Synthesis, X-ray Crystal Structure, and Stability of Novel Trialkylalane−Triorganylbismuthane Adducts

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Dedicated to Prof. Dr. Wolfgang W. Schoeller on the occasion of his 60th birthday

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Reactions of trialkylalanes AlR_3 (R = Me, Et, *t*Bu) and triorganylbismuthanes BiR'_3 (R′ = *i*Pr, $SiMe_3$) were performed and the products investigated both in solution and in the solid state. $Et_3Al–Bi(SiMe_3)_3$ (**2**), $tBu_3Al–Bi(SiMe_3)_3$ (**3**), and $tBu_3Al–Bi(iPr)_3$ (**6**) are stable Lewis acid–base adducts in pure form while only **3** and **6** are adducts in solution. Their dissociation enthalpies, as determined by temperature-dependent NMR spectroscopy, were estimated to 6.3 (**3**) and 6.9 kcal/mol (**6**). In contrast, $Me_3Al–Bi(SiMe_3)_3$ (**1**), $Et_3Al–Bi(SiMe_3)_3$ (**2**), $Me_3Al–Bi(iPr)_3$ (**4**), and $Et_3Al–Bi(iPr)_3$ (**5**) are fully dissociated in solution. Compounds **1**–**6** were characterized by multinuclear NMR spectroscopy (^{1}H, ^{13}C), mass spectrometry, and elemental analysis. In addition, the crystal structures of **2** and **6** were determined by single-crystal X-ray diffraction. Compounds **2** and **6** are the first structurally characterized alane–triorganylbismuthane Lewis acid–base adducts.

Introduction

Group-13 trialkyl compounds generally tend to form adducts with Lewis bases by utilizing their vacant p-valence orbital.[1] This basic reaction, in particular toward group-15 compounds, has been widely studied, not only due to the interesting structural features that have been discovered during the last decades, but also to the potential application of so-formed Lewis acid−base adducts to serve as single source precursors for the preparation of the corresponding binary III−V materials by CVD processes. Both the influence of the central group-13 and -15 element as well as the role of the substituents on the adduct stability, which usually is expressed by their dissociation energy, has been studied experimentally and theoretically.[2] As generally accepted, the Lewis basicity of triorganyl pnicogenides R'_3E decreases with increasing atomic number of the central pnicogenide E. Consequently, amine and phosphane adducts of a constant Lewis acid R_3M (M = B, Al, Ga, In) are much more stable than stibane and bismuthane adducts. Experimental studies strongly support these findings. While numerous adducts of boranes (BR_3) and alanes (AlR_3) (R = halogen, H or Me) with amines (R_3N) and phosphanes (R_3P) have been prepared and structurally characterized, adducts with the higher homologues of group 15, such as stibanes (R_3Sb)[3] and bismuthanes (R_3Bi), have been studied to a far lesser extend. Coates described in the early 1950s the reaction of $GaMe_3$ with trimethyl pnicogenides EMe_3 (E = N, P, As, Sb, and Bi)[4] and experimentally verified the steadily decreasing Lewis basicity of EMe_3 toward $GaMe_3$ with increasing atomic number. This tendency reaches its maximum at Me_3Bi, which did not react with Me_3Ga. The decrease of the Lewis basicity results from the increased s-character of the *lone pair*. Detailed investigations show two significant steps within the decrease of the basicity: Arsanes AsR_3 exhibit a much lower basicity than phosphanes PR_3 due to the post transition metal effect (d-contraction) and bismuthanes BiR_3 are less basic than stibanes SbR_3 both due to the lanthanoid contraction (inert pair effect) and to relativistic effects.[5]

We and others have focused on the coordination chemistry of the heavier group-15 elements during the last few years, leading to the synthesis and structural characterization of several group-13−stibane adducts.[6] Very recently, we reported on the synthesis and structural characterization of the first stable trialkylgallane−triorganylbismuthane adducts.[7]

In an attempt to expand these studies to other group-13 elements and to gain further insights into the structural properties of adducts containing a group-13−Bi linkage, we studied reactions of trialkylalanes with triorganylbismuthanes. Herein, we describe the synthesis and structural characterization of trialkylalane−bismuthane adducts. In addition, temperature-dependent NMR studies were performed to estimate the stability of these adducts in solution.

Results and Discussion

Equimolar amounts of pure trialkylalanes R_3Al (R = Me, Et, *t*Bu) and triorganylbismuthanes R'_3Bi (R′ = $SiMe_3$, *i*Pr) were combined in a glovebox. While tBu_3Al immediately formed white solids with both bismuthanes, clearly indicating the formation of the adducts

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tBu$_3$Al−Bi(SiMe$_3$)$_3$ (**3**) and tBu$_3$Al−Bi(iPr)$_3$ (**6**), analogous reactions of Me$_3$Al yielded colorless liquids Me$_3$Al/Bi(SiMe$_3$)$_3$ (**1**) and Me$_3$Al/Bi(iPr)$_3$ (**4**). Et$_3$Al, however, reacted with Bi(SiMe$_3$)$_3$ to give the solid adduct Et$_3$Al−Bi(SiMe$_3$)$_3$ (**2**), while the combination with iPr$_3$Bi led to a colorless liquid [Et$_3$Al/Bi(iPr)$_3$ (**5**)].

$$R_3Al + R'_3Bi \longrightarrow R_3Al\text{–}BiR'_3$$

$$R = Me, Et, tBu;\ R' = SiMe_3, iPr$$

Pure **1**−**6** have been characterized by elemental analysis. In addition, mass spectra were recorded in the electron impact (EI) mode at 10 eV to obtain further information about the stability of the adducts in the gas phase. However, the peaks with the highest mass observed for **1**−**6** correspond to the respective trialkylalane and triorganylbismuthane fragments. The adduct molecular ion peak was never detected.

