Reactions of Distibines Sb_2R_4 and Dibismuthine Bi_2Et_4 with Trialkyltrieles MR_3

A. Kuczkowski, S. Fahrenholz, S. Schulz,* and M. Nieger

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

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Distibines Sb_2R_4 react with trimethylgallane and -indane (MMe_3; M = Ga, In) with formation of heterocycles of the general type $[Me_2MSbR'_2]_3$ (R′ = Me, M = Ga (**2**), In (**3**); R′ = *i*-Pr, M = Ga (**4**)), whereas only decomposition reactions were observed for reactions with trialkylalanes. However, the mononuclear distibine−alane adduct $[Al(t\text{-}Bu)_3][Sb_2(i\text{-}Pr)_4]$ (**1**) with the distibine serving as monodentate ligand could be isolated and structurally characterized. In addition, reactions of the dibismuthine Bi_2Et_4 with $M(t\text{-}Bu)_3$ (M = Al, Ga) were investigated, resulting in the formation of the simple Lewis acid−base adducts $Et_3Bi\text{-}M(t\text{-}Bu)_3$ (M = Al (**5**), Ga (**6**)). **1**−**6** were characterized by multinuclear NMR and mass spectroscopy and elemental analysis as well as single-crystal X-ray diffraction.

Introduction

Reactions of Lewis bases ER'_3 (E = N, P, As, Sb, Bi) with Lewis acids MR_3 (M = B, Al, Ga, In, Tl) have been investigated for almost two centuries.[1] In sharp contrast, reactions of dipenteles of the type $R'_2E-ER'_2$, which may serve as both monodentate[2] and bidentate ligands,[3] as was shown in several reactions with transition-metal complexes, and MR_3 have been studied to a far lesser extent. Only two dinuclear diphosphine−borane adducts ($[Me_4P_2][BH_3]_2$, $[Me_4P_2][BH_2Br]_2$)[4] have been synthesized and structurally characterized prior to our studies. We became only recently interested in such types of compounds and reported on the synthesis and single-crystal X-ray structures of the first dinuclear distibine[5] and dibismuthine adducts,[6] with the dipentele serving as a bidentate ligand. These adducts were found to be fairly stable in their pure forms, whereas they tend to undergo consecutive reactions in solution. The distibine−gallane adducts $[R_4Sb_2]$-$[Ga(t\text{-}Bu)_3]_2$ (R = Me, Et) were found to react at ambient temperature with formation of the heterocyclic stibinogallanes $[t\text{-}Bu_2GaSbMe_2]_3$ and $[t\text{-}Bu_2GaSbEt_2]_2$.[5] This reaction, which has also been observed by Breunig et al. on the reaction of Sb_2Me_4 with $In(CH_2SiMe_3)_3$,[7] is most likely based on the lability of the Sb−Sb bond toward electrophilic compounds.[8] Comparable reactions have been previously observed for distibine transition-metal complexes.[9]

Due to our interest in completely alkyl-substituted Ga−Sb and In−Sb heterocycles, which are promising candidates for the deposition of thin films of the corresponding binary antimonides GaSb and InSb by the MOCVD (*metal organic chemical vapor deposition*) process,[10] we investigated the general applicability of this reaction pathway for the synthesis of the desired class of M−Sb heterocycles. In addition, reactions of the dibismuthine Bi_2Et_4 with $M(t\text{-}Bu)_3$ (M = Al, Ga) were studied in order to investigate whether this reaction type can also be assigned for the synthesis of M−Bi heterocycles.

Experimental Section

General Considerations. All manipulations were performed in a glovebox under a N_2 atmosphere or by standard Schlenk techniques. $Al(t\text{-}Bu)_3$,[11] $GaMe_3$,[12] $InMe_3$,[13] Sb_2Me_4,[14] Sb_2Et_4,[15] $Sb_2(i\text{-}Pr)_4$,[16] and Bi_2Et_4[17] were prepared according to literature methods. ^1H and $^{13}C\{^1H\}$ spectra were recorded using a Bruker AMX 300 spectrometer and are referenced to internal C_6D_5H ($\delta(^1H)$ 7.154, $\delta(^{13}C)$ 128.0). Melting points were measured in sealed capillaries and are not corrected. Mass spectra were recorded on a VG Masslab 12-250 spectrometer

* 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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in the electron ionization mode at 20 eV. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn.

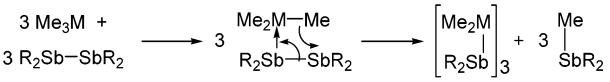
[*i*-Pr$_4$Sb$_2$][Al(*t*-Bu)$_3$] (1; M_r = 614.19). Pure Al(*t*-Bu)$_3$ (2 mmol, 0.40 g) and Sb$_2$(*i*-Pr)$_4$ (2 mmol, 0.83 g) were combined in the glovebox. The resulting yellow oil was dissolved in pentane (5 mL) and stored at −60 °C, resulting in the formation of light yellow crystals of **1**. Yield: 0.59 g, 0.96 mmol, 48%. Mp: ca. −30 °C. Anal. Found (calcd) for $C_{44}H_{55}AlSb_2$: C, 46.78 (46.90); H, 9.22 (9.35). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 1.17 (s, 27 H, *Me*$_3$C/Al), 1.42 (d, $^3J_{HH}$ = 7.3 Hz, 6 H, *Me*$_2$CH/Sb), 1.48 (d, $^3J_{HH}$ = 7.3 Hz, 6 H, *Me*$_2$CH/Sb), 2.34 (sept, $^3J_{HH}$ = 7.3 Hz, 4 H, Me$_2$CH/Sb). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ 14.4 (Me$_2$*C*H/Sb), 20.3 (Me$_3$*C*/Al), 24.9 (*Me*$_2$-CH/Sb), 31.4 (*Me*$_3$C/Al).

