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Synthesis and X-ray Crystal Structures of Novel Al−Bi and Ga−Bi Compounds[†]

Andreas Kuczkowski, Florian Thomas, Stephan Schulz,* and Martin Nieger

Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Strasse 1,
D-53121 Bonn, Germany

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Reactions between trialkylgallanes GaR_3 (R = Me, Et, *t*-Bu) and triorganobismuthanes BiR'_3 (R′ = *i*-Pr, $SiMe_3$) lead to the formation of six Lewis acid−base adducts of the type $R_3Ga{\cdot}BiR'_3$ ($Me_3Ga{\cdot}Bi(SiMe_3)_3$, **1**, $Et_3Ga{\cdot}Bi(SiMe_3)_3$, **2**, *t*-$Bu_3Ga{\cdot}Bi(SiMe_3)_3$, **3**, $Me_3Ga{\cdot}Bi$(*i*-Pr)$_3$, **4**, $Et_3Ga{\cdot}Bi$(*i*-Pr)$_3$, **5**, *t*-$Bu_3Ga{\cdot}Bi$(*i*-Pr)$_3$, **6**). **2** and **6** are the first structurally characterized main group element−triorganobismuthane Lewis acid−base adducts. In addition, the synthesis and structural characterization of two Lewis base-stabilized, monomeric aluminum bismuthides of the type base−Al(R_2)Bi($SiMe_3$)$_2$ (base = 4-(dimethylamino)pyridine (dmap); R = Me **7**, Et **8**) is reported.

Introduction

"*On the other hand, there are still many "white areas" challenging future research, e.g., ..., organobismuth-main group metal compounds, ...*" This final statement of Breunig et al. in their review article about organobismuth compounds[1] clearly reveals the underexplored status of main group−bismuth chemistry in general. This can also undoubtly be seen in group 13/15 chemistry. While numerous simple Lewis acid−base adducts $R_3M{\cdot}ER'_3$, monomers, heterocycles, and cages $[R_2MER'_2]_x$ (*x* = 1, 2, 3, 4, ...) containing the lighter pnicogenides, N, P, As, and Sb, have been prepared and structurally characterized, the analogous Bi-containing compounds remain almost unknown. Very recently, we described the synthesis and X-ray structure of the first example of such a compound. The six-membered heterocycle $[Me_2AlBi(SiMe_3)_2]_3$ was obtained by a dehydrosilylation reaction between Me_2AlH and $Bi(SiMe_3)_3$.[2] Further attempts to synthesize additional compounds by this reaction pathway failed.[3] Interestingly, even no simple Lewis acid−base adduct of the type $R_3M{\cdot}BiR'_3$ has been synthesized until now. To the best of our knowledge, only Coates almost 50 years ago described the reaction between $GaMe_3$ and $BiMe_3$, which did not yield a stable adduct.[4] This was surprising because the simple coordination of a Lewis base is a general reaction of group13 trialkyls due to their tendency, when possible, to complete their valence octet of electrons and to increase their coordination number from three to four.[5] This result indicates a decreased Lewis basicity of trimethylbismuthane compared to the other trimethyl pnicogenes, which form the corresponding adducts $Me_3Ga{\cdot}EMe_3$.[6]

In an attempt to explore the uncharted area of compounds containing the group13−Bi linkage and to obtain a deeper insight into structural properties, we were interested in the synthesis and structural characterization of such compounds containing either dative bonds or regular σ-bonds. Herein, we present our results on Lewis acid−base reactions between trialkylgallanes and triorganobismuthanes. In addition, we describe the synthesis of monomeric, Lewis base-stabilized aluminum bismuthides of the type dmap−Al(R_2)Bi($SiMe_3$)$_2$ (dmap = 4-(dimethylamino)pyridine).

Experimental Section

General Considerations. All manipulations were performed in a glovebox under a N_2 atmosphere or by standard Schlenk techniques. 4-(Dimethylamino)pyridine was commercially available from Aldrich and used as received. Me_3Ga,[7] Et_3Ga,[7] *t*-Bu_3Ga,[8] $Bi(SiMe_3)_3$,[9] Bi(*i*-Pr)$_3$,[10] Et_2AlH,[11] and $[Me_2AlBi(SiMe_3)_2]_3$[2] were prepared by literature methods. ^1H and $^{13}C\{^1H\}$ spectra were recorded using a Bruker AMX 300 spectrometer and are referenced to internal C_6D_5H (δ ^1H 7.154,

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[†] Dedicated to Prof. Herbert W. Roesky on the occasion of his 65th birthday.

* To whom correspondence should be addressed. Phone: (+49)228-73-5326. Fax: (+49)228-73-5327. E-mail: sschulz@uni-bonn.de.

