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Reactions of $t\mathrm{Bu_2AlH}$ and $\mathrm{RE(SiMe_3)_2}$ (R = H, $\mathrm{SiMe_3}$) – Synthesis and X-ray Crystal Structures of $[t\mathrm{Bu_2AlP(H)SiMe_3}]_2$ and $[t\mathrm{Bu_2AlE(SiMe_3)_2}]_2$ (E = Sb, Bi)

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Dehydrosilylation reactions between $t\mathrm{Bu_2AlH}$ and $\mathrm{E(SiMe_3)_3}$ yielded the four-membered heterocycles $[t\mathrm{Bu_2AlE(SiMe_3)_2}]_2$ (E = Sb, **1**; Bi, **2**), whereas no reaction was observed with $\mathrm{P(SiMe_3)_3}$. In contrast, the reaction of $t\mathrm{Bu_2AlH}$ with $\mathrm{HP(SiMe_3)_2}$ also proceeds with elimination of $\mathrm{Me_3SiH}$ and subsequent formation of $[t\mathrm{Bu_2AlP(H)SiMe_3}]_2$ (**3**). Complexes **1**–**3** were characterized by multinuclear NMR (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) and mass spectroscopy, elemental analysis, and single-crystal X-ray diffraction.

Introduction

Heterocyclic group 13/15 compounds of the type $[\mathrm{R_2MER'_2}]_x$ have been studied for many years. In particular, amino-, phosphanyl- and arsinoalanes, -gallanes and -indanes $[\mathrm{R_2MER'_2}]_x$ (M = Al, Ga, In; E = N, P, As) have been synthesized in large numbers by standard synthetic procedures such as alkane, hydrogen, and salt elimination reactions and structurally characterized.[1] Unfortunately, these reaction types almost completely failed to synthesize analogous group 13 stibides and bismuthides $[\mathrm{R_2MER'_2}]_x$ (M = Al, Ga, In; E = Sb, Bi).[2] Therefore, alternative synthetic pathways had to be developed. The dehalosilylation reaction, which was introduced by Wells et al. for the synthesis of arsinogallanes in 1986,[3] was found to be suitable for the preparation of stibinogallanes and -indanes,[4] whereas the corresponding stibinoalanes,[5] as well as bismuthinoalanes[6] and -gallanes,[7] were synthesized by the dehydrosilylation reaction. This particular reaction sequence, which was introduced by Nöth et al. for the synthesis of phosphanylboranes $[\mathrm{H_2BPR_2}]_3$,[8] is generally applicable for the synthesis of the desired group 13/15 heterocycles $[\mathrm{R_2MER'_2}]_x$ (M = Al, Ga; E = P, As, Sb, Bi), as the reaction can be performed under kinetically controlled reaction conditions at low reaction temperatures,[9] which were found to be essential for the synthesis of group 13/Bi heterocycles such as $[\mathrm{Me_2GaBi(SiMe_3)_2}]_3$ and $[\mathrm{Me_2InBi(SiMe_3)_2}]_3$.[10] Mechanistic studies on the reactions of $\mathrm{Et_2PSiMe_3}$ with $\mathrm{HAlCl_2}$ and $\mathrm{H_2AlCl}$ clearly demonstrated that the dehydrosilylation reaction is favored over the dehalosilylation reaction.[11] In addition, the reaction of $\mathrm{Me_2AlH}$ with $\mathrm{HP(SiMe_3)_2}$ also proceeds preferably with dehydrosilylation rather than $\mathrm{H_2}$ elimination, even though subsequent transphosphanation reactions resulted in the formation of several $\mathrm{Me_2AlP(SiMe_3)_2}$-containing species such as the trimeric phosphanylalane $[(\mathrm{Me_2Al})_3(\mathrm{P(H)SiMe_3})_2\mathrm{P(SiMe_3)_2}]$, which could be isolated[12] and structurally characterized.[13] In remarkable contrast to these findings, $i\mathrm{Bu_2AlH}$ preferably reacts with $\mathrm{HP(SiMe_3)_2}$ with $\mathrm{H_2}$ elimination and subsequent formation of $[i\mathrm{Bu_2AlP(SiMe_3)_2}]_2$.[14] An analogous reaction sequence was observed for the reaction of $i\mathrm{Bu_2AlH}$ with $\mathrm{Ph_3SiPH_2}$, also yielding the $\mathrm{H_2}$ elimination product $[i\mathrm{Bu_2AlP(H)SiPh_3}]_2$.[15] Obviously, the reaction mode is strongly influenced by the organic substituents bound to the Al atom.

