dustrie, the Stiftung Volkswagenwerk, and Convex Computer GmbH.

Registry No. EDA, 107-15-3; TMEDA, 110-18-9; PDA, 109-76-2; TMPDA, 110-95-2; DTA, 111-40-0; PMDTA, 3030-47-5; PHT, 110-90-7; TMPHT, 108-74-7; TACN, 4730-54-5; TMTACN, 96556-05-7; THF, 109-99-9; GLY, 107-21-1; 9C3, 27725-91-3; Li^+, 17341-24-1; CH_3Li, 917-54-4; NH_3, 7664-41-7; NMe_3, 75-50-3; H_2O, 7732-18-5; Me_2O, 115-10-6; Et_2O, 60-29-7; $[Li(NH_3)]^+$, 52472-72-7; $[Li(NH_3)_2]^+$, 43415-98-1; $[Li(NH_3)_3]^+$, 68011-04-1; $[Li(NH_3)_4]^+$, 44013-01-6; $[Li(NMe_3)]^+$, 87311-90-8; $[Li(NMe_3)_2]^+$, 122677-10-5; $[Li(TMPHT)]^+$, 122677-11-6; $[Li(TACN)]^+$, 122677-12-7; $[Li(TMTACN)]^+$, 122677-13-8; $[Li(H_2O)]^+$, 63313-34-8; $[Li(H_2O)_2]^+$, 30051-05-9; $[Li(H_2O)_3]^+$, 43567-59-5; $[Li(H_2O)_4]^+$, 40791-36-4; $[Li(Me_2O)]^+$, 53259-64-6; $[Li(Me_2O)_2]^+$, 53259-69-1; $[Li(Et_2O)]^+$, 44387-74-8; $[Li(THF)]^+$, 53307-59-8; $[Li(GLY)]^+$, 122677-14-9; $[Li(GLY)_2]^+$, 122677-15-0; $[Li(9C3)]^+$, 122677-16-1; $CH_3Li(NH_3)$, 63448-35-1; $CH_3Li(NH_3)_2$, 122677-17-2; $CH_3Li(NH_3)_3$, 122677-18-3; $CH_3Li(NMe_3)$, 63448-39-5; $CH_3Li(EDA)$, 122677-19-4; $CH_3Li(EDA)_2$, 122677-20-7; $CH_3Li(TMEDA)$, 106563-74-0; $CH_3Li(TMPHT)$, 122677-21-8; $CH_3Li(TACN)$, 122677-22-9; $CH_3Li(TMTACN)$, 122677-23-0; $CH_3Li(H_2O)$, 117317-80-3; $CH_3Li(H_2O)_2$, 122677-24-1; $[Li(EDA)]^+$, 82268-60-8; $[Li(EDA)_2]^+$, 110556-22-4; $[Li(EDA)_3]^+$, 122677-25-2; $[Li(TMEDA)]^+$, 45651-70-5; $[Li(PDA)]^+$, 89960-63-4; $[Li(TMPDA)]^+$, 122677-26-3; $[Li(DTA)]^+$, 122677-27-4; $[Li(PMDTA)]^+$, 57444-53-8; $[Li(PHT)]^+$, 122677-28-5; $CH_3Li(H_2O)_3$, 122677-29-6; $CH_3Li(Me_2O)$, 122677-30-9; $CH_3Li(Et_2O)$, 122677-31-0; $CH_3Li(THF)$, 122677-32-1; $CH_3Li(THF)_2$, 122677-33-2; $CH_3Li(GLY)$, 122677-34-3; $CH_3Li(GLY)_2$, 122677-35-4; $CH_3Li(9C3)$, 122677-36-5.

Reaction of Organoaluminum Species with Macrocyclic and Open-Chain Tetradentate Amines: Synthesis and Molecular Structure of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ and $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$. An Examination of Aminoalanes Containing Six-Coordinate Aluminum Atoms

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Reaction of diethylaluminum chloride with *N,N′*-bis(3-aminopropyl)ethylenediamine in a toluene/methylene chloride mixture affords the crystalline product $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ (I). I crystallizes in the monoclinic space group $C2/c$ with unit-cell parameters a = 17.056 (4) Å, b = 10.855 (3) Å, c = 11.050 (4) Å, β = 116.77 (2)°, V = 1826.6 (9) Å^3, and D_{calcd} = 1.29 g cm^{-3} for Z = 4. Least-squares refinement based upon 970 observed reflections (1354 collected reflections; 1200 unique reflections; R_{int} = 0.018) with intensities $I > 3\sigma(I)$ in the range $3.50 < 2\theta < 45.0°$ converged at R = 0.044 (R_w = 0.059). The two terminal primary amine nitrogen atoms of *N,N′*-bis(3-aminopropyl)ethylenediamine are bridged by a dichloroaluminum unit and a diethylaluminum unit, thereby constituting a planar Al_2N_2 four-membered ring with an Al···Al contact of 2.819 (2) Å. The mean Al–N bond distance in I is 1.97 (3) Å while the independent Al–Cl distance is 2.394 (1) Å. Additionally, I contains a crystallographic 2-fold axis coincident with Al(1) and Al(2). The crystalline product $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II) is obtained from reaction of the methanol adduct of cyclam, $C_{10}H_{24}N_4{\cdot}CH_3OH$, trimethylaluminum, and $ZrCl_4$. II crystallizes in the triclinic space group $P\bar{1}$ with unit-cell parameters a = 9.234 (3) Å, b = 10.681 (3) Å, c = 15.021 (5) Å, α = 96.23 (3)°, β = 108.78 (3)°, γ = 97.34 (3)°, V = 1373.3 (8) Å^3, and D_{calcd} = 1.30 g cm^{-3} for Z = 2. Least-squares refinement based on 2976 observed reflections (3887 collected reflections; 3616 unique reflections; R_{int} = 0.017) with intensities $I > 3\sigma(I)$ in the range $3.50 < 2\theta < 45.0°$ converged at R = 0.056 (R_w = 0.074). II also contains an Al_2N_2 four-membered ring with an Al···Al contact of 2.889 (2) Å. The central aluminum atom of both I and II are six-coordinate residing in octahedral environments. The coordination sphere of the octahedral aluminum atom in I consists of the four nitrogen atoms of the open-chain amine in addition to two chloride atoms residing on either side of the equatorial N_4 plane. The coordination sphere of the core aluminum atom in II consists of the four nitrogen atoms of the macrocycle, one chlorine atom, and a μ-bridging methoxide fragment. The mean Al–N distance in II is 1.98 (4) Å while Al–Cl distances of 2.368 (1) and 2.130 (3) Å were observed. The mean Al–O bond distance in the Al_2ON four-membered ring in II is quite short at 1.88 (6) Å.

