

Organoaluminates with Three Terminal Phenylethynyl Groups and Their Interactions with Alkali Metal Cations[†]

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Summary: The synthesis of $[K^+ \cdot THF(2,6\text{-}iPr_2C_6H_3N\text{-}(SiMe_3)Al(C\equiv CPh)_3)^-]_2$ (**1**), $[Na^+ \cdot THF(2,6\text{-}iPr_2C_6H_3N\text{-}(SiMe_3)Al(C\equiv CPh)_3)^-]_2$ (**2**), and $[Li^+ \cdot dioxane(2,6\text{-}iPr_2C_6H_3N\text{-}(SiMe_3)Al(C\equiv CPh)_3)^-]_2 \cdot 2dioxane$ (**3**) respectively by the reaction of $[2,6\text{-}iPr_2C_6H_3N(SiMe_3)AlCl_2]_2$ (**4**) with the corresponding phenylethynyl alkali metal salt is reported. In compound **1** the potassium (2, sodium) interacts with the $C\equiv C$ bonds of four phenylethynyl groups. A further coordination site of the potassium (sodium) is occupied by a THF molecule. Thus, the cation therein acts as a bridging moiety to form the dimer. In compound **3** each of the lithium cations is 2-fold coordinated by phenylethynyl ligands and two dioxane molecules. One of the dioxane molecules in **3** functions as a bridge forming the dimer. The herein described compounds are the first structurally characterized species having three terminal phenylethynyl groups bound to the aluminum atom.

Introduction

The cation π -interaction is of importance within the numerous known noncovalent interactions and is the subject of several publications.¹ There are only three known potassium compounds of this type of bonding that are structurally characterized,² but nevertheless **1** is the first example of a compound in which potassium is coordinated exclusively to alkynyl groups and a THF molecule.

In the case of sodium there are three known alkynyl compounds with such π -interactions that have been structurally characterized.³ Furthermore, lithium alkynyl π -interactions have been observed in compounds of transition metals and main group elements.⁴ To the best of our knowledge there is no known aluminum alkynyl compound in which the alkynyl group interacts with an

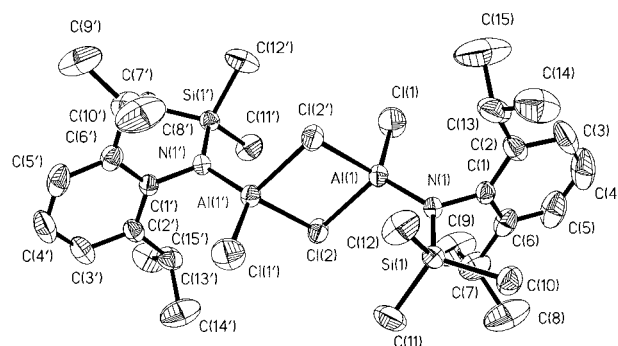


Figure 1. Molecular structure of **4**. For clarity, the hydrogen atoms have been omitted. Non-hydrogen atoms are represented by thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) for **4**: Al(1)–Cl(1) 2.0667(12), Al(1)–Cl(2) 2.2813(11), Al(1)–Cl(2) 2.2855(11), Cl(1)–Al(1)–Cl(2) 106.58(5), Cl(2)–Al(1)–Cl(2) 89.38(4), Al(1)–Cl(2)–Al(1) 90.41(4).

alkali metal ion. The centrosymmetric compounds $[K^+ \cdot THF(2,6\text{-}iPr_2C_6H_3N(SiMe_3)Al(C\equiv CPh)_3)^-]_2$ (**1**), $[Na^+ \cdot THF(2,6\text{-}iPr_2C_6H_3N(SiMe_3)Al(C\equiv CPh)_3)^-]_2$ (**2**), and $[Li^+ \cdot dioxane(2,6\text{-}iPr_2C_6H_3N(SiMe_3)Al(C\equiv CPh)_3)^-]_2 \cdot 2dioxane$ (**3**) are unique. Only a few aluminum alkynyl complexes have been structurally characterized, and compounds **1**, **2**, and **3** are the first in which an aluminum center is bonded to three alkynyl groups.⁵

In a previous report^{5d} it was shown that aluminum alkynyl compounds are not very soluble in organic solvents or give oily products. Therefore we used an aluminum compound with a sterically demanding ligand (2,6-*iPr*₂C₆H₃N(SiMe₃)). The resulting products usually give well-formed single crystals. The reaction of $[2,6\text{-}iPr_2C_6H_3N(SiMe_3)AlMe_2]_2$ with Me₃SnCl yielded $[2,6\text{-}iPr_2C_6H_3N(SiMe_3)AlCl_2]_2$ (**4**) with elimination of Me₄Sn. The single-crystal X-ray structural analysis of **4** shows a dimeric compound containing a four-membered Al₂Cl₂ ring (Figure 1). The Al–Cl bond lengths (2.0667–2.2855 Å) correspond to those of known Al–Cl com-

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[†] Dedicated to Professor Walter Siebert on the occasion of his 65th birthday.

