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Reactions of Group 13 Organometallics tBu$_3$M with Distibanes Sb$_2$R$_4$

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Tetraalkyldistibanes Sb$_2$R$_4$ (R = *n*Pr, *i*Bu) react with tBu$_3$M (M = Al, Ga) at –30 °C with the formation of the Lewis acid–base adducts [tBu$_3$M]$_2$[Sb$_2$R$_4$] [M = Al, R = *n*Pr (**1**), *i*Bu (**2**); M = Ga, R = *n*Pr (**3**), *i*Pr **4**)]. Compounds **1** and **2** are stable in solution whereas **3** undergoes a Sb–Sb bond-breakage reaction with the subsequent formation of [tBu$_2$GaSb(*n*Pr)$_2$]$_2$ (**5**). The same trend was observed for the reaction of Sb$_2$(*i*Bu)$_4$ with tBu$_3$Ga, which yielded the heterocyclic stibanylgallane [tBu$_2$GaSb(*i*Bu)$_2$]$_2$ (**6**). In addition, the simple trialkylstibane adduct tBu$_3$Al–Sb(*i*Bu)$_3$ (**7**) was obtained as a byproduct from the reaction of Sb$_2$(*i*Bu)$_4$ with tBu$_3$Al. Compounds **1**–**7** were characterized by multinuclear NMR (^{1}H, ^{13}C{^{1}H}) and mass spectroscopy and elemental analysis. Compounds **1**, **3**, **5**, and **7** were also investigated by single-crystal X-ray diffraction.

Introduction

Lewis basic tetraalkyldipenteles R′$_2$E–ER′$_2$ (E = N to Bi) are capable of acting as monodentate[1] or bidentate ligands[2] as was shown in several reactions with transition metal complexes.[3] Surprisingly, reactions with main group Lewis acids such as group 13 organometallics MR$_3$ (M = B to Tl) have been studied to a far lesser extent even though Lewis acid–base adducts of trialkylpenteles ER′$_3$ are long known in group 13/15 chemistry. Only two diphosphane-borane adducts ([Me$_4$P$_2$][BH$_3$]$_2$ and [Me$_4$P$_2$][BH$_2$Br]$_2$)[4] have been structurally characterized prior to our studies. We started to investigate reactions of distibanes R′$_2$Sb–SbR′$_2$ and dibismuthines R′$_2$Bi–BiR′$_2$ with group 13 organometallics MR$_3$ (M = Al, Ga, In) because of our general interest in group 13/15 chemistry. These reactions typically yielded bisadducts of the type [R$_3$M]$_2$[E$_2$R′$_4$] (M = Al, Ga; E = Sb,[5] Bi[6]), with the dipenteles serving as bidentate ligands. Only tetraisopropyldistibane was found to form the monoadduct [tBu$_3$Al][Sb$_2$(*i*Pr)$_4$] when reacted with tBu$_3$Al, most likely because of the increased repulsive interactions caused by the bulky *i*Pr substituents.[7] The distibane alane adducts [R$_3$Al]$_2$[Sb$_2$R′$_4$] were found to be stable in their pure form and in solution,[8] whereas the corresponding gallane and indane adducts [R$_3$M]$_2$[Sb$_2$R′$_4$] (M = Ga, In) tended to undergo Sb–Sb bond-breakage reactions in solution with the subsequent formation of heterocyclic stibanylgallanes and -indanes [R$_2$MSbR′$_2$]$_x$ (x = 2, 3). Comparable findings have previously been observed by Breunig et al. in reactions with main group[9] and transition metal complexes.[10]

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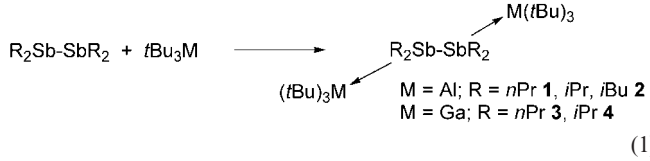
Because of our interest in completely alkyl-substituted heterocycles [R$_2$MSbR′$_2$]$_x$, which are promising candidates for the deposition of MSb thin films by the MOCVD process (metal organic chemical vapor deposition),[11] we extended our studies to the reaction of Sb$_2$R′$_4$ (R′ = *n*Pr, *i*Pr, *i*Bu) with trialkylalanes and gallanes MR$_3$. The influence of the organic ligand on the stability of the initially formed distibane adducts was of particular interest.