The adduct formation is obvious in case of the solid products **2**, **3**, and **6**, while it is questionable for the liquid reaction products **1**, **4**, and **5**, which could merely be simple 1:1 mixtures in pure form. Since gas phase measurements could not be performed due to the lack of suitable instrumentation, it was not possible for us to distinguish between these two possible forms. However, to the best of our knowledge, **2**, **3**, and **6** are the first stable Lewis acid−base adducts in pure form.

1−**6** have also been consequently investigated in solution by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR spectra of **1**−**6** show signals due to the organic groups almost at the same chemical shift as the starting compounds.[8]

Table 1. Selected ^{1}H and ^{13}C NMR shifts and Δ(H) and Δ(C) values of the trialkylalanes and the adducts **1**−**6** as obtained from solutions in C$_6$D$_6$

Compound	δ = ^{1}H[a]	δ = ^{13}C[b]	Δ(H)[c]	Δ(C)[d]
Me$_3$Al	−0.36	−6.8	−	−
Et$_3$Al	0.31	0.9	−	−
tBu$_3$Al	1.08	21.1	−	−
Me$_3$Al−Bi(SiMe$_3$)$_3$ (**1**)	−0.35	−6.7	0.01	0.1
Et$_3$Al−Bi(SiMe$_3$)$_3$ (**2**)	0.31	0.9	0	0
tBu$_3$Al−Bi(SiMe$_3$)$_3$ (**3**)	1.08	21.1	0	0
Me$_3$Al−Bi(iPr)$_3$ (**4**)	−0.36	−6.9	0	0.1
Et$_3$Al−Bi(iPr)$_3$ (**5**)	0.30	0.9	0.01	0
tBu$_3$Al−Bi(iPr)$_3$ (**6**)	1.10	21.1	0.02	0

[a] Me$_3$Al and Et$_3$Al: δ = ^{1}H(α-H); tBu$_3$Al: δ = ^{1}H(β-H). − [b] δ = ^{13}C(α-C). − [c] Me$_3$Al and Et$_3$Al: Δ(H) = δ(α-H)$_{\text{adduct}}$ − δ(α-H)$_{\text{trialkylalane}}$; tBu$_3$Al: Δ(H) = δ(β-H)$_{\text{adduct}}$ − δ(β-H)$_{\text{trialkylalane}}$. − [d] Δ(C) = δ(α-C)$_{\text{adduct}}$ − δ(α-C)$_{\text{trialkylalane}}$.

This is in contrast to the corresponding alane−stibane adducts[6b,6d] and to alane−phosphane adducts,[9] which show resonances typically shifted to lower field (ligands bound to Al) and higher field (ligands bound to P and Sb), respectively. These results strongly indicate **1**−**6** to be at least extensively dissociated in solution at ambient temperature. Unfortunately, we were not able to study the degree of dissociation by cryoscopic molecular mass determination, due to the extreme sensitivity of **1**−**6** in solution toward traces of oxygen and water. Therefore, temperature-dependent NMR studies were performed. These clearly proved the products of the reaction of Bi(iPr)$_3$ and Bi(SiMe$_3$)$_3$ with Me$_3$Al (**1**, **4**) and Et$_3$Al (**2**, **5**) to be fully dissociated in solution. While at ambient temperature the ^{1}H NMR spectra only show one resonance due to the Al−Me and Al−Et groups, at −70 °C two resonances of the Me and Et groups of relative intensities of 1:2 were observed. This clearly show the presence of (Me$_3$Al)$_2$ and (Et$_3$Al)$_2$ dimers (terminal and bridging substituents), eliminating the possibility for the presence of the desired adduct in solution. The two resonances coalesce between −25 and −40 °C. In contrast, the tBu$_3$Al−BiR$_3$ adducts **3** and **6** are not fully dissociated in solution. This was also demonstrated by temperature-dependent ^{1}H NMR spectroscopy. The dissociation enthalpy of the adducts R$_3$Bi−Al(tBu)$_3$ (R = SiMe$_3$, iRr) may be derived from the temperature dependence of the equilibrium constant K_{eq}, with Equations (1) and (2).

$$tBu_3Al + Bi(R)_3 \overset{K_{\text{eq}}}{\rightleftharpoons} R_3Bi\text{–}Al(tBu)_3 \qquad (1)$$

$$\ln K_{\text{eq}} = \frac{-\Delta H_{\text{D}}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S_{\text{D}}}{R} \qquad (2)$$

The equilibrium constant can be expressed in terms of the mol fraction of the alane present as free tBu$_3$Al and the total initial concentration, [total], with Equation (3).

$$K_{\text{eq}} = \frac{[\text{total}]\cdot(\chi_{\text{free}})^2}{(1-\chi_{\text{free}})} \qquad (3)$$

