

Preliminary communication

Synthesis and structure of the dimeric organo-antimony (V) imido complex $[\text{Ph}_3\text{Sb}(\mu\text{-NCH}_2\text{CH}_2\text{Ph})]_2$

Andrew J. Edwards, Michael A. Paver, Philip Pearson, Paul R. Raithby, Moira-Ann Rennie, Christopher A. Russell, Dominic S. Wright *

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

Received 3 May 1995

Abstract

The amine $\text{PhCH}_2\text{CH}_2\text{NH}_2$ undergoes dimetallation by $[\text{Ph}_3\text{Sb}(\text{NMe}_2)_2]$ (1) under mild conditions to give the first structurally authenticated example of an organo-Sb(V) imido complex, $[\text{Ph}_3\text{Sb}(\mu\text{-NCH}_2\text{CH}_2\text{Ph})]_2$ (2).

Keywords: Antimony; Imido; Crystal structure; Group 15; Metallation; Dimer

Our recent investigations of the reactivities of Group 15 dimethylamido derivatives, $(\text{Me}_2\text{N})_x\text{ECl}_{3-x}$ (E = Sb, Bi; $x = 1 - 3$), have shown that these species are valuable precursors for the synthesis of a host of Group 15 imido complexes [1–7]. Such species are highly potent reagents, as witnessed by the complete deprotonation of primary amines, RNH_2 , by $\text{E}(\text{NMe}_2)_3$ to give the dimeric complexes $[\text{Me}_2\text{NE}(\mu\text{-NR})]_2$ [2]. The use of Group 15 dimethylamido derivatives as metallating agents with mono-lithiated primary amines, $(\text{RNHLi})_n$, gave a series of novel polyamido Group 15 anion complexes [3–7]. Recently we have sought to extend this versatile route to other elements and oxidation states. Thus the reaction of $\text{Sn}(\text{NMe}_2)_2$ with RNH_2 , proved to be a clean, low temperature route to the Sn_4N_4 cubanes, $[\text{Sn}(\text{NR})]_4$, which were inaccessible by existing higher temperature routes [8].

We report here that organo-Sb(V) imido complexes $[\text{R}_3\text{Sb}(\text{NR})]_n$, are readily accessible using Sb(V) dimethylamido reagents. Exemplifying this route, the

reaction of $\text{Ph}_3\text{Sb}(\text{NMe}_2)_2$ (1) with phenylethylamine, $\text{PhCH}_2\text{CH}_2\text{NH}_2$, gives $[\text{Ph}_3\text{Sb}(\mu\text{-NCH}_2\text{CH}_2\text{Ph})]_2$ (2).¹ Complex (2) is the first structurally characterised

¹ Synthesis of $\text{Ph}_3\text{Sb}(\text{NMe}_2)_2$ (1). A solution of triphenylantimony (17.65 g, 50 mmol) in 400 ml of dry ether was cooled to -78°C and chlorine gas was slowly bubbled through for 30 mins. The volume of the solution was then reduced to ca. 200 ml, yielding a white precipitate of Ph_3SbCl_2 . This was isolated and 10.6 g (25 mmol) of it was added to a slurry of LiNMe_2 (2.55 g, 50 mmol) in 200 ml of ether at -78°C . After the initial exothermic reaction, the mixture was refluxed for 2 h. Filtration (Celite, P3 cinter) yielded a colourless solution. Reduction of the volume to ca. 50 ml yielded colourless microcrystals of $\text{Ph}_3\text{Sb}(\text{NMe}_2)_2$ in 80% yield (8.8 g); m.p. 115°C to a colourless liquid; IR (Nujol mull) $3070\text{--}3050\text{ cm}^{-1}$ (aryl C–H); Elemental Anal. Found C 59.5% H 6.0% N 5.8%, Calc. C 59.9% H 6.1% N 6.3%; ¹H NMR (+25°C, 250 MHz, d_6 benzene) δ ppm: 8.00 (6H, d, *o*- Ph_3Sb -), 7.20 (6H, dd, *m*- Ph_3Sb -), 7.14 (3H, t, *p*- Ph_3Sb -), 2.38 (12H, s, –Me).

