Dimeric Antimony Complexes capturing Dimethylamine as a Neutral Donor; Syntheses and Structural Characterisation of $[SbCl_2(NHMe_2)(\mu\text{-}OEt)]_2$ and $[SbCl(NHMe_2)(\mu\text{-}NBu^t)]_2$†

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The two dimeric antimony complexes, $[SbCl_2(NHMe_2)(\mu\text{-}OEt)]_2$ and $[SbCl(NHMe_2)(\mu\text{-}NBu^t)]_2$ have been synthesised by the reaction of $SbCl_x(NMe_2)_{3-x}$ with EtOH ($x = 2$) or NH_2Bu^t ($x = 1$) respectively; both complexes exhibit the co-ordination of a dimethylamine ligand to antimony and intricate intermolecular association in the solid state.

The search for stable precursors to a range of novel organometallic anion complexes and mixed-ligand organometallic species has recently led us to the successful application of nucleophilic addition and substitution reactions of heavy p-block metal cyclopentadienyl derivatives of Group 13 (MC_5H_5; M = In or Tl)[1] and Group 14 [$M(C_5H_5)_2$; M = Sn or Pb].[2] However, to date our attempts to extend this work to Group 15 (M = Sb or Bi) have been unsuccessful owing to the extreme thermal instability of the precursor metal cyclopentadienides, *e.g.*, $M(C_5H_5)_3$ (M = Sb or Bi).[3] Recently we reported the synthesis and structural characterisation of the first tris(imino) antimony species, $Sb(N{=}CPh_2)_3$,[4] with a view to utilising this as a stable precursor to antimony organometallics. Our attention has now switched to the use of $M(NMe_2)_3$ (M = Sb or Bi) and related species, on which only limited studies have previously been reported,[5,6] as suitable Group 15 metallating agents. Our reinvestigations of the use of these species as reagents has unexpectedly resulted in the isolation of antimony complexes containing dimethylamine as a ligand from these reactions, a result which has not previously been reported. The co-ordination of this ligand to antimony is surprisingly durable, surviving both in the solid state and in solution.

We now report the syntheses of the two dimeric antimony species $[SbCl_2(NHMe_2)(\mu\text{-}OEt)]_2$ **1** and $[SbCl(NHMe_2)(\mu\text{-}NBu^t)]_2$ **2** *via* metallation reactions of EtOH or NH_2Bu^t with $SbCl_x(NMe_2)_{3-x}$ (for **1**, $x = 2$; for **2**, $x = 1$) (see Experimental section). Complexes **1** and **2** are dimeric in the solid state and have $NHMe_2$, a gas at room temperature (b.p. 7 °C), co-ordinated to their Sb centres both in the solid state and in solution. They are the first structurally characterised complexes to contain such a small protic ligand bonded to Sb.

Results and Discussion

The complexes $[SbCl_2(NHMe_2)(\mu\text{-}OEt)]_2$ **1** and $[SbCl(NHMe_2)(\mu\text{-}NBu^t)]_2$ **2** are prepared in relatively low, though reproducible, first-batch, yield by the reactions of EtOH with $SbCl_2(NMe_2)$ and NH_2Bu^t with $SbCl(NMe_2)_2$ respectively. The Sb metallation reagents were prepared *in situ* by the equilibration reactions of $Sb(NMe_2)_3$ with $SbCl_3$ (1 : 2 for **1**, and 2 : 1 for **2**) prior to their reactions with the organic acids.[5] The syntheses of **1** and **2** are rapid and lead to little or no decomposition of the Sb reagents. However, it is essential that the Et_2O used as the reaction solvent and the organic precursors (EtOH and NH_2Bu^t) are particularly dry and oxygen-free since otherwise $SbCl_2(NMe_2)$, $SbCl(NMe_2)_2$ and the products **1** and **2** decompose (apparently giving antimony oxides and Sb metal). The reactions are summarized in equations (1)–(3).