Introduction

The interactions of aluminum species with amines represents one of the most extensively investigated facets of organoaluminum chemistry. Investigations may be traced to 1930 when Krause and Dittmar[1] reported the synthesis of $H_3N{\cdot}Al(p\text{-tolyl})_3$ and $H_3N{\cdot}AlPh_3$. In terms of more recent studies, seminal work has been reported concerning both aluminum–nitrogen oligomers[2-10] and poly(*N*-alkylimino)alanes.[11-25] Although these studies often resulted

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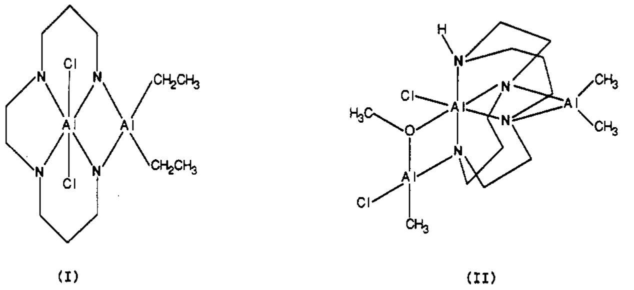

Figure 1. Schematic illustrations of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$, (I) and $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II).

in unusual Al–N cages, the coordination chemistry, relative to aluminum, was generally unspectacular as the typical four-coordinate tetrahedral coordination was largely observed. Additionally, it is important to point out that the aforementioned investigations were exclusively concerned with reactions of aluminum species with monodentate primary and secondary amines. The corresponding chemistry of macrocyclic and multidentate open-chain amines consequently remained a largely unexplored segment of organoaluminum chemistry.

Table I. Summary of the Crystallographic Data for $[Cl_2Al{\bullet}C_8H_{20}N_4][Al(C_2H_5)_2]$ (I) and $[Al(CH_3)_2][ClAl{\bullet}C_{10}H_{21}N_4{\bullet}OCH_3][ClAl(CH_3)]$ (II)

	I	II
empirical formula	$C_{12}H_{30}N_4Al_2Cl_2$	$C_{20}H_{38}N_4OAl_3Cl_3$
color; habit	colorless; parallelepiped	
space group	$C2/c$	$P\bar{1}$
unit-cell dimens		
a, Å	17.056 (4)	9.234 (3)
b, Å	10.855 (3)	10.681 (3)
c, Å	11.050 (4)	15.021 (5)
α, deg		96.23 (3)
β, deg	116.77 (2)	108.78 (3)
γ, deg		97.34 (3)
V, Å^3	1826.6 (9)	1373.3 (8)
molecules/cell	4	2
mol wt	355.32	537.91
D(calcd), g/cm^3	1.29	1.30
diffractometer	Nicolet R3/m	
radiatn	Mo Kα (g = 0.71073 Å)	
temp. °C	21	
2θ range, deg	3.50–45.0	
reflectns collected	1354 (1200 unique; R_{int} = 0.018)	3887 (3616 unique; R_{int} = 0.017)
reflectns obsd ($I > 3\sigma(I)$)	970	2976
GOF	1.65	2.82
data to parameter ratio	6.38:1	11.1:1
R	0.044	0.056
R_w	0.059	0.074

Recently, this laboratory initiated an investigation into the organoaluminum chemistry of macrocyclic[26-31] and multidentate open-chain amines.[32-35] These studies, characterized by alkane elimination and reaction products possessing Al_2N_2 fragments with extensive Al–N association, proved to be exceedingly fruitful particularly with regard to the organometallic coordination chemistry of aluminum. Herein, we report the synthesis and molecular structures of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ (I) and $[Al(CH_3)_2][ClAl{\cdot}C_8H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II). I was isolated from reaction of diethylaluminum chloride with the tetradentate open-chain amine *N,N′*-bis(3-aminopropyl)ethylenediamine, $C_8H_{22}N_4$. II resulted from reaction of the methanol adduct of cyclam[36] with trimethylaluminum in the presence of $ZrCl_4$. Interestingly, as illustrated by Figure 1, both I and II contain core aluminum atoms residing in six-coordinate octahedral environments.

