# **Inorganic Chemistry**

# **Prototypical Phosphine Complexes of Antimony(III)**

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**S** Supporting Information

**ABSTRACT:** Complexes of the generic formula  $[Cl_n(PR_3)_mSb]^{(3-n)+}$  (n = 1, 2, 3, or 4 and <math>m = 1 or 2) have been prepared featuring  $[ClSb]^{2+}$ ,  $[Cl_2Sb]^{1+}$ ,  $Cl_3Sb$ , or  $[Cl_4Sb]^{1-}$  as acceptors with one or two phosphine ligands  $\{PMe_3, PPh_3, PCy_3 (Cy = C_6H_{11})\}$ . The solid-state structures of the complexes reveal foundational features that define the coordination chemistry of a lone pair bearing stibine acceptor site. The experimental observations are interpreted with dispersion-corrected density functional theory calculations to develop an understanding of the bonding and structural diversity.



# INTRODUCTION

The vast array of transition metal coordination complexes involving neutral two-electron donors is the foundation of classical coordination chemistry, which usually involves multiple ligands and is understood by invoking acceptor d-orbitals at the metal center. The donor-acceptor (Lewis acid-base) concept is extrapolated to describe adducts between p-block elements, referring to an acceptor with a single or multiple ligands [e.g., H<sub>3</sub>NBH<sub>3</sub> and (THF)<sub>2</sub>AlH<sub>3</sub>, respectively]. For the relatively rare examples of electron-rich centers behaving as Lewis acceptors, the presence of a lone pair of electrons at the acceptor site<sup>1</sup> offers interesting structural and electronic features and some demonstrated applications in catalysis.<sup>2</sup> The most diverse array of complexes involving an electron-rich acceptor site is reported for monoantimony acceptors with phosphine ligands, including examples of neutral compounds,  $^{3-5}$  anions,  $^6$  and a broad array of cations. Stibenium cations can accommodate a single phosphine ligand to give the general structure  $1^{7-9}$  chelating diphosphine ligands to impose either structure 2 or  $3^{10}$  or two phosphine ligands in structural types  $4^8$  and  $5^{10}$  In addition, two examples of the dication chelate complex structure  $6^{10}$  and the unique tris-phosphine tricationic complex 7 have been reported.<sup>11</sup>

The structural diversity demonstrated by complexes of the type 1–7 prompted us to perform a systematic assessment of PR<sub>3</sub> complexes of chloro-antimony acceptors (R = Me, Ph, Cy). The potentially broad configurational variety for such compounds is illustrated in Chart 1 for the generic formula  $[Cl_n(PR_3)_mSb]^{(3-n)+}$  (n = 2, 3, or 4 and m = 1 or 2) using an octahedral frame that includes a lone pair at the antimony acceptor site and in some cases a vacant coordination site. Our observations reveal substantial configurational versatility for antimony including examples of 9 of the 12 configurations listed in Chart 1. More importantly, the data provide for a

rationalization of configurational preferences that define the coordination chemistry of a lone pair bearing stibine acceptor site, and this is confirmed by analogous observations for select derivatives of  $Cl_2PhSb$  and  $[Ph_2Sb]^{1+}$  acceptors. The experimental observations are interpreted with dispersion-corrected density functonal theory (DFT) calculations to develop an understanding of the bonding and structural diversity. Together, the study debuts a coordination chemistry for antimony that has the potential to be as extensive and diverse as many transition metals.

# EXPERIMENTAL SECTION

Reagents and Apparatus. All reagents were handled in a MBraun Labmaster 130 glovebox (dry  $N_2$ ) or on a grease-free dual manifold argon and vacuum (base vacuum =  $2 \times 10^{-2}$  mbar) Schlenk line. Prior to use, HPLC-grade CH<sub>3</sub>CN (Aldrich) was refluxed over CaH<sub>2</sub> for at least 48 h and distilled under an atmosphere of argon directly onto 3 Å molecular sieves, which had been freshly activated at 300 °C under dynamic vacuum for 24 h. All other solvents were obtained from an MBraun Solvent purification system and stored for at least 48 h over activated 4 Å molecular sieves prior to use. All reagents were purchased from Sigma-Aldrich. Deuterated solvents were dried using the same procedure as  $CH_3CN$ .  $SbCl_3$  (99.99%) was purified by sublimation and Sb(OTf)<sub>3</sub> was prepared in situ from the metathesis of SbF<sub>3</sub> and Me<sub>3</sub>SiO<sub>3</sub>SCF<sub>3</sub> (TMSOTf). SbF<sub>3</sub> (99.99%), Ph<sub>3</sub>P (97%), and Cy<sub>3</sub>P (97%) were used as received. PMe<sub>3</sub> (97%) and TMSOTf (99%) were distilled before use. Reactions were carried out inside the glovebox in screw-cap glass vials that had been dried at 200 °C for at least 1 h and placed under dynamic vacuum (glovebox antechamber) while still hot. NMR tubes fitted with J-Young valves were charged and sealed inside the glovebox. Elemental analyses were carried out by Canadian Microanalytical Ltd. in Delta, British Columbia, Canada. All

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Chart 1. Potential Structural Variety (VSEPR-Inconsistent Structures Are Not Considered) in an Octahedral Frame for Antimony Complexes Composed of Four (Anion), Three (Neutral) or Two (Monocation) Chloride Substituents and One or Two Phosphine Ligands  $(P = PR_3)^a$ 



<sup>*a*</sup>The labels denote the abbreviated generic formula and distinguish between each configuration of the chloride substituents and the phosphine ligands. Bold line = lone pair;  $\Box$  = vacant coordination site.

quantum chemical calculations were carried out using Gaussian 09. See Supporting Information for complete citation.

**Preparation Procedures and Characterization Data.** [*Cl<sub>3</sub>(PMe<sub>3</sub>)Sb*]. PMe<sub>3</sub> (0.08 g, 1.0 mmol) and SbCl<sub>3</sub> (0.23 g, 1.0 mmol) were combined in CH<sub>3</sub>CN. The resulting white suspension was stirred for 1 h and then allowed to settle. Crystals were obtained from the supernatant by slow evaporation. Yield: 0.27 g, 88%. Elemental analysis for C<sub>3</sub>H<sub>9</sub>Cl<sub>3</sub>PSb (calcd./expt.): C (11.85/11.87), H (2.98/ 3.22). Melting point: 188–190 °C. NMR (CD<sub>3</sub>CN, 298 K, 7.05 T field strength): <sup>1</sup>H: 1.98 ppm (*d*, <sup>2</sup>J<sub>H-P</sub> = 14.3 Hz), <sup>13</sup>C{<sup>1</sup>H}: 10.1 ppm, (*d*, <sup>1</sup>J<sub>C-P</sub> = 35 Hz), <sup>31</sup>P{<sup>1</sup>H}: 9.6 ppm (s).

[Cl<sub>3</sub>(PPh<sub>3</sub>)Sb]. SbCl<sub>3</sub> (0.23 g, 1.0 mmol) and PPh<sub>3</sub> (0.26 g, 1.0 mmol) were combined in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) to obtain a clear, golden yellow solution, which was stirred for 1 h. The reaction mixture was filtered and concentrated under a vacuum to ca. 2 mL and stored at room temperature for 24 h, which led to the formation of small yellow crystals. The reaction mixture was removed from vacuum and allowed to sit at room temperature for 24 h, which led to the formation of small yellow club block-shaped crystals that were washed with 0.5 mL of cold CH<sub>2</sub>Cl<sub>2</sub> and dried under a vacuum. Yield: 0.41 g, 84%. Melting point: 120–122 °C. Elemental analysis for C<sub>18</sub>H<sub>15</sub>Cl<sub>3</sub>PSb (calcd/expt): C (44.09/44.97), H (3.08/3.23). NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, 7.0 T field strength): <sup>1</sup>H: 7.1–7.9 (*m*, Ph<sub>3</sub>P), <sup>13</sup>C{<sup>1</sup>H}: 128.4 ppm (*d*, <sup>1</sup>J<sub>C-P</sub> = 25.0 Hz), <sup>31</sup>P{<sup>1</sup>H}: 5.6 ppm (*s*).

 $[Cl_3(PCy_3)Sb]$ . SbCl<sub>3</sub> (0.11 g, 0.50 mmol) and PCy<sub>3</sub> (0.14 g, 0.50 mmol) were combined in 3 mL of CH<sub>2</sub>Cl<sub>2</sub> to obtain a light yellow solution. The reaction mixture was stirred for 20 min, filtered through

5 6 7 glass wool, and concentrated under a vacuum to 1 mL. Very pale yellow block-like crystals were obtained over 48 h at -30 °C, isolated by decantation, washed with 0.5 mL of cold CH<sub>2</sub>Cl<sub>2</sub> and dried under a vacuum. Yield: 0.21 g, 82%. Melting point: 142–145 °C (dec). Elemental analysis for C<sub>18</sub>H<sub>33</sub>Cl<sub>3</sub>SbP (calcd/expt): C (42.51/42.73), H (6.54/6.63). NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, 8.45 T field strength): <sup>1</sup>H: 1.36–1.92 ppm (*m*, 10H), 3.23 ppm (*tq*, 12.9 Hz, 2.6 Hz, 1H),  $^{13}C{}^{1}H{}$ : 26.3 ppm, (s), 27.82 (*d*,  $^{3}J_{C-P} = 11.2$  Hz), 29.65 (*d*,  $^{2}J_{C-P} =$ 4.8 Hz), 33.85 (*d*,  $^{1}J_{C-P} = 15.0$  Hz),  $^{31}P{}^{1}H{}$ : 25.1 ppm (s).

[*Cl*<sub>3</sub>(*PMe*<sub>3</sub>)<sub>2</sub>*Sb*]. A solution of PMe<sub>3</sub> (0.46 g, 6.0 mmol) in 4 mL of CH<sub>3</sub>CN was added to SbCl<sub>3</sub> (0.68 g, 3.0 mmol) dissolved in 4 mL of CH<sub>3</sub>CN. Midway through the addition a large amount of white precipitate appeared. By the end of the addition a clear, pale yellow solution was obtained which was allowed to stir for 30 min, concentrated under a vacuum to ca. 2 mL and filtered through glass wool. Colorless blocks were obtained by diffusion of Et<sub>2</sub>O into the concentrated CH<sub>3</sub>CN solution. The crystals were washed with cold CH<sub>3</sub>CN and dried under a vacuum. Yield: 1.10 g, 97%. Melting point: 110–113 °C (dec). Elemental analysis for C<sub>6</sub>H<sub>18</sub>Cl<sub>3</sub>SbP<sub>2</sub> (calcd/expt): C (18.95/18.84), H (4.77/4.59). NMR (CD<sub>3</sub>CN, 298 K, 8.45 T field strength): <sup>1</sup>H: 1.76 ppm (*d*, <sup>2</sup>*J*<sub>H–P</sub> = 11.33 Hz), <sup>13</sup>C{<sup>1</sup>H}: 11.9 ppm (*d*, <sup>1</sup>*J*<sub>C–P</sub> = 25.0 Hz), <sup>31</sup>P: -10.2 ppm (*m*, <sup>2</sup>*J*<sub>P–H</sub> = 11.2 Hz).