Since the time-dependent ^{1}H NMR spectra only show a single resonance due to the Al(tBu) group over the complete temperature range, and assuming the ^{1}H NMR shift of the Al(tBu) group to be directly proportional to the mol fraction of the total species present as free tBu$_3$Al, χ_{free} may be calculated by the ^{1}H NMR chemical shift of Al(tBu) at a given temperature with Equation (5); δ_{free} is the chemical shift of the uncomplexed tBu$_3$Al and δ_{sample} is obtained directly from the sample. The "real" chemical shift of the adduct (fully coordinated species) is given by δ_{coord}. This was estimated by addition of a fivefold excess of the corresponding bismuthane R$_3$Bi to tBu$_3$Al, which was then measured at −70 °C, assuming tBu$_3$Al to be fully coordinated under these conditions.[10]

$$\chi_{\text{free}} = \frac{\delta_{\text{sample}} - \delta_{\text{coord}}}{\delta_{\text{free}} - \delta_{\text{coord}}} \qquad (4)$$

Table 2. Temperature-dependent ^{1}H NMR chemical shifts and thermodynamic data of **3** and **6** in [D$_8$]toluene

*t*Bu$_3$Al−Bi(SiMe$_3$)$_3$ (**3**)

T [K]	1/*T*	$\delta_{exp.}$ [ppm][a]	χ_{free}	K_{eq}	ln *K*
303	3.30 10^{-3}	1.32	0.606	3.72 10^{-2}	−3.29
263	3.80 10^{-3}	1.41	0.352	7.65 10^{-3}	−4.87
243	4.12 10^{-3}	1.45	0.239	3.02 10^{-3}	−5.80
223	4.48 10^{-3}	1.49	0.141	9.24E-04	−6.99
203	4.93 10^{-3}	1.51	0.070	2.13E-04	−8.45
δ_{coord} [ppm]	δ_{free} [ppm]	Concentration		Δ*H* [kJ/mol]	Δ*S* [J/Kmol]
1.53	1.18	0.04 M		26.3	59.6

*t*Bu$_3$Al−Bi(*i*Pr)$_3$ (**6**)

T [K]	1/*T*	$\delta_{exp.}$ [ppm][a]	χ_{free}	K_{eq}	ln *K*
303	3.30 10^{-3}	1.21	0.90	3.24 10^{-1}	−1.13
263	3.80 10^{-3}	1.26	0.70	6.53 10^{-2}	−2.73
243	4.12 10^{-3}	1.31	0.48	1.77 10^{-2}	−4.03
223	4.48 10^{-3}	1.36	0.30	5.14 10^{-3}	−5.27
203	4.93 10^{-3}	1.39	0.16	1.22 10^{-3}	−6.71
δ_{coord} [ppm]	δ_{free} [ppm]	Concentration		Δ*H* [kJ/mol]	Δ*S* [J/Kmol]
1.43	1.18	0.04 M		28.9	86.2

[a] β-H resonance of *t*Bu$_3$Al.

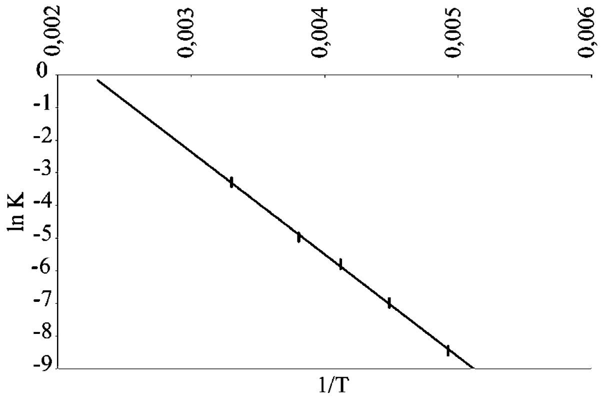

Figure 1. Temperature dependence of the equilibrium constant K_{eq} for the dissociation of **3** ($R = 0.999$)

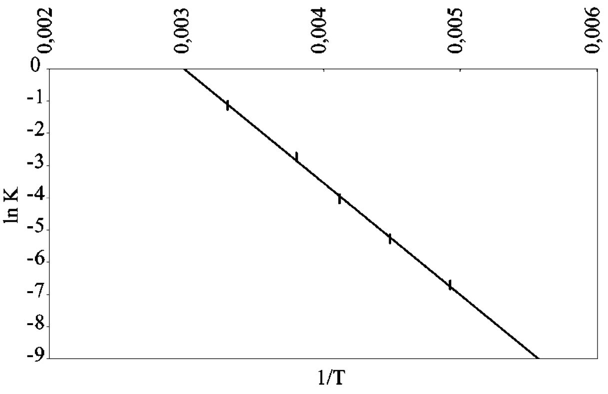

Figure 2. Temperature dependence of the equilibrium constant K_{eq} for the dissociation of **6** ($R = 0.998$)

The dissociation enthalpies of **3** and **6** were calculated to 26.3 kJ/mol (6.3 kcal/mol) and 28.9 kJ/mol (6.9 kcal/mol), respectively, indicating the interaction between *t*Bu$_3$Al and the bismuthanes to be weak in solution. The Δ*S* values of 59.6 kJ/mol (14.2 kcal/mol) and 86.2 kJ/mol (20.6 kcal/mol) are very large and positive, as is typical for a dissociative process. However, the absolute values are erroneous due to several potential sources of errors, in particular the values for the "real" adducts. A small variation in these so-calculated values of only $\delta = 0.01$ would lead to Δ*H* values which differ by about ± 2 kJ/mol.

