value of 102 ± 2° is measured. From analogy with similar species, and with SiF where $\omega_e x_e = 6.2\ \text{cm}^{-1}$, the anharmonic correction to the frequency values can be assumed to be of the order of 5–10 cm^{-1}, and one finds the anharmonic correction to have only a small effect on the bond angle in this case. For example, using an anharmonic factor of 8 cm^{-1}, the neon matrix angle increases to 100.5 ± 1°, as compared to the gas-phase value of 100.9°. Thus it can be concluded that within the limits of experimental uncertainty the calculated geometry of matrix-isolated SiF_2 is essentially the same as that in the gas phase.

A verification of the ν_3 and ν_1 assignments is given by the fact that if the ν_1 isotopic frequencies were assumed to be ν_3, a bond angle calculation would indicate values of only 81 ± 2°. This differs too much from the gas-phase value for this alternative assignment to be correct. The assignment verifies the current literature[2] where the higher frequency is taken to be the ν_3. The following comparison of frequencies for ν_3 of 872 cm^{-1} in the gas phase, 864.6 cm^{-1} in the neon matrix at ~5°K, and 852.9 cm^{-1} in the argon matrix at ~15°K and similarly for ν_1 of 855, 851.5, and 842.8 cm^{-1} indicates that neon matrices give SiF_2 stretching frequencies that are only slightly shifted to the red from the gas-phase values. This has also been found to be the case for other inorganic species such as SO_2, SeO_2, SiO, and GeF_2.[5,7] Also the sharpness of the bands, as shown in Figure 2, indicates another advantage of using neon as compared with other rare gases for the matrix in this type of spectroscopy.

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Stereochemistry of Polynuclear Compounds of the Main Group Elements. VII.[1] The Structure of Octamethyldialuminummonomagnesium[2]

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Abstract: Dimethylmagnesium dissolves in trimethylaluminum to give two crystalline compounds with melting points of 39 and 54°. The crystal structure of the lower melting electron-deficient product octamethyldialuminummonomagnesium, $Mg[Al(CH_3)_4]_2$, has been determined by three-dimensional, single-crystal X-ray diffraction techniques. The compound crystallizes in the triclinic space group $P\bar{1}$, with two molecules per unit cell. The cell parameters are $a = 6.955$, $b = 10.802$, and $c = 10.287$ Å and $\alpha = 102.35$, $\beta = 105.03$, and $\gamma = 92.49°$. The average magnesium–carbon(bridge)–aluminum angle is 77.7°, and the average magnesium–aluminum distance, 2.704 Å. The conventional discrepancy index for the structure is 7.2%. Nuclear magnetic resonance studies on the trimethylaluminum–dimethylmagnesium and trimethylaluminum–dimethylberyllium systems are reported. In the latter, low-temperature spectra are interpreted in terms of the formation of a complex with the empirical formula $Be[Al(CH_3)_4]_2$.

The heterocyclic four-membered ring systems formed by group II and III metals with two one-electron alkyl and aryl donors are unusual in having metal–metal distances approximately equal to their single bond metallic diameters, and relatively small metal–carbon–metal bridge angles ranging from 66 to 78°.[3] These features together with bond lengths, the observed phenyl ring distortions in triphenylaluminum,[4] and the terminal carbon–aluminum–terminal carbon angle of 123.1° in trimethylaluminum[5] have been used as the basis for speculation concerning the bonding in group II and III electron-deficient compounds.

In order to learn more about the relative stereochemical importance of (1) metal–metal interactions, (2) steric effects of groups external to the heterocyclic ring, (3) steric effects across the ring between bridging atoms, (4) dative ligand–metal π bonding, (5) the electron distribution about the bridging atom in isoelectronic series of the type R_3C–, R_2N–, RO–, and F^-, and (6) intermolecular forces within the crystal lattice, we have initiated a systematic investigation of a number of polynuclear systems. In addition, it is hoped that such a study will provide realistic models for the extensive synthetic chemistry involving group II and III organometallic complexes as intermediates. In this paper the structural features of $(CH_3)_8MgAl_2$, and the nuclear magnetic resonance spectra of $(CH_3)_2Mg$–$Al(CH_3)_3$ and $(CH_3)_2Be$–$Al(CH_3)_3$ systems are discussed.