[Me$_2$GaSbMe$_2$]$_3$ (2; M_r = 754.83). A 2 mmol portion of Sb$_2$-Me$_4$ (0.60 g) was added to a solution of 3.8 mmol of GaMe$_3$ (0.44 g) dissolved in 40 mL of pentane. The resulting yellow solution was stirred for 5 days at ambient temperature in the absence of light, yielding a colorless solution. The solvent was reduced to 5 mL and the solution stored at −60 °C. After 72 h, **2** was obtained as a colorless powder. Yield: 0.34 g, 0.45 mmol, 68% (based on the distibine). Mp: 92−94 °C dec. Anal. Found (calcd) for $C_{12}H_{36}Ga_3Sb_3$: C, 18.99 (19.10); H, 4.66 (4.80). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.19 (s, 6H, *Me*/Ga), 0.84 (s, 6H, *Me*/Sb). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ −6.1 (*Me*/Sb), 1.4 (*Me*/Ga). EI-MS (*m*/*z* (%)): 485 (3) [Me$_7$Sb$_2$Ga$_2$]$^+$, 304 (100) [Me$_3$SbGa$_2$]$^+$, 289 (76) [Me$_2$SbGa$_2$]$^+$, 274 (15) [MeSbGa$_2$]$^+$, 259 (5) [SbGa$_2$]$^+$, 153 (89) [MeGa$_2$]$^+$, 151 (29) [Me$_2$Sb]$^+$, 136 (27) [MeSb]$^+$, 84 (5) [MeGa]$^+$.

[Me$_2$InSbMe$_2$]$_3$ (3; M$_r$ = 890.12). A 4 mmol portion of InMe$_3$ (0.64 g) and 2 mmol of Sb$_2$Me$_4$ (0.60 g) were dissolved in 30 mL of toluene and stirred for 5 days at ambient temperature in the absence of light. After evaporation of the solvent, the resulting colorless solid was dissolved in 30 mL of hexane. After filtration, a colorless solution was obtained, which was concentrated to 10 mL and stored at −30 °C. After 72 h, **3** was obtained as colorless crystals. Yield: 0.77 g, 0.86 mmol, 43% (based on the distibine). Mp: 64−66 °C dec. Anal. Found (calcd) for $C_{12}H_{36}In_3Sb_3$: C, 16.56 (16.21); H, 4.24 (4.01). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.93 (s, 6H, Me/Sb), 0.19 (s, 6H, Me/In). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ −11.2 (Me/Sb), 1.4 (Me/In). EI-MS (*m*/*z* (%)): 304 (68) [Me$_4$Sb$_2$]$^+$, 289 (24) [Me$_3$Sb$_2$]$^+$, 250 (21) [MeSbIn]$^+$, 166 (7) [Me$_3$Sb]$^+$, 151 (23) [Me$_2$Sb]$^+$, 145, (100) [Me$_2$In]$^+$, 136 (3) [MeSb]$^+$.

[Me$_2$GaSb(*i*-Pr)$_2$]$_3$ (4; M_r = 923.15). A 2 mmol portion of Sb$_2$(*i*-Pr)$_4$ (2 mmol, 0.83 g) was added to a solution of 3.8 mmol of GaMe$_3$ (0.44 g) dissolved in 40 mL of pentane. The resulting yellow solution was stirred for 48 h at ambient temperature in the absence of light, yielding colorless solutions. The solvent was reduced to 5 mL and the solution stored at −30 °C. After 4 weeks, colorless crystals of **4** formed. Yield: 0.23 g, 0.25 mmol, 12% (based on the distibine). Mp: 84−89 °C dec. Anal. Found (calcd) for $C_{24}H_{60}Ga_3Sb_3$: C, 30.94 (31.24); H, 6.16 (6.61). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.32 (s, 6 H, *Me*/Ga), 1.4 (d, $^3J_{HH}$ = 7.8 Hz, 12 H, *Me*$_2$CH/Sb), 2.37 (sept, $^3J_{HH}$ = 7.8 Hz, 2 H, Me$_2$C*H*/Sb). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ 14.4 (s, Me$_2$*C*H/Sb), 20.3 (s, b, Me$_3$*C*/Al), 24.9 (s, *Me*$_2$CH/Sb), 31.4 (*Me*$_3$C/Al). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ 1.4 (s, Me/Ga), 24.9 (s, *Me*$_2$CH/Sb), 25.8 (s, Me$_2$*C*H/Sb).

Scheme 1



After filtration of **2**−**4** the solvent of each resulting solution was removed in vacuo. Oily residues were obtained, which were investigated by ^{1}H NMR. Resonances due to unconsumed MMe$_3$ (M = Ga (**2**, **4**), δ −0.15; M = In (**3**), δ −0.18) were observed. Additional resonances due to the formation of SbMe$_3$ (**2**, **3**, δ 0.60) were found, strongly supporting the proposed reaction mechanism (Scheme 1). The oily residue obtained from the synthesis of **4** showed several signals due to the presence of *i*-Pr (δ 1.20−1.37 (d, CH*Me*$_2$), 1.65−1.83 (sept, C*H*Me$_2$)) and Me groups (δ 0.54−0.62). To the best of our knowledge, *i*-Pr$_2$SbMe has not been identified by ^{1}H NMR, to date, allowing no comparison with these data. The presence of several resonances can be explained by ligand exchange reactions, leading to a mixture of several stibines of the type *i*-Pr$_{3-x}$SbMe$_x$ (x = 0−3).