The results obtained from temperature-dependent ^{1}H NMR spectroscopy prove the dimerization of Me$_3$Al and Et$_3$Al to be thermodynamically more favored in solution compared to the formation of a bismuthane adduct. Therefore, the preparative key for the synthesis of stable alane−bismuthane adducts in solution seems to be the use of trialkylalanes, which do not dimerize. In addition, bismuthanes containing sterically bulky and electropositive substituents, which increase the Lewis basicity due to steric (partial rehybridization of the lone pair leading to a higher p-character) and electronic reasons (+*I* effect of the substituents), lead to more stable adducts.[11] Repulsive interactions between the ligands of the Lewis base and acid, which play an important role for the stability of borane− and alane−amine adducts,[12] seem to be less important due to the bigger central pnicogen atom, leading to reduced steric interactions.

However, the results obtained in solution do not necessarily mean that Me$_3$Al and Et$_3$Al cannot form stable adducts with bismuthanes in general. This is obvious for the reaction product of Et$_3$Al and Bi(SiMe$_3$)$_3$, which is a solid, indicating the formation of the adduct Et$_3$Al−Bi(SiMe$_3$)$_3$ (**2**). Unfortunately, the reactions of Me$_3$Al with both bismuthanes and of Et$_3$Al with Bi(*i*Pr)$_3$ led to liquid products. Whether these compounds are adducts or only mixtures of the starting compounds could not be determined conclusively.

X-ray quality single crystals of $Et_3Al-Bi(SiMe_3)_3$ (**2**) and $(tBu)_3Al-Bi(iPr)_3$ (**6**) were grown from solutions in pentane at −30 °C. Figures 3 and 4 show the solid-state structures of **2** and **6.**

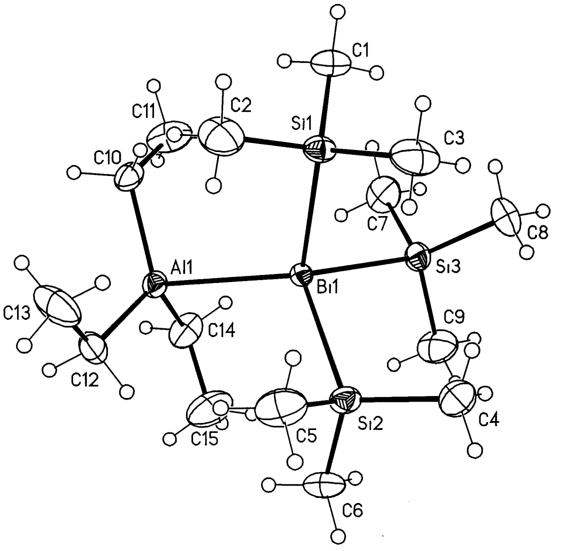

Figure 3. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for $Et_3Al-Bi(SiMe_3)_3$ (**2**); selected bond lengths [Å] and angles [°]: Al1−Bi1 2.921(2), Al1−C10 1.989(6), Al1−C12 1.973(5), Al1−C14 1.972(5), Bi1−Si1 2.634(2), Bi1−Si2 2.628(2), Bi1−Si3 2.635(2); C10−Al1−C12 116.0(2), C10−Al1−C14 117.3(2), C12−Al1−C14 117.5(3), Si1−Bi1−Si2 103.2(1), Si1−Bi1−Si3 100.5(1), Si2−Bi1−Si3 101.9(1)

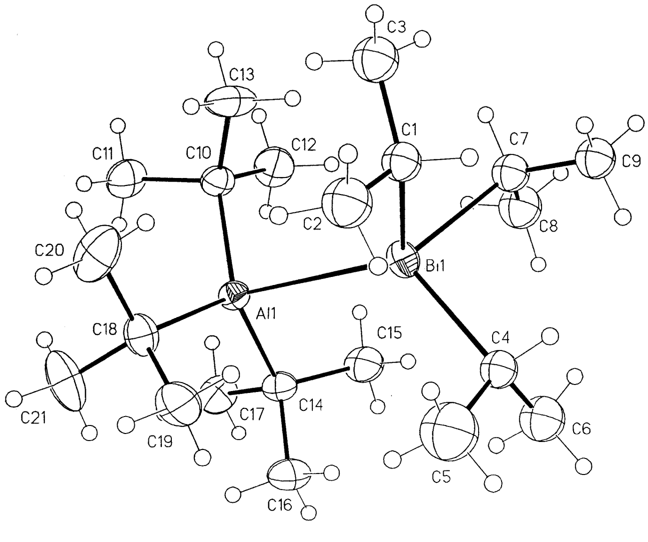

Figure 4. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for $tBu_3Al-Bi(iPr)_3$ (**6**); selected bond lengths [Å] and angles [°]: Al1−Bi1 308.8(2), Al1−C10 2.014(5), Al1−C14 2.014(5), Al1−C18 2.025(5), Bi1−C1 2.313(5), Bi1−C4 2.246(5), Bi1−C7 2.326(5); C10−Al1−C14 117.4(2), C10−Al1−C18 116.7(2), C14−Al1−C18 116.3(2), C1−Bi1−C4 95.8(2), C1−Bi1−C7 93.1(2), C4−Bi1−C7 97.6(2); only one orientation of the disordered *i*Pr groups is shown; in addition, only the data of the major compound are included in the tables