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[1] Previous papers in this series are: (a) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 4821 (1964); (b) J. L. Atwood and G. D. Stucky, *ibid.*, **89**, 5362 (1967); (c) J. L. Atwood and G. D. Stucky, *Chem. Commun.*, 1169 (1967); (d) J. Toney and G. D. Stucky, *ibid.*, 1168 (1967); (e) V. R. Magnuson and G. D. Stucky, *J. Am. Chem. Soc.*, **90**, 3269 (1968); (f) J. L. Atwood and G. D. Stucky, *J. Organometal. Chem.* (Amsterdam), **3**, 53 (1968).

[2] This work was supported by the National Science Foundation and by the Advanced Research Projects Agency under Contract SD-131.

[3] V. R. Magnuson and G. D. Stucky, *J. Am. Chem. Soc.*, **90**, 3269 (1968).

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

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

Table I. Final Observed and Calculated Structure Factors[a]

[a] Unobserved reflections are indicated by an asterisk.

Ziegler and Holzkamp[6] reported in 1957 the preparation of two compounds from the reaction of trimethylaluminium with dimethylmagnesium: a viscous oil formulated as $MgAl_2(CH_3)_8$, and a crystalline solid (mp 88°) referred to as $MgAl(CH_3)_5$. This same reaction produced compounds with significantly different properties in our laboratory.

Experimental Section

$(CH_3)_2Mg$ was prepared by the reaction of excess Mg metal with

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(6) K. Ziegler and E. Holzkamp, *Ann.*, **605**, 93 (1957).

Table II. Final Atomic Positional Parameters for Octamethyldialuminummonomagnesium

Atom	*x/a*	*y/b*	*z/c*
Mg	0.0114 (4)	−0.2552 (3)	0.2648 (3)
Al(1)	−0.2309 (4)	−0.2438 (3)	0.0165 (3)
Al(2)	0.2549 (4)	−0.2568 (3)	0.5166 (2)
C(1)	−0.5052 (14)	−0.1978 (10)	0.0050 (10)
C(2)	−0.1379 (14)	−0.2807 (10)	−0.1521 (9)
C(3)	−0.0287 (13)	−0.0966 (8)	0.1611 (9)
C(4)	−0.2034 (15)	−0.4024 (9)	0.1021 (9)
C(5)	0.3213 (13)	−0.3015 (10)	0.3251 (9)
C(6)	−0.0511 (13)	−0.2230 (9)	0.4698 (9)
C(7)	0.2735 (14)	−0.4081 (9)	0.5935 (9)
C(8)	0.4156 (15)	−0.0975 (10)	0.6261 (10)
H1 (C(1))	−0.5251	−0.1842	0.0947
H2 (C(1))	−0.5202	−0.1212	−0.0267
H3 (C(1))	−0.5973	−0.2642	−0.0568
H4 (C(2))	0.0001	−0.2990	−0.1288
H5 (C(2))	−0.2030	−0.3500	−0.2192
H6 (C(2))	−0.4020	−0.2047	−0.1891
H7 (C(3))	−0.0010	−0.0410	0.2608
H8 (C(3))	0.0800	−0.0920	0.1315
H9 (C(3))	−0.1323	−0.0410	0.1521
H10 (C(4))	−0.1619	−0.4795	0.1409
H11 (C(4))	−0.2830	−0.4160	0.1583
H12 (C(4))	−0.1629	−0.4466	0.0235
H13 (C(5))	0.3700	−0.3060	0.2510
H14 (C(5))	0.4356	−0.2319	0.3648
H15 (C(5))	0.3300	−0.3750	0.3611
H16 (C(6))	−0.1500	−0.1621	0.4520
H17 (C(6))	−0.0760	−0.2400	0.5516
H18 (C(6))	−0.0142	−0.1415	0.5333
H19 (C(7))	0.2300	−0.4773	0.5102
H20 (C(7))	0.4090	−0.4030	0.5709
H21 (C(7))	0.2410	−0.3930	0.6804
H22 (C(8))	0.3882	−0.0315	0.5750
H23 (C(8))	0.3825	−0.0702	0.7109
H24 (C(8))	0.5540	−0.1049	0.6439