Results and Discussion

In order to establish the distibane 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) and to verify the influence of both the central group 13 metal and the organic ligands bound to the metal centers on the formation of the M–Sb heterocycles, reactions of three different distibanes Sb$_2$R$_4$ (R = *n*Pr, *i*Pr, *i*Bu) with tBu$_3$Al and tBu$_3$Ga, respectively, were investigated. The reaction of Sb$_2$(*i*Pr)$_4$ with tBu$_3$Al was previously shown to yield [tBu$_3$Al][Sb$_2$(*i*Pr)$_4$].[7]

Reactions of Sb$_2$R$_4$ (R′ = *n*Pr, *i*Pr, *i*Bu) with tBu$_3$M (M = Al, Ga) yielded Lewis acid–base adducts [tBu$_3$M]$_2$[Sb$_2$R$_4$] [M = Al, R = *n*Pr (**1**), *i*Bu (**2**); M = Ga, R = *n*Pr (**3**), *i*Pr (**4**)], which were isolated as light-yellow, crystalline solids after crystallization from solutions in pentane at –40 °C [Equation (1)].



(1)

^{1}H NMR spectra of **1**–**4** show resonances from the organic ligands in a 2:3 molar ratio as was expected from the formation of the bisadducts $[t\mathrm{Bu_3M}]_2[\mathrm{Sb_2R_4}]$. The Sb centers in the distibane adducts are prochiral, leading to two separated sets of resonances of the diasterotropic α-CH_2 protons of the *n*Pr and *i*Bu groups in **1**, **2**, and **3**. Mass spectra of **1**–**4** only show signals arising from the dissociation into Sb_2R_4 and $t\mathrm{Bu_3M}$ as well as from typical fragmentation reactions. Single crystals of **1** suitable for an X-ray structure determination were obtained from a solution in pentane at –30 °C. In addition, the trialkylstibane adduct $t\mathrm{Bu_3Al–Sb}(i\mathrm{Bu})_3$ (**7**) was isolated from the reaction of $t\mathrm{Bu_3Al}$ with $\mathrm{Sb}_2(i\mathrm{Bu})_4$, which was contaminated with $\mathrm{Sb}(i\mathrm{Bu})_3$ (about 10%) as was shown by NMR spectroscopy. Figure 1, Figure 2 and Figure 3 show solid-state structures of **1**, **3**, and **7**, respectively [Equation (2)].

$$\mathrm{R_2Sb\text{-}SbR_2} + t\mathrm{Bu_3Ga} \xrightarrow[-t\mathrm{BuSbR_2}]{} 1/2\,[t\mathrm{Bu_2GaSbR_2}]_2 \quad \mathrm{R} = n\mathrm{Pr}\ \mathbf{5},\ i\mathrm{Bu}\ \mathbf{6} \tag{2}$$

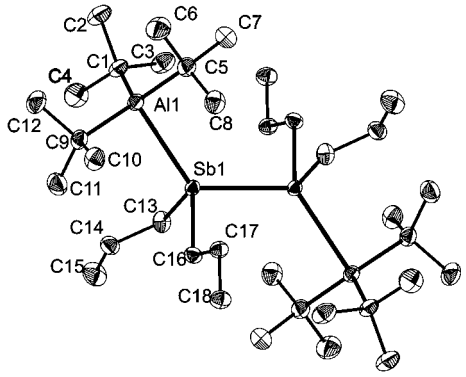


Figure 1. ORTEP plot (50% probability level; H omitted for clarity) showing the solid-state structure and atom-numbering scheme for **1**. Selected bond lengths [Å] and angles [°]: Sb1–Sb1a 2.839(1), Sb1–Al1 2.964(1), Al1–C1 2.009(2), Al1–C5 2.018(2), Al1–C9 2.038(2), Sb1–C13 2.158(2), Sb1–C16 2.153(2), C1–Al1–C5 116.5(1), C1–Al1–C9 117.1(1), C5–Al1–C9 116.6(1), C13–Sb1–C16 96.4(1), C13–Sb1–Sb1a 97.1(1), C16–Sb1–Sb1a 98.7(1), Sb1a–Sb1–Al1 126.8(2).