Because of our general interest in group 13/15 chemistry of the heavier group 15 elements (Sb, Bi), we investigated reactions of $t\mathrm{Bu_2AlH}$ with $\mathrm{E(SiMe_3)_3}$ (E = P, Sb, Bi) and $\mathrm{HP(SiMe_3)_2}$ and report herein on the synthesis and single-crystal X-ray analyses of $[t\mathrm{Bu_2AlE(SiMe_3)_2}]_2$ (E = Sb, **1**; Bi, **2**) and $[t\mathrm{Bu_2AlP(H)SiMe_3}]_2$ (**3**), respectively.

Results and Discussion

Equimolar amounts of $t\mathrm{Bu_2AlH}$ and $\mathrm{E(SiMe_3)_3}$ (E = Sb, Bi) react at ambient temperature with elimination of $\mathrm{Me_3SiH}$ and subsequent formation of $[t\mathrm{Bu_2AlE(SiMe_3)_2}]_2$ (E = Sb, **1**; Bi, **2**). In contrast, no reaction was observed with $\mathrm{P(SiMe_3)_3}$, even at 180 °C.[16] Complex **2** was formed in only 25% yield because of decomposition reactions with subsequent formation of $\mathrm{Bi_2(SiMe_3)_4}$, which has been previously shown to be the typical decomposition product of $[\mathrm{Me_2MBi(SiMe_3)_2}]_3$ (M = Al,[6] Ga,[7] In[10]). To the best of our knowledge, **2** represents only the second structurally characterized heterocyclic bismuthinoalane to date [Equation (1)].

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$$2\ t\mathrm{Bu_2AlH} + 2\ \mathrm{E(SiMe_3)_3} \xrightarrow[-\,2\ \mathrm{Me_3SiH}]{} [t\mathrm{Bu_2AlE(SiMe_3)_2}]_2 \qquad \mathrm{E = Sb}\ \mathbf{1},\ \mathrm{Bi}\ \mathbf{2} \qquad (1)$$

Complexes **1** and **2** were characterized in detail by multinuclear NMR spectroscopy. ^{1}H and ^{13}C{^{1}H} NMR spectra of both compounds each show two sets of resonances due to the organic substituents (tBu, SiMe$_3$). Mass spectra of **1** and **2** do not show the molecular ion peaks. The peak with the highest mass observed in both spectra corresponds to the monomeric unit (M$^+$/2).

Single crystals of **1** and **2** suitable for X-ray structure determination were obtained from solutions in toluene at –40 °C (Figures 1 and 2).

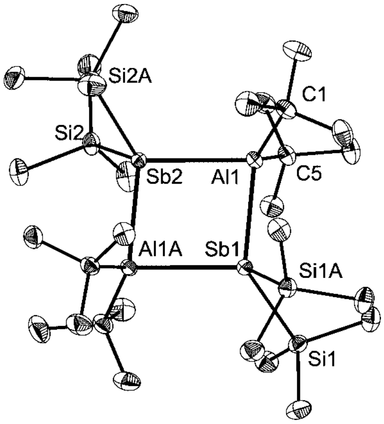

Figure 1. ORTEP plot (50% probability level; H omitted for clarity) showing the solid-state structure and atom-numbering scheme for **1**. Selected bond lengths [Å] and angles [°]: Al1–Sb1 2.786(1), Al1–Sb2 2.781(1), Sb1–Si1 2.587(1), Sb1–Si1A 2.587(1), Al1–C1 2.004(2), Al1–C5 2.005(2); Al1–Sb1–Al1A 94.1(1), Al1–Sb2–Al1A 94.3(1), Sb1–Al1–Sb2 85.8(1), C1–Al1–C5 117.5(1), Si1–Sb1–Si1A2 96.7(1), Si2–Sb2–Si2A2 96.2(1).

