

Stereochemistry of Polynuclear Compounds of the Main Group Elements.¹ X. μ -Diphenylamino- μ -methyl-tetramethyldialuminum²

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Abstract: μ -Diphenylamino- μ -methyl-tetramethyldialuminum, $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$, has been prepared and the crystal and molecular structure determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by a full-matrix least-squares technique to a final R_1 factor of 4.4% on F . The complex crystallizes in the space group $C_{2h}^2-P2_1/c$ of the monoclinic system, with four molecules in a cell of dimensions $a = 7.850 \text{ \AA}$, $b = 10.61 \text{ \AA}$, $c = 21.855 \text{ \AA}$; $\beta = 91.74^\circ$. The basic structural feature of the complex is a nonplanar four-membered heterocyclic ring system composed of two aluminum atoms, one carbon atom, and one nitrogen atom. $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$ consists of molecules resembling those found in $[\text{Al}(\text{CH}_3)_3]_2$ but with one bridging methyl group removed and a diphenylamino group substituted in its place. The geometry around each Al atom is distorted from tetrahedral symmetry. The Al(1)-N-Al(2) bridge angle is 85.6° , while the Al(1)-C(5)-Al(2) bridge angle is 78.9° . The average bond lengths are: Al-N, 2.00 \AA ; Al-C(bridge), 2.14 \AA ; and Al-C(terminal), 1.95 \AA . The presence of the diphenylamino group in the bridging position increases the metal-metal distance from 2.60 \AA for $[\text{Al}(\text{CH}_3)_3]_2$ to 2.72 \AA for this complex. The overall symmetry of the molecule is very nearly C_s -m.

Mixed electron-deficient–nonelectron-deficient bridges have been proposed by a number of workers in order to explain proton magnetic spectra obtained from mixtures of $[\text{Al}(\text{CH}_3)_3]_2$ with $(\text{R}_n\text{AlX}_{3-n})_2$ where X represents a base and R is an alkyl or aryl group. Kawai, *et al.*,⁴ explain the high-temperature nmr spectrum obtained from a mixture of $[\text{Al}(\text{CH}_3)_3]_2$ and $[(\text{CH}_3)_2\text{-AlN}(\text{C}_6\text{H}_5)_2]_2$ by invoking an equilibrium between the above two species and the mixed-bridge species $(\text{CH}_3)_5\text{-Al}_2\text{N}(\text{C}_6\text{H}_5)_2$. Mixed-bridge dimers of $(\text{CH}_3)_5\text{Al}_2\text{Cl}$ have been proposed by Jeffery, *et al.*,⁵ and Zambelli, *et al.*,⁶ to explain low-temperature spectra obtained from mixtures of $[\text{Al}(\text{CH}_3)_3]_2$ and $[\text{ClAl}(\text{CH}_3)_2]_2$.

During studies of the system $(\text{CH}_3)_3\text{Al}$ with $(\text{C}_6\text{H}_5)_2\text{-NH}$, the mixed electron-deficient–nonelectron-deficient compound $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$ was isolated, as later determined by chemical analysis and single-crystal X-ray analysis. Since no previous solid-state work on mixed bridging systems for the representative elements had been reported, it seemed of particular interest to determine the molecular structure of this complex and to study the stereochemistry and bridging within the four-membered heterocyclic ring system.

Experimental Section

Preparation of the Complex. μ -Diphenylamino- μ -methyl-tetramethyldialuminum, $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$, was prepared by the vacuum distillation of trimethylaluminum into a cold tube (-196°) containing diphenylamine. The reaction was performed on a

vacuum line in a closed system consisting of a U-tube fitted with two standard joints to which were attached two glass tubes equipped with vacuum stopcocks. The U-tube in turn was attached to a vacuum line equipped with a mercury bubbler and a gas inlet.

One of the tubes was loaded with 0.020 mol (1.44 g) of trimethylaluminum in the glove box and the second with 0.010 mol (1.68 g) of diphenylamine. Both tubes were then attached to the U-tube on the vacuum line, and the entire system with the exception of the tube containing the trimethylaluminum was evacuated and filled with nitrogen gas four times. Then the tube containing the trimethylaluminum was cooled to liquid nitrogen temperature and evacuated. At this time the stopcock to the vacuum line was closed and the vacuum distillation of the trimethylaluminum was performed by cooling the tube containing the diphenylamine while allowing the trimethylaluminum to warm to room temperature. After the completion of the distillation the tube now containing both the trimethylaluminum and the diphenylamine at -196° was opened to the mercury bubbler and placed under a slight positive pressure of nitrogen. The reaction tube was allowed to warm slowly to room temperature and then heated to 100° . During the course of the reaction gas was given off. After alternate heating (100°) and cooling of the reaction mixture any excess trimethylaluminum was pumped off at 50° (10^{-3} mm). The resulting product was a snow-white powder.

Purification of the compound was carried out by vacuum sublimation onto a cold trap. All transfers of the complex were made in a glove box as the complex is easily oxidized and hydrolyzed. No sharp melting point was observed as the compound decomposes between 130 and 150° . A chemical analysis of the complex was obtained from Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The results of this analysis are shown in Table I.

Collection and Reduction of Intensity Data. Single crystals of the clear, colorless complex, sublimed in a sealed tube at 70° (10^{-3} mm), were mounted in glass capillaries in the glove box. Initial X-ray data were taken on a precession camera with Mo $K\alpha$ radiation. These photographs showed the Laue symmetry to be $2/m$. Extinctions were observed for $h0l$ data, $l = 2n + 1$, and $0k0$ data,

Table I. Chemical Analysis for $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$

Element	Obsd, %	Calcd, %
Al	17.65	18.15
N	4.82	4.71
C	65.76	68.67
H	8.01	8.47

(1) Part IX: J. L. Atwood and G. D. Stucky, submitted for publication.

(2) (a) For preliminary communication concerning this work see: V. R. Magnuson and G. D. Stucky, *J. Am. Chem. Soc.*, **90**, 3269 (1968).

