Organometallics **2003,** *22,* 3637−3638

Synthesis and Structural Characterization of an Exclusively N-Based Tetrameric Aluminum(I) Compound

Marcus Schiefer, N. Dastagiri Reddy, Herbert W. Roesky,* and Denis Vidovic

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany

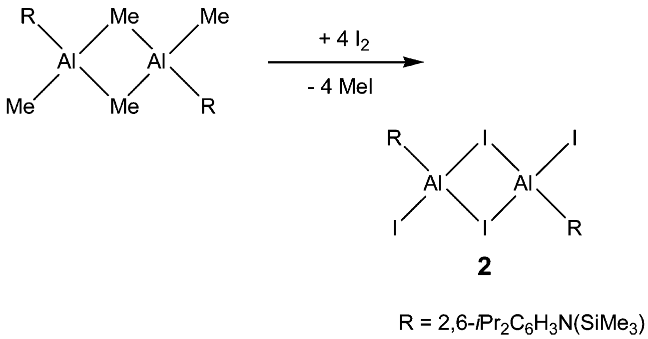
Received April 15, 2003

*Summary: The synthesis and X-ray structure of the first exclusively N-based tetrameric complex $[RAl]_4$ (**1**; R = 2,6-$iPr_2C_6H_3N(SiMe_3)$) are reported. **1** was prepared by the reduction of $[RAlI_2]_2$ (**2**) with Na/K alloy.*

Even though the synthesis of the first Al(I) tetramer, $(RAl)_4$ (R = Cp*), was reported in 1991, only a few compounds of this type have been synthesized to date,[1] despite their ability to form novel coordination complexes with d-block metals which involve σ(Al−M) donor bonds.[2] One of the reasons may be the difficulty involved in their syntheses, due to the tendency of these compounds to disproportionate to elemental aluminum and AlR_3 in the absence of a suitable stabilizing R group. Therefore, choosing an appropriate R group has always been a key factor in the synthesis of aluminum(I) compounds of the general type $(RAl)_4$. In the structurally characterized compounds, the ligands Cp*,[1a,c,f,g] tris(trimethylsilyl)methyl,[1b] tris(trimethylsilyl)silyl,[1e] and tri-*tert*-butylsilyl[1d] have been employed to stabilize the aluminum tetrahedron. It has also been reported that one of the Cp* groups in $(Cp^*Al)_4$ can be substituted by a N-based ligand to obtain the unsymmetrical compound $[(Cp^*Al)_3AlN(SiMe_3)_2]$.[1c] In our continuing efforts to explore this class of compounds, we have chosen a ligand to obtain an exclusively N-based aluminum tetrahedron, and herein we report the synthesis and crystal structure of $[RAl]_4$ (**1**) and its precursor $[RAlI_2]_2$ (**2**) (R = 2,6-$iPr_2C_6H_3N(SiMe_3)$).

Al(I) compounds of the composition $(RAl)_4$ may be obtained by the reductive dehalogenation of aluminum(III) diiodides. Previously, we have reported an aluminum(III) diiodide with coordinated THF as starting material that lowers the reactivity and decreases the yield, due to the formation of THF ring-opening products during the reduction process.[1b] Therefore, in the present work, we have employed a donor-free dimeric aluminum(III) diiodide (**2**). Addition of iodine to a solution of $[RAlMe_2]_2$[3] in toluene afforded **2** in good yield (Scheme 1).[4] The X-ray structural analysis of **2**[5] revealed that the molecule exists as a dimer in the solid state, forming an Al_2I_2 four-membered ring and thereby distorting the tetrahedral geometry around the Al atoms (Figure 1). The I(1A)−Al(1)−I(1) angle is only 93.83(7)°, while the N(1)−Al(1)−I(2) angle is 120.59(19)°. As with the previously studied structures,[6] the bond distances between the Al atoms and the bridging I atoms are longer (2.645(2) and 2.687(2) Å) than those of known $RAlI_2$ compounds,[7] while the bond distances between Al and the terminal I atoms (2.464(2) Å) are shorter.

Scheme 1



Reduction of **2** with Na/K alloy in hexane gave the pale yellow product **1** (Scheme 2).[8] The compound is stable at room temperature and decomposes at 270 °C.

---

* To whom correspondence should be addressed. Fax: (+49)551-393373. E-mail: hroesky@gwdg.de.

