Reaction of trimethylaluminum with aza-18-crown-6 (HN18C6): structure of Me2Al[N18C6]AlMe3

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matography using 15% EtOAc/hexanes to provide 1.0 g (63% yield) of a yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 5 H), 5.87 (s, 10 H), 3.49 (s, 2 H), 3.12 (s, 4 H), 0.15 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 188.9, 138.5, 129.1, 128.2, 127.1, 126.9, 108.6, 64.5, 59.9, 1.1. Anal. Calcd for $C_{29}H_{39}NSi_2Zr$: C, 63.50; H, 7.11; N, 2.55. Found: C, 61.82; H, 7.26; N, 2.13. FABMS: (M^+) *m/z* 548.

3-(Phenylsulfonyl)-7,7-bis(η^5-cyclopentadienyl)-6,8-bis(trimethylsilyl)-3-aza-7-zirconabicyclo[3.3.0]octa-1(8),5(6)-diene (5). To a solution of bis(η^5-cyclopentadienyl)zirconium(IV) dichloride (0.77 g, 2.7 mmol) in 35 mL of anhydrous THF under nitrogen at −78 °C was added *n*-BuLi (4.1 mL of 1.3 M in hexanes, 5.3 mmol). After stirring at room temperature for 1 h, 1,7-bis(trimethylsilyl)-4-aza-4-(phenylsulfonyl)hepta-1,6-diyne (1.0 g, 2.7 mmol) was added and the mixture stirred at room temperature for 2 h. The reaction was concentrated in vacuo and purified by flash chromatography using 5% EtOAc/hexanes to provide 0.57 g (36% yield) of a yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.78 (m, 2 H), 7.54 (m, 3 H), 5.82 (s, 10 H), 3.90 (s, 4 H), 0.14 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 193.5, 137.4, 132.8, 129.1, 127.9, 109.5, 109.2, 56.6, 0.8. Anal. Calcd for $C_{28}H_{37}NO_2SSi_2Zr$: C, 56.19; H, 6.18; N, 2.34. Found: C, 55.93; H, 6.20; N, 2.28. FABMS: (M^+) *m/z* 598.

3-Benzyl-7,7-bis(η^5-cyclopentadienyl)-6,8-bis(triisopropylsilyl)-3-aza-7-zirconabicyclo[3.3.0]octa-1(8),5(6)-diene (6). To a solution of bis(η^5-cyclopentadienyl)zirconium(IV) dichloride (0.15 g, 0.50 mmol) in 15 mL of anhydrous THF under nitrogen at −78 °C was added *n*-BuLi (0.72 mL of 1.4 M in hexanes, 1.0 mmol). After stirring at room temperature for 1 h, 1,7-bis(triisopropylsilyl)-4-aza-4-benzylhepta-1,6-diyne (0.25 g, 0.5 mmol) was added and the mixture stirred at room temperature for 2 h. The reaction was concentrated in vacuo and purified by flash chromatography using 5% EtOAc/hexanes to provide 0.055 g (16% yield)[12] of a yellow solid. ^{1}H NMR (C_6D_6): δ 7.34 (d, *J* = 8 Hz, 2 H), 7.16 (dd, *J* = 8, 8 Hz, 2 H), 7.09 (d, *J* = 8 Hz, 1 H), 5.78 (s, 10 H), 3.50 (s, 4 H), 3.23 (s, 2 H), 1.24 (m, 42 H). ^{13}C NMR (C_6D_6): δ 183.1, 138.6, 123.7, 108.9, 68.6, 59.7, 20.6, 14.4. Anal. Calcd for $C_{41}H_{63}NSi_2Zr$: C, 68.71; H, 8.79; N, 1.95. Found: C, 66.99; H, 8.70; N, 1.94. FABMS: ($M^+ - 1$) *m/z* 715.

