Reactivity of Distibanes toward Trialkylalanes and -gallanes: Syntheses and X-ray Structures of Bisadducts and Heterocycles

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Reactions between distibanes of the type Sb_2R_4 and trialkylalanes and -gallanes R'_3M in 1:2 stoichiometry yield eight bisadducts of the type $[Sb_2R_4][MR'_3]_2$ (R = Me, R′ = *t*-Bu, M = Al **1**, Ga **2**; R = Et, M = Al, R′ = Me **3**, Et **4**, *t*-Bu **5**; M = Ga, R′ = Me **6**, Et **7**, *t*-Bu **8**), which were characterized by multinuclear NMR studies and elemental analysis. In addition, **1**, **2**, **5**, and **8** are the first structurally characterized neutral main group Lewis acid−distibane bisadducts. **1**−**8** are unstable in solution toward the formation of heterocycles of the type $[R_2SbMR'_2]_x$. $[Me_2SbGa(t\text{-}Bu)_2]_3$ (**9**) and $[Et_2SbGa(t\text{-}Bu)_2]_2$ (**10**) have been isolated and their solid state structures determined by single-crystal X-ray diffraction.

1. Introduction

The tendency of group 13 trialkyls to form simple Lewis acid−base adducts $R_3M{-}ER'_3$ is a central aspect of their chemistry. Numerous adducts, mainly with amines and phosphanes, have been reported. Within the past few years, we[1] and other groups[2] have expanded these studies on the heavier elements of group 15 and reported on the synthesis and crystal structures of simple Lewis acid−base adducts of the type $R_3M{-}ER'_3$ (M = Al, Ga; E = Sb, Bi). In contrast, the coordination properties of dipnicogenides of the type $R_2E{-}ER_2$ (E = P, As, Sb, Bi), which contain a central element−element bond, have been investigated to a far lesser extent. Most of the studies have concentrated on diphosphanes and diarsanes. To the best of our knowledge, only five distibane complexes have been structurally characterized, while adducts of dibismuthanes are unknown, so far.[3] Reactions of $R_2Sb{-}SbR_2$ (R = Ph, Et) with transition metal complexes lead to mono- and bimetallic complexes of the type $[R_4Sb_2][ML_n]_x$ (M = transition metal; *x* = 1, 2).[3c] In addition, heterocycles of the type $(R_2SbML_n)_2$ were obtained by Sb−Sb bond-cleavage reaction.[4] However, reactions with main group element Lewis acids are much more rare. Breunig et al. obtained $[Me_2Sb{-}SbMe_2{-}SbMe_2]^+[Me_2SbBr_2]^-$ by reaction of Me_4Sb_2 and Me_2SbBr. The cation can be described as an adduct of Me_4Sb_2 and Me_2Sb^+.[5] Recently, they reported on the synthesis of $[Me_3Sb{-}SbMe_2]^+[MeSbBr_3]^-$. The cation, which is formally the product of the reaction of Me_4Sb_2 and Me^+,[6] is not available by a direct quaternizing reaction of Me_4Sb_2 with MeI[7] due to the low stability of the Sb−Sb bond, leading to the formation of Me_3Sb and Me_2SbI.[8]

Reactions of $R_2E{-}ER_2$ (E = N, P, As, Sb, Bi) with group 13 compounds R_3M (R = H, alkyl, aryl, halogen, M = B, Al, Ga, In) are almost unknown. Nöth and Burg described 40 years ago for the first time the synthesis of such a compound. $[Me_4P_2][BH_3]_2$, the borane bisadduct of tetramethyldiphosphane, was obtained by reaction of Me_4P_2 and B_2H_6.[9] However, only two complexes, $Me_4P_2(BH_3)_2$[10] and $Me_4P_2(BH_2Br)_2$,[11] have been structurally charactized, so far. Compounds with heavier elements of group 15 are still unknown. Recently, Breunig et al. described the reaction of Me_4Sb_2 with $(Me_3SiCH_2)_3In$, leading to the formation of the six-membered heterocycle $[(Me_3SiCH_2)_2InSbMe_2]_3$.[12] Again,

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its formation is based on the well-known lability of the Sb−Sb bond toward electrophilic compounds.[13] The formation of a bisadduct could not be observed.

In an attempt to investigate the reactivity of distibanes toward electrophilic group 13 trialkyls in more detail, we performed several reactions with trialkylalanes and -gallanes. Depending on the reaction conditions, bisadducts of the type $[R_4Sb_2][MR'_3]_2$ and heterocycles $[R_2SbGa(t\text{-Bu})_2]_x$ were obtained.

2. Experimental Section

2.1. General Considerations. All manipulations were performed in a glovebox under a N_2 atmosphere or by standard Schlenk techniques. Me_3Al and Et_3Al were commercially available from Aldrich and used as received. t-Bu_3Al[14] $GaMe_3$,[15] $GaEt_3$,[15] t-Bu_3Ga,[16] Me_4Sb_2,[17] and Et_4Sb_2[18] were prepared according to literature methods. ^{1}H and ^{13}C{^{1}H} spectra were recorded using a Bruker AMX 300 spectrometer and are referenced to internal C_6D_5H (δ ^{1}H 7.154, δ ^{13}C 128.0). Spectra were recorded within minutes after the freshly prepared bisadducts were dissolved in C_6D_6. Melting points were measured in sealed capillaries and are not corrected. Mass spectra were recorded on a VG Masslab 12-250 spectrometer in the electron ionization mode at 20 eV. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn.