(b) This work was supported by the Advanced Research Projects Agency under Contract SD-131 and the National Science Foundation.

(3) (a) NASA trainee, 1966–1968.

(4) M. Kawai, T. Ogawa, and K. Hirota, *Bull. Chem. Soc. Japan*, **37**, 1302 (1964).

(5) E. A. Jeffery, T. Mole, and J. K. Saunders, *Australian J. Chem.*, **21**, 649 (1968).

(6) A. Zambelli, A. L. Segre, A. Marinangelli, and G. Gatti, *Chem. Ind. (Milan)*, **48**, 1 (1966).

$k = 2n + 1$. This unambiguously defines the space group to be $C_{2h}^5-P2_1/c$. The lattice constants and standard deviations obtained by a least-squares refinement⁷ of the $\sin \theta$ values of 11 reflections which had been carefully centered on a Picker four-circle diffractometer are: $a = 7.850 \pm 0.003 \text{ \AA}$; $b = 10.613 \pm 0.004 \text{ \AA}$; $c = 21.855 \pm 0.009 \text{ \AA}$; $\beta = 91.74 \pm 0.06^\circ$ ($t = 25^\circ$; $\lambda(\text{Cu K}\alpha_1) 1.540462^\circ$). The observed density, measured by the flotation method in cyclohexane and bromobenzene, 1.08 g/cc, agrees well with a density of 1.09 g/cc calculated for four molecules of $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$ per unit cell.

Intensity data were gathered using a Picker manual diffractometer equipped with a scintillation counter and a pulse height analyzer. The crystal used was a rectangular box of approximate dimensions $0.35 \times 0.30 \times 0.70 \text{ mm}$. Nickel-filtered copper radiation was used as a source. Attenuators were inserted into the diffracted beam if its intensity exceeded about 7000 counts/sec during the scan. The intensity record was taken at a take-off angle of 1.3° using the $\theta-2\theta$ scan technique. A total of 1850 symmetry independent reflections were collected with 2θ values less than 100° . Of these, 128 intensities were judged as unobservables ($I_{\text{obsd}} \leq 3\sigma(I)$) and seven intensities for which $I_{\text{obsd}} \leq (I_{\text{bkg}}) - 3\sigma(I_{\text{bkg}})$ were rejected. Only observed reflections were included in the subsequent analysis. All data were corrected for Lorentz polarization effects with program ACAC.⁹ Backgrounds were measured before and after the scan, and corrections were made by assuming that the background is linear with respect to the $\theta-2\theta$ scan. Incident beam and diffracted beam collimators of 1.0 and 2.0 mm, respectively, were used in data collection. A 0.0005-in. nickel foil filter was placed between the crystal and the scintillation counter mounted 21 cm from the crystal. Two standard peaks were measured periodically throughout the data-taking process to monitor decomposition, crystal shifting, and diffractometer stability. No systematic variation in intensity was observed. No secondary extinction correction or absorption correction ($\mu = 13.4/\text{cm}^{-1}$) was applied. The maximum error in the structure factors due to the omission of the absorption correction was less than 6%. The average error was estimated to be less than 4%.

Solution and Refinement of the Structure

An attempt was made to solve the structure by the heavy atom method. Although the Patterson map was sharpened,¹⁰ no vector interpretation could be made. The symbolic addition procedure of Karle and Karle¹¹ was used to solve the structure by means of the computer programs FAME-MAGIC-LINK-SYMP.¹²

The starting set of vectors used in the phase determination are listed in Table II. The first three vectors listed were assigned a symbol of + and used as origins. Also listed in Table II are the vectors for which symbolic signs were used in the Σ_2 relationship as described elsewhere.¹³

On the basis of this assignment of origins, MAGIC generated a total of 200 known E 's in nine iterations. The symbol C was used in less than 3% of the knows, so it was rejected. This meant that an assignment of + or - could be made to the remaining unknowns

Table II. Starting Set of Vectors for the Symbolic Addition Phase Determination

Symbol	h	k	l	E
+	-2	1	12	2.55
+	-2	3	19	2.52
+	-3	1	16	3.14
A	5	2	8	3.34
B	2	4	19	2.81
C	-3	6	11	2.67

(7) J. Gvildys and M. Mueller, "B-101, Orientation and Angle Setting Generation Program," Argonne National Laboratory, Lemont, Ill.

(8) J. A. Bearden, *Rev. Mod. Phys.*, **39**, 68 (1967).

(9) L. J. Guggenberger and C. Prewitt, "Program ACAC," E. I. du Pont de Nemours and Co., Wilmington, Del.

(10) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell, London, 1966.

(11) I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).

(12) D. K. Dewar, A. L. Stone, and E. B. Fleischer, private communication, 1966.

(13) G. H. Stout and L. H. Jensen, "X-Ray Structural Determination," The Macmillan Co., New York, N. Y., 1968.

A and B . These were tried in the four possible combinations of + and -. For each combination the number of inconsistencies in the symbol equivalence found by MAGIC is given in Table III. An E map was calculated¹⁴ using the signs assigned by combinations 1 to 200 data.

The coordinates of 15 nonhydrogen atoms were determined from this E map. An initial structure factor calculation based on only these 15 nonhydrogen atoms produced an R_1 factor of 48.5% ($R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$) and R_2 of 47% ($R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w F_o^2)^{1/2}$). A Fourier map calculated from these phases was used to locate the remaining five nonhydrogen atoms in the asymmetric unit.