$$Sb(NMe_2)_3 + SbCl_3 \xrightarrow{\substack{2:1\ (x = 1)\\ 1:2\ (x = 2)}} SbCl_x(NMe_2)_{3-x} \quad (1)$$

$$SbCl_2(NMe_2) + EtOH \longrightarrow [SbCl_2(NHMe_2)(\mu\text{-}OEt)]_2\ \mathbf{1} \quad (2)$$

$$SbCl(NMe_2)_2 + NH_2Bu^t \longrightarrow [SbCl(NHMe_2)(\mu\text{-}NBu^t)]_2\ \mathbf{2} + Me_2NH \quad (3)$$

Before obtaining the crystal structures of **1** and **2** both complexes were characterised by elemental analyses (C, H, N), solid-state IR spectroscopy, and by ^1H NMR spectroscopy. This preliminary work clearly illustrated that one $NHMe_2$ ligand, produced as a byproduct in the syntheses of both complexes per formula unit of **1** and **2**, had been incorporated into their structures. Thus, the IR spectra of both complexes exhibit intense N–H stretching bands, at 3000–3100 cm^{-1} for **1** and 3122 cm^{-1} for **2**, and in the ^1H NMR spectra the $NHMe_2$ ligands of both complexes appear in the expected (1 : 1) ratio to the EtO and NBu^t groups. Somewhat unexpectedly, the methyl resonances of the $NHMe_2$ ligands are found at markedly different chemical shifts in both complexes (δ 2.62 in **1**, and 1.16 in **2**). Although large, this difference may simply reflect the very different co-ordination spheres (geometries and the nature of attached ligands) of the Sb centres in **1** and **2**. In contrast to the methyl resonances, the N–H resonances of the $NHMe_2$ ligands exhibit concentration-dependent chemical shifts presumably as a consequence of the varying degree of hydrogen bonding occurring at different concentrations.

As mentioned above, previously only limited synthetic work has been undertaken on the products of metallation reactions employing $SbCl_x(NMe_2)_{3-x}$ (x = 0–2) as reagents with organic acids. In fact, none of these species has been subjected to rigorous (NMR or X-ray structural) analysis and the potential incorporation of $NHMe_2$ as a ligand to antimony in these reactions has not been observed or apparently realised.[5,6] Conceivably, the reasons for the observation of $NHMe_2$ acting as a Lewis-base ligand in **1** and **2** lie in the particular steric and electronic environments of their Sb centres and/or in the choice of reaction conditions employed in their syntheses (*e.g.*, solvent polarity). Nonetheless, the analytical and spectroscopic data illustrate that $NHMe_2$, which is a gas at room temperature (b.p. 7 °C), is a highly durable ligand to antimony in these complexes

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: atm = 101 325 Pa.

and survives in the solid state and in solution. The ligand is only removed from **1** and **2** by sustained evacuation (10^{-2} atm). Although $SbCl_3(NHMe_2)$ and other mononuclear Sb and Bi complexes containing small protic amines have been prepared and characterised by elemental analysis and IR spectroscopy,[7] none has been structurally characterised and, to our knowledge, **1** and **2** are the first structurally characterised complexes containing such ligands.

Low-temperature (153 K) X-ray crystallographic studies were undertaken on complexes **1** and **2**. Details of the structural refinements of both complexes are given in Table 1, and Tables 2 and 3 list the atomic coordinates for **1** and **2**, respectively. Selected bond lengths and bond angles are given in Table 4.