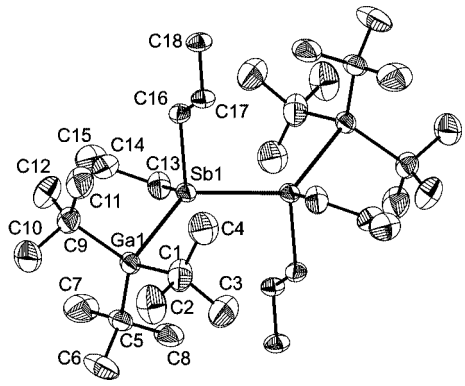


Figure 2. ORTEP plot (50% probability level; H omitted for clarity) showing the solid-state structure and atom-numbering scheme for **3**. Selected bond lengths [Å] and angles [°]: Sb1–Sb1a 2.822(1), Sb1–Ga1 2.988(1), Ga1–C1 2.056(5), Ga1–C5 2.030(4), Ga1–C9 2.033(4), Sb1–C13 2.172(4), Sb1–C16 2.160(3), C1–Ga1–C5 116.5(2), C1–Ga1–C9 116.7(2), C5–Ga1–C9 117.3(2), C13–Sb1–C16 96.2(2), C13–Sb1–Sb1a 97.1(1), C16–Sb1–Sb1a 97.4(1), Sb1a–Sb1–Ga1 127.5(2).

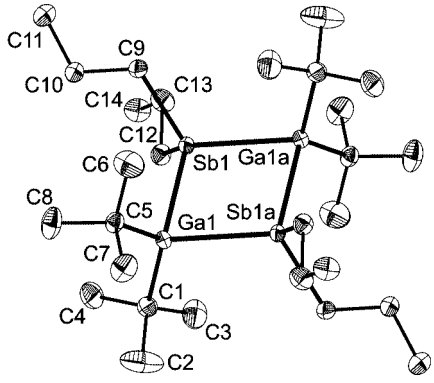


Figure 3. ORTEP plot (50% probability level; H omitted for clarity) showing the solid-state structure and atom-numbering scheme for **7**. Al1–Sb1 2.903(2), Sb1–C1 2.159(4), Sb1–C5 2.153(4), Sb1–C9 2.157(4), Al1–C13 2.028(4), Al1–C17 2.016(5), Al1–C21 2.013(4); C1–Sb1–C5 106.91(16), C1–Sb1–C9 95.84(15), C5–Sb1–C9 99.61(16), C13–Al1–C17 116.20(19), C13–Al1–C21 115.96(18), C17–Al1–C21 115.01(18).

Compounds **1** and **3** crystallize in the monoclinic space group $P2_1/n$ (No. 14) and **7** in $P2_1/c$ (No. 14), respectively. Compounds **1** and **3** possess crystallographic C_i symmetry with the center of symmetry at the Sb–Sb bond. The central Sb–Sb bond lengths observed in **1** [2.839(1) Å] and **3** [2.822(5) Å] are almost identical to those of pure distibanes Sb_2R_4 {R = Me 2.862(2) Å,[12] 2.830(1), 2.838(1) Å;[13] *t*Bu 2.817(1) Å;[14] Ph 2.844(1) Å;[15] $SiMe_3$ 2.867(1) Å;[15] $SnMe_3$ 2.866(1) Å[16]}. There is no sign of any Sb–Sb bond weakening upon coordination to Lewis acidic $t\mathrm{Bu_3M}$. Comparable findings have been previously observed for other distibane adducts $[t\mathrm{Bu_3Al}]_x[\mathrm{Sb_2R_4}]$ [R = Me 2.811(1),[5] Et 2.838(1),[5] *i*Pr 2.855(1) Å[7]]. The most significant structural change of the distibane moiety due to the adduct formation is the increase of the degree of pyramidalization of the central Sb atoms. The sums of the C–Sb–C and C–Sb–Sb bond angles observed for **1** (292.2°) and **3** (290.6°) are significantly increased compared with uncomplexed distibanes such as Me_4Sb_2 (283.1°), resulting from 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 electrons pairs. The Al–Sb bond length observed for **1** [2.964(1) Å] is elongated compared to that of $[t\mathrm{Bu_3Al}]_2[\mathrm{Sb_2Me_4}]$ [2.919(1) Å],[5] whereas $[t\mathrm{Bu_3Al}]_2[\mathrm{Sb_2Et_4}]$ [3.001(1) Å][5] and $[t\mathrm{Bu_3Al}][\mathrm{Sb}_2(i\mathrm{Pr})_4]$ [3.003(2) Å][7] exhibit slightly longer intermetallic Al–Sb distances. In particular the longer Al–Sb distance of $[t\mathrm{Bu_3Al}]_2[\mathrm{Sb_2Et_4}]$ is somehow surprising since repulsive interactions between the organic substituents were expected to be more pronounced for the *n*Pr substituents than the sterically slightly less demanding Et substituents. Comparable trends are observed for gallane adduct **3** [2.988(1) Å], which shows a slightly shorter inter-