The structure was refined by the method of least squares using the full-matrix, least-squares program of Busing, *et al.*,¹⁵ which minimizes the function $\sum w(|F_o| - |F_c|)^2$. Hartree-Fock-Slater atomic scattering factors were used in all structure factor calculations.¹⁶ Several cycles of least-squares refinement with unit weights, in which the positional coordinates and isotropic temperature factors of all 20 nonhydrogen atoms were varied as well as the over-all scale factor, gave an R_1 value of 13.6%. Hydrogen atoms on the phenyl rings were located by a difference Fourier and were included at this point in the refinement. Subsequent anisotropic refinement of all nonhydrogen atoms resulted in an R_1 value of 9.0%. The 15 hydrogen atoms on the methyl groups were located by using difference Fourier calculations and confirmed by program HYGEM.¹⁷ Refinement of these hydrogen atom positions as well as further anisotropic refinement of the 20 nonhydrogen atoms resulted in convergence with $R_1 = 4.4\%$ and $R_2 = 5.0\%$. Unit weights were used for all data as a weighting scheme based on counting statistics was found to give too small a weight for medium and strong intensities. A plot of $|F_o|$ vs. $w(|F_o| - |F_c|)^2$ where $w = 1$ showed

Table III. Summary of Data from Phase-Determining Program

Combination	Origins	A	B	C	Contradictions
1	+ + +	-	+	R	2
2	+ + +	-	-	R	35
3	+ + +	+	-	R	48
4	+ + +	+	+	R	49

Table IV. Final Nonhydrogen Atom Positional Parameters

Atom	x	y	z
Al(1)	0.5854 (2) ^a	0.7375 (1)	0.3802 (1)
Al(2)	0.2847 (2)	0.8082 (1)	0.3252 (1)
C(5)	0.5181 (6)	0.9118 (5)	0.3368 (2)
N	0.3438 (4)	0.6823 (3)	0.3908 (1)
C(1)	0.6994 (6)	0.6366 (5)	0.3192 (3)
C(2)	0.7082 (6)	0.7670 (6)	0.4574 (2)
C(3)	0.2850 (6)	0.7342 (5)	0.2438 (2)
C(4)	0.0965 (6)	0.9207 (5)	0.3433 (2)
AC(1)	0.3179 (5)	0.5505 (4)	0.3746 (2)
AC(2)	0.4320 (5)	0.4615 (4)	0.3953 (2)
AC(3)	0.4088 (7)	0.3346 (5)	0.3799 (3)
AC(4)	0.2694 (9)	0.3002 (5)	0.3450 (3)
AC(5)	0.1553 (7)	0.3875 (6)	0.3256 (2)
AC(6)	0.1776 (6)	0.5217 (4)	0.3404 (2)
BC(1)	0.2753 (5)	0.7130 (4)	0.4508 (2)
BC(2)	0.1972 (5)	0.6236 (4)	0.4858 (2)
BC(3)	0.1303 (6)	0.6572 (5)	0.5419 (2)
BC(4)	0.1396 (7)	0.7785 (6)	0.5627 (2)
BC(5)	0.2187 (8)	0.8664 (5)	0.5289 (2)
BC(6)	0.2871 (7)	0.8348 (4)	0.4724 (2)

^a Numbers in parentheses here and in succeeding discussions are estimated standard deviations in the least significant digits.

(14) I. C. Karle, H. Hauptman, J. Karle, and A. B. Wing, *Acta Cryst.*, **11**, 257 (1958).

(15) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least Squares Program," U. S. Atomic Energy Commission, Report No. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(16) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

(17) Program HYGEM, which generates desired atomic positions based on the geometry and distances specified by the user when given as input an arbitrary set of lattice parameters and atomic coordinates, was written by F. K. Ross and G. D. Stucky.

Table V. Final Nonhydrogen Atom Anisotropic Thermal Parameters ($\times 10^4$)

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al(1)	180 (3)	127 (2)	31 (0)	-24 (2)	-7 (1)	17 (1)
Al(2)	203 (3)	101 (1)	23 (0)	8 (2)	-2 (1)	9 (1)
C(5)	263 (11)	165 (7)	37 (1)	-14 (7)	-12 (3)	19 (3)
N	189 (6)	94 (4)	22 (1)	-8 (4)	1 (2)	2 (1)
C(1)	223 (10)	198 (7)	46 (2)	30 (7)	16 (3)	16 (3)
C(2)	291 (11)	211 (8)	41 (2)	-74 (8)	-24 (4)	24 (3)
C(3)	312 (11)	180 (7)	22 (1)	34 (7)	0 (3)	9 (2)
C(4)	286 (11)	148 (6)	38 (1)	38 (7)	-3 (3)	5 (3)
AC(1)	187 (8)	91 (5)	21 (1)	-12 (5)	4 (2)	3 (2)
AC(2)	221 (9)	111 (5)	33 (1)	4 (6)	13 (3)	8 (2)
AC(3)	335 (14)	119 (6)	43 (2)	18 (7)	26 (4)	3 (3)
AC(4)	500 (19)	114 (7)	38 (2)	-62 (10)	50 (5)	-12 (3)
AC(5)	358 (14)	161 (8)	28 (1)	-101 (9)	3 (3)	-6 (3)
AC(6)	238 (10)	132 (6)	26 (1)	-36 (6)	-8 (3)	5 (2)
BC(1)	191 (8)	103 (5)	20 (1)	0 (5)	-10 (2)	2 (2)
BC(2)	220 (9)	121 (5)	23 (1)	-10 (6)	2 (2)	1 (2)
BC(3)	253 (10)	182 (7)	25 (1)	-21 (7)	9 (3)	-3 (3)
BC(4)	327 (12)	196 (8)	25 (1)	11 (8)	4 (3)	-13 (3)
BC(5)	436 (15)	130 (6)	30 (1)	2 (8)	3 (3)	-14 (3)
BC(6)	390 (13)	115 (6)	25 (1)	-30 (7)	-1 (3)	-4 (2)