$(CH_3)_2Hg$ in ether solution. The ether was then driven off by heating the residue at 130° under vacuum (10^{-5} mm pressure) for 4 hr. Analysis[7] of the $(CH_3)_2Mg$ showed a maximum of 0.07 ethyl ether molecule per $(CH_3)_2Mg$ unit. $(CH_3)_2Be$ was prepared by the sealed tube reaction of an excess of Be powder with $(CH_3)_2Hg$. The resulting $(CH_3)_2Be$ was twice sublimed over Au foil before use.

$(CH_3)_2Be$ dissolves to some extent in $(CH_3)_3Al$, but no solid other than recrystallized $(CH_3)_2Be$ could be isolated. Equimolar mixtures of $(CH_3)_2Mg$ and $(CH_3)_3Al$ yield a substance which readily sublimes at 40° to form colorless, fragile, needle-like crystals (mp 54°). A 1:2 molar mixture of $(CH_3)_2Mg$ and $(CH_3)_3Al$ yields a different complex which sublimes at room temperature to form colorless, rod-shaped crystals (mp 39°). Chemical analyses indicated that this material was $MgAl_2(CH_3)_8$. This was verified by the three-dimensional X-ray structural study.

Single crystals of $MgAl_2(CH_3)_8$ were grown by slow sublimation, and sealed in thin-walled glass capillaries. Preliminary unit cell dimensions were determined from Weissenberg (Cu Kα) and precession (Mo Kα) photographs. The crystal system is triclinic and statistical tests indicate the space group to be $P\bar{1}$. Lattice constants and standard deviations were obtained by a least-squares refinement of the angular settings of 12 reflections which were carefully centered on a Picker four-circle diffractometer. The unit cell parameters are $a = 6.955 \pm 0.002$, $b = 10.802 \pm 0.002$, and $c = 10.287 \pm 0.002$ Å; $\alpha = 102.35 \pm 0.02$, $\beta = 105.03 \pm 0.01$, and $\gamma = 92.49 \pm 0.01°$; $V = 725.1$ Å^3 with $Z = 2$. The calculated density, 0.91 g cm^{-3}, agrees well with the observed density, 0.93 g cm^{-3}.

Data were collected with Ni-filtered Cu radiation. The diffracted intensities were collected by the θ–2θ scan technique with a take-off angle of 2.5° and a scan rate of 1° min^{-1}. The mosaicity of the crystal used was satisfactorily small. Intensity data were collected up to 80° in 2θ for a total of 889 independent reflections. Background, Lorentz, and polarization corrections reduced the observed intensities to squared structure factors. Unobserved reflections ($I_{obsd} < 3\sigma(I)$) were given a raw intensity of $\sigma(I)$. The linear absorption coefficient (μ) for this compound is 18.59 cm^{-1} with Cu Kα radiation. This gives a maximum range of calculated values of 9% for μR for the crystal used and absorption corrections were deemed unnecessary. Fourier calculations were made with the Sly, Shoemaker, and Van den Hende ERFR3[8] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[9] No corrections were made for extinction or anomalous dispersion. The function $\Sigma W(|F_o| - |F_c|)^2$ was minimized. Neutral atom-scattering factors were taken from the compilations of Ibers[10] for H, C, Mg, and Al. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE[11] program. Johnson's program ORTEP[12] was used for the crystal structure illustrations.

Nmr spectra were measured on the Varian A-60A and HA-100 spectrometers.

