$[Me_2AlBi(SiMe_3)_2]_3$—The First Structurally Characterized Organometallic Compound Containing a Bond between an Element of Group 13 and Bi**

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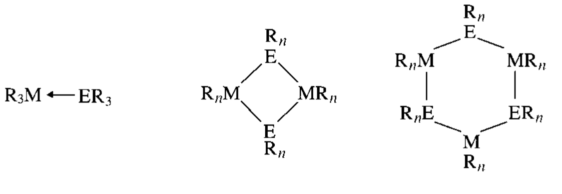
Dedicated to Professor Edgar Niecke
on the occasion of his 60th birthday

Over the past two decades compounds containing elements of Groups 13 and 15 (III–V compounds) have attracted much attention due to their potential applications as single-source precursors for the deposition of thin films of the corresponding semiconducting material by metal organic chemical vapor deposition (MOCVD). Numerous amides, phosphides, and arsenides of Al, Ga, and In, usually in the form of simple 1:1 Lewis acid–base adducts (type I) or ring compounds (type II and III), have been synthesized.[1]



I II III

M = Al, Ga, In; E = N, P, As, Sb; R = Alkyl

Fundamental investigations concerning the synthesis and structural characterization of Ga and In antimonides were performed by Wells et al.[2] and by other groups.[3] Bisorganogallium and -indium chlorides reacted with $Sb(SiMe_3)_3$ under elimination of Me_3SiCl (dehalosilylation) to form four-membered ring systems (type II). Recently, we described the synthesis and structural characterization of the first organometallic Al–Sb compounds.[4] $Sb(SiMe_3)_3$ reacted with bisorganoaluminum hydrides R_2AlH under elimination of Me_3SiH (dehydrosilylation) to give the ring systems $[R_2AlSb(SiMe_3)_2]_x$, while trialkylaluminum compounds form simple adducts $R_3Al \leftarrow Sb(SiMe_3)_3$.

Organometallic Bi heterocycles $[R_xBiMR_x]_x$ containing Bi and the main group element M in 1:1 stochiometry were synthesized and structurally characterized in form of four-membered ring systems (type II; M = main group element, E = Bi). In these compounds the Bi atoms are linked by an electronegative element such as oxygen[5] or nitrogen.[6] $[Cp^*_2SmBi]_2$, the only structurally characterized ring compound showing Bi atoms linked by an electropositive element, also contains a four-membered Sm_2Bi_2 core.[7]

We report herein on the synthesis of the first III–V compound with the higher homologue Bi. Equimolar amounts of Me_2AlH and $Bi(SiMe_3)_3$ react quantitatively under dehydrosilylation to give $[Me_2AlBi(SiMe_3)_2]_3$, a six-membered ring system of type III containing Al–Bi bonds [Eq. (1)]. $[Me_2AlBi(SiMe_3)_2]_3$, which is very sensitive towards air and moisture,

$$3\ Me_2AlH + 3\ Bi(SiMe_3)_3 \xrightarrow[-\ 3Me_3SiH]{} [Me_2AlBi(SiMe_3)_2]_3 \qquad (1)$$

was characterized by elemental analysis, as well as ^1H NMR, ^{13}C NMR, and IR spectroscopy. In addition, the solid-state structure was determined by a single-crystal X-ray diffraction study .

The ^1H NMR spectrum shows resonances for the Me and $SiMe_3$ groups at $\delta = 0.32$ and 0.76, respectively, the ^{13}C NMR spectrum only shows the resonance for the $SiMe_3$ groups at $\delta = 7.02$.[8] In the mass spectra the peaks with the highest mass observed are at m/z 710 ($Bi_2(SiMe_3)_4^+$) and m/z 428 ($Bi(SiMe_3)_3^+$). A signal at m/z 57 corresponds to the $AlMe_2^+$ fragment. The molecular ion peak $[Me_2AlBi(SiMe_3)_2]_3^+$ could not be detected. Evidently, $[Me_2AlBi(SiMe_3)_2]_3$ is thermally unstable and decomposes under the measurement conditions to the observed compounds. The ^1H NMR spectrum of $[Me_2AlBi(SiMe_3)_2]_3$ showed no contamination with $Bi(SiMe_3)_3$ or $Bi_2(SiMe_3)_4$.[9]

Single crystals suitable for an X-ray structure analysis were obtained from pentane at 0 °C.[10] $[Me_2AlBi(SiMe_3)_2]_3$ crystallizes in the monoclinic space group $P2(1)/n$ (Figure 1). Within the six-membered Al_3Bi_3 ring, the Al and Bi atoms adopt a distorted tetrahedral environment. The Al–Bi bond lengths range from 2.755(3) to 2.793(3) Å, which is slightly longer