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Scheme 1

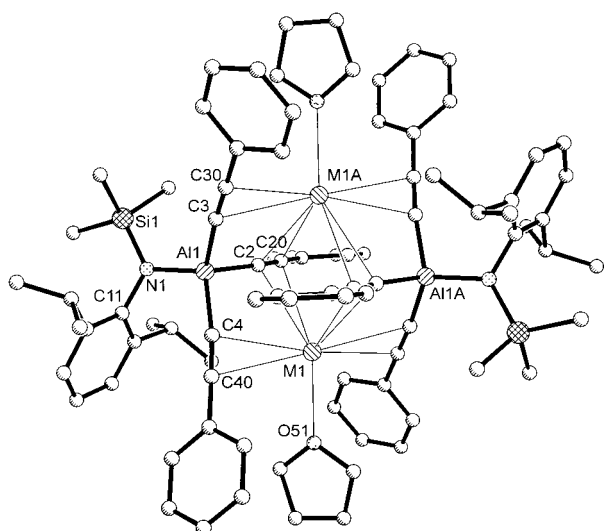
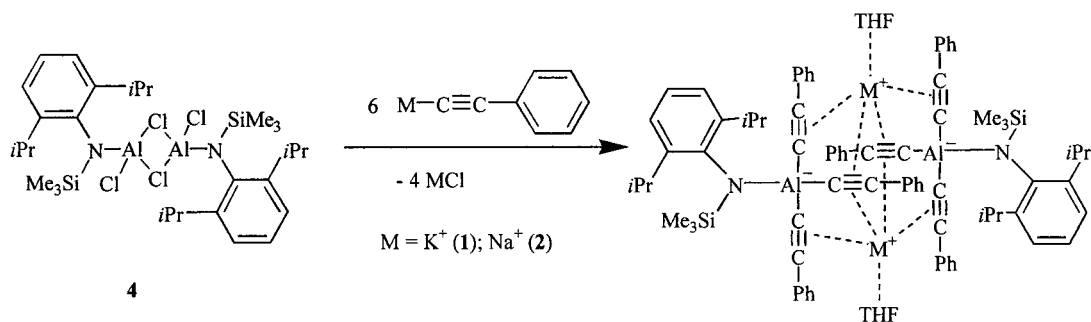


Figure 2. Stick and ball model of isomorphous compounds **1** and **2** ($M = K^+$ (**1**); Na^+ (**2**)).

pounds.⁶ The reaction of **4** with 6 equiv of potassium or sodium phenylacetylide in THF at 50 °C yielded the aluminum phenylethynyl complex **1** or **2** (Scheme 1, Figure 2), while the reaction of lithium phenylacetylide with **4** gave an oily product. However, a colorless crystalline compound **3** was obtained when the latter was treated with dioxane (Figure 3).

The single-crystal X-ray structural analysis of **1** and **2** revealed that the potassium and sodium ions, respectively, are π -coordinated by four phenylethynyl groups. The fifth coordination site is occupied by a THF molecule. Compounds **1** and **2** have an inversion center. The $(2,6\text{-}iPr_2C_6H_3N(SiMe_3)Al(C\equiv CPh)_3)^-$ cores are connected by two alkali metal ions. Moreover, the three phenylethynyl groups and one $2,6\text{-}iPr_2C_6H_3N(SiMe_3)$ group are situated in a slightly distorted tetrahedral environment about the aluminum center. The Al–C bond lengths (Al–C_{alkynyl} 1.960–1.988 Å) are comparable to those found in the literature.^{5a,d} The angle between the aluminum and the two alkynyl carbon atoms (Al–C–C) ranges from 164.2° to 176.7°. This strong deviation from linearity of the Al–C≡C unit, coordinated by two potassium or two sodium atoms, respectively (Al(1)–C(2)–C(20) 165.7° (**1**); 164.2° (**2**)), is a rare example in main group chemistry.^{3a,5d} The reason for this bending might be the small energy difference between a linear and a nonlinear Al–C≡C unit.