^a The form of the anisotropic thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table VI. Final Hydrogen Atom Parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
AC(2)H	0.5368 (66)	0.4824 (52)	0.4221 (24)	5.3 (1.4) ^a
AC(3)H	0.4903 (71)	0.2737 (58)	0.3957 (27)	7.7 (1.7)
AC(4)H	0.2565 (68)	0.2147 (55)	0.3381 (25)	6.9 (1.6)
AC(5)H	0.0618 (62)	0.3613 (48)	0.3019 (23)	4.7 (1.3)
AC(6)H	0.0958 (53)	0.5730 (41)	0.3254 (19)	3.1 (1.1)
BC(2)H	0.1847 (45)	0.5337 (35)	0.4702 (17)	2.0 (0.86)
BC(3)H	0.0789 (71)	0.5933 (55)	0.5710 (26)	7.0 (1.6)
BC(4)H	0.0932 (77)	0.8094 (59)	0.5959 (29)	9.3 (1.9)
BC(5)H	0.2269 (60)	0.9564 (47)	0.5400 (22)	4.5 (1.3)
BC(6)H	0.3373 (57)	0.9015 (44)	0.4478 (21)	3.9 (1.2)
C(5)H(1)	0.5006 (60)	0.9627 (45)	0.3690 (22)	4.0
C(5)H(2)	0.4843 (60)	0.9525 (44)	0.3019 (22)	4.0
C(5)H(3)	0.6266 (61)	0.9144 (45)	0.3334 (22)	4.0
C(1)H(1)	0.6327 (54)	0.6188 (42)	0.2918 (19)	4.0
C(1)H(2)	0.7957 (58)	0.6771 (46)	0.3075 (21)	4.0
C(1)H(3)	0.7380 (61)	0.5530 (47)	0.3330 (22)	4.0
C(2)H(1)	0.6438 (59)	0.8256 (46)	0.4856 (22)	4.0
C(2)H(2)	0.6962 (58)	0.6893 (46)	0.4878 (22)	4.0
C(2)H(3)	0.8175 (58)	0.7974 (44)	0.4459 (21)	4.0
C(3)H(1)	0.3679 (58)	0.6593 (45)	0.2331 (21)	4.0
C(3)H(2)	0.1690 (59)	0.7094 (45)	0.2234 (21)	4.0
C(3)H(3)	0.3050 (59)	0.7984 (46)	0.2110 (21)	4.0
C(4)H(1)	0.1121 (58)	0.9712 (45)	0.3835 (22)	4.0
C(4)H(2)	0.0796 (59)	0.9782 (46)	0.3162 (22)	4.0
C(4)H(3)	-0.0081 (58)	0.8793 (46)	0.3406 (22)	4.0

^a Isotropic temperature factors are given by $\exp[-B(\sin^2 \theta)/\lambda^2]$.

no systematic variation as a function of F_o . Final positional parameters and final anisotropic thermal parameters for all non-hydrogen atoms are given in Tables IV and V, respectively. Final hydrogen atom parameters are given in Table VI. Observed and calculated structure factors for observed data only are listed in Table VII.

Discussion of the Structure

The basic structural feature of the complex is the four-membered heterocyclic ring system composed of two Al atoms, one C atom, and one N atom. This work represents the first description of the preparation and structure in the solid state of a mixed electron-deficient–nonelectron-deficient bridging situation for the representative elements. Mixed bridging systems have been previously proposed in solutions to explain nmr data for mixtures of $[(CH_3)_2AlN(C_6H_5)_2]_2$,⁴ $[Al(C_6H_5)_3]_2$,¹⁸ $[(CH_3C_6H_4)_3Al]_2$,¹⁸ and $[ClAl(CH_3)_2]_2$,^{5,6} with $[Al(CH_3)_3]_2$.

(18) E. A. Jeffery, T. Mole, and J. K. Saunders, *Australian J. Chem.*, **21**, 137 (1968).

Trimethylaluminum^{19,20} and triphenylaluminum²¹ have been shown to crystallize as dimers with electron-deficient Al–C–Al bridge angles of 74.7 and 76.5°, respectively. $(CH_3)_5Al_2N(C_6H_5)_2$ consists of molecules resembling those found in $[Al(CH_3)_3]_2$ but with one bridging methyl group removed and a diphenylamino group substituted in its place. The basic molecular arrangement as well as selected bond lengths and angles are shown in Figure 2, which is a tracing of a Calcomp plot generated by ORTEP.²² The geometry around each Al atom is distorted from tetrahedral symmetry with exterior C(2)–Al(1)–C(1) and C(3)–Al(2)–C(4) angles of 117.32 (24) and 117.09° (21), respectively, and interior N–Al(1)–C(5) and N–Al(2)–C(5) angles of 94.70 (16) and 94.50° (16), respectively.

(19) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **16**, 552 (1948).

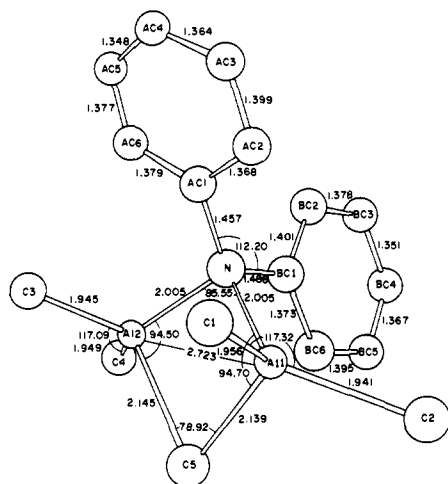
(20) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, **89**, 3121 (1967).

(21) J. F. Malone and W. S. McDonald, *Chem. Commun.*, 444 (1967).