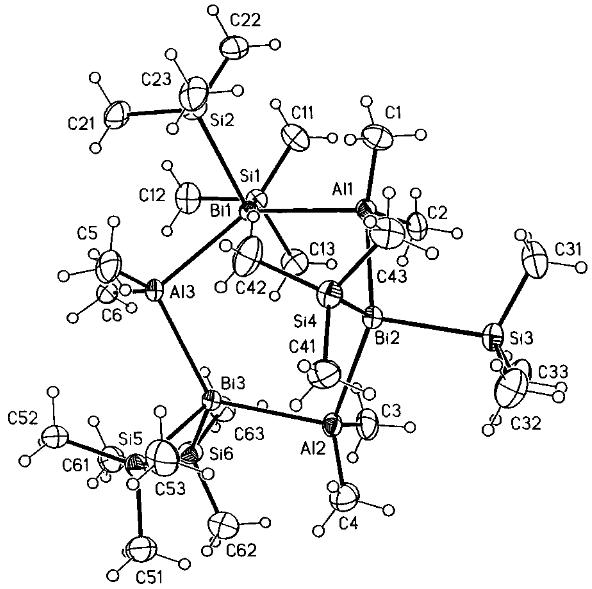


Figure 1. Solid-state structure of $[Me_2AlBi(SiMe_3)_2]_3$. Selected bond lengths [Å] and angles [°]: Bi1–Al1 2.793(3), Bi1–Al3 2.790(3), Bi2–Al1 2.755(3), Bi2–Al2 2.766(3), Bi3–Al2 2.766(3), Bi3–Al3 2.773(3), Bi1–Si1 2.646(3), Bi1–Si2 2.640(3), Al1–C1 1.967(9), Al1–C2 1.960(9); Al1-Bi1-Al3 130.48(9), Al1-Bi2-Al2 121.67(9), Al2-Bi3-Al3 128.40(8), Bi1-Al1-Bi2 101.00(9), Bi2-Al2-Bi3 101.78(9), Bi1-Al3-Bi3 104.13(8), C1-Al1-C2 122.4(4), Si1-Bi1-Si2 100.75(8).

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than the sum of the covalent radii of these atoms (2.72 Å).[11] The Al – Bi distances observed at Bi2 and Bi3 are about 3 pm shorter than those found at Bi1. Analogous structural findings were observed in the isostructural compounds $[Me_2GaSb(SiMe_3)_2]_3$[12] and $[Me_2AlSb(SiMe_3)_2]_3$.[4b] Due to the lack of organometallic Al – Bi compounds, only a comparison with the Zintl phase anion $[Al_2Bi_6]^{10-}$ in $Ca_5Al_2Bi_6$, showing comparable bond lengths of 2.800 – 2.869 Å, can be made.[13] The endocyclic Al-Bi-Al bond angles span a wide range of 121.7(1) to 130.5(1)°, while the Bi-Al-Bi bond angles only vary between 101.0(1) and 104.1(1)°. The greater angle at Al and the smaller angle at Bi are in agreement with the VSEPR model. Comparable values were found in six-membered rings with an Al_3E_3 core (E = element of Group 15), such as $[Me_2AlNH_2]_3$,[14] $[(Me_3Si)_2AlP(H)(cyclo\text{-}C_6H_{11})]_3$,[15] $[H_2AlP(SiMe_3)_2]_3$,[16] $[Me_2AlAsPh_2]_3 \cdot 2\,C_7H_8$,[17] and $[Me_2AlSb(SiMe_3)_2]_3$.[4b] The average Al – C (1.958(9) Å) and Bi – Si (2.635(3) Å) bond lengths are within the expected range.

The dehydrosilylation pathway allows a ready access to Al compounds with the higher homologues of Group 15, Sb and Bi, which could not be synthesized by established methods like salt and alkane elimination or dehalosilylation. Since the corresponding P and As compounds can also be synthesized by dehydrosilylation, this pathway seems generally applicable for the synthesis of Al – pnicogen compounds. Its potential with respect to the synthesis of the corresponding Ga and In compounds is currently under investigation.

Experimental Section

Neat Me_2AlH[18] (0.12 g, 2 mmol) and $Bi(SiMe_3)_3$[19] (0.86 g, 2 mmol) were combined at room temperature. Gas evolution followed immediately, and after 30 s, a light brown solid was formed, which was heated to 50 °C (10 min) and then dissolved in hot pentane. Colorless crystals (0.78 g, 0.63 mmol, 94 %) were formed at 0 °C. M.p. 132 °C (decomp). Elemental analysis for $C_{24}H_{72}Al_3Bi_3Si_6$ (%): calcd: C 23.30, H 5.87; found. C 23.09, H 5.78; ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 0.32$ (s, 3 H, Me), 0.76 (s, 9 H, $SiMe_3$); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 7.02$ ($SiMe_3$); MS (EI, 20 eV): m/z (%): 710 (5) $[Bi_2(SiMe_3)_4^+]$, 428 (60) $[Bi(SiMe_3)_3^+]$, 73 (100) $[SiMe_3^+]$, 57 (40) $[Me_2Al^+]$; IR (Nujol): $\tilde{\nu} = 1259$, 1245, 1172, 1100, 842, 822, 670, 622 cm^{-1}.

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[8] The absence of the Me resonance is not unusual for Me-substituted Al compounds.

[9] The mass spectra of a single crystal did not show different peaks.

[10] $[Me_2AlBi(SiMe_3)_2]_3$ ($C_{24}H_{72}Al_3Bi_3Si_6$), colorless crystals, crystal size 0.18 × 0.12 × 0.05 mm, $M_r = 1237.2$, monoclinic, space group $P2(1)/n$ (no. 14), $a = 9.5523(3)$, $b = 20.9233(8)$, $c = 24.4374(6)$ Å, $\beta = 96{,}257(2)°$, $V = 4855.1(3)$ Å^3, $Z = 4$, λ ($Mo_{K\alpha}$) = 0.71073 Å, μ = 11.06 mm^{-1}, $\rho_{calcd} = 1.69$ g cm^{-3}, T = 123(2) K, $F(000) = 2352$. Using a Nonius Kappa CCD diffractometer, 34105 reflections ($2\theta_{max} = 50°$) were collected (8158 unique, $R_{int} = 0.0978$). The structure was solved by direct methods (SHELXS-90)[20] and refined by full-matrix least-squares on F^2 (SHELXL-97).[21] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. $R_1 = 0.043$ ($I > 2\sigma(I)$), $wR_2 = 0.093$, 331 parameters, largest min./max. residual electron density in the final difference Fourier synthesis: -3.021 e Å^{-3}/2.308 e Å^{-3} (absorption effects). An empirical absorption correction was applied (min./max. transmission 0.2890/0.4466) Crystallographic data (exluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-106174. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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