[*Cl*<sub>3</sub>(*PPh*<sub>3</sub>)<sub>2</sub>*Sb*]. PPh<sub>3</sub> (0.52 g, 2.0 mmol) and SbCl<sub>3</sub> (0.23 g, 1.0 mmol) were combined in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. The resulting clear yellow solution was stirred for 1 h, filtered through glass wool, concentrated under a vacuum to 2 mL, and recrystallized at -30 °C to obtain light yellow translucent crystals. The crystals were isolated by decantation, washed with 0.5 mL of cold CH<sub>2</sub>Cl<sub>2</sub>, and dried under a vacuum. Yield: 0.65 g 86%. Melting point: 115–118 °C. Elemental analysis for C<sub>36</sub>H<sub>30</sub>Cl<sub>3</sub>SbP<sub>2</sub> (calcd/expt): C (57.45/57.75), H (4.02/4.39). NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, 7.0 T field strength): <sup>1</sup>H: 7.1–7.9 (*m*, PPh<sub>3</sub>), <sup>13</sup>C{<sup>1</sup>H}: 128.4 ppm (*d*, <sup>1</sup>*J*<sub>C-P</sub> = 25.0 Hz), <sup>31</sup>P{<sup>1</sup>H}: 5.6 ppm (*s*).

 $[Cl_3(PCy_3)_2Sb]$ . SbCl<sub>3</sub> (0.11 g, 0.50 mmol) and PCy<sub>3</sub> (0.28 g, 1.0 mmol) were combined in a 3 mL of CH<sub>3</sub>CN. The reaction mixture was stirred for 16 h to get a light yellow suspension. The supernatant was removed, and the precipitate was washed with 3 mL of cold CH<sub>3</sub>CN and pumped dry. The supernatant was concentrated under a vacuum to obtain yellow needle-shaped crystals. The crystals and bulk powder exhibited identical NMR spectra, although trace amounts of [Cl<sub>3</sub>(PCy<sub>3</sub>)Sb] was also found in the bulk and could not be separated by recrystallization. Yield (impure): 0.66 g. Melting point: 135–138 °C. Elemental analysis for C<sub>36</sub>H<sub>66</sub>Cl<sub>3</sub>P<sub>2</sub>Sb (calcd/expt): C (54.80/ 52.38), H (8.43/8.07). NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, 7.0 T field strength): <sup>1</sup>H: 1.34–2.56 ppm (*m*), <sup>31</sup>P{<sup>1</sup>H}: 15.7 ppm (*s*).

 $[Cl_2(PMe_3)Sb][OTf].$  SbCl<sub>3</sub> (0.11 g, 0.50 mmol) and TMSOTf (0.11 g, 0.50 mmol) were combined in 2.5 mL of CH<sub>3</sub>CN and stirred for 1 h. A solution of PMe<sub>3</sub> (0.04 g, 0.50 mmol) in 2 mL of CH<sub>3</sub>CN was added, and the reaction mixtures were stirred for 1 h to obtain a clear, colorless solution. All volatiles were removed under a vacuum to obtain a white powder (0.207 g, calcd. for product 0.209 g), which was recrystallized from CH<sub>3</sub>CN at -30 °C to obtain colorless block-shaped crystals, which were washed with cold CH<sub>3</sub>CN and dried under a vacuum. Yield: 0.19 g, 91%. Melting point: 108–111 °C. Elemental analysis for C<sub>4</sub>H<sub>9</sub>Cl<sub>2</sub>F<sub>3</sub>O<sub>3</sub>PSSb (calcd/expt): C (11.49/11.37), H (2.17/2.19). NMR (CD<sub>3</sub>CN, 298 K, 8.45 T field strength): <sup>1</sup>H: 1.99 ppm (d, <sup>2</sup>J<sub>H-P</sub> = 14.7 Hz), <sup>13</sup>C{<sup>1</sup>H}: 9.7 ppm (d, <sup>1</sup>J<sub>C-P</sub> = 34.1 Hz), <sup>31</sup>P{<sup>1</sup>H}: 14.6 ppm (s), <sup>19</sup>F{<sup>1</sup>H}: -80.0 ppm (s).

 $[Ph_2(PMe_3)Sb][OTf]$ . Sb(OTf)<sub>3</sub> (0.29 g, 0.50 mmol) and SbPh<sub>3</sub> (0.35 g, 1.0 mmol) were combined in CH<sub>3</sub>CN (4 mL) and stirred for 1 h to get a pale yellow solution of Ph<sub>2</sub>SbOTf. Neat PMe<sub>3</sub> (0.11 g, 1.5 mmol) was added in three portions to obtain a clear, light yellow solution. This reaction mixture was stirred for 40 min, filtered through glass wool, concentrated under a vacuum to approximately 2 mL.

# Table 1. Crystal Data for the Featured Compounds

	[Cl <sub>3</sub> (PMe <sub>3</sub> )Sb]	[Cl <sub>3</sub> (PPh <sub>3</sub> )Sb]	[Cl <sub>3</sub> (PCy <sub>3</sub> )Sb]	$[Cl_3(PMe_3)_2Sb]$	$[Cl_3(PPh_3)_2Sb]$	$[Cl_3(PCy_3)_2Sb]$
formula	C <sub>3</sub> H <sub>9</sub> Cl <sub>3</sub> PSb	C <sub>18</sub> H <sub>15</sub> Cl <sub>3</sub> PSb	C <sub>18</sub> H <sub>33</sub> Cl <sub>3</sub> PSb	$C_6H_{18}Cl_3P_2Sb$	C36H30Cl3P2Sb	C <sub>36</sub> H <sub>66</sub> Cl <sub>3</sub> P <sub>2</sub> Sb
fw	304.17	490.37	508.51	380.24	752.64	788.93
space grp	$P2_1/n$	$P\overline{1}$	$P\overline{1}$	$P2_1/n$	I2/a	$P\overline{1}$
a /Å	7.9261 (11)	10.5374 (8)	10.376 (3)	7.6594 (4)	15.8017 (12)	9.7577 (7)
b/Å	19.089 (3)	10.5630 (8)	15.895 (4)	11.4178 (6)	9.5425 (8)	10.3383 (7)
c /Å	13.1115 (18)	10.6579 (8)	20.641 (5)	16.0941 (8)	22.4802 (18)	11.2342 (8)
$\alpha$ /deg		92.9183 (8)	85.320 (4)			115.1065 (7)
$\beta$ / deg	100.8495 (17)	115.7836 (7)	80.800 (4)	96.3001 (5)	101.4987 (9)	104.6530 (7)
γ /deg		113.9875 (7)	73.177 (4)			94.0515 (8)
$V/Å^3$	1948.3 (5)	937.79 (12)	3214.2 (14)	1398.98 (12)	3321.7 (5)	972.13 (12)
Z	8	2	6	4	4	1
$\rho / g \text{ cm}^{-3}$	2.074	1.737	1.576	1.805	1.505	1.348
λ /Α	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T/K	1/3	173	173	173	173	1/3
GOF	1.036	1.102	0.872	1.048	1.068	1.079
$K_1$	0.0259	0.0190	0.0394	0.0123	0.0204	0.0250
WK <sub>2</sub>	$[C1 (DM_{2}) \text{Sh}]$	$[Dh (DM_{2})Sh]$	$\left[ C_{1} \left( \text{DD}_{1} \right) \text{ sh} \right]$	[Dh (DMa) Sh]	$\left[Cl(DM_{2}), Sh\right]$	$[M_{\alpha}(CH CN)]$
	[OTf]	[Pfl_2(PMe_3)Sb] [OTf]	[OTf]	[Ph <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> Sb] [OTf]	$[OTf]_2$	$\begin{bmatrix} Mg(CH_3CN)_6 \end{bmatrix} \\ \begin{bmatrix} Cl_4(PMe_3)Sb \end{bmatrix}_2 \end{bmatrix}$
formula	$C_4H_9Cl_2F_3O_3PSSb$	$\mathrm{C_{16}H_{19}F_3O_3PSSb}$	$C_{37}H_{30}Cl_2F_3O_3P_2SSb$	$C_{19}H_{28}F_3O_3P_2SSb$	$C_8H_{18}ClF_6O_6P_2S_2Sb$	$C_{18}H_{36}Cl_8MgN_6P_2Sb_2$
fw	417.79	501.09	866.26	577.16	607.48	949.88
space grp	$P2_1/c$	P1	P1	$P2_1/c$	$P2_1/n$	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a /A	10.798 (2)	8.2553 (2)	9.5641 (7)	8.2974 (3)	13.5151 (8)	10.9776 (15)
b /A	11.059 (2)	10.8326 (3)	12.0248 (8)	11.1805 (4)	11.4915 (7)	10.9983 (15)
c /A	12.214 (3)	11.1367 (3)	17.5876 (12)	26.4962 (9)	13.9937 (8)	32.060 (4)
$\alpha$ /deg	114,202 (2)	98.4361 (3)	94.0493 (9)	22.205((1))	105 5000 (/)	
$\beta$ / deg	114.382 (2)	97.6027 (3)	96.8668 (10)	93.3876 (4)	105.7092 (6)	
$\gamma / \text{deg}$	1220 5 (5)	93.1231 (3)	110.3615 (9)	2452 52 (15)	2002.2 (2)	2050 5 (0)
V/A°	1328.5 (5)	9/3./0 (4)	1869.0 (2)	2453./3 (15)	2092.2 (2)	38/0.7 (9)
Z	4	2	2	4	4	4
$\rho/g \text{ cm}^{-1}$	2.089	1.709	1.539	1.502	1.929	1.030
λ / A T / V	0./10/5	0./10/5	0.710 75	0./10/5	0.710 75	0./10/5
	1/5	1/5	1/5	1/5	1/3	1/5
D	0.0212	0.0157	0.0280	0.0201	0.0175	0.0267
K <sub>1</sub>	0.0313	0.0137	0.0289	0.0201	0.0173	0.0307
wik <sub>2</sub>	0.0010	$[Cl_{*}(Ph)(PMe_{*})]$	56.0719 Sh]	$[Cl_{*}(Pb)(PPb_{*})Sb]$	0.0 <del>1</del> .01.1	$(Ph)(PPh_),Sh]$
fam	aula	C H C l DSh	50]	C H C DSh		U CIDSh
form	nuia	245.92		$C_{24}\Pi_{20}CI_2PSD$	7	42 <sup>H</sup> 35 <sup>Cl</sup> 2 <sup>P</sup> 2 <sup>SD</sup>
IW		345.82 D2 /#		532.02 D2 /m	/: 	94.29 2 / a
spac	å	$PZ_1/n$		$PZ_1/n$ 10.2222 (4)	11	$\frac{2}{l}$
u / 1	Å	0.0302(2)		10.3232(4) 11.6723(4)	14	2.9097 (2) 1.2568 (2)
0 / I	n İ	17.8313(3) 10.5339(3)		11.0723(4) 18.4318(7)	1-	(2)
c /1	dea	10.3339 (3)		10.4510 (7)	1;	.9243 (3)
B/ 0	dea	93 8302 (3)		90 4966 (4)	90	5 6050 (7)
p/ (	lea	75.6562 (5)		JU.4JUU (4)		
V /	Å <sup>3</sup>	1281.52 (6)		2220.87 (14)	34	542.78 (9)
v /. Z		4		4	4	
n /a	$\sigma$ cm <sup>-3</sup>	1.792		1.591	1	448
λ / λ	\$ Å	0.710 73		0.710 73	0	710 73
T /	K	173		173	0. 17	73
GO	F	1,173		1.149	1	111
R.	-	0.0163		0.0230	0	0185
wR.		0.0411		0.0555	0.	0474
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Colorless crystals were obtained upon storage -30 °C for 24 h, isolated by removing the supernatant by pipet and washed with 0.5 mL of cold CH<sub>3</sub>CN and dried under a vacuum. Yield: 0.42 g, 83%. Melting point: 117–119 °C. Elemental analysis for C<sub>16</sub>H<sub>19</sub>F<sub>3</sub>O<sub>3</sub>PSSb (calcd/expt): C (38.35/38.66) H (3.82/3.88). NMR (CD<sub>3</sub>CN, 298 K, 7.05 T field strength): <sup>1</sup>H: 1.60 ppm (*d*, <sup>2</sup>J<sub>H-P</sub> = 13.5 Hz, 9H), 7.52–7.57