3-Benzyl-7,7-bis(η^5-cyclopentadienyl)-6,8-bis(*tert*-butyldiphenylsilyl)-3-aza-7-zirconabicyclo[3.3.0]octa-1(8),5(6)-diene (7). To a solution of bis(η^5-cyclopentadienyl)zirconium(IV) dichloride (0.11 g, 0.38 mmol) in 15 mL of anhydrous THF under nitrogen at −78 °C was added *n*-BuLi (0.47 mL of 1.3 M in hexanes, 0.76 mmol). After stirring at room temperature for 1 h, 1,7-bis(*tert*-butyldiphenylsilyl)-4-aza-4-benzylhepta-1,6-diyne (0.25 g, 0.38 mmol) was added and the mixture stirred at room temperature for 2 h. The reaction was concentrated in vacuo and purified by flash chromatography using 5% EtOAc/hexanes to provide 0.25 g (62% yield) of a yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.84 (m, 1 H), 7.62 (m, 5 H), 7.38 (m, 14 H), 7.14 (m, 3 H), 7.02 (m, 2 H), 5.50 (s, 10 H), 3.22 (s, 2 H), 3.12 (s, 4 H), 1.14 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 181.6, 138.4, 138.0, 136.4, 135.6, 129.5, 128.7, 128.6, 128.4, 127.9, 127.7, 127.5, 126.7, 109.4, 69.2, 59.2, 30.37, 27.2, 19.1. Anal. Calcd for $C_{55}H_{59}NSi_2Zr$: C, 74.94; H, 6.74; N, 1.59. Found: C, 75.20; H, 7.00; N, 1.51. FABMS: (M^+) *m/z* 880.

Registry No. 3, 138856-02-7; 4, 138856-03-8; 5, 138856-04-9; 6, 138856-05-0; 7, 138856-06-1; Cp_2ZrCl_2, 1291-32-3; $Me_3SiC{\equiv}CCH_2OCH_2C{\equiv}CSiMe_3$, 18036-67-4; $Me_3SiC{\equiv}CCH_2N(CH_2Ph)CH_2C{\equiv}CSiMe_3$, 138835-25-3; $Me_3SiC{\equiv}CCH_2N(SO_2Ph)CH_2C{\equiv}CSiMe_3$, 138856-01-6; $(i\text{-}Pr)_3SiC{\equiv}CCH_2N(CH_2Ph)CH_2C{\equiv}CSi(Pr\text{-}i)_3$, 138835-26-4; $(t\text{-}Bu)Ph_2SiC{\equiv}CCH_2N(CH_2Ph)CH_2C{\equiv}CSiPh_2(t\text{-}Bu)$, 138835-27-5.

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(12) The yield of this reaction is ~70%, but coelution of an impurity complicates the isolation of pure material.

Reaction of Me_3Al with Aza-18-crown-6 (HN18C6): Structure of $Me_2Al[N18C6]AlMe_3$

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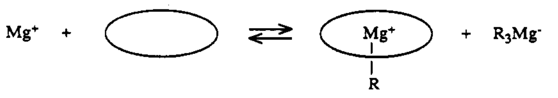
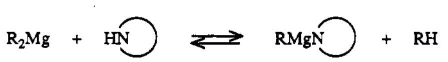
Summary: Reaction of Me_3Al and aza-18-crown-6 furnished a solid, $Me_2Al[N(CH_2CH_2O)_5CH_2CH_2]AlMe_3$, whose structure was determined by X-ray diffraction. In the crystal structure (monoclinic, $P2_1/m$, a = 9.709 (2) Å, b = 11.697 (3) Å, c = 10.767 (2) Å, β = 111.92 (2)°, Z = 2), one Al atom is bonded to two Me groups, the N atom, and the two crown ether O atoms nearest to the N atom; the other Al atom is bonded to three Me groups and the N atom.

Organomagnesium compounds react with appropriate crown ethers and cryptands to form coordinated organomagnesium cations and organomagnesiate anions (e.g., eq 1).[2,3] As part of that study we investigated the use of aza crown ethers.[2,4] Organomagnesium compounds metalate the secondary amine functions of these, of course, as shown in eq 2.[5] We wanted particularly to determine the



(1)



(2)

structures of the species that would be present in such solutions that had been prepared with an *excess* of R_2Mg. Defining the structures proved to be complicated, however.

Because the results could themselves be interesting and also might help us to understand the solutions prepared from R_2Mg, we decided to investigate reactions with aza

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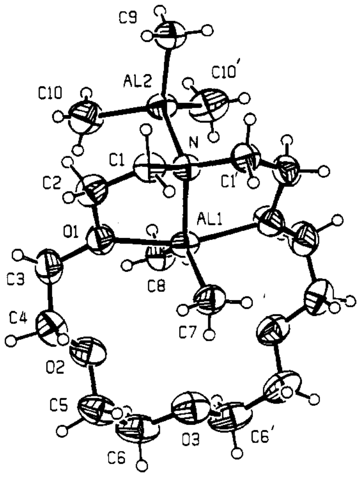
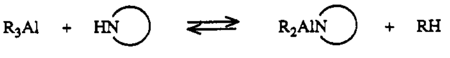