Experimental Section

General Comments. The extreme air and water sensitivity of reactants and products warranted concerted effort to exclude oxygen and moisture during the synthesis and subsequent manipulations. Thus, standard Schlenk technique was employed in conjunction with an inert-atmosphere glovebox (Vacuum Atmospheres HE--43 Dri-Lab). Toluene, methylene chloride, and chlorobenzene were distilled under prepurified argon prior to use. Diethylaluminum chloride, *N,N′*-bis(3-aminopropyl)ethylenediamine, trimethylaluminum, and $ZrCl_4$ were purchased from Aldrich Chemical Co. and used as received. Cyclam was prepared by the Ni-template synthesis described by Barefield.[37] The macrocycle was isolated as the alcohol adduct after recrystallization from methanol. Single-crystal X-ray data were collected

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Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for $[Cl_2Al \bullet C_8H_{20}N_4][Al(C_2H_5)_2]$ (I)

atom	*x*	*y*	*z*	*U*(eq)[a]
Cl(1)	4155 (1)	1566 (1)	5088 (1)	58 (1)
Al(1)	5000	1661 (1)	7500	44 (1)
Al(2)	5000	4257 (2)	7500	47 (1)
N(1)	4304 (2)	2967 (3)	7770 (4)	46 (1)
N(2)	4242 (3)	299 (4)	7635 (5)	69 (2)
C(1)	3339 (3)	2863 (5)	7098 (5)	65 (2)
C(2)	3028 (4)	1690 (7)	7465 (7)	84 (3)
C(3)	3261 (4)	515 (7)	7003 (6)	92 (3)
C(4)	4509 (5)	−869 (5))	7230 (6)	106 (4)
C(5)	4276 (4)	5242 (5)	5879 (6)	73 (3)
C(6)	3575 (4)	5994 (5)	5999 (8)	87 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

on a Nicolet R3m/V diffractometer. NMR data were recorded on a JEOL 90-MHz spectrometer.

Synthesis of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ (I). A reaction vessel was charged with toluene/methylene chloride (10 and 5 mL, respectively) and *N,N'*-bis(3-aminopropyl)ethylenediamine (8.2 mmol) in the drybox. Diethylaluminum chloride (8.2 mmol) was slowly added via syringe. Reaction was immediate and exothermic. The reaction vessel was removed from the drybox and heated (110 °C) in an oil bath for 24 h. The reaction vessel was vented periodically. After the system was allowed to stand undisturbed for several hours at room temperature, a multitude of small, colorless, extremely air-sensitive crystals (mp 251–54 °C; 45% yield) were obtained. ^1H NMR ($CDCl_3$): δ −0.110 (q, 4 H, $AlCH_2CH_3$), 1.01 (t, 6 H, $AlCH_2CH_3$), 1.65–3.35 (m, 16 H, $N(CH_2)_3N(CH_2)_2N(CH_2)_3N$). In addition to the crystalline material, a small amount of an insoluble amorphous substance was also present.

Synthesis of $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II). A 100-mL Schlenk flask was charged with cyclam (2.49 mmol) and admitted to the drybox where chlorobenzene (25 mL) was added. Zirconium tetrachloride (2.49 mmol) was added to the flask and the milky white mixture was allowed to stir for 1 h. Trimethylaluminum (8.35 mmol) was slowly added to this system. Reaction was immediate and exothermic resulting in a yellowish solution. The system was removed from the drybox and allowed to stir for several hours at room temperature. The solution was filtered via cannula and concentrated under vacuo. Upon cooling overnight colorless, air-sensitive crystals were obtained; 46% yield (based on cyclam) (mp 208–210 °C dec). ^1H NMR ($CDCl_3$): δ −0.56 (s, 3 H, $Al(CH_3)_2$), −0.43 (s, 3 H, $Al(CH_3)_2$), 0.065 (s, 3 H, $Al(CH_3)Cl$), 1.25–3.00 (m, 21 H, $C_{10}H_{20}N_4$), 3.65 (s, 3 H, OCH_3).

Structure Solution and Refinement for $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ (I). A colorless parallelepiped crystal of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ was mounted in a thin walled glass capillary under an inert atmosphere of argon. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement of the setting angles of 35 carefully centered reflections in the range 26.17 < 2θ < 39.65°, corresponded to a monoclinic cell. The space group was determined to be *C*2/*c* (No. 15). The structure was solved by direct methods and refined, based on 970 observed reflections with intensities $I > 3\sigma(I)$, using SHELXTL PLUS.[38] Non-hydrogen atoms were refined by using anisotropic thermal parameters; hydrogen atoms, located by standard difference Fourier techniques, were refined by using isotropic thermal parameters. The weighting scheme was based on counting statistics and included a factor (p = 0.0005) to downweight the intense reflections. The maximum and minimum peaks on the final difference map corresponded to 0.39 and −0.33 e/Å^3, respectively. Refinement converged at R = 0.044 (R_w = 0.059). Relevant crystallographic data are given in Table I. Final fractional atomic coordinates for I are given in Table II while selected bond distances and angles are given in Table III.