ppm (*m*, 6H), 7.67–7.72 (*m*, 4H),  ${}^{13}C{}^{1}H$ : 10.3 ppm (*d*,  ${}^{1}J_{C-P}$  = 31.9 Hz), 130.9 ppm (*s*), 131.6 ppm (*s*), 138.1 ppm (*s*),  ${}^{31}P{}^{1}H$ : -21.2 ppm (*s*),  ${}^{19}F$ : ppm (*s*): -79.2 ppm (*s*).

 $[Cl_2(PMe_3)_2Sb][OTf]$ . SbCl<sub>3</sub> (0.23 g, 1.0 mmol) and TMSOTf (0.22 g, 1.0 mmol) were combined in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) and stirred for 30 min to yield a clear and colorless solution. This was added dropwise to a

#### Scheme 1. Synthetic Approaches to Prototypical Complexes of Antimony(III)

a)	$n PR_3 + SbCl_3 \longrightarrow [Cl_3(PR_3)_nSb]$ $n = 1 \text{ or } 2, R = Me, Ph \text{ or } Cy$
b)	$nPR_3 + SbCl_3 + Me_3SiOTf \longrightarrow [Cl_2(PR_3)_nSb][OTf] + Me_3SiCl $ $n = 1, R = Me$ n = 2, R = Me  or  Ph
c)	$PMe_3 + Ph_2SbCI + Me_3SiOTf \longrightarrow [Ph_2(PMe_3)Sb][OTf] + Me_3SiCI$
d)	Sb(OTf) <sub>3</sub> + 2SbPh <sub>3</sub> $\longrightarrow$ 3Ph <sub>2</sub> Sb(OTf) $\xrightarrow{\text{xs.PMe}_3}$ 3[Ph <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> Sb][OTf]
e)	$2PMe_3 + SbCl_3 + xsMe_3SiOTf \longrightarrow [Cl(PMe_3)_2Sb][OTf]_2 + 2Me_3SiCl$
f)	$MgCl_2 + 2SbCl_3 \xrightarrow{CH_3CN} [(CH_3CN)_6Mg][SbCl_4]_2 \xrightarrow{2PMe_3} [(CH_3CN)_6Mg][Cl_4(PMe_3)Sb]_2$

stirring solution of PMe<sub>3</sub> (0.228 g, 3.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) over 30 s to produce a cloudy white suspension. The reaction mixture was allowed to stir for 1 h yielding a fine white powder and a clear and colorless supernatant, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of which exhibited two signals (5.8 ppm, 85% and -2.2 ppm, 15%). Removal of solvent under dynamic vacuum at room temperature over 4 h yielded a fine white powder (0.515 g), which was recrystallized in CH<sub>3</sub>CN (10 mL) at -30 °C. Highly reflective colorless block-shaped crystals were obtained after 5 days, isolated by decantation, washed with cold CH<sub>3</sub>CN (3 × 3 mL); Yield: 0.40 g, 80%; melting point: 135 °C dec.; elemental analysis calcd (found): C 17.02 (16.97), H 3.67 (3.41); NMR: <sup>1</sup>H (CD<sub>3</sub>CN, 500 MHz, 293 K): 2.08 (*d*, 18H, <sup>2</sup>J<sub>PH</sub> = 14.1 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125.76 MHz, 293 K): 11.6 (*d*, <sup>1</sup>J<sub>PC</sub> = 34.4 Hz), 118.5 (*s*); <sup>19</sup>F NMR (CD<sub>3</sub>CN, 282.44 MHz, 293 K): -79.1 (*s*); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 202.46 MHz, 293 K): 6.2 (*s*).

[*Cl*<sub>2</sub>(*PPh*<sub>3</sub>)<sub>2</sub>*Sb*][*OTf*]. To a solution of SbCl<sub>3</sub> (0.09 g, 0.40 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added a solution of PPh<sub>3</sub> (0.11 g, 0.40 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). Neat TMSOTf (0.09 g, 0.40 mmol) was added, and the clear, bright yellow solution was stirred at room temperature. Following filtration through glass wool and concentration under reduced vacuum, crystalline yellow blocks were obtained after storage at room temperature for 24 h. The crystals were washed with 0.5 mL of cold CH<sub>2</sub>Cl<sub>2</sub> and dried under a vacuum. Yield: 0.66 g, 76%. Melting point: 105 °C (dec.). Elemental analysis for C<sub>37</sub>H<sub>30</sub>Cl<sub>2</sub>F<sub>3</sub>O<sub>3</sub>P<sub>2</sub>SSb (calcd/expt): C (51.30/51.05), H (3.49/3.01). NMR (298 K, 11.7 T field strength): <sup>1</sup>H (CDCl<sub>3</sub>): 7.46–7.57 ppm (*m*, Ph), <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>): 128.4 (*d*, <sup>1</sup>*J*<sub>C-P</sub> = 24 Hz), 129.2 (*d*, <sup>3</sup>*J*<sub>C-P</sub> = 10 Hz), 131.3 (*s*), 134.0 (*d*, <sup>2</sup>*J*<sub>C-P</sub> = 13 Hz), <sup>31</sup>P{<sup>1</sup>H}(CD2Cl<sub>2</sub>): -5.0 ppm (*s*, broad).

[Ph<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Sb][OTf]. A solution of Sb(OTf)<sub>3</sub> (0.29 g, 0.50 mmol) and SbPh<sub>3</sub> (0.35 g, 1.0 mmol) were combined in CH<sub>3</sub>CN (4 mL) and stirred for 1 h to get a pale yellow solution. All volatiles were removed under a vacuum to yield an off-white powder, which was not isolated. The powder was redissolved in  $CH_2Cl_2$  (3 mL), and a solution of PMe3 (0.34 g, 4.5 mmol) in CH2Cl2 (3 mL) was dropwise added to get a clear, very light brown solution. This reaction mixture was stirred for 10 min, filtered, concentrated under a vacuum to approximately 3 mL. Large, colorless blocks, obtained upon recrystallization at -30 °C over 24 h, were isolated by removing the supernatant by pipet and were washed with 0.5 mL cold CH<sub>2</sub>Cl<sub>2</sub> and dried under a vacuum. Yield: 0.69 g, 80%. Melting point: 98-100 °C. Elemental analysis for C<sub>19</sub>H<sub>29</sub>F<sub>3</sub>O<sub>3</sub>P<sub>2</sub>SSb (calcd/expt): C (39.54/39.96), H (4.89/4.68). NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, 8.45 T field strength): <sup>1</sup>H: 1.19 ppm (d, <sup>2</sup>J<sub>H-P</sub> = 7.9 Hz, 18H), 7.53-7.59 ppm (m, 6H), 7.65-7.69 (m, 4H), <sup>13</sup>C{<sup>1</sup>H}: 12.2 ppm (d, <sup>1</sup>J<sub>C-P</sub> = 12.1 Hz), 130.6 ppm (s), 131.0 ppm (s), 136.6 ppm (s), <sup>31</sup>P{<sup>1</sup>H}: -41.3 ppm (s), <sup>19</sup>F: -79.2 ppm (s).

[*Cl*(*PMe*<sub>3</sub>)<sub>2</sub>*Sb*][*OTf*]<sub>2</sub>. A solution of excess TMSOTf (0.67 g, 3.0 mmol) in 4 mL of CH<sub>3</sub>CN was added to solid [(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>*Sb*] (0.38 g, 1.0 mmol), and the clear, colorless solution was allowed to stir for 1 h. Volatiles were removed under a vacuum to yield a sticky powder, which was redissolved in a minimum of CH<sub>3</sub>CN and recrystallized via diffusion of Et<sub>2</sub>O at -30 °C to give colorless block-shaped crystals that were washed with 0.5 mL of cold CH<sub>3</sub>CN. Yield: 0.50 g, 82%. Melting point: 157–160 °C. Elemental analysis for C<sub>8</sub>H<sub>18</sub>ClF<sub>6</sub>O<sub>6</sub>P<sub>2</sub>S<sub>2</sub>Sb (calcd/expt): C (15.81/15.45), H (2.99/2.83). NMR (CD<sub>3</sub>CN, 298 K, 8.45 T field strength): <sup>1</sup>H: 2.0 ppm (d, <sup>2</sup><sub>JH-P</sub> = 14.6 Hz), <sup>13</sup>C{<sup>1</sup>H}: 9.6 ppm (d, <sup>1</sup><sub>C-P</sub> = 34.0 Hz), <sup>31</sup>P{<sup>1</sup>H}: 15.8 (*s*, broad).