[1] (a) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem.* **1991**, *103*, 594−595; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564−565. (b) Schnitter, C.; Roesky, H. W.; Röpken, C.; Herbst-Irmer, R.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem.* **1998**, *110*, 2059−2062; *Angew. Chem., Int. Ed.* **1998**, *37*, 1952−1955. (c) Sitzmann, H.; Lappert, M. F.; Dohmeier, C.; Üffing, C.; Schnöckel, H. *J. Organomet. Chem.* **1998**, *561*, 203−208. (d) Purath, A.; Dohmeier, C.; Ecker, A.; Schnöckel, H.; Amelunxen, K.; Passler, T.; Wiberg, N. *Organometallics* **1998**, *17*, 1894−1896. (e) Purath, A.; Schnöckel, H. *J. Organomet. Chem.* **1999**, *579*, 373−375. (f) Schormann, M.; Klimek, K. S.; Hatop, H.; Varkey, S. P.; Roesky, H. W.; Lehmann, C.; Röpken, C.; Herbst-Irmer, R.; Noltemeyer, M. *J. Solid State Chem.* **2001**, *162*, 225−236. (g) Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem.* **1993**, *105*, 1828−1830; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729−1731.

[2] Fischer, R. A.; Weiss, J. *Angew. Chem.* **1999**, *111*, 3002−3022; *Angew. Chem., Int. Ed.* **1999**, *38*, 2831−2850.

[3] Waezsada, S. D.; Liu, F.-Q.; Murphy, E. F.; Roesky, H. W.; Teichert, M.; Usón, I.; Schmidt, H.-G.; Albers, T.; Parisini, E.; Noltemeyer, M. *Organometallics* **1997**, *16*, 1260−1264.

[4] *Synthesis of $(RAlI_2)_2$ (**2**; R = 2,6-$iPr_2C_6H_3N(SiMe_3)$)*: to a solution of (2,6-$iPr_2C_6H_3N(SiMe_3)AlMe_2)_2$[3] (12.22 g, 20 mmol) in toluene (30 mL) was added slowly a solution of iodine (20.30 g, 80 mmol) in toluene (200 mL) at −78 °C. The reaction mixture was stirred at this temperature for 2 h and then slowly warmed to room temperature with continued stirring overnight while it was protected from light. The volatiles were removed under vacuum, and to the residue was added cold pentane (75 mL). After filtration, removal of pentane from the filtrate afforded compound **2** as a colorless solid in good yield (16.5 g, 78%). Suitable crystals for X-ray analysis were grown by slow evaporation of a toluene solution. Mp: 167 °C dec. ^1H NMR (200 MHz, C_6D_6): δ 7.00−7.10 (m, 3 H, Ar *H*), 3.55 (sept, $J = 6.9$ Hz, 2 H, C*H*$(CH_3)_2$), 1.35 (d, $J = 6.9$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.22 (d, $J = 6.9$ Hz, 6 H, CH(C*H*$_3$)$_2$), 0.34 (s, 9 H, $SiMe_3$). MS (EI) corresponds to the monomer: *m/z* (%) 529 (M^+, 70), 402 ([$M^+ - I - H$], 100). IR (Nujol): $\tilde{\nu}$ 1614, 1554, 1313, 1250, 1164, 1101, 1041, 925, 888, 869, 801, 746, 540 cm^{-1}. Anal. Calcd for $C_{30}H_{52}Al_2I_4N_2Si_2$ (1058.51): C, 34.04; H, 4.95; N, 2.65. Found: C, 33.76; H, 4.81; N, 2.83.

[5] Crystallographic data for compound **2**: $C_{15}H_{26}AlI_2NSi$ (fw = 529.24), monoclinic, space group $P2_1/c$, $a = 12.957(5)$ Å, $b = 9.282(2)$ Å, $c = 17.541(14)$ Å, $\beta = 96.21(5)°$, $V = 2.110(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.676$ g cm^{-3}, μ(Mo Kα) = 3.091 mm^{-1}, $T = 200(2)$ K, R1 (wR2) ($I > 2\sigma(I)$) = 0.0539 (0.1385), R1 (wR2) (all data) = 0.0602 (0.1463).

[6] Allegra, G.; Perego, G.; Immirzi, A. *Makromol. Chem.* **1963**, *61*, 69−79.