2.2. General Preparation of Bisadducts $[R_4Sb_2][MR'_3]_2$. Pure R_3M (2 mmol) and R_4Sb_2 (1 mmol) were combined in the glovebox. **1**, **2**, **5**, and **8** were obtained as yellow solids, while **3**, **4**, **6**, and **7** are yellow liquids even at −30 °C. **1**, **2**, **5**, and **8** were dissolved in cold pentane (−10 °C, 10 mL) and immediately stored at −30 °C, resulting in the formation of colorless crystals. Compounds **3**, **4**, **6**, and **7** were characterized without further purification.

$$2\ t\text{-}Bu_3M + Sb_2Me_4 \rightarrow [Me_4Sb_2][M(t\text{-}Bu)_3]_2\ (M = Al\ \mathbf{1},\ Ga\ \mathbf{2})$$

$$2\ R_3Al + Sb_2Et_4 \rightarrow [Et_4Sb_2][AlR_3]_2\ (R = Me\ \mathbf{3},\ Et\ \mathbf{4},\ t\text{-}Bu\ \mathbf{5}) \quad (1)$$

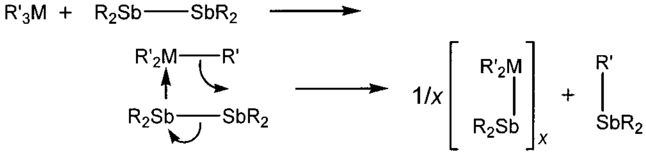
$$2\ R_3Ga + Sb_2Et_4 \rightarrow [Et_4Sb_2][GaR_3]_2\ (R = Me\ \mathbf{6},\ Et\ \mathbf{7},\ t\text{-}Bu\ \mathbf{8})$$

$[Me_4Sb_2][Al(t\text{-}Bu)_3]_2$, 1 (M = 700.31 g/mol): 0.41 g, 0.58 mmol, 58%. Mp: 101−104 °C. $C_{28}H_{66}Al_2Sb_2$, found (calc): C 48.02 (47.86); H 9.42 (9.35). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.82 (s, 12 H, *Me*Sb), 1.19 (s, 54 H, *t*-Bu). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ −9.0 (MeSb), 20.0 ($Me_3\mathit{C}Al$), 32.0 (Me_3CAl).

$[Me_4Sb_2][Ga(t\text{-}Bu)_3]_2$, 2 (M = 785.77 g/mol): 0.50 g, 0.64 mmol, 64%. Mp: 75 °C. $C_{28}H_{66}Ga_2Sb_2$, found (calc): C 42.33 (42.80); H 8.20 (8.47). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 1.02 (s, 12 H, *Me*Sb), 1.27 (s, 54 H, *t*-Bu). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ −10.9 (MeSb), 33.6 (Me_3CGa).

$[Et_4Sb_2][AlMe_3]_2$, 3 (M = 483.65 g/mol): 0.48 g, 1 mmol, 100%. $C_{14}H_{38}Al_2Sb_2$, found (calc): C 34.43 (34.77); H 7.65 (7.86). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ −0.33 (s, 18 H, MeAl), 1.28 (t, $^3J_{HH}$ = 7.7 Hz, 12 H, CH_3CH_2Sb), 1.52−1.71 (m, 8 H, $CH_3\mathit{CH}_2Sb$). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ −6.6 (MeAl), 1.6 ($CH_3\mathit{C}H_2Sb$), 14.8 ($\mathit{C}H_3CH_2Sb$).

Scheme 1. Possible Reaction Pathway for the Formation of 9 and 10



$[Et_4Sb_2][AlEt_3]_2$, 4 (M = 587.72 g/mol): 0.59 g, 1 mmol, 100%. $C_{20}H_{50}Al_2Sb_2$, found (calc): C 40.68 (40.87); H 8.39 (8.51). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.34 (q, $^3J_{HH}$ = 8.1 Hz, 12 H, $CH_3\mathit{CH}_2Al$), 1.23 (t, $^3J_{HH}$ = 7.9 Hz, 12 H, CH_3CH_2Sb), 1.24 (t, $^3J_{HH}$ = 8.1 Hz, 18 H, CH_3CH_2Al), 1.52−1.71 (m, 8 H, $CH_3\mathit{CH}_2Sb$). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ 1.8 ($CH_3\mathit{C}H_2Al$), 2.2 ($CH_3\mathit{C}H_2Sb$), 10.0 ($\mathit{C}H_3CH_2Al$), 14.5 ($\mathit{C}H_3CH_2Sb$).

$[Et_4Sb_2][Al(t\text{-}Bu)_3]_2$, 5 (M = 756.42 g/mol): 0.63 g, 0.83 mmol, 83%. Mp: 75 °C. $C_{32}H_{74}Al_2Sb_2$, found (calc): C 50.63 (50.81); H 9.68 (9.86). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 1.19 (t, $^3J_{HH}$ = 7.9 Hz, 12 H, $\mathit{Me}CH_2Sb$), 1.22 (s, 54 H, *t*-Bu), 1.61−1.80 (m, 8 H, $Me\mathit{CH}_2Sb$). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ 3.4 ($Me\mathit{CH}_2Sb$), 14.1 ($\mathit{Me}CH_2Sb$), 20.0 (q-C/Al), 32.5 (Me_3CAl).

$[Et_4Sb_2][GaMe_3]_2$, 6 (M = 589.39 g/mol): 0.59 g, 1 mmol, 100%. $C_{14}H_{38}Ga_2Sb_2$, found (calc): C 28.41 (28.53); H 6.41 (6.50). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ −0.01 (s, 18 H, MeGa), 1.26 (t, $^3J_{HH}$ = 7.7 Hz, 12 H, CH_3CH_2Sb), 1.50−1.69 (m, 8 H, $CH_3\mathit{CH}_2Sb$). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ 0.3 (MeGa), 1.5 ($CH_3\mathit{C}H_2Sb$), 14.4 ($\mathit{C}H_3CH_2Sb$).

$[Et_4Sb_2][GaEt_3]_2$, 7 (M = 673.56 g/mol): 0.67 g, 1 mmol, 100%. $C_{20}H_{50}Ga_2Sb_2$, found (calc): C 35.32 (35.66); H 7.32 (7.48). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.63 (q, $^3J_{HH}$ = 7.9 Hz, 12 H, $CH_3\mathit{CH}_2Ga$), 1.25 (t, $^3J_{HH}$ = 7.9 Hz, 18 H, CH_3CH_2Ga), 1.30 (t, $^3J_{HH}$ = 8.1 Hz, 12 H, CH_3CH_2Sb), 1.51−1.73 (m, 8 H, $CH_3\mathit{CH}_2Sb$). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ 2.1 ($CH_3\mathit{C}H_2Sb$), 8.0 ($CH_3\mathit{C}H_2Ga$), 11.4 ($\mathit{C}H_3CH_2Ga$), 14.2 ($\mathit{C}H_3CH_2Sb$).

