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Synthesis and X-ray Crystal Structure of $[Me_2GaBi(SiMe_3)_2]_3$

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*Summary: $[Me_2GaBi(SiMe_3)_2]_3$ (**1**) was synthesized in high yield by the equimolar reaction of Me_2GaH and $Bi(SiMe_3)_3$ and characterized by mass and multinuclear NMR spectroscopy and by single-crystal X-ray diffraction. $[Me_2GaBi(SiMe_3)_2]_3$ represents the first Ga−Bi heterocycle, closing the gap on structurally characterized Ga−pnicogen compounds. The described reaction demonstrates the potential application of dialkylgallanes to serve as powerful synthons in organometallic syntheses requiring mild reaction conditions.*

Introduction

Group 13/15 compounds belong to the most intensively studied classes of inorganic main-group-element compounds. Besides the simple Lewis acid−base adducts $R_3M\cdot ER'_3$ (M = B, Al, Ga, In; E = N, P, As), which have been known for almost two centuries,[1] ME heterocycles and cages $[R_2MER'_2]_x$ and $[RMER']_x$ have been synthesized in large numbers. Four general synthetic pathways, proceeding by H_2, alkane, salt, or halosilane elimination reactions, have been developed for the synthesis of amines, phosphines, and arsines of B, Al, Ga, and In.[2] The corresponding MSb heterocycles were initially reported in 1988 by Cowley et al.,[3] but only within the last 5 years have dehalosilylation,[4] dehydrosilylation,[5] and distibine cleavage reactions[6] been established as general synthetic pathways. In sharp contrast, organometallic group 13−Bi compounds have remained almost unknown,[7] most likely resulting from their decreased thermodynamic stability.[8] However, the highly underexplored status of group 13−Bi compounds is not surprising, since organometallic main-group-element−Bi compounds containing electropositive elements in general have only been scarcely investigated.[9]

A few years ago we started our investigations on the synthesis of group 13−Bi compounds in an attempt to gain the first insights into their thermodynamic stability, chemical reactivity, and solid-state structures. Stable Lewis acid−base adducts of the types $R_3M\cdot BiR'_3$[10] and $[R_3M]_2[Bi_2R'_4]$[11] containing dative M−Bi bonds (M = Al, Ga) were obtained by reaction of bismuthines R_3Bi and dibismuthines R_4Bi_2 with trialkylalanes and -gallanes R_3M, respectively. In addition, $[Me_2AlBi(SiMe_3)_2]_3$, to date the only structurally characterized group 13−Bi heterocycle,[12] and monomeric Lewis base stabilized compounds of the type dmap−$(R_2)AlBi(SiMe_3)_2$ (dmap = 4-(dimethylamino)pyridine; R = Me, Et)[10a] were synthesized by dehydrosilylation reactions between R_2AlH and $Bi(SiMe_3)_3$. All these reactions were performed under very mild conditions, which were found to be essential for the synthesis of the desired Al−Bi compounds due to their facile thermal decomposition. We expected the synthesis of Ga−Bi heterocycles, which are unknown to date, also to require such mild reaction conditions. Since the dehalosilylation reaction between Me_2GaCl and $Bi(SiMe_3)_3$ failed in our hands to give $[Me_2GaBi(SiMe_3)_2]_3$, we investigated the utility of the dehydrosilylation method in the synthesis of the desired heterocycles. Ga−H bonds ($D°_{298}$ < 274 kJ/mol) have much lower bonding energies than Ga−Cl bonds ($D°_{298} = 481 \pm 13$ kJ/mol), rendering gallanes such as dimethylgallane, Me_2GaH, very attractive reagents.[13] However, to the best of our knowledge, Me_2GaH, whose synthesis was reported in 1986,[14] has not been used in

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(1) $F_3B\cdot NH_3$ was first synthesized by Gay-Lussac (Gay-Lussac, J. L.; Thenard, J. L. *Mem. Phys. Chim. Soc. d'Arcueil* **1809**, *2*, 210. As cited in: Jonas, V.; Frenking, G. *J. Chem. Soc., Chem. Commun*. **1994**, 1489).

(2) For references see: (a) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl*. **1989**, *28*, 1208. (b) Wells, R. L. *Coord. Chem. Rev*. **1992**, *112*, 237. (c) Carmalt, C. J. *Coord. Chem. Rev*. **2001**, *223*, 217.