metallic Ga–Sb bond length compared with $[t\mathrm{Bu_3Ga}]_2$-$[\mathrm{Sb_2Et_4}]$ [3.022(1) Å], whereas that observed for $[t\mathrm{Bu_3Ga}]_2$-$[\mathrm{Sb_2Me_4}]$ [2.919(1) Å] is significantly shorter. The Al–Sb bond length of **7** [2.903(2) Å] is slightly shorter than that of **1** and in between those observed for $t\mathrm{Bu_3Al–SbEt_3}$ [2.845(1)] and $t\mathrm{Bu_3Al–Sb}(i\mathrm{Pr})_3$ [2.927(1) Å]. The average Al–C bond lengths [average values of **1** (2.022) and **7** (2.019 Å)] and C–Al–C bond angles [**1** (116.7°) and **7** (115.7°)] are comparable to those of previously reported alane adducts of trialkylstibanes.[17]

Distibane adducts of trialkylgallanes and -indanes have been previously found to tend to undergo consecutive Sb–Sb bond-cleavage reactions in solution with subsequent formation of heterocyclic stibanylgallanes and -indanes $[\mathrm{R_2MSbR'_2}]_x$, whereas the corresponding Al–Sb heterocycles were not formed.[5,7] The same trends were observed for the distibane adducts **1**–**4**. Alane adducts **1** and **2** remained unchanged in solutions of pentane or hexane and can be stirred for days without any sign of decomposition whereas $t\mathrm{Bu_3Ga}$ reacts with $\mathrm{Sb_2R_4}$ (R = *i*Pr, *i*Bu) with almost quantitative formation of the corresponding Ga–Sb heterocycles $[t\mathrm{Bu_2GaSb}(n\mathrm{Pr})_2]_2$ (**5**) and $[t\mathrm{Bu_2GaSb}(i\mathrm{Bu})_2]_2$ (**6**) within four days.[18] In contrast, the reaction of $t\mathrm{Bu_3Ga}$ with $\mathrm{Sb_2}(i\mathrm{Pr})_4$ proceeds much slower. Even after the reaction mixture was stirred for 10 days there is still some distibane adduct **4** detectable in solution. Unfortunately, $[t\mathrm{Bu_2GaSb}(i\mathrm{Pr})_2]_2$ could not be isolated from byproducts, to date, but its formation is clearly indicated by NMR spectroscopy. Obviously, the steric demand of the organic substituents bound to the Sb centers plays the key role for the required reaction time. Sterically less hindered distibanes such as $\mathrm{Sb_2Me_4}$ and $\mathrm{Sb_2Et_4}$ react with $t\mathrm{Bu_3Ga}$ within two days with almost quantitative formation of the corresponding stibanylgallanes $[t\mathrm{Bu_2GaSbMe_2}]_3$ and $[t\mathrm{Bu_2GaSbEt_2}]_2$,[5] whereas the formation of **5** and **6** requires longer reaction times. Compounds **5** and **6** were obtained as colorless crystalline solids in almost quantitative yields, which were recrystallized from solutions in hexane.

^{1}H and ^{13}C NMR spectra of **5** and **6** show resonances of the organic ligands in the expected 1:1 molar ratio. Since the Sb centers in the distibane adducts are no longer prochiral only a single resonance of the α-CH_2 protons of the *n*Pr and *i*Bu groups occurs. The mass spectra of **5** and **6** show typical fragmentation patterns of the heterocycles, whereas no molecular ion peak could be detected. Suitable crystals of **5** for a single-crystal X-ray diffraction study were obtained from a solution in hexane at –30 °C. (Figure 4).

Compound **5** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) and adopts a planar four-membered ring. The metal atoms reside in distorted tetrahedral environments. The Ga–Sb bond lengths [2.736(1), 2.738(1) Å] are almost identical to those observed for $[t\mathrm{Bu_2GaSbEt_2}]_2$ [2.731(1)–2.735(1) Å] and $[\mathrm{Et_2GaSb(SiMe_3)_2}]_2$ [2.718(1), 2.729(1) Å],[19] whereas $[t\mathrm{Bu_2GaSb(SiMe_3)_2}]_2$ [2.768(1) Å][20] shows slightly longer Ga–Sb distances due to increased repulsive interactions between the sterically more demanding organic substituents. The C–Sb–C bond angles [97.3(2)°] are smaller than the C–Ga–C bond angles [122.2(2)°] as is typical for this type of compound and the Ga–C [2.016(4), 2.011(3) Å] and Sb–C bond lengths [2.161(3), 2.166(3) Å] are within typical ranges.