 $[Mg(CH_3CN)_6][Cl_4(PMe_3)Sb]_2$ . MgCl<sub>2</sub> (0.10 g, 1.0 mmol) and SbCl<sub>3</sub> (0.46 g, 2.0 mmol) were combined in 8 mL of CH<sub>3</sub>CN. The reaction

mixture was stirred for 16 h to obtain a white suspension. Neat PMe<sub>3</sub> (0.16 g, 2.0 mmol) was added to obtain a clear solution, which became cloudy upon stirring for an additional 1 h. The supernatant was removed from the white precipitate and filtered. Slow removal of CH<sub>3</sub>CN at room temperature yielded colorless crystalline blocks. The dried precipitate and crystals gave identical <sup>31</sup>P, <sup>1</sup>H, and <sup>13</sup>C NMR spectra. Yield: 0.78 g, 74%. Melting point: 175–178 °C (dec). Samples prepared for elemental analysis (dynamic vacuum for 24 h) show loss of one molecule of CH<sub>3</sub>CN giving [Mg(CH<sub>3</sub>CN)<sub>5</sub>][Cl<sub>4</sub>(PMe<sub>3</sub>)Sb]<sub>2</sub>, C<sub>16</sub>H<sub>33</sub>N<sub>5</sub>Sb<sub>2</sub>MgCl<sub>8</sub>P (calcd/expt): C (21.14/21.27), H (3.66/3.49), N(7.71/7.84). NMR (CD<sub>3</sub>CN, 298 K, 8.45 T field strength): <sup>1</sup>H: 1.95 ppm (*d*, 18H, <sup>2</sup>J<sub>H-P</sub> = 14.2 Hz, PMe<sub>3</sub>); 1.99 ppm (*s*, 18H, CH<sub>3</sub>CN), <sup>13</sup>C{<sup>1</sup>H}: 10.4 ppm (*d*, <sup>1</sup>J<sub>C-P</sub> = 36.2 Hz), <sup>31</sup>P{<sup>1</sup>H}: 7.7 ppm (*s*, broad).

[*Cl*<sub>2</sub>(*Ph*)(*PMe*<sub>3</sub>)*Sb*]. A solution of PMe<sub>3</sub> (0.04 g, 0.50 mmol) in 1 mL of CH<sub>3</sub>CN was added to PhSbCl<sub>2</sub> (0.13 g, 0.50 mmol) dissolved in 3 mL of CH<sub>3</sub>CN. The clear colorless reaction mixture was allowed to stir for 15 min, filtered, and concentrated under a vacuum at room temperature to obtain clear colorless crystalline blocks that were washed with 0.5 mL of cold CH<sub>3</sub>CN and dried under a vacuum. Yield: 0.30 g, 86%. Melting point: 147–149 °C. Elemental analysis for C<sub>9</sub>H<sub>14</sub>C<sub>12</sub>PSb (calcd/expt): C (31.26/31.53), H (4.08/4.19). NMR (CD<sub>3</sub>CN, 298 K, 7.05 T field strength): <sup>1</sup>H: 1.75 ppm (*d*, <sup>2</sup>*J*<sub>H–P</sub> = 13.9 Hz, 9H), 7.38–7.52 ppm (*m*, 3H), 8.29 ppm (*m*, 2H), <sup>13</sup>C{<sup>1</sup>H}: 10.2 ppm, (*d*, <sup>1</sup>*J*<sub>C–P</sub> = 35 Hz), <sup>31</sup>P{<sup>1</sup>H}: -9.2 ppm (*s*).

 $[Cl_2(Ph)(PPh_3)Sb]$ . A solution of PPh<sub>3</sub> (0.262 g, 1 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to PhSbCl<sub>2</sub> (0.260 g, 1 mmol) dissolved in 2 mL of DCM. The clear golden yellow reaction mixture was allowed to stir for 15 min, filtered, and concentrated under vacuum to ca. 1 mL. Yellow crystalline blocks were obtained by diffusion of pentane vapor into this solution at -30 °C over 24 h and isolated by decanting the supernatant. Yield: 0. 217 g, 42%. Melting point: 118 °C dec; NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, 8.45 T field strength): <sup>1</sup>H: 7.1–7.9 (*m*, Ph<sub>3</sub>P), <sup>13</sup>C{<sup>1</sup>H}: 128.4 ppm (*d*, <sup>1</sup>J<sub>C-P</sub> = 25.0 Hz), <sup>31</sup>P{<sup>1</sup>H}: 5.6 ppm (*s*).

Structure Determination of  $[Cl_2(Ph)(PPh_3)_2Sb]$ . This product could not be isolated as a pure substance and was formed together with  $[Cl_2(Ph)(PPh_3)Sb]$ . A solution of PPh<sub>3</sub> (0.262 g, 1 mmol) in 2 mL of CH<sub>3</sub>CN was added to PhSbCl<sub>2</sub> (0.130 g, 1 mmol) to obtain a yellow solution, which was allowed to stir for 40 min. Upon concentration to 1 mL at -30 °C for 72 h, a mixture of yellow and colorless crystals was obtained, and the colorless crystals were identified as  $[Cl_2(Ph)-(PPh_3)_2Sb]$  by X-ray crystallography. It was not possible to manually isolate a sufficient quantity of the colorless crystals to characterize the compound as a pure substance.

# RESULTS AND DISCUSSION

**Preparation of Phosphine Complexes of Antimony.** A series of  $PR_3$  (R = Me, Ph, Cy) complexes on  $[ClSb]^{2+}$ ,  $[Cl_2Sb]^{1+}$ ,  $Cl_3Sb$ , or  $[Cl_4Sb]^{1-}$  acceptors have been prepared and structurally characterized. As illustrated in Scheme 1a, reactions of  $PR_3$  with SbCl<sub>3</sub> yield the corresponding derivatives of  $[Cl_3(PR_3)Sb]$ . In the presence of excess phosphine the bisphosphine complexes,  $[Cl_3(PR_3)_2Sb]$ , are formed. Analogous reactions of  $Cl_2(Ph)Sb$  with  $PR_3$  give the corresponding derivatives of  $[Cl_2(Ph)(PR_3)Sb]$ . Attempts to prepare  $[Cl_2(Ph)(PMe_3)_2Sb]$  yielded only  $[Cl_2(Ph)(PMe_3)Sb]$  and free  $PMe_3$  even in the presence of a 6-fold excess of phosphine.



Figure 1. Views of the solid-state structures for (a)  $[mer-Cl_3(PMe_3)Sb]$  (showing Sb–Cl intermolecular interactions that results in a polymeric array), (b)  $[fac-Cl_3(PPh_3)Sb]$  (dimeric structure), (c)  $[mer-Cl_3(PCy_3)Sb]$ , (d)  $[mer-Cl_3-cis-(PMe_3)_2Sb]$ , (e)  $[mer-Cl_3-trans-(PPh_3)_2Sb]$ , and (f)  $[mer-Cl_3-trans-(PCy_3)_2Sb]$ .

We speculate that the Lewis acidity of the antimony center in  $[Cl_2(Ph)(PR_3)Sb]$  is quenched by PMe<sub>3</sub>, but not by PPh<sub>3</sub>.

Reaction of PMe<sub>3</sub> with SbCl<sub>3</sub> in the presence of 1 equivalent of TMSOTf gives  $[Cl_2(PMe_3)Sb][OTf]$  with elimination of TMSCl as illustrated in Scheme 1b, while attempts to obtain  $[Cl_2(PPh_3)Sb][OTf]$  were unsuccessful, giving only  $[Cl_2(PPh_3)_2Sb][OTf]$ . The corresponding  $[Cl_2(PMe_3)_2Sb]$ -[OTf] is formed in the presence of 2 equivalents or excess PMe<sub>3</sub>. The analogous reaction of PMe<sub>3</sub> with Ph<sub>2</sub>SbCl and TMSOTf gives  $[Ph_2(PMe_3)Sb][OTf]$  according to Scheme 1c, and  $[Ph_2(PMe_3)_2Sb][OTf]$  is formed according to Scheme 1d from Ph<sub>2</sub>(OTf)Sb [generated *in situ* via substituent exchange between  $(OTf)_3Sb$  and Ph<sub>3</sub>Sb].

In the presence of excess TMSOTf, mixtures of PMe<sub>3</sub> with  $SbCl_3$  yield  $[Cl(PMe_3)_2Sb][OTf]_2$ , as in Scheme 1e. Attempts to prepare the PPh<sub>3</sub> derivative were unsuccessful, resulting in formation of  $[Cl_2(PPh_3)_2Sb][OTf]$  even in the presence of a large excess of TMSOTf. Reaction of PMe<sub>3</sub> with MgCl<sub>2</sub> and  $SbCl_3$  in CH<sub>3</sub>CN yields  $[Mg(CH_3CN)_6][Cl_4(PMe_3)Sb]_2$ , according to Scheme 1f. However, there is no evidence of an analogous reaction occurring with PPh<sub>3</sub>.

Structure and Bonding in Neutral Phosphine Complexes of Antimony. The structural features of the neutral complexes  $[Cl_3(PMe_3)Sb]$ ,  $[Cl_3(PPh_3)Sb]$ ,  $[Cl_3(PCy_3)Sb]$ ,  $[Cl_3(PMe_3)_2Sb]$ ,  $[Cl_3(PPh_3)_2Sb]$ , and  $[Cl_3(PCy_3)_2Sb]$  are illustrated in Figure 1, and selected structural parameters are listed in Table 2. In the solid state,  $[Cl_3(PMe_3)Sb]$  adopts a polymeric arrangement in which antimony centers are bridged by chlorine centers that impose a distorted square planar SbCl<sub>4</sub> frame with a phosphine center in an axial position. The Sb–Cl distances involving the bridging chlorine centers are predictably longer than those involving the terminal chlorine centers. Considering the shortest Sb–Cl interactions (Figure 2), we envisage a lone pair of electrons occupying the site *trans* to the phosphine ligand in the square-based pyramid, representing the configuration [*mer*-Cl<sub>3</sub>PSb] A, illustrated in Chart 1.

Dimeric arrangements are observed for  $[Cl_3(PPh_3)Sb]$  and  $[Cl_3(PCy_3)Sb]$  in the solid state, which represent config-

urations [*fac*-Cl<sub>3</sub>PSb] and [*mer*-Cl<sub>3</sub>PSb] B, respectively (Chart 1). In each case, two chlorine atom bridges result from edgesharing, square-based pyramids with a chlorine substituent in the axial position. Interestingly,  $[Cl_3(PPh_3)Sb]$  adopts a centrosymmetric dimer, while  $[Cl_3(PCy_3)Sb]$  adopts a dimer with  $C_2$  symmetry. The bridging Sb–Cl distances are longer than those involving the terminal chlorine centers.