Structure Determination and Refinement

The position of one metal atom was found from a three-dimensional Patterson map. A three-dimensional electron density synthesis phased by the one metal atom revealed the positions of the other two metal atoms. At this point, $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| - \times 100 = 37\%$. Subsequent Fourier syntheses yielded the coordinates of all nonhydrogen atoms. Several cycles of isotropic least-squares refinement with unit weights resulted in a discrepancy factor of $R_1 = 13.8\%$ for observed data. A difference Fourier map did not unambiguously reveal the hydrogen atom positions, but did indicate anisotropic behavior. After two cycles of anisotropic refinement ($R_1 = 10.1\%$), a difference map was calculated and showed peaks which could be ascribed to hydrogen atoms. The hydrogen atom positions were not refined, but were moved after each subsequent cycle by an amount equal to the shift of the carbon atom to which they are attached. Three cycles of refinement in this fashion yielded a discrepancy factor of $R_1 = 7.6\%$. Unit weights had been used up to this time, and a check of Cruickshank's criterion[13] that data should be so weighted as to make $W(|F_o| - |F_c|)^2$ constant over the entire range of $|F_o|$ values indicated a divergence only with the six most intense reflections and with the unobserved reflections. This was corrected by giving these reflections a weight of 0.10 that of the others. Two more cycles of refinement gave $R_1 = 7.2\%$, $R_2 = [\sum(|F_o| - |F_c|)^2/\sum(F_o)^2]^{1/2} \times 100 = 6.8\%$.

The final cycle of refinement showed no parameter shift greater than 0.04 of one estimated standard deviation. A difference Fourier map computed at this point did not have any feature greater than 0.5 e/Å^3. The final value of the function $[\sum W(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m is the number of reflections included in the refinement and n is the number of parameters varied, is 1.19. The final observed and calculated structure factors are listed in

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(7) Analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

(8) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, CBRL-22M-62, Esso Research and Engineering Co., 1962.

(9) W. R. Busing, K. O. Martin, and H. A. Levy, Report No. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(10) J. A. Ibers, "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202, 203.

(11) W. R. Busing, K. O. Martin, and H. A. Levy, Report No. ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(12) C. K. Johnson, Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(13) D. W. J. Cruickshank, "Computing Methods in the Phase Problem," Pergamon Press, Oxford, 1961.

Table III. Anisotropic Temperature Factors ($\times 10^4$) for Octamethyldialuminummonomagnesium

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Mg	254 (9)	132 (4)	112 (4)	26 (4)	18 (4)	31 (3)
Al(1)	246 (9)	124 (4)	116 (4)	6 (4)	16 (5)	35 (3)
Al(2)	226 (8)	125 (4)	122 (4)	20 (4)	24 (4)	40 (3)
C(1)	304 (31)	201 (16)	214 (16)	37 (18)	67 (18)	47 (13)
C(2)	388 (33)	181 (15)	149 (14)	36 (18)	65 (17)	29 (11)
C(3)	336 (30)	117 (12)	188 (15)	−7 (15)	56 (17)	3 (10)
C(4)	523 (38)	120 (13)	193 (16)	−22 (18)	67 (20)	55 (11)
C(5)	324 (30)	221 (16)	162 (14)	45 (18)	132 (17)	62 (12)
C(6)	303 (29)	173 (14)	164 (14)	82 (17)	96 (17)	43 (11)
C(7)	371 (32)	159 (14)	180 (15)	3 (17)	46 (12)	45 (11)
C(8)	434 (35)	151 (14)	217 (17)	12 (18)	68 (20)	26 (12)

Table I. Final atomic parameters and standard deviations are tabulated in Table II. Anisotropic thermal parameters are shown in Table III. Interatomic distances, angles, and errors are listed in Table IV.

Discussion

The molecular configuration, shown in Figure 1, is that of a 2:1 complex. As Table V indicates, $Mg[Al(CH_3)_4]_2$ has the features characteristic of an electron-deficient compound: the metal–carbon–metal bridge angle is 77.7°, and the metal–metal approach is 2.70 Å. The extent to which this compound could be considered an -ate complex had been subject to speculation. The structure does have some characteristics very similar to those found in $LiAl(C_2H_5)_4$[14] (Table V); however, the longer aluminum–carbon(bridge) bond length in $Mg[Al(CH_3)_4]_2$ suggests a greater degree of covalency in the latter complex. On the other hand, the magnesium–aluminum approach is 0.04 Å longer than might be predicted on the basis of a purely covalent model and the metal–carbon–metal bond angle of 77.7° is significantly larger than that found in either parent species. Further, the average aluminum–carbon(bridge) bond length of 2.10 Å is shorter than that found in trimethylaluminum. All but the last of the comparisons hinge on the reliability of the reported values for dimethylmagnesium,[15,16] a structure done by powder diffraction methods. However, in the dimethylmagnesium structure, the magnesium atoms lie on special positions so that the accuracy of the Mg–Mg distance depends only on the accuracy of the unit cell parameters. The bonding in the mixed complex is therefore seen to exhibit an observable amount of ionic character relative to that in $[Al(CH_3)_3]_2$ and $[Mg(CH_3)_2]_n$.