Preparation of Et$_3$Bi-M(*t*-Bu)$_3$. A 1 mmol portion of Bi$_2$-Et$_4$ and 2 mmol of M(*t*-Bu)$_3$ (M = Al, Ga) were dissolved in 30 mL of pentane and stirred for 72 h at ambient temperature in the absence of light. The resulting black suspension was filtered and the light yellow filtrate was reduced to 5 mL and stored at −30 °C. After 48 h, **5** and **6** were obtained as colorless crystals.

Et$_3$Bi−Al(*t*-Bu)$_3$ (5; M_r = 494.50). Yield: 0.32 g, 0.65 mmol, 65%. Mp: 72−73 °C. Anal. Found (calcd) for $C_{18}H_{42}AlBi$: C, 42.86 (43.71); H, 8.11 (8.63). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 1.13 (s, 27 H, *Me*$_3$C/Al), 1.65−1.76 (m, 15 H, *Et*/Bi). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ 10.4 (s, b, CH$_3$*C*H$_2$/Bi), 13.0 (s, *C*H$_3$CH$_2$/Bi), 20.7 (s, b, Me$_3$*C*/Al), 31.0 (s, *Me*$_3$C/Al).

Et$_3$Bi−Ga(*t*-Bu)$_3$ (6; M$_r$ = 537.23). Yield: 0.21 g, 0.34 mmol, 39%. Mp: 46−48 °C. Anal. Found (calcd) for $C_{18}H_{42}$-GaBi: C, 39.78 (38.78); H, 7.11 (6.75). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 1.20 (s, 27 H, *Me*$_3$C/Ga), 1.63−1.77 (m, 15 H, *Et*/Bi). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ = 10.3 (s, b, CH$_3$*C*H$_2$/Bi), 13.1 (s, *C*H$_3$CH$_2$/Bi), 22.6 (s, b, Me$_3$*C*/Ga), 31.4 (s, *Me*$_3$C/Ga).

X-ray Structure Solution and Refinement. Crystallographic data of **1**−**4** are summarized in Table 1 and those of **5** and **6** in Table 2. Selected bond lengths and angles are given in Table 3 (**2**−**4**) and Table 4 (**5** and **6**). Figures 1−6 show ORTEP diagrams of the solid-state structures of **1**−**6**. Data were collected on a Nonius Kappa-CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å) at T = −150 °C, and the structures were solved by direct methods (**1**−**4**, **6**) and Patterson methods (SHELXS-97; **5**),[18] respectively, and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied for all compounds. All non-hydrogen atoms in **1**−**6** were refined anisotropically, and hydrogen atoms were refined by a riding model (SHELXL-97).[19]

Results and Discussion

To establish the distibine cleavage reaction as a general reaction type for the formation of completely alkyl substituted heterocycles of the type [R$_2$MSbR′$_2$]$_x$ (M = Al, Ga, In) and to verify the influence of the organic ligands bound to the metal centers on the formation of the M-Sb heterocycles, reactions of three distibines Sb$_2$R′$_4$ (R′ = Me, Et, *i*-Pr) with AlR$_3$ (R = Me, Et, *t*-Bu), GaMe$_3$, and InMe$_3$ were investigated. Unfor-

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Table 1. Crystallographic Data and Measurement Details for [*i*-Pr_4Sb_2][Al(*t*-Bu)$_3$] (1), [$Me_2GaSbMe_2$]$_3$ (2), [$Me_2InSbMe_2$]$_3$ (3), [Me_2GaSb(*i*-Pr)$_2$]$_3$ (4)

	1	2	3	4
mol formula	$C_{24}H_{55}AlSb_2$	$C_{12}H_{36}Ga_3Sb_3$	$C_{12}H_{36}In_3Sb_3$	$C_{24}H_{60}Ga_3Sb_3$
fw	614.16	754.82	890.12	923.13
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.7698(5)	10.3280(3)	13.3859(3)	16.3795(2)
b, Å	10.2089(6)	10.4400(4)	10.6226(2)	10.4832(2)
c, Å	15.4554(9)	13.4815(6)	17.7192(4)	21.2972(3)
α, deg	78.255(3)	101.056(1)		
β, deg	78.374(3)	97.883(1)	100.684(1)	98.716(1)
γ, deg	89.431(3)	119.513(1)		
V, Å^3	1477.49(14)	1195.01(8)	2475.87(9)	3614.70(10)
Z	2	2	4	4
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	1.865	6.664	5.963	4.423
temp. K	123(2)	123(2)	123	123(2)
D_{calcd}, g cm^{-3}	1.380	2.098	2.388	1.696
cryst dimens (mm)	0.15 × 0.10 × 0.10	0.20 × 0.15 × 0.15	0.20 × 0.10 × 0.05	0.50 × 0.30 × 0.25
$2\theta_{max}$, deg	50	50	55	55
no. of rflns measd	12 969	10 162	13 172	20 662
no. of nonequiv rflns measd	4967	4165	5500	8002
R_{merge}	0.067	0.044	0.047	0.053
no. of params refined	244	163	163	271
R1,[a] wR2[b]	0.038, 0.067	0.046, 0.104	0.026, 0.064	0.027, 0.0608
goodness of fit[c]	0.899	1.064	1.021	0.992
final max, min $\Delta\rho$, e Å^{-3}	0.993, −0.711	2.693, −1.603	0.994, −1.215	0.982, −1.186

