Communications

A Novel Zwitterionic Species Containing an Aluminum(III) Cation and a Planar Carbanion. Crystal Structure of [$Et_3AlNMe_2SiMe_2C(SiMe_2NMe_2)_2AlEt_2$]·$C_6H_6$

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Summary: Reaction of ($Me_2NMe_2Si)_3CLi$ *with* $AlEt_2Cl$ *in toluene followed by recrystallization of the product from benzene has given the unprecedented title compound, in which a tetrahedral cationic Al(III) center and a planar carbanion center form part of a six-membered ring. The corresponding reaction with* $AlCl_3$ *has given* [$Al\{C(SiMe_2NMe_2)(SiMe_2NMe_2)_2\}Cl_2$]. *Crystal structures of both products are reported.*

In an extension of our studies of the use of the bulky ligand $(Me_3Si)_3C$ to give a wide range of novel organometallic species[1] we recently turned to related ligands of the type $(Me_3Si)_2(XMe_2Si)C$ and $(XMe_2Si)_3C$, in which X is a donor group such as OMe,[2] SMe,[3] and NMe_2.[4] In particular, attachment of the ligand $(Me_2NMe_2Si)_3C$ to Li gave the linear polymeric species $\{(Me_2NMe_2Si)_3CLi\}_n$, in which each Li atom is attached to two Me_2N groups from one such ligand and to one Me_2N group from another,[4] and its attachment to Mg gave the highly unusual Grignard reagent $(Me_2NMe_2Si)_3CMgI$, in which all three Me_2N groups of the ligand are attached to a single metal center to produce a planar carbanionic center apparently without specific bonding with the Mg.[5] We have now further demonstrated the versatility of the ligand by attaching it to Al.

Reaction of the lithium derivative with 1 equiv of $AlCl_3$[6] gave the relatively simple species [$Al\{C(SiMe_2NMe_2)(SiMe_2NMe_2)_2\}Cl_2$] (**1**) with the structure shown in Figure 1,[7] one NMe_2 group being coordinated to the metal to give a four-membered ring and two NMe_2 groups, with planar geometry at N, left free. The ring is almost planar (sum of internal angles 359.9°; fold angle 3°), with angles of 87.1(2), 88.5(2), 88.3(2),

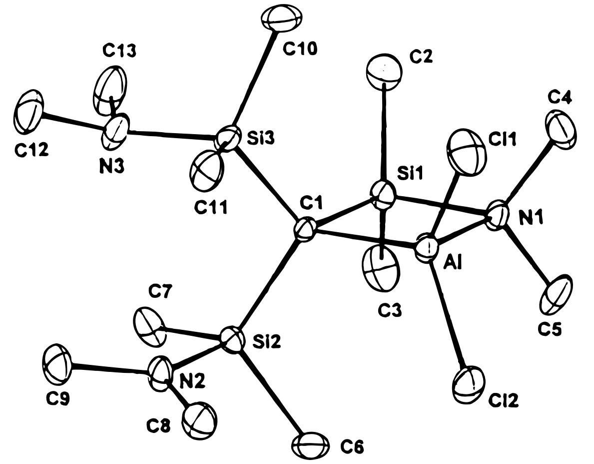

Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (deg): C1−Al, 2.006(5); C1−Si1, 1.867(5); C1−Si2, 1.899(5); C1−Si3, 1.881(5); Si1−N1, 1.861(4); Si2−N2, 1.731(4); Si3−N3, 1.741(5); Al−N1, 1.968(4); Al−Cl1, 2.128(2); Al−Cl2, 2.128(2); mean Si1−Me, 1.848(6); mean Si2,3−Me, 1.874(5); mean N1−Me, 1.499(7); mean N2,3−Me, 1.443(8); Si−C1−Si3, 120.3(3); Al−C1−Si2, 115.7(2); Si2−C1−Si3, 109.3(2); Al−C1−Si1, 87.1(2); C1−Si1−N1, 96.1(2); N1−Al−C1, 88.5(2); Cl1−Al−Cl2, 105.3(1).