10.1021/om0302793 CCC: $25.00

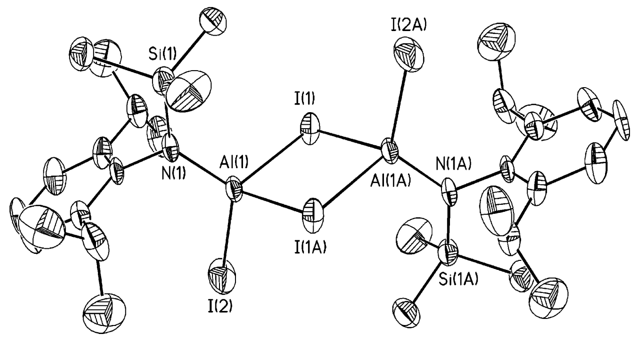
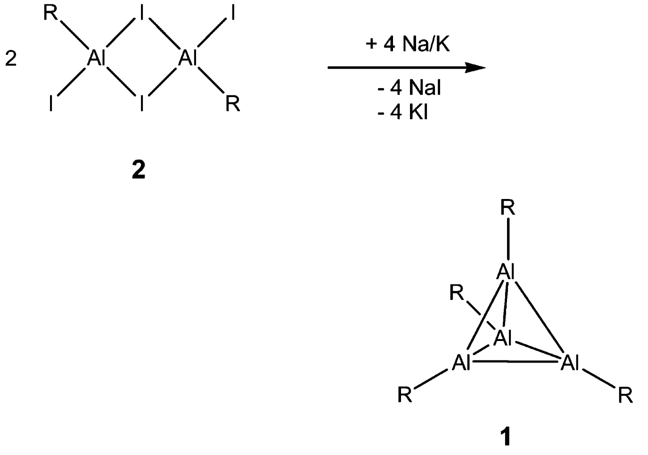


Figure 1. Molecular structure of **2**. For clarity, all the hydrogen atoms are omitted. Non-hydrogen atoms are represented by thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): Al(1)−N(1) = 1.784(6), Al(1)−I(2) = 2.464(2), Al(1)−I(1A) = 2.645(2), Al(1)−I(1) = 2.687(2), I(1)−Al(1A) = 2.645(2); N(1)−Al(1)−I(2) = 120.59(19), N(1)−Al(1)−I(1A) = 113.34(19), I(2)−Al(1)−I(1A) = 106.81(8), N(1)−Al(1)−I(1) = 114.7(2), I(2)−Al(1)−I(1) = 103.92(8), I(1A)−Al(1)−I(1) = 93.83(7).

Scheme 2



R = 2,6-iPr$_2$C$_6$H$_3$N(SiMe$_3$)

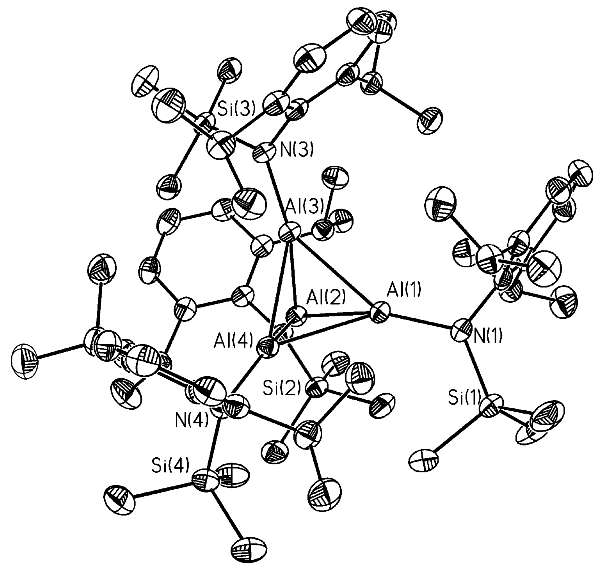


Figure 2. Molecular structure of **1**. For clarity, all the hydrogen atoms are omitted. Non-hydrogen atoms are represented by thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): Al(2)−N(2) = 1.808(2), Al(1)−N(1) = 1.821(2), Al(2)−Al(3) = 2.601(1), Al(1)−Al(3) = 2.635(1); N(3)−Al(3)−Al(2) = 141.79(7), N(1)−Al(1)−Al(3) = 149.54(8), Al(2)−Al(4)−Al(3) = 59.37(3), Al(3)−Al(2)−Al(1) = 60.79(3).

Single-crystal X-ray structural analysis[9] showed a nearly perfect tetrahedral Al$_4$ framework (Figure 2). No Al−Al−Al angle differs more than 1° from the ideal angle of 60°. The average Al−Al bond length (2.619 Å) is relatively short compared to (Cp*Al)$_4$ (2.769 Å) but is in good agreement with the calculated length (SCF) for the model compound (AlNH$_2$)$_4$ (2.646 Å).[1c] The EI mass spectrum of **1** shows the molecular ion peak with a relative intensity of 16%. This result is quite surprising, since the mass spectrum of (Cp*Al)$_4$ exhibits only the monomeric species Cp*Al under similar conditions.[1g] The ^{1}H NMR spectrum recorded at room temperature shows broad signals, which can be attributed to the hindered rotation of the sterically bulky 2,6-iPr$_2$C$_6$H$_3$N(SiMe$_3$) groups. However, at 70 °C the signals are so resolved that the coupling constants of the isopropyl protons could be determined. A partial dissociation of **1** to the monomeric species in solution at 70 °C cannot be ruled out.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Göttinger Akademie der Wissenschaften. N.D.R. thanks the Alexander von Humboldt-Stiftung for a research fellowship.

