Synthesis and Crystal Structure of Sb(N=CPh$_2$)$_3$

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Monomers of Sb(N=CPh$_2$)$_3$ **1**, the first tris(imino) antimony compound characterised in the solid state, exhibit unusual packing in the crystal in which short aromatic *meta*-C–H • • • Sb intermonomer contacts are present.

Nucleophilic addition and substitution reactions of heavy p-block metal cyclopentadienyl derivatives of Group 13 [M(C$_5$H$_5$), M = In or Tl][1] and Group 14 [M(C$_5$H$_5$)$_2$, M = Sn or Pb][2] have been employed by us in the synthesis of novel organometallic anion complexes and mixed-ligand organometallic species. 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$_5$H$_5$)$_3$ (M = Sb or Bi).[3] Recently we have switched our attention to the possibility of utilising heteroatom (N, P, O, S, *etc.*) stabilised antimony and bismuth complexes as precursors for nucleophilic addition and substitution reactions. Our first target has been the synthesis of complexes containing [M(C$_5$H$_5$)R$_3$]$^-$ anions by nucleophilic addition of C$_5$H$_5$ to SbR$_3$. For this purpose we have synthesised and characterised a range of simple SbR$_3$ derivatives that contain heteroatomic organic groups (R) which were likely to be sterically uncrowded in the vicinity of the metal centre, in the hope of allowing sufficient room for a cyclopentadienyl ligand to add on to the metal. We here report the synthesis and structure of Sb(N=CPh$_2$)$_3$ **1**, the first structurally characterised tris(imino) antimony complex. Monomers of **1** exhibit unusual packing in the solid state, in which short intermolecular aryl *meta*-C–H • • • Sb contacts are present.

Complex **1** was prepared by the room-temperature reaction of SbCl$_3$ with 3 equivalents of LiN=CPh$_2$ in tetrahydrofuran (thf). The resulting yellow powder was crystallised from toluene in good yield.[†]

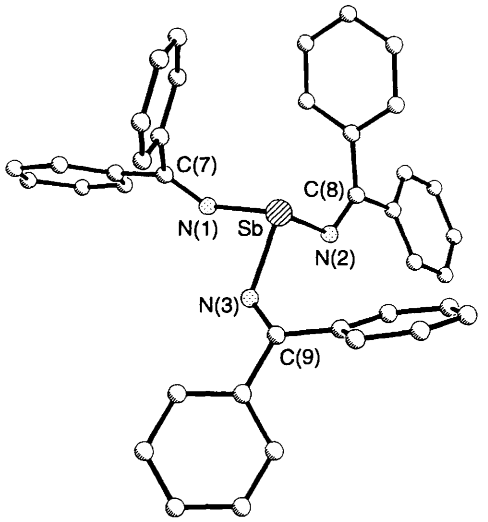

Fig. 1 Molecular structure of complex **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sb–N(1) 2.081(7), Sb–N(2) 2.074(7), Sb–N(3) 2.077(7), N(1)–C(7) 1.277(11), N(2)–C(8) 1.273(10), N(3)–C(9) 1.273(10), av. (imino)C–Ph 1.503, N(1)–Sb–N(2) 90.7(3), N(2)–Sb–N(3) 98.3(3), N(3)–Sb–N(1) 87.1(3), C(7)–N(1)–Sb 118.2(6), C(8)–N(2)–Sb 118.1(5), C(9)–N(3)–Sb 123.0(6)

An X-ray crystallographic study of **1**[‡] shows that Sb(N=CPh$_2$)$_3$ exists as discrete monomer molecules in the solid state (Fig. 1). The central Sb atom, which forms three nearly equivalent Sb–N bonds with the three imino N centres [av. Sb–N 2.077 Å; *cf.* sum of covalent radii of Sb and N *ca.* 2.11 Å[5]], has a typical pyramidal geometry (av. N–Sb–N 92.0°). Overall, the observation of a pyramidal geometry for the Sb centre in **1** is

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[†] A solution of benzonitrile (0.78 cm^3, 7.5 mmol) in thf (10 cm^3) was treated with LiPh (4.17 cm^3, 1.8 mol dm^{-3} in ether, 7.5 mmol) at 0 °C and stirred for 15 min to yield a blood red solution. To this was added a solution of antimony trichloride (0.57 g, 2.5 mmol) in thf (5 cm^3) and the mixture stirred (10 min), producing a yellow solution. The yellow solid produced after evaporation of this to dryness was almost completely dissolved in toluene (10 cm^3) by heating (70 °C, 10 min). After filtration (porosity 4), the resulting solution was reduced to half its original volume under vacuum. The precipitate formed was gently warmed so as to redissolve it and storage at room temperature (24 h) yielded large yellow faceted crystals of **1**. Yield 65% (after second batch crystallisation): the complex darkens at *ca.* 150 °C and melts at 170–172 °C. IR (Nujol): *ca.* 3060w (aryl C–H) and 1590m cm^{-1} [ν(C=N)]. ^{1}H NMR (250 MHz, C$_6$D$_6$, 25 °C): δ 7.3–6.9 (m, Ph$_2$C=N). The complex was too insoluble in benzene at 6 °C for cryoscopic molecular mass measurements. Satisfactory analyses (C, H, N) were obtained for all samples of **1**.