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(6) A mixture of $AlCl_3$ (0.50 g, 3.75 mmol) and toluene (40 cm^3) was stirred at room temperature for 2 h, after which only a small amount of solid remained undissolved. The solution was cooled to 0 °C and added dropwise to a stirred solution of $LiC(SiMe_2NMe_2)_3$ (1.14 g, 3.50 mmol) in toluene (40 cm^3) containing a few drops of THF and that was also cooled to 0 °C. The mixture was subsequently allowed to warm to room temperature and the solvent removed under vacuum. The residue was extracted with light petroleum (bp 40−60 °C; 4 × 15 cm^3), and the extract was filtered and then slowly concentrated under vacuum to give colorless crystals, which were filtered off and washed with light petroleum to yield compound **1** (1.43 g, 98%). Mp: 163−165 °C dec. ^1H NMR (C_6D_6): δ 0.30 (s, 18H, $SiMe_2$), 2.27 (s, 18H, NMe_2). ^{13}C NMR (C_6D_6): δ 3.8 ($SiMe_2$), 40.3 (NMe_2). ^{15}N NMR (C_6D_6): δ −380. ^{27}Al NMR (toluene-d_8): δ 114 ($\Delta\nu_{1/2}$ 1150 Hz)). ^{29}Si NMR (C_6D_6): δ 11.52 (at 20 °C; 11.95 at −20 °C, 11.34 at +60 °C; *endo*-$SiMe_2$) and 10.13 (−20 to +60 °C, *exo*-$SiMe_2$). MS (EI, 70 eV): *m/z* 415 (5, M), 400 (10, [M − Me]), 371 (100, M − NMe_2), 355 (M − Me − NMe_2), 274 (60, $(Me_2NMe_2Si)_2C{=}SiMe_2$), 230 (60), 216 (70, $(Me_2NMe_2Si)_2C$), 102 (65, Me_2NMe_2Si). Although the spectra indicated that the bulk product was essentially pure, a satisfactory analysis could not be obtained.

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and 96.1(2)° at C, Al, N, and Si, respectively. The exocyclic Si−C1−Si angle, 109.3(2)°, is smaller than might have been expected (compare the Si−C−Si angle of 123.2° in $(Me_3Si)_2CH_2$)[8]), but opening of this angle is inhibited by interactions between the substituents on the ring atoms; e.g. the C3···C6 and C2···C10 contacts are 3.51 and 3.38 Å, respectively. The difference between the lengths of the exocyclic Si−N bonds (mean 1.736(4) Å) and that of the endocyclic bond to the coordinated N atom (1.861(4) Å) is noteworthy. The ^1H, ^{13}C, and ^{29}Si NMR spectra in C_6D_6, all showing the expected sharp peaks, are consistent with persistence of the solid-state stucture in solution, and the ^{27}Al NMR spectrum shows a broad peak centered at δ 114, in the range reported for $(EtAlCl_2)_2$ (δ 122),[9a] $(Me_3Si)_3CAlCl_2$·THF (δ 123),[9b] and 2,4,6-t-$Bu_3C_6H_2AlCl_2$·THF (δ 108),[9c] in all of which the Al is four-coordinate.

More surprising was the product, **2**, isolated from the reaction of the lithium reagent with 1 equiv of $AlEt_2Cl$ in toluene.[10] The product isolated as its benzene solvate after recrystallization from heptane and then benzene proved to have the unprecedented structure shown in Figure 2,[11] two NMe_2 groups of the $(Me_2NMe_2Si)_3C$ ligand being bound in chelating fashion to an $AlEt_2$ center, to produce a six-membered ring, and the other NMe_2 group bound to an $AlEt_3$ fragment. The compound is a zwitterionic species, with a cationic Al(III) center clearly separated (by 3.65 Å) from a planar carbanionic center (sum of angles 359.7°). The NMR spectra of **2** indicate that the observed structure is maintained in toluene solution.

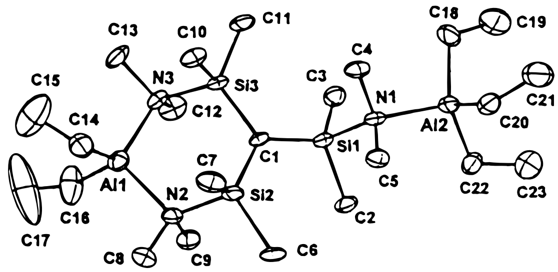

Figure 2. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): C1−Si1, 1.790(7); C1−Si2, 1.798(6); C1−Si3, 1.793(6); Si−Me (mean), 1.867(2); Si1−N1, 1.868(6); Si2−N2, 1.869(6); Si3−N3, 1.872(6); N1−Al2, 2.043(6); N2−Al1, 1.998(6); N3−Al1, 1.996(6); N−Me (mean), 1.505(2); Si2−C1−Si3, 115.3(4); Si2−N2−Al1, 115.3(3); Si3−N3−Al1, 115.1(3); N2−Al−N3, 106.1(2); C14−Al1−C16, 113.2(4); C1−Si1−N1, 111.5(3); Si1−N1−Al2, 121.5(3); Me−N−Me, (mean) 106.4(2); Me−Si−Me (mean), 102.8(2).