Synthesis of $[\text{Ph}_3\text{Sb}(\mu\text{-NCH}_2\text{CH}_2\text{Ph})]_2$ (2). A Solution of $\text{Ph}_3\text{Sb}(\text{NMe}_2)_2$ (1.10 g, 2.5 mmol) in 20 ml of toluene was treated at 0°C with $\text{H}_2\text{NCH}_2\text{CH}_2\text{Ph}$ (0.31 ml, 2.5 mmol). The mixture was heated under reflux and stirred for 15 mins, giving a yellow solution. Filtration (Celite, P3 cinter) and subsequent reduction of the volume in vacuo produced a white precipitate, which was redissolved by gentle warming. Storage at 5°C for 24 h, yielded a crop of colourless crystals of (2) in 60% yield (0.71 g); Melting point $205\text{--}207^\circ\text{C}$ to a red oil; IR (Nujol mull) 3060 cm^{-1} (aryl C–H), 1574 and 1600 cm^{-1} (aryl C=C); Elemental Anal., Found C 63.3% H 5.0% N 2.9%, Calc. C 66.1% H 5.1% N 3.0%; ¹H NMR (+25°C, 250 MHz, d_6 benzene) δ ppm: 8.08 (2H, dd, *m*- PhCH_2CH_2 -), 7.98 (6H, d, *o*- Ph_3Sb -), 7.24 (6H, dd, *m*- Ph_3Sb -), 7.10 (3H, t, *p*- Ph_3Sb -), 6.92 (1H, t, *p*- PhCH_2CH_2 -), 6.27 (2H, d, *o*- PhCH_2CH_2 -), 3.07 (2H, t, – NCH_2), 2.09 (2H, t, – CH_2Ph).

* Corresponding author.

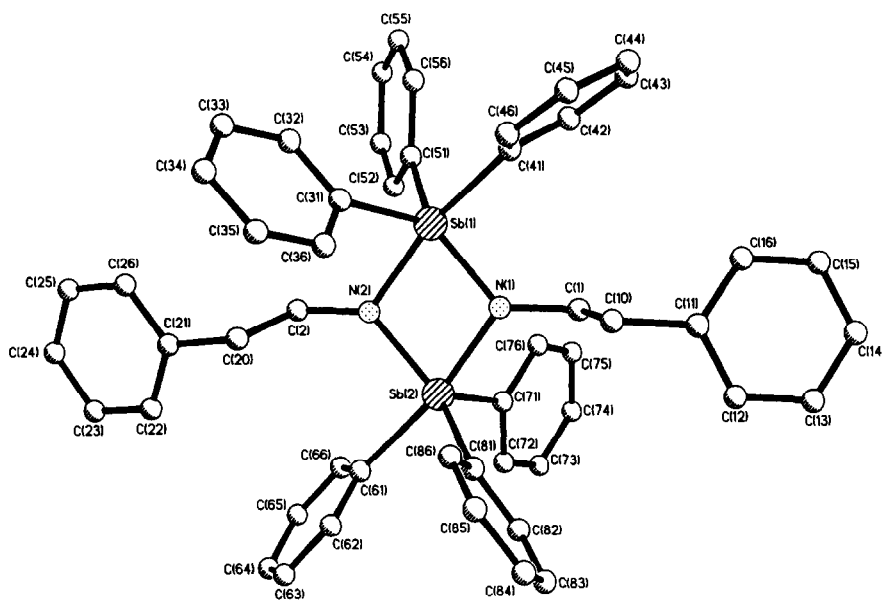
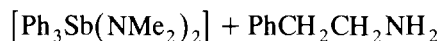


Fig. 1. Molecular Structure of (2). Hydrogen atoms have been omitted for clarity. Bond lengths (Å) and bond angles (°); Sb(1)–N(1) 1.997(3), Sb(1)–N(2) 2.122(3), Sb(2)–N(2) 1.990(3), Sb(2)–N(1) 2.116(3), av. Sb–C(α) 2.17, Sb(1)–N(1)–Sb(2) 105.2(1), Sb(1)–N(2)–Sb(2) 105.3(1), N(1)–Sb(1)–N(2) 74.6(1), N(1)–Sb(2)–N(2) 74.9(1), range C–Sb–C 93.4(1)–112.3(1)°, range N–Sb–C 88.5(1)–170.4(1)°.

example of an organo-Sb(V) imido complex (formally containing RN^{2-} ligands).



(1)



(2)

Scheme 1.