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(5) This reaction has been extensively studied since Gay-Lussac almost 200 years ago synthesized the first compound of this type, $F_3B{\cdot}NH_3$ (Gay-Lussac, J. L.; Thenard, J. L. *Mem. Phys. Chim. Soc. d'Arcueil* **1809**, *2*, 210. Citation in: Jonas, V.; Frenking, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1489−1490.). Since then, numerous group 13/15 adducts have been investigated both experimentally and theoretically. (See the following and the references therein: (a) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992−1007. (b) Haaland, A. In *Coordination Chemistry of Aluminum*, Robinson, G. H., Ed.; VCH Verlagsgesellschaft: Weinheim, 1993. (c) Gardiner, M. G.; Raston, C. L. *Coord. Chem. Rev.* **1997**, *166*, 1−34. (d) Brunel, J. M.; Faure, B.; Maffei, M. *Coord. Chem. Rev.* **1998**, *178*−*180*, 665−698. (e) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741−8753. (f) Timoshkin, A. Y.; Suvorov, A. V.; Bettinger, H. F.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1999**, *121*, 5687−5699.)

(6) The poor donor properties of triorganylbismuthanes in general are also indicated by the fact that compared with the almost uncountable number of transition-metal phosphane complexes, much fewer bismuthane complexes are known. In addition, up to now only three neutral transition metal complexes $L_nM{\cdot}BiR_3$ have been structurally characterized: (a) Carty, A. J.; Taylor, N. J.; Coleman, A. W.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 639−640. (b) Holmes, N. J.; Levason, W.; Webster, M. *J. Organomet. Chem.* **1997**, *545*, 111−115.

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δ ^{13}C 128.0). Melting points were measured in sealed capillaries and are not corrected. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn.

General Preparation of $R_3Ga\cdot BiR'_3$. Pure R_3Ga (2 mmol) and R'_3Bi (2 mmol) were combined in the glovebox. **2** and **3** immediately formed a white solid, while **1**, **4**, **5**, and **6** stayed liquid at ambient temperature. At −30 °C, **6** also solidified. **2**, **3**, and **6** were dissolved in pentane (5 mL) and stored at −30 °C, resulting in the formation of colorless crystals in almost quantitative yield. **1**, **4**, and **5** were characterized without further purification.

$Me_3Ga\cdot Bi(SiMe_3)_3$, **1** (M = 544.95 g/mol): 1.11 g, 2.00 mmol, 100%. $C_{12}H_{36}AlBiSi_3$, found (calc): C 25.98 (26.45); H 6.53 (6.66). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ −0.06 (s, 3 H, MeGa), 0.63 (s, 9 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ 1.7 (MeGa), 6.4 ($SiMe_3$).

$Et_3Ga\cdot Bi(SiMe_3)_3$, **2** (M = 585.46 g/mol): 1.10 g, 1.88 mmol, 94%. Mp: 66−68 °C. $C_{15}H_{42}BiGaSi_3$, found (calc): C 30.11 (30.77); H 7.18 (7.23). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.52 (q, $^3J_{HH}$ = 7.9 Hz, 2 H, MeCH_2Ga), 0.64 (s, 9 H, $SiMe_3$), 1.21 (t, $^3J_{HH}$ = 7.9 Hz, 3 H, $MeCH_2Ga$). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ 6.3 ($SiMe_3$), 9.9 (MeCH_2Ga), 10.5 (MeCH$_2$Ga).

t-$Bu_3Ga\cdot Bi(SiMe_3)_3$, **3** (M = 671.19 g/mol): 1.29 g, 1.92 mmol, 96%. Mp: 88−90 °C. $C_{21}H_{54}BiGaSi_3$, found (calc): C 37.13 (37.58); H 7.98 (8.11). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.66 (s, 9 H, $SiMe_3$), 1.20 (s, 9 H, *t*-Bu). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ 6.5 ($SiMe_3$), 31.4 (Me_3CGa).

i-$Pr_3Bi-GaMe_3$, **4** (M = 453.07 g/mol): 0.91 g, 2.00 mmol, 100%. $C_{12}H_{30}BiGa$, found (calc): C 31.03 (31.81); H 6.31 (6.67). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ −0.14 (s, 3H, MeGa), 1.82 (d, $^3J_{HH}$ = 7.2 Hz, 6 H, Me_2CHBi), 2.15 (sep, $^3J_{HH}$ = 7.2 Hz, 1 H, $Me_2$$CH$Bi). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ 1.6 (MeGa), 23.9 (Me_2CHBi), 29.0 ($Me_2$$CH$Bi).