The bis-phosphine complexes  $[Cl_3(PR_3)_2Sb]$  all adopt monomeric structures in the solid state with meridionally configured chlorine substituents. The phosphine ligands are *cis*configured in  $[mer-Cl_3-cis-(PMe_3)_2Sb]$ , while a *trans* configuration is observed for  $[mer-Cl_3-trans-(PPh_3)_2Sb]$  and  $[mer-Cl_3$  $trans-(PCy_3)_2Sb]$ . We envisage that the sixth coordination site at antimony in these complexes is occupied by a lone pair of electrons. The alternative configuration  $[fac-Cl_3-cis-(PR_3)_2Sb]$ is not observed.

The P-Sb and Sb-Cl bond lengths in derivatives of [Cl<sub>3</sub>(PR<sub>3</sub>)Sb] and [Cl<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>Sb] are compared graphically in Figure 3, coded according to the substituent (or lone pair) that is trans to the P-Sb and Sb-Cl bonds, respectively. Derivatives of [Cl<sub>3</sub>(PR<sub>3</sub>)Sb] exhibit average P–Sb lengths (horizontal lines in Figure 3 left) that are consistent with the relative Lewis basicity of the phosphine. Longer P-Sb bonds are observed in the analogous derivatives of  $[Cl_3(PR_3)_2Sb]$ , imposed in the PPh<sub>2</sub> and PCv<sub>2</sub> derivatives by the *trans* configuration and influence of the phosphines. The cis configuration of the phosphines observed in [mer-Cl<sub>3</sub>-cis-(PMe<sub>3</sub>)<sub>2</sub>Sb] avoids the trans influence of the phosphines with the greatest basicity, resulting in the shortest average P-Sb bonds within the  $[Cl_3(PR_3)_2Sb]$  series. The significantly longer bonds in [mer- $Cl_3$ -trans- $(PCy_3)_2Sb$ ] is due to a greater basicity and steric presence of PCy<sub>3</sub>. The P-Sb or Sb-Cl bonds trans to a chlorine atom  $(2, \bigcirc)$  are observed with intermediate length between those trans to a phosphine and those trans to a lone pair (Figure 3,  $\langle \rangle$ ). Consequently, *trans* Cl-Sb-Cl arrangements are preferred over trans P-Sb-Cl and trans P-Sb-P arrangements. The trans P-Sb-Cl arrangement is tolerated by the relatively low basicity of PPh<sub>3</sub> in [fac-Cl<sub>3</sub>(PPh<sub>3</sub>)Sb] and is

Table 2. Selected (	Structural Parameters fo	or Derivatives of [Cl <sub>3</sub> (PR <sub>3</sub> )	Sb] and $[Cl_3(PR_3)_2Sb]$			
	[Cl <sub>3</sub> (PMe <sub>3</sub> )Sb]	$[Cl_3(PPh_3)Sb]$	$[Cl_3(PCy_3)Sb]$	[Cl <sub>3</sub> (PMe <sub>3</sub> ) <sub>2</sub> Sb]	$[Cl_3(PPh_3)_2Sb]$	$[Cl_3(PCy_3)_2Sb]$
P <sub>A</sub> -Sb D_Sb	2.5951(9) Sb <sub>A</sub> 2.5967(0) Sb	2.7576(5)	2.6516(14)	2.5757(4) 2.7778(4)	2.7934(4) 2.7034(4)	2.848(2) 2.871(2)
P-C	1.791(3) - 1.800(3)	1.8047(18) - 1.8124(18)	1.828(5) - 1.836(5)	1.7953(15) - 1.8136(16)	1.8082(17) - 1.8144(16)	1.8514(16) - 1.8553(17)
$Sb-Cl_A$	2.7656(9)	2.7562(5) Cl <sub>A</sub>	2.3362(14)	2.6046(4)	2.5571(5)	2.568(2)
	Sb <sub>A</sub> -Cl <sub>A</sub>	2.8949(5) Cl <sub>Å'</sub>				
	2.8204(9) ShCl.					
	2.95/04(9)					
	Sb <sub>A</sub> -Cl <sub>A</sub>					
	2.7083(9)					
	$Sb_B-Cl_{A'}$					
Sb-Cl <sub>B</sub>	2.4062(9)	2.4037(5)	2.5773(15)	2.5653(4)	2.5572(5)	2.556(2)
	$Sb_A-Cl_B$					
	2.5093(9)					
	$Sb_B-Cl_{B'}$					
Sb-Cl <sub>C</sub>	2.4783(9)	2.3569(5)	2.5939(14)	2.7096(4)	2.3849(6)	2.3773(12)
	$Sb_A - Cl_C$		$Sb_A-Cl_C$			
	2.4688(9)		3.269(2)			
	$Sb_B-Cl_{C'}$		$Sb_A-Cl_{C'}$			
$P_A-Sb-P_B$				93.078(12)	171.862(17)	172.95(4)
$P_A-Sb-Cl_A$	77.55(3) Cl <sub>A</sub>	170.589(14)	94.96(4)	82.194(12)	85.936(15)	90.60(6)
	$76.68(3) \text{ Cl}_{A'}$					
$P_{A}-Sb-Cl_{B}$	90.32(3)	91.732(16)	86.64(5)	86.846(12)	93.727(15)	89.42(6)
$P_A-Sb-Cl_C$	87.67(3)	86.517(16)	86.43(5)	78.331(12)	85.931(9)	86.41(5)
$P_B-Sb-Cl_A$	77.04(3) Cl <sub>A</sub>			86.805(12)	93.727(15)	89.17(6)
	79.65(3) Cl <sub>A"</sub>					
$P_B-Sb-Cl_B$	87.73(3) Cl <sub>B'</sub>			80.240(12)	85.938(15)	89.85(6)
$P_B-Sb-Cl_C$	88.54(3) Cl <sub>C'</sub>			170.333(12)	85.931(9)	86.56(5)
Cl <sub>A</sub> -Sb-Cl <sub>B</sub>	88.91(3)	94.561(17) Cl <sub>A</sub>	89.15(5)	162.547(13)	175.27(2)	172.12(4)
	$CI_A - Sb_A - CI_B$	$176.645(15) \text{ Cl}_{A'}$				
	89.62(3)					
	$CI_A - Sb_B - CI_{B'}$					
$CI_A-Sb-CI_C$	165.22(3)	86.235(17)	87.68(5)	96.297(14)	87.635(11)	84.45(6)
	$CI_A - Sb_A - CI_C$					
	165.58(3)					
	$CI_A - Sb_B - CI_{C'}$					
$Cl_B - Sb - Cl_C$	90.77(4)	92.406(19)	171.90(5)	94.726(14)	87.635(11)	87.68(6)
	$CI_B - Sb_A - CI_C$					
	89.85(3)					
	$Cl_{B'}-Sb_B-Cl_{C'}$					

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Figure 2. Illustrating the local configuration at antimony for the dimeric [*fac*-Cl<sub>3</sub>(PPh<sub>3</sub>)Sb] (top) and polymeric [*mer*-Cl<sub>3</sub>(PCy<sub>3</sub>)Sb] (bottom).



Figure 3. P-Sb (left) and Sb-Cl (right) bond lengths in derivatives of  $[Cl_3(PR_3)Sb]$  and  $[Cl_3(PR_3)_2Sb]$ , coded according to the substituent *trans* to that bond. Horizontal bars indicate the average value for the compound.

enforced in [*mer*-Cl<sub>3</sub>-*cis*-(PMe<sub>3</sub>)<sub>2</sub>Sb] to avoid the *trans* configuration of the more basic PMe<sub>3</sub> ligands. The *trans* P–Sb–P arrangements observed for [*mer*-Cl<sub>3</sub>-*trans*-(PPh<sub>3</sub>)<sub>2</sub>Sb] and [*mer*-Cl<sub>3</sub>-*trans*-(PCy<sub>3</sub>)<sub>2</sub>Sb] are unavoidable due to the greater steric presence of PPh<sub>3</sub> and PCy<sub>3</sub>, compared to PMe<sub>3</sub>. On the basis of these structural comparisons, we conclude that in the coordination sphere of antimony in neutral phosphine complexes, the magnitude of *trans* influence has the trend: lone pair < PPh<sub>3</sub>  $\leq$  Cl<sup>-</sup> < Cy<sub>3</sub>P  $\approx$  PMe<sub>3</sub>.

Calculations on gas-phase models using dispersion-corrected DFT (B3LYP-D<sup>12</sup>) were carried out to determine the reaction enthalpies ( $\Delta H_r$ ) and free energies ( $\Delta G_r$ ) for the formation of [Cl<sub>3</sub>(PR<sub>3</sub>)Sb] (R = Me, Ph) according to Scheme 1a, under standard conditions. Geometry optimization revealed the global minimum as a trigonal pyramidal  $C_{3\nu}$  symmetry configuration, [*pyr*-Cl<sub>3</sub>(PR<sub>3</sub>)Sb] **8**, with the phosphine in the apical position and the antimony below the basal plane, consistent with previous theoretical investigations.<sup>31</sup> However, there are no experimental data for such a non-VSEPR geometry, and the observed [*mer*-Cl<sub>3</sub>(PMe<sub>3</sub>)Sb] is a shallow minimum, observed only when using the strictest convergence criterion and when the angle between two chlorine substituents is restricted to greater than 175 degrees. We conclude that the *fac*- and *mer*-

configurations observed for  $[Cl_3(PR_3)Sb]$  result from intermolecular interactions evidenced in the solid state.

The reaction enthalpies (Table 3) for complexes of PMe<sub>3</sub> are negative (exothermic) and small, as expected for closed-shell interactions. However, the entropic costs of complexation are sufficiently high that the overall free-energy changes for the observed *mer* and *fac* isomers are positive (nonspontaneous).

Table 3. Calculated (B3LYP-D with Counterpoise Correction) Enthalpies and Free Energies for Reaction of  $Cl_3Sb$  with  $PR_3$  to give  $[Cl_3(PR_3)Sb]$  in kJ mol<sup>-1</sup>

	[Cl <sub>3</sub> (PMe <sub>3</sub> )Sb]		[Cl <sub>3</sub> (PPh <sub>3</sub> )Sb]	
	$\Delta H_{ m r}$	$\Delta G_{ m r}$	$\Delta H_{ m r}$	$\Delta G_{ m r}$
[fac-Cl <sub>3</sub> (PR <sub>3</sub> )Sb]	-18.0	+21.8	+105.9	+151.9
[mer-Cl <sub>3</sub> (PR <sub>3</sub> )Sb]	-9.2	+33.1	+140.6	+192.9
$[pyr-Cl_3(PR_3)Sb]$ 8	-93.7	-11.8	-49.4	+10.5



**Figure 4.** Variations in selected calculated bond lengths for  $[mer-Cl_3-cis-(PMe_3)_2Sb]$  as a function of the dielectric constant ( $\varepsilon$ ) of the applied PCM solvent field.