(22) C. K. Johnson, "ORTEP. A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," U. S. Atomic Energy Commission, Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table VIII. Bond Lengths for Nonhydrogen Atoms

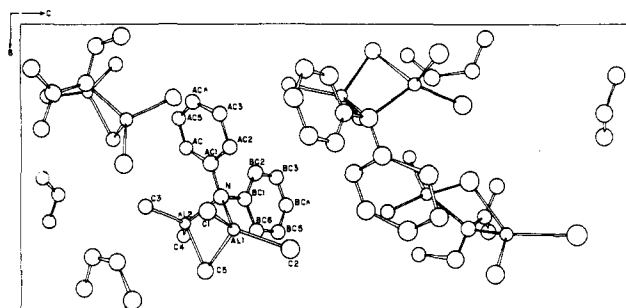
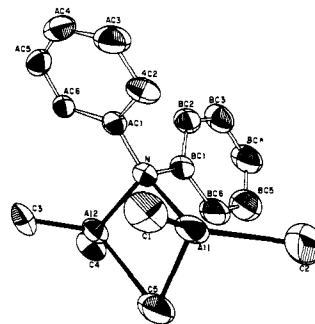
Bond	Distance, Å	Bond	Distance, Å
Al(2)-C(5)	2.145 (5)	AC(3)-AC(4)	1.364 (8)
Al(2)-N	2.005 (3)	AC(4)-AC(5)	1.348 (8)
Al(1)-N	2.005 (3)	AC(5)-AC(6)	1.377 (7)
Al(1)-C(5)	2.139 (5)	AC(6)-AC(1)	1.379 (5)
Al(1)-C(1)	1.956 (5)	N-BC(1)	1.468 (5)
Al(1)-C(2)	1.941 (5)	BC(1)-BC(2)	1.373 (5)
Al(1)-C(3)	1.945 (5)	BC(2)-BC(3)	1.395 (6)
Al(2)-C(4)	1.949 (5)	BC(3)-BC(4)	1.367 (7)
N-AC(1)	1.456 (5)	BC(4)-BC(5)	1.351 (7)
AC(1)-AC(2)	1.368 (5)	BC(5)-BC(6)	1.401 (6)
AC(2)-AC(3)	1.399 (7)	BC(6)-BC(1)	1.378 (6)

Figure 1. Molecular structure of $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$ with hydrogen atoms omitted for clarity.

distance is shorter than it would be if the ring were planar, and that in the distorted ring the $\text{Al}(1)-\text{C}(5)-\text{Al}(2)$ angle is smaller than it would be if the ring were planar with the same intramolecular distances found for the nonplanar ring. This suggests that the nonplanarity of the ring might arise because of enhanced metal-metal bonding and the sharp bridging angle required for three-center electron-deficient bonding. It should be noted, however, that there is considerable steric interaction between the phenyl groups and the terminal methyl groups on the Al atoms. For example, the nonbonded distances between $\text{BC}(6)-\text{C}(2)$, $\text{BC}(6)-\text{C}(4)$, $\text{BC}(6)-\text{Al}(1)$, and $\text{BC}(6)-\text{Al}(2)$ are only 3.408 (7) Å, 3.284 (6) Å, 3.300 (5) Å, and 3.230 (5) Å, respectively (Figure 1). The packing of the contents of the unit cell is shown in Figure 2. This implies that the lack of planarity may be due to the result of an in-plane bending distortion of the $\text{Al}_2(\text{CH}_3)_4$ group to accommodate the benzene ring which is nearly normal to it.

Examination of the thermal ellipsoids (Figure 3) and the root-mean-square thermal displacements along the principle axes (Table X) of these thermal ellipsoids shows that the thermal motion is large for the bridging methyl carbon, C(5), and the four terminal methyl carbons, C(1), C(2), C(3), and C(4). Al-C bond lengths with and without a correction for thermal motion, respectively, are given (in Å) as: $\text{Al}(1)-\text{C}(1)$, 1.956 (5), 1.975 (6); $\text{Al}(1)-\text{C}(2)$, 1.941 (5), 1.966 (5); $\text{Al}(2)-\text{C}(3)$, 1.945 (5), 1.963 (5); $\text{Al}(2)-\text{C}(4)$, 1.949 (3), 1.969 (5); $\text{Al}(2)-\text{C}(5)$, 2.145 (5), 2.162 (5). In each case the carbon atom is assumed to ride on the aluminum atom.²⁶ Because of the larger thermal vibration of these methyl groups, carbon-hydrogen bond distances in the complex show a fairly large scatter about a mean value of 0.96 (06) Å.

The average C-C distance is 1.372 ± 0.012 Å in phenyl ring A and 1.378 ± 0.014 Å in phenyl ring B. Each phenyl ring is nearly planar, with the equation of the mean plane being $AX + BY + CZ + D = 0$, where X, Y, and Z are orthogonal coordinates related to fractional coordinates in the monoclinic cell by $X = xa + zc \cos \beta$, $Y = yb$, and $Z = zc \sin \beta$. The distances of the ring atoms and phenyl protons from the best plane are given in Table XI.

(26) W. R. Busing and H. A. Levy, *Acta Cryst.*, 17, 142 (1964).Figure 2. Contents of the unit cell in $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$ as viewed along [100].Figure 3. Perspective view of $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$ with root-mean-square displacements indicated (hydrogen atoms omitted).

As mentioned above mixed electron-deficient-nonelectron-deficient bridging systems have been postulated by a number of workers⁴⁻⁶ to interpret proton magnetic spectra from mixtures of $[\text{Al}(\text{CH}_3)_3]_2$ and $(\text{R}_n\text{AlX}_{3-n})_2$ where X represents a base and R is an alkyl or aryl. Mixed bridge dimers of $(\text{CH}_3)_5\text{Al}_2\text{Cl}$ have been proposed^{5,6} to explain the low-temperature spectra obtained from mixtures of $[\text{Al}(\text{CH}_3)_3]_2$ and $[\text{ClAl}(\text{CH}_3)_2]_2$. A poorly resolved peak at 110 cps upfield from the methyl resonance of toluene has been assigned to the protons of the bridging methyl group in $(\text{CH}_3)_5\text{Al}_2\text{Cl}$. In order to affirm the assignment of this peak to a bridging methyl group in a mixed-bridge complex, nmr spectra were recorded for pure $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$. All spectra were run on a Varian A-60A with toluene as the solvent. A copper-constantan thermocouple was used to record the temperature. Exchange takes place at room temperature as only one signal at 154 cps upfield from the methyl resonance in toluene is observed. However, at about -5° exchange has apparently stopped and an assignment of a small peak at 104 cps has been made to the proton of the bridging methyl group in $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$. A larger peak at 161-162 cps has been assigned to the terminal methyl protons in $(\text{CH}_3)_5\text{AlN}(\text{C}_6\text{H}_5)_2$. Further work in this area is being carried out by Dr. Paul Oliver at Wayne State University.