i-$Pr_3Bi-GaEt_3$, **5** (M = 495.07 g/mol): 0.99 g, 2.00 mmol, 100%. $C_{15}H_{36}BiGa$, found (calc): C 35.99 (36.39); H 7.13 (7.33). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.51 (q, $^3J_{HH}$ = 7.9 Hz, 2 H, MeCH_2Ga), 1.19 (t, $^3J_{HH}$ = 7.9 Hz, 3 H, MeCH$_2$Ga), 1.82 (d, $^3J_{HH}$ = 7.7 Hz, 6 H, Me_2CHBi), 2.16 (sep, $^3J_{HH}$ = 7.7 Hz, 1 H, $Me_2$$CH$Bi). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ 9.9 (MeCH_2Ga), 10.4 (MeCH$_2$Ga), 23.9 (Me_2CHBi), 28.9 ($Me_2$$CH$Bi).

i-$Pr_3Bi-Ga(t\text{-}Bu)_3$, **6** (M = 579.29 g/mol): 1.03 g, 1.78 mmol, 89%. Mp: −15 °C. $C_{21}H_{48}BiGa$, found (calc): C 43.19 (43.54); H 4.99 (5.22). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 1.17 (s, 9 H, *t*-Bu), 1.82 (d, $^3J_{HH}$ = 7.4 Hz, 6 H, Me_2CHBi), 2.15 (sep, $^3J_{HH}$ = 7.4 Hz, 1 H, $Me_2$$CH$Bi). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ 23.9 (Me_2CHBi), 31.1 ($Me_2$$CH$Bi), 31.6 ($Me_3$CGa).

Synthesis of dmap−$Al(Me_2)Bi(SiMe_3)_2$, 7: 4-(Dimethylamino)pyridine (3 mmol) was added to a solution of $[Me_2AlBi(SiMe_3)_2]_3$ (1 mmol) in hexane. The resulting suspension was heated at 50 °C. The resulting clear yellow solution was stored at −30 °C. After 10 h, **7** was obtained as a yellow solid. Yield: 1.20 g, 2.24 mmol, 75%. Mp: 68 °C. $C_{15}H_{34}AlBiN_2Si_2$ (M = 534.58 g/mol), found (calc): C 33.32 (33.65); H 6.19 (6.38). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.23 (s, 6 H, $AlMe_2$), 0.98 (s, 18 H, $SiMe_3$), 1.91 (s, 6 H, NMe_2), 5.55 (d, $^3J_{H-H}$ = 5.6 Hz, 2 H, C(3)−H), 8.06 (d, $^3J_{H-H}$ = 5.8 Hz, 2 H, C(2)−H). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): δ 8.3 ($SiMe_3$), 38.1 (NMe_2), 106.5 (C(3)−H), 146.3 (C(2)−H), 155.0 (C(4)).

Synthesis of dmap−$Al(Et_2)Bi(SiMe_3)_2$, 8. To a solution of equimolar amounts of 4-(dimethylamino)pyridine (2 mmol) and Et_2AlH (2 mmol) in hexane was added $Bi(SiMe_3)_3$ (2 mmol). The solution was heated at 50 °C for 30 min. Then, the resulting clear yellow solution was stored at −30 °C. After 10 h, **8** was obtained as a yellow solid. Yield: 1.11 g, 1.32 mmol, 66%. Mp: 72 °C. $C_{17}H_{38}AlBiN_2Si_2$ (M = 562.63 g/mol), found (calc): C 36.03 (36.27); H 6.52 (6.77). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.72 (q, $^3J_{H-H}$ = 8.0 Hz, 4 H, CH$_3$$CH_2$Al), 0.96 (s, 18 H, $SiMe_3$), 1.52 (t, $^3J_{H-H}$ = 7.9 Hz, 6 H, CH_3CH$_2$Al), 1.96 (s, 6 H, NMe_2), 5.61 (d, $^3J_{H-H}$ = 6.1 Hz, 2 H, C(3)−H), 8.04 (d, $^3J_{H-H}$ = 6.5 Hz, 2 H, C(2)−H). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): δ 7.3 (CH_2), 8.9 ($SiMe_3$), 11.5 (CH_3), 38.7 (NMe_2), 107.0 (C(3)−H), 147.1 (C(2)−H), 155.5 (C(4)).

X-ray Structure Solution and Refinement. Crystallographic data of **2**, **6**, **7**, and **8** are summarized in Table 1. Figures 1−4 show the ORTEP diagrams of the solid-state structures including selected bond lengths and angles of **2**, **6**, **7**, and **8**. Data were collected on a Nonius Kappa-CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) at T = −150 °C. The structures of **2**, **6**, **7**, and **8** were solved by Patterson methods (SHELXS-97)[12] and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[13] The *i*-Pr groups in **6** are disordered (60:40).