$[Et_4Sb_2][Ga(t\text{-}Bu)_3]_2$, 8 (M = 841.85 g/mol): 0.73 g, 0.87 mmol, 87%. Mp: 54 °C. $C_{32}H_{74}Ga_2Sb_2$, found (calc): C 45.32 (45.66); H 8.64 (8.79). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 1.23 (s, 54 H, *t*-Bu), 1.26 (t, $^3J_{HH}$ = 7.7 Hz, 12 H, $\mathit{Me}CH_2Sb$), 1.58−1.78 (m, 8 H, $Me\mathit{CH}_2Sb$). ^{13}C{^{1}H} NMR (80 MHz, C_6D_5H, 25 °C): δ 2.6 ($Me\mathit{CH}_2Sb$), 14.5 ($\mathit{Me}CH_2Sb$), 31.9 (Me_3CGa).

2.3. General Preparation of Heterocycles $[R_2SbGa(t\text{-}Bu)_2]_x$. One millimole of the bisadduct $[R_4Sb_2][Ga(t\text{-}Bu)_3]_2$ (R = Me **2**, Et **8**) was dissolved in 30 mL of pentane, giving a yellow solution, and the reaction mixture was stirred for 72 h at ambient temperature in the absence of light. The resulting clear solution was reduced to 15 mL and stored at −30 °C. After 48 h, **9** and **10** were obtained as colorless crystals.

$$[R_4Sb_2][t\text{-}Bu_3Ga]_2 \rightarrow [R_2SbGa(t\text{-}Bu)_2]_x + R_2Sb(t\text{-}Bu) + Ga(t\text{-}Bu)_3,\ R = Me,\ x = 3\ \mathbf{9};\ R = Et,\ x = 2\ \mathbf{10} \quad (2)$$

$[Me_2SbGa(t\text{-}Bu)_2]_3$, 9 (M = 1002.25 g/mol): 0.27 g, 0.27 mmol, 82% (based on the starting distibane bisadduct). Mp: 146−151 °C (dec). $C_{30}H_{72}Ga_3Sb_3$, found (calc): C 35.91 (35.93); H 7.15 (7.18). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 1.21 (s, 6H, SbMe), 1.28 (s, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ −10.9 (SbMe), 33.6 (GaMe). EI-MS (*m*/*z*, %): 945 ($M^+ - (t\text{-}Bu)$, 2), 663 ($M^+ - 6(t\text{-}Bu)$, 5), 304 ($(t\text{-}Bu)_2GaSb^+$, 100), 183 ($(t\text{-}Bu)_2Ga^+$, 33), 151 (Me_2Sb^+, 27), 57 ($t\text{-}Bu^+$, 95).

$[Et_2SbGa(t\text{-}Bu)_2]_2$, 10 (M = 727.65 g/mol): 0.28 g, 0.39 mmol, 78%. Mp: 180−182 °C (dec). $C_{24}H_{56}Ga_2Sb_2$, found (calc): C 39.55 (39.62); H 7.72 (7.76). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 1.28 (s, 18H, *t*-Bu), 1.33 (t, $^3J_{HH}$ = 7.5 Hz,

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Table 1. Crystallographic Data and Measurements for $[Me_4Sb_2][Al(t\text{-}Bu)_3]_2$ (1), $[Me_4Sb_2][Ga(t\text{-}Bu)_3]_2$ (2), $[Et_4Sb_2][Al(t\text{-}Bu)_3]_2$ (5), and $[Et_4Sb_2][Ga(t\text{-}Bu)_3]_2$ (8)

	1	**2**	**5**	**8**
mol formula	$C_{28}H_{66}Al_2Sb_2$	$C_{28}H_{66}Ga_2Sb_2$	$C_{32}H_{74}Al_2Sb_2$	$C_{32}H_{74}Ga_2Sb_2$
fw	700.27	785.75	756.37	841.85
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.6774(1)	14.6677(1)	8.4701(2)	8.4647(3)
b, Å	11.4300(1)	9.5208(1)	16.1248(3)	16.0772(5)
c, Å	18.5338(2)	25.9501(3)	14.8614(4)	14.9124(4)
β, deg	99.414(1)	90	104.558(1)	104.736(2)
V, $Å^3$	1813.47(3)	3623.89(6)	1964.58(8)	1962.66(11)
Z	2	4	2	2
radiation (wavelength, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ, mm^{-1}	1.551	2.959	1.437	2.737
temp, K	123(2)	123(2)	123(2)	123(2)
D_{calcd}, g cm^{-3}	1.282	1.440	1.279	1.425
cryst dimens (mm)	0.25 × 0.20 × 0.20	0.50 × 0.40 × 0.20	0.15 × 0.10 × 0.07	0.30 × 0.25 × 0.20
$2\theta_{max}$, deg	55.0	50.0	56.6	56.6
no. of rflns rec	38 599	24 994	34 707	20 110
no. of nonequiv rflns rec	4141	3178	4836	4742
R_{merg}	0.051	0.045	0.047	0.041
no. of params refined	145	145	163	163
R1;[a] wR2[b]	0.016, 0.043	0.024, 0.062	0.021, 0.048	0.020, 0.049
goodness of fit[c]	1.051	1.085	0.994	1.042
final max, min $\Delta\rho$, e $Å^{-3}$	0.535; −0.459	1.099; −0.849	0.458; −0.645	0.854; −0.735

[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 Measurements for $[Me_2SbGa(t\text{-}Bu)_2]_3$ (9) and $[Et_2SbGa(t\text{-}Bu)_2]_2$ (10)