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

Table 2. Crystallographic Data and Measurement Details for $Et_3Bi{-}Al(t\text{-}Bu)_3$ (5) and $Et_3Bi{-}Ga(t\text{-}Bu)_3$ (6)

	5	6
mol formula	$C_{18}H_{42}AlBi$	$C_{18}H_{42}BiGa$
fw	494.48	537.22
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	14.1961(2)	14.1630(2)
b, Å	9.6925(1)	9.7255(1)
c, Å	16.0793(2)	16.0724(2)
β, deg	91.0310(10)	90.848(1)
V, Å^3	2212.08(5)	2213.61(5)
Z	4	4
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	8.004	9.149
temp. K	123(2)	123(2)
D_{calcd}, g cm^{-3}	1.485	1.612
crystal dim. (mm)	0.50 × 0.40 × 0.30	0.60 × 0.55 × 0.50
$2\theta_{max}$, deg	50.0	50.0
no. of rflns measd	40 217	40 044
no. of nonequiv rflns measd	3881	3890
R_{merge}	0.058	0.077
no. of params refined	181	181
R1,[a] *w*R2[b]	0.018, 0.044	0.0249, 0.067
goodness of fit[c]	1.080	1.073
final max, min $\Delta\rho$, e Å^{-3}	0.560, −1.154	1.748, −1.164

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

tunately, reactions with AlR_3 in pentane at ambient temperature occurred with decomposition of the distibine and formation of insoluble black residues which could not be identified. However, the Lewis acid−base adduct [*i*-Pr_4Sb_2][Al(*t*-Bu)$_3$] (**1**) was isolated as a crystalline solid in moderate yield from the reaction of Sb_2(*i*-Pr)$_4$ with either 1 or 2 equiv of Al(*t*-Bu)$_3$ (eq 1). To the best of our knowledge, **1** is the first mononuclear distibine complex to be structurally characterized to date.

$$(i\text{-Pr})_2\text{Sb-Sb}(i\text{-Pr})_2 + t\text{-Bu}_3\text{Al} \xrightarrow{\text{Al}(t\text{-Bu})_3} (i\text{-Pr})_2\text{Sb-Sb}(i\text{-Pr})_2 \quad (1)$$

The ^{1}H NMR spectrum of **1** showed resonances due to the organic ligands (*i*-Pr, *t*-Bu) in a 4:3 molar ratio, indicating the formation of a mononuclear adduct. Its mass spectrum only showed signals due to fragmentation reactions (Sb_2(*i*-Pr_4) and Al(*t*-Bu)$_3$). Single crystals of **1** suitable for an X-ray structure determination were obtained from a solution in pentane at −60 °C. Figure 1 shows the solid-state structure of **1**.

1 crystallizes in the triclinic space group $P\bar{1}$ (No. 2). The Sb−Sb bond distance in **1** (2.855(1) Å) is comparable to those observed for dinuclear distibine adducts [R_4Sb_2][Al(*t*-Bu)$_3$]$_2$ (R = Me, 2.811(1) Å; R = Et, 2.838(1) Å) and the uncomplexed distibines (Sb_2Me_4, 2.862(2) Å[20] and 2.830(1), 2.838(1) Å;[21] $Sb_2(SiMe_3)_4$, 2.867(1) Å;[22] $Sb_2(SnMe_3)_4$, 2.866(1) Å;[23] Sb_2(*t*-Bu)$_4$, 2.817(1) Å;[24] Sb_2Ph_4, 2.844(1) Å[22]). The Al−Sb bond length observed for **1** (3.003(2) Å) is elongated compared to those observed for [Me_4Sb_2][Al(*t*-Bu_3)]$_2$ (2.919(1) Å) and [Et_4Sb_2][Al(*t*-Bu_3)]$_2$ (3.001(1) Å), clearly reflecting the increased repulsive interactions between the organic substituents. The most interesting structural feature of **1** is displayed by the degree of pyramidalization observed at the central Sb atoms. The sum of the C−Sb−C and C−Sb−Sb bond angles found for the uncomplexed Sb center (Sb1, 300.9°) is significantly larger than that of the Sb atom which is coordinated to the alane (Sb2, 288.2°). It is also much larger than that observed for