Results and Discussion

The reactions of equimolar amounts of trialkylgallanes R_3Ga (R = Me, Et, *t*-Bu) and triorganobismuthanes R'_3Bi (R = $SiMe_3$, *i*-Pr) at ambient temperature lead to Lewis acid−base adducts ($Me_3Ga\cdot Bi(SiMe_3)_3$, **1**, $Et_3Ga\cdot Bi(SiMe_3)_3$, **2**, *t*-$Bu_3Ga\cdot Bi(SiMe_3)_3$, **3**, $Me_3Ga\cdot Bi(i\text{-}Pr)_3$, **4**, $Et_3Ga\cdot Bi(i\text{-}Pr)_3$, **5**, *t*-$Bu_3Ga\cdot Bi(i\text{-}Pr)_3$, **6**). To the best of our knowledge, these compounds are the first bismuthane adducts with a main group element Lewis acid. Compared to Coates' unsuccessful reaction of Me_3Ga with Me_3Bi,[14] the basicity of both bismuthanes we used is greater due to steric (partial rehybridization of the lone pair) and electronic reasons (+I-effect of the substituents).

$$R_3Ga + BiR'_3 \rightarrow R_3Ga-BiR'_3 \qquad (1)$$

$$R' = SiMe_3,\ R = Me\ \mathbf{1};\ Et\ \mathbf{2},\ t\text{-}Bu\ \mathbf{3}$$

$$R' = i\text{-}Pr,\ R = Me\ \mathbf{4};\ Et\ \mathbf{5},\ t\text{-}Bu\ \mathbf{6}$$

Complexes **1**−**6** have been characterized by multinuclear NMR spectroscopy (^{1}H and ^{13}C) and elemental analysis. Compared with the resonances of the starting compounds, the ^{1}H NMR spectra of **1**−**6** show signals due to the organic groups almost at the same chemical shift (**3**, **4**, **6**) or slightly shifted to lower field (ligands bound to gallium) and higher field (ligands bound to bismuth) (**1**, **2**, **5**). Obviously, **1**−**6** are extensively dissociated in solution. Unfortunately, we were not able to study the degree of dissociation by cryoscopic molecular weight determination due to the extreme sensitivity of **1**−**6** in solution toward traces of oxygen and water. In addition, temperature-dependent ^{1}H NMR studies between 218 and 298 K did not give reliable results.

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(14) We also reacted $BiMe_3$ with GaR_3 (R = Me, Et, *t*-Bu). The products obtained remained liquid even at −30 °C and showed resonances in the ^{1}H and ^{13}C NMR spectra at exactly the same chemical shift as the starting trialkyls.

Table 1. Crystallographic Data and Measurements for $Et_3Ga-Bi(SiMe_3)_3$ (2), $(t\text{-}Bu)_3Ga-Bi(i\text{-}Pr)_3$ (6), dmap$-Al(Me_2)Bi(SiMe_3)_2$ (7), and dmap$-Al(Et_2)Bi(SiMe_3)_2$ (8)

	2	**6**	**7**	**8**
mol formula	$C_{15}H_{42}BiGaSi_3$	$C_{21}H_{48}BiGa$	$C_{15}H_{38}AlBiN_2Si_2$	$C_{17}H_{38}AlBiN_2Si_2$
fw	585.46	579.29	534.58	562.63
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	15.0169(10)	8.9595(4)	14.3850(5)	9.6324(4)
b, Å	10.0777(7)	10.2084(4)	9.9173(4)	10.3942(4)
c, Å	17.0582(8)	14.9286(4)	17.4500(7)	14.1440(4)
α, deg		85.081(2)		77.476(2)
β, deg	91.649(4)	89.859(2)	110.512(2)	76.342(2)
γ, deg		67.948(2)		69.756(2)
V, $Å^3$	2580.4(3)	1260.20(8)	2331.59(16)	1276.80(8)
Z	4	2	4	2
radiation (wavelength, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ, mm^{-1}	7.988	8.042	7.700	7.034
temp, K	123(2)	123(2)	123(2)	123(2)
D_{calcd}, g cm^{-3}	1.507	1.527	1.523	1.463
cryst dimens (mm)	0.10 × 0.08 × 0.05	0.25 × 0.15 × 0.10	0.35 × 0.20 × 0.10	0.40 × 0.12 × 0.08
$2\theta_{max}$, deg	50.0	50.0	56.6	56.6
no. of rflns rec	12 908	18 104	35 028	18 773
no. of nonequiv rflns rec	4531	4428	5762	6090
R_{merg}	0.070	0.078	0.128	0.077
no. of params refined	181	191/177 restraints	192	210
R1;[a] wR2[b]	0.043, 0.102	0.025, 0.058	0.041, 0.097	0.040, 0.108
goodness of fit[c]	0.981	1.023	1.012	1.101
final max, min $\Delta\rho$, e $Å^{-3}$	4.521 (near Bi), −1.428	1.310, −0.872	1.984, −4.657	2.380, −3.381

[a] R1 = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ (for $I > 2\sigma(I)$). [b] wR2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] Goodness of fit = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{observns} - N_{params})\}^{1/2}$.