	9	**10**
mol formula	$C_{30}H_{72}Ga_3Sb_3$	$C_{24}H_{56}Ga_2Sb_2$
fw	1007.29	727.63
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	9.2837(2)	9.0217(2)
b, Å	22.0286(4)	11.7686(3)
c, Å	20.3563(4)	14.8729(3)
β, deg	91.269(1)	90.085(1)
V, $Å^3$	4161.98(14)	1579.10(6)
Z	4	2
radiation (wavelength, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ, mm^{-1}	3.849	3.388
temp, K	123	123
D_{calcd}, g cm^{-3}	1.608	1.530
cryst dimens (mm)	0.15 × 0.15 × 0.10	0.65 × 0.55 × 0.45
$2\theta_{max}$, deg	50.0	50.0
no. of rflns rec	28 739	12 773
no. of nonequiv rflns rec	7295	2719
R_{merg}	0.084	0.071
no. of params refined	325	127
R1;[a] wR2[b]	0.038, 0.066	0.029, 0.074
goodness of fit[c]	0.981	1.195
final max, min $\Delta\rho$, e $Å^{-3}$	0.794; −0.920	0.534; −1.099

[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 3. Selected Bond Lengths (Å) and Angles (deg) for 1, 2, 5, and 8[a]

	$[Me_4Sb_2][Al(t\text{-}Bu)_3]_2$ (**1**); M = Al	$[Me_4Sb_2][Ga(t\text{-}Bu)_3]_2$ (**2**); M = Ga
Sb1−Sb1a	2.811(1)	2.814(1)
Sb1−M1	2.919(1)	2.919(1)
Sb1−C1	2.145(2)	2.150(3)
Sb1−C2	2.147(2)	2.138(3)
M1−C3	2.025(2)	2.029(3)
C3−M1−C7	117.0(1)	117.4(2)
C1−Sb1−C2	97.8(1)	96.6(2)
M1−Sb1−Sb1a	127.2(1)	129.8(1)
C3−M1−Sb1	98.4(1)	99.6(1)
C1−Sb1−M1	112.2(1)	113.5(1)
C2−Sb1−M1	117.2(1)	114.8(1)

	$[Et_4Sb_2][Al(t\text{-}Bu)_3]_2$ (**5**); M = Al	$[Et_4Sb_2][Ga(t\text{-}Bu)_3]_2$ (**8**); M = Ga
Sb1−Sb1a	2.838(1)	2.839(1)
Sb1−M1	3.001(1)	3.022(1)
Sb1−C1	2.163(2)	2.165(2)
Sb1−C3	2.171(2)	2.171(2)
M1−C9	2.023(2)	2.032(2)
C5−M1−C13	117.4(1)	116.8(1)
C1−Sb1−C3	96.8(1)	96.1(1)
M1−Sb1−Sb1a	125.5(1)	126.4(1)
C9−M1−Sb1	101.9(1)	101.7(1)
C1−Sb1−M1	117.4(1)	117.7(1)
C3−Sb1−M1	115.7(1)	115.9(1)

[a] Symmetry generated by −*x*, −*y* + 1, −*z* (**1**); −*x* + 1, −*y*, −*z* + 1 (**2**); −*x* + 1, −*y* + 1, −*z* + 1 (**5**, **8**).

12 H, *Me*CH$_2$Sb), 1.94 (q, $^3J_{HH}$ = 7.5 Hz, 8 H, Me*CH*$_2$Sb). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ −1.2 (Me*C*H$_2$Sb), 14.5 (*Me*CH$_2$Sb), 28.6 (Me$_3$*C*Ga), 32.4 (*Me*$_3$CGa). EI-MS (*m*/*z*, %): 523 (((t-Bu)$_2$Ga$_2$Sb$_2$Et$^+$, 5), 454 ((t-Bu)$_2$GaSb$_2$Et$^+$, 20), 304 ((t-Bu)$_2$GaSb$^+$, 20), 236 ((t-Bu)SbEt$_2^+$, 25), 183 ((t-Bu)$_2$Ga$^+$, 100), 57 (t-Bu$^+$, 65).

X-ray Structure Solution and Refinement. Crystallographic data of **1**, **2**, **5**, and **8** are summarized in Table 1; those of **9** and **10** in Table 2. Selected bond lengths and angles are given in Tables 3 (**1**, **2**, **5**, and **8**) and 4 (**9** and **10**). Figures 1−6 show ORTEP diagrams of the solid state structures of **1**, **2**, **5**, and **8**−**10**. Data were collected on a Nonius Kappa-CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) at T = −150 °C, and the structures were solved by direct methods (**1**, **10**) and Patterson methods (SHELXS-97; **2**, **5**, **8**, **9**),[19] respectively, and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied for all compounds except **5**. All non-hydrogen atoms in **1**, **2**, **5**, **8**, **9**, and **10** were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[20]

3. Results and Discussion

Reactions of trialkylalanes and -gallanes R_3M (M = Al, Ga; R = Me, Et, *t*-Bu) with distibanes R_4Sb_2 (R =

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[19] Sheldrick, G. M. *SHELXS-97*, Program for Structure Solution. *Acta Crystallogr. Sect. A* **1990**, *46*, 467−473.

