Synthesis and structural characterization of the first metal organic thallium antimonide

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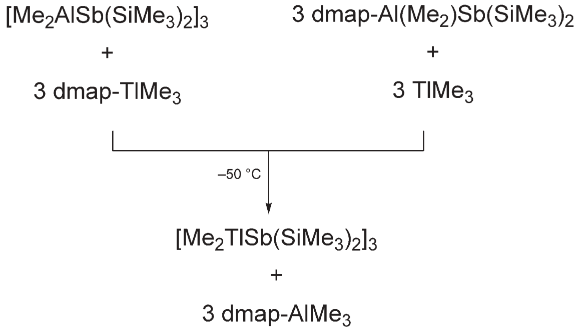
Received (in Cambridge, UK) 20th December 2005, Accepted 10th March 2006
First published as an Advance Article on the web 20th March 2006
DOI: 10.1039/b518072d

The first metal organic thallium antimonide, the heterocycle $[Me_2TlSb(SiMe_3)_2]_3$, was synthesized by reaction of $[Me_2AlSb(SiMe_3)_2]_3$ with the Lewis acid–base adduct dmap-$TlMe_3$ (dmap = 4-dimethylaminopyridine). The analogous TlBi heterocycle $[Me_2TlBi(SiMe_3)_2]_3$ couldn't be isolated due to its limited thermal stability in solution.

Metal organic compounds between elements of groups 13 and 15 have a long standing history in main group organometallic chemistry. Several reaction pathways such as salt metathesis, H_2 and alkane elimination and dehalosilylation reactions have been established for the synthesis of group 13 metal (Al, Ga, In, Tl) amides, phosphides and arsenides,[1] but they almost completely failed for the synthesis of the corresponding antimonides (except Ga, In) and bismuthides. To date, the most valuable reaction for the synthesis of such compounds, whose thermal stability is significantly reduced compared to their lighter congeners, is the dehydrosilylation reaction between $E(SiMe_3)_3$ (E = Sb, Bi) and dialkylmetal hydrides R_2MH (M = Al, Ga).[2] Unfortunately, this specific reaction can't be applied for the synthesis of In and Tl heterocycles since dialkylindanes and -thallanes R_2MH (M = In, Tl) are almost unknown, to date.[3] Consequently, we became interested in the developement of new reaction pathways and reported on the metathesis reaction of dmap–$Al(Me_2)E(SiMe_3)_2$ (dmap = 4-dimethylaminopyridine; E = P, As, Sb, Bi) and Me_3M (M = Ga, In), which proceed with Al/M exchange and subsequent formation of the corresponding group 13/15 heterocycles $[Me_2ME(SiMe_3)_2]_3$.[4] This specific reaction can be performed at very low temperature and allows the synthesis of extremely temperature sensitive group 13/15 compounds such as $[Me_2InBiSiMe_3)_2]_3$ and $[Me_2TlE(SiMe_3)_2]_2$ (E = P, As).[5] We now report on the synthesis and X-ray crystal structure analysis of the first organometallic Tl–Sb compound and on our studies concerning the synthesis of a Tl–Bi heterocycle.†

The reaction of Me_3Tl–dmap[6] with $[Me_2AlSb(SiMe_3)_2]_3$[7] at −50 °C proceeds with formation of dmap-$AlMe_3$ and the novel six-membered TlSb heterocycle $[Me_2TlSb(SiMe_3)_2]_3$ **1** (eqn (1)).[8] **1** is very sensitive toward moisture, air and light and only stable in solution at temperatures below −30 °C, whereas in its pure form **1** can be stored in the dark at −30 °C for weeks. Consequently, NMR spectra were recorded in toluene-d_8 at −40 °C. The ^1H NMR spectrum shows a singlet of the $SiMe_3$ and a doublet of the $TlMe_2$ groups with a typical $^2J_{TlH}$ coupling constant of 315 Hz. The recording of a ^{13}C NMR spectrum was complicated by the low solubility of **1** under these conditions. Only a single resonance due to the $SiMe_3$ groups was observed in very low intensity whereas the $TlMe_2$ groups, which should give a doublet in even lower intensity compared to the $SiMe_3$ groups (intensity 1 : 1 : 6), were not detected. Mass spectrometry studies indicate a very limited stability of **1** in the gas phase since only signals due to a complete fragmentation of the six-membered heterocycle were detected.