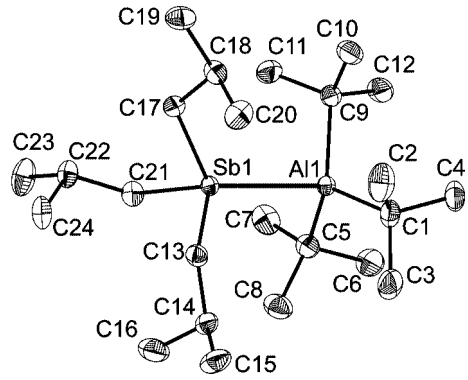


Figure 4. ORTEP plot (50% probability level; H omitted for clarity) showing the solid-state structure and atom-numbering scheme for **5**. Ga1–Sb1 2.736(1), Ga1a–Sb1 2.738(1), Sb1–C9 2.161(3), Sb1–C12 2.166(3), Ga1–C1 2.016(4), Ga1–C5 2.011(3), Sb1–Ga1–Sb1a 83.4(1), Ga1–Sb1–Ga1a 96.6(1), C9–Sb1–Ga1 117.1(1), C12–Sb1–Ga1 113.8(1), C1–Ga1–Sb1 108.8(1), C5–Ga1–Sb1 113.4(1), C1–Ga1–C5 122.2(2), C9–Sb1–C12 97.3(2).

Conclusions

Distibanes $\mathrm{Sb_2R_4}$ (R = *n*Pr, *i*Pr, *i*Bu) react with trialkylalanes and -gallanes $t\mathrm{Bu_3M}$ with the initial formation of Lewis acid–base adducts $[t\mathrm{Bu_3M}]_2[\mathrm{Sb_2R_4}]$. The gallane adducts were found to tend to undergo Sb–Sb bond-cleavage reactions with the subsequent formation of heterocyclic stibanylgallanes $[t\mathrm{Bu_2GaSbR_2}]_2$, whereas the alane adducts remained unchanged in solution.

Experimental Section

General: All manipulations were performed in a glovebox under an Ar atmosphere or by standard Schlenk techniques. $t\mathrm{Bu_3Al}$,[21] $t\mathrm{Bu_3Ga}$,[22] $\mathrm{Sb_2}(n\mathrm{Pr})_4$,[23] $\mathrm{Sb_2}(i\mathrm{Pr})_4$,[23] and $\mathrm{Sb_2}(i\mathrm{Bu})_4$[23] were prepared according to literature methods. ^{1}H and ^{13}C{^{1}H} spectra were recorded using a Bruker Avance 500 spectrometer and are referenced to internal C_6D_5H (^{1}H NMR: δ = 7.154, ^{13}C NMR: δ = 128.0 ppm). Melting points were measured in sealed capillaries and are not corrected. Mass spectra (EI) were recorded with a Finnigan MAT 8230 spectrometer. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the Elementaranalyse Labor of the University of Paderborn. Yields are given for the pure products after recrystallization.

Synthesis of $[t\mathrm{Bu_3M}]_2[\mathrm{Sb_2R_4}]$: $t\mathrm{Bu_3M}$ (1 mmol) and $\mathrm{Sb_2R_4}$ (0.5 mmol) were combined in the glovebox, and the resulting yellow oil was dissolved in *n*-pentane (5 mL) and stored at –40 °C. Light yellow crystals of **1**–**4** were formed within 2 d. Yields are given for isolated compounds after recrystallization.

$[t\mathrm{Bu_3Al}]_2[\mathrm{Sb_2}(n\mathrm{Pr})_4]$ (1): Yield 0.22 g, 0.35 mmol, 70%. M.p. 85 °C. $C_{36}H_{82}Al_2Sb_2$ (812.51): calcd. C 53.2, H 10.2; found C 54.2, H 9.5. ^{1}H NMR (500 MHz; C_6D_5H, 25 °C): δ = 0.89 [t, $^3J_{H,H}$ = 7.2 Hz, 12 H, $CH_3CH_2CH_2Sb$], 1.22 [s, 54 H, Me_3CAl], 1.53–1.62 [m, 8 H, $CH_3CH_2CH_2Sb$], 1.75–1.81 [m, 4 H, $CH_3CH_2CH_2Sb$], 1.88–1.93

