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Mass Spectra of Bridge-Bonded Aluminum Compounds

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The mass spectra of trimethylaluminum, dimethylaluminum chloride, methylaluminum dichloride, aluminum trichloride, and dimethylaluminum hydride have been determined. The existence of a dimer is clearly shown for dimethylaluminum chloride and methylaluminum dichloride. Mass spectrometry is incapable of demonstrating the existence of a dimer of trimethylaluminum. Aluminum trichloride exhibits a large number of fragments with many peaks at m/e values greater than the dimer. The dimethylaluminum hydride spectrum indicates species characterized as monomers, dimers, trimers, tetramers, pentamers, and hexamers. Some possible implications of this with respect to hydrogen bridge bonding in aluminum compounds are discussed.

Introduction

The mass spectra of boron hydrides,¹⁻³ alkylboranes,⁴⁻⁷ and boron trihalides⁸⁻¹¹ have been studied. In the boron series only the hydride exhibits a bridge bond.^{4,12} These bridge bonds survive electron impact to give a distribution of ions extending downward from the molecule ion.³ The analogous aluminum compounds exhibit methyl, hydrogen, and halogen bridging. The mass spectral study¹³ of these compounds is therefore of interest for information it might yield regarding bridge bonding.

Trimethylaluminum is a dimer in the vapor phase to 70°.¹⁴ After a shaky start at structural determination involving electron diffraction¹⁵⁻¹⁷ and Raman data,¹⁸ the correct structure was proposed by Kohlrausch and Wagner on the basis of the Raman spectra.¹⁹ Lewis and Rundle²⁰ unequivocally showed the presence of a methyl bridge in crystalline trimethylaluminum by X-ray diffraction. Nmr data in hydrocarbon solvents have shown that there is a single peak for methyl protons at room temperature

but the peak splits when the temperature is lowered to -75°.²¹⁻²³ This indicates that in a solution at room temperature a rapid exchange between terminal and bridged methyl groups renders all protons magnetically equivalent on an nmr time scale. When the temperature is lowered to -75°, the exchange is slowed sufficiently for the detection of protons in different chemical environments by nmr spectroscopy. On the basis of the vapor-phase infrared spectra, Gray²⁴ has confirmed the D_{2h} symmetry proposed earlier.¹⁹

Fischer and Rahlfs²⁵ established that aluminum chloride vapor is a dimer by vapor pressure and vapor density measurements. The structure, consisting of two chlorine bridges, was established by electron diffraction.^{26,27} The mass spectra of aluminum trifluoride showed, among other fragments, the peaks corresponding to the monomer, dimer, and trimer.²⁸

Methylaluminum dichloride and dimethylaluminum chloride are dimeric in the vapor phase. Brockway and Davidson²⁹ proposed that the structures consist of two aluminum atoms and two bridging halogens. Although the proposal for the existence of methyl bridges on the basis of the Raman spectra³⁰ confused the situation for a while,^{23,31} the most recent infrared²⁴ and nmr²² evidence supports Brockway's earlier conclusion. Gray²⁴ further states that the methyl groups in methylaluminum dichloride are in the *trans* configuration. Laubengayer and Lengnick³² have reported that diethylaluminum fluoride exists as a

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tetramer with the fluorine nmr spectrum indicating a cyclic structure of aluminum with fluorine bridge bonds.

Dimethylaluminum hydride has not been studied as extensively as the above compounds. Wartik and Schlesinger³³ found a degree of association of about 2.4 on the basis of vapor density molecular weight in the temperature range of 83–95°. The dimeric value was approached at 167°. When the molecular weight was determined in isopentane solution by vapor tension lowering, values corresponding to the trimer were observed.

Experimental Section

Instrumentation.—The mass spectra were obtained on an AEI MS-12 single-focus instrument which was operated at 70 eV and a resolution of about 1000 for the routine spectra with the source temperature kept as low as possible. This was accomplished by keeping the source heater off and the filament off until just prior to a run. The indicated source temperature was between 60 and 100° for all runs. All of the samples except aluminum chloride were admitted to the source through the standard gas leak. A solid probe was used for aluminum chloride.

Trimethylaluminum.—This compound was used as obtained from the Ethyl Corp. without further purification.