It is well to note the carbon(terminal)–aluminum–carbon(terminal) angles of 119.2 and 119.9°. Vranka and Amma found the same angle to be 123.1° in trimethylaluminum,[5] and used this as a basis to postulate that the aluminum atoms could be employing sp^2 hybrid orbitals with one lobe directed at the opposing aluminum atom. On this basis, it was suggested that metal-metal interactions are important in the stabilization of these compounds. Such an argument might be used for $Mg[Al(CH_3)_4]_2$, but other factors such as intra- and intermolecular electrostatic interactions cannot be ruled out.

Table IV. Interatomic Distances (Å) and Angles (degrees) for Octamethyldialuminummonomagnesium

	Bonded		
Mg–Al(1)	2.702 (4)	Al(1)–C(2)	1.973 (10)
Mg–Al(2)	2.706 (4)	Al(1)–C(3)	2.104 (9)
Mg–C(5)	2.194 (9)	Al(1)–C(4)	2.082 (9)
Mg–C(6)	2.222 (9)	Al(2)–C(5)	2.100 (9)
Mg–C(3)	2.195 (10)	Al(2)–C(6)	2.123 (9)
Mg–C(4)	2.218 (10)	Al(2)–C(7)	1.957 (10)
Al(1)–C(1)	1.972 (10)	Al(2)–C(8)	1.958 (10)
	Nonbonded Intramolecular Distances		
C(1)–C(2)	3.41 (1)	C(2)–C(3)	3.28 (1)
C(3)–C(4)	3.34 (1)	C(2)–C(4)	3.29 (1)
C(5)–C(6)	3.36 (1)	C(5)–C(7)	3.29 (1)
C(7)–C(8)	3.38 (1)	C(5)–C(8)	3.28 (1)
C(1)–C(3)	3.31 (1)	C(6)–C(7)	3.27 (1)
C(1)–C(4)	3.25 (1)	C(6)–C(8)	3.31 (1)
	Bond Angles		
Al(1)–Mg–Al(2)	178.5 (1)	Al(1)–C(3)–Mg	77.8 (2)
C(1)–Al(1)–C(2)	119.9 (3)	Al(1)–C(4)–Mg	77.8 (2)
C(7)–Al(2)–C(8)	119.2 (3)	Al(2)–C(5)–Mg	78.1 (2)
		Al(2)–C(6)–Mg	77.1 (2)

Table V. Comparison of Structural Properties of Electron-Deficient Compounds

Compound	M–M, Å	Al–C bridge	Mg–C bridge	Al–C terminal	M–C–M, deg
$[(CH_3)_2Mg]_\infty$	2.72	....	2.24	....	75
$[(CH_3)_3Al]_2$	2.60	2.14	....	1.97	74.7
$Mg[Al(CH_3)_4]_2$	2.70	2.10	2.21	1.97	77.7
$Li[Al(C_2H_5)_4]$	2.71	2.02	....	....	77.2

Table VI. Mean Plane Calculation for the Four-Membered Ring Systems in Octamethyldialuminummonomagnesium

Atom	Displacement, Å
A. Equation of Plane Defined by Mg, Al(1), C(3), and C(4) of the Form $AX + BY + CZ - D = 0$[a]	
Mg	−0.008 (4)
Al(1)	−0.009 (3)
C(3)	0.008 (10)
C(4)	0.008 (11)
B. Equation of Plane Defined by Mg, Al(2), C(5), and C(6) of the Form $AX + BY + CZ - D = 0$[b]	
Mg	−0.036 (3)
Al(2)	−0.037 (3)
C(5)	0.036 (10)
C(6)	0.035 (10)

[a] $A = 0.8762$, $B = -0.2164$, $C = -0.4306$, $D = 0.9431$.
[b] $A = 0.2713$, $B = 0.9518$, $C = 0.1431$, $D = 3.0265$.