Table III. Selected Bond Distance (Å) and Angles (deg) for $[Cl_2Al \bullet C_8H_{20}N_4][Al(C_2H_5)_2]$ (I)

Bond Distances			
Cl(1)–Al(1)	2.394 (1)	Al(1)–Al(2)	2.819 (2)
Al(1)–N(1)	1.957 (4)	Al(1)–N(2)	2.012 (5)
Al(2)–N(1)	1.945 (4)	Al(2)–C(5)	1.971 (5)
N(1)–C(1)	1.474 (5)	N(2)–C(3)	1.513 (8)
N(2)–C(4)	1.482 (8)	C(1)–C(2)	1.503 (9)
C(2)–C(3)	1.493 (10)	C(4)–C(4A)	1.505 (16)
C(5)–C(6)	1.502 (10)		
Bond Angles			
Cl(1)–Al(1)–N(1)	95.7 (1)	Cl(1)–Al(1)–N(2)	88.1 (1)
Cl(1)–Al(1)–Cl(1A)	175.1 (1)	Cl(1)–Al(1)–N(1A)	87.9 (1)
Cl(1)–Al(1)–N(2A)	88.3 (1)	N(1)–Al(1)–N(2)	93.8 (2)
N(1)–Al(1)–N(1A)	87.1 (2)	N(1)–Al(1)–N(2A)	175.9 (2)
N(2)–Al(1)–N(2A)	85.5 (3)	N(1)–Al(2)–C(5)	110.8 (2)
N(1)–Al(2)–N(1A)	87.9 (2)	C(5)–Al(2)–N(1A)	115.3 (2)
C(5)–Al(2)–C(5A)	114.3 (3)	Al(1)–N(1)–Al(2)	92.5 (2)
Al(1)–N(1)–C(1)	118.9 (3)	Al(2)–N(1)–C(1)	126.7 (3)
Al(1)–N(2)–C(3)	117.7 (4)	Al(1)–N(2)–C(4)	108.1 (5)
C(3)–N(2)–C(4)	114.8 (4)	N(1)–C(1)–C(2)	112.2 (4)
C(1)–C(2)–C(3)	116.8 (7)	N(2)–C(3)–C(2)	112.6 (5)
N(2)–C(4)–C(4A)	108.6 (3)	Al(2)–C(5)–C(6)	114.3 (5)

Structure Solution and Refinement for $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II). A single crystalline sample of $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ was prepared for X-ray examination in the same manner employed for I. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement of the setting angles of 40 carefully centered reflections in the range 27.32 < 2θ < 42.21°, afforded a triclinic cell. The space group was determined to be $P\bar{1}$ (No. 2). The structure was solved by direct methods using SHELXTL PLUX.[38] Non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation in difference map orientations; C–H distances were constrained to 0.96 Å. An isotropic group thermal parameter (U_{iso} = 0.064 (3) Å^2) was refined for all of the hydrogen atoms. The final cycle of full-matrix least-squares refinement, based on 2976 observed reflections ($I > 3\sigma(I)$) and 269 variable parameters, converged at R = 0.056 and R_w = 0.074. The asymmetric unit contains one chlorobenzene solvent molecule that is disordered. The parameters of the organoaluminum species were little affected (no shifts greater than 2 esd's) by the nature of the modeling of the disorder. The final model of the solvent molecule consisted of a benzene ring constrained to idealized values (d_{C-C} = 1.395 Å; C–C–C = 120°); the position of the chlorine atom was not constrained. All of the solvent atoms were assigned anisotropic thermal parameters to correct for extreme librational motion. Crystallographic data concerning II are given in Table I. Final fractional atomic coordinates for II are given in Table IV while selected bond distances and angles are given in Table V.

Results and Discussion

Smith reported that the nature of Al–N cages and oligomers resulting from interactions of organoaluminum species with primary and secondary amines was greatly dependent upon reaction temperature.[2] Reaction of N–H amines with aluminum alkyls at low temperatures was reported to produce simple 1:1 addition compounds of the type which Davidson and Brown studied (eq 1).[39] However, Smith demonstrated that when such systems having N–H and Al–R bonds are pyrolyzed intermolecular condensation occurs with the elimination of alkane, resulting in Al–N oligomers possessing Al_2N_2 fragments and substantial Al–N association (eq 2).[2,9] A similar class of

$$Al(CH_3)_3 + (CH_3)_2HN \rightarrow (CH_3)_2HN{\cdot}Al(CH_3)_3 \quad (1)$$

$$3Al(CH_3)_3 + 3NH_2(CH_3) \xrightarrow{70\ °C} [(CH_3)_2AlNH(CH_3)]_3 + 3CH_4 \quad (2)$$

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Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Al(CH_3)_2][ClAl \bullet C_{10}H_{21}N_4 \bullet OCH_3][ClAl(CH_3)]$ (II)