[‡] Crystal data: C$_{39}$H$_{30}$N$_3$Sb, M = 662.41, monoclinic, space group $P2_1/c$, a = 9.952(2), b = 17.606(4), c = 18.622(4) Å, U = 3131.4(12) Å^3, Z = 4, D_c = 1.405 Mg m^{-3}, λ = 0.710 73 Å, T = 153(2) K, μ(Mo-Kα) = 0.913 mm^{-1}. Data were collected on a Stoe AED diffractometer using an oil-coated rapidly cooled crystal of dimensions 0.34 × 0.31 × 0.25 mm by the 2θ–ω method ($5 \leqslant 2\theta \leqslant 45°$). Of a total of 4206 reflections collected, 4060 were independent. The structure was solved by direct methods (SHELX 92)[4] and refined by full-matrix least squares on F^2 with final R [$F > 4\sigma(F)$] and $wR2$ (all data) values of 0.047 and 0.2105 respectively {$R = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$}. Largest peak and hole in the final difference map are 1.131 and −1.394 e Å^{-3}. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

consistent with a high degree of 5p character being present in the Sb–N bonds and with the lone pair on the metal having a significant proportion of 5s character.[6] The $Ph_2C=N$ ligands of **1** are bent towards the antimony lone pair (av. Sb–N–C 119.8°) and their phenyl rings intermesh so that molecules of **1** adopt a 'propeller' shape. However, there are distinct angular distortions at the imino ligand associated with N(3). Notably, the angle at C(9)–N(3)–Sb is significantly less acute than at the other imino ligands [123.0(6)°, *cf.* average of *ca.* 118.2° at N(1) and N(2)] and there is also a significant distortion at N(2)–Sb–N(3) [98.3(3)°, *cf.* average of 88.9° for the other two N–Sb–N angles]. Within the three $Ph_2C=N$ ligands, the C$\overline{\cdots}$N bond lengths are close to that expected for double bonds (av. 1.274 Å in **1**; predicted 1.27 Å[5]) and the (imino)C–Ph bonds are approximately single (av. 1.503 Å in **1**; predicted 1.54 Å[5]).

As a structural type, monomeric pyramidal complexes similar to **1** are well known in Group 15 and the synthesis of imino complexes of the non-metallic elements has been investigated earlier, notably by Wade and co-workers.[7] Imino–phosphorus complexes have been most commonly studied and a few solid-state structures are known.[8] However, although a bidentate imino ligand is present in the structures of $Sb[(Me_3Si)N\overline{\cdots}C(Ph)\overline{\cdots}N(SiMe_3)]_nCl_{3-n}$ (n = 1 or 2),[9] there is only one other structurally characterised Group 15 tris(imino) complex, $As[N{=}CS_2C(CF_3)]_3$.[10] Complex **1** is the first simple imino- and the first tris(imino)-antimony (or bismuth) complex to be structurally characterised.

Monomers of **1** are stacked into apparent vertical strands along the *b* axis in the solid state (Fig. 2). One of the phenyl rings of each monomer (strand A) slots into the gap left between the phenyl rings of two successive monomers of a neighbouring strand (strand B). There do not appear to be any graphitic interactions between the interlocking phenyl rings judging from the intermolecular ring–ring distances involved (*ca.* 4.4 Å; *cf. ca.* 3.3 Å in graphite[5]) and by the twisted orientation of these rings with respect to each other. The penetrating phenyl ring of a neighbouring strand forces the N(2)–Sb–N(3) angle of each monomer to enlarge presumably, at least in part, in order to accommodate inter-strand packing. In so doing, short intermolecular *meta*-C–H ··· Sb contacts are established between the Sb centre and this phenyl ring (Sb ··· H, *ca.* 3.26 Å; *cf.* sum of van der Waals radii of Sb and H, 3.4–3.6 Å[5]). Although it is not clear whether these contacts are *real* interactions and the Sb ··· H–C-*meta* contact is far from linear (*ca.* 140°), it is noticeable that the lone pair on Sb is pointing directly at this H. The situation found in **1** is somewhat similar to that observed by us recently in $Pb[\mu\text{-}N{=}C(Bu^t)Ph]_3Li\cdot thf$, the Pb centre of which is isoelectronic with the Sb centre of **1**, where the phenyl rings of two separate monomers intermesh and long range intermolecular *ortho*-C–H ··· Pb contacts are established.[2e]

We can find no precedents for the intricate intermolecular association observed in **1** for any Group 15 (III oxidation state) metallo-organic compounds, including the aryl derivatives. Generally such derivatives are separate monomers such as $BiPh_3$,[11] or else in some cases they are polymers such as $(Ph_2SbNCS)_\infty$.[12]

We are currently investigating the use of **1** and related complexes as acceptor molecules for nucleophilic addition reactions with various anionic π ligands ($C_5H_5^-$, allyl$^-$, *etc.*).

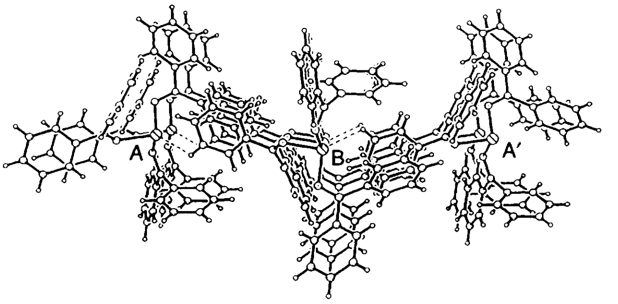

Fig. 2 Association of vertical strands of complex **1** viewed down the *b* axis; *meta*-C–H ··· Sb, 3.26 Å (*ca.* 140°)

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