The X-ray crystallographic study of **1** shows it to have a dimeric structure in the solid state (Fig. 1), with the dimeric unit lying on a crystallographic centre of symmetry. Molecules of **1** contain an Sb_2O_2 core with the antimony centres bridged by ethoxy groups [Sb–O 2.005(4) and 2.478(4) Å, O–Sb–O 68.9(2) and Sb–O–Sb 111.1(2)°] and attached to two terminal chlorine atoms [Sb–Cl 2.445(2) and 2.572(2) Å]. Interestingly, the gaseous dimethylamine produced during the course of the reaction is captured as an adduct with antimony, the two neutral $NHMe_2$ fragments having the expected *trans* arrangement about the dimeric framework [Sb–N 2.402(5) Å]. The $NHMe_2$ hydrogen atoms were located in the electron-density difference map. The angle about each antimony, between the amine and the chlorine atom *trans* to it, is distorted away from linearity by approximately 12° [N(1)–Sb(1)–Cl(1) 168.41(13)°].

Table 1 Crystal data and structure solution of $[SbCl_2(NHMe_2)(\mu\text{-}OEt)]_2$ **1** and $[SbCl(NHMe_2)(\mu\text{-}NBu^t)]_2$ **2**[a]

	1	**2**
Empirical formula	$C_4H_{12}Cl_2NOSb$	$C_6H_{16}ClN_2Sb$
M	282.80	273.41
Crystal size/mm	0.41 × 0.41 × 0.37	0.34 × 0.29 × 0.26
a/Å	7.437(1)	6.848(1)
b/Å	8.314(2)	9.491(2)
c/Å	15.158(3)	15.830(3)
β/°	97.19(3)	101.38(3)
$U/Å^{-3}$	929.9(3)	1008.6(3)
$D_c/Mg\ m^{-3}$	2.020	1.800
θ range	$3.62 \leqslant \theta \leqslant 22.50$	$3.60 \leqslant \theta \leqslant 22.50$
Reflections collected	1256	1373
Independent reflections	1204 (R_{int} = 0.0124)	1317 (R_{int} = 0.0160)
Goodness of fit	1.296	1.095
R, *R′*[b] [$F > 4\sigma(F)$]	0.029, 0.086	0.022, 0.059
R, *R′*[b] (all data)	0.029, 0.086	0.024, 0.061
Final difference peak, hole/e $Å^{-3}$	0.741, −1.148	0.631, −1.106

[a] Details in common: $T = 153(2)$ K, $\lambda = 0.710\,73$ Å, monoclinic, space group $P2_1/c$, $Z = 4$, refinement by full-matrix least squares. [b] $R' = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.[8]

Table 2 Atomic coordinates (× 10^4) for **1**

	x	*y*	*z*
Sb(1)	5 070(1)	4 372(1)	13 832(1)
Cl(1)	8 399(1)	3 512(2)	14 209(1)
Cl(2)	5 773(2)	5 886(2)	12 536(1)
O(1)	5 732(5)	6 214(5)	14 663(2)
N(1)	2 181(7)	5 699(6)	13 584(4)
C(1)	2 139(9)	7 463(8)	13 574(4)
C(2)	1 199(9)	5 023(9)	12 752(4)
C(3)	6 953(9)	7 490(8)	14 464(5)
C(4)	7 283(10)	8 654(9)	15 202(5)

Table 3 Atomic coordinates (× 10^4) for **2**

	x	*y*	*z*
Sb(1)	2 920(1)	373(1)	5 214(1)
Cl(1)	2 247(1)	−2 244(1)	5 698(1)
N(1)	3 436(5)	2 949(3)	4 930(2)
N(2)	4 156(4)	−255(3)	4 220(2)
C(1)	2 746(6)	3 502(4)	4 057(3)
C(2)	2 566(6)	3 747(4)	5 565(3)
C(3)	4 664(7)	−601(5)	2 751(3)
C(4)	2 437(7)	−2 233(4)	3 339(3)
C(5)	1 403(8)	237(5)	2 999(3)
C(6)	3 170(5)	−723(4)	3 341(2)