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2−4

		$[Me_2GaSbMe_2]_3$ (**2**)	
Sb1−Ga1	2.682(1)	Sb2−C6	2.134(8)
Sb1−Ga2	2.676(1)	Sb3−C9	2.147(8)
Sb2−Ga2	2.668(1)	Sb3−C10	2.160(9)
Sb2−Ga3	2.669(1)	Ga1−C3	1.983(9)
Sb3−Ga1	2.666(1)	Ga1−C4	1.983(9)
Sb3−Ga3	2.671(1)	Ga2−C7	2.000(10)
Sb1−C1	2.170(9)	Ga2−C8	2.003(9)
Sb1−C2	2.150(9)	Ga3−C11	1.989(8)
Sb2−C5	2.157(8)	Ga3−C12	1.979(9)
Ga1−Sb1−Ga2	130.8(1)	C1−Sb1−C2	99.0(4)
Ga1−Sb3−Ga3	136.7(1)	C5−Sb2−C6	98.2(4)
Ga2−Sb2−Ga3	129.7(1)	C10−Sb3−C9	97.2(4)
Sb1−Ga1−Sb3	97.3(1)	C3−Ga1−C4	118.2(4)
Sb1−Ga2−Sb2	107.8(1)	C7−Ga2−C8	119.3(5)
Sb2−Ga3−Sb3	98.5(1)	C11−Ga3−C12	117.7(4)
		$[Me_2InSbMe_2]_3$ (**3**)	
Sb1−In1	2.845(1)	Sb2−C6	2.154(4)
Sb1−In3	2.852(1)	Sb3−C9	2.152(4)
Sb2−In1	2.842(1)	Sb3−C10	2.162(4)
Sb2−In2	2.869(1)	In1−C3	2.185(4)
Sb3−In2	2.858(1)	In1−C4	2.175(4)
Sb3−In3	2.844(1)	In2−C7	2.188(4)
Sb1−C1	2.150(5)	In2−C8	2.178(4)
Sb1−C2	2.143(4)	In3−C11	2.176(4)
Sb2−C5	2.151(4)	In3−C12	2.178(4)
In1−Sb1−In3	133.9(1)	C1−Sb1−C2	98.3(2)
In1−Sb2−In2	132.5(1)	C5−Sb2−C6	95.5(2)
In2−Sb3−In3	137.5(1)	C9−Sb3−C10	98.3(2)
Sb1−In1−Sb2	104.6(1)	C3−In1−C4	118.0(2)
Sb2−In2−Sb3	102.1(1)	C7−In2−C8	123.5(2)
Sb1−In3−Sb3	103.5(1)	C11−In3−C12	122.2(2)
		$[Me_2GaSb(i\text{-}Pr)_2]_3$ (**4**)	
Sb1−Ga1	2.669(1)	Sb2−C12	2.182(3)
Sb1−Ga3	2.669(1)	Sb3−C17	2.177(3)
Sb2−Ga1	2.677(1)	Sb3−C20	2.174(3)
Sb2−Ga2	2.687(1)	Ga1−C7	1.994(4)
Sb3−Ga2	2.694(1)	Ga1−C8	1.972(4)
Sb3−Ga3	2.692(1)	Ga2−C15	1.985(3)
Sb1−C1	2.178(3)	Ga2−C16	1.973(3)
Sb1−C4	2.186(3)	Ga3−C23	1.983(3)
Sb2−C9	2.178(3)	Ga3−C24	1.990(3)
Ga1−Sb1−Ga3	118.9(1)	C1−Sb1−C4	102.0(1)
Ga1−Sb2−Ga2	127.7(1)	C9−Sb2−C12	97.4(1)
Ga2−Sb3−Ga3	130.5(1)	C17−Sb3−C20	97.8(1)
Sb1−Ga1−Sb2	104.1(1)	C7−Ga1−C8	119.8(2)
Sb1−Ga3−Sb3	102.2(1)	C15−Ga2−C16	117.5(2)
Sb2−Ga2−Sb3	103.7(1)	C23−Ga3−C24	118.6(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 5 and 6

		$Et_3Bi{-}Al(t\text{-}Bu)_3$ (**5**)	
Al1−Bi1	2.940(1)	Bi1−C13	2.249(3)
Al1−C1	2.019(3)	Bi1−C15	2.240(3)
Al1−C5	2.027(3)	Bi1−C17	2.249(3)
Al1−C9	2.017(3)		
C1−Al1−C5	116.9(1)	C13−Bi1−C15	96.2(2)
C1−Al1−C9	117.1(1)	C13−Bi1−C17	95.9(2)
C5−Al1−C9	117.5(1)	C15−Bi1−C17	96.2(2)
		$Et_3Bi{-}Ga(t\text{-}Bu)_3$ (**6**)	
Ga1−Bi1	2.966(1)	Bi1−C13	2.244(5)
Ga1−C1	2.025(4)	Bi1−C15	2.255(5)
Ga1−C5	2.038(4)	Bi1−C13	2.264(5)
Ga1−C9	2.048(5)		
C1−Ga1−C5	117.2(2)	C13−Bi1−C15	95.2(2)
C1−Ga1−C9	117.6(2)	C13−Bi1−C17	95.4(2)
C5−Ga1−C9	117.5(2)	C15−Bi1−C17	95.3(2)

Sb_2Me_4 (average 283.1°). These findings do not agree with the structural trends previously observed for stibine[25] and distibine adducts,[5] which typically show an increase of the sum of bond angles upon coordination to a Lewis acid due to an increase in p character of the former Sb electron *lone pair* and an increase in s character of the former Sb−C and Sb−Sb bonding electron pairs.[26] Obviously, repulsive interactions between the bulky *i*-Pr groups bound to the Sb center and the sterically demanding Lewis acid Al(*t*-Bu)$_3$ significantly influence the complex geometry. In addition, these repulsive steric interactions seem to prevent $Sb_2(i\text{-}Pr)_4$ from serving as a bidentate ligand, as was observed for Sb_2Me_4 and Sb_2Et_4. **1** shows Al−C bond distances (average 2.029 Å) and C−Al−C bond angles (average 115.8°) comparable to those of the dinuclear adducts $[R_4Sb_2][Al(t\text{-}Bu)_3]_2$ (R = Me, Et).[5]