However, in the absence of solvent, we believe **1**−**6** to be adducts, which in the case of **2**, **3**, and **6** is clearly indicated by the fact that these compounds are solids, while the both starting compounds are liquids. Complexes **1**, **4**, and **5**, which are liquids even at −30 °C, should also be adducts, because **1** contains the same Lewis base but a stronger Lewis acid (Me_3Ga) compared with **2** and **3**. The same is true for **4** and **5** compared with **6** (t-Bu_3Ga is the weakest Lewis acid due to electronic (+I-effect of t-Bu groups) and steric reasons (ligand repulsion)).

Mass spectra of **1**−**6** do not show the molecular ion peaks. The peaks with the highest mass observed corrrespond to the respective trialkylgallane and triorganobismuthane fragments.

Single crystals of **2** and **6** suitable for an X-ray structure determination were obtained from solutions in pentane at −30 °C. Figures 1 and 2 show the solid-state structures of **2** and **6**.

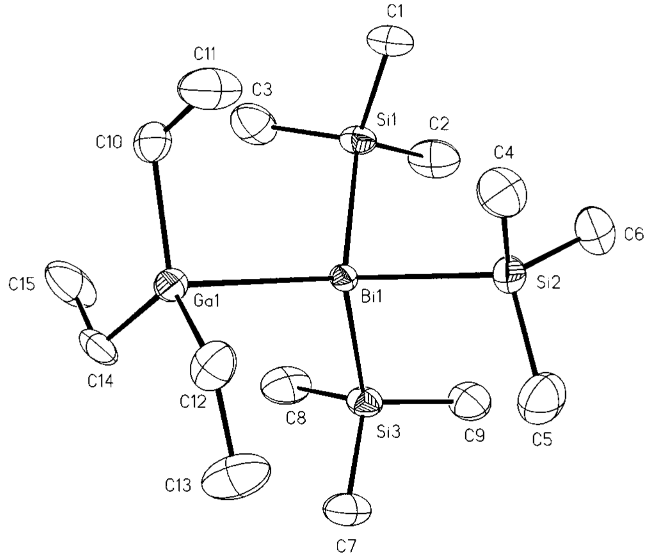

Figure 1. Molecular structure of **2** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga1−Bi1 2.966(1), Ga1−C10 1.994(8), Ga1−C12 1.978(8), Ga1−C14 1.997(8), Bi1−Si1 2.639(2), Bi1−Si2 2.638(2), Bi1−Si3 2.628(2), C10−Ga1−C12 118.2(4), C10−Ga1−C14 117.3(4), C12−Ga1−C14 118.4(4), Si1−Bi1−Si2 99.8(1), Si1−Bi1−Si3 102.5(1), Si2−Bi1−Si3 101.2(1).

As expected, the Ga and Bi atoms reside in distorted tetrahedral environments with their substituents adopting a staggered conformation relative to one another. Even in the solid state, the acid−base interactions seem to be very weak. This is indicated by the long Ga−Bi bond distances of 2.966(1) Å in **2** and 3.135(1) Å in **6** (sum of the covalent radii is 2.76 Å[15]). In particular, the distance observed for **6** is very long. Compared with the analogously substituted stibane adducts $Et_3Ga{\cdot}Sb(SiMe_3)_3$[16] and $(t\text{-}Bu)_3Ga{\cdot}Sb(i\text{-}Pr)_3$,[17] which show Ga−Sb distances of 2.846(5) and 2.962(1) Å, the Ga−Bi bonds in **2** and **6** are elongated by 0.12 and 0.17 Å, respectively. However, the difference of the covalent radii of Bi (1.50 Å) and Sb (1.41 Å) is only 0.09 Å.[15] The relative bond lengthening of 0.03 and 0.08 Å, respectively, clearly shows the lower Lewis basicity of the triorganobismuthanes compared with the corresponding triorganostibanes. The same is indicated by the decreased Si−Bi−Si and C−Bi−C angles (sum of the bond angles: 303.5° **2**, 286.1° **6**) compared with the Si−Sb−Si and C−Sb−C angles (sum of the bond angles: Si−Sb−Si 310.8°; C−Sb−C 300.5°), which might express the degree of hybridization and the Lewis basicity of the pnicogenides.[18] Unfortunately, the structures of the pure