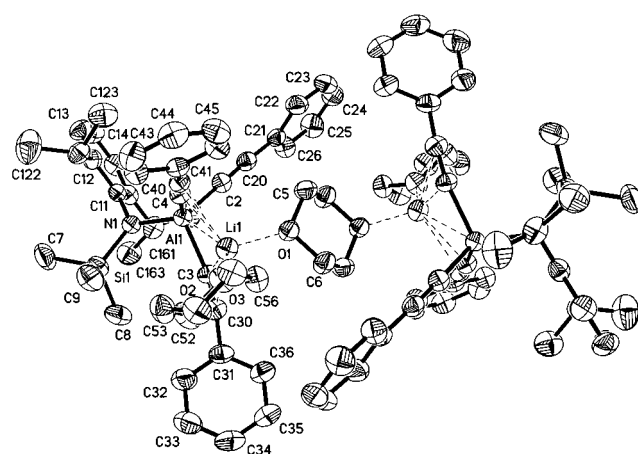


Figure 3. Molecular structure of **3**. For clarity, the hydrogen atoms have been omitted. Non-hydrogen atoms are represented by thermal ellipsoids drawn at the 50% probability level. One additional dioxane is not shown.

The bond distances between the alkynyl carbon atom and the potassium ion in **1** and the sodium ion in **2** are in the range from 2.969 to 3.473 Å (**1**) and 2.651 to 3.358 Å (**2**), respectively, which are slightly longer than the reported values (K–C_{alkynyl} 2.868–3.197 Å; Na–C_{alkynyl} 2.533–2.891 Å).^{2,3} It is quite obvious that the difference of the latter bond distances in **2** (0.707 Å) is more distinct than the corresponding one in **1** (0.504 Å). However, there is a lack of comparable data due to the fact that **1** and **2** are the first potassium and sodium aluminum alkynyl compounds (other examples are Mg,^{3a} Ti,^{3b} Sm^{2b,3c}). The C–M–C angles are in the range 20.23–22.68° (**1**) and 20.6–24.76° (**2**), respectively, and are comparable with those of other alkali metal alkynyl compounds.^{2a,3}

In contrast to compounds **1** and **2**, the lithium ion in **3** is bound to two phenylethynyl groups and two solvent molecules, whereas the alkali metal ions in **1** and **2** are coordinated to four phenylethynyl ligands. Thus the alkali metal ion in compound **3** is not a bridging unit. Moreover, the $[Li^+ \cdot dioxane(2,6\text{-}iPr_2C_6H_3N(SiMe_3)Al(C\equiv CPh)_3)^-]$ cores in **3** are connected by a dioxane molecule. The Al–C bond lengths (1.943–1.998 Å) and the Al–C≡C angles (166.6–175.6°) are similar to those of compounds **1** and **2**. One additional dioxane molecule in the lattice is not shown in Figure 3.

The results of the structural analysis of compounds **1**, **2**, and **3** are surprising. The hard metal cations coordinate as well to the hard oxygen of the THF and dioxane molecule, respectively, as to the four softer coordination sites of the alkynyl groups. Obviously, the

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Table 1. Summary of Crystal Data for Complexes 1, 2, 3, and 4