[20] Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; Universität Göttingen, 1997.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 9 and 10[a]

[$Me_2SbGa(t\text{-}Bu)_2]_3$ (**9**)

Sb1−Ga1	2.713(1)	Sb3−C21	2.147(5)	Ga2−Sb3−Ga3	133.3(1)
Sb1−Ga3	2.750(1)	Sb3−C22	2.163(5)	Sb1−Ga1−Sb2	97.0(1)
Sb2−Ga1	2.713(1)	Ga1−C3	2.030(5)	Sb2−Ga2−Sb3	96.7(1)
Sb2−Ga2	2.718(1)	Ga1−C7	2.009(5)	Sb1−Ga3−Sb3	102.8(1)
Sb3−Ga2	2.726(1)	Ga2−C13	2.036(5)	C1−Sb1−C2	95.4(2)
Sb3−Ga3	2.751(1)	Ga2−C17	2.040(5)	C11−Sb2−C12	99.1(2)
Sb1−C1	2.161(5)	Ga3−C23	2.029(5)	C21−Sb3−C22	95.4(2)
Sb1−C2	2.155(5)	Ga3−C27	2.023(5)	C3−Ga1−C7	120.0(2)
Sb2−C11	2.155(5)	Ga1−Sb1−Ga3	127.3(1)	C13−Ga2−C17	119.0(2)
Sb2−C12	2.157(5)	Ga1−Sb2−Ga2	131.4(1)	C23−Ga3−C27	119.4(2)

[$Et_2SbGa(t\text{-}Bu)_2]_2$ (**10**)

Ga1−Sb1	2.731(1)	Sb1−Ga1−Sb1a	83.4(1)
Ga1a-Sb1	2.735(1)	C1−Sb1−C3	97.8(2)
Sb1−C1	2.169(3)	C1−Sb1−Ga1	114.8(1)
Sb1−C3	2.162(4)	C3−Sb1−Ga1	116.8(1)
Ga1−C5	2.019(3)	C5−Ga1−C9	123.4(2)
Ga1−C9	2.019(3)	C5−Ga1−Sb1	109.6(1)
Ga1−Sb1−Ga1a	96.6(1)	C9−Ga1−Sb1	112.0(1)

[a] Symmetry generated by $-x + 1, -y + 1, -z + 1$ (**10**).

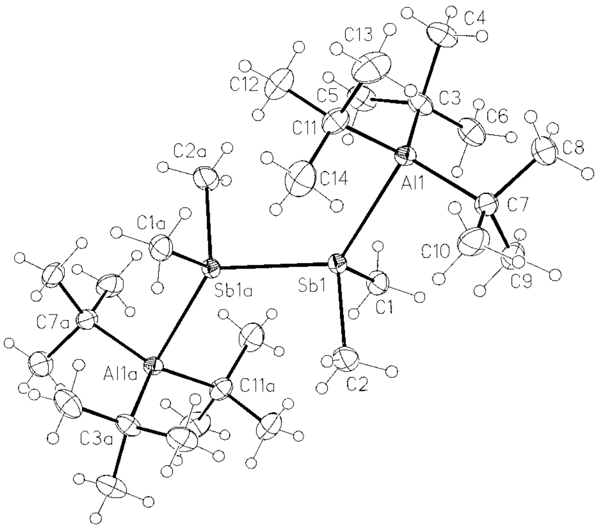

Figure 1. ORTEP plot (50% probability level; H omitted for clarity) showing the solid state structure and atom-numbering scheme for **1**.

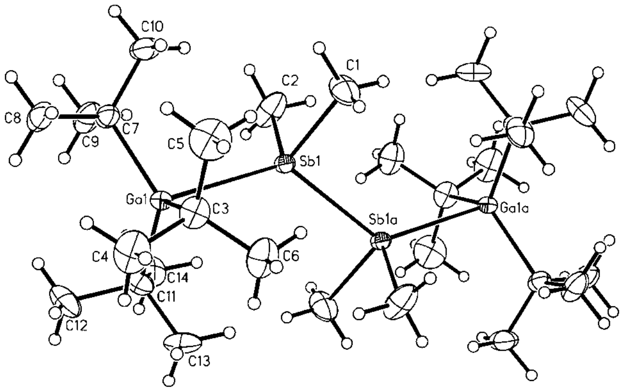

Figure 2. ORTEP plot (50% probability level; H omitted for clarity) showing the solid state structure and atom-numbering scheme for **2**.

Me, Et) in a 2:1 molar ratio resulted in the formation of Lewis acid−base bisadducts of the type $[Sb_2R_4][MR'_3]_2$ (R = Me, R′ = *t*-Bu, M = Al **1**, Ga **2**; R = Et, M = Al, R′ = Me **3**, Et **4**, *t*-Bu **5**; M = Ga, R′ = Me **6**, Et **7**, *t*-Bu **8**). To the best of our knowledge, **1**−**8** are the first neutral distibane bisadducts with a main group element Lewis acid.

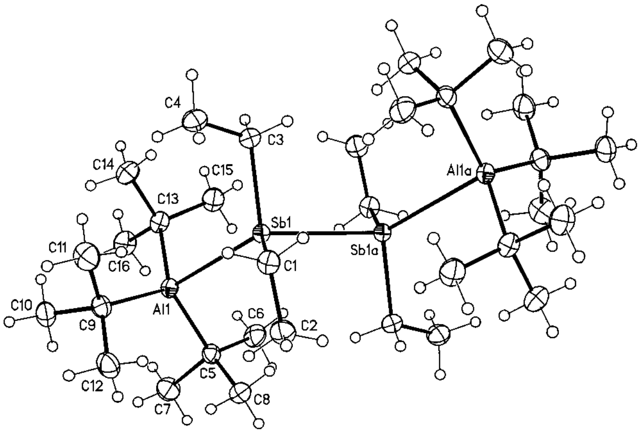

Figure 3. ORTEP plot (50% probability level; H omitted for clarity) showing the trans conformation and atom-numbering scheme for **5**.

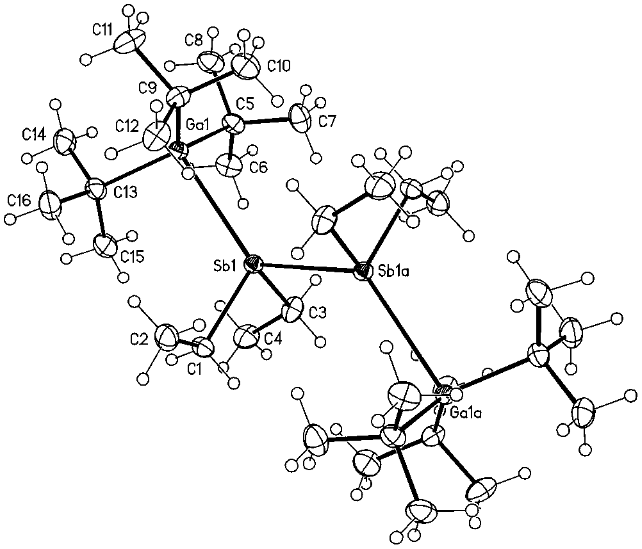

Figure 4. ORTEP plot (50% probability level; H omitted for clarity) showing the solid state structure and atom-numbering scheme for **8**.