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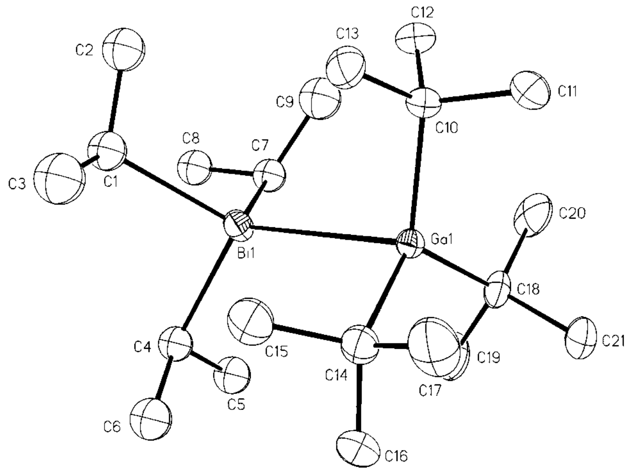

Figure 2. 2. Molecular structure of **6** (50% thermal ellipsoids). [Only one orientation of the disordered *i*-Pr groups is shown. In addition, only the data of the major compound are included in the tables.] Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)−Bi(1) 3.135(1), Bi(1)−C(1) 2.278(9), Bi(1)−C(4) 2.299(8), Bi(1)−C(7) 2.300(6), Ga(1)−C(10) 2.031(3), Ga(1)−C(14) 2.030(4), Ga(1)−C(18) 2.029(4), C(1)−Bi(1)−C(4) 95.9(4), C(1)−Bi(1)−C(7) 100.6(3), C(4)−Bi(1)−C(7) 90.6(3), C(10)−Ga(1)−C(14) 117.1(2), C(10)−Ga(1)−C(18) 118.1(2), C(14)−Ga(1)−C(18) 117.0(2).

bismuthanes are unknown, so far, and can therefore not be compared with the adducts.

Haaland demonstrated for boranes and alanes that the adduct formation process between a group 13 trialkyl and an amine or phosphane is accompanied by a decrease of the C−M−C bond angle (from 120° toward tetrahedral) and an increase of the M−C bond distance (M = B, Al).[5a,b] The smaller the decrease of the C−M−C angle and the increase of the M−C distance within analogously substituted group 13/15 adducts, the weaker the adduct. Following this model, the larger C−Ga−C bond angles in **2** and **6** (sum of the bond angles: 353.9° **2**, 352.1° **6**) compared with the stibane adducts ($Et_3Ga{\cdot}Sb(SiMe_3)_3$ 348.3°, $(t\text{-Bu})_3Ga{\cdot}Sb(i\text{-Pr})_3$ 347.6°) and the shorter Ga−C bond lengths (average values: 1.99 Å **6**, 2.03 Å **6**; $Et_3Ga{\cdot}Sb(SiMe_3)_3$ 2.01 Å, $(t\text{-Bu})_3Ga{\cdot}Sb(i\text{-Pr})_3$ 2.04 Å) also indicate that **2** and **6** are weaker adducts than the corresponding stibane adducts. Carty and Lappert have synthesized a series of pentacarbonylchromium complexes of the type $(OC)_5Cr(EPh_3)$ (E = P, As, Sb, Bi) and determined their solid-state structures.[6a] Interestingly, they observed an increase of the M−E bond order with increasing s-character of the metal−pnicogen bond.[19] This is in sharp contrast with our results observed for trialkylgallane adducts, which show a *decreasing* bond strength from Sb to Bi.

In addition to the synthesis of simple Lewis acid−base adducts, we are particularly interested in the synthesis of compounds containing group 13-Bi σ-bonds. Unfortunately, only a single compound, $[Me_2AlBi(SiMe_3)_2]_3$, could be synthesized and structurally characterized, so far. Recently, we described the synthesis of monomeric, Lewis base-stabilized group 13-pnicogenides of the type dmap−$M(R_2)E(SiMe_3)_2$ (R = Me, Et; M = Al, Ga; E = P, As, Sb) by reaction of four- and six-membered heterocycles with the strong Lewis base 4-(dimethylamino)pyridine (dmap).[20] Previous to our studies, a handful of compounds of this type have been reported, but their synthesis was limited to reactions of Me_3N-stabilized alanes and chloroalanes $Me_3N{\cdot}Al(H_2)X$ (X = H, Cl) with amines,[21] phosphanes, or arsanes,[22] and the reaction products (base-stabilized monomers or heterocycles) were unpredictable. Very recently, Gladfelter et al. described the synthesis of $quin{\cdot}Ga(Cl_2)H$ and $quin{\cdot}Ga(H_2)Cl$ (quin = quinuclidine) and demonstrated their potential to serve as starting compounds for monomeric, quinuclidine-stabilized amidogallanes $quin{\cdot}Ga(H_2)N(SiMe_3)_2$ and $quin{\cdot}Ga(H)[N(SiMe_3)_2]_2$.[23] Applying the ring cleavage reaction to $[Me_2AlBi(SiMe_3)_2]_3$, we obtained the first Lewis base-stabilized, monomeric Al−Bi compound dmap−$Al(Me_2)Bi(SiMe_3)_2$ (**7**) in good yield. In addition, the reaction of Et_2AlH with $Bi(SiMe_3)_3$ *in the presence* of a stoichoimetric amount of dmap also gave the monomer dmap−$Al(Et_2)Bi(SiMe_3)_2$ (**8**).[24] X-ray quality single crystals of **7** and **8** were obtained at −30 °C from solutions in hexane.