(3) (a) Barron, A. R.; Cowley, A. H.; Jones, R. A.; Nunn, C. M.; Westmoreland, D. L. *Polyhedron* **1988**, *7*, 77. (b) Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M.; Westmoreland, D. L. *J. Organomet. Chem*. **1988**, *341*, C1. (c) Cowley, A. H.; Jones, R. A.; Nunn, C. M.; Westmoreland, D. L. *Chem. Mater*. **1990**, *2*, 221.

(4) See the following and references therein: (a) Foos, E. E.; Jouet, R. J.; Wells, R. L.; White, P. S. *J. Organomet. Chem*. **2000**, *598*, 182. (b) Schulz, S. *Coord. Chem. Rev*. **2001**, *215*, 1. (c) Thomas, F.; Schulz, S.; Nieger, M. *Z. Anorg. Allg. Chem*. **2002**, *628*, 235.

(5) (a) Schulz, S.; Nieger, M. *Organometallics* **1998**, *17*, 3398. (b) Schulz, S.; Nieger, M. *Organometallics* **1999**, *18*, 315. (c) Schulz, S.; Kuczkowski, A.; Nieger, M. *Organometallics* **2000**, *19*, 699. Dialkylchloroalanes and $Sb(SiMe_3)_3$ react with formation of the simple Lewis acid−base adducts.

(6) (a) Breunig, H. J.; Stanciu, M.; Rösler, R.; Lork, E. *Z. Anorg. Allg. Chem*. **1998**, *624*, 1965. (b) Kuczkowski, A.; Schulz, S.; Nieger, M.; Saarenketo, P. *Organometallics* **2001**, *20*, 2000.

(7) Only some Zintl ions containing $AlBi_4$ tetrahedra (Cordier, G.; Schäfer, H.; Stelter, M. *Z. Naturforsch*. **1984**, *39b*, 727) and MBi deltahedral clusters (M = In, Ga; Xu, L.; Sevov, S. C. *Inorg. Chem*. **2000**, *39*, 5383) have been synthesized and structurally characterized.

(8) For instance, the stability of simple Lewis acid−base adducts was found to decrease with increasing atomic number of the pnicogen. Kuczkowski, A.; Schulz, S.; Nieger, M.; Schreiner, P. R. *Organometallics* **2002**, *21*, 1408.

(9) Organometallic main-group-element−Bi compounds are almost limited to those containing electronegative elements such as N, P, O, S, and halides. Prior to our studies, $[Cp^*{}_2SmBi]_2$ (Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc*. **1991**, *113*, 9880) and $(Me_2Si)_6Bi_2$ (Kollegger, G. M.; Siegel, H.; Hassler, K.; Gruber, K. *Organometallics* **1996**, *15*, 4337) were the only structurally characterized heterocycles featuring Bi atoms linked by electropositive elements.

(10) (a) Kuczkowski, A.; Thomas, F.; Schulz, S.; Nieger, M. *Organometallics* **2000**, *19*, 5758. (b) Kuczkowski, A.; Schulz, S.; Nieger, M. *Eur. J. Inorg. Chem*. **2001**, 2605.

(11) Kuczkowski, A.; Schulz, S.; Nieger, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4222.

(12) Schulz, S.; Nieger, M. *Angew. Chem., Int. Ed. Engl*. **1998**, *38*, 967.

(13) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 78th ed.; CRC Press: New York, 1997; pp 9−53 and 9−54.

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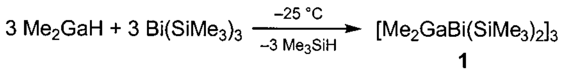
Scheme 1. Synthesis of $[Me_2GaBi(SiMe_3)_2]_3$ (1) by Dehydrosilylation Reaction



$$3\ Me_2GaH + 3\ Bi(SiMe_3)_3 \xrightarrow[-3\ Me_3SiH]{-25\ °C} [Me_2GaBi(SiMe_3)_2]_3$$

1

synthetic chemistry, so far.[15] In contrast to base-stabilized gallanes such as $H_3Ga{\cdot}NMe_3$,[16] the reactivity of dialkyl- and diarylgallanes R_2GaH generally has not been investigated in detail, most likely a consequence of the small number of stable compounds of this type known to date as well as their lability toward further decomposition reactions.[17] However, our purpose regarding the synthesis of Ga−Bi heterocycles under mild reaction conditions required such a highly reactive reagent. We now report on our initial studies using Me_2GaH in preparative metalloorganic chemistry, leading to the synthesis of $[Me_2GaBi(SiMe_3)_2]_3$ (**1**), the first Ga−Bi heterocycle. **1** was investigated in detail by mass and multinuclear NMR spectroscopy (^1H, ^{13}C) as well as by single-crystal X-ray diffraction.