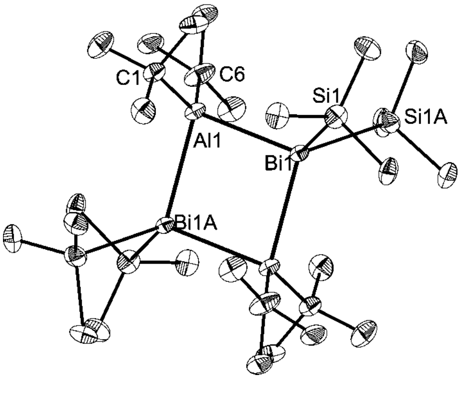

Figure 2. ORTEP plot (50% probability level; H omitted for clarity) showing the solid-state structure and atom-numbering scheme for **2**. Selected bond lengths [Å] and angles [°]: Al1–Bi1 2.840(2), Al1–Bi1A 2.840(2), Bi1–Si1 2.660(2), Bi1–Si1A 2.660(2), Al1–C1 2.008(7), Al1–C6 1.999(8); Al1–Bi1–Al1A 94.1(1), Al1–Bi2–Al1A 95.9(1), Bi1–Al1–Bi1A 84.1(1), C1–Al1–C6 118.9(3), Si1–Bi1–Si1A2 95.6(1).

Complexes **1** and **2** crystallize in the monoclinic space group *C*2/*c* (no. 15) **1** and *C*2/*m* (no. 12) **2** and adopt planar four-membered rings. The ring atoms reside in distorted tetrahedral environments, as is typical for this type of compound. The Al–Sb bond length (av. 2.784 Å **1**) is elongated compared to that of other heterocyclic stibinoalanes [R$_2$AlSb(SiMe$_3$)$_2$]$_x$ (av. values: R = Me, 2.719;[5b] Et, 2.726;[5a] iBu, 2.744 Å[5a]) and base-stabilized monomeric derivatives dmap–AlR$_2$Sb(SiMe$_3$)$_2$ [R = Me, 2.691(1); Et, 2.680(1) Å],[17] most likely because of increased repulsive interactions between the sterically demanding organic substituents. Analogous trends are observed for the average Al–Bi bond length in **2** [2.840(2) Å], which is also longer than the average Al–Bi bond length observed in [Me$_2$AlBi(SiMe$_3$)$_2$]$_3$ (2.774 Å)[6] and dmap–AlR$_2$Bi(SiMe$_3$)$_2$ [R = Me, 2.755(2); Et, 2.750(2) Å],[18] the only structurally characterized organometallic Al–Bi compounds to date. The endocyclic Al–E–Al bond angles (94.2°, **1**; 95.9°, **2**) are bigger than the Al–E–Al bond angles (85.8°, **1**; 84.1°, **2**), as is typical for this type of heterocycle. The presence of bulky tBu substituents leads to elongated Al–C bond lengths (av. 2.005 Å, **1**) compared to other four-membered Al–Sb heterocycles [R$_2$AlSb(SiMe$_3$)$_2$]$_2$ [R = Et, 1.971 Å, 117.3(1)°; iBu, 1.983 Å, 121.3(1)°], as was previously reported for heterocyclic phosphanylalanes [R$_2$AlP(SiMe$_3$)$_2$]$_2$ (R = Me,[19] Et,[20] iBu[12]). Surprisingly, the C–Al–C bond angle in **1** [117.5(1)°] is smaller than that observed for [iBu$_2$AlSb(SiMe$_3$)$_2$]$_2$ [121.3(1)°] and almost identical to that of [Et$_2$AlSb(SiMe$_3$)$_2$]$_2$ [117.3(1)°] despite the increased steric demand of the tBu groups. The Al–C bond length (av. 2.004 Å) and C–Al–C bond angle in **2** [118.9(3)°] are comparable to those in **1**. The Sb–Si and Bi–Si bond lengths (av. 2.587 Å, **1**; 2.660 Å, **2**) are within the expected ranges; the average Si–Sb–Si bond angle in **1** (96.5°) is slightly bigger than the Si–Bi–Si bond angle of **2** (95.6°).

