Synthesis and Structure of the First Chiral Tetracoordinated Aluminum Cation

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Low-coordinate aluminum compounds, especially cationic derivatives, are highly electron deficient species of great interest as "living" polymerization catalysts[1] as well as in the Lewis acid-promoted reduction of carbonyl groups.[2] In the former case, such compounds in a chiral version, even if not enantiomerically pure,[3] should be of significant importance, and here we report the synthesis and single-crystal X-ray diffraction study of the first chiral low-valent aluminum cation.

Very few examples of tetracoordinated aluminum cations are known.[4] They are synthesized by abstraction of a halogen atom from a pentacoordinated aluminum center. Our strategy was totally different. Taking into account the topological analogy with the well-known tetradentate triamidoamine ligands $[(RNCH_2CH_2)_3N]^{3-}$,[5] the tridentate diamidoamine $[(Me_3SiNCH_2CH_2)_2NSiMe_3]^{2-}$ **1**, recently prepared by Cloke *et al.*,[6] should stabilize electron deficient centers. Therefore, it seemed reasonable to first prepare a monomeric[7] aluminum(III) derivative **2**, which by subsequent transformation of a potentially reactive amido group into an amino group should give the desired chiral tetracoordinated aluminum cation **3** (Scheme 1).

The bislithium salt of $(Me_3SiNHCH_2CH_2)_2NSiMe_3$ **1** reacted in THF at −78 °C with $AlCl_3$ to give the derivative **2**,[8] which was isolated in 55% yield after sublimation under vacuum. A single-crystal X-ray diffraction study of **2** confirmed that **1** acts as a tridentate ligand (Figure 1, Table 1).[9] Note that **2** crystallizes as a pair of enantiomers due to the conformation of the rings.[5a,b] Derivative **2** is monomeric, with the aluminum center exhibiting a distorded trigonal monopyramidal (TMP) geometry (*vide infra*), which is rare for main group elements,[5ab,10] and even for transition metal complexes.[11]

Due to the coordination of the amino nitrogen to the aluminum center, a regioselective quaternarization of one of the amido nitrogen atoms was achieved by reacting at room temperature a toluene solution of **2** with an anhydrous ether solution of HCl. The resulting salt **3a** precipitated as a white powder. Exchanging the anion Cl^- with $AlCl_4^-$, by adding a stoichiometric amount of $AlCl_3$, gives **3b**, which is soluble in toluene. According to multinuclear NMR spectroscopy, several diastereomers were present in solution. Colorless crystals of

Scheme 1

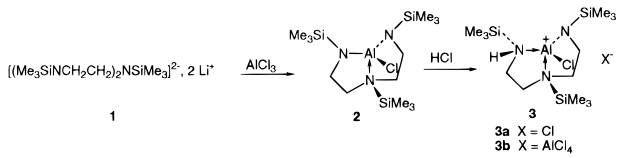

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds **2** and **3b**

	2	**3b**
Al(1)−Cl(1)	2.144(1)	2.103(2)
Al(1)−N(1)	1.811(1)	1.947(3)
Al(1)−N(2)	1.998(1)	1.963(3)
Al(1)−N(3)	1.803(1)	1.782(3)
N(1)−Al(1)−N(2)	92.8(1)	91.8(1)
N(1)−Al(1)−N(3)	124.4(1)	114.8(1)
N(1)−Al(1)−Cl(1)	113.1(1)	109.4(1)
N(2)−Al(1)−N(3)	92.8(1)	95.0(1)
N(2)−Al(1)−Cl(1)	116.5(1)	117.9(1)
N(3)−Al(1)−Cl(1)	113.1(1)	123.0(1)

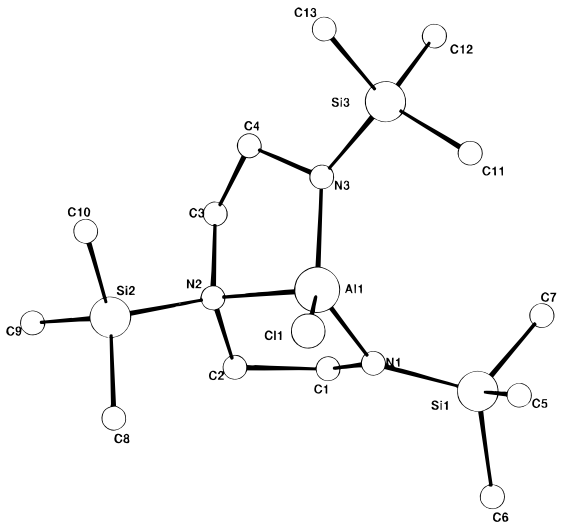

Figure 1. CAMERON[13] plot of derivative **2** showing the numbering scheme used. For clarity, hydrogen atoms have been omitted.