An X-ray crystallographic study of (2)² shows it to consist of dimeric molecules, $[\text{Ph}_3\text{Sb}(\mu\text{-NCH}_2\text{CH}_2\text{Ph})]_2$. The Sb_2N_2 core of (2) has a rhombic shape [$\text{N}-\text{Sb}-\text{N}$ 74.8(1)° and $\text{Sb}-\text{N}-\text{Sb}$ 105.2(1)°], in which the Sb(V) centres have similar highly distorted five-co-

ordinate geometries [range C–Sb–C 93.4(1)–112.3(1)°, range N–Sb–C 88.5(1)–170.4(1)°]. Surprisingly the $\text{CH}_2\text{CH}_2\text{Ph}$ chains of the bridging imido groups adopt a *cisoid* orientation with respect to the Sb_2N_2 core, presumably as a result of steric and/or crystal packing effects. The angles within the Sb_2N_2 core are similar to those that have been observed in the antimony (III) dimers $[\text{Me}_2\text{NSb}(\mu\text{-NR})]_2$ (av. Sb–N–Sb 105.2° and av. N–Sb–N 74.8°) [2]. Although symmetrical, the Sb–N bond lengths within the core of (2) alternate ‘long’ (av. 2.12 Å) and ‘short’ (av. 2.00 Å). These bonds are of similar lengths to those in a range of Sb(V)–N complexes [9]. However, the presence of alternate long and short Sb–N bonds observed in (2) contrasts with the situation for other dimeric Sb(V) Sb_2N_2 species, in which there is little variation in the ring Sb–N distances, e.g., in $[\text{Cl}_4\text{Sb}(\mu\text{-N}\cdots\text{C}\cdots\text{NSiMe}_3)]_2$ Sb–N av. 2.11–2.12 Å [9f].

Complex (2) (Fig. 1) is the first structurally characterised example of an organo-imino stiborane formally consisting of ylidic monomer units $[\text{Ph}_3\text{Sb}=\text{NR} \rightleftharpoons \text{Ph}_3\text{Sb}^+-\text{N}^-\text{R}]$. The most closely related complex to (2) is that of the inorganic azastibacubane $[\text{Cl}_3\text{SbNMe}_3]_4$, the only other structurally characterised example of an Sb(V) imido compound, produced by elimination of Me_3SiCl in the reaction of SbCl_5 with $[(\text{Me}_3\text{Si})_2\text{NMe}]$ [10]. In order to investigate the potential monomer–dimer equilibrium for (2) in solution in which ylidic monomer units would be formed, $[\text{Ph}_3\text{Sb}(\mu\text{-NCH}_2\text{CH}_2\text{Ph})]_2 \rightleftharpoons 2[\text{Ph}_3\text{Sb}=\text{NCH}_2\text{CH}_2\text{Ph}]$, cryoscopic molecular mass determinations were carried out over a range of concentrations. These showed that the molecule is largely dimeric in solution even at low

² Crystal data for (2): $\text{C}_{52}\text{H}_{48}\text{N}_2\text{Sb}_2$, $M = 944.42$, triclinic, space group $\text{P}\bar{1}$, $a = 11.224(2)$, $b = 13.662(3)$, $c = 15.133(5)$ Å, $\alpha = 80.18(3)^\circ$, $\beta = 79.52(3)^\circ$, $\gamma = 71.83(3)^\circ$, $V = 2151.9(7)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.458$ Mg m⁻³, $\lambda = 0.71073$ Å, $T = -120^\circ\text{C}$, $\mu(\text{Mo K}\alpha) = 1.293$ mm⁻¹. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly-cooled crystal of dimensions $0.45 \times 0.44 \times 0.26$ mm in an oil drop [12] by the θ/ω method ($7.20^\circ \leq 2\theta \leq 45.00^\circ$). Of a total of 7189 collected reflections, 5583 were independent. The data were corrected for absorption by a semi-empirical method based on Ψ -scans. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R_1(F > 4\sigma(F)) = 0.0206$, $\omega R_2 = 0.0638$ for 4912 reflection with $F > 46(F)$ and $R_1 = 0.0292$, $\omega R_2 = 0.1076$ for all data [$R_1 = \sum |F_0 - F_c| / \sum F_0$ and $\omega R_2 = (\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2)^{0.5}$] [13]; largest peak and hole in the final difference map 0.490 and -0.463 eÅ⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

concentrations [for $[\text{Ph}_3\text{SbNCH}_2\text{CH}_2\text{Ph}]_n$; $n = 1.88 \pm 0.13$ ($0.00233 \text{ mol. dm}^{-3}$) and $n = 1.96 \pm 0.04$ ($0.0132 \text{ mol. dm}^{-3}$)].