Dimethylaluminum Chloride.—Methylaluminum sesquichloride obtained from the Ethyl Corp. was treated with sodium chloride in order to complex the methylaluminum dichloride in the mixture.^{34,35} Several drops of sesquichloride were condensed into a large excess of sodium chloride dried by heating to about 80° under vacuum for several hours. All operations were carried out in a standard vacuum line. After 12 hr, the dimethylaluminum chloride was distilled from the sodium chloride.

Methylaluminum Dichloride.—Methylaluminum sesquichloride obtained from the Ethyl Corp. was condensed into aluminum trichloride on a vacuum line. Because of the difficulty of measuring exact amounts of sesquichloride, the aluminum chloride was present in less than a stoichiometric amount. The reaction was slow. After 12 hr of heating at 60°, there was still a bit of solid aluminum chloride left even though it was in contact with unreacted dimethylaluminum chloride. The reaction mixture was distilled at room temperature into a liquid nitrogen cooled trap. After removal of the excess sesquichloride, a residue of methylaluminum dichloride remained. The compound was analyzed by condensing water above the aluminum compound and allowing the trap to warm gradually from –195° to room temperature. The methane generated was toepolymerized and measured. The chloride was determined gravimetrically as silver chloride.

Anal. Calcd: CH₃:Cl⁻ = 1:2. Found: CH₄, 1.04 mmol; Cl⁻, 75.3 mg; CH₃:Cl⁻ = 1:2.04.

Aluminum Trichloride.—ACS Reagent grade aluminum trichloride was sublimed under vacuum. The solid probe of the mass spectrometer was filled with the material on the sublimator cold finger by carrying out the operation in a glove bag filled with dry nitrogen. The retracted probe was removed from the glove bag and immediately placed in the antechamber of the solid probe introduction system.

Dimethylaluminum Hydride.—Dimethylaluminum hydride was prepared from trimethylaluminum and lithium aluminum hydride according to the method of Wartik.³³ The product was analyzed by hydrolyzing with water, toepolymerizing the meth-

ane and hydrogen mixture, and analyzing the mixture on a mass spectrometer.

Anal. Calcd: H₂:CH₄ for (CH₃)₂AlH = 0.50. Found: H₂:CH₄ = 0.51.

Results

Because the cracking patterns of the aluminum compounds were not studied with the view of obtaining data for analytical determinations, the fragmentation patterns listed should be used only for gauging relative intensities.

Aluminum Chloride.—Table I shows the monoisotopic spectrum for aluminum chloride. Species assignments are shown with intensities normalized to the Al₂Cl₅⁺ peak. There is no sharp termination of peaks in the spectra. At higher *m/e* values than the dimer peak, peaks occur in groups of 12–15. There are at least 20 such groupings distinctly identifiable in the *m/e* range 261–630. The intensities are of the order of 1% but range as high as 3% of the base peak. Chlorine isotope patterns for six and seven chlorines can be picked out in some of the groups below *m/e* 470. However, no satisfactory species assignment could be made. At *m/e* values higher than 630, an order of magnitude drop in peak intensities is observed. These small peaks seem to continue in a pattern similar to those found in the *m/e* 261–630 region.

TABLE I
MONOISOTOPIC PATTERN OF ALUMINUM CHLORIDE (Cl³⁵)

<i>m/e</i>	Species	Rel intens
27	Al ⁺	13.6
62	AlCl ⁺	23.4
97	AlCl ₂ ⁺	64.1
132	AlCl ₃ ⁺	20.7
229	Al ₂ Cl ₅ ⁺	100.0
264	Al ₃ Cl ₈ ⁺	1.04

Methylaluminum Dichloride.—The monoisotopic spectrum for methylaluminum dichloride is shown in Table II. Unlike the spectrum for aluminum trichloride, the region above the dimer peak was essentially clean. The CH₃AlCl⁺ peak was arbitrarily chosen as the normalizing peak. The important peaks are attributable to species formed by loss of one substituent, either a methyl or chlorine from the monomer or dimer. As in the group IVa organometallics, carbon–hydrogen cleavage to give species of the type MCH₂⁺ is relatively rare. Also consistent with the other organometallics is the observation that metal hydride species are formed. The analyses of the metastable peaks give definite evidence for the formation of hydrides by electron-impact processes. However, there is also the possibility that they might be formed by thermal reactions in the source.