Molecules of **1** are associated by intermolecular Sb ⋯ Cl interactions between neighbouring molecules which afford a pseudo-octahedral geometry about each Sb atom [Sb ⋯ Cl 3.57 Å; *cf.* sum of covalent radii of Sb and Cl 4.0 Å[9]] (Fig. 2). Such a structural motif as observed in **1** has been previously reported in the closely related dimer $[SbCl_2(\mu\text{-}OEt)]_2$.[10] Although the fundamental dimeric unit is almost identical, the absence here of the co-ordinated $NHMe_2$ group opens up another potential co-ordination site, hence allowing the further association of dimeric units by means of another set of intermolecular Sb ⋯ Cl interactions which bring about a more three-dimensional polymeric array than in **1** in the solid state. Unlike $[SbCl_2(\mu\text{-}OEt)]_2$ where the terminal Sb–Cl bond lengths are almost identical (ranging from 2.40 to 2.46 Å), in

Table 4 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Complex **1**		Complex **2**	
Sb(1)–O(1)	2.005(4)	Sb(1)–N(2)	2.018(3)
Sb(1)–Cl(1)	2.445(2)	Sb(1)–N(2a)	2.028(3)
Sb(1)–Cl(2)	2.572(2)	Sb(1)–Cl(1)	2.666(1)
Sb(1a)–O(1)	2.478(4)	Sb(1)–N(1)	2.524(3)
Sb(1)–O(1a)	2.478(4)	Sb ⋯ Cl*	3.97
Sb(1)–N(1)	2.402(5)	Sb ⋯ Sb*	3.99
Sb ⋯ Cl*	3.57		
O(1)–Sb(1)–O(1a)	68.9(2)	Sb(1)–N(2)–Sb(1a)	101.6(1)
Sb(1)–O(1)–Sb(1a)	111.1(2)	N(2)–Sb(1)–N(2a)	78.4(1)
N(1)–Sb(1)–Cl(1)	168.4(1)	N(1)–Sb(1)–Cl(1)	172.80(7)
N(1)–Sb(1)–Cl(2)	85.1(1)	N(1)–Sb(1)–N(2a)	88.3(1)
Cl(1)–Sb(1)–Cl(2)	91.46(6)	N(1)–Sb(1)–Sb(1a)	90.86(7)
		Cl(1)–Sb(1)–Sb(1a)	93.89(2)

Symmetry equivalent atoms generated by symmetry transformation $1 - x$, $1 - y$, $3 - z$ (**1**) or $1 - x$, $-y$, $1 - z$ (**2**). * Intermolecular bonds.