$$1/3\ [Me_2AlBi(SiMe_3)_2]_3 + dmap \rightarrow dmap{-}Al(Me_2)Bi(SiMe_3)_2\ (\mathbf{7}) \qquad (2)$$

$$Et_2AlH + Bi(SiMe_3)_3 + dmap \xrightarrow{-Me_3SiH} dmap{-}Al(Et_2)Bi(SiMe_3)_2\ (\mathbf{8}) \qquad (3)$$

The average Bi−Si distance in **7** and **8** is 2.63 Å, which is comparable with those reported previously.[25] The Al−C (1.972 **7**; 1.988 Å **8**) and Al−N distances (1.972(4) **7**; 1.978(5) Å **8**) are almost the same as those found in the analogues compounds with the lighter pnicogenides dmap−$Al(R_2)E(SiMe_3)_2$ (R = Me, Et; E = P, As, Sb).[20] Despite the reduced coordination number of the Bi center (four-coordinate in $[Me_2AlBi(SiMe_3)_2]_3$ and three-coordinate in **7** and **8**), which usually leads to shortened bond distances, the Al−Bi distances (2.755(2) **7**; 2.750(2) Å **8**) are comparable with those found in $[Me_2AlBi(SiMe_3)_2]_3$ (average 2.774 Å). The analogous

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[18] For a detailed review dealing with this problem see: Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262−286; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272−296.

[19] The relative Cr−Bi bond length, obtained by subtraction of the covalent radii of the pnicogen E from the observed Cr−E bond distances, is about 0.01 Å shorter than the Cr−Sb bond and almost 0.07 Å shorter than the Cr−P bond length.

[20] (a) Schulz, S.; Nieger, M. *Organometallics* **2000**, *19*, 2640−2642. (b) Thomas, F.; Schulz, S.; Nieger, M. *Eur. J. Inorg. Chem.* **2000**, in press.

[21] (a) Atwood, J. L.; Koutsantonis, G. A.; Lee, F.-C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 91−92. (b) Gardiner, M. G.; Koutsantonis, G. A.; Lawrence, S. M.; Lee, F.-C.; Raston, C. L. *Chem. Ber.* **1996**, *129*. 545−549. (c) Janik, J. F.; Duesler E. N.; Paine, R. T. *J. Organomet. Chem.* **1997**, *539*, 19−25.

[22] (a) Janik, J. F.; Wells, R. L.; White, P. S. *Inorg. Chem.* **1998**, *37*, 3561−3566. (b) Atwood, D. A.; Contreras, L.; Cowley, A. H.; Jones, R. A.; Mardones, M. A. *Organometallics* **1993**, *12*, 17−18.

[23] Luo, B.; Young, V. G., Jr.; Gladfelter, W. L. *Inorg. Chem.* **2000**, *39*, 1705−1709.

[24] The corresponding heterocycle $[Et_2AlBi(SiMe_3)_2]_x$ cannot be synthesized due to decomposition problems. The reaction of Et_2AlH and $Bi(SiMe_3)_3$ leads in almost quantitative yield to $Bi_2(SiMe_3)_4$ and so far unidentified side products.

[25] Becker et al. found Si−Bi bond distances of 2.633(14) Å in $LiBi(SiMe_3)_2{\leftarrow}DME$ and 2.679(13) and 2.687(16) Å in $Bi_2(SiMe_3)_4$ (Mundt, O.; Becker, G.; Rössler, M.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1983**, *506*, 42−58), while Hassler et al. observed a mean distance of 2.657(4) Å in $Bi_2(SiMe_2)_5$ (Kolleger, G. M.; Siegl, H.; Hassler, K.; Gruber, K. *Organometallics* **1996**, *15*, 4337−4338). In $[Me_2AlBi(SiMe_3)_2]_3$, the distances range from 2.615(2) to 2.646(3) Å.