	1	2	3	4
formula	C ₈₆ H ₉₈ Al ₂ K ₂ N ₂ O ₂ Si ₂	C ₈₆ H ₉₈ Al ₂ N ₂ Na ₂ O ₂ Si ₂	C ₉₄ H ₁₁₄ Al ₂ Li ₂ N ₂ O ₈ Si ₂	C ₁₅ H ₂₆ AlCl ₂ NSi
fw	1380.00	1347.78	1523.89	346.34
temp, K	200(2)	200(2)	203(2)	200(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	12.3241(16)	12.403(3)	12.216(14)	13.7686(16)
<i>b</i> , Å	19.54.8(3)	19.036(4)	13.039(18)	18.803(3)
<i>c</i> , Å	17.333(3)	17.193(3)	15.551(14)	15.258(3)
<i>a</i> , deg	90	90	106.92(12)	90
β , deg	92.084(15)	91.24(3)	106.731(18)	98.075(14)
γ , deg	90	90	95.89(3)	90
<i>V</i> , Å ³	4172.9(12)	4058.4(14)	2221	3911.0(10)
<i>Z</i>	2	2	1	8
ρ_{calcd} , g cm ⁻³	1.098	1.103	1.139	1.176
abs coeff, mm ⁻¹	0.208	0.121	0.114	0.430
no. of reflns collected	8317	7175	8051	9844
no. of indep reflns	7363 (<i>R</i> _{int} = 0.1240)	7175 (<i>R</i> _{int} = 0.0000)	7596 (<i>R</i> _{int} = 0.1647)	6877 (<i>R</i> _{int} = 0.0292)
data/restraints/params	7363/0/440	7175/4/441	7596/0/503	6877/0/375
GOF/ <i>F</i> ²	1.042	1.034	1.023	1.026
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0518 w <i>R</i> 2 = 0.1224	<i>R</i> 1 = 0.0720 w <i>R</i> 2 = 0.1704	<i>R</i> 1 = 0.0603 w <i>R</i> 2 = 0.1614	<i>R</i> 1 = 0.0471 w <i>R</i> 2 = 0.1181
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0728 w <i>R</i> 2 = 0.1405	<i>R</i> 1 = 0.1087 w <i>R</i> 2 = 0.2000	<i>R</i> 1 = 0.0736 w <i>R</i> 2 = 0.1800	<i>R</i> 1 = 0.0659 w <i>R</i> 2 = 0.1310
largest diff peak/ hole, e Å ⁻³	0.302/-0.310	0.822/-0.480	0.589/-0.439	0.380/-0.536

potassium and the sodium ions prefer to coordinate to the alkynyl groups even in the presence of an excess of THF. The products formed by the alkynyl groups seem to be energetically more favorable in comparison to completely solvated cations such as [K(THF)₆]⁺.

Experimental Section

All experiments were carried out using standard Schlenk techniques under a dry nitrogen atmosphere due to the sensitivity of the reactants and products toward air and moisture. A Braun MB 150-GI box was used to store the compounds and to prepare the samples for spectroscopic characterization. All solvents were distilled from sodium/benzophenone and degassed prior to use. [2,6-*i*-Pr₂C₆H₃N-(SiMe₃)AlMe₂]₂ was prepared as described in the literature.⁷ NMR spectra were recorded on a Bruker Avance 200 or Bruker AC 250 and were referenced to Me₄Si and LiCl, respectively. FT-IR spectra were measured on a Bio-Rad FTS-7 instrument as Nujol mulls in the range 4000–400 cm⁻¹. Mass spectra were obtained on a Finnigan MAT 95. Melting points were measured in sealed glass tubes on a Büchi 540 instrument.

Crystal structure solutions and refinements for compounds **1**, **2**, **3**, and **4** are shown in Table 1. Data for all compounds were collected on a Stoe four-circle diffractometer. Mo K α radiation (λ = 0.71073 Å) was used in all cases. All structures were solved by direct methods and refined anisotropically with SHELXTL.⁸

[K⁺·THF(2,6-*i*-Pr₂C₆H₃N(SiMe₃)Al(C≡CPh)₃]₂ (**1**). To a solution of **4** in THF (200 mL) (1.73 g, 2.5 mmol) were added 6 equiv of potassium phenylacetylide (2.10 g, 15 mmol) and the mixture stirred overnight at 50 °C. After cooling to room temperature the solvent was removed in vacuum. To the slightly soluble residue was added hexane (35 mL). The suspension was stirred for 5 min and then was filtered. The residue was extracted with THF (250 mL) to yield 1.48 g (2.15 mmol, 43%) of **1** after removing the THF. Single crystals of **1** were obtained by dissolving the crude product in THF. The latter solution, in a small flask, was placed in a larger vessel containing 10 mL of *n*-hexane. Due to the slow diffusion of

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1, 2, and 3 (M = K⁺ (1); Na⁺ (2); Li⁺ (3))