[m, 4 H, $CH_3CH_2CH_2Sb$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz; C_6D_5H, 25 °C): δ = 13.4 (s, *Me*CH_2CH_2Sb), 17.8 [s, Me*CH*$_2CH_2Sb$], 19.5 [s, Me_3CAl], 23.1 [s, $MeCH_2CH_2Sb$], 31.9 [s, *Me*$_3$CAl] ppm. EI-MS (70 eV, 70 °C): *m*/*z* (%) = 416 (35) $[Sb_2(nPr)_4]^+$, 375 (5) $[Sb_2(nPr)_3]^+$, 331 (25) $[Sb_2(nPr)_2]^+$, 288 (40) $[Sb_2(nPr)H]^+$, 141 (35) $[tBu_2Al]^+$, 84 (5) $[tBuAl]^+$, 57 (100) $[tBu]^+$.

[*t*Bu$_3$Al]$_2$[Sb$_2$(*i*Bu)$_4$] (2): Yield 0.40 g, 0.46 mmol, 92%. M.p. < 0 °C. $C_{40}H_{90}Al_2Sb_2$ (868.61): calcd. C 55.3, H 10.4; found C 56.1, H 10.2. ^1H NMR (500 MHz; C_6D_5H, 25 °C): δ = 1.00 [d, $^3J_{H,H}$ = 7.2 Hz, 24 H, $(CH_3)_2CHCH_2Sb$], 1.14 [s, 54 H, *Me*$_3$CAl], 1.75–1.78 [m, $^3J_{H,H}$ = 6.7 Hz, 4 H, $(CH_3)_2CHCH_2Sb$], 1.93 [sept, $^3J_{H,H}$ = 6.7 Hz, 4 H, $(CH_3)_2CHCH_2Sb$], 2.01–2.05 [m, $^3J_{H,H}$ = 6.7 Hz, 4 H, $(CH_3)_2CHCH_2Sb$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz; C_6D_5H, 25 °C): δ = 22.8 [s, Me_2CHCH_2Sb], 25.7 [s, *Me*$_2$CHCH$_2$Sb], 27.7 [s, Me$_3$*C*Al], 29.1 [s, Me_2CHCH_2Sb], 30.8 [s, *Me*$_3$CAl] ppm.

[*t*Bu$_3$Ga]$_2$[Sb$_2$(*n*Pr)$_4$] (3): Yield 0.28 g, 0.31 mmol, 62%. M.p. 37 °C. $C_{36}H_{82}Ga_2Sb_2$ (897.98) calcd. C 48.2, H 9.2; found C 47.1, H 8.8. ^1H NMR (500 MHz; C_6D_5H, 25 °C): δ = 0.93 [t, $^3J_{H,H}$ = 7.2 Hz, 12 H; $CH_3CH_2CH_2Sb$], 1.26 [s, 54 H, *Me*$_3$CGa], 1.62 [m, 8 H, $CH_3CH_2CH_2Sb$], 1.71–1.77 [m, 4 H, $CH_3CH_2CH_2Sb$], 1.84–1.88 [m, 4 H, $CH_3CH_2CH_2Sb$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz; C_6D_5H, 25 °C): δ = 13.1 [s, Me*CH*$_2$CH$_2$Sb], 18.2 [s, *Me*CH$_2$CH$_2$Sb], 23.7 [s, $MeCH_2CH_2Sb$], 29.7 [s, Me$_3$*C*Ga], 31.9 [s, *Me*$_3$CGa] ppm.

[*t*Bu$_3$Ga]$_2$[Sb$_2$(*i*Pr)$_4$] (4): Yield 0.42 g, 0.47 mmol, 94%. M.p. < 0 °C. $C_{36}H_{82}Ga_2Sb_2$ (897.98) calcd. C 48.2, H 9.2; found C 47.1, H 8.9. ^1H NMR (500 MHz; C_6D_5H, 25 °C): δ = 1.18 [s, 54 H, *Me*$_3$CGa], 1.42 [d, $^3J_{H,H}$ = 7.3 Hz, 12 H, $(CH_3)_2CHSb$], 1.49 [d, $^3J_{H,H}$ = 7.3 Hz, 12 H, $(CH_3)_2CHSb$], 2.31 [sept, 4 H, $(CH_3)_2CHSb$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz; C_6D_5H, 25 °C): δ = 13.9 [s, Me$_2$*CH*Sb], 24.7 [s, *Me*$_2$CHSb], 25.6 [s, *Me*$_2$CHSb], 30.7 [s, *Me*$_3$CGa] ppm.