Me_4Sb_2 is more reactive than Et_4Sb_2 toward trialkylalanes. Only the reaction with the sterically hindered

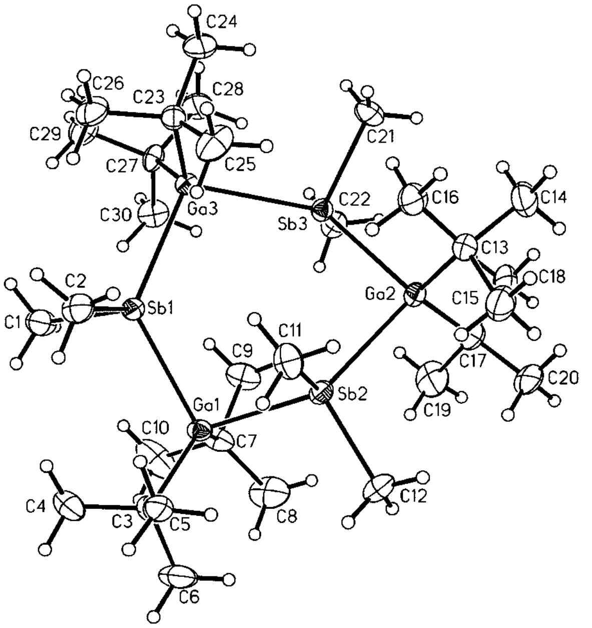

Figure 5. ORTEP plot (50% probability level; H omitted for clarity) showing the solid state structure and atom-numbering scheme for **9**.

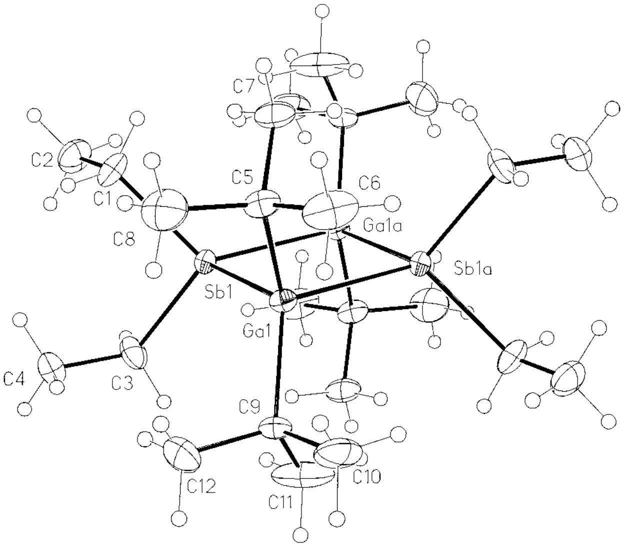

Figure 6. ORTEP plot (50% probability level; H omitted for clarity) showing the solid state structure and atom-numbering scheme for **10**.

and less electrophilic t-Bu_3Al leads to the formation of a stable bisadduct (**1**), while reactions with Me_3Al and Et_3Al immediately yield black, insoluble solids, which could not be characterized. With trialkylgallanes, no decomposition occurs. In the case of Me_3Ga and Et_3Ga, yellow liquids were formed, while the reaction with t-Bu_3Ga yields **2** as a yellow solid. Obviously, the reactivity of distibanes toward group 13 trialkyls depends on the stability of the distibane, which is kinetically controlled by the substituents bound to the Sb centers and by the electrophilic nature of the group 13 trialkyl. Pure **1**−**8** are stable compounds at 0 °C and can be stored in the dark without decomposition for weeks. However, they are instable in solution and undergo consecutive reactions, which was shown by time-dependent NMR studies. Again, the Me_4Sb_2 adducts **1** and **2** are more reactive than the Et_4Sb_2 adducts **3**−**8**.

Compounds **1**−**8** were characterized by ^1H and ^{13}C NMR studies. Compared to the starting compounds, the signals due to the organic ligands are shifted to lower field (MR'_3) and higher field (Sb_2R_4). The same tendency was observed for simple trialkylstibane adducts of the type $R_3Sb{-}MR'_3$ (M = Al, Ga).[1c,d] Due to the low stability of **1**−**8** in solution, neither temperature-dependent NMR studies nor cryoscopic molecular weight determinations could be performed. Therefore, reliable information about the stability and the degree of dissociation of the bisadducts in solution is not experimentally available. Mass spectra of **1**−**8** do not show molecular ion peaks due to fragmentation into the corresponding distibane and the trialkylalane and -gallane fragment, respectively.

Single crystals of **1**, **2**, **5**, and **8** suitable for an X-ray structure determination were obtained from solutions in pentane at −30 °C. Figures 1−4 show the solid state structures of **1**, **2**, **5**, and **8**.