To our surprise, no reaction occurred when tBu$_2$AlH and P(SiMe$_3$)$_3$ were heated up to 180 °C.[16] In contrast, iBu$_2$AlH was reported to react slowly with P(SiMe$_3$)$_3$ at ambient temperature with formation of [iBu$_2$AlP(SiMe$_3$)$_2$]$_2$.[14,21] This finding prompted our interest in the reaction of tBu$_2$AlH and HP(SiMe$_3$)$_2$, yielding [tBu$_2$AlP(H)SiMe$_3$]$_2$ **3** in high yield. ^{31}P NMR spectroscopic studies gave no sign of any transphosphanation reaction involving species such as PH$_3$ and Me$_3$SiPH$_2$ as was reported for the reaction of Me$_2$AlH and HP(SiMe$_3$)$_2$[12] [Equation (2)].

$$2\ t\mathrm{Bu_2AlH} + 2\ \mathrm{HP(SiMe_3)_2} \xrightarrow[-\,2\ \mathrm{Me_3SiH}]{} [t\mathrm{Bu_2AlP(H)SiMe_3}]_2\ \ \mathbf{3} \qquad (2)$$

Complex **3** was characterized in detail by multinuclear NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}). The NMR spectra clearly proved the presence of a mixture of the *cis* and *trans* isomers of the four-membered ring in solution. The integration of the three resonances of the tBu groups in the ^{1}H NMR spectrum revealed the formation of a 1:1 mixture of the *trans* (one signal) and *cis* isomer (two signals). The ^{31}P spectrum of **3** shows two multiplets of the AA′XX′ spin system (AA′ parts) and the ^{31}P{^{1}H} spectrum shows two singlets of almost equal intensity at –229.6 and –232.8 ppm, respectively, for the *cis* and the *trans* isomer. The $^{31}P\{^1H\}$ spectra of the mother liquor and the recrystallized product show the same relative intensities of both isomers (Figure 3).

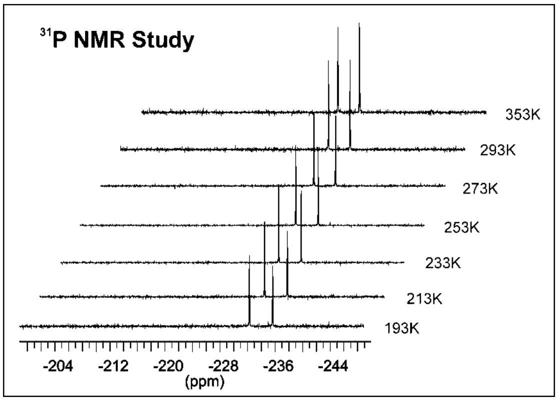

Figure 3. Temperature-dependent $^{31}P\{^1H\}$ NMR study of **3** in [D$_8$]toluene.

The formation of *cis* and *trans* isomers has been described previously for four-membered M_2P_2 heterocycles of the type $[R_2MP(H)R']_2$ such as [Et$_2$InP(H)Si(*i*Pr)$_3$]$_2$,[22] [Et$_2$GaP(H)SiMe$_2$(CMe$_2$*i*Pr)]$_2$,[23] and [*t*Bu$_2$InP(H)SiMe$_3$]$_2$.[24] Surprisingly, a temperature-dependent $^{31}P\{^1H\}$ NMR study in [D$_8$]toluene of recrystallized **3** clearly revealed that there is no dynamic equilibrium between both isomers in solution in the temperature range from –80 to +80 °C. The relative concentrations of both isomers do not change and no coalescence was observed. A powder X-ray diffraction study proved the crystalline material to be exclusively the *trans* isomer (Figure 4). According to this result, cocrystallization of the *trans* and the *cis* isomer can be excluded.[25]

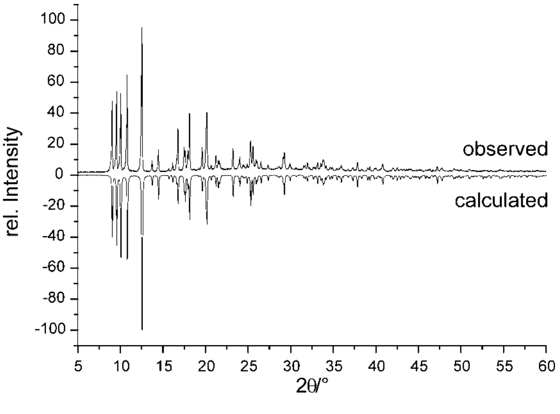

Figure 4. Experimental and calculated powder X-ray diffraction pattern of **3**.

The mass spectrum of **3** does not show the molecular ion peak but M$^+$/2 as was observed for **1** and **2**. An additional signal at *m/z* 363 ([*t*BuAl$_2$P$_2$(SiMe$_3$)H]$^+$) at very high intensity indicates the stability of the central four-membered Al_2P_2 ring under these specific conditions.