(1)

Single crystals of **1** were obtained from a solution of freshly prepared **1** in toluene at −60 °C. **1**, which is the first structurally characterized TlSb metal organic compound, crystallizes in the monoclinic space group $P2_1/n$ (No. 14) and is isostructural to comparable six-membered heterocycles of the general type $[Me_2MSbSiMe_3)_2]_3$ (M = Al,[7] Ga,[9] In[10]) (Fig. 1). The Tl and Sb centers show distorted tetrahedral coordination spheres. They form a six-membered ring, which adopts a distorted boat-type conformation (Fig. 2). The endocyclic Tl–Sb–Tl-bond angles (121.5(1)–129.1(1)°) of **1** are significantly larger than the Sb–Tl–Sb bond angles (100.0(1)–104.9(1)°) as was previously observed for analogous six-membered MSb heterocycles (M = Al, Ga, In). The Tl–Sb bond distances range from 2.889(1)–2.941(1) Å, which is significantly shorter than the Tl–Sb distances in the Zintl anions $[Tl_4Sb_6]_x^{12-11}$ and $[Tl_2Sb_8]_x^{12-}$ (2.99–3.25 Å).[12] The Tl–C bond distances of **1** (Ø 2.212 Å) are almost identical to those observed in $TlMe_3$ (2.206 Å)[13] and dmap-$TlMe_3$ (2.224 Å).[6]

The thermal stability of the TlE heterocycles $[Me_2TlE(SiMe_3)_2]_x$ (E = P, As, x = 2; Sb, x = 3) in solution was found to steadily decrease with increasing atomic number of the group 15 element. A solution of $[Me_2TlP(SiMe_3)_2]_2$ in toluene can be handled at room temperature for almost 30 min without decomposition whereas solutions of $[Me_2TlAs(SiMe_3)_2]_2$ and $[Me_2TlSb(SiMe_3)_2]_3$ in toluene decompose at temperatures above −20 °C and −30 °C,

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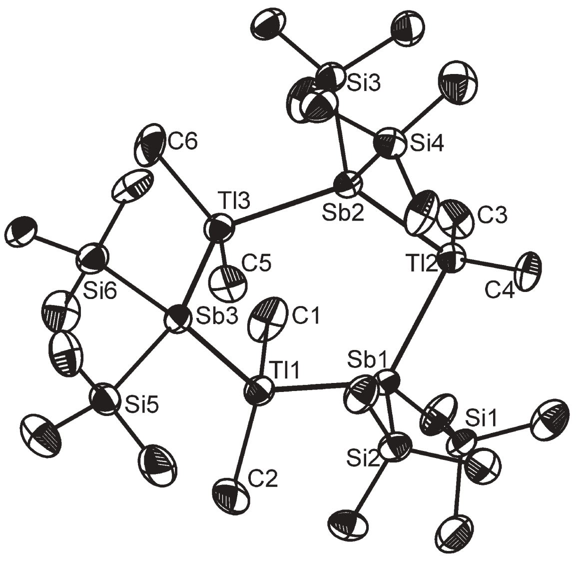

Fig. 1 Thermal ellipsoid (50%) drawing of **1**, H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sb1–Tl1 2.904(1), Sb1–Tl2 2.895(1), Sb2–Tl2 2.941(1), Sb2–Tl3 2.896(1), Sb3–Tl1 2.910(1), Sb3–Tl3 2.889(1), Sb1–Si1 2.545(3), Sb1–Si2 2.539(3), Tl1–C1 2.205(10), Tl1–C2 2.231(11), Sb2–Si3 2.566(3), Sb2–Si4 2.558(3), Tl2–C3 2.207(10), Tl2–C4 2.205(10), Sb3–Si5 2.560(3), Sb3–Si6 2.551(4), Tl3–C5 2.227(10), Tl3–C6 2.199(13); Tl1–Sb1–Tl2 121.5(1), Tl2–Sb2–Tl3 129.1(1), Tl1–Sb3–Tl3 128.3(1), Sb1–Tl1–Sb3 100.0(1), Sb1–Tl2–Sb2 100.1(1), Sb2–Tl3–Sb3 104.9(1), C1–Tl1–C2 132.0(5), Si1–Sb1–Si2 103.5(1), C3–Tl2–C4 132.7(4), Si3–Sb2–Si4 102.3(1), C5–Tl3–C6 116.9(5), Si5–Sb3–Si6 101.0(1).

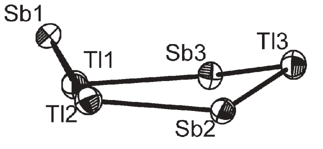

Fig. 2 ORTEP diagram (50% probability ellipsoids) showing the distorted boat-type conformation of the six-membered Tl_3Sb_3 ring.

respectively, within a few minutes. This tendency consequently continues for $[Me_2TlBi(SiMe_3)_2]_3$ **2**, the heaviest congener of this class of compounds. Several attempts to synthesize **2** by reaction of $[Me_2AlBi(SiMe_3)_2]_3$ with three equivalents of dmap-$TlMe_3$ failed. Even though a reaction was observed at −90 °C, **2** couldn't be isolated and characterized due to its low thermal stability. **2** decomposes in solution above −90 °C with subsequent formation of $Bi_2(SiMe_3)_4$, which was identified according to its characteristic green-metallic color and by ^1H NMR spectrometry (after isolation). $Bi_2(SiMe_3)_4$ is known to be the typical decomposition product of group 13 metal-Bi heterocycles of the type $[Me_2MBi(SiMe_3)_2]_3$ (M = Al, Ga, In)[14] and its formation strongly indicates the presence of $[Me_2TlBi(SiMe_3)_2]_3$ **2** as highly unstable reaction intermediate.