In an attempt to prepare $[(\text{CH}_3)_2\text{AlN}(\text{C}_6\text{H}_5)_2]_2$, a 1:1 molar ratio of trimethylaluminum and diphenylamine was allowed to react as described in the preparation of $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$. The white solid that resulted was easy to sublime and single crystals were mounted and studied by diffraction techniques. Preliminary precession photographs showed the crystalline complex to belong to the space group $\text{P}2_1/c$. Lattice constants were determined by a least-squares fit of 2θ values from the Picker diffractometer and are $a = 16.211$ (5) Å, $b = 13.146$ (4) Å, $c = 16.564$ (5) Å; $\beta = 97.345$ (47) Å. Based on a cell volume of 3500.27 Å³ and an observed density of 1.13 g/cc, the formula weight for the unknown complex is 594. This implies that the complex is either $(\text{CH}_3)_3\text{Al}_2(\text{N}(\text{C}_6\text{H}_5)_2)_3$ or $[(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2]_n$ ($n = 1$ or 2), and not 1:1 as had been expected. If n is equal to 1 then the complex may be just a different crystalline modification of the structure previously discussed in this section. Further structural work is in progress.

Molecular Orbital Calculations

As pointed out previously the geometries of the four-membered heterocyclic ring systems formed by group II and III metals depend

Table IX. Bond Angles for Nonhydrogen Atoms

Atoms	Angle, deg	Atoms	Angle, deg
C(2)-Al(1)-C(1)	117.32 (24)	N-BC(1)-BC(6)	119.38 (38)
C(2)-Al(1)-N	113.20 (18)	AC(6)-AC(1)-AC(2)	119.10 (39)
C(2)-Al(1)-C(5)	110.85 (23)	AC(1)-AC(2)-AC(3)	120.38 (44)
C(1)-Al(1)-N	111.76 (18)	AC(2)-AC(3)-AC(4)	119.24 (50)
C(1)-Al(1)-C(5)	106.45 (22)	AC(3)-AC(4)-AC(5)	120.41 (50)
N-Al(1)-C(5)	94.70 (16)	AC(4)-AC(5)-AC(6)	120.98 (49)
C(3)-Al(2)-C(4)	117.09 (21)	AC(5)-AC(6)-AC(1)	119.84 (46)
C(3)-Al(2)-N	112.22 (18)	BC(6)-BC(1)-BC(2)	118.92 (39)
C(3)-Al(2)-C(5)	106.90 (21)	BC(1)-BC(2)-BC(3)	119.92 (42)
C(4)-Al(2)-N	115.04 (18)	BC(2)-BC(3)-BC(4)	120.99 (46)
C(4)-Al(2)-C(5)	108.18 (22)	BC(3)-BC(4)-BC(5)	119.29 (46)
N-Al(2)-C(5)	94.50 (16)	BC(4)-BC(5)-BC(6)	120.69 (47)
Al(1)-C(5)-Al(2)	78.92 (17)	BC(5)-BC(6)-BC(1)	120.16 (45)
Al(1)-N-Al(2)	85.55 (13)	Al(1)-N-AC(1)	112.24 (19)
AC(1)-N-BC(1)	112.20 (30)	Al(1)-N-BC(1)	114.27 (20)
N-AC(1)-AC(2)	119.85 (36)	Al(2)-N-AC(1)	116.07 (26)
N-AC(1)-AC(6)	121.00 (38)	Al(1)-N-BC(1)	114.08 (19)
N-BC(1)-BC(2)	121.69 (36)		

Table X. Root-Mean-Square Components of Thermal Vibration (\AA) for $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$

Al(1)	0.224 (2)	0.234 (2)	0.312 (2)
Al(2)	0.213 (2)	0.254 (2)	0.259 (2)
C(5)	0.258 (6)	0.283 (6)	0.345 (6)
N	0.223 (4)	0.232 (4)	0.247 (4)
C(1)	0.252 (6)	0.293 (7)	0.365 (6)
C(2)	0.264 (6)	0.281 (7)	0.403 (7)
C(3)	0.226 (6)	0.296 (6)	0.340 (6)
C(4)	0.262 (6)	0.308 (6)	0.321 (6)
AC(1)	0.213 (6)	0.232 (6)	0.247 (6)
AC(2)	0.241 (6)	0.255 (6)	0.298 (6)
AC(3)	0.258 (7)	0.292 (7)	0.353 (7)
AC(4)	0.240 (7)	0.267 (7)	0.426 (8)
AC(5)	0.236 (7)	0.267 (7)	0.382 (7)
AC(6)	0.241 (6)	0.248 (6)	0.306 (6)
BC(1)	0.207 (6)	0.242 (6)	0.257 (5)
BC(2)	0.237 (6)	0.254 (6)	0.271 (6)
BC(3)	0.243 (7)	0.278 (6)	0.327 (6)
BC(4)	0.237 (6)	0.317 (6)	0.343 (7)
BC(5)	0.239 (7)	0.300 (7)	0.369 (7)
BC(6)	0.238 (7)	0.258 (6)	0.353 (6)