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(14) R. L. Gerteis, R. E. Dickerson, and T. L. Brown, *Inorg. Chem.*, **3**, 872 (1964).

(15) E. Weiss, *J. Organometal. Chem.* (Amsterdam), **2**, 314 (1964).

(16) G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 4825 (1964).

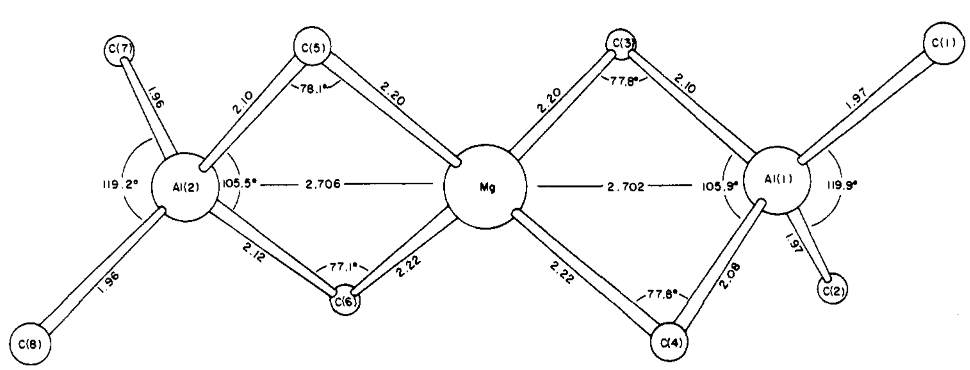

Figure 1. Molecular structure of octamethyldialuminummonomagnesium.

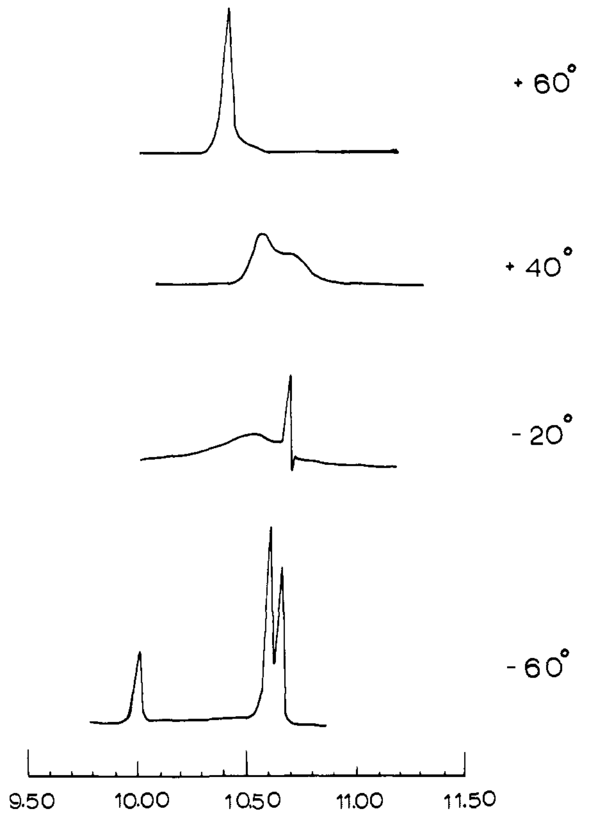

Figure 2. Temperature dependence of the exchange process between trimethylaluminum and octamethyldialuminummonomagnesium in cyclopentane.