Figure 1. ORTEP[9] drawing of $Me_2Al[N18C6]AlMe_3$, indicating the atom-labeling scheme. H atoms are assigned arbitrary radii; other atoms are shown with 50% probability ellipsoids.

crown ethers of trialkylaluminum compounds (R_3Al), which are isoelectronic with dialkylmagnesium compounds. When we began this study, there already were reports of reactions between organoaluminum compounds and crown ethers or aza crown ethers, and more have since appeared. These studies mainly concern structures of solids isolated from the reactions. In many of these studies,[6] however, the crown ethers either have no nitrogen atoms or only tertiary nitrogen atoms; therefore, metalation (eq 3) corresponding to that in eq 2 is not involved. A smaller number of studies[7,8] involve aza crown ethers having secondary nitrogen atoms. The crown ethers, however, have either two or four such atoms, and the Al atoms are bonded to two or three "metalated" nitrogen atoms and retain only one bond or no bond to an alkyl group.



(3)

Results and Discussion

Reactions of Me_3Al and HN15C5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) in benzene–toluene solutions must proceed as in eq 3 (R = Me). The ^1H NMR spectra of solutions having (after reaction) two methyl groups per crown ether showed one significant methyl absorption (δ –0.48) and crown ether absorptions shifted from those of free crown ether. When more Me_3Al was used (methyl:crown ratio significantly greater than 2), one or two additional methyl absorptions were seen. The spectra of solutions obtained from reactions of Me_3Al and HN18C6 (1,4,7,10,13-pentaoxa-16-azacyclooctadecane) were generally more complicated. Two methyl absorptions (–0.38 and –0.46 in a ~5:1 ratio) were seen at a methyl:crown ratio of 2, and as many as six methyl absorptions at higher methyl:crown ratios. With either crown ether, the correlation between solution composition and number and areas of absorptions was unclear.

Table I. Final Atomic Coordinates[a] (Esd's in Parentheses) and Isotropic Thermal Parameters[b]

atom	x	y	z	B_{eq},[b] Å^2
Al (1)	0.6827 (1)	0.2500	0.3982 (1)	3.34 (2)
Al (2)	0.6137 (1)	0.2500	0.0627 (1)	3.61 (3)
O(1)	0.6511 (2)	0.0690 (2)	0.3645 (2)	4.48 (5)
O(2)	0.8744 (2)	0.0490 (2)	0.6357 (2)	4.85 (5)
O(3)	0.9122 (3)	0.2500	0.7969 (3)	5.43 (8)
N	0.5349 (3)	0.2500	0.2130 (3)	3.24 (7)
C(1)	0.4391 (3)	0.1484 (2)	0.2016 (3)	3.89 (6)
C(2)	0.5294 (3)	0.0423 (3)	0.2444 (3)	4.34 (7)
C(3)	0.7514 (3)	–0.0253 (3)	0.4201 (3)	5.07 (8)
C(4)	0.7806 (3)	–0.0387 (3)	0.5642 (3)	5.07 (8)
C(5)	0.8974 (3)	0.0495 (3)	0.7733 (3)	5.37 (8)
C(6)	0.9932 (3)	0.1484 (4)	0.8372 (3)	5.97 (9)
C(7)	0.5837 (4)	0.2500	0.5279 (4)	4.26 (9)
C(8)	0.8916 (4)	0.2500	0.4273 (4)	4.13 (9)
C(9)	0.5679 (4)	–0.2500	0.1019 (4)	4.5 (1)
C(10)	0.7370 (3)	0.1153 (3)	0.0733 (3)	5.75 (8)

[a] Since the structure has a mirror plane, y coordinates of atoms in this plane were not allowed to refine; these atoms were allowed 0.5 occupancy factors. [b] Anistropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table II. Bond Lengths (Å) and Angles (deg) (Esd's in Parentheses)[a]