Supporting Information Available: Tables giving X-ray crystallographic data for the structures of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0302793

---

(7) (a) Schnitter, C.; Klimek, K.; Roesky, H. W.; Albers, T.; Schmidt, H.-G.; Röpken, C.; Parisini, E. *Organometallics* **1998**, *17*, 2249−2257. (b) Ecker, A.; Köppe, R.; Üffing, C.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 817−822. (c) Üffing, C.; Baum, E.; Köppe, R.; Schnöckel, H. *Angew. Chem.* **1998**, *110*, 2488−2491; *Angew. Chem., Int. Ed.* **1998**, *37*, 2397−2400. (d) Krossing, I.; Nöth, H.; Schwenk-Kircher, H. *Eur. J. Inorg. Chem.* **1998**, 927−939. (e) Böker, C.; Noltemeyer, M.; Gornitzka, H.; Kneisel, B. O.; Teichert, M.; Herbst-Irmer, R.; Meller, A. *Main Group Met. Chem.* **1998,** *21*, 565−579. (f) Ecker, A.; Baum, E.; Friesen, M. A.; Junker, M. A.; Üffing, C.; Köppe, R.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 513−516.

(8) *Synthesis of [RAl]$_4$ (**1**)*: compound **2** (0.53 g, 0.50 mmol) in hexane (60 mL) was treated with Na/K alloy, made from sodium (0.024 g, 1 mmol) and potassium (0.041 g, 1 mmol). The mixture was stirred for 12 days at room temperature and filtered through Celite. The yellow residue, which was obtained after the removal of hexane from the filtrate, was treated with dimethoxyethane (4 mL), and the white solid was filtered through Celite. The solvent was removed under vacuum, diisopropyl ether (0.7 mL) was added, and the mixture was stored for 3 days at 12 °C to obtain yellow crystals of **1**·(diisopropyl ether) (0.096 g, 32%). Mp: 270 °C dec. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 7.05 (AB$_2$, 12 H, Ar H), 3.68 (br, 8 H, CH(CH$_3$)$_2$), 3.44 (sept, J = 6.1 Hz, 2 H, OCH(CH$_3$)$_2$), 1.27 (d, br, 24 H, CH(CH_3)$_2$), 1.20 (d, J = 6.1 Hz, 12 H, CH(CH_3)$_2$), 1.14 (d, br, 12 H, CH(CH_3)$_2$), 1.06 (d, br, 12 H, CH(CH_3)$_2$), 0.20 (s, br, 36 H, Si(CH_3)$_3$). ^{1}H NMR (200 MHz, C$_6$D$_6$, 70 °C): δ 7.15 (AB$_2$, 12 H, Ar H), 3.67 (sept, J = 6.9 Hz, 8 H, CH(CH$_3$)$_2$), 3.45 (sept, J = 6.1 Hz, 2 H, OCH(CH$_3$)$_2$), 1.24 (d, J = 6.9 Hz, 24 H, CH(CH_3)$_2$), 1.10 (d, J = 6.9 Hz, 24 H, CH(CH_3)$_2$), 1.06 (d, J = 6.1 Hz, 12 H, CH(CH_3)$_2$), 0.21 (s, 27 H, Si(CH_3)$_3$). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 146.2, 138.8, 124.7, 124.1 (arom C), 28.1, 27.5 (CH), 23.8, 23.0 (CH$_3$), 3.9 (Si(CH$_3$)$_3$). MS (EI): m/z (%) 1100 (M$^+$, 16), 550 ($^1/_2$ M$^+$, 100). IR (Nujol): $\tilde{\nu}$ 3176, 1587, 1433, 1363, 1314, 1249, 1237, 1176, 1103, 1052, 1041, 884, 836, 796, 749, 680, 539, 435 cm^{-1}. Anal. Calcd for C$_{66}$H$_{118}$Al$_4$N$_4$OSi$_4$ (1203.96): C, 65.84; H, 9.88; N, 4.65. Found: C, 64.48; H, 9.09; N, 4.19.

(9) Crystallographic data for compound **1**·(diisopropyl ether): C$_{66}$H$_{118}$Al$_4$N$_4$Si$_4$ (fw = 1187.92), triclinic, space group $P1$, a = 13.0801(9) Å, b = 13.7352(10) Å, c = 20.8205(15) Å, α = 83.173(6)°, β = 96.21(5)°, γ = 81.883(6)°, V = 3669.6(5) Å^3, Z = 2, ρ_{calcd} = 1.075 g cm^{-3}, μ(Mo Kα) = 0.167 mm^{-1}, T = 133(2) K, R1 (wR2) ($I > 2\sigma(I)$) = 0.0492 (0.1153), R1 (wR2) (all data) = 0.0714 (0.1209).