General Synthesis of [tBu$_2$GaSbR$_2$]$_2$: Sb_2R_4 (1 mmol) was added to a solution of *t*Bu$_3$Ga (1.5 mmol, 0.35 g) dissolved in hexane (10 mL). The resulting yellow solution was stirred for 4 d at ambient temperature. Storage at –30 °C under the absence of light yielded colorless crystals of **5** and **6** within 12 h.

[*t*Bu$_2$GaSb(*n*Pr)$_2$]$_2$ (5): Yield 0.30 g, 0.39 mmol, 78%. M.p. 160 °C. $C_{28}H_{64}Ga_2Sb_2$ (783.75) calcd. C 42.9, H 8.2; found C 42.2, H 8.1. ^1H NMR (500 MHz; C_6D_5H, 25 °C): δ = 0.95 [t, $^3J_{H,H}$ = 7.3 Hz, 12 H, $CH_3CH_2CH_2Sb$], 1.34 [s, 36 H, *Me*$_3$CGa], 1.66–1.73 [m, 8 H, $CH_3CH_2CH_2Sb$], 2.05–2.08 [m, 8 H, $CH_3CH_2CH_2Sb$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz; C_6D_5H, 25 °C): δ = 9.9 [s, $MeCH_2CH_2Sb$], 18.3 [s, *Me*CH$_2$CH$_2$Sb], 24.1 [s, Me*CH*$_2$CH$_2$Sb], 28.5 [s, Me$_3$*C*Ga], 32.2 [s, *Me*$_3$CGa] ppm. EI-MS (70 eV, 70 °C): *m*/*z* (%) = 527 (8) $[GaSb_2(nPr)tBu_3]^+$, 416 (30) $[Sb_2(nPr)_4]^+$, 345 (30) $[Sb_2(nPr)tBuH]^+$, 288 (40) $[Sb_2(nPr)H]^+$, 57 (100) $[tBu]^+$.

[*t*Bu$_2$GaSb(*i*Bu)$_2$]$_2$ (6): Yield 0.36 g, 0.43 mmol, 86%. M.p. 162 °C (dec.). $C_{32}H_{72}Ga_2Sb_2$ (839.86): calcd. C 45.8, H 8.6; found C 45.2; H, 8.5. ^1H NMR (500 MHz; C_6D_5H, 25 °C): δ = 1.06 [d, $^3J_{H,H}$ = 6.3 Hz, 24 H, $(CH_3)_2CHCH_2Sb$], 1.39 [s, 36 H, *Me*$_3$CGa], 2.15 [m, 4 H, $(CH_3)_2CHCH_2Sb$], 2.22 [d, $^2J_{H,H}$ = 7.2 Hz, 8 H, $(CH_3)_2CHCH_2Sb$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz; C_6D_5H, 25 °C): δ = 19.7 [s, $(CH_3)_2CHCH_2Sb$], 25.3 [s, $(CH_3)_2CHCH_2Sb$], 29.2 [s, Me$_3$*C*Ga], 29.9 [s, $(CH_3)_2CHCH_2Sb$], 32.1 [s, *Me*$_3$CGa] ppm. EI-MS (70 eV, 100 °C): *m*/*z* (%) = 472 (20) $[Sb_2(iBu)]^+$, 420 (15) $[tBu_2GaSb(iBu)_2]^+$, 363 (40) $[GaSb(i/tBu)_3]^+$, 307 (35) $[GaSb(i/tBu)_2]^+$, 251 (15) $[GaSb(i/tBu)]^+$, 236 (5) $[iBu_2Sb]^+$, 183 (65) $[tBu_2Ga]^+$, 178 (15) $[iBuSb]^+$, 127 (25) $[tBuGa]^+$, 69 (55) $[Ga]^+$, 57 (100) $[i/tBu]^+$.