Results and Discussion

1 was obtained by reaction of equimolar amounts of Me_2GaH and $Bi(SiMe_3)_3$ at −25 °C in pentane (Scheme 1). Pure **1** is stable at ambient temperature under inert conditions for several hours, whereas solutions of **1** can be stored even at low temperatures only for short periods of time. Depending on the solvent, **1** decomposes at −20 °C within 1 h (pentane or THF) or a couple of minutes (toluene). Interestingly, the decomposition pathway differs significantly. Temperature-dependent ^1H NMR spectroscopic studies clearly reveal that in noncoordinating solvents (pentane, toluene), $Bi_2(SiMe_3)_4$, Me_3Ga, and some elemental Ga are formed in almost quantitative yield, whereas in coordinating solvents (e.g. THF), $Bi(SiMe_3)_3$, Me_3Ga, and a large amount of dark precipitate is obtained.

Due to the extreme sensitivity of **1** toward air and moisture also in its pure form, no satisfactory elemental analyses could be obtained. The mass spectrum of **1** (EI, 12 eV, 40 °C) displays signals due to $SiMe_3^+$ (*m/z* 73), $GaMe_2^+$ (*m/z* 99), $Si_2Me_5^+$ (*m/z* 131), $BiSiMe_3^+$ (*m/z* 282), and $Bi(SiMe_3)_3^+$ (*m/z* 428), indicating the excessive fragmentation of **1** under such conditions. The peak with the highest mass corresponds to the fragment $Me_4Ga_2Bi_2(SiMe_3)_3^+$ (*m/z* 836); the molecular ion peak was not detected. NMR spectra of **1** in pentane show resonances due to the Ga−Me and Si−Me groups (^1H, δ 0.43 ($GaMe_2$), 0.61 ($SiMe_3$); ^{13}C, δ 5.1 ($GaMe_2$), 6.1 ($SiMe_3$); ^{29}Si, δ −17.7), whereas in THF the Ga−Me resonances are shifted to higher field (^1H, δ 0.04 ($GaMe_2$), 0.65 ($SiMe_3$); ^{13}C, δ 3.5 ($GaMe_2$), 7.4 ($SiMe_3$)).

Table 1. Crystallographic Details for 1

empirical formula	$C_{24}H_{72}Bi_3Ga_3Si_6$
fw	1365.46
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a (Å)	9.5769(1)
b (Å)	20.8442(2)
c (Å)	24.4343(3)
β (deg)	96.077(1)
V (Å^3)	4850.23(9)
Z	4
T (K)	123(2) K
radiation (λ (Å))	Mo Kα (0.710 73)
D_{calcd} (g cm^{-3})	1.870
μ (mm^{-1})	12.649
$2\theta_{max}$ (deg)	50
F(000)	2568
cryst dimens (mm)	0.40 × 0.20 × 0.10
no. of rflns	65 519
no. of unique rflns	8512
R_{merg}	0.1092
no. of params refined/restraints	325/0
abs cor	empirical from multiple rflns
max and min transmission	0.2534 and 0.1193
refinement method	full-matrix least squares on F^2
goodness of fit on F^2 [a]	0.950
final R indices ($I > 2\sigma(I)$)[b]	R1 = 0.0309, wR2 = 0.0681
R indices (all data)	R1 = 0.0483, wR2 = 0.0720
largest diff peak and hole (e Å^{-3})	1.067 and −1.808