The Al and Bi atoms in **2** and **6** reside in distorted tetrahedral environments with their substituents adopting a staggered conformation relative to one another. The same was observed for the corresponding gallane−bismuthane adducts $Et_3Ga-Bi(SiMe_3)_3$ and $(tBu)_3Ga-Bi(iPr)_3$,[7] and alane−stibane adducts $Et_3Al-Sb(SiMe_3)_3$ [6b] and $(tBu)_3Al-Sb(iPr)_3$ [6d] The Al−Bi bond lengths of 2.921(2) Å in **2** and 3.088(1) Å in **6** are significantly elongated compared to the sum of the covalent radii of 2.75 Å (Al: 1.25 Å; Bi: 1.50 Å).[13] $[Me_2AlBi(SiMe_3)_2]_3$, $(dmap)Al(Me_2)Bi(SiMe_3)_2$ and $(dmap)Al(Et_2)Bi(SiMe_3)_2$ [dmap = 4-(dimethylamino)pyridine], so far the only structurally characterized organometallic compounds containing Al−Bi σ-bonds, also show significantly shorter Al−Bi distances [2.774 Å (average),[14] 2.755(2) Å and 2.750(2) Å[7]]. In particular the Al−Bi distance observed in **6** is very long. However, the Al−Bi bond lengths in **2** and **6** are shorter than the Ga−Bi distances found in the analogously substituted gallane−bismuthane adducts $Et_3Ga-Bi(SiMe_3)_3$ [2.966(1) Å] and $(tBu)_3Ga-Bi(iPr)_3$ [3.135(1) Å], respectively.[7] These findings agree with the decreased Lewis acidity of the gallanes compared to the alanes, leading to weaker acid−base interactions. As was found for the gallane−bismuthane adducts, the lower Lewis basicity of the triorganylbismuthanes R_3Bi compared to the corresponding triorganylstibanes R_3Sb can be observed by comparison of **2** and **6** with the analogously substituted alane−stibane adducts $Et_3Al-Sb(SiMe_3)_3$ and $(tBu)_3Al-Sb(iPr)_3$, showing Al−Sb bond lengths of 2.841(1) and 2.927(1) Å, respectively. In particular the difference of 16 pm for the $(tBu)_3Al-E(iPr)_3$ adducts [E = Sb: 2.927(1) Å, Bi: 3.088(1) Å] is significantly increased relative to the difference of the covalent radii (Sb: 1.41 Å, Bi: 1.50 Å[13]). The lower basicity of the bismuthanes in relation to the corresponding stibanes is also indicated by the smaller Si−Bi−Si and C−Bi−C angles (sum of the bond angles: 305.7° for **2** and 286.4° for **6**) compared to the Si−Sb−Si and C−Sb−C angles (sum of the bond angles: Si−Sb−Si = 310.8°; C−Sb−C = 301.5°), which might express the degree of hybridization, and therefore the Lewis basicity of the pnicogenides. The same tendency was found for trihydrides EH_3 and triorganyl pnicogenides ER_3 (R = Me, Ph). The H−E−H and C−E−C angles steadily decrease from almost tetrahedral (amines) to 90° (bismuthanes), indicating a significant increase in s-character of the *lone pair*.[15]

Haaland[2a][2b] and Frenking et al.[2e] demonstrated for borane and alane adducts, that the adduct formation between a group-13 trialkyl compound and an amine or a phosphane leads to a decrease of the C−M−C bond angle (from 120° towards tetrahedral) and an increase of the M−C bond length (M = B, Al). According to this model, a smaller C−M−C angle and a longer M−C bond within analogously substituted group-13/15 adducts indicate a weakening of the adduct. According to this model, the slightly larger C−Al−C bond angles in **2** and **6** (sum of the bond angles: 350.8° for **2** and 350.4° for **6**) compared to those of the stibane adducts [$Et_3Al-Sb(SiMe_3)_3$ 347.3°, $(tBu)_3Al-Sb(iPr)_3$ 346.9°] and the shorter Al−C bonds [average values: 1.978 Å (**2**), 2.019 Å (**6**); $\mathrm{Et_3Al{-}Sb(SiMe_3)_3}$ = 1.984 Å, $(t\mathrm{Bu})_3\mathrm{Al{-}Sb}(i\mathrm{Pr})_3$, = 2.030 Å] also demonstrate **2** and **6** to be weaker adducts than the corresponding stibane adducts. This is in agreement with the generally accepted decreasing donor capacity of triorganyl pnicogenides with increasing atomic number of the central group-15 element.[16]

Experimental Section

General Remarks: All manipulations were performed in a glovebox under $\mathrm{N_2}$, or by standard Schlenk techniques. $\mathrm{Me_3Al}$ and $\mathrm{Et_3Al}$ were commercially available from Aldrich and used as received, while $t\mathrm{Bu_3Al}$,[17] $\mathrm{Bi(SiMe_3)_3}$,[18] and $\mathrm{Bi}(i\mathrm{Pr})_3$ [19] were prepared by literature methods. − ^{1}H and ^{13}C{^{1}H} spectra were recorded using a Bruker AMX 300 spectrometer and are referenced to internal $\mathrm{C_6D_5H}$ (δ^{1}H = 7.154; δ^{13}C = 128.0), while low-temperature NMR spectra are referenced to internal [D$_8$]toluene (δ^{1}H = 7.20). − Melting points were measured in sealed capillaries and are not corrected. − Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn.