	x	y	z	U(eq)[a]
Cl(1)	2940 (1)	4220 (1)	4929 (1)	40 (1)
Cl(2)	3171 (3)	−417 (2)	6190 (1)	92 (1)
Cl(3)	8810 (11)	1470 (7)	11483 (6)	455 (7)
Al(1)	3783 (2)	3862 (1)	6530 (1)	29 (1)
Al(2)	2798 (2)	1287 (1)	5598 (1)	47 (1)
Al(3)	3459 (2)	5026 (1)	8268 (1)	35 (1)
O(1)	4609 (4)	2423 (3)	6091 (2)	43 (1)
N(1)	2006 (4)	2440 (3)	6308 (3)	35 (1)
N(2)	2788 (4)	5258 (3)	6925 (2)	33 (1)
N(3)	5651 (4)	5228 (4)	6756 (3)	37 (2)
N(4)	4476 (4)	3643 (3)	7916 (3)	33 (1)
C(1)	454 (6)	2749 (5)	5804 (3)	43 (2)
C(2)	74 (6)	3906 (5)	6298 (4)	48 (2)
C(3)	1101 (6)	5177 (5)	6405 (3)	43 (2)
C(4)	3562 (6)	6474 (4)	6761 (3)	45 (2)
C(5)	5288 (6)	6499 (5)	7025 (4)	47 (2)
C(6)	7199 (6)	5077 (6)	7394 (3)	51 (2)
C(7)	7212 (6)	4862 (6)	8378 (3)	51 (2)
C(8)	6155 (6)	3674 (5)	8395 (3)	46 (2)
C(9)	3696 (6)	2336 (5)	7937 (3)	43 (2)
C(10)	2054 (6)	2050 (5)	7243 (3)	43 (2)
C(11)	4754 (7)	6533 (5)	9160 (3)	53 (2)
C(12)	1800 (6)	4546 (6)	8783 (3)	53 (2)
C(13)	1861 (7)	898 (5)	4229 (3)	64 (3)
C(14)	5753 (7)	2319 (6)	5744 (5)	67 (3)
C(15)	8587 (16)	1229 (11)	10324 (7)	332 (22)
C(16)	9474	1666	9788	237 (17)
C(17)	8978	1238	8810	288 (22)
C(18)	7594	374	8367	201 (12)
C(19)	6706	−63	8903	208 (14)
C(20)	7203	365	9882	243 (12)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

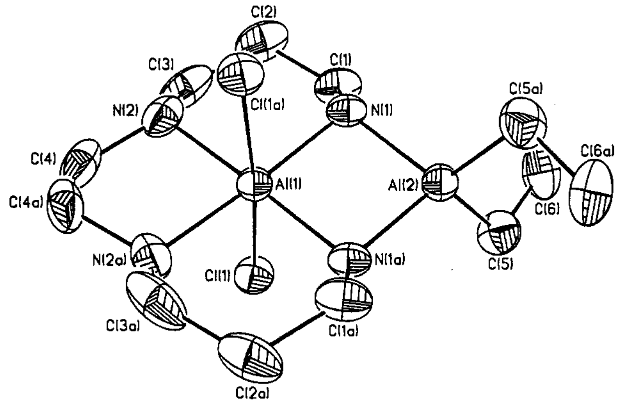


Figure 2. A view of the $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ (I) molecule showing the atom-labeling scheme. Thermal ellipsoids show 35% probability levels. Hydrogen atoms have been omitted.

aluminum–nitrogen cage compounds known as poly(N-alkyliminoalanes), prepared from reaction of aluminum hydride or lithium aluminum hydride with primary and secondary amines, has also been reported and extensively studied.[11-25] Notably, the four-coordinate tetrahedral coordination of the aluminum atoms observed in the aforementioned Al–N oligomers and poly(N-alkyliminoalanes) generated little interest as such coordination was expected for aluminum. Indeed, four-coordinate tetrahedral is the predominant coordination of aluminum throughout organometallic chemistry. With this in mind, it is interesting to observe the core aluminum atoms in the structures of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ (I) and $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II) given in Figure 2 and Figure 3, respectively.

Table V. Bond Distances (Å) and Angles (deg) for $[Al(CH_3)_2][ClAl \bullet C_{10}H_{21}N_4 \bullet OCH_3][ClAl(CH_3)]$ (II)

Bond Distances

Cl(1)–Al(1)	2.368 (2)	Cl(2)–Al(2)	2.130 (3)
Al(1)–O(1)	1.944 (4)	Al(1)–N(1)	2.003 (4)
Al(1)–N(2)	1.982 (4)	Al(1)–N(3)	2.023 (4)
Al(1)–N(4)	2.021 (4)	Al(2)–O(1)	1.818 (3)
Al(2)–N(1)	1.907 (5)	Al(2)–C(13)	1.930 (5)
Al(3)–N(2)	1.965 (4)	Al(3)–N(4)	1.962 (4)
Al(3)–C(11)	1.956 (5)	Al(3)–C(12)	1.963 (6)
O(1)–C(14)	1.332 (9)	N(1)–C(1)	1.488 (6)
N(1)–C(10)	1.496 (7)	N(2)–C(3)	1.486 (6)
N(2)–C(4)	1.485 (6)	N(3)–C(5)	1.484 (7)
N(3)–C(6)	1.483 (6)	N(4)–C(8)	1.478 (6)
N(4)–C(9)	1.495 (6)	C(1)–C(2)	1.510 (8)
C(2)–C(3)	1.514 (7)	C(4)–C(5)	1.510 (8)
C(6)–C(7)	1.517 (8)	C(7)–C(8)	1.507 (8)
C(9)–C(10)	1.507 (6)		