Figure 5. Solid-state structures of the cation in (a)  $[fac-Cl_2(PMe_3)Sb][OTf]$ , showing Sb---O contacts, (b)  $[trans-Cl_2-cis-(PMe_3)_2Sb][OTf]$ , showing the dimeric interactions and Sb---O contacts, (c)  $[cis-Cl_2-trans-(PPh_3)_2Sb][OTf]$ , showing Sb---O contacts, (d)  $[fac-Ph_2(PMe_3)Sb][OTf]$ , (e)  $[cis-Ph_2-trans-(PMe_3)_2Sb][OTf]$ , showing Sb---O contact, (f)  $[fac-Ph_2(PPh_3)Sb][PF_6]$ , and (g)  $[cis-Ph_2-trans-(PPh_3)_2Sb][PF_6]$ .

The polymeric solid-state structure of  $[Cl_3(PMe_3)Sb]$  results from intermolecular coordination of a chlorine center from an adjacent  $[Cl_3(PMe_3)Sb]$  complex. The gas-phase reaction free energies predict that all three configurations of  $[Cl_3(PPh_3)Sb]$ are unstable with respect to the starting reagents, consistent with the importance of intermolecular lattice interactions in the stability of the complex.

The calculated gas-phase structures for derivatives of  $[Cl_3(PR_3)_2Sb]$  failed to reproduce the experimental geometric parameters. For instance, the calculated gas-phase (vacuum) structure of  $[mer-Cl_3-cis-(PMe_3)_2Sb]$  (Figure 4) shows good agreement with the experimentally observed  $Sb_A-P_A$  ( $\Delta = 0.01$  Å;  $\Delta = calcd - expt$ ),  $Sb_A-Cl_A$  ( $\Delta = 0.01$  Å), and  $Sb_A-Cl_B$  ( $\Delta = 0.05$  Å) distances, but the calculations overestimate the  $Sb_A-P_B$  distance by 0.19 Å and underestimate the  $Sb_A-Cl_C$  distance

by 0.17 Å. In the gas phase, one ligand is bound only weakly, affecting a relatively short  $Sb_A - Cl_C$  bond *trans* to the long  $P_B - Sb_A$  bond. One calculated imaginary frequency is associated with  $S_N$ 2-type displacement of  $Cl_C$  from the metal center by  $P_B$ . Calculations in a simulated solvent field (PCM) of pentane (dielectric constant,  $\varepsilon = 1.84$ ), acetonitrile ( $\varepsilon = 37.5$ ), or water ( $\varepsilon = 80.1$ ) show that greater solvent field polarity recovers the experimentally observed structural parameters (Figure 4). We conclude that calculated gas-phase  $Sb_A - P_B$  and  $Sb_A - Cl_C$  distances for [*mer*-Cl<sub>3</sub>-*cis*-(PMe<sub>3</sub>)<sub>2</sub>Sb] model the initial steps of an  $SN_2$ -type nucleophilic displacement of a chloride anion by a phosphine ligand at the antimony center. In solvents of greater polarity, the minimum energy structure is farther along the reaction coordinate toward [Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Sb]<sup>1+</sup>.

Table 4. Selected Structural Parameters for [*fac*-Cl<sub>2</sub>(PMe<sub>3</sub>)Sb][OTf], [*trans*-Cl<sub>2</sub>-*cis*-(PMe<sub>3</sub>)<sub>2</sub>Sb][OTf], [*cis*-Cl<sub>2</sub>-*trans*-(PPh<sub>3</sub>)<sub>2</sub>Sb][OTf], [*fac*-Ph<sub>2</sub>(PMe<sub>3</sub>)Sb][OTf], [*cis*-Ph<sub>2</sub>-*trans*-(PMe<sub>3</sub>)<sub>2</sub>Sb][OTf], [*fac*-Ph<sub>2</sub>(PPh<sub>3</sub>)Sb][PF<sub>6</sub>], [*cis*-Ph<sub>2</sub>-*trans*-(PMe<sub>3</sub>)<sub>2</sub>Sb][PF<sub>6</sub>]

	[Cl <sub>2</sub> (PMe <sub>3</sub> )Sb] [OTf]	[Ph <sub>2</sub> (PMe <sub>3</sub> )Sb] [OT	$[Ph_2(PPh_3)Sb] [PF_6]$	$[Ph_2(PMe_3)Sb]_4 \ [Cl][PF_6]_3$	$[Ph_2(PMe_3)Sb]_4 [Br][PF_6]_3$
P <sub>A</sub> -Sb P-C Sb-X <sub>A</sub> Sb-X <sub>B</sub>	2.6043(9) 1.797(3)-1.809(3) 2.3719(9) 2.3926(8)	2.5584(4) 1.7981(16)-1.8047(1 2.1487(15) 2.1549(15)	$\begin{array}{c} 2.5950(12) \\ 1.794(4) - 1.805(5) \\ 2.152(5) \\ 2.153(5) \end{array}$	2.5906(14) 1.800(6)-1.804(6) 2.153(4) 2.153(4)	2.5846(13) 1.798(5)-1.799(4) 2.153(3) 2.153(3)
SbO <sub>A</sub> SbO <sub>B</sub> P <sub>4</sub> SbX <sub>4</sub>	2.705(2) 2.755(2) 90.71(3)	3.5475(16) 3.6882(14) 89.55(4)	93 70(12)	89.08(9)	89 43(8)
$P_A - Sb - X_B$ $X_A - Sb - X_B$	90.62(3) 92.78(3)	94.74(4) 96.35(6)	97.61(12) 100.14(18)	89.08(9) 107.64(19)	89.43(8) 107.08(16)
ref	this work [Cl <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> S	this work b] [OTf] [O	8 Cl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> Sb] [OTf]	$\frac{7}{[Ph_2(PMe_3)_2Sb]}[OTf]$	$\frac{7}{[Ph_2(PPh_3)_2Sb]}[PF_6]$
$P_{A}-Sb$ $P_{B}-Sb$ $P-C$ $Sb-X_{A}$ $Sb-X_{B}$ $SbO_{A}$ $SbO_{B}$ $P_{A}-Sb-P_{B}$	2.5890(4) 2.5805(4) 1.7914(18)-1. 2.6707(4) 2.5079(4) 2.996(1) 101.754(13)	8005(16)	2.8621(5) 2.8042(5) 1.810(2)-1.818(2) 2.3643(6) 2.4083(6) 2.6793(17) 3.2332(18) 160.901(17)	2.8034(4) 2.7559(4) 1.8047(19)-1.812(2) 2.1594(17) 2.1558(16) 3.4951(19) 177.142(13)	2.8694(8) $2.8426(9)$ $1.811(12)-1.833(11)$ $2.157(2)$ $2.157(3)$ $170.11(8)$
$P_{A}-Sb-Y_{B}$ $P_{A}-Sb-X_{A}$ $P_{B}-Sb-X_{B}$ $P_{B}-Sb-X_{B}$ $X_{A}-Sb-X_{B}$ ref	79.283(13) 87.027(14) 79.634(14) 87.122(14) 158.504(14) this work		81.519(18) 84.404(19) 82.142(18) 88.230(19) 98.27(3) this work	86.64(4) 89.60(4) 90.51(4) 90.90(4) 95.06(6) this work	87.9(2) 86.9(3) 86.2(3) 101.1(3) 8

Structure and Bonding in Cationic Phosphine Complexes of Antimony. The solid-state structures of the cations in [fac-Cl<sub>2</sub>(PMe<sub>3</sub>)Sb][OTf], [trans-Cl<sub>2</sub>-cis-(PMe<sub>3</sub>)<sub>2</sub>Sb][OTf], [cis-Cl<sub>2</sub>-trans-(PPh<sub>3</sub>)<sub>2</sub>Sb][OTf], [fac-Ph<sub>2</sub>(PMe<sub>3</sub>)Sb][OTf], and [cis-Ph2-trans-(PMe3)2Sb][OTf] are illustrated in Figure 5 and are compared with the structures of the previously reported  $[fac-Ph_2(PPh_3)Sb][PF_6]$  and  $[cis-Ph_2-trans-(PPh_3)_2Sb][PF_6]$ . Selected structural parameters for these compounds are listed in Table 4. All triflate derivatives in Table 4 are considered to be ionic, exhibiting Sb---O contacts that are substantially greater than the sum of the covalent radii ( $\Sigma_{CR}$  Sb–O = 2.05 Å). The cation in [fac-Cl<sub>2</sub>(PMe<sub>3</sub>)Sb][OTf] (Figure 5a) involves two interion Sb---O contacts imposing a square pyramidal geometry at antimony. Similar structures are observed for the cations in  $[fac-Ph_2(PMe_3)Sb][OTf]$  (Figure 5d) and  $[fac-Ph_2(PMe_3) Sb_{4}[Cl][PF_{6}]_{3}$  (Figure Sf).<sup>7</sup> The bisphosphine cations in [trans-Cl<sub>2</sub>-cis-(PMe<sub>3</sub>)<sub>2</sub>Sb][OTf] (Figure 5b) and [cis-Cl<sub>2</sub>-trans-(PPh<sub>3</sub>)<sub>2</sub>Sb][OTf] (Figure 5c) illustrate further structural variety for antimony. The cis configuration of the more basic PMe<sub>3</sub> ligands in the structure of in the cation of [trans-Cl<sub>2</sub>-cis- $(PMe_3)_2Sb][OTf]$  is consistent with that of [mer-Cl<sub>3</sub>-cis- $(PMe_3)_2Sb$  and contrasts the *trans* configuration of the phosphines in the cation of [cis-Cl<sub>2</sub>-trans-(PPh<sub>3</sub>)<sub>2</sub>Sb][OTf], made possible by the less basic PPh<sub>3</sub> ligands and the steric stress imposed by phenyl substituents. A trans configuration of two PMe<sub>3</sub> ligands is uniquely observed in the cation of [*cis*-Ph<sub>2</sub>trans-(PMe<sub>3</sub>)<sub>2</sub>Sb][OTf] (Figure 5e), suggesting that aryl substituents are the most strongly trans-labilizing of the groups discussed here, and the trend in the magnitude of trans influence: lone pair <  $PPh_3 \leq Cl^- < Cy_3P \approx PMe_3 < Ph^-$ .

Derivatives of  $[Ph_2(PR_3)_2Sb]^{1+}$  (R = Me, Ph) adopt P–Sb distances that are shorter by approximately 0.08 Å when R =

Me. The Sb–Cl distances are more sensitive (range of 0.21 Å) to the substitution pattern around Sb. Complexes with shorter P–Sb distances show longer Sb–Cl bond lengths. By comparison, in complexes featuring Ph<sub>2</sub>Sb centers, the Sb– $C_{\rm phenyl}$  distances are relatively unperturbed by the variation of the number or type of phosphine ligand (range of 0.01 Å), consistent with the greater elasticity in the more polarized (more ionic) Sb–Cl bond than in the less polarized (more covalent) Sb–C bond.