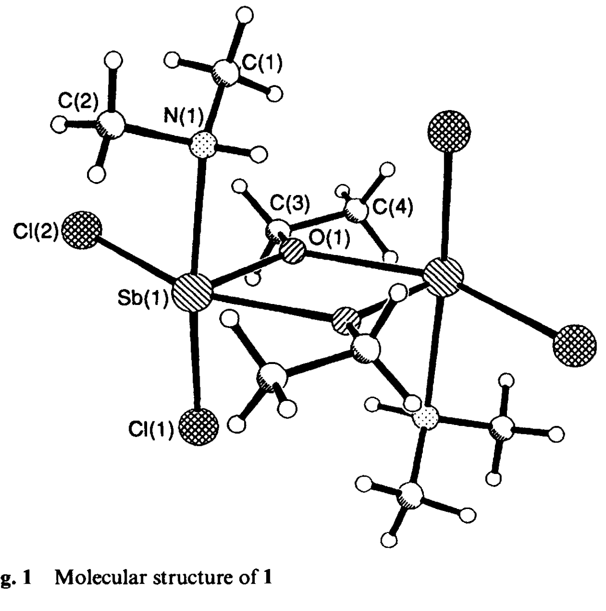

Fig. 1 Molecular structure of **1**

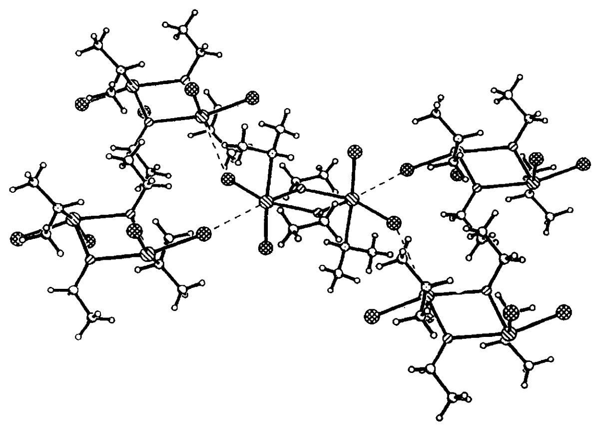

Fig. 2 Association of molecules of **1** in the solid state

molecules of **1** the Sb–Cl bond lengths show a more substantial variation [Sb(1)–Cl(1) 2.445(2) and Sb(1)–Cl(2) 2.572(2) Å]. The elongation in the latter indicates intermolecular Sb–Cl ··· Sb bridging, whereas the shorter bond is consistent with a non-bridging chlorine atom.

The solid-state structure of **2** (Fig. 3) shows it to possess a dimeric Sb_2N_2 framework with two $\mathrm{NBu^t}$ fragments bridging the antimony centres together. The dimeric unit lies on a crystallographic centre of symmetry. Unlike **1**, where the Sb–O bond lengths alternate, the Sb–N bond lengths of the core in **2** are almost identical [2.018(3) and 2.028(3) Å], with associated angles within the dimeric core of Sb–N–Sb 101.62(13) and N–Sb–N 78.38(13)°. The *tert*-butylamine precursor has undergone dimetallation producing two equivalents of $NHMe_2$ in the process. As in **1**, one of these amines co-ordinates to antimony [Sb(1)–N(1) 2.524(3) Å], the second equivalent presumably escaping from the reaction system. The $NHMe_2$ hydrogen atoms were located in the electron-difference density map. It is somewhat surprising that a neutral secondary amine ($NHMe_2$), with a relatively acidic proton, can co-exist with apparently extremely basic bridging $\mathrm{NBu^t}$ groups of **2**.

Within molecules of **2** the co-ordination of the $NHMe_2$ ligands and the terminal chlorines is approximately perpendicular to the Sb_2N_2 plane, the angle about antimony between the co-ordinated amine and the chlorine atom being substantially more linear than in **1** [N(1)–Sb(1)–Cl(1) 172.80(7), N(1)–Sb(1)–Sb(1a) 90.86(7), Cl(1)–Sb(1)–Sb(1a) 92.89(2)°]. The solid-state association of molecules of **2** is of interest (Fig. 4), there being close intermolecular Sb ··· Sb contacts. The Sb ··· Sb approach of 3.99 Å is substantially less than the sum of the van der Waals radii (4.4 Å), while the Sb ··· Cl contacts are at the upper limit for Sb ··· Cl interactions (3.97 Å; *cf.* sum of van der Waals radii, 4.0 Å).[9] However, the intermolecular Sb ··· Sb contacts are longer than the inter- (Sb ··· Sb) and intra-molecular (Sb–Sb) bonds observed in $(SbMe_2)_2$ (2.86 and 3.64 Å respectively).[11]

The literature provides only a handful of structurally characterised examples of such a dimetallated framework as in **2**. Although the related complex $\mathrm{[SbCl(\mu\text{-}NBu^t)]_2}$ has been synthesised and spectroscopically characterised,[12] the solid-state structure has not been determined. In the crystal structure of $\mathrm{[SbBu^t(\mu\text{-}NBu^t)]_2}$ a similar dimeric core to **2** is observed (average Sb–N 2.047 Å, Sb–N–Sb 101.7, N–Sb–N 78.3°). However, there are no apparent close intermolecular contacts.[13] Other related examples containing dimetallated primary amine bridges are the tricyclic complex $\mathrm{Sb_2SeCl_2(NBu^t)_4}$ and the tetrameric cubane $(SbCl_3NMe)_4$.[14,15]

Conclusion

The syntheses of **1** and **2** illustrate for the first time that $NHMe_2$ produced as a gaseous byproduct in the reaction of $SbCl_x(NMe_2)_{3-x}$ (x = 1 or 2) with organic acids can be captured by the metallo-organic products of the reactions. Complexes **1** and **2** are, to our knowledge, the first structurally characterised complexes to contain a small protic Lewis-base ligand bonded to antimony. The $NHMe_2$ ligand is shown by this work to be a surprisingly durable ligand and survives in the solid state and in solution.