***t*Bu$_3$Al–Sb(*i*Bu)$_3$ (7):** Compound **7** was obtained in the form of colorless crystals as a byproduct from the reaction of *t*Bu$_3$Al with $Sb_2(iBu)_4$, which contained about 10% Sb(*i*Bu)$_3$ according to NMR spectroscopic studies. Compound **7** was also independently prepared by the reaction of *t*Bu$_3$Al (1.5 mmol, 0.18 g) with Sb(*i*Bu)$_3$ (1.5 mmol, 0.28 g). Yield 0.23 g, 0.5 mmol, 50%. M.p. 47 °C. $C_{24}H_{54}AlSb$ (491.42): calcd. C 58.7, H 11.1; found C 57.3, H 10.9. ^1H NMR (500 MHz; C_6D_5H, 25 °C): δ = 0.96 [d, $^3J_{H,H}$ = 6.6 Hz, 18 H, $(CH_3)_2CHCH_2Sb$], 1.18 [s, 27 H, *Me*$_3$CAl], 1.49 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, $(CH_3)_2CHCH_2Sb$], 1.90 [sept, $^3J_{H,H}$ = 6.6 Hz, 3 H, $(CH_3)_2CHCH_2Sb$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz; C_6D_5H, 25 °C): δ = 20.4 [s, Me$_3$*C*Al], 26.0 [s, *Me*$_2$CHCH$_2$Sb], 27.6 [s, Me$_2$CH*CH*$_2$Sb], 27.8 [s, Me$_2$*CH*CH$_2$Sb], 31.4 [s, *Me*$_3$CAl] ppm.

Table 1. Crystallographic data for [*t*Bu$_3$Al]$_2$[Sb$_2$(*n*Pr)$_4$] (**1**), [*t*Bu$_3$Ga]$_2$[Sb$_2$(*n*Pr)$_4$] (**3**), [*t*Bu$_2$GaSb(*n*Pr)$_2$]$_2$ (**5**), and *t*Bu$_3$Al–Sb(*i*Bu)$_3$ (**7**).

	[*t*Bu$_3$Al]$_2$[Sb$_2$(*n*Pr)$_4$] (**1**)	[*t*Bu$_3$Ga]$_2$[Sb$_2$(*n*Pr)$_4$] (**3**)	[*t*Bu$_2$GaSb(*n*Pr)$_2$]$_2$ (**5**)	*t*Bu$_3$Al–Sb(*i*Bu)$_3$ (**7**)
Molecular formula	$C_{36}H_{82}Al_2Sb_2$	$C_{36}H_{82}Ga_2Sb_2$	$C_{28}H_{64}Ga_2Sb_2$	$C_{24}H_{54}AlSb$
Formula mass [g mol^{-1}]	812.48	897.96	783.73	491.40
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	12.916(5)	12.8845(9)	12.4726(8)	10.2575(16)
b [Å]	13.122(5)	13.3124(9)	8.9185(6)	14.503(2)
c [Å]	12.971(5)	12.9979(9)	15.8908(10)	18.631(3)
β [deg]	90.103(2)	91.633(1)	92.574(1)	96.590(3)
V [Å^3]	2198.4(14)	2228.5(3)	1765.9(2)	2753.3(7)
Z	2	2	2	4
μ [mm^{-1}]	1.289	2.415	3.036	1.040
D_{calcd} [g cm^{-3}]	1.227	1.338	1.474	1.185
Crystal dim. [mm]	0.39 × 0.24 × 0.21	0.48 × 0.43 × 0.39	0.43 × 0.09 × 0.08	0.40 × 0.32 × 0.27
Reflections recorded	18798	19346	15141	24588
Nonequiv. reflections recorded	5318	5315	4272	6689
R_{merg}	0.0430	0.0448	0.0469	0.0714
Parameters refined/restraints	181	181	145	235
R_1[a]; wR_2[b]	0.0253; 0.0599	0.0379; 0.1032	0.0343; 0.0699	0.0506; 0.0844
Goodness of fit[c]	1.048	1.064	1.014	0.925
Final max., min. $\Delta\rho$ (e Å^{-3})	1.063, –0.532	0.937, –0.905	0.898, –0.610	0.985, –0.960

[a] $R_1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$ [for $I > 2\sigma(I)$]. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. [c] Goodness of fit = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2] / N_{obs} - N_{param})\}^{1/2}$.

X-ray Structure Solution and Refinement: Crystallographic data of **1**, **3**, **5**, and **7** are summarized in Table 1. Figures 1–4 show ORTEP diagrams of the solid-state structures of **1**, **3**, **5**, and **7**. Data were collected with a Bruker SMART APEX CCD diffractometer[24] using Mo-K_α radiation (λ = 0.71073 Å) at T = 120(2) K and the structures were solved by Direct and Fourier Methods (SHELXTL),[24] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms in **1**, **3**, **5** and **7** were refined anisotropically and hydrogen atoms were located from ΔF maps and refined at idealized positions with a riding model (SHELXTL).

CCDC-623814 (for **1**), -623815 (for **3**), -623816 (for **5**), and -623813 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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