Single crystals of **3** suitable for X-ray structure determination were obtained from a solution in *n*-hexane at –40 °C. Figure 5 shows the solid-state structure of **3**.

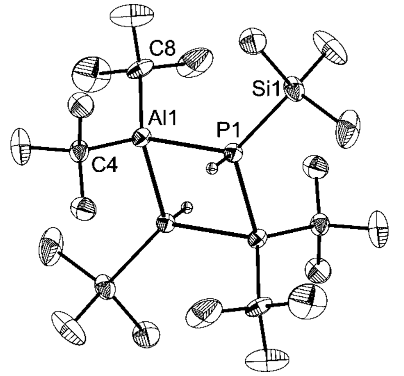

Figure 5. ORTEP plot (50% probability level; H omitted for clarity) showing the solid-state structure and atom-numbering scheme for **3**. Selected bond lengths [Å] and angles [°]: Al1–P1 2.465(1), Al1–P1A 2.459(1), P1–Si1 2.255(1), Al1–C4 1.998(2), Al1–C8 1.994(2); Al1–P1–Al1A 94.4(1), P1–Al1–P1A 85.6(1), C4–Al1–C8 121.0(2), Si1–P1–Al1 129.9(1), Si1–P1–Al1A 127.3(1).

Complex **3** crystallizes in the triclinic space group $P\bar{1}$ (no. 2) and adopts a planar four-membered heterocyclic structure. To the best of our knowledge, **3** represents the first structurally characterized dimeric phosphanylalane containing primary phosphido ([RPH]$^-$) bridges.[26] Comparable phosphanylgallanes $[R_2GaPHR']_2$ were shown to form either planar ([Cl$_2$GaP(H)Si(*t*Bu)$_3$]$_2$,[27] [*t*Bu$_2$GaP(H)*t*Bu]$_2$,[28] [*t*Bu$_2$GaP(H)Cp]$_2$[29]) or butterfly-type ring structures ([Me$_2$GaP(H)Si(*t*Bu)$_3$]$_2$[27]). The formation of a four-membered ring is caused by the steric demand of the *t*Bu substituents, as can be seen when comparing **3** with sterically less hindered phosphanylalanes [(Me$_2$Al)$_3$(P(H)SiMe$_3$)$_2$P(SiMe$_3$)$_2$][13] and [Me$_2$AlP(H)Si(*i*Pr)$_3$]$_2$,[30] which form six-membered rings in the solid state. The Al–P bond length in **3** (av. 2.462 Å) is comparable to those reported for [Me$_2$AlP(SiMe$_3$)$_2$]$_2$ (2.457 Å), [Et$_2$AlP(SiMe$_3$)$_2$]$_2$ (2.458 Å), and [*i*Bu$_2$AlP(SiMe$_3$)$_2$]$_2$ (2.476 Å). The central ring atoms reside in distorted tetrahedral environments with the SiMe$_3$ groups and H atoms bound to the P atoms showing a *transoid* orientation. The endocyclic Al–P–Al bond angle of 94.4(1)° is bigger than the P–Al–P angle of 85.6(1)°, as was expected. Both bond angles significantly deviate from those of [R$_2$AlP(SiMe$_3$)$_2$]$_2$ [Al–P–Al: R = Me, 90.6(1); Et, 90.2(1); *i*Bu, 91.0(1); P–Al–P: R = Me, 89.4(1); Et, 89.8(1); *i*Bu, 89.0(1)°]. The average Al–C bond length as observed for **3** (1.996 Å) is elongated and the C–Al–C bond angle [121.0(2)°] is bigger than in [R$_2$AlP(SiMe$_3$)$_2$]$_2$ [R = Me, 1.959 Å, 113.4(2)°; Et, 1.972 Å, 114.2(2)°; *i*Bu, 1.977 Å, 117.1(2)°], in accordance with the higher steric demand of the *t*Bu groups, whereas the P–Si bond lengths [2.255(1) Å] are almost identical.

Experimental Section

General: All manipulations were performed in a glovebox under N$_2$ or by standard Schlenk techniques. *t*Bu$_2$AlH,[31] HP(SiMe$_3$)$_2$,[32] P(SiMe$_3$)$_3$,[33] Sb(SiMe$_3$)$_3$,[33] and Bi(SiMe$_3$)$_3$[33] were prepared according to literature methods. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra were recorded with a Bruker Avance 500 spectrometer and are referenced to internal C_6D_5H (^1H δ = 7.154, ^{13}C δ = 128.0 ppm) and external H_3PO_4, respectively. 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. The results obtained for **1** and **2** deviate from the calculated values because of their expressed sensitivity toward air and moisture.