Table XI. Distances of Atoms from Mean Plane of Phenyl Rings

Atom	Distance, \AA	Atom	Distance, \AA
Phenyl Ring A			
AC(1)	0.012	N	0.007
AC(2)	-0.009	AC(2)H	-0.030
AC(3)	0.001	AC(3)H	-0.030
AC(4)	0.004	AC(4)H	-0.041
AC(5)	-0.001	AC(5)H	0.004
AC(6)	-0.008	AC(6)H	0.010
$0.5416X + 0.1316Y - 0.8303Z + 4.8210 = 0$			
Phenyl Ring B			
BC(1)	0.006	N	0.043
BC(2)	-0.001	BC(2)H	0.027
BC(3)	-0.007	BC(3)H	-0.080
BC(4)	0.009	BC(4)H	0.070
BC(5)	-0.005	BC(5)H	0.039
BC(6)	-0.003	BC(6)H	0.043
$-0.8611X + 0.2141Y - 0.4612Z + 4.5309 = 0$			

in a very systematic way upon the bridging atom.^{2a} Furthermore, in the dimeric species the bridging angle changes only slightly as the metal atoms and the groups exterior to the ring are varied. Bridging angles in polymeric dimethylberyllium and diethylmagnesium and trimeric bis(dimethylamino)beryllium are anomalous due to steric interactions between the bridging groups of the heterocyclic ring in question and adjacent bridging atoms. The net over-all effect is to force the atoms away from the line defined by

the metal-metal vector and to thus decrease the bridging angle. Disregarding the above three complexes in Table I of ref 2a the mean metal-carbon-metal, M-C-M, bridge angle is $76.3 \pm 1.2^\circ$, the mean M-N-M (amino nitrogen) bridge angle is $87.9 \pm 1.2^\circ$ the mean M-N-M (immino nitrogen) bridge angle is $94.0 \pm 0.6^\circ$, and the mean M-O-M bridge angle is $98.4 \pm 2.3^\circ$. Thus, we can see that the bridging angle increases by about 21° in going from C to N to O atoms in the bridge. The next member of this series is exemplified by $(\text{CH}_3)_2\text{AlF}$ which has been reported to be a tetramer.²⁷

The most important consideration in the stereochemistry of chloride and bromide bridge complexes appears to be anion repulsions "across" the heterocyclic ring and to a lesser extent the coordination number of the metal atom rather than preferred hybridization of the bridging atoms.²⁸

A number of workers, Cusachs,²⁹ Carroll, *et al.*,³⁰ and Allen and Russell,³¹ have shown that the geometries of simple molecules like H_2 , H_2O , and H_2S can be predicted by applying semiempirical extended Hückel theory. These calculations have been very successful in predicting equilibrium bond angles but have not been quite as successful in predicting good bond lengths. For example, the equilibrium H-O-H angle for water has been obtained.^{29,30} In addition Cusachs suggests in his paper that a minimum in energy vs. a variation of bond angles might be found for more complex systems. In view of this, it seemed possible that molecular orbital calculations might be able to confirm the angles that have been found experimentally by X-ray analysis and suggest some possible explanations for the observed trends in the four-membered heterocyclic ring systems.

Extended Hückel calculations were performed by program IICO5, a modified version of the original Hoffman program,³² which was supplied for our use by Drago.³³ The procedure was to pick an initial charge and configuration for each atom in the molecule and then calculate the corresponding terms of the Hamiltonian matrix. The diagonal terms, H_{ii} , were given by Basch, *et al.*,³⁴ and the off-diagonal terms were approximated by Cusachs' formula.²⁹

$$H_{ij} = \frac{1}{2} S_{ij}(H_{ii} + H_{jj})(2 - |S_{ij}|)$$

This approximation for H_{ij} has been the most successful approximation in connection with configuration studies. After calculation of the appropriate H_{ii} and H_{ij} terms, the resulting secular equation, $|H_{ij} - S_{ij}E| = 0$, was solved for eigenvectors and eigenvalues, and a Mulliken population analysis³⁵ was performed.

(27) J. Weidlein and V. Krug, *J. Organometal. Chem.*, **11**, 9 (1968).

(28) J. Toney and G. Stucky, to be published; L. F. Dahl, private communication.

(29) L. C. Cusachs, *J. Chem. Phys.*, **43**, 5157 (1965).

(30) D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *ibid.*, **44**, 1865 (1966).

(31) L. C. Allen and J. D. Russell, *ibid.*, **46**, 1029 (1967).

(32) R. Hoffman, *ibid.*, **39**, 1397 (1963).

(33) R. S. Drago, private communication, 1968.

(34) H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta* (Berlin), **3**, 458 (1965).

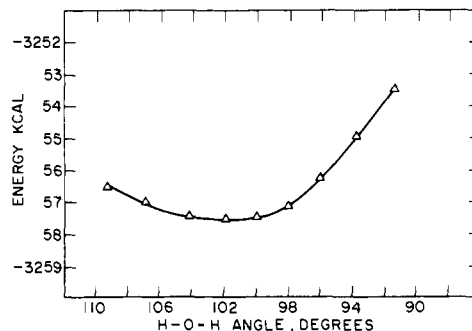
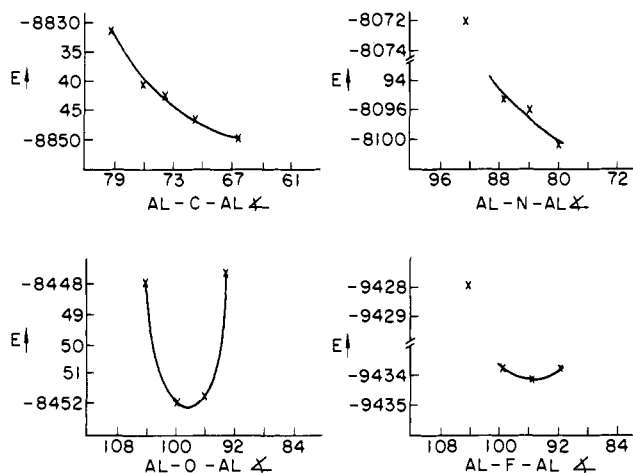
Table XII. Reduced Overlap Population Analysis for Planar and Nonplanar $H_4Al_2CH_3NH_2$

	$[H_2AlCH_3]_2$	Planar $H_4AlNH_2CH_3$	Nonplanar $H_4AlNH_2CH_3$	$[H_2AlN_2]_2$
Al-N		0.44	0.44	0.45
Al-C	0.35	0.36	0.46	
Al-Al	0.23	0.04	0.05	-0.13
Al-H (av)	0.74	0.73	0.72	0.73

A new set of charges thus resulted and was used in a second iterative cycle. When the difference between the input and output charges was less than 0.01 or 0.02 charge unit, depending upon the size of the problem, the calculation was self-consistent. Clementi double ζ orbitals³⁶ were used as wave functions for all orbitals except hydrogen for which a single Slater wave function was used with an exponent of 1.2. Aluminum d-orbital wave functions were not used.