There are several examples of salts containing separated Al(III) cations and counteranions,[12−14] and it has been shown that these may have potential in organic synthesis and catalysis.[14] None of them, however, contains a carbanion counterion, and there appears to be no other example of a zwitterion. It is noteworthy that the Grignard reagent $(Me_2NMe_2Si)_3CMgI$ can also be regarded as a zwitterionic species, though one with a much shorter metal−carbanion distance.

The ring system in **2** is analogous to that in $\{(Me_2NMe_2Si)_3CLi\}_n$.[4] All the Si−N bonds are long (mean 1.869(6) Å). The endocyclic Al−N bonds to the cationic center (mean 1.997(6) Å) are probably slightly shorter than the Al−N bond to the neutral N center (2.043(6)° Å). Since silicon-substituted amines are normally thought to be much less basic and thus much weaker donors than alkylamines,[15] it is noteworthy that even the longest Al−N bond in **2** is similar in length to that (2.058(3) Å) in, for example, the alkylamine−Al complex $[Al(CH_2SiMe_3)_3NMe_3]$.[16] The lengths of the C1−Si bonds (mean 1.794(6) Å) are similar to those in $\{(Me_2NMe_2Si)_3CLi\}_n$ (mean 1.793(6) Å) and in the free anion of the salt $[Li(THF)_4][C\{SiMe_2C_6H_4Me\text{-}o\}]$ (mean 1.800(3) Å).[17]

We emphasize that although **2** was the species that separated from the recrystallization from benzene, it was not necessarily the main product from the reaction in which it was formed, and the other constituents of the initial product mixture have not yet been established. The appearance of the $AlEt_3$ entity in **2** can be

(7) Crystal data for **1**: $C_{13}H_{36}AlCl_2N_3Si_3$, M_r = 416.6, orthorhombic, a = 29.601(6) Å, b = 11.651(2) Å, c = 13.231(3) Å, V = 4563(2) Å^3, space group *Pbcn* (No. 60), Mo Kα radiation, λ = 0.710 73 Å, Z = 8, D_c = 1.21 Mg m^{-3}, F(000) = 1792, crystal dimensions 0.3 × 0.3 × 0.2 mm, μ = 0.48 mm^{-1}, CAD4 diffractometer, θ−2θ mode, T = 173(2) K, 2 < θ < 23°, 3169 unique reflections measured, 2303 with $I > 2\sigma(I)$, structure analysis by direct methods (SHELXS-86), full-matrix-least squares refinement on F^2 (SHELXL-93) with non-H atoms anisotropic, H atoms in riding mode, R1($I > 2\sigma(I)$) = 0.063, wR2(all data) = 0.181, S = 1.051.