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

Colorless crystals of **1**, suitable for a single-crystal X-ray diffraction study, were obtained from a solution in pentane at −30 °C. **1** is isostructural with $[Me_2AlBi(SiMe_3)_2]_3$,[12] crystallizing in the monoclinic space group $P2_1/n$ (No. 14). The Ga and Bi atoms adopt distorted tetrahedral environments, forming a distorted boat-type ring, as was observed for other six-membered group 13/15 heterocycles. The Ga−Bi bond distances range from 2.744(1) to 2.783(1) Å, which corresponds well to the sum of the covalent radii for Ga and Bi (2.76 Å). Comparable bond distances were found for $[Me_2AlBi(SiMe_3)_2]_3$ (2.755(3)−2.793(3) Å). As was observed in isomorphous heterocycles such as $[Me_2MSb(SiMe_3)_2]_3$ (M = Al,[5a] Ga,[18] In[4c]) and $[Me_2AlBi(SiMe_3)_2]_3$, the central ring of **1** features two long (at Bi1) and four short Ga−Bi distances (Bi2 and Bi3). Due to the lack of any other organometallic compounds containing Ga−Bi σ-bonds, only comparisons to Lewis acid−base adducts $R_3Ga{-}BiR'_3$[10] and $[R_3Ga]_2[Bi_2R'_4]$[11] are possible. As expected, these show significantly elongated Ga−Bi distances (2.97−3.14 Å) according to their dative bonding character. The endocyclic Ga−Bi−Ga bond angles found for **1** are significantly larger than the Bi−Ga−Bi bond angles, ranging from 121.6(1) to 130.7(1)° and from 100.7(1) to 103.8(1)°, respectively. The exocyclic C−Ga−C (115.4(3)−123.4(3)°) and Si−Bi−Si bond angles (99.2(1)−101.1(1)°) consequently show the opposite trend. The Ga−C (average 1.990 Å) and Bi−Si bond lengths (average 2.640 Å) are within typical ranges.

Our studies reveal the dehydrosilylation reaction to be the most versatile pathway for the synthesis of group 13/15 heterocycles. Its high synthetic potential is based on the use of highly reactive reagents, allowing the syntheses to be performed under very mild reaction conditions. These were found to be essential for the

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(14) Baxter, P. L.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1986**, 805.

(15) Only some reactions of Me_2GaH with NH_3, B_2H_6, and Lewis bases were performed for the purpose of its characterization.

(16) For references see: (a) Jones, C.; Koutsantonis, G. A.; Raston, C. L. *Polyhedron* **1993**, *12*, 1829. (b) Gardiner, M. G.; Raston, C. L. *Coord. Chem. Rev.* **1997**, *166*, 1. (c) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, *101*, 3305.

(17) (a) Eisch, J. J. *J. Am. Chem. Soc.* **1962**, *84*, 3830. (b) Uhl, W.; Cuypers, L.; Graupner, R.; Molter, J.; Vester, A.; Neumüller, B. *Z. Anorg. Allg. Chem.* **2001**, *627*, 607. (c) Wehmschulte, R. J.; Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 6300.

(18) Schulz, S.; Nieger, M. *J. Organomet. Chem.* **1998**, *570*, 275.

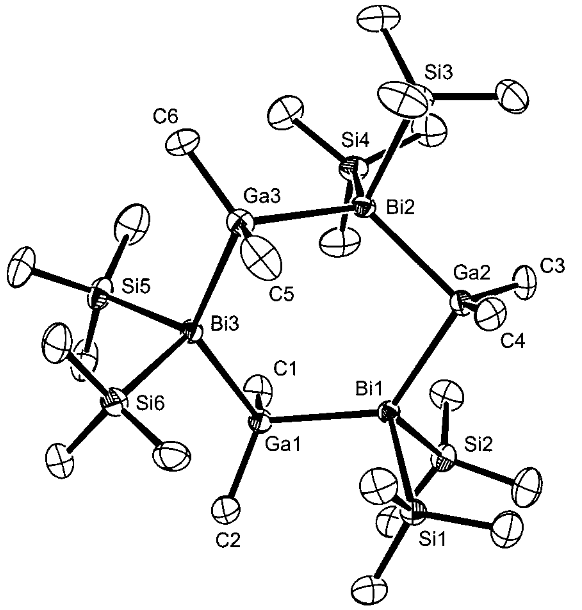

Figure 1. Molecular structure and atom numbering scheme of **1**; thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi1−Ga1 2.773(1), Bi1−Ga2 2.783(1), Bi2−Ga2 2.744(1), Bi2−Ga3 2.751(1), Bi3−Ga1 2.757(1), Bi3−Ga3 2.761(1), Bi1−Si1 2.649(2), Bi1−Si2 2.647(2), Ga1−C1 2.002(7), Ga1−C2 1.978(7); Ga1−Bi1−Ga2 130.7(1), Ga1−Bi3−Ga3 128.6(1), Ga2−Bi2−Ga3 121.6(1), Bi1−Ga1−Bi3 103.8(1), Bi1−Ga2−Bi2 100.7(1), Bi2−Ga3−Bi3 101.5(1), C1−Ga1−C2 115.4(3), Si1−Bi1−Si2 100.7(1).