Structure and Bonding in a Dicationic Phosphine Complex of Antimony. Two views of the dication in the solid-state structure of [fac-Cl(PMe<sub>3</sub>)<sub>2</sub>Sb][OTf]<sub>2</sub> are shown in Figure 6, one illustrating the three closest contacts to oxygen atoms of anions (a), and the other showing the dimeric association of the formula units through bridging O-S-O units of the anions (b). The definitive facial configuration of the chlorine substituent and two phosphine ligands and the oxygen centers of three separate triflate units impose a distorted octahedral environment for antimony. The Sb---O contacts are comparable in length to the shorter contacts in the monocationic salts (Table 4) and are substantially greater than the sum of the covalent radii ( $\Sigma_{CR}$  Sb–O = 2.07 Å), defining an ionic formulation. The P-Sb bond lengths in the dication are predictably short but are in the range that is observed for neutral and cationic phosphine complexes of antimony. The very short Sb-Cl bond [2.3511(4) Å] is inside the sum of the covalent radii for the two elements ( $\Sigma_{CR}$  Sb–Cl = 2.38 Å).

The *trans* Influence in Phosphine Complexes of Antimony. The trend in the magnitude of *trans* influence at the antimony acceptor site (lone pair <  $PPh_3 \le Cl^- < PCy_3 \approx PMe_3 < Ph^-$ ) is further demonstrated in the neutral complexes



**Figure 6.** Solid-state structural features in [*fac*-Cl(PMe<sub>3</sub>)<sub>2</sub>Sb][OTf]<sub>2</sub>, showing (a) the cation with Sb---O contacts and (b) the Sb---OSO---Sb interion contacts between adjacent cations. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Select bond lengths (Å) and angles (deg):  $P_A$ -Sb<sub>A</sub> = 2.5950(4),  $P_B$ -Sb<sub>A</sub> = 2.5843(4),  $Sb_A$ -Cl<sub>A</sub> = 2.3511(4),  $Sb_A$ -O<sub>A</sub> = 2.7922(13),  $Sb_A$ -O<sub>B</sub> = 2.8459(14),  $Sb_A$ -O<sub>C</sub> = 2.7114(13),  $P_A$ -Sb<sub>A</sub>-P<sub>B</sub> = 102.026(15), Cl<sub>A</sub>-Sb<sub>A</sub>-P<sub>A</sub> = 90.111(15), Cl<sub>A</sub>-Sb<sub>A</sub>-P<sub>B</sub> = 91.812(15), O<sub>A</sub>-Sb<sub>A</sub>-O<sub>B</sub> = 103.36(5), Cl<sub>A</sub>-Sb<sub>A</sub>-O<sub>C</sub> = 153.19(3).

featuring PR<sub>3</sub>, Cl<sup>-</sup>, and Ph<sup>-</sup> on the same antimony center. The solid-state structures of  $[Cl_2(Ph)(PMe_3)Sb]$ ,  $[Cl_2(Ph)(PPh_3)-Sb]$ , and  $[Cl_2(Ph)(PPh_3)_2Sb]$  are shown in Figure 7, and selected structural parameters are listed in Table 5. The weakly *trans*-labilizing chlorine substituents in the three compounds allow for the observed *trans* Cl–Sb–Cl configurations in all three structures. Consistently, the more *trans*-labilizing PMe<sub>3</sub> ligand and Ph<sup>-</sup> substituent are *cis* configured. In this context, the *trans* labilizing trend defined above enables rationalization and prediction of the configurations even with the variety of VSEPR-consistent configurational options available for derivatives of  $[Cl_2(Ph)(PR_3)Sb]$  and  $[Cl_2(Ph)(PR_3)_2Sb]$  illustrated in Chart 2.

Structure and Bonding in an Anionic Phosphine Complex of Antimony. Hypervalent centers such as those in pnictogen pentafluorides are powerful Lewis acids and react with halides to give weakly coordinating hexahalopnictogen anions. Indeed anionic  $[SbCl_4]^{1-}$  is sufficiently Lewis acidic to form the square-based pyramidal  $(AX_4E)$  dianion  $[SbCl_5]^{2-}$  in the presence of excess chloride anions.<sup>13</sup> The anions  $[dmpeSbI_4]^{1-}$  and  $[(Et_3P)_2Sb_2Br_7]^{1-}$  have also been reported as serendipitous products of a hydrolysis reaction.<sup>6</sup> In this context, preparation of  $[Mg(CH_3CN)_6][Cl_4(PMe_3)Sb]_2$  from PMe<sub>3</sub> and  $[Mg(CH_3CN)_6][Cl_4Sb]_2$  represents a rational synthesis of the complex anion. Formation of  $[Cl_4(PPh_3)Sb]^{1-}$  is precluded by the relatively low basicity of PPh<sub>3</sub>.

The molecular structure of the  $[Cl_4(PMe_3)Sb]^{1-}$  anion is derived from  $[Cl_5Sb]^{2-}$  by replacing the apical chloride ion with a PMe<sub>3</sub> ligand (Figure 8). The Sb–Cl bonds [2.555(2)-2.634(2) Å, average 2.593 Å] are on average shorter than the basal Sb–Cl bonds in  $[Cl_5Sb]^{2-}$  [2.4775(12)-2.8847(12) Å, average 2.646 Å]<sup>14</sup> and those in  $[Cl_4Sb]^{1-}$  [2.4317(7)-2.6395(11) Å, average 2.536 Å].<sup>15</sup> The magnesium center is not engaged by the phosphine due to encapsulation of the hard  $[Mg]^{2+}$  atom with hard CH<sub>3</sub>CN ligands (solvent), leaving the soft  $[Cl_4Sb]^{1-}$  anion as the sole coordination site for the soft phosphine donor.

Coordination of a Lewis base to cationic or neutral haloantimony centers is understood as donor occupation of vacant p-orbitals or low-lying  $\sigma^*$  Sb–X antibonding orbitals at antimony. As shown in Figure 9, phosphine coordination to anionic  $[Cl_4Sb]^{1-}$  also involves overlap of the Me<sub>3</sub>P lone pair and a vacant p-orbital perpendicular to the SbCl<sub>4</sub> plane (HOMO-1). Bonding within the  $SbCl_4$  plane involves overlap between the chlorine lone pairs and the two remaining porbitals (HOMO-11, HOMO-12), a small degree of Cl---Cl bonding via in-phase overlap of the chlorine p-orbitals in a ring around Sb (HOMO-9), and delocalized  $\pi$ -bonding involving the chlorine lone-pairs and the p-orbital that is used for P-Sb bonding (HOMO-10). A nonbonding lone pair is evident as the HOMO, thereby accounting for the five bonding pairs and one nonbonding pair of electrons around Sb in six molecular orbitals.

A Charge-Variant Series of PMe<sub>3</sub> Complexes of Chloroantimony Centers. The compounds described above, together with  $[(PMe_3)_3Sb]^{3+}$ ,<sup>11</sup> include the extensive charge-variant series  $[Cl_4(PMe_3)Sb]^{1-}$ ,  $[Cl_3(PMe_3)Sb]$ ,  $[Cl_2(PMe_3)Sb]^{1+}$ ,  $[Cl_3(PMe_3)_2Sb]$ ,  $[Cl_2(PMe_3)_2Sb]^{1+}$ ,  $[Cl_3(PMe_3)_2Sb]^{3+}$ , for which selected bond lengths are illustrated graphically in Figure 10. Notwithstanding the outlier long P–Sb bond for  $[Cl_3(PMe_3)_2Sb]$  corresponding to the only P–Sb bond that is *trans* to a chloride substituent, the Sb–Cl bonds adopt a substantially broader range than the P–Sb bonds. A similar effect is evident for phosphine complexes of tin<sup>16</sup> and bismuth halides.<sup>17</sup>

While a greater positive charge is expected to result in stronger and shorter coordinate bonds, the P–Sb bonds are slightly longer for complexes with greater charge. These results are borne out by the calculations (MP2/Def2-TZVPP) of electronic structure for select complexes (see Supporting Information). For example, the calculated gas-phase geometry of [Cl<sub>3</sub>(PMe<sub>3</sub>)Sb] shows a P–Sb bond (2.542 Å) that is slightly shorter than that calculated for [Cl<sub>2</sub>(PMe<sub>3</sub>)Sb]<sup>1+</sup> (2.561 Å). The corresponding Sb–Cl distances for the netural (2.491 Å)



Figure 7. Solid state structures of (a)  $[Cl_2(Ph)(PMe_3)Sb]$ , II (b)  $[Cl_2(Ph)(PPh_3)Sb]$ , III and (c)  $[Cl_2(Ph)(PPh_3)_2Sb]$ , VI. The Roman numerals refer to labels in Chart 2.

	$[Cl_2(Ph)(PMe_3)Sb]$	$[Cl_2(Ph)(PPh_3)Sb]$	$[Cl_2(Ph)(PPh_3)_2Sb]$
P <sub>A</sub> -Sb	2.5612(4)	2.9656(5)	2.8741(4)
P <sub>B</sub> -Sb			2.8741(4)
Р-С	1.7971(17) - 1.7992(19)	1.819(2) - 1.822(2)	1.8174(15) - 1.8204(15)
Sb-Cl <sub>A</sub>	2.6286(5)	2.3965(6)	2.5989(4)
		$Sb_A-Cl_A$	
		3.3152(6)	
		$Sb_A-Cl_{A'}$	
Sb-Cl <sub>B</sub>	2.5566(5)	2.5463(6)	2.5989(4)
Sb-C <sub>A</sub>	2.1640(16)	2.146(2)	2.163(2)
P <sub>A</sub> -Sb-P <sub>B</sub>			169.098(16)
P <sub>A</sub> -Sb-Cl <sub>A</sub>	78.952(15)	169.437(19)	85.722(15)
		$P_A - Sb_A - Cl_{A'}$	
		100.920(15)	
		$P_A - Sb_A - Cl_{A'}$	
P <sub>A</sub> -Sb-Cl <sub>B</sub>	87.297(15)	83.233(18)	94.419(15)
P <sub>A</sub> -Sb-C <sub>A</sub>	95.85(4)	84.04(6)	84.549(8)
P <sub>B</sub> -Sb-Cl <sub>A</sub>			94.418(15)
P <sub>B</sub> -Sb-Cl <sub>B</sub>			85.721(15)
$P_B-Sb-C_A$			84.548(8)
Cl <sub>A</sub> -Sb-Cl <sub>B</sub>	165.789(16)	90.09(2)	178.53(2)

# Table 5. Selected Structural Parameters for [Cl<sub>2</sub>(Ph)(PMe<sub>3</sub>)Sb], [Cl<sub>2</sub>(Ph)(PPh<sub>3</sub>)Sb], and [Cl<sub>2</sub>(Ph)(PPh<sub>3</sub>)<sub>2</sub>Sb]

Chart 2. VSEPR-Consistent Configurational Options for  $[Cl_2(Ph)(PR_3)Sb]$  and  $[Cl_2(Ph)(PR_3)_2Sb]^a$ 



<sup>*a*</sup>P = phosphine; bold line = lone pair;  $\Box$  = vacant coordination site.