Bond Angles

Cl(1)–Al(1)–O(1)	86.7 (1)	Cl(1)–Al(1)–N(1)	93.7 (1)
O(1)–Al(1)–N(1)	79.7 (2)	Cl(1)–Al(1)–N(2)	91.8 (1)
O(1)–Al(1)–N(2)	175.8 (1)	N(1)–Al(1)–N(2)	96.6 (2)
Cl(1)–Al(1)–N(3)	87.0 (1)	O(1)–Al(1)–N(3)	97.5 (2)
N(1)–Al(1)–N(3)	177.0 (2)	N(2)–Al(1)–N(3)	86.3 (2)
Cl(1)–Al(1)–N(4)	177.1 (1)	O(1)–Al(1)–N(4)	96.2 (2)
N(1)–Al(1)–N(4)	87.3 (2)	N(2)–Al(1)–N(4)	85.4 (2)
N(3)–Al(1)–N(4)	92.0 (2)	Cl(2)–Al(2)–O(1)	107.6 (1)
Cl(2)–Al(2)–N(1)	113.0 (2)	O(1)–Al(2)–N(1)	85.5 (2)
Cl(2)–Al(2)–C(13)	110.6 (2)	O(1)–Al(2)–C(13)	117.7 (2)
N(1)–Al(2)–C(13)	120.0 (2)	N(2)–Al(3)–N(4)	87.5 (2)
N(2)–Al(3)–C(11)	114.5 (2)	N(4)–Al(3)–C(11)	118.4 (2)
N(2)–Al(3)–C(12)	116.2 (2)	N(4)–Al(3)–C(12)	116.5 (2)
C(11)–Al(3)–C(12)	104.0 (2)	Al(1)–O(1)–Al(2)	97.9 (2)
Al(1)–O(1)–C(14)	134.0 (3)	Al(2)–O(1)–C(14)	120.0 (3)
Al(1)–N(1)–Al(2)	93.1 (2)	Al(1)–N(1)–C(1)	114.3 (3)
Al(2)–N(1)–C(1)	116.8 (3)	Al(1)–N(1)–C(10)	109.0 (2)
Al(2)–N(1)–C(10)	112.3 (3)	C(1)–N(1)–C(10)	110.2 (4)
Al(1)–N(2)–Al(3)	94.1 (2)	Al(1)–N(2)–C(3)	116.7 (3)
Al(3)–N(2)–C(3)	118.5 (3)	Al(1)–N(2)–C(4)	107.8 (3)
Al(3)–N(2)–C(4)	113.5 (2)	C(3)–N(2)–C(4)	105.9 (4)
Al(1)–N(3)–C(5)	109.5 (3)	Al(1)–N(3)–C(6)	119.8 (3)
C(5)–N(3)–C(6)	110.8 (3)	al(1)–N(4)–Al(3)	93.0 (2)
Al(1)–N(4)–C(8)	116.9 (3)	Al(3)–N(4)–C(8)	120.6 (3)
Al(1)–N(4)–C(9)	105.7 (2)	Al(3)–N(4)–C(9)	113.9 (3)
C(8)–N(4)–C(9)	105.8 (4)	N(1)–C(1)–C(2)	114.2 (3)
C(1)–C(2)–C(3)	116.9 (5)	N(2)–C(3)–C(2)	116.5 (4)
N(2)–C(4)–C(5)	110.6 (4)	N(3)–C(5)–C(4)	111.9 (4)
N(3)–C(6)–C(7)	113.0 (5)	C(6)–C(7)–C(8)	114.9 (4)
N(4)–C(8)–C(7)	115.8 (4)	N(4)–C(9)–C(10)	110.9 (4)
N(1)–C(10)–C(9)	110.3 (4)		

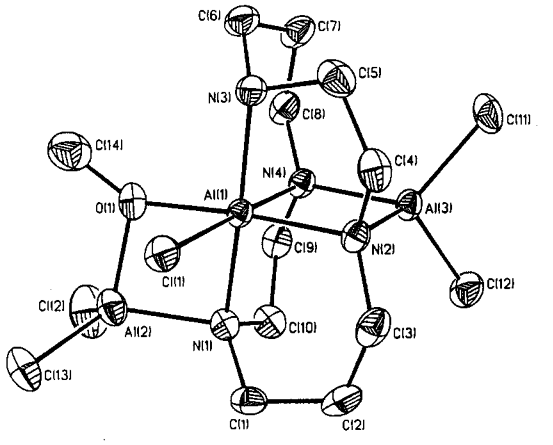
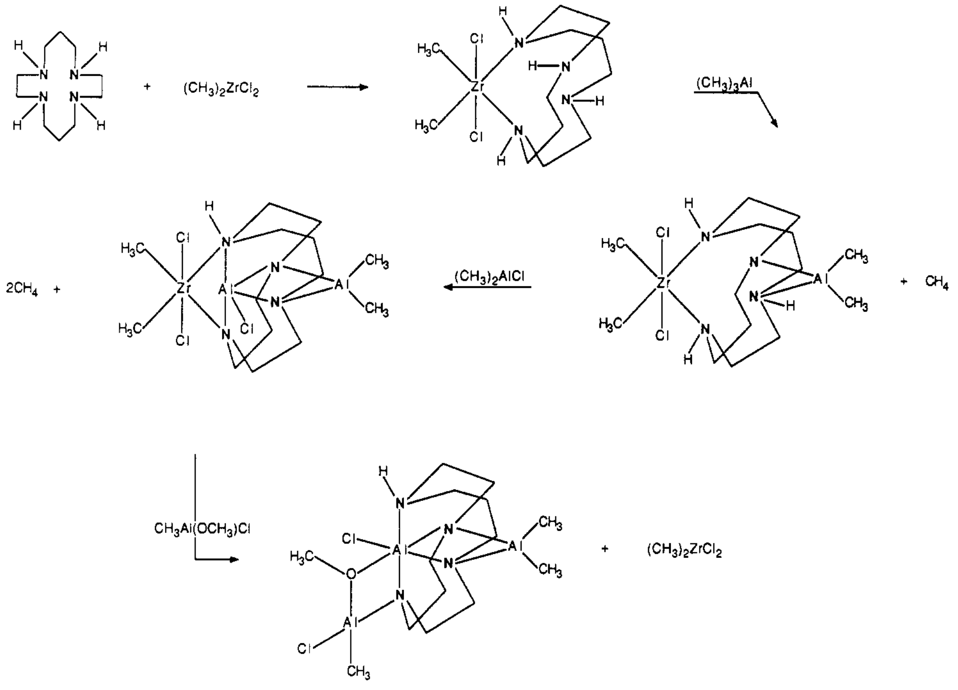


Figure 3. A view of the $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II) molecule showing the atom-labeling scheme. Thermal ellipsoids show 35% probability levels. Hydrogen atoms have been omitted.