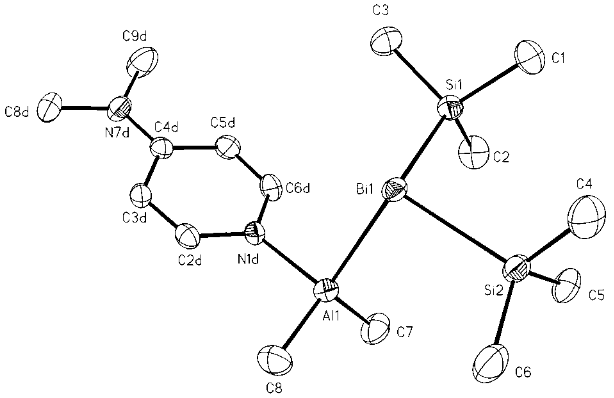

Figure 3. Molecular structure of **7** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−Bi(1) 2.755(2), Bi(1)−Si(1) 2.635(2), Bi(1)−Si(2) 2.632(1), Al(1)−C(7) 1.967(5), Al(1)−C(8) 1.976(6), Al(1)−N(1d) 1.972(4); Si(1)−Bi(1)−Si(2) 95.7(1), C(7)−Al(1)−C(8) 116.4(3).

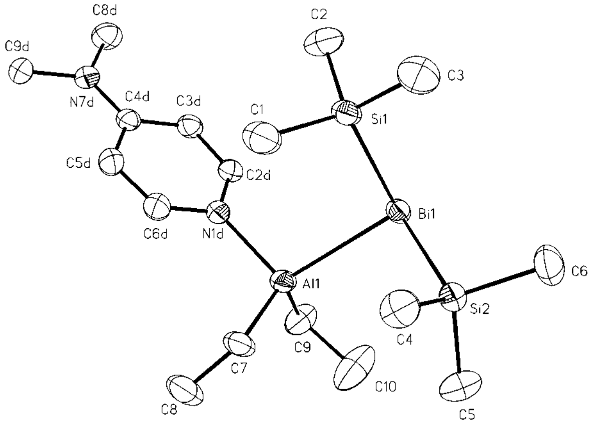

Figure 4. Molecular structure of **8** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−Bi(1) 2.750(2), Bi(1)−Si(1) 2.630(2), Bi(1)−Si(2) 2.637(2), Al(1)−C(7) 1.983(6), Al(1)−C(9) 1.992(7), Al(1)−N(1d) 1.978(5); Si(1)−Bi(1)−Si(2) 97.4(1), C(7)−Al(1)−C(9) 115.6(3).

compounds containing the lighter group 15 elements, dmap−Al(R_2)E($SiMe_3$)$_2$ (R = Me, Et; E = P, As, Sb), showed a greater shortening of the Al−E distance compared with the starting heterocycles. However, the degree of the shortening steadily decreases from the phosphane dmap−Al(Me_2)P($SiMe_3$)$_2$ (0.08 Å) and arsanes dmap−Al(R_2)As($SiMe_3$)$_2$ (0.06 Å) to the stibanes dmap−Al(R_2)Sb($SiMe_3$)$_2$ (R = Me: 0.03 Å; Et: 0.05 Å). This tendency reaches its minimum for the bismuthanes reported herein (0.02 Å). These observations clearly demonstrate that steric repulsion, which generally leads to elongated bond distances, is very important for heterocycles containing small elements (e.g., P), but less so for heterocycles containing the larger elements (e.g., Bi). Therefore, the ring cleavage, which reduces the coordination number and therefore the steric pressure at the pnicogene atom, leads to significantly shortened Al−P, but almost unchanged Al−Bi distances. A second major structural difference within this particular group of compounds is displayed by the Si−E−Si bond angles. The Si−Bi−Si angles (95.7(1)° **7**, 97.4(1)° **8**) are significantly smaller than those of the other pnicogenides (dmap−Al(Me_2)P($SiMe_3$)$_2$: 104.8(1)° and 102.9(1)°; dmap−Al(R_2)As($SiMe_3$)$_2$: R = Me 101.1(1)° and 101.9(1)°, Et 101.3(1)°; dmap−Al(R_2)Sb($SiMe_3$)$_2$: R = Me 97.6(2)°, Et 99.1(1)°).[20] This tendency, which was also found within group 15 trihydrides H_3E (H−E−H angles decrease from 106.8° (NH_3)[26] to 91.3° (SbH_3)[27] and triphenyl derivatives EPh_3 (C−E−C angles decrease from 102.8° (PPh_3), 100.1° ($AsPh_3$), 97.8° ($SbPh_3$) to 93.9° ($BiPh_3$))[28]), results from the decreased steric repulsion between the $SiMe_3$ groups due to the increased E−Si bond length and from the increased s-character of the *lone pair* and the increased p-character of the bonding electron pairs due to relativistic effects and the lanthanide contraction (inert-pair effect).[18,29]

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **2**, **6**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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