**Figure 8.** Molecular structure of the anion in  $[Mg(CH_3CN)_6]$ - $[Cl_4(PMe_3)Sb]_2$ . One of two asymmetric units is shown. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms have been omitted for clarity. Select bond lengths (Å) and angles (deg):  $P_A-Sb_A = 2.582(2)$ ,  $Sb_A-Cl_A = 2.580(2)$ ,  $Sb_A-Cl_B = 2.634(2)$ ,  $Sb_A-Cl_C = 2.601(2)$ ,  $Sb_A-Cl_D = 2.555(2)$ ,  $P_A-Sb_A-Cl_A = 82.10(7)$ ,  $P_A-Sb_A-Cl_B = 85.53(8)$ ,  $P_A-Sb_A-Cl_C = 88.89(7)$ ,  $P_A-Sb_A-Cl_D = 81.05(8)$ ,  $Cl_A-Sb_A-Cl_B = 90.93(8)$ ,  $Cl_A-Sb_A-Cl_C = 170.93(7)$ ,  $Cl_A-Sb_A-Cl_D = 90.91(7)$ ,  $Cl_B-Sb_A-Cl_C = 89.45(8)$ ,  $Cl_B-Sb_A-Cl_D = 166.08(7)$ ,  $Cl_C-Sb_A-Cl_D = 86.58(7)$ .

and cationic (2.315 Å) complexes show the opposite trend. Similarly, the P–Sb distance in the calculated structure of  $[Cl_2(PMe_3)_2Sb]^{1+}$  (2.555 Å) is shorter than in  $[Cl-(PMe_3)_2Sb]^{2+}$  (2.561 Å), whereas the Sb–Cl distance is shorter for the greater charge (2.507 and 2.317 Å, respectively). These observations are consistent with strengthening of the Sb–Cl bond with increasing charge, predicted by increased electrostatic attraction across the polar Sb–Cl bond. In addition, electronic structure calculations on the model complex  $[Cl_2(PMe_3)Sb]^{1+}$  also show (Figure 11) increased Sb–Cl covalency via two  $\pi$ -type bonding MOs (HOMO-4, HOMO-5) delocalized over the Cl–Sb–Cl fragment, evidencing a competitive occupation of a p-orbital at Sb by the phosphine and chlorine lone pairs. This  $\pi$ -type interaction is in addition to two Sb–Cl  $\sigma$ -bonding MOs (HOMO-6, HOMO-8) and may explain preferential shortening of the Sb–Cl bonds at the cost of elongated P–Sb bonds.

The sum of bond angles around the trigonal pyramidal Sb centers in  $[Cl_2(PMe_3)Sb]^{1+}$  (274.1°),  $[Cl(PMe_3)_2Sb]^{2+}$  (283.9°), and  $[(PMe_3)_3Sb]^{3+}$  (305.8°) increase drastically with steric bulk upon stepwise substitution of chlorides with phosphines. For comparison, the sum of the Cl–Sb–Cl bond angle in solid and gaseous SbCl<sub>3</sub> is 285.6° and 291.57°, respectively.<sup>18,19</sup> As expected, the extent of pyramidalization around phosphorus decreases only slightly upon successive removal of chlorides in  $[Cl_4(PMe_3)Sb]^{1-}$  (319.1°),  $[Cl_3(PMe_3)Sb]$  (320.5°), and  $[Cl_2(PMe_3)Sb]^{1+}$  (322.2°).

The <sup>31</sup>P NMR spectra of derivatives of  $[Cl_n(PMe_3)_mSb]^{(3-n)+}$ (n = 1-4, m = 1, 2) in CD<sub>3</sub>CN at 298 K are plotted in Figure 12 as a function of the formal charge on the stibine complex. The phosphorus centers in  $[Cl_2(PMe_3)_2Sb]^{1+}$  and  $[Cl_3(PMe_3)_2Sb]^{1+}$ 



Figure 9. Molecular orbitals (MP2/Def2-TZVPP) relevant to the bonding in  $[Cl_4(PMe_3)Sb]^{1-}.$  Hydrogen atoms have been omitted for clarity.

 $(PMe_3)_2Sb]^{2+}$  are isochronous by symmetry and give rise to a single chemical shift value. For [*mer*-Cl<sub>3</sub>-*cis*-(PMe<sub>3</sub>)<sub>2</sub>Sb], only one signal is observed, despite the nonequivalence of the phosphorus centers in its solid-state structure, indicating a dynamic process that exchanges the two phosphines. However, in a low-temperature NMR experiment, the slow-exchange limit

characterized by decoalescence and peak separation was not reached at -90 °C, preventing a determination of the chemical shifts for the two environments.

The <sup>31</sup>P NMR results are consistent with greater deshielding of the phosphorus nucleus for complexes of higher positive charge. The monophosphine complexes show chemical shifts that are further downfield than their bisphosphine analogues, indicating a distribution of the charge over two phosphines. The effect is most pronounced in complexes of  $[Ph_2Sb]^{1+}$ , which show <sup>31</sup>P chemical shifts of -21.2 ppm and -41.3 ppm for the mono-PMe<sub>3</sub> and bis-PMe<sub>3</sub> complexes, respectively. Similarly, the shift for [Cl<sub>3</sub>(PCy<sub>3</sub>)Sb] (+25.1 ppm) is 10 ppm downfield of  $[Cl_3(PCy_3)_2Sb]$  (+15.7 ppm). By comparison, the <sup>31</sup>P chemical shifts of PPh<sub>3</sub> complexes are essentially independent of charge or geometry and are almost identical to that of free  $PPh_3$  (-5.6 ppm). We conclude that even in weakly polar solvents (e.g., CD<sub>2</sub>Cl<sub>2</sub>), solutions of the PPh<sub>3</sub> complexes consist of dissociated phosphine ligands and solvated SbCl<sub>3</sub>, Cl<sub>2</sub>Sb(OTf), or Ph<sub>2</sub>Sb(OTf). The solvation enthalpies of these individual species are therefore approximately equal to the strength of the phosphine-stibine interaction, and in the absence of solvent, crystalline products with P-Sb bonds are obtained in the solid state. Consistently, all observed PPh<sub>3</sub> complexes are soluble in CH<sub>2</sub>Cl<sub>2</sub>.

# CONCLUSIONS

A series of cationic, neutral, and anionic prototypical phosphine complexes of antimony(III) have been prepared and structurally characterized. On the basis of the observed configurations of substituents and ligands at antimony in this series, the relative *trans*-labilizing influence exerted by a lone pair, a substituent or a ligand is concluded to be lone pair < PPh<sub>3</sub>  $\leq$  Cl<sup>-</sup> < PCy<sub>3</sub>  $\approx$  PMe<sub>3</sub> < Ar<sup>-</sup>. Consistent with this model, all previously reported adducts of SbCl<sub>3</sub> with Lewis bases weaker than PMe<sub>3</sub> adopt a facial configuration of chloride substituents,<sup>20,21</sup> while complexes with the strong donors 2,2-bipyridine, 1,3-dimethyl-2-imidazolethione,<sup>22</sup> tetramethylthiourea,<sup>23</sup> or PCy<sub>3</sub> show the meridional configuration of chloride substituents, and the distinction is also evident in the solid-state



Figure 10. P-Sb (left) and Sb-Cl (right) bond lengths in PMe<sub>3</sub> complexes of chloroantimony acceptors.



Figure 11. Molecular orbitals (MP2/Def2-TZVPP) relevant to the bonding in  $[Cl_2(PMe_3)Sb]^{1+}$ . Hydrogen atoms have been omitted for clarity.



**Figure 12.** <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts in CD<sub>3</sub>CN for observed complexes in the series  $[Cl_n(PMe_3)_mSb]^{(3-n)+}$ ; n = 1-4, m = 1, 2 plotted as a function of the formal charge of the complex.

structures of other antimony halides.<sup>3,24</sup> We expect that the relative *trans*-labilizing influence of these fragments will be

broadly applicable to analogous complexes of other main-group acceptor centers bearing a lone pair. We further predict that carbene complexes of the type  $[Cl_3(NHC)Sb]$  (NHC = N-heterocyclic carbene) will feature a  $[mer-Cl_3(NHC)Sb]$  A configuration, since carbenes are stronger donors than the most basic phosphines. By corollary, donors weaker than phosphines, such as dialkylsulfides, will adopt a  $[fac-Cl_3LSb]$  configuration.

Calculations on molecules in the gas phase suggest that the 1:1 neutral complexes are stable, but the 1:2 stibine/phosphine complexes are unstable with respect to dissociation of one of the phosphine ligands. Nevertheless, they are observed in the solution and solid state due to additional stabilization from intermolecular interactions. We therefore urge caution when interpreting statements regarding the stability of such weakly bound complexes in cases when such conclusions are drawn exclusively from gas-phase modeling. Comparison of the experimental structural data for a charge-variant series of PMe<sub>3</sub> complexes of haloantimony centers reveals counterintuitive differences in the P-Sb and Sb-Cl bond lengths, which are explained with reference to increased ionic and covalent Sb-Cl bonding, as borne out in computational models. For PMe<sub>3</sub> complexes, solution-phase <sup>31</sup>P NMR spectroscopy is a sensitive probe of the overall charge on the complex, while PPh<sub>3</sub> complexes dissociate in solution and show only the free ligand.

There is renewed interest in the development of ligandstabilized main-group halides, with a view toward using their reduction chemistry to access species featuring multiply-bonded elements. While most efforts have been directed toward carbene-stabilized main-group centers,<sup>25–28</sup> we have successfully demonstrated analogous reductive coupling chemistry for phosphine-stabilized cationic halophosphine<sup>29,30</sup> and halostibine<sup>11,31</sup> centers. Moreover, a recent theoretical investigation has made specific predictions about the viability of accessing phosphine-stabilized group 15 element dimers (E-E triplebonded molecules) from phosphine-ECl<sub>3</sub> adducts.<sup>32</sup> The complexes presented here represent ideal precursors to test these predictions.

# ASSOCIATED CONTENT

# **S** Supporting Information

IR/Raman characterization of selected compounds; Cartesian coordinates for calculated structures; crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

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