As can be seen from Figure 2, $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ (I) contains two aluminum fragments: one dichloroaluminum unit and one diethylaluminum unit. I resides upon a crystallographic 2-fold axis coincident with the two aluminum atoms Al(1) and Al(2) and bisecting the planar Al_2N_2 four-membered ring. The independent Al–N



(II)

Figure 4. Preparative reaction scheme for $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II).

distances for the Al_2N_2 ring are 1.957 (4) and 1.945 (4) Å for Al(1)–N(1) and Al(2)–N(1), respectively. The Al(1)···Al(2) contact of 2.819 (2) Å is not indicative of significant metal–metal interaction. The mean Al–N bond distance in I is 1.971 (4) Å. The Al(1)–N(1)–Al(2) bond angle is 92.5 (2)° while the N(1)–Al(2)–N(1a) bond angle is 87.9 (2)°. The mean N–Al–Cl(1) bond angle is 90.0 (1)°. The Cl(1)–Al(1)–Cl(1a) bond angle is 175.1 (1)° whereas that for N(1)–Al(1)–N(2a) is 175.9 (2)°. The four nitrogen atoms of the amine are coplanar with Al(1) while the two chlorine atoms, with a unique Al–Cl bond distance of 2.394 (1) Å, are situated in axial positions relative to the AlN_4 plane. The coordination of Al(1) in $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ can thus be described as six-coordinate octahedral.

The absence of a diethylaluminum chloride moiety in I is significant and may easily be accounted for by considering the disproportionation of $[(C_2H_5)_2AlCl]_2$ to provide $(C_2H_5)AlCl_2$ and $(C_2H_5)_3Al$. Such disproportionation of dialkylaluminum halides in the presence of base to give alkylaluminum dihalides and trialkylaluminum has been previously noted[40] and was initially suggested by Ziegler nearly 30 years ago.[41] Indeed, we have recently observed this behavior in our laboratory while studying the reaction of diethylaluminum chloride with the macrocyclic tetradentate amine cyclam.[29] I could thus be obtained by the interaction of ethylaluminum dichloride, the stronger Lewis acid, with the four nitrogen atoms along the amine cavity while triethylaluminum is left to react with the primary amine units of the ligand. It is important to note that *N,N′*-bis(3-aminopropyl)ethylenediamine is quite versatile in organoaluminum coordination chemistry as we have recently reported the unique ability of this ligand to also stabilize a five-coordinate organoaluminum species in a trigonal bipyramidal geometry.[34]

The X-ray crystal structure of $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II) is given in Figure 3. II contains three aluminum units: one chloroaluminum fragment, one dimethylaluminum fragment, and one methylaluminum chloride unit. As the four nitrogen atoms in uncomplexed cyclam are coplanar,[28] it is evident that the macrocycle has experienced considerable distortion as it has assumed a folded "envelope" conformation in accommodating the three aluminum species in II. Particularly noteworthy is the fact that the core aluminum atom Al(1) is six-coordinate residing in an octahedral environment. The coordination sphere of Al(1) consists of the four nitrogen atoms of the macrocyclic amine and one chlorine atom in addition to a bridging methoxide fragment. II results from a unique reaction involving the chlorination of trimethylaluminum by $ZrCl_4$ and the cleavage of N–H and Al–R bonds.

It is proposed that the first step in the process involves reaction of trimethylaluminum with the methanol adduct of cyclam to yield dimethylaluminum methoxide (eq 3).

$$(CH_3)_3Al + CH_3OH \rightarrow CH_4 + (CH_3)_2Al(OCH_3) \quad (3)$$

Zirconium tetrachloride in turn is proposed to react with dimethylaluminum methoxide and trimethylaluminum to produce $(CH_3)_2ZrCl_2$, $(CH_3)_2AlCl$, and $(CH_3)Al(OCH_3)Cl$ (eq 4). It is important to note that no zirconium species

$$ZrCl_4 + (CH_3)_3Al + (CH_3)_2Al(OCH_3) \rightarrow (CH_3)_2ZrCl_2 + (CH_3)_2AlCl + (CH_3)Al(OCH_3)Cl \quad (4)$$

were isolated. It is well-documented that alkylzirconium derivatives such as $(CH_3)_4Zr$ are inherently unstable and reportedly decompose, with blackening, above −15 °C.[42] Similarly, $(CH_3)_2ZrCl_2$ has been reported to be quite unstable. While earlier attempts at preparing $(CH_3)_2ZrCl_2$ from reaction of ZrX_4 and ZnR_4 (X = Cl, Br; R = CH_3, C_2H_5) failed, the workers were able to isolate the bipyridine adduct of $(CH_3)_2ZrCl_2$.[43] Thus, it is reasonable that cyclam could be employed in a similar capacity, as illustrated in Figure 4, to stabilize the zirconium moiety. Subsequent reaction of the cyclam adduct of dimethylzirconium di-

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chloride, $(CH_3)_2ZrCl_2{\cdot}C_{10}H_{24}N_4$, with trimethylaluminum, dimethylaluminum chloride, and $(CH_3)Al(OCH_3)Cl$, as illustrated in Figure 4, could readily provide $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II).