Bond Distances			
Al(1)–O(1)	2.151 (2)	O(1)–C(3)	1.446 (3)
Al(1)–N	1.975 (3)	O(2)–C(4)	1.397 (3)
Al(1)–C(7)	1.969 (3)	O(2)–C(5)	1.413 (3)
Al(1)–C(8)	1.933 (3)	O(3)–C(6)	1.402 (3)
Al(2)–N	2.032 (3)	N–C(1)	1.485 (3)
Al(2)–C(9)	1.979 (4)	C(1)–C(2)	1.490 (3)
Al(2)–C(10)	1.957 (3)	C(3)–C(4)	1.478 (4)
O(1)–C(2)	1.423 (3)	C(5)–C(6)	1.483 (4)
Bond Angles			
O(1)–Al(1)–O(1)′	159.76 (9)	C(2)–O(1)–C(3)	114.3 (2)
O(1)–Al(1)–N	79.94 (5)	C(4)–O(2)–C(5)	113.3 (2)
O(1)–Al(1)–C(7)	92.49 (5)	C(6)–O(3)–C(6)′	116.0 (3)
O(1)–Al(1)–C(8)	95.86 (5)	Al(1)–N–Al(2)	117.2 (1)
N–Al(1)–C(7)	110.7 (1)	Al(1)–N–C(1)	106.3 (1)
N–Al(1)–C(8)	119.1 (1)	Al(2)–N–C(1)	110.1 (1)
C(7)–Al(1)–C(8)	130.2 (2)	C(1)–N–C(1)′	106.2 (2)
N–Al(2)–C(9)	103.8 (1)	N–C(1)–C(2)	111.3 (2)
N–Al(2)–C(10)	110.9 (1)	O(1)–C(2)–C(1)	107.0 (2)
C(9)–Al(2)–C(10)	111.9 (1)	O(1)–C(3)–C(4)	110.5 (2)
C(10)–Al(2)–C(10)′	107.3 (2)	O(2)–C(4)–C(3)	109.4 (2)
Al(1)–O(1)–C(2)	112.8 (1)	O(2)–C(5)–C(6)	108.4 (2)
Al(1)–O(1)–C(3)	130.5 (2)	O(3)–C(6)–C(5)	109.6 (2)

[a] Primed atoms are related to unprimed atoms by the symmetry operations x, $^1/_2 - y$, z.

A crystalline solid was isolated from a concentrated toluene solution prepared from Me_3Al and HN18C6 in a 2:1 ratio. The ^1H NMR spectrum of the solution obtained from dissolving (benzene-d_6) this solid resembled but was somewhat simpler than the spectra of solutions prepared directly from HN18C6 and excess Me_3Al (without isolation of a solid). The areas of the methyl and crown ether absorptions showed the presence of five methyl groups per crown ether, the composition expected for the solution

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from which the solid precipitated. Methyl absorptions (relative areas in parentheses) were at δ −0.23 (1), −0.28 (3), −0.30 (1), −0.44 ($<^1/_3$), and −0.60 (1), and crown ether multiplets lay between δ 2.3 and 4.1.

As had been expected, the crystal structure (Figure 1) has a Me_2Al unit bonded to the N atom. The structure has a mirror plane, which passes through the N atom, the O atom most remote from N, and the Al atom and both C atoms of the Me_2Al group. This Al atom is pentacoordinate, and all bond distances involving it are normal. Besides the bonds to the N atom (1.975 (3) Å) and the methyl C atoms (1.969 (3) and 1.933 (3) Å), the other two bonds are to the two crown ether O atoms (2.151 (2) Å) nearest to the N atom. The remaining ring O atoms are well out of bonding distance. The geometry about this Al can be regarded as distorted trigonal bipyramidal, with the N atom and the two Me groups having equatorial positions and the O atoms occupying apical positions (O(1)–Al(1)–O(1)′ 159.76 (9)°). The other Al atom, which also lies in the mirror plane, is tetracoordinate. Three bonds are to methyl C atoms (1.979 (4) and 1.957 (3) Å) and the fourth bond is to the N atom (2.032 (3) Å). As would be expected, these bonds are somewhat longer than those to the other Al atom. The geometry about the tetracoordinate Al atom is very nearly tetrahedral. The disposition of groups around the Al atoms and the substantial distance between them (3.420 (1) Å) indicate the absence of Al–Al bonding.

Structures of crystalline solids are influenced by crystal-packing considerations that do not apply in solution. Nevertheless, it is noteworthy that in spite of the congestion around the N atom, Me_3Al is bonded to it rather than to an O atom. This is in accord with the strong donor abilities of N atoms of the type R_2NM, where M is a polar metal or organometallic fragment. Other crystal structures containing Me_3Al bonded to a N atom[8] of this sort or to a similar O atom (ROM)[10] have been observed. While consistent with a major component in the solutions having this structure, the NMR observations are insufficient to establish its presence.

Experimental Section

All operations were carried out under an atmosphere of nitrogen in a glovebox equipped with an efficient system to circulate and purify the nitrogen. The aza crown ethers, HN15C5[11] and HN18C6,[12] were prepared using previously reported procedures.