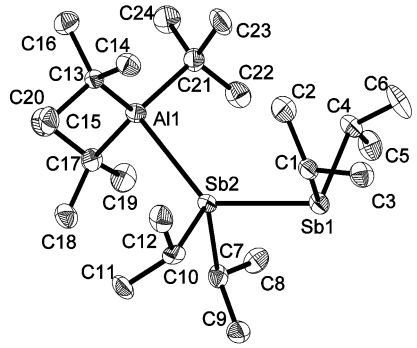

Figure 1. Ortep plot (ellipsoids at the 50% probability level; H atoms omitted for clarity) showing the solid-state structure and atom-numbering scheme for **1**. Selected bond lengths (Å) and angles (deg): Sb1−Sb2 = 2.855(1), Sb2−Al1 = 3.003(2), Al1−C13 = 2.024(5), Al1−C17 = 2.022(6), Al1−C21 = 2.040(5), Sb1−C1 = 2.191(5), Sb1−C4 = 2.208(5), Sb2−C7 = 2.179(5), Sb2−C10 = 2.204(5); C13−Al1−C17 = 116.0(2), C13−Al1−C21 = 115.0(2), C17−Al1−C21 = 116.4(2), C1−Sb1−C4 = 100.7(2), C1−Sb1−Sb2 = 97.5(2), C4−Sb1−Sb2 = 102.7(2), C7−Sb2−C10 = 96.3(2), C7−Sb2−Sb1 = 92.8(2), C10−Sb2−Sb1 = 99.1(2).

Whereas the distibine cleavage reaction in our hands remained unsuccessful for the formation of Al−Sb heterocycles, reactions of Sb_2R_4 (R = Me, *i*-Pr) with 2 equiv of $GaMe_3$ and $InMe_3$ proceeded with cleavage of the Sb−Sb bond and subsequent formation of the corresponding six-membered Ga−Sb and In−Sb heterocycles $[Me_2GaSbMe_2]_3$ (**2**), $[Me_2InSbMe_2]_3$ (**3**), and $[Me_2GaSbi\text{-}Pr_2]_3$ (**4**) according to the mechanism described in Scheme 1.[27]

However, the reactions described occurred much more slowly compared to those of Sb_2R_4 (R = Me, Et) with the sterically more demanding Lewis acid Ga(*t*-Bu)$_3$, which was found to react completely within 2 days.[5] Solutions of Sb_2R_4 (R = Me, *i*-Pr) with 2 equiv of $GaMe_3$ and $InMe_3$ in pentane or toluene had to be stirred for 5−7 days at ambient temperature until a colorless solution was formed. Thereafter, the solvent was evacu-

(25) See the following and references therein: (a) Schulz, S.; Kuczkowski, A.; Nieger, M. *J. Organomet. Chem.* **2000**, *604*, 202. (b) Schulz, S.; Nieger, M. *J. Chem. Soc., Dalton Trans.* **2000**, 639.

(26) Unfortunately, the solid-state structure of $Sb_2(i\text{-}Pr)_4$ has not been determined, to date, allowing no structural comparisons between the sum of the bond angles of the uncomplexed distibine and **1**.

(27) Only 1 equiv of MMe_3 is formally necessary for the formation of the heterocycles. However, the reaction proceeds faster with 1.8−2 equiv of MMe_3, most likely due to the complexation of the trialkylstibine R_2SbMe (R = Me, Et, *i*-Pr) formed according to the reaction mechanism.

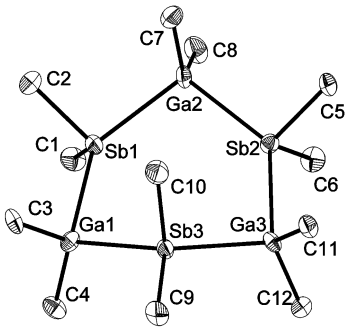

Figure 2. Ortep plot (ellipsoids at the 50% probablity level; H atoms omitted for clarity) showing the solid-state structure and atom-numbering scheme for **2**.

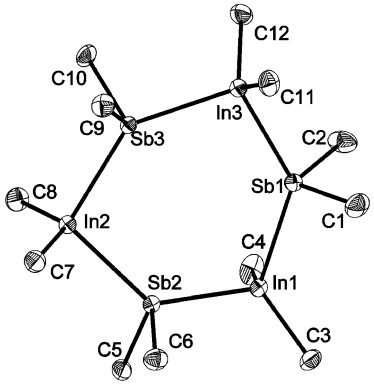

Figure 3. Ortep plot (ellipsoids at the 50% probablity level; H atoms omitted for clarity) showing the solid state structure and atom-numbering scheme for **3**.

ated in vacuo, and the resulting waxy residues were dissolved in pentane (5 mL) and stored at −60 °C. Colorless solids of **2**−**4** were formed within 3 days in moderate yields (eq 2).

$$R_2Sb{-}SbR_2 + 2MMe_3 \xrightarrow[-R_2SbMe,\ -MMe_3]{} {}^1/_3[Me_2MSbR_2]_3 \quad \mathbf{2{-}4} \qquad (2)$$

M = Ga, R = Me (**2**), *i*-Pr (**4**); M = In, R = Me (**3**)

^{1}H and ^{13}C NMR spectra of **2**−**4** show signals due to the organic ligands in a 1:1 molar ratio, indicating the formation of the heterocycles. Mass spectra of **2**−**4** do not show molecular ion peaks due to fragmentation reactions. Single crystals of **2**−**4** suitable for X-ray diffraction were obtained from solutions in pentane at −60 °C (Figures 2−4).