Several points regarding structure and bonding in I and II are worthy of note. The Al–Cl bond distance of 2.130 (3) Å involving the four-coordinate aluminum atom Al(2) in II is considerably shorter than the corresponding Al–Cl bond distance of 2.368 (2) Å involving the six-coordinate aluminum atom Al(1). Moreover, it is interesting to note that the six-coordinate aluminum–chlorine bond distance in II is shorter than the analogous Al(1)–Cl(1) bond distance of 2.394 (1) Å observed in I. Indeed, the Al–Cl bond distances involving the six-coordinate aluminum atoms in I and II are considerably longer than the Al–Cl distances of 2.202 (5) and 2.197 (7) Å reported for the seven-coordinate aluminum atom in the $[Cl_2Al{\cdot}15\text{-crown-}5]^+$ complex.[44]

Organoaluminum chemistry relative to amines is currently experiencing great activity principally due to the utilization of Al–N compounds as potential precursors to ceramic materials.[45–47] For example, a novel six-coordinate aminoalane complex has recently been reported that, upon pyrolysis, provides aluminum nitride and silicon carbide.[48] Future contributions from this laboratory will continue to examine the interactions of organoaluminum species with various amines.

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Registry No. I, 122699-35-8; II, 122699-37-0; *N*,*N*-bis(3-aminopropyl)ethylenediamine, 10563-26-5; diethylaluminum chloride, 96-10-6; cyclam, 295-37-4; trimethylaluminum, 75-24-1.

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters, molecular plots, and a summary of data collection and refinement (33 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Isocyanide Insertion Reactions of Manganese(I) Alkyl and Iminoacyl Complexes

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The reaction of $(CO)_5MnCH_2C_6H_4$-*p*-X (X = Cl, OMe) with *p*-tolyl isocyanide in the presence of PdO affords the products of double insertion $(CO)_4Mn[C({=}N$-*p*-tolyl$)C({=}N$-*p*-tolyl$)CH_2C_6H_4$-*p*-X] (**2a,b**). Also isolated was **3a**, $(CO)_4Mn[C\{{=}CH(C_6H_4$-*p*-Cl$)\}N($*p*-tolyl$)C(NH$-*p*-tolyl$)]$, the product of intramolecular imino N attack on a coordinated *p*-tolyl isocyanide. **2a,b** react with an additional equivalent of isocyanide affording products which depend on the identity of the isocyanide. With *p*-tolyl isocyanide and cyclohexyl isocyanide, carbene complexes $(CO)_4Mn[C({=}N$-*p*-tolyl$)C\{{=}CH(C_6H_4$-*p*-X$)\}N($*p*-tolyl$)C(NHR)]$ (**4a**, X = Cl, R = *p*-tolyl; **4b**, X = OMe, R = C_6H_{11}; **4c**, X = Cl, R = C_6H_{11}) and $(CO)_4Mn[C({=}N$-*p*-tolyl$)C(NH$-*p*-tolyl$)C(C_6H_4$-*p*-X$)C(NHR)]$ (**5a**, X = Cl, R = *p*-tolyl; **5b**, X = OMe, R = C_6H_{11}) are isolated. With bulky *t*-BuNC, $(CO)_4(CN$-*t*-Bu$)Mn[C({=}N$-*p*-tolyl$)C({=}N$-*p*-tolyl$)CH_2C_6H_4$-*p*-Cl] (**7a**) and $(CO)_3(CN$-*t*-Bu$)$-$Mn[C({=}N$-*p*-tolyl$)C({=}N$-*p*-tolyl$)CH_2C_6H_4$-*p*-Cl] (**8a**) are obtained. **4a** can be protonated at the iminoacyl N giving a bis(carbene) complex, **6a**. Mechanisms for the formation of **2**, **3**, and **4** are proposed. The last is supported by isolation of **7**. The structures of **2b**, **3a**, **4a**, **4b**, **4c**, and **6a** have been solved by single-crystal X-ray diffraction methods. Crystallographic data [space group, *a* (Å), *b* (Å), *c* (Å), β (deg), *Z*, observed reflections, R_w]: for **2b**, $P2_1/n$, 19.616 (2), 12.287 (2), 11.368 (2), 103.13 (1), 4, 1985, 0.0379; for **3a**, $P2_1/c$, 6.611 (1), 18.937 (2), 20.510 (2), 90.111 (8), 4, 2119, 0.0407; for **4a**, $P2_1/n$, 16.354 (5), 13.273 (2), 15.513 (4), 108.96 (2), 4, 2292, 0.0388; for **4b**, $P2_1/n$, 15.986 (2), 13.748 (2), 15.681 (2), 108.01 (1), 4, 2033, 0.0370; for **4c**, $P2_1/n$, 15.915 (2), 13.550 (2), 15.611 (2), 108.723 (9), 4, 3303, 0.0382; and for **6a**, $P2_1/c$, 13.054 (2), 15.721 (2), 17.798 (3), 104.79 (1), 4, 2026, 0.0392.

Introduction

Insertion reactions are of fundamental importance in organometallic chemistry.[1,2] The most completely studied insertion reaction is that of carbon monoxide which plays a key role in many reactions homogeneously catalyzed by transition-metal species—for example, hydroformylation,[3] homologation,[4] and oxygenate production by hydrogenation of CO.[5] CO insertion chemistry has been reviewed.[6–8]

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