NMR Spectra. The crown ether (0.2 mmol) was dissolved in benzene-d_6 (0.4 mL, distilled from CaH_2), and a toluene solution of Me_3Al (2.0 M) was added. The resulting solution was allowed to stand for 24 h and then placed in an NMR tube. The tube was sealed and then heated at 80 °C for 30 min to further increase the probability that no NH remained. The ^1H NMR spectra (200 MHz) were taken at 25 °C; chemical shifts are relative to the CH_3 of toluene (δ 2.10). The methyl:crown ratios that are cited were determined from the relative areas of ^1H NMR absorptions due to Me–Al groups and absorptions due to the crown ether; these experimental values are similar to the ratios that are calculated on the basis of the amounts of reactants that were used.

X-ray Crystal Structure Determination.[13] A toluene solution of trimethylaluminum (1.0 mL, 2.0 M, 2.0 mmol) was added to a solution of HN18C6 (219 mg, 1.0 mmol) in toluene (1.0 mL) that was stirred with a magnetic stirring bar. After 24 h, the solution was transferred to a glass tube which then was sealed. The tube was heated at 80 °C for 30 min, brought back into the glovebox, and opened. The contents were placed in a vial, and the cap was left slightly loose so that the solvent could evaporate slowly. After 1 week, a significant amount of clear, colorless, platelike crystals (mp 174–175 °C) had deposited from the solution. The reported ^1H NMR chemical shifts of a solution of this solid are relative to benzene-d_5 (δ 7.15).

The crystals were cut to an appropriate size, and one with approximate dimensions 0.42 × 0.52 × 0.70 mm was sealed in a glass capillary. Diffraction data for this crystal ($C_{17}H_{39}NO_5Al_2$, mol wt = 391.47) were collected at 20 °C with an Enraf-Nonius CAD-4 automatic diffractometer using graphite-monochromatized Mo Kα (0.710 73 Å) radiation. Lattice constants were obtained by least-squares refinement of the setting angles of 25 reflections with $10 < \theta < 15°$: $a = 9.709$ (2) Å, $b = 11.697$ (3) Å, $c = 10.767$ (2) Å, $\beta = 111.92$ (2)°, $V = 1134.4$ Å^3, $Z = 2$, $D_{calcd} = 1.146$ g cm^{-3}, $F(000) = 428$. Unit cell parameters indicated a monoclinic crystal system. Systematic absences indicated that the space group was $P2_1/m$ or $P2_1$; solution and refinement in the former was successful. Intensity data were collected by the $\omega/2\theta$ scan technique, scan width $(1.20 + 0.35 \tan \theta)°$, using variable scan speed (1.83–2.35° min^{-1}) in the range $2 < \theta < 23°$. The intensities of 1661 unique reflections were measured, of which 1266 had $I > 3\sigma(I)$ and were used. The intensities of 3 reflections, chosen as standards and measured at regular intervals, decreased by 2.4%; the data were corrected for decay by appropriate scaling. Data were also corrected for Lorentz and polarization effects but, since the value of μ (0.146 mm^{-1}) indicated that absorption was not severe, were not corrected for absorption.

The structure was solved by direct methods using MULTAN82 and refined by full-matrix least-squares calculations on F's. In the final cycles of least-squares refinement, 124 parameters were varied including the positional parameters and anisotropic thermal parameters of all non-hydrogen atoms. Hydrogens were located from a difference map and fixed at geometrically idealized positions[13] with C–H = 0.95 Å and fixed isotropic temperature factors ($B = 4.0$ Å^2) in the final rounds of the refinement cycles. The refinement converged with $R = 0.056$ and $R_w = (\Sigma\Delta^2/\Sigma wF_o^2)^{1/2} = 0.070$ where $w = [(\sigma^2F_o + (0.080F_o)^2]^{-1}$. At the conclusion of the refinement, $(\Delta/\sigma)_{max} < 0.01$, the difference map had no peak larger than 0.37 e Å^{-3}, and $S = 1.55$. Atomic scattering factors for non-H atoms were taken from Cromer and Mann[14] and for H atoms from Stewart, Davidson, and Simpson.[15] Allowance was made for anomalous dispersion.[16]

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Registry No. HN15C5, 66943-05-3; HN18C5, 33941-15-0; $Me_2Al[N18C6]AlMe_3$, 138856-43-6; Me_3Al, 75-24-1.

Supplementary Material Available: Tables of hydrogen atom coordinates and of anisotropic thermal parameters (2 pages); a table of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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