2 crystallizes in the triclinic space group $P\bar{1}$ (No. 2), and **3** and **4** crystallize in the monoclinic space groups $P2_1/n$ (No. 14; **3**) and $P2_1/c$ (No. 14; **4**). The central structural motifs are the six-membered M−Sb rings, which adopt distorted-twist-boat conformations. The central group 13 metal and Sb atoms reside in distorted-tetrahedral environments. As was found previously, the ring size of the M−Sb heterocycles in the solid state depends on the steric bulk of the substituents bound to the metal centers, with the small Me groups favoring the formation of six-membered rings.[28] The Ga−Sb bond distances in **2** and **4** range from 2.668(1) to 2.694(1) Å. These distances are comparable to those found for other six-membered rings $[Me_2GaSb(SiMe_3)_2]_3$ (2.677(1)−2.714(1) Å),[29] $[Cl_2GaSb(t\text{-}Bu)_2]_3$[30] (2.659(1)−2.662(1) Å),

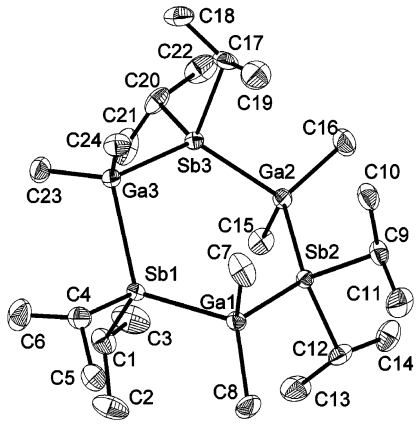

Figure 4. Ortep plot (ellipsoids at the 50% probablity level; H atoms omitted for clarity) showing the solid-state structure and atom-numbering scheme for **4**.

and $[t\text{-}Bu_2GaSbMe_2]_3$ (2.713(1)−2.751(1) Å).[5] The endocyclic Ga−Sb−Ga bond angles observed for **2** (129.7(1)−136.7(1)°) are significantly increased compared to those observed for **4** (118.9(1)−130.5(1)°), whereas the Ga−C bond distances of **2** and **4** (average values: 1.983 Å, **2**; 1.985 Å, **4**) are almost the same. In contrast, the average Sb−C bond length observed for **2** (2.153 Å) is significantly shorter than that of **4** (2.179 Å), clearly demonstrating the influence of the larger *i*-Pr substituents.

The In−Sb bond distances in **3** range from 2.842(1) to 2.869(1) Å, which are comparable to those previously reported for six-membered stibinoindanes $[Me_2InSb(SiMe_3)_2]_3$ (2.844(1)−2.870(1) Å),[28] $[Et_2InSb(SiMe_3)_2]_3$ (2.824(2)−2.911(2) Å),[31] and $[Me_2InSb(CH_2SiMe_3)_2]_3$ (2.852(2)−2.869(2) Å).[7] In contrast, those observed for the four-membered heterocycle $[t\text{-}Bu_2InSb(SiMe_3)_2]_2$ are significantly longer (2.927(1)−2.934(2) Å) due to increased repulsive interactions between the larger organic substituents.[32] As was observed for the Ga−Sb heterocycles **2** and **4**, the endocyclic In−Sb−In bond angles of **3** (132.5(1)−137.5(1)°) are larger than the Sb−In−Sb angles (102.1(1)−104.6(1)°). The In−C bond distances (average value 2.179 Å) and Sb−C bond lengths (average value 2.152 Å) are within the expected ranges.

Since the distibine cleavage reaction gives an easy access to completely alkyl substituted, heterocyclic stibinogallanes and -indanes, we became interested in whether this reaction pathway also allows the generation of group 13−Bi heterocycles of the general type $[R_2MBiR'_2]_x$ (M = Al, Ga). To date, only three compounds of the desired type have been prepared by dehydrosilylation reactions between $Bi(SiMe_3)_3$ and Me_2MH (M = Al,[33] Ga[34]) as well as by a novel meta-

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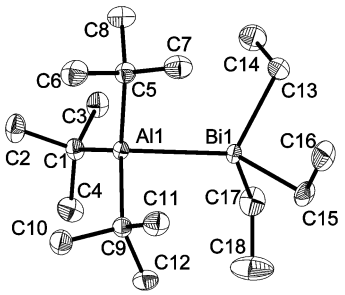

Figure 5. Ortep plot (ellipsoids at the 50% probablity level; H atoms omitted for clarity) showing the solid-state structure and atom-numbering scheme for **5**.

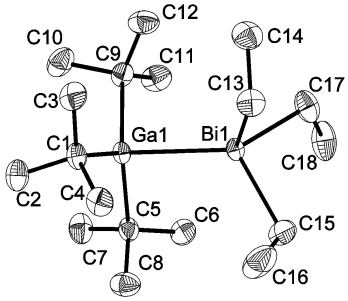

Figure 6. Ortep plot (ellipsoids at the 50% probablity level; H atoms omitted for clarity) showing the solid-state structure and atom-numbering scheme for **6**.

thesis reaction between $[Me_2AlBi(SiMe_3)_2]_3$ and dmap-$InMe_3$.[35] Since the stability of the E−E bond of dipenteles $E_2R'_4$ steadily decreases with increasing atomic number of the group 15 element, dibismuthines $Bi_2R'_4$ are even less stable than distibines $Sb_2R'_4$. Consequently, complexes of dibismuthines remained unknown until we reported only recently on the synthesis and single-crystal X-ray structures of the first stable dinuclear dibismuthine−alane and −gallane adducts $[Et_4Bi_2][M(t\text{-}Bu)_3]_2$ (M = Al, Ga).[6] However, the lability of the Bi−Bi bond renders dibismuthines very interesting starting compounds for further reactions, and we now report on the reaction of Bi_2Et_4 with $M(t\text{-}Bu)_3$.