5 and **8** are isomorphic and crystallize in the monoclinic space group $P2_1/c$ (No. 14), while **1** (monoclinic space group $P2_1/c$, No. 14) and **2** (orthorhombic space group $Pbca$, No. 61) crystallize in different space groups. In **1**, **2**, **5**, and **8**, the ligands bound to the Sb centers adopt a staggered conformation in relation to one another with the $M(t\text{-}Bu)_3$ fragments in a trans position, which is likely due to sterical effects. The compounds possess crystallographic C_i-symmetry, with the center of symmetry in the Sb−Sb bond. The Sb−Sb bond distances in **1** (2.811(1) Å) and **2** (2.814(1) Å) are slightly shorter than those in **5** (2.838(1) Å) and **8** (2.839(1) Å). Despite the increased steric pressure within the adducts compared to the pure distibanes, the Sb−Sb bond distances within **1**, **2**, **5**, and **8** remain almost unchanged. The crystal structure data give no evidence for a Sb−Sb bond weakening. Typical Sb−Sb bond lengths in distibanes range from 2.82 to 2.87 Å (Me_4Sb_2, 2.862(2),[21] 2.830(1) and 2.838(1) Å;[22] $(Me_3Si)_4Sb_2$, 2.867(1) Å;[23] $(Me_3Sn)_4Sb_2$, 2.866(1) Å;[24] $(t\text{-}Bu)_4Sb_2$, 2.817(1) Å;[25] $(Ph)_4Sb_2$, 2.844(1) Å).[23] Compared to the polymeric bisadduct $\{[Sb_2Et_4][I_2Cd]_2\}_n$ (2.784(2) Å),[3e] the intramolecular Sb−Sb bond lengths in **1**, **2**, **5**, and **8** are elongated by about 5 pm, while $[Sb_2Ph_4][W(CO)_5]_2$ (2.861(1) Å) and $[Sb_2Ph_4][Cr(CO)_5]_2$ (2.866(1) Å) show slightly longer Sb−Sb distances. Distibanes are usually arranged in the form of endless chains in the solid state with short intermolecular Sb−Sb contacts (e.g., 3.645(2)[21] and 3.678(1) Å[22] for Me_4Sb_2). Compared to the starting distibanes, these intermolecular Sb−Sb distances are significantly elongated by coordination to the Lewis acid fragment. The shortest values observed are 8.68 (**1**), 7.43 (**2**), 7.66 (**5**), and 7.68 Å (**8**), indicating the loss of attractive intermolecular Sb···Sb interactions. The Al−Sb (2.919(1) Å **1**; 3.001(1) Å **5**) and Ga−Sb bond lengths (2.919(1) Å **2**; 3.022(2) Å **8**) of the Me_4Sb_2 bisadducts (**1**, **2**) are significantly shorter than those of

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(21) Ashe, A. J., III; Ludwig, E. G., Jr.; Oleksyszyn, J.; Huffman, J. C. *Organometallics* **1984**, *3*, 337−338.

(22) Mundt, O.; Riffel, H.; Becker, G.; Simon, A. *Z. Naturforsch.* **1984**, *39b*, 317−322.

(23) Becker, G.; Freudenblum, H.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1982**, *492*, 37−51.

(24) Becker, G.; Meiser, M.; Mundt, O.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1989**, *569*, 62−82.

(25) Mundt, O.; Becker, G.; Wessely, H.-J.; Breunig, H. J.; Kischkel, H. *Z. Anorg. Allg. Chem.* **1982**, *486*, 70−89.

the Et_4Sb_2 bisadducts (**5**, **8**) due to reduced sterical interactions. **5** shows the longest Al−Sb bond length ever observed, while the Ga−Sb distance found in **8** is comparable to those of $(Me_3Si)_3Sb{-}Ga(t\text{-}Bu)_3$ (302.7(2) pm). The Ga−Sb and Ga−C distances (average 2.028 Å **2**; 2.038 Å **8**) are slightly longer than the Al−Sb and Al−C distances (average 2.020 Å **1**; 2.023 Å **5**) of similar bisadducts, which might express the reduced Lewis acidity of $t\text{-}Bu_3Ga$ compared to $t\text{-}Bu_3Al$.[26] The same was found for simple stibane adducts of the type $R_3Sb{-}MR'_3$[1] and agrees with a model originally described by Haaland et al.[27] The Sb−C distances in **1** and **2** are slightly shorter than those in **5** and **8** (average 2.146 Å **1**; 2.144 Å **2**; 2.167 Å **5**; 2.168 Å **8**). They are comparable to the average Sb−C distance observed for Me_4Sb_2 (2.162 Å; structure of Et_4Sb_2 is unknown). In contrast, the sum of the C−Sb−C and C−Sb−Sb bond angles for **1** (295.1°), **2** (292.9°), **5** (292.9°), and **8** (291.1°) is significantly increased compared to those of Me_4Sb_2 (average 283.1°). The same was found for simple M−Sb Lewis acid base adducts (M = Al, Ga)[1] and points to a partial rehybridization of the Sb-center. The former *lone pair* of the distibane, which had a high s-character, gets more p-character in the adducts. Simultaneously, the s-character of the former Sb−C and Sb−Sb bonding electron pairs increases, resulting in widened C−Sb−C and C−Sb−Sb bond angles.

While pure **1**−**8** can be stored at 0 °C without decomposition, their stability in solution is significantly reduced. Due to Breunig's observations that distibanes react with group 13 trialkyls under Sb−Sb bond cleavage to give M−Sb heterocycles of the type $[R_2SbMR'_2]_x$, we also suggested the formation of M−Sb heterocycles in solution. This is of potential interest, because to date, M−Sb heterocycles are generally available only by dehalosilylation (Ga−Sb) and dehydrosilylation reaction (Al−Sb heterocycles), respectively. Both reaction pathways suffer from the lack of stable silylstibanes as starting compounds. Most reactions have been performed using $Sb(SiMe_3)_3$. Besides this compound, only a few compounds of the type $R_2SbSiMe_3$ and $RSb(SiMe_3)_2$, respectively, are known. The reaction of distibanes with trialkylalanes and -gallanes would offer an alternative pathway, in particular for the synthesis of all-alkyl-substituted heterocycles, which might be useful precursors for the synthesis of thin films of the corresponding semiconducting materials by the MOCVD (metal organic chemical vapor deposition) process.[28] The first step of a possible reaction pathway includes the formation of a 1:1 adduct, followed by M−C and Sb−Sb bond cleavage reactions. Following this reaction type, stibanes of the type R_2SbR' should be obtained as byproducts. The formation of 1:1 adduct intermediates in solution starting from 2:1 adducts seems to be reasonable due to the weak M−Sb bonds and the expected extensive degree of dissociation of **1**−**8** in solution.[29]

The bisadducts **2** and **8** were stirred in pentane for 3 days, followed by storage at −30 °C. Colorless crystals of **9** and **10** were formed within 48 h. ^{1}H and ^{13}C NMR spectra show signals due to the organic ligands.[30] Compared to the starting bisadducts, the resonance of the Sb−R groups is significantly shifted to lower field. In addition, the Sb(R)/Ga(*t*-Bu) ratio changes as expected from 2:3 (bisadducts) to 1:1 (**9**, **10**). Mass spectra of **9** and **10** do not show molecular ion peaks due to fragmentation. The peaks with the highest mass are $[M^+ - (t\text{-Bu}) - 2Me]$ (*m*/*z* 917 **9**) and $[M^+ - 2(t\text{-Bu}) - 3Et]$ (*m*/*z* 523 **10**).