Notes and references

† Crystal data for **1**: $C_{24}H_{72}Sb_3Si_6Tl_3$, $M = 1507.72$, space group $P2_1/n$ (No. 14), monoclinic, $a = 9.6404(4)$, $b = 20.7836(9)$, $c = 24.7602(12)$ Å, $\beta = 96.761(2)°$, $V = 4926.5(4)$ Å^3; $Z = 4$; $T = 123$ K; $\rho_{ber.} = 2.033$ g cm^{-3}; $\mu(MoK\alpha) = 11.557$ mm^{-1}, $F(000) = 2784$, 20129 reflections ($2\theta_{max} = 50°$) measured (8547 unique), R (for $I > 2\sigma(I)$) = 0.0440, $wR2$(all data) = 0.0831, GOF = 0.824 for 325 parameters, max./min. difference electron density 1.331 eÅ^{-3}/–1.395 eÅ^{-3}; an empirical absorption correction was applied (max./min. transmission 0.2356/0.1877). The structure was solved by direct methods (SHELXS-97; G. M. Sheldrick SHELXS-90/96, Program for Structure Solution, *Acta Crystallogr. Sect. A* 1990, **46**, 467) and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97; G. M. Sheldrick SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, 1997).

$[Me_2TlSb(SiMe_3)_2]_3$ (1): A solution of 0.56 g (1.5 mmol) Me_3Tl–dmap in 10 ml toluene was added dropwise at −30 °C to a suspension of 0.49 g (0.5 mmol) $[Me_2AlSb(SiMe_3)_2]_3$ in 15 ml toluene and stirred for 30 min. The resulting light brown solution was stored for 12 h at −30 °C. dmap-$AlMe_3$ was removed by decanting and the remaining solution was stored at −60 °C. **1** was obtained after 24 h as colorless crystals. Yield: 0.36 g, 0.24 mmol, 48%. Mp. 50–60 °C (dec.). **1** was also obtained from the equimolar reaction of dmap-$Al(Me_2)Sb(SiMe_3)_2$ and $TlMe_3$, but this reaction requires the isolation of the very air and moisture sensitive, base-stabilized aluminium stibide dmap-$Al(Me_2)Sb(SiMe_3)_2$.

^1H-NMR (300 MHz, toluene-d_8, −40 °C): $\delta = 0.56$ (s, 18 H; $SiMe_3$), 0.92 (d, $^2J_{Tl–H} = 315$ Hz, 6 H; $TlMe_2$). $^{13}C\{^1H\}$-NMR (75 MHz, toluene-d_8, −40 °C): $\delta = 5.9$ ($SiMe_3$). MS (EI, 12 eV, 75 °C) m/z (%) = 340 (35) $[Sb(SiMe_3)_3]^+$, 267 (18) $[Sb(SiMe_3)_2]^+$, 203 (8) $[Tl]^+$, 73 (100) $[SiMe_3]^+$.

CCDC 262592. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b518072d

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8 **1** was also obtained from the reaction of dmap-$Al(Me_2)Sb(SiMe_3)_2$ (S. Schulz and M. Nieger, *Organometallics*, 2000, **19**, 2640) with $TlMe_3$. The first step of the reaction was found to be the formation of the adduct dmap-$Al(Me_2)Sb(SiMe_3)_2$-$TlMe_3$, which subsequently undergoes Al–Sb and Tl–Me bond breaking reactions with formation of dmap-$AlMe_3$ and **1**.

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12 B. Li, L. S. Chi and J. D. Corbett, *Inorg. Chem.*, 2003, **42**, 3036.

13 Electron diffraction (F. Tjeldberg, A. Haaland, R. Seip, Q. Shen and J. Weidlein, *Acta Chem. Scand. Ser. A*, 1982, **36**, 495) and single crystal X-ray analyses (R. Boese, A. J. Downs, T. M. Greene, A. W. Hall, C. A. Morrison and S. Parsons, *Organometallics*, 2003, **22**, 2450) of $TlMe_3$ gave identical Tl–C distances.

14 The decomposition temperatures of toluene solutions of $[Me_2MBi(SiMe_3)_2]_3$ (M = Al, Ga, In) were also found to steadily decrease with increasing atomic number of the group 13 metal (M = Al 40 °C, Ga −20 °C, In −35 °C). In each case, the formation of $Bi_2(SiMe_3)_4$ was observed. Very recently, Fenske *et al.* observed the formation of $Bi_2(SiMe_3)_4$ in the reaction of Cu^I halides and Cu^I acetates, respectively, with $Bi(SiMe_3)_3$ (D. Fenske, A. Rothenberger and S. Wieber, *Z. Anorg. Allg. Chem.*, 2003, **629**, 929).