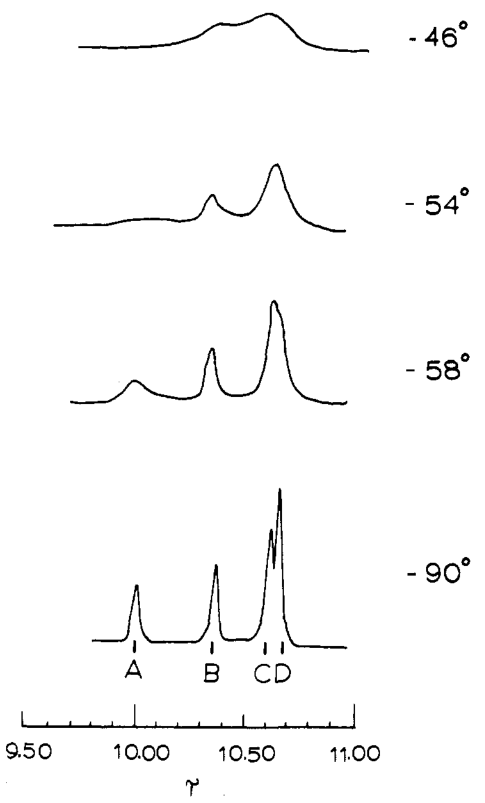

Figure 3. Temperature dependence of the exchange process between trimethylaluminum and octamethyldialuminummonoberyllium in toluene.

The Al(1)-Mg-Al(2) angle is 178.5°. In Table VI, Mg, Al(1), C(3), C(4) are seen to be nearly coplanar while with Mg, Al(2), C(5), C(6) the deviation from planarity is much greater. Further calculations show that Al(2) lies 0.13 Å out of the plane defined by Mg, C(5), and C(6).

Solution studies of $\mathrm{Mg[Al(CH_3)_4]_2}$ are complicated by the existence of the equilibrium

$$2\mathrm{Mg[Al(CH_3)_4]_2} \rightleftarrows [\mathrm{MgAl(CH_3)_5}]_2 + 2\mathrm{Al(CH_3)_3} \qquad (1)$$

The two mixed group II and III compounds readily interconvert at room temperature and it is therefore difficult to isolate a pure sample of either complex. Nuclear magnetic resonance spectra of the two compounds in different concentration ratios show in all cases a sharp singlet at room temperature (τ 10.50 in cyclopentane). It is evident that each species undergoes some type of rapid exchange process and that the average sites are close to being magnetically equivalent. Below −60°, in samples of one of the compounds with a small impurity of the other, two resonances separated by 4 Hz have been recorded. Thus, although the role of the solvent has not been exhaustively studied, it appears that exchange occurs between the two species at room temperature. Each complex continues to show evidence of exchange with itself to −100°.

If $\mathrm{Mg[Al(CH_3)_4]_2}$ or $[\mathrm{MgAl(CH_3)_5}]_2$ is dissolved in $\mathrm{(CH_3)_3Al}$, the nmr spectrum of the resultant solution shows two broadened methyl resonances. The one downfield corresponds to the average resonance in tri-

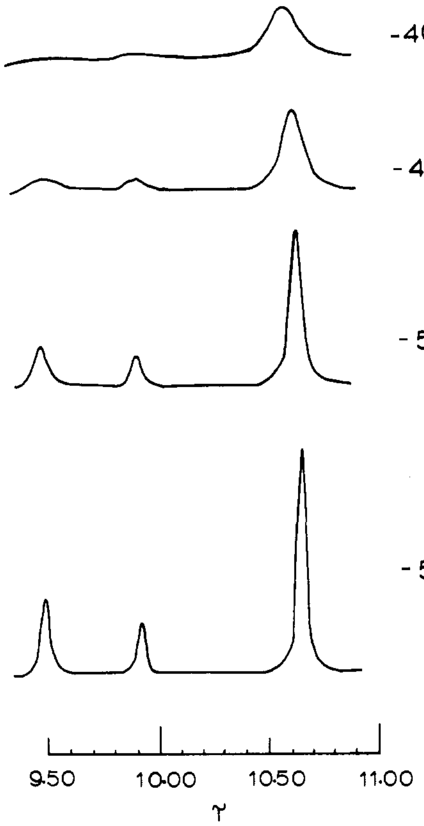

Figure 4. Temperature dependence of the exchange process between trimethylaluminum and octamethyldialuminummonoberyllium in cyclopentane.