General Experimental Procedure: Pure $\mathrm{R_3Al}$ (2 mmol) and $\mathrm{R_3Bi}$ (2 mmol) were combined in the glovebox in 10-mL flasks. $\mathrm{Bi(SiMe_3)_3}$ immediately formed a white solid with $\mathrm{Et_3Al}$ and $t\mathrm{Bu_3Al}$, while the same occurred between $\mathrm{Bi}(i\mathrm{Pr})_3$ and $t\mathrm{Bu_3Al}$, indicating the formation of the adducts $\mathrm{Et_3Al{-}Bi(SiMe_3)_3}$ (**2**), $t\mathrm{Bu_3Al{-}Bi(SiMe_3)_3}$ (**3**), and $t\mathrm{Bu_3Al{-}Bi}(i\mathrm{Pr})_3$ (**6**). In contrast, the products of the reaction of both bismuthanes with $\mathrm{Me_3Al}$ and of $\mathrm{Bi}(i\mathrm{Pr})_3$ with $\mathrm{Et_3Al}$ stayed liquid at ambient temperature. Compounds **2**, **3**, and **6** were dissolved in pentane (5 mL) and stored at −30 °C, resulting in the formation of colorless crystals in almost quantitative yield. Compounds **1**, **4**, and **5** were characterized without further purification.

$\mathbf{Me_3Al/Bi(SiMe_3)_3}$ (1): Yield 1.00 g (100%). − $\mathrm{C_{12}H_{36}AlBiSi_3}$ (502.21): calcd. C 28.70, H 7.23, found C 28.13 H 6.99. − ^{1}H NMR (300 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = − 0.35 (s, 3 H, MeAl), 0.65 (s, 9 H, $\mathrm{SiMe_3}$). − ^{13}C{^{1}H} NMR (80 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = − 6.7 (MeAl), 6.5 ($\mathrm{SiMe_3}$). − Temperature-dependent ^{1}H NMR spectra (300 MHz, [D$_8$]toluene); 303 K: δ = − 0.25 (s, 9 H, MeAl), 0.75 (s, 27 H, $\mathrm{SiMe_3}$); 263 K: δ = − 0.27 [s (broad), 3 H, MeAl], 0.74 (s, 9 H, $\mathrm{SiMe_3}$). 243 K, δ = − 0.34 [s (very broad), 9 H, MeAl], 0.74 (s, 27 H, $\mathrm{SiMe_3}$). 223 K, δ = − 0.49 [s (broad), 6 H, MeAl], 0.10 [s (very broad), 3 H, MeAl], 0.73 (s, 27 H, $\mathrm{SiMe_3}$); 203 K: δ = − 0.49 [s (broad), 3 H, MeAl], 0.07 [s (broad), 6 H, MeAl], 0.73 (s, 27 H, $\mathrm{SiMe_3}$).

$\mathbf{Et_3Al{-}Bi(SiMe_3)_3}$ (2): Yield 0.98 g (90%). M.p. 50−51 °C. − $\mathrm{C_{15}H_{42}AlBiSi_3}$ (542.72): calcd. C 33.20, H 7.80; found C 32.83, H 7.63. − ^{1}H NMR (300 MHz. $\mathrm{C_6D_5H}$, 25 °C): δ = 0.31 (q, $^{3}J_{\mathrm{HH}}$ = 8.1 Hz, 2 H, MeCH_2Al), 0.64 (s, 9 H, $\mathrm{SiMe_3}$), 1.18 (t, $^{3}J_{\mathrm{HH}}$ = 8.1 Hz, 3 H, *Me*$\mathrm{CH_2}$Al). − ^{13}C{^{1}H} NMR (80 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = 2.0 (Me$\mathrm{CH_2}$Al), 6.3 ($\mathrm{SiMe_3}$), 9.5 (*Me*$\mathrm{CH_2}$Al). − Temperature-dependent ^{1}H NMR spectra (300 MHz, [D$_8$]toluene); 303 K: δ = 0.39 (q, $^{3}J_{\mathrm{HH}}$ = 8.1 Hz, 6 H, MeCH_2Al), 0.75 (s, 27 H, $\mathrm{SiMe_3}$), 1.27 (t, $^{3}J_{\mathrm{HH}}$ = 8.1 Hz, 9 H, *Me*$\mathrm{CH_2}$Al); 263 K: δ = 0.44 [“q” (broad), 6 H, MeCH_2Al], 0.72 (s, 27 H, $\mathrm{SiMe_3}$), 1.34 [“t” (broad), 9 H, *Me*$\mathrm{CH_2}$Al]. 243 K, δ = 0.44 [s (broad), 6 H, MeCH_2Al], 0.70 (s, 27 H, $\mathrm{SiMe_3}$), 1.34 [s (broad), 9 H, *Me*$\mathrm{CH_2}$Al]; 223 K: δ = 0.68 (s, 27 H, $\mathrm{SiMe_3}$), 1.42 [s (very broad), 9 H, *Me*$\mathrm{CH_2}$Al]; 203 K: δ = 0.17 [s (very broad), 2 H, MeCH_2Al], 0.66 (s, 27 H, $\mathrm{SiMe_3}$), 0.98 [s (very broad), 4 H, MeCH_2Al], 1.30 [s (very broad), 3 H, *Me*$\mathrm{CH_2}$Al], 1.61 [s (very broad), 6 H, *Me*$\mathrm{CH_2}$Al].