Synthesis of [*t*Bu$_2$AlE(SiMe$_3$)$_2$]$_2$: Equimolar amounts of *t*Bu$_2$AlH (0.14 g, 1 mmol) and E(SiMe$_3$)$_3$ (E = Sb, 0.34 g; Bi, 0.43 g) were combined at ambient temperature and stirred until gas evolution had stopped. The resulting solids were dissolved in toluene (10 mL) and stored at –40 °C. Colorless crystals of **1** and **2** were formed within 24 h. Yields are given for isolated compounds after recrystallization.

[*t*Bu$_2$AlSb(SiMe$_3$)$_2$]$_2$ (1): Yield 0.37 g, 0.45 mmol, 90%. *M* = 818.68 g/mol; m.p. 220 °C (dec.). Found: C 40.2, H 8.6; $C_{28}H_{72}Al_2Sb_2Si_4$ requires C 41.1, H 8.9. ^1H NMR (500 MHz, C_6D_5H, 25 °C): δ = 0.59 (18 H, s, *Me*$_3$Si), 1.29 (18 H, s, *Me*$_3$CAl) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_5H, 25 °C): δ = 6.0 [s, *Me*$_3$Si], 31.4 [s, *Me*$_3$CAl] ppm. EI-MS (70 eV, 70 °C): *m*/*z* (%) = 534 (5) [Sb$_2$(SiMe$_3$)$_4$]$^+$, 498 (5) [M/2 + H]$^+$, 408 (55) [M/2]$^+$, 351 (75) [M/2 – (*t*Bu)]$^+$, 295 (60) [M/2 – 2*t*Bu]$^+$, 221 (60) [M/2 – 2*t*Bu – SiMe$_3$]$^+$, 73 (100) [SiMe$_3$]$^+$, 58 (80) [*t*BuH]$^+$, 43 (65) [*t*BuH – Me]$^+$.

[*t*Bu$_2$AlBi(SiMe$_3$)$_2$]$_2$ (2): Yield 0.13 g, 0.13 mmol, 25%. *M* = 993.14 g/mol; m.p. 165 °C (dec.). Found: C 32.8, H 6.9; $C_{28}H_{72}Al_2Bi_2Si_4$ requires C 33.9, H 7.3. ^1H NMR (500 MHz, C_6D_5H, 25 °C): δ = 0.82 (18 H, s, *Me*$_3$Si), 1.30 (18 H, s, *Me*$_3$CAl) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_5H, 25 °C): δ = 7.1 (s, *Me*$_3$Si), 31.1 (s, *Me*$_3$CAl) ppm. EI-MS (70 eV, 70 °C): *m*/*z* (%) = 498 (5) [M/2 + H]$^+$, 423 (15) [M/2 – SiMe$_3$]$^+$, 366 (25) [M/2 – SiMe$_3$ – (*t*Bu)]$^+$, 146 (65) [Si$_2$Me$_6$]$^+$, 73 (100) [SiMe$_3$]$^+$, 58 (45) [*t*BuH]$^+$, 43 (70) [*t*BuH – Me]$^+$.

