight new directions in the chemistry of the pnictogen elements.

Reactions of PMe₃, dmpm, dppm, dmpe or dppe, with SbCl₃ in the presence of AlCl₃ or Me₃SiSO₃CF₃ occur rapidly at room temperature. Compounds [dppmSbCl₂] **1b** [AlCl₄], [dmpeSbCl₂] **2a** [SO₃CF₃], [dppeSbCl₂] **2b** [AlCl₄] and [(Me₃P)₂SbCl₂] **4** [SO₃CF₃] have been isolated from the respective reaction mixture and comprehensively characterized (Table 1). The ³¹P NMR spectrum of each reaction mixture shows the isolated compound to be the quantitative product (**1** and **2**) or the dominant species (**4**). Solid state structures of the cations **1b**, **2a**, **2b** and **4**, as determined by X-ray crystallography, are shown in Fig. 1, and selected structural parameters are listed in Table 1.

The cations 1b, 2a and 2b all adopt a cyclic structure in which each phosphorus center can be considered as a

phosphonium environment, although the structure of 1b is distinguished from those of 2a and 2b by the non-symmetric P-Sb-P interaction [P-Sb = 2.6011(4) and 3.0272(4) Å]. Therefore, 1b is best considered as a stibinophosphonium, analogous to 3,^{4,6} with a weak secondary P-Sb contact that imposes only minor distortion on the trigonal pyramidal environment of antimony. Consistently, the shorter P(1)-Sb(1) distance in 1b is similar to the P-Sb bonds in 2a, 2b and 3, and the distinct geometry at antimony in 1b is due to a frustrated Sb-P Lewis pair imposed by the three atom P-C-P restriction of dppm. In contrast to 1b, 2a and 2b exhibit a tetra-coordinate, disphenoidal geometry at antimony, with chlorine atoms in the axial positions and a symmetric P-Sb-P interaction, which is unusual for an interpnictogen framework and reveals a flexible new bonding environment for antimony. The structural features observed for derivatives of 2 and 4 are analogous to the features observed for isoelectronic neutral diphosphine-GeX₂ adducts.9



The geometry at antimony (P–Sb–P and Cl–Sb–Cl angles) is very similar in compounds **2a**, **2b**, and **4**, indicating that the cyclic structures of **2a** and **2b** impose only minor restriction on the geometry at antimony. Cation **4** accommodates the phosphorus centers in the equatorial positions of a distorted disphenoidal geometry at the antimony, in contrast to $[(Ph_3P)_2SbPh_2]$ **5** $[PF_6]^4$ in which the phosphorus centers occupy the axial positions. Consequently, the *trans* influence of the phosphine ligands in **5** imposes substantially longer [2.8694(8) Å and 2.8426(9) Å] Sb–P bonds relative to the equatorial P–Sb bonds in **4** [2.5890(4) Å and 2.5805(4) Å]. The differences between the ³¹P NMR chemical shifts of the

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	1b [AlCl ₄]	2a [SO ₃ CF ₃]	2b [AlCl ₄]	4 [SO ₃ CF ₃]	6b [AlCl ₄] ₂	7b [Al ₂ Cl ₇] ₂
Sb(1)–P(1)	2.6011(4)	2.5655(4)	2.6121(5)	2.5890(4)	2.6270(11)	2.6191(6)
Sb(1) - P(2)	3.0272(4)	2.5658(4)	2.6164(5)	2.5805(4)	2.6101(11)	2.6074(6)
Sb(1)-Cl(1)	2.4088(4)	2.5729(4)	2.6791(5)	2.6707(4)	2.3397(11)	2.3187(9)
Sb(1)-Cl(2)	2.3718(4)	2.5520(4)	2.4640(5)	2.5079(4)	_ ``	_ ()
Shortest	Sb-Cl	Sb–O	Sb-Cl	Sb-O	Sb-Cl	Sb-Cl
Cation-Anion	3.5596(6)	2.9436(14)	3.1255(5)	2.996(1)	3.086(1)	3.3415(7)
P-Sb-P	61.215(12)	81.190(11)	80.933(16)	101.754(13)	65.77(3)	80.60(2)
Cl-Sb-Cl	96.328(17)	165.527(14)	162.004(19)	158.504(14)	_ ()	_ ()
$\Delta\delta$ (³¹ P)	5.2	34.1	17.5	6.2	-2.3	49.1
$\Delta\delta$ (³¹ P) ligand	-22.8	-48.4	-13.1	-55	-22.8	-13.1
$\Delta\Delta\delta$ (³¹ P) ^a	28.0	82.5	30.6	61.2	20.5	62.2
$^{a}\Delta\Delta\delta$ (³¹ P) = $\Delta\delta$ (³	P _{complexed phosphine})	$-\Delta\delta$ (³¹ P _{free phosphine})				

Table 1 Selected interatomic distances (Å), bond angles (°) and ³¹P NMR shifts (ppm) for title compounds and ³¹P NMR shifts for free ligands