$\boldsymbol{t}\mathbf{Bu_3Al{-}Bi(SiMe_3)_3}$ (3): Yield 1.15 g (92%). M.p. 41 °C. − $\mathrm{C_{21}H_{54}AlBiSi_3}$ (626.82): calcd. C 40.20, H 8.62; found C 39.84, H 8.49. − ^{1}H NMR (300 MHz. $\mathrm{C_6D_5H}$, 25 °C): δ = 0.64 (s, 9 H, $\mathrm{SiMe_3}$), 1.08 (s, 9 H, *t*Bu). − ^{13}C{^{1}H} NMR (80 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = 6.3 ($\mathrm{SiMe_3}$), 21.1 ($\mathrm{Me_3}\mathit{C}$Al), 32.5 (Me_3CAl). − Temperature-dependent ^{1}H NMR spectra (300 MHz, [D$_8$]toluene); 303 K: δ = 0.74 (s, 27 H, $\mathrm{SiMe_3}$), 1.32 (s, 27 H, *t*Bu); 263 K: δ = 0.69 (s, 27 H, $\mathrm{SiMe_3}$), 1.41 (s, 27 H, *t*Bu); 243 K: δ = 0.66 (s, 27 H, $\mathrm{SiMe_3}$), 1.45 (s, 27 H, *t*Bu). 223 K, δ = 0.63 (s, 27 H, $\mathrm{SiMe_3}$), 1.49 (s, 27 H, *t*Bu); 203 K: δ = 0.58 (s, 27 H, $\mathrm{SiMe_3}$), 1.51 (s, 27 H, *t*Bu). $t\mathrm{Bu_3Al{-}Bi(SiMe_3)_3}$ (1:5; 203 K, [D$_8$]toluene): δ = 1.53. $t\mathrm{Bu_3Al}$ (298 K, [D$_8$]toluene): δ = 1.18.

$\mathbf{Me_3Al/Bi}(\boldsymbol{i}\mathbf{Pr})_3$ (4): Yield 0.82 g (100%). − $\mathrm{C_{12}H_{30}AlBi}$ (410.33): calcd. C 35.13, H 7.37; found C 34.98, H 7.29. − H NMR (300 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = −0.36 (s, 3 H, MeAl), 1.82 (d, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 6 H, Me_2CHBi), 2.15 (sept, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 1 H, $\mathrm{Me_2}\mathit{CH}$Bi). − ^{13}C{^{1}H} NMR (80 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = −6.9 (MeAl), 23.9 (Me_2CHBi), 29.1 ($\mathrm{Me_2}\mathit{C}$HBi). − Temperature-dependent ^{1}H NMR spectra (300 MHz, [D$_8$]toluene); 303 K: δ = −0.26 (s, 9 H, MeAl), 1.92 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 18 H, Me_2CHBi), 2.22 (sept, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi). 263 K, δ = − 0.27 [s (broad), 9 H, MeAl], 1.99 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 18 H, Me_2CHBi), 2.20 (sept, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi); 243 K: δ = − 0.38 [s (very broad), 9 H, MeAl], 1.89 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 18 H, Me_2CHBi), 2.19 (sept, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi). 223 K, δ = − 0.50 [s (broad), 3 H, MeAl], 0.12 [s (very broad), 6 H, MeAl], 1.89 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 18 H, Me_2CHBi), 2.18 (sept, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi); 203 K: δ = − 0.49 (s, 3 H, MeAl), 0.07 (s, 6 H, MeAl), 1.88 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 18 H, Me_2CHBi), 2.16 (sept, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi).

$\mathbf{Et_3Al/Bi}(\boldsymbol{i}\mathbf{Pr})_3$ (5): Yield 0.90 g (100%). − $\mathrm{C_{15}H_{36}AlBi}$ (452.42): calcd. C 39.82, H 8.02; found C 39.67, H 7.99. − ^{1}H NMR (300 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = 0.30 (q, $^{3}J_{\mathrm{HH}}$ = 7.9 Hz, 2 H, MeCH_2Al), 1.10 (t, $^{3}J_{\mathrm{HH}}$ = 7.9 Hz, 3 H, *Me*$\mathrm{CH_2}$Al), 1.82 (d, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 6 H, Me_2CHBi), 2.15 (sept, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 1 H, $\mathrm{Me_2}\mathit{CH}$Bi). − ^{13}C{^{1}H} NMR (80 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = 0.9 (MeCH$_2$Al), 9.1 (*Me*$\mathrm{CH_2}$Al), 23.9 (Me_2CHBi), 29.2 ($\mathrm{Me_2}\mathit{C}$HBi). − Temperature-dependent ^{1}H NMR spectra (300 MHz, [D$_8$]toluene); 303 K: δ = 0.38 (q, $^{3}J_{\mathrm{HH}}$ = 7.9 Hz, 6 H, MeCH_2Al), 1.21 (t, $^{3}J_{\mathrm{HH}}$ = 7.9 Hz, 9 H, *Me*$\mathrm{CH_2}$Al), 1.92 (d, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 18 H, Me_2CHBi), 2.23 (sept, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi); 263 K: δ = 0.37 [“s” (broad), 6 H, MeCH_2Al], 1.19 (“t”, $^{3}J_{\mathrm{HH}}$ = 8.1 Hz, 9 H, *Me*$\mathrm{CH_2}$Al), 1.90 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 18 H, Me_2CHBi), 2.20 (sept, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi); 243 K: δ = 1.19 [“s” (very broad), 9 H, *Me*$\mathrm{CH_2}$Al], 1.89 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 18 H, Me_2CHBi), 2.19 (sept, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi); 223 K: δ = 0.19 [s (very broad), 2 H, MeCH_2Al], 1.26 [s (broad), 9 H, *Me*$\mathrm{CH_2}$Al], 1.89 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 18 H, Me_2CHBi), 2.18 (sept, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi). 203 K, δ = 0.18 [s (broad), 2 H, MeCH_2Al], 0.73 [s (broad), 4 H, MeCH_2Al], 0.99 [s (broad), 3 H, *Me*$\mathrm{CH_2}$Al], 1.29 [“t” (broad), 9 H, *Me*$\mathrm{CH_2}$Al], 1.88 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 18 H, Me_2CHBi), 2.17 (sept, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3 H, $\mathrm{Me_2}\mathit{CH}$Bi).