Synthesis of [*t*Bu$_2$AlP(H)SiMe$_3$]$_2$ (3): *t*Bu$_2$AlH (1 mmol, 0.14 g) was added to HP(SiMe$_3$)$_2$ (1 mmol, 0.17 g) at ambient temperature. Immediately, a gas evolution was observed and after a few minutes the mixture solidified. The colorless solid was dissolved in *n*-hexane (10 mL) and stored at –40 °C. Colorless crystals of **3** were formed within 48 h. The yield is given for the isolated compound after recrystallization. Yield 0.21 g, 0.43 mmol, 86%. *M* = 492.75 g/mol; m.p. 98–100 °C. Found: C 53.4, H 11.3; $C_{22}H_{56}Al_2Si_2P_2$ requires C 53.6, H 11.5. ^1H NMR (500 MHz, C_6D_5H, 25 °C): δ = 0.26–0.28 (18 H, *Me*$_3$Si), 1.22 (9 H, s, *Me*$_3$CAl, *cis* isomer), 1.23 (18 H, s, *Me*$_3$CAl, *trans* isomer), 1.26 (9 H, s, *Me*$_3$CAl, *cis* isomer) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_5H, 25 °C): δ = 3.1 [dt, ^2J(C-P) = 4.2, ^4J(C-P) = 2.0 Hz, *Me*$_3$Si], 30.9 (s, *Me*$_3$CAl), 31.3 (s, *Me*$_3$CAl), 31.8 (s, *Me*$_3$CAl) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, C_6D_5H, 25 °C): δ = –229.6 [dd, ^1J(P-H) = 167.6, ^2J(P-P) = 67.7 Hz, *cis* isomer], –232.8 [dd, ^1J(P-H) = 171.3, ^2J(P-P) = 71.4 Hz, *trans* isomer] ppm. EI-MS (70 eV, 70 °C): *m*/*z* (%) = 363 (90) [*t*BuAl$_2$P$_2$(SiMe$_3$)H]$^+$, 246 (50) [M/2]$^+$, 147 (80) [Si$_2$Me$_6$]$^+$, 73 (75) [SiMe$_3$]$^+$, 58 (60) [*t*BuH]$^+$, 43 (100) [*t*BuH – Me]$^+$.

X-ray Structure Solution and Refinement: Crystallographic data of **1**–**3** are summarized in Table 1. Figures 1, 2 and 5 show ORTEP diagrams of the solid-state structures of **1**–**3**. Data were collected with a Bruker SMART APEX CCD diffractometer[34] using Mo-K_α radiation (λ = 0.71073 Å) at *T* = 120(2) K, and data reduction and absorption corrections were done with SAINT[34] and SADABS.[34] The structures were solved by direct and Fourier methods (SHELXTL),[34] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms in **1**–**3** were refined anisotropically and hydrogen atoms were located from ΔF maps and refined at idealized positions with a riding model (SHELXTL). The Si–C distances of the disordered SiMe$_3$ group in **2** have been restrained with the SADI command of SHELX.

CCDC-626081 (for **1**), -626082 (for **2**), and -626083 (for **3**) 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.

Table 1. Crystallographic data for [*t*Bu$_2$AlSb(SiMe$_3$)$_2$]$_2$ (**1**), [*t*Bu$_2$AlBi(SiMe$_3$)$_2$]$_2$ (**2**) and [*t*Bu$_2$AlP(H)SiMe$_3$]$_2$ (**3**).

	[*t*Bu$_2$AlSb(SiMe$_3$)$_2$]$_2$ (**1**)	[*t*Bu$_2$AlBi(SiMe$_3$)$_2$]$_2$ (**2**)	[*t*Bu$_2$AlP(H)SiMe$_3$]$_2$ (**3**)
Molecular formula	$C_{28}H_{72}Al_2Sb_2Si_4$	$C_{28}H_{72}Al_2Bi_2Si_4$	$C_{22}H_{56}Al_2P_2Si_2$
Formula mass	818.68	993.14	492.75
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2/*c* (no. 15)	*C*2/*m* (no. 12)	$P\bar{1}$ (no. 2)
a [Å]	19.6350(8)	18.3305(12)	8.4864(9)
b [Å]	13.2645(5)	13.3815(9)	10.4671(11)
c [Å]	18.2399(7)	9.9129(6)	10.7269(11)
α [°]			63.790(2)
β [°]	117.121(1)	117.869(1)	80.170(2)
γ [°]			73.546(2)
V [Å^3]	4228.2(3)	2149.5(2)	818.7(2)
Z	4	2	1
μ [mm^{-1}]	1.448	8.343	0.267
$D_{\text{calcd.}}$ [g/cm^3]	1.286	1.534	0.999
Crystal dimensions [mm]	0.22 × 0.20 × 0.13	0.22 × 0.08 × 0.07	0.41 × 0.38 × 0.32
Measured reflections	18182	9501	7070
Unique reflections	5018	2652	3709
R_{merg}	0.0199	0.0466	0.0574
No. of parameters refined/restraints	164/0	138/21	131/0
R_1[a]; wR_2[b]	0.0207, 0.0524	0.0303, 0.0659	0.0418, 0.1368
Gof[c]	1.043	1.040	1.118
Final max, min $\Delta\rho$ [e/Å^3]	0.768, –0.273	1.577, –1.073	0.349, –0.349

[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 = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{\text{obs}} - N_{\text{param}})\}^{1/2}$.

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