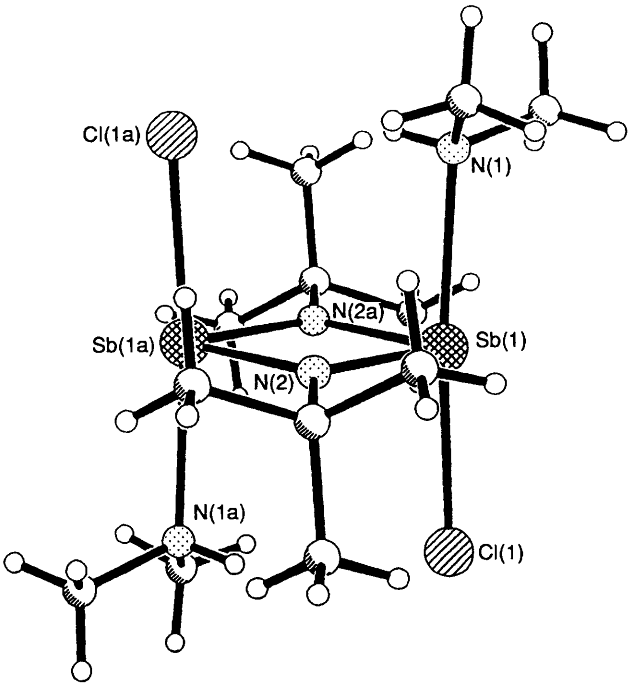

Fig. 3 Molecular structure of **2**

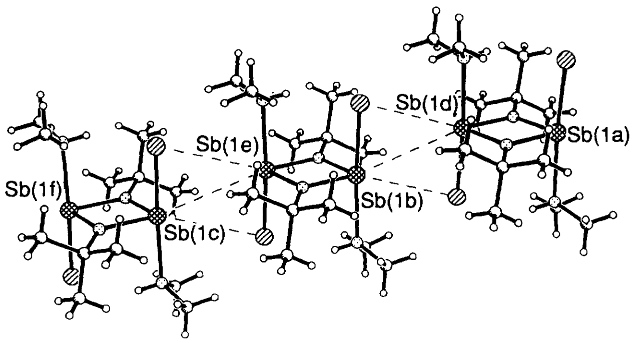

Fig. 4 Association of molecules of **2** in the solid state

We are continuing to investigate the uses of $MCl_x(NMe_2)_{3-x}$ (M = Sb or Bi; x = 0–2) as Group 15 metallating agents for the synthesis of a range of organometallic derivatives and mixed-metal complexes.

Experimental

The compound $Sb(NMe_2)_3$[5] and the products **1** and **2** are air- and/or moisture-sensitive. They were handled on a vacuum line using standard inert atmosphere techniques[16] and under dry, oxygen-free argon. Diethyl ether was dried using sodium–benzophenone and degassed prior to the reactions. The compound $Sb(NMe_2)_3$ was prepared in the manner described in the literature from $SbCl_3$ and $LiNMe_2$ (Aldrich) in diethyl ether, the product being purified by distillation.[5] Ethanol was distilled over sodium and degassed prior to use in the synthesis of **1**, and degassed $\mathrm{NH_2Bu^t}$ was stored in a Schlenk tube over a molecular sieve (13X). Complexes **1** and **2** were isolated and characterised using an argon-filled glove box (Faircrest Mark 4A) fitted with an O_2 and H_2O recirculation system (Type B). Melting points were determined by using a conventional apparatus and sealing samples in capillaries under argon. IR spectra were recorded as Nujol mulls using NaCl windows and were run on a Perkin-Elmer 2400 spectrophotometer. Elemental analyses were performed by firstly sealing samples under argon in air-tight aluminium boats (1–2 mg) and C, H, N content determined using a Perkin-Elmer 240 elemental analyser. Proton NMR spectra were recorded on a Bruker WH 250 MHz spectrometer in dry [$^2H_5$]pyridine (using the resonances of C_5D_4HN as the internal reference standard).