$\boldsymbol{t}\mathbf{Bu_3Al{-}Bi}(\boldsymbol{i}\mathbf{Pr})_3$ (6): Yield 1.01 g (94%). M.p. 44−46 °C. − $\mathrm{C_{21}H_{48}AlBi}$ (536.55): calcd. C 47.01, H 9.02; found C 46.96, H 8.55. − ^{1}H NMR (300 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = 1.10 (s, 9 H, *t*Bu), 1.82 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 6 H, Me_2CHBi), 2.16 (sept, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 1 H, $\mathrm{Me_2}\mathit{CH}$Bi). − ^{13}C{^{1}H} NMR (80 MHz, $\mathrm{C_6D_5H}$, 25 °C): δ = 21.1 ($\mathrm{Me_3}\mathit{C}$Al), 23.9 (Me_2CHBi), 30.9 ($\mathrm{Me_2}\mathit{C}$HBi), 32.3

Table 3. Crystallographic data and measurements for $Et_3Al{-}Bi(SiMe_3)_3$ (**2**) and $tBu_3Al{-}Bi(iPr)_3$ (**6**)

	2	**6**
Empirical formula	$C_{15}H_{42}AlBiSi_3$	$C_{21}H_{48}AlBi$
Molecular mass	542.72	536.55
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	15.0063(6)	8.9756(3)
b [Å]	10.0800(4)	10.1879(4)
c [Å]	17.0467(6)	14.9615(4)
α [°]	90	85.063(2)
β [°]	91.624(2)	89.830(2)
γ [°]	90	67.926(2)
V [Å^3]	2577.51(17)	1262.49(7)
Z	4	2
Radiation (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)
μ [mm^{-1}]	7.008	7.018
T [K]	123(2)	123(2)
$D_{calcd.}$ [g cm^{-3}]	1.399	1.411
crystal dimensions (mm)	0.30 × 0.20 × 0.10	0.15 × 0.10 × 0.05
$2\theta_{max}$ [°]	50.0	50.0
No. of reflections	20387	19044
No. of nonequiv. reflections	4525	4440
R_{merg}	0.095	0.091
No. of parameters refined/restraints	181/0	191/253
$R1$[a]; $wR2$[b]	0.031, 0.079	0.027, 0.062
Goodness of fit[c]	1.051	1.057
Final max/min. Δρ [e·Å^{-3}]	2.991/−1.864	1.238/−1.094

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

(Me_3CAl). − Temperature-dependent ^{1}H NMR spectra (300 MHz, [D$_8$]toluene); 303 K: δ = 1.21 (s, 9 H, *t*Bu), 1.91 (d, $^3J_{HH}$ = 7.2 Hz, 6 H, Me_2CHBi), 2.24 (sept, $^3J_{HH}$ = 7.2 Hz, 1 H, Me$_2$*CH*Bi); 263 K: δ = 1.26 (s, 9 H, *t*Bu), 1.84 (d, $^3J_{HH}$ = 7.4 Hz, 6 H, Me_2CHBi), 2.29 (sept, $^3J_{HH}$ = 7.4 Hz, 1 H, Me$_2$*CH*Bi). 243 K, δ = 1.31 (s, 9 H, *t*Bu), 1.77 (d, $^3J_{HH}$ = 7.2 Hz, 6 H, Me_2CHBi), 2.30 (sept, $^3J_{HH}$ = 7.2 Hz, 1 H, Me$_2$*CH*Bi); 223 K: δ = 1.36 (s, 9 H, *t*Bu), 1.71 (d, $^3J_{HH}$ = 7.3 Hz, 6 H, Me_2CHBi), 2.27 (sept, $^3J_{HH}$ = 7.3 Hz, 1 H, Me$_2$*CH*Bi); 203 K: δ = 1.39 (s, 9 H, *t*Bu), 1.67 (d, $^3J_{HH}$ = 7.1 Hz, 6 H, Me_2CHBi), 2.23 (sept, $^3J_{HH}$ = 7.1 Hz, 1 H, Me$_2$*CH*Bi); $tBu_3Al{-}Bi(iPr)_3$ (1:5; 203 K, [D$_8$]toluene): δ = 1.43 (s, 9 H, *t*Bu), 1.84 (d, $^3J_{HH}$ = 7.4 Hz, 6 H, Me_2CHBi), 2.15 (sept, $^3J_{HH}$ = 7.4 Hz, 1 H, Me$_2$*CH*Bi); tBu_3Al (298 K, [D$_8$]toluene): δ = 1.18.

X-ray Structure Solution and Refinement: Crystallographic data for **2** and **6** are summarized in Table 3. The ORTEP diagrams of the solid state structures including selected bond lengths and angles of **2** and **6** are shown in Figures 3 and 4. Data were collected with a Nonius Kappa CCD diffractometer. The structures of **2** and **6** were solved by Patterson methods (SHELXS-97)[20] and refined by full-matrix least squares on F^2 (SHELXL-97).[21] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. The *i*Pr groups in **6** are disordered (58:42). Empirical absorption corrections were applied. The crystallographic data of **2** and **6** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158549 (**2**) and -158550 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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