In order to determine whether this particular combination of wave function orbital energies and off-diagonal terms would be appropriate for use, calculations were made for the water molecule as a function of the H-O-H angle. An interatomic O-H distance of 0.958 Å was used. Results of these calculations predict an equilibrium angle of 102° (Figure 4), which is in very good agreement with the experimental value of 104.5°. Similar calculations were then made on the isoelectronic series of hypothetical complexes $(H_2AlX)_2$ (X = CH₃, NH₂, OH, and F) in order to determine if a minimum energy could be obtained for a bridging angle, α , equal to the experimental average value for that particular type of complex. The use of the hydrogen atoms in the terminal position was justified by the experimental observation that the bridging angles were independent (to about 2°) of the terminal group and by a desire to keep computation costs at a minimum. Bond lengths were chosen as follows: $r_{Al-H} = 1.55$ Å; $r_{Al-C} = 2.14$ Å; $r_{Al-N} = 2.00$ Å; $r_{Al-O} = 1.80$ Å; $r_{Al-F} = 1.90$ Å; $r_{C-H} = 1.10$ Å; $r_{N-H} = 1.05$ Å; $r_{O-H} = 1.00$ Å. These values are based on both X-ray and spectroscopic results. In all cases the atomic coordinates for each atom were generated such that the four-membered heterocyclic ring, Al-X-Al-X, was planar. The H-Al-H angle was held at a constant value of 120°. Figure 5 shows the results of these calculations. A minimum in energy was obtained for only two members of the series, $(H_2AlOH)_2$ and $(H_2AlF)_2$. Although the predicted equilibrium angle, α , agrees quite well with the experimentally expected value for $(H_2AlOH)_2$ (see Table I of ref 1a), the result may be fortuitous since no minimum was found for either $(H_2AlCH_3)_2$ or $(H_2AlNH_2)_2$. It is interesting to note that the predicted equilibrium angle for $(H_2AlF)_2$ is about 96°, which implies a F-F distance of only 2.44 Å. Anion-anion repulsion may be the reason that $(CH_3AlF)_x$ is tetrameric rather than dimeric;²⁸ at any rate, it did not appear that repulsion energies were adequately accounted for in the model. In an attempt to find a reason for the unsuccessful minimization for $(H_2AlCH_3)_2$ and $(H_2AlNH_2)_2$, a variation in orbital exponents and energies was tried for $(H_2AlCH_3)_2$. Analysis of the wave functions showed that the molecular orbitals with large coefficients for carbon Slater orbitals were becoming too stable as the Al-C-Al angle decreased. Single Slater orbitals with coefficients 20% larger than calculated by the method of Burns³⁷ were substituted for Clementi wave functions in order to decrease the contribution of the carbon orbitals. However, no minimum in energy was obtained.

Amma has suggested that the terminal C-Al-C angle of 123° in $[Al(CH_3)_3]_2$ implies sp^2 aluminum hybridization and significant metal-metal bonding. In this connection we have carried out a $1/r_{ij}$ minimization for trimethylaluminum in which the angular positions of the hydrogen atoms were varied considering both intra- and intermolecular electrostatic terms.³⁸ A minimum in the potential energy was found at 120° for the terminal carbon-aluminum-terminal carbon angle which is in good agreement with the observed value of 123°. The charges used for this calculation were obtained from a complete extended Hückel calculation of the type discussed above. For trimethylaluminum the reduced overlap populations are aluminum-terminal carbon, 0.75; aluminum-bridging carbon, 0.38; and aluminum-aluminum, 0.23. These values agree well

Figure 4. Total energy vs. bond angle for H_2O .Figure 5. Total energy vs. X-M-X angle for $(H_2AlX)_2$ when X = CH₃, NH₂, OH, and F.

with previous values of reduced overlap populations and support the argument for metal-metal bonding.^{39,40}

Additional calculations were carried out to determine the amount of Al-Al overlap in a mixed bridge system. In order to save computing time, the calculation was carried out on $H_4Al_2NH_2CH_3$ rather than on $(CH_3)_5Al_2N(C_6H_5)_2$. The orthogonal coordinates used for $H_4Al_2NH_2CH_3$ were determined by transforming the X-ray coordinates of $(CH_3)_5Al_2N(C_6H_5)_2$ and linearly interpolating to allow for short Al-H and N-H distances compared to Al-C and N-C distances. Calculations were also carried out for $H_4Al_2NH_2CH_3$ containing a planar four-membered heterocyclic ring with the coordinates generated using the X-ray bond lengths found in $(CH_3)_5Al_2N(C_6H_5)_2$. The results are tabulated in Table XII. Comparison of the reduced overlap populations shows a small amount of Al-Al bonding in the mixed-bridge complex for both the "planar" and "nonplanar" configurations.⁴¹ The total energy for planar $H_4Al_2NH_2CH_3$ was 83 kcal lower than the total energy for nonplanar $H_4Al_2NH_2CH_3$ despite the fact that the analogous complex, $(CH_3)_5Al_2N(C_6H_5)_2$, is nonplanar in the solid state. In all the complexes which were examined and which contain non-electron-deficient four-membered heterocyclic ring systems, there is net antibonding between metal atoms as shown by the negative reduced overlap population for Al-Al in $(H_2AlNH_2)_2$.

(35) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955).

(36) E. Clementi, "Tables of Atomic Functions," International Business Machines, New York, N. Y., 1965.

(37) G. Burns, *J. Chem. Phys.*, **41**, 1521 (1964).

(38) A. R. E. Bates and G. Stucky, unpublished results.

(39) H. Kato, K. Yamaguchi, and T. Yonezawa, *Bull. Chem. Soc. Japan*, **39**, 1377 (1966).

(40) A. Schreiner, private communication, 1968.

(41) "Planar" and "nonplanar" refer only to the four-membered heterocyclic ring system, Al-N-Al-C.