Syntheses.—Compound **1**. Tris(dimethylamido)antimony (0.635 g, 2.5 mmol) was added to a solution of $SbCl_3$ (1.14 g, 5.0 mmol) in diethyl ether (30 cm^3) at −40 °C. The resultant white precipitate was then allowed to warm to room temperature and stirred for 30 min. This was then cooled to −70 °C and dry, oxygen-free ethanol (0.345 g, 7.5 mmol) was added. Warming to reflux with subsequent stirring for 5 min resulted in the bulk of the material dissolving. The reaction mixture was then filtered to yield a colourless solution which was reduced under vacuum to about 20 cm^3, whereupon a white precipitate developed. This was warmed into solution and storage at 20 °C for 24 h yielded colourless crystalline blocks of **1** in 30% yield (first batch): m.p. 115–117 °C, decomp. *ca.* 180 °C to black solid (Found: C, 16.2; H, 3.8; N, 4.9. Calc. for $C_8H_{24}Cl_4N_2O_2Sb_2$: C, 17.0; H, 4.2; N, 5.0%). IR ν(Nujol): 3000–3100 cm^{-1} (N–H); ^1H NMR (250 MHz, [$^2H_5$]pyridine, +25 °C): δ 4.94 (s, 1 H, Me_2NH), 4.67 (q, 2 H, CH_2 of μ-OEt), 2.62 (s, 6 H, Me_2NH), 1.30 (t, 3 H, CH_3 of μ-OEt).

Compound **2**. Tris(dimethylamido)antimony (1.27 g, 5.0 mmol) was added to a solution of $SbCl_3$ (0.57 g, 2.5 mmol) in diethyl ether (30 cm^3) at −40 °C. This was allowed to warm to room temperature and stirred for 30 min. Cooling to −70 °C, followed by addition of *tert*-butylamine (0.55 g, 7.5 mmol) resulted in a yellow colouration developing and after stirring at 30 °C for 10 min a yellow solution was obtained. This was reduced under vacuum to about 15 cm^3, whereupon a yellow precipitate developed. Gentle warming led to dissolution of the solid. Storage at 5 °C for 48 h yielded yellow crystalline rods of **2** in 35% yield (first batch): m.p. 75–77 °C, decomp. *ca.* 110 °C to black solid (Found: C, 25.9; H, 5.5; N, 10.0. Calc. for $C_{12}H_{32}Cl_2N_4Sb_2$: C, 26.3; H, 5.8; N, 10.2%). IR ν(Nujol): 3122 cm^{-1} (N–H); ^1H NMR (250 MHz, [$^2H_5$]pyridine, +25 °C) δ 2.57 (br, s, 1 H, Me_2NH), 1.30 (s, 9 H, Bu^t), 1.16 (s, 6 H, Me_2NH).

X-Ray Structure Determinations of **1** *and* **2**.—Crystals were mounted directly from solution under argon using a perfluorocarbon oil which protects them from atmospheric O_2 and moisture.[17] The oil 'freezes' at reduced temperatures and holds the crystals static in the X-ray beam. Data were collected on a Stoe-Siemens AED diffractometer by the θ/ω method. Semi-empirical absorption corrections based on psi scans were employed for both complexes. Details of the structure solution and refinement of both complexes are shown in Table 1. Both structures were solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares on F^2 (SHELXL-93).[8]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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