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(10) Liquid $AlEt_2Cl$ (0.40 cm^3, 3.08 mmol) was added to a stirred suspension of $LiC(SiMe_2NMe_2)_3$ (1.00 g, 3.08 mmol) in toluene (40 cm^3) kept at −85 °C. The stirred mixture was subsequently allowed to warm to room temperature and then filtered and the solvent removed under vacuum. The solid residue was recrystallized from heptane and then from benzene to give the solvate **2** as colorless crystals, in ca. 30% yield. Mp: 109−112 °C. One crystal was taken for the X-ray study, and when the remainder were kept under vacuum the benzene was readily removed and the spectroscopic data were recorded for the residue. ^1H NMR (C_6D_6): δ *ca.* 0 (10H, broad unresolved $AlCH_2$), 0.30 (s, 6H, *exo*-$SiMe_2$), 0.44 (s, 12H, *endo*-$SiMe_2$), 1.16 (t, 6H, CH_2CH_3), 1.68 (t, 9H, CH_2CH_3), 1.84 (s, 6H, *exo*-NMe_2), 2.20 (s, 6H), 2.26 (s, 6H) (*endo*-NMe_2). ^{13}C NMR (C_6D_6): δ *ca.* 3 (very broad, $AlCH_2$), 4.12 ($SiMe_2$), 6.0 ($SiMe_2$), 10.7 and 11.6 ($AlCH_2CH_3$), 39.9 (*exo*-NMe_2), and 40.0, 40.3 (*endo*-NMe_2). ^{27}Al NMR (C_6D_6): δ 165 (unsymmetrical, $\Delta\nu_{1/2}$ 3520 Hz). ^{29}Si NMR (C_6D_6): δ 9.6 (*endo*), 20.5 (*exo*). MS (EI, 70 eV): *m/z* 374 (30, $[(Me_2NMe_2Si)_3CAlEt_2)]$ (M′) − Et]), 359 (100, M′ − NMe_2), 345 (80, M′ − 2Et), 316 (70), 274 (50, $(Me_2NMe_2Si)_2C{=}SiMe_2$), 259 (30), 230 (50), 73 (70), 102 (45, Me_2NMe_2Si). Although the spectra indicated that the product was essentially pure, a satisfactory C/H analysis could not be obtained (Anal. Calcd for $C_{23}H_{61}Al_2N_3Si_3$: N, 8.1. Found: N, 8.2).

(11) Crystal data for **2**: $C_{23}H_{61}Al_2N_3Si_3$·C_6H_6, M_r = 596.1, monoclinic, a = 13.001(5) Å, b = 10.277(5) Å, c = 28.197(9) Å, β = 103.16(5)°, V = 3669(3) Å^3, space group $P2_1/n$ (No. 14)), Mo Kα radiation, λ = 0.710 73 Å, Z = 4, D_c = 1.08 Mg m^{-3}, F(000) = 1320, crystal dimensions 0.4 × 0.4 × 0.1 mm, μ = 0.20 mm^{-1}, CAD4 diffractometer, θ−2θ mode, T = 173(2) K, 2 < θ < 22°, 4484 unique reflections measured, 2826 with $I > 2\sigma(I)$, no absorption, structure analysis by direct methods (SHELXS-86), full-matrix least-squares refinement on F^2 (SHELXL-93) with non-H atoms anisotropic, H atoms in riding mode, R1($I > 2\sigma(I)$) = 0.082, wR2(all data) 0.265, S = 1.035. (The high value of wR2 is a consequence of the large number of weak reflections.)

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readily understood in terms of the ready redistribution of of AlR_xCl_{3-x} species in the presence of alkali-metal halides, but it is not obvious why the endocyclic N atom should prefer to coordinate to an $AlEt_3$ rather than to a more acidic $AlEt_xCl_{3-x}$ molecule having $x < 3$. (It should be of interest to observe the outcome of the addition of of, for example, $AlEt_3$ or $AlCl_3$ to a solution of **1**, which has two NMe_2 groups available for coordination.) The formation of a cationic Al species from $AlEt_2Cl$ but not from $AlCl_3$ is consistent with a stabilization of the positive center by the electron-releasing Et groups much larger than that by the electron-withdrawing Cl substituents.

So far the ligand $(Me_2NMe_2Si)_3C$ has been shown to form (i) the mercury compound $Hg\{C(SiMe_2NMe_2)_3\}_2$, in which none of the NMe_2 groups are used for coordination (and which is thus itself a potentially hexadentate ligand), (ii) the lithium complex $\{(Me_2NMe_2Si)_3CLi\}_n$, in which two NMe_2 groups are coordinated in a chelating fashion to one lithium atom and one NMe_2 group is coordinated to another Li atom,[4] (iii) the magnesium complex $(Me_2NMe_2Si)_3CMgI$, in which all three Me_2N groups are coordinated to the same Mg atom,[5] (iv) the Al compound **1**, in which one NMe_2 group is attached in chelating fashion to a single Al atom, leaving two available for further coordination, and (v) compound **2**, in which two NMe_2 groups are coordinated in chelating fashion to one Al center and the third NMe_2 group is coordinated to a second Al center. The potential for obtaining a wide range of novel species of other metals is apparent.

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Supporting Information Available: Tables giving details of the crystal structure determinations, atom coordinates, bond lengths and angles, and anisotropic displacement parameters for **1** and **2** (7 pages). Ordering information is given on any current masthead page.

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