	1	2	3
Al(1)–C(2)	1.984(3)	1.988(4)	1.943(3)
Al(1)–C(3)	1.963(3)	1.965(4)	1.998(3)
Al(1)–C(4)	1.962(3)	1.960(4)	1.992(3)
M(1)–C(2)	3.097(2)	2.876(4)	
M(1)–C(20)	3.473(3)	3.358(4)	
M(1)–C(2A)	3.063(2)	2.772(4)	
M(1)–C(20A)	3.399(3)	3.221(4)	
M(1)–C(3A)	3.035(2)	2.707(4)	2.350(5) ^a
M(1)–C(30A)	3.089(2)	2.888(4)	2.594(6)
M(1)–C(4)	2.969(2)	2.651(4)	2.287(5)
M(1)–C(40)	3.191(3)	2.968(4)	2.464(6)
C(2)–C(20)	1.212(3)	1.211(5)	1.209(4)
C(3)–C(30)	1.205(3)	1.213(5)	1.209(4)
C(4)–C(40)	1.207(3)	1.203(5)	1.210(4)
C(3)–Al–C(2)	104.7(1)	103.7(1)	113.0(1)
C(3)–Al–C(4)	110.5(1)	110.9(1)	97.1(1)
C(4)–Al–C(2)	107.3(1)	106.1(1)	106.6(1)
C(2)–M(1)–C(20)	20.23(6)	20.6(1)	
C(3A)–M(1)–C(30A)	22.68(6)	24.8(1)	27.8(1) ^a
C(4)–M(1)–C(40)	22.22(6)	23.9(1)	29.2(1)
Al(1)–C(2)–C(20)	165.7(2)	164.2(3)	175.6(2)
Al(1)–C(3)–C(30)	175.0(2)	176.7(3)	166.6(2)
Al(1)–C(4)–C(40)	173.6(2)	172.2(3)	173.8(2)

^a [C(3A)=C(3); C(30A)=C(30)].

the hexane into the THF solution, the single crystals are formed after 18 days. ¹H NMR (200 MHz, THF-*d*₆): δ 7.3–6.6 (m, 18 H), 4.12 (qq, 2 H, *J*_{HH} = 7.0 Hz), 3.6 (m, 4 H), 1.8 (m, 4 H), 1.29 (d, 6 H, *J*_{HH} = 7.0 Hz), 1.18 (d, 6 H, *J*_{HH} = 7.0 Hz), 0.18 (s, 9 H). ²⁹Si NMR (99 MHz, THF-*d*₆): δ -2.2. ¹³C NMR (125 MHz, THF-*d*₆): δ 149.38 (q), 147.71 (q), 132.17, 128.51, 127.73 (q), 127.01, 122.85, 121.58 (s, arom. C), 113.5 (br, Al-C), 106.11 (s, C-Ph), 68.24 (s, THF), 28.20 (s, THF), 28.11 (s, CH), 26.46 (s, CH₃), 3.37 (SiMe₃). IR: $\tilde{\nu}$ 2118, 2099, 1654, 1315, 1263, 1240, 1183, 1158, 1053, 927, 798, 759, 691, 576, 539 cm⁻¹. MS(FAB): *m/z* (%) 578 (1/2[M⁺ - 2THF - K⁺], 100), 1195 ([M⁺ - 2THF - K⁺], 10). Anal. Calcd for C₈₆H₉₈Al₂K₂N₂·Si₂O₂ (1380.07): C, 74.85; H, 7.16; N, 2.03. Found: C, 74.08; H, 7.33; N, 1.87.

[Na⁺·THF(2,6-*i*-Pr₂C₆H₃N(SiMe₃)Al(C≡CPh)₃]₂ (**2**). To a solution of **4** in THF (200 mL) (1.73 g, 2.5 mmol) were added 6 equiv of sodium phenylacetylide (1.86 g, 15 mmol), and the resulting mixture was stirred overnight at 50 °C. After cooling

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to room temperature, the solvent was removed in vacuum. To the slightly soluble product was added toluene (35 mL). The mixture was stirred for 5 min and then was filtered. A slightly yellow residue (3.39 g) containing NaCl and product **2** was obtained. Due to its low solubility in organic solvents, compound **2** cannot be separated completely from the NaCl. Single crystals were obtained by adding THF to the crude product, and the resulting supernatant phase was decanted in a small flask. This flask was placed in a larger vessel containing 10 mL of *n*-hexane. A few single crystals of **2**, suitable for X-ray structure analysis, were obtained after 20 days by slow diffusion of *n*-hexane into the THF solution of **2**. ¹H NMR (200 MHz, C₆D₆): δ 7.5–6.7 (m, 18 H), 4.45 (qq, 2 H, *J*_{HH} = 6.9 Hz), 3.27 (m, 4 H), 1.57 (d, 6 H, *J*_{HH} = 6.9 Hz), 1.55 (d, 6 H, *J*_{HH} = 6.9 Hz), 1.06 (m, 4 H), 0.67 (s, 9 H). ¹³C NMR (125 MHz, THF-*d*₆): δ 149.69 (q), 147.75 (q), 132.22, 128.50, 128.34 (q), 128.26, 122.76, 121.38 (s, arom. C), 112.5 (br, Al-C), 105.40 (s, C-Ph), 68.20 (s, THF), 28.08 (s, THF), 28.04 (s, CH), 26.36 (s, CH₃), 3.38 (SiMe₃). ²⁹Si NMR (99 MHz, C₆D₆): δ 0.6. IR: $\tilde{\nu}$ 2120, 2098, 1597, 1572, 1240, 1184, 1156, 1049, 925, 759, 691, 576, 539 cm⁻¹. The amount of pure **2** was not sufficient enough for elemental analysis.