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(8) Spectroscopic data: **2**, ^{1}H NMR (C_6D_6) δ 0.48 (s, 9 H, $SiCH_3$), 0.36 (s, 18 H, $SiCH_3$), 1.97 (ddd, 2 H, J_{HH} = 12.1, 5.4, and 5.4 Hz, CH_2), 2.42 (ddd, 2 H, J_{HH} = 12.1, 7.6, and 5.4 Hz, CH_2), 2.76 (ddd, 2 H, J_{HH} = 12.3, 5.3, and 5.3 Hz, CH_2), 2.92 (ddd, 2 H, J_{HH} = 12.3, 7.6, and 5.3 Hz, CH_2); ^{27}Al NMR (C_6D_6) δ +125.

(9) Crystal data: **2**, $[C_{13}H_{35}N_3Si_3AlCl]$, monoclinic, $P2_1/c$, a = 16.361(11) Å, b = 10.237(4) Å, c = 13.353(6) Å, β = 92.04(4)°, V = 2235.04(10) Å^3, Z = 4, with 331 parameters refined on 3435 reflections having $F > 4\sigma(F_o)$, R1 = 0.028 and wR2 = 0.078; **3b**, $[C_{13}H_{36}N_3Si_3Al_2Cl_5]$, triclinic, P1, a = 9.992(4) Å, b = 11.970(4) Å, c = 13.160(5) Å, α = 82.62(3)°, β = 68.94(3)°, γ = 89.17(3)°, V = 1455.84(9) Å^3, Z = 2, with 248 parameters refined on 3312 reflections having $F > 4\sigma(F_o)$, R1 = 0.037 and wR2 = 0.103.

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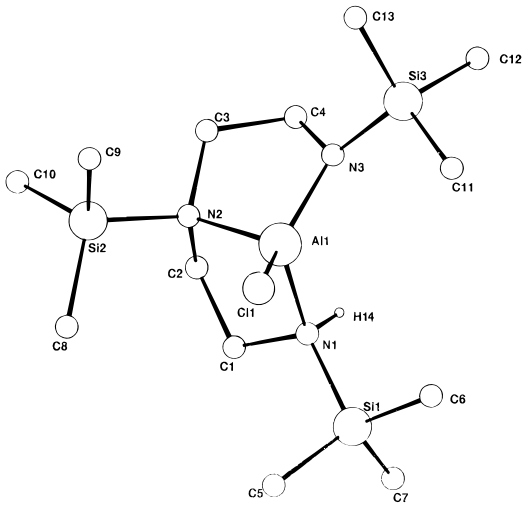

Figure 2. CAMERON[13] plot of derivative **3b** showing the numbering scheme used. For clarity, hydrogen atoms have been omitted, exept the NH.

3b (50% yield) were obtained from a saturated benzene solution, and the structure of one of the diastereomers was clearly established by a single-crystal X-ray diffraction study (Figure 2, Table 1).[9]

Derivative **3b** is monomeric; no interaction with the counteranion $AlCl_4^-$ is observed. The hydrogen atom of the NH moiety was located and refined. The molecular structures of **2** and **3b** offer the opportunity to compare structural parameters in related neutral and cationic tetracoordinated aluminum compounds. In both cases, the aluminum atom is only slightly displaced from the trigonal plane Cl(1)N(1)N(3) in the direction of the apically coordinated donor (0.34 and 0.40 Å for **2** and **3b**, respectively), and the endocyclic N−Al−N angles are close to 90°; therefore, **2** and **3b** feature central aluminum atoms approaching a TMP coordination environment. As expected the protonation induces a lengthening of the Al(1)−N(1) bond distance (0.137 Å) and a shortening of the Al(1)−Cl(1), Al(1)−N(2), and Al(1)−N(3) bond lengths (0.041, 0.035, and 0.022 Å, respectively).

This is the first example of a protonation reaction at the amido nitrogen of a coordinated *N*-silylated amidoamine ligand; this suggest that such a ligand could be involved in removing or adding a proton to coordinated hydrocarbon fragments (a possible alternative mechanism for the α,α-dehydrogenation of transition metal alkyl complexes).[5d,e]

Due to its TMP coordination environment, the cationic aluminum center of **3b** is accessible for additional ligands. Indeed, one molecule of diethyl ether or THF coordinates to **3b** as shown by ^{1}H and ^{13}C NMR spectroscopies. The aptitude of **3b** to coordinate an oxygen-containing substrate is of particular interest for future development in catalysis,[1] and especially for the polymerization of propylene oxide.[1,12]

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Supporting Information Available: Tables of crystal and intensity collection data, position and thermal parameters, interatomic distances and angles (13 pages). Ordering information is given on any current masthead page.

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