preparation of $[Me_2GaBi(SiMe_3)_2]_3$, on account of its facile thermal decomposition in solution. The X-ray structure analysis of $[Me_2GaBi(SiMe_3)_2]_3$ closes the gap on structurally characterized Ga−pnicogen compounds. The utility of the dehydrosilylation pathway with respect to the synthesis of so far unknown In−Bi heterocycles is currently under investigation.

Experimental Section

All manipulations were performed in a glovebox under an N_2 atmosphere or by standard Schlenk techniques. Me_2GaH[14] was prepared similar to the synthesis of Me_2AlH by reaction of equimolar amounts of $LiGaH_4$ and Me_3Ga followed by fractionation in vacuo. $Bi(SiMe_3)_3$[19] was prepared by literature methods. ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were recorded using a Bruker DPX 300 spectrometer. The mass spectrum was recorded on a VG Masslab 12-250 spectrometer in the electron ionization mode.

$[Me_2GaBi(SiMe_3)_2]_3$ (1). At −30 °C $Bi(SiMe_3)_3$ (2 mmol, 0.86 g) was added dropwise to a solution of Me_2GaH (2 mmol, 0.20 g) in pentane (10 mL) and slowly warmed to −25 °C. The initially colorless solution turns brown, and a white solid precipitates. This suspension is stirred for another 30 min at −20 °C and then quickly warmed to room temperature to dissolve the solid. Storage of the resulting brown solution at −30 °C yields $[Me_2GaBi(SiMe_3)_2]_3$ (**1**) as colorless crystals (0.49 mmol, 0.67 g, 74%).

M_r = 1365.4 g/mol for $C_{24}H_{72}Bi_3Ga_3Si_6$. ^1H NMR (300 MHz, pentane, −20 °C): δ 0.43 (s, 6H, $GaMe_2$), 0.61 (s, 18H, $SiMe_3$). ^{13}C NMR (75 MHz, pentane, −20 °C): δ 5.1 ($GaMe_2$), 6.1 ($SiMe_3$). ^{29}Si NMR (60 MHz, pentane, −20 °C): δ −17.7 ($SiMe_3$). ^1H NMR (300 MHz, THF-d_8, −50 °C): δ 0.04 (s, 6H, $GaMe_2$), 0.65 (s, 18H, $SiMe_3$). ^{13}C NMR (75 MHz, THF-d_8, −50 °C): δ 3.5 ($GaMe_2$), 7.4 ($SiMe_3$). MS (EI, 12 eV, 40 °C): m/z (%) 836 (2) $[Me_4Ga_2Bi_2(SiMe_3)_3]^+$, 710 (1) $[Bi_2(SiMe_3)_4]^+$, 627 (2) $[Me_4Ga_2Bi(SiMe_3)_3]^+$, 428 (28) $[Bi(SiMe_3)_3]^+$, 282 (24) $[BiSiMe_3]^+$, 267 (18) $[BiSiMe_2]^+$, 157 (23) $[Me_2GaSiMe_3]^+$, 131 (100) $[Me_5Si_2]^+$, 99 (92) $[Me_2Ga]^+$, 73 (90) $[SiMe_3]^+$.

X-ray Structure Solution and Refinement. Crystallographic data of **1** are summarized in Table 1. Figure 1 shows an ORTEP diagram of its solid-state structure. Data were collected on a Nonius Kappa-CCD diffractometer. The structure was solved by Patterson methods (SHELXS-97)[20] and refined by full-matrix least squares on F^2. An empirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[21]

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Supporting Information Available: Tables of bond lengths, bond angles, anisotropic temperature factor parameters, and fractional coordinates for $[Me_2GaBi(SiMe_3)_2]_3$ (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Becker, G.; Rössler, M. *Z. Naturforsch.* **1982**, *37b*, 91.

(20) Sheldrick, G. M. SHELXS-97, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(21) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen, Göttingen, Germany, 1997.