methylaluminum. The upfield signal must arise from $Mg[Al(CH_3)_4]_2$ since the excess trimethylaluminum should drive the equilibrium (1) well to the left. Figure 2 shows the temperature dependence of the exchange process between trimethylaluminium and octamethyldialuminummonomagnesium. At 60° exchange is rapid; by −20° $(CH_3)_3Al$–$Mg[Al(CH_3)_4]_2$ exchange has ceased and that of $[(CH_3)_3Al]_2$ has been slowed. By −60° only the complex itself continues to show evidence of exchange. This suggests that the rate-determining process in the trimethylaluminum–octamethyldialuminummonomagnesium exchange is the dissociation of the trimethylaluminum dimer. However, more detailed kinetic studies of these systems are needed in order to fully explain the observed behavior.

As in the case of dimethylmagnesium, dimethylberyllium will dissolve to some extent in trimethylaluminum. Repeated attempts to isolate a solid from the resultant solution yielded only recrystallized dimethylberyllium. At room temperature the equilibrium

$$(CH_3)_3Al + (CH_3)_2Be \rightleftarrows \text{complex} \qquad (2)$$

must lie well to the left, since dimethylberyllium will dissolve only in far more than stoichiometric amounts of trimethylaluminum. At 30° nmr spectra of different

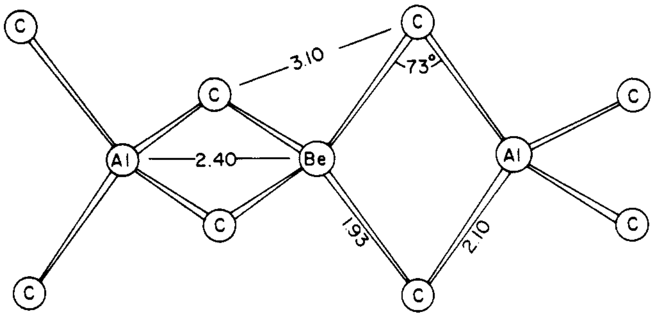

Figure 5. Proposed structure for octamethyldialuminummonoberyllium.

concentrations of dimethylberyllium in trimethylaluminum show a sharp singlet with the same τ value as pure trimethylaluminum (τ 10.27 in cyclopentane). Apparently, both trimethylaluminum and complex undergo rapid exchange and the average sites are magnetically equivalent.

Figures 3 and 4 show the temperature dependence of the exchange process in cyclopentane and in toluene. In both cases essentially all exchange is stopped by −60°. The −90° spectrum in toluene shows four resonances. The one farthest downfield (A) is assigned to the protons on the bridging methyl groups in trimethylaluminum and the one farthest upfield (D) results from the protons on the terminal methyl groups in trimethylaluminum. By analogy, B must arise from the protons on the bridge methyl groups in the complex and C from the ones on the terminal groups in the complex.

The stoichiometry of the complex may be deduced from an integration of the three peaks (in toluene, both terminal resonances are treated as one peak). If twice the area under the bridge methyl peak of trimethylaluminum is subtracted from the total area under the terminal peak, the resonances associated with the complex are found to be in the ratio 1:1. Therefore, there must be equal numbers of bridge and terminal methyl groups, and the structure of a 2:1 complex, as seen in Figure 5, may be assigned. The bond distances and angles were calculated from values obtained from the structures of dimethylberyllium,[17] trimethylaluminum,[5] and octamethyldialuminummonomagnesium. A very short methyl(bridge)–methyl(bridge) distance of 3.10 Å is expected. Methyl–methyl distances of the same magnitude (3.12 Å) are found in $[Be[N(CH_3)_2]_2]_3$ and are postulated to be the reason that $[Be[N(CH_3)_2]_2]_3$ is trimeric rather than polymeric.[1c] In the corresponding magnesium compound this approach is 3.6 Å. The steric interactions in octamethyldialuminummonoberyllium, as formulated in Figure 5, would be much more severe than those in octamethyldialuminummonomagnesium and probably explain its instability relative to that of the organomagnesium derivative.

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(17) A. I. Snow and R. E. Rundle, *Acta Cryst.*, 4, 348 (1951).