[Li⁺·dioxane (2,6-*i*Pr₂C₆H₃N(SiMe₃)Al(C≡CPh)₃]⁻]₂·2dioxane (3**).** To a solution of phenylethyne (3.06 g, 30 mmol) in ether (100 mL) was added at -78 °C a solution of *n*-BuLi in hexane (30 mmol). The reaction mixture was stirred at room temperature overnight. Compound **4** (3.46 g, 5 mmol) was added to this solution at -78 °C. Subsequently, the solution was stirred and warmed slowly to room temperature. After filtration the filtrate was evaporated in vacuum. To the resulting oily crude residue was added dioxane (50 mL) and the resulting mixture stirred for 4 h. Finally the dioxane was removed in vacuum and the remaining solid was washed with hexane (35 mL) to yield 4.31 g (3 mmol, 60%) of **3**. ¹H NMR (200 MHz, C₆D₆): δ 7.4–6.8 (m, 18 H), 4.40 (qq, 2 H, *J*_{HH} = 6.8 Hz), 3.38 (s, 18 H), 1.61 (d, 6 H, *J*_{HH} = 6.8 Hz), 1.51 (d, 6 H, *J*_{HH} = 6.8 Hz), 0.66 (s, 9 H). ²⁹Si NMR (99 MHz, C₆D₆): δ 0.2. ¹³C NMR (125 MHz, C₆D₆): δ 147.41 (q), 147.30 (q), 131.78,

128.60, 128.05 (s, arom. C), 109.0 (br, Al-C), 108.82 (s, C-Ph), 67.17 (s, dioxane), 28.11 (s, CH), 26.49 (s, CH₃), 3.36 (SiMe₃). ⁷Li NMR (97.2 MHz, C₆D₆): δ 0.2. IR: $\tilde{\nu}$ 2123, 2111, 1597, 1572, 1486, 1272, 1239, 1181, 1122, 1109, 1079, 925, 872, 796, 759, 693, 445 cm⁻¹. MS(FAB): *m/z* (%): 592 (1/2[M⁺ - 4 dioxane], 100), 585 (1/2[M⁺ - 4 dioxane - Li⁺], 25). Anal. Calcd for C₉₄H₁₁₄Al₂Li₂N₂O₈Si₂ (1523.89): C, 74.09; H, 7.54; N, 1.84. Found: C, 73.86; H, 7.85; N, 1.88.

[2,6-*i*Pr₂C₆H₃N(SiMe₃)AlCl₂]₂ (4**).** [2,6-*i*Pr₂C₆H₃N(SiMe₃)AlMe₂]₂ (30.6 g, 50 mmol) was treated under stirring with trimethyltin chloride (39.9 g, 200 mmol) in toluene (200 mL) at -78 °C. The reaction mixture was warmed slowly to room temperature and stirred overnight. All volatiles were removed in vacuum. The crude product was washed with pentane (40 mL). After filtration 24.2 g of **4** (35 mmol, 70%) were obtained as a colorless solid. ¹H NMR (200 MHz, C₆D₆): δ 7.1–6.8 (m, 3 H), 3.56 (qq, 2 H), 1.35 (d, 6 H, *J*_{HH} = 7.5 Hz), 1.26 (d, 6 H, *J*_{HH} = 7.5 Hz), 0.29 (s, 9 H). IR (Nujol): $\tilde{\nu}$ 2120, 2097, 1597, 1572, 1241, 1181, 925, 759, 723, 691, 576, 539 cm⁻¹. MS(EI): *m/z* (%) 345 (1/2[M⁺], 50), 249 (1/2[M⁺ - AlCl₂], 100). Anal. Calcd for C₃₀H₅₂Al₂Cl₄N₂Si₂ (692.70): N, 4.04. Found: N, 3.36.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 172242 (**1**), 163134 (**2**), 166025 (**3**), and 163133 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.ac-ac.uk>].

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **1**, **2**, **3**, and **4** are available free of charge via the Internet at <http://pubs.acs.org>.

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