Bi_2Et_4 was reacted with 1 or 2 equiv of $M(t\text{-}Bu)_3$ in pentane, toluene, or THF in the temperature range from −30 to 25 °C, resulting in the formation of black residues. Filtration of the insoluble material yielded light yellow filtrates, which were stored at −60 °C. Colorless crystals of $Et_3Bi\text{-}M(t\text{-}Bu)_3$ (M = Al (**5**), Ga (**6**)) were formed within 48 h (eq 3).

$$3Et_2Bi{-}BiEt_2 + 4M(t\text{-}Bu)_3 \xrightarrow{-2Bi} 4(t\text{-}Bu)_3M{\leftarrow}BiEt_3 \quad (3)$$

^1H and ^{13}C NMR spectra of **5** and **6** show resonances due to the Et and *t*-Bu groups in a 1:1 molar ratio. Peaks with the highest mass found in the mass spectra of **5** and **6** correspond to $[M(t\text{-}Bu)_3]^+$ (*m*/*z* 198, **5**; *m*/*z* 240, **6**) and $[BiEt_3]^+$ (*m*/*z* 296). The solid-state structures of **5** and **6** were determined by single-crystal X-ray diffraction. Figures 5 and 6 show the solid-state structures of **5** and **6**.

5 and **6** are isostructural and crystallize in the monoclinic space group $P2_1/c$ (No. 14). The central metal atoms reside in distorted-tetrahedral environments with their substituents adopting a staggered conformation relative to one another, as is typical for such adducts. The central M−Bi bond distances are significantly elongated (2.940(1) Å, **5**; 2.966(1) Å, **6**) compared to the sum of the covalent radii (2.75 Å (AlBi), 2.76 Å (GaBi)[36]). They are comparable to those found for $Et_3M{-}Bi(SiMe_3)_3$ adducts (M = Al, 2.921(2) Å; M = Ga, 2.966(1) Å) but significantly shorter than those reported for the sterically more hindered bismuthine and dibismuthine adducts of the type $(t\text{-}Bu)_3M\text{-}Bi(i\text{-}Pr)_3$ (M = Al, 3.088(1) Å; M = Ga, 3.135(1) Å)[37] and $[Et_4Bi_2][M(t\text{-}Bu)_3]_2$ (M = Al, 3.084(1) Å; M = Ga, 3.099(2) and 3.114(2) Å[6]). The sum of the C−M−C bond angles of the $M(t\text{-}Bu)_3$ units (351.5°, **5**; 352.3°, **6**), which deviate only by 8° from planarity, indicate only weak Lewis acid−base interactions, as was previously observed for the bismuthine and dibismuthine adducts. The M−C (average values: 2.011 Å, **5**; 2.037 Å, **6**) and Bi−C bond lengths (average values: 2.246 Å, **5**; 2.254 Å, **6**) are within typical ranges.

The formation of **5** and **6** clearly shows the strong tendency of Bi_2Et_4 to disproportionate with formation of elemental Bi and $BiEt_3$.[17] This trend, which has also been observed for Bi_2Ph_4,[38] is typical for dibismuthines. $BiEt_3$ reacts with the Lewis acid $M(t\text{-}Bu)_3$ with formation of the corresponding adducts.

Summary. Reactions of distibines $Sb_2R'_4$ with trialkylalanes, -gallanes, and -indanes MR_3 were investigated in detail, clearly demonstrating the distibine cleavage reaction to be a powerful reaction pathway for the synthesis of Ga−Sb and In−Sb heterocycles $[R_2MSbR'_2]_x$, whereas the corresponding Al−Sb heterocycles $[R_2AlSbR'_2]_x$ could not be obtained. However, for the first time the mononuclear distibine complex $[i\text{-}Pr_4Sb_2][Al(t\text{-}Bu)_3]$ was synthesized and structurally characterized. The organic substituents R bound to the group 13 metal center were found to play a key role in the distibine cleavage reaction. Distibines $Sb_2R'_4$ (R = Me, Et) readily react with $Ga(t\text{-}Bu)_3$, whereas reactions with $GaMe_3$ occur much more slowly and give the corresponding heterocycles in lower yields. These findings correlate with the Ga−C bond energy decreasing as the branching of the organic substituent increases.[39] In addition, the reactivity of the distibines $Sb_2R'_4$ toward ring formation was found to decrease with increasing steric demand of their substituents R′, most likely due to their increased stability (principle of kinetic stabilization). Consequently, Sb_2Me_4 was found to be more reactive than $Sb_2(i\text{-}Pr)_4$.

Reactions of Bi_2Et_4 with $M(t\text{-}Bu)_3$ (M = Al, Ga) did not occur with formation of the corresponding M−Bi heterocycles $[t\text{-}Bu_2MBiEt_2]_x$ but with disproportionation yielding elemental Bi and $BiEt_3$. $BiEt_3$ reacts with $M(t\text{-}Bu)_3$ to give the corresponding Lewis acid−base adducts $Et_3Bi\text{-}M(t\text{-}Bu)_3$ (M = Al, Ga).

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isterium für Bildung, Wissenschaft, Forschung und Technologie (BMBF) and Prof. E. Niecke.

Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **1**−**6**; these data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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