Fig. 1 Views of the cations in (i) **1b** [AlCl₄], (ii) **2b** [AlCl₄], (iii) **2a** [SO₃CF₃], (iv) **4** [SO₃CF₃], (v) **6b** [AlCl₄]₂, and (vi) **7b** [Al₂Cl₇]₂. Thermal ellipsoids correspond to 50% probability, and hydrogen atoms are omitted for clarity.

complexed and free forms of the diphosphines $[\Delta\Delta\delta(^{31}P)$ in ppm, Table 1] for **1b**, **2b**, and **5** $[\Delta\Delta\delta(^{31}P) = 28.0, 30.6, and 1.5,$ respectively] are uniformly smaller than those for **1a**, **2a** and **4** $[\Delta\Delta\delta(^{31}P) = 55.9, 82.5, and 61.2, respectively], which$ correlates with the relative length of the P–Sb bonds, andthe relative donor strength of the phosphine centers.

Reactions of dppm or dppe with SbCl₃ in the presence of excess AlCl₃ occur rapidly at room temperature and the ³¹P NMR spectrum of each reaction mixture shows a single phosphorus containing species (Table 1), assigned as [dppmSbCl] **6b** [AlCl₄]₂ and [dppeSbCl] **7b** [Al₂Cl₇]₂, respectively. The solid state structures of the cations **6b** and **7b**, shown in Fig. 1, reveal symmetric P–Sb–P interactions in both cases with acute P–Sb–P angles [65.77(3) and 80.60(2)°, respectively]. The structural adjustment from **1b** to **6b** upon abstraction of the chloride ion is more dramatic than observed from **2b** to **7b**, and is borne out in the observed ³¹P NMR shifts, which for **7b** [49.1 ppm] is at a higher frequency than that for **2b** [17.5 ppm], but the shift for **6b** [–2.3 ppm] is at a lower frequency than that for **1b** [5.2 ppm].

The P–Sb–P frameworks of **6** and **7** represent the first examples of stibinodiphosphonium cations, analogous to the rare examples of 2-phosphino-1,3-diphosphonium cations.^{10–12} The central Sb–Cl bonds in **6b** [2.3397(11) Å] and **7b** [2.3187(9) Å] are very short compared to those in **1b** [2.4088(4) Å], **2a** [2.5520(4) Å], **2b** [2.4640(5) Å] and **4** [2.5079(4) Å], and the Sb–P bonds in **6b** and **7b** are essentially identical to those in the monocationic analogues **1b** and **2b**. The Sb–Cl unit can be considered as accommodating the dicationic charge, invoking a chelate coordination complex

model 9 for frameworks 6b and 7b, in which the acceptor is a stibinidenium cation, $[Sb-Cl]^{2+}$ (Sb-R = stibinidene). In this context, cations 2a and 2b are examples of 8, chelate complexes of a stibenium cation $[SbCl_2]^+$. Consistently, ³¹P NMR spectra of reaction mixtures containing 1b or 2b with either PMe₃ or dmpe show quantitative formation of 4 and 2a, respectively, together with free dppm or dppe, illustrating the coordinative nature of the interaction. Similarly, the ³¹P NMR spectrum of a reaction mixture of dppm with 7b shows broadened signals due to 7b, 6b, free dppm and free dppe, demonstrating facile ligand redistribution.



Examples of coordination complexes involving a phosphine ligand on a stibenium cation^{4,6} represent part of a developing series of interpnictogen compounds,^{2,3,5,7,8} however chelate complexes are rare for any pnictenium acceptor. For example, the phosphorus center in **10** represents an iminophosphenium

cation interacting with a chelating bipyridine ligand,¹³ the arsenic center in **11** represents an arsenium cation in which the amine substituent is tethered to an imine donor, and in **12**, an arsenidenium dication is supported by both a pendant imine donor and achelating bipyridine ligand.¹⁴ Classification of **6** and **7** as chelate complexes of $[Sb-Cl]^{2+}$ is consistent with the structure of $[SbCl(15\text{-crown-5})][SbCl_6]_2$, which also contains $[Sb-Cl]^{2+}(Sb-Cl = 2.365 \text{ Å})$ shrouded by a crown ether.¹⁵ The new complexes provide a ready access to $[Sb-Cl]^{2+}$ as a synthon for the systematic development of new antimony frameworks.

In summary, we have prepared a series of diphosphinestabilized cations that are rare examples of the $[R_3P-Sb(X_2)-PR_3]^+$ framework and the first examples of the $[R_3P-Sb(X)-PR_3]^{2+}$ frameworks including the first chelate complexes featuring a stibenium or stibinidenium acceptor. Ring strain and phosphine donor strength are determinants of the geometry at the antimony centre. We are exploiting the coordination chemistry of pnictinidenium cations and more highly charged pnictogen centers as a means to systematically develop new interpnictogen frameworks.

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