Compounds **9** and **10** crystallize in the monoclinic space group $P2_1/c$ (**9**) and $P2_1/n$ (**10**). Central units of the heterocycles are the six-membered ring (**9**), which adopts a distorted twist-boat conformation, and the planar four-membered ring (**10**). The Ga and Sb atoms reside in distorted tetrahedral environments. The ring size of the Ga−Sb heterocycles **9** and **10** in the solid state depends on the steric bulk of the substituents. Small Me groups lead to the formation of a six-membered ring (**9**), while the somewhat larger Et groups favor the formation of a four-membered ring (**10**). Analogous results were observed in compounds with different sterical demand of the group 13 element substituent.[31] The Ga−Sb bond distances in **9** range from 2.713(1) to 2.751(1) Å, which is slightly elongated compared to those found in $[Me_2GaSb(SiMe_3)_2]_3$ (2.677(1)−2.714(1) Å)[1a] and $[Cl_2GaSb(t\text{-}Bu)_2]_3$ (2.659(1)−2.662(1) Å).[32] As expected, the Ga−Sb bond lengths within the four-membered ring (**10**) are elongated (2.731(1)−2.735(1) Å). They are comparable to those of $[Et_2GaSb(SiMe_3)_2]_2$ (2.718(1), 2.729(1) Å)[33] and $[(t\text{-}Bu)_2GaSb(SiMe_3)_2]_2$ (2.765(1), 2.768(1) Å),[34] the only structurally characterized four-membered Ga_2Sb_2 rings, so far. Compared to the bisadducts **2** and **8**, the Ga−Sb bond distances are significantly shortened. In contrast, the Ga−C (average 2.028 Å **9**; 2.019 Å **10**) and Sb−C bond lengths (average 2.156 Å **9**; 2.166 Å **10**) in **9** and **10** are almost the same as those in **2** and **8**. The C−Sb−C bond angles are relatively small (96.6° **9** (average); 97.8(2)° **10**), while the sterically crowding *t*-Bu groups lead to wide C−Ga−C bond angles (119.5° **9** (average); 123.4(2)° **10**). The Ga−Sb−Ga (127.3(1)−133.3(1)° **9**; 96.6(1)° **10**) and Sb−Ga−Sb bond angles (96.7(1)−102.8(1)° **9**; 83.4(1)° **10**) are comparable to those of similar group 13/15 four- and six-membered rings.

4. Conclusions

Eight group 13-distibane bisadducts of the type $[Sb_2R_4][MR'_3]_2$ (M = Al, Ga) have been synthesized for the first time by reaction of distibanes Sb_2R_4 with trialkylalanes and -gallanes in the absence of solvent.

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[26] The covalent radii of Al (1.25 Å) and Ga (1.26 Å) are almost the same. Holleman, A. F.; Wiberg, E. In *Lehrbuch der Anorganischen Chemie*, 101st ed.; Walter de Gruyter: Berlin, 1995; 1838 ff.

[27] Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992−1007.

[28] (a) Cowley, A. H.; Jones, R. A.; Nunn, C. M.; Westmoreland, D. L. *Chem. Mater.* **1990**, *2*, 221−222. (b) Park, H. S.; Schulz, S.; Wessel, H.; Roesky, H. W. *Chem. Vap. Deposition* **1999**, *5*, 179−184.

[29] This is supported by the NMR studies which show only slight differences of the chemical shift of the pure group 13 trialkyls compared to those of the bisadducts, indicating **1**−**8** to be extensively dissociated in solution.

[30] The solvent of the remaining solution was evacuated in vacuo to give an oily residue. ^{1}H and ^{13}C NMR spectra showed signals that correspond to those of **9** and **10**, respectively. In addition, signals due to $Me_2Sb(t\text{-}Bu)$ and $Et_2Sb(t\text{-}Bu)$ were observed.

[31] See for example: (a) Schulz, S.; Nieger, M. *Organometallics* **1998**, *17*, 3398−3400. (b) Schulz, S.; Nieger, M. *Organometallics* **2000**, *19*, 699−702.

[32] Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M.; Westmoreland, D. L. *J. Organomet. Chem.* **1988**, *341*, C1−C5.

[33] Foos, E. E.; Jouet, R. J.; Wells, R. L.; Rheingold, A. L.; Liable-Sands, L. M. *J. Organomet. Chem* **1999**, *582*, 45−52.

[34] Wells, R. L.; Foos, E. E.; White, P. S.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 4771−4775.

Four bisadducts have been structurally characterized by single-crystal X-ray diffraction studies. So prepared bisadducts are stable compounds in the pure form and can be stored at 0 °C without decomposition. However, in solution consecutive reactions occur. They react under Sb−Sb and M−C bond cleavage to form heterocycles of the type $[R_2SbMR'_2]_x$ and mixed stibanes of the type R_2SbR'. Depending on the sterical demand of the substituent bound to the Sb atom, four- and six-membered rings, respectively, were obtained in good yields. This reaction scheme offers an alternative pathway for the synthesis of MSb heterocycles. Its generality concerning the formation of Al−Sb and In−Sb heterocycles is currently under investigation.

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **1**, **2**, **5**, and **8**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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