The synthesis of (2) from (1) and phenylethylamine, an amine in which there is no conjugative stabilisation, is worthy of note. Complexes with Sb(V)–N bond are only formed by traditional routes if the basicity of the nitrogen centre is reduced by electron withdrawing substituents and the nitrogen containing precursor is stable to oxidation [10]. Aliphatic amines, for example, react with SbCl_5 to give mixed-valence compounds [11]. The new route to (2) should provide a versatile method for making organo-Sb(V) imido complexes ($[\text{R}_3\text{Sb}(\text{NR})_n]$) in general. By changing the steric bulk of the organic substituents (R and R' in $[\text{R}_3\text{Sb}(\text{NR}')_n]$), we are attempting to produce larger imido-Sb(V) cages and monomeric (multiply-bonded) complexes.

Acknowledgements

We gratefully acknowledge support by the EPSRC (A.J.E., M.A.P., P.R.R., C.A.R., D.S.W.), the Associated Octel Co., Ltd., Ellesmere Port, U.K. (M.A.P., D.S.W.), the Royal Society (P.R.R., D.S.W.), the Nuffield Foundation (D.S.W.), and the Cambridge Crystallography Data Centre (M.-A.R.).

References

- [1] A.J. Edwards, N.E. Leadbeater, M.A. Paver, P.R. Raithby, C.A. Russell and D.S. Wright, *J. Chem. Soc., Dalton Trans.*, (1994) 1479.
- [2] A.J. Edwards, M.A. Paver, P.R. Raithby, M. Rennie, C.A. Russell and D.S. Wright, *J. Chem. Soc., Dalton Trans.*, (1994) 2963.
- [3] A.J. Edwards, M.A. Paver, M. Rennie, P.R. Raithby, C.A. Russell and D.S. Wright, *Angew. Chem.*, 106 (1994) 1334.; *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 1277.
- [4] M.A. Beswick, A.J. Edwards, J.R. Galsworthy, M.A. Paver, P.R. Raithby, M. Rennie, C.A. Russell, K.L. Verhorevoort and D.S. Wright, *J. Chem. Soc., Dalton Trans.*, submitted.
- [5] R.A. Alton, D. Barr, A.J. Edwards, M.A. Paver, P.R. Raithby, M. Rennie, C.A. Russell and D.S. Wright, *J. Chem. Soc., Chem. Commun.*, (1994) 1481.
- [6] D. Barr, A.J. Edwards, M.A. Paver, P.R. Raithby, M. Rennie, C.A. Russell and D.S. Wright, *Angew. Chem.*, in press.
- [7] D. Barr, A.J. Edwards, M.A. Paver, S. Pullen, P.R. Raithby, M. Rennie, C.A. Russell and D.S. Wright, *Angew. Chem.*, 106 (1994) 1960; *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 1875.
- [8] R.E. Allan, M.A. Beswick, A.J. Edwards, M.A. Paver, P.R. Raithby, M. Rennie and D.S. Wright, *J. Chem. Soc., Dalton Trans.*, in press.
- [9] See for example; (a) U. Müller, *Z. Anorg. Allg. Chem.*, 388 (1972) 207; (b) G. Ferguson and D.R. Ridley, *J. Chem. Soc., Dalton Trans.*, (1975) 1288; (c) U. Müller, *Z. Anorg. Allg. Chem.*, 422 (1976) 134; (d) W. Schwarz and H.J. Guder, *Acta Cryst. A*, 34 (1978) S123; (e) K. Dehnicke, K. Hartke, J. Pebler, F. Weller and H. Wolff, *Z. Anorg. Allg. Chem.*, 486 (1982), 61; (f) C. Rajca, W. Schwarz and J. Weidlein, *Z. Naturforsch.*, 39B (1984) 1219; (g) W. Kolandra, W. Schwarz and J. Weidlein, *Z. Naturforsch.*, 40B (1985) 87; (h) G.E. Forster, G. Southerington, M. Begley and D.B. Sowerby, *J. Chem. Soc., Chem. Commun.*, (1991) 54.
- [10] W. Neubert, H. Pritskow and H.P. Latscha, *Angew. Chem.*, 100 (1988) 298; *Angew. Chem., Int. Ed. Engl.*, 27 (1988) 287.
- [11] G. Birke, H.P. Latscha, H. Pritskow, *Z. Naturforsch.*, B31 (1976) 1285; W. Dietrich, H. Eisinger, H.P. Latscha, J. Pebler and K. Schmid, *Z. Naturforsch.*, B34 (1979) 1454; H. Eisinger and H.P. Latscha, *Z. Naturforsch.*, B34 (1979) 1059.
- [12] T. Kottke, D. Stalke, *J. Appl. Crystallogr.*, 26 (1993) 615.
- [13] G.M. Sheldrick, SHELXL-93, Göttingen, 1992.