Dimethylaluminum Chloride.—The monoisotopic spectrum for dimethylaluminum chloride with species assignment is shown in Table III. As in the methylaluminum dichloride spectrum, the CH₃AlCl⁺ peak was chosen as the normalizing peak. The spectrum com-

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TABLE II

MONOISOTOPIC MASS SPECTRUM OF METHYLALUMINUM DICHLORIDE		
<i>m/e</i>	Species	Pattern coeff
12	C ⁺	4.3
13	CH ⁺	14.0
14	CH ₂ ⁺	30.5
15	CH ₃ ⁺	54.3
16	CH ₄ ⁺	29.9
26	C ₂ H ₂ ⁺	1.3
27	Al ⁺	164.0
	C ₂ H ₃ ⁺	5.0
28	AlH ⁺	2.7
	C ₂ H ₄ ⁺	0.8
29	AlH ₂ ⁺	1.1
	C ₂ H ₅ ⁺	2.0
35	Cl ⁺	5.6
36	HCl ⁺	3.2
41	AlCH ₂ ⁺	4.0
42	AlCH ₃ ⁺	12.1
43	HAICH ₃ ⁺	2.9
49	CH ₂ Cl ⁺	6.7
57	Al(CH ₃) ₂ ⁺	54.9
62	AlCl ⁺	62.2
63	HAICl ⁺	12.4
77	CH ₃ AlCl ⁺	100.0
92	(CH ₃) ₂ AlCl ⁺	1.8
97	AlCl ₂ ⁺	230.5
112	AlCH ₃ Cl ₂ ⁺	18.6
132	AlCl ₃ ⁺	9.6
153	Al ₃ Cl ₃ H ₂ ⁺ or Al ₂ Cl ₂ C ₂ H ₅ ⁺	0.5
169	Al ₂ (CH ₃) ₃ Cl ₂ ⁺	4.1
189	Al ₂ (CH ₃) ₂ Cl ₃ ⁺	22.0
209	Al ₂ CH ₃ Cl ₄ ⁺	39.6

TABLE III

MONOISOTOPIC MASS SPECTRUM OF DIMETHYLALUMINUM CHLORIDE		
<i>m/e</i>	Species	Rel intens
12	C ⁺	0.1
13	CH ⁺	0.2
14	CH ₂ ⁺	0.9
15	CH ₃ ⁺	3.6
16	CH ₄ ⁺	1.1
26	C ₂ H ₂ ⁺	0.5
27	Al ⁺	36.5
	C ₂ H ₃ ⁺	2.6
28	AlH ⁺	0.8
	C ₂ H ₄ ⁺	0.4
29	AlH ₂ ⁺	0.8
	C ₂ H ₅ ⁺	1.8
35	Cl ⁺	0.5
36	HCl ⁺	0.9
41	AlCH ₂ ⁺	1.4
	C ₃ H ₅ ⁺	3.3
42	AlCH ₃ ⁺	7.7
43	HAICH ₃ ⁺	3.0
	C ₃ H ₇ ⁺	2.3
57	Al(CH ₃) ₂ ⁺	100.0
62	AlCl ⁺	9.1
63	HAICl ⁺	4.0
69	Al ₂ CH ₃ ⁺	0.5
70	HAAl ₂ CH ₃ ⁺	0.4
71	H ₂ Al ₂ CH ₃ ⁺	1.2
72	H ₃ Al ₂ CH ₃ ⁺	0.3
73	H ₄ Al ₂ CH ₃ ⁺	0.7
77	AlCH ₃ Cl ⁺	50.7
85	Al ₂ (CH ₃) ₂ H ⁺	0.5
92	Al(CH ₃) ₂ Cl ⁺	5.4
97	AlCl ₂ ⁺	8.1
149	Al ₂ (CH ₃) ₄ Cl ⁺	1.4
153	Al ₂ Cl ₃ C ₂ H ₅ ⁺ or Al ₃ Cl ₂ H ₂ ⁺	4.8
169	Al ₃ (CH ₃) ₃ Cl ₂ ⁺	48.4
189	Al ₂ (CH ₃) ₂ Cl ₃ ⁺	4.2

compares in many respects to the methylaluminum dichloride spectrum. The AlCl⁺ and AlCl₂⁺ peaks are smaller and the AlCH₃⁺ and Al(CH₃)₂⁺ peaks are larger as expected. It is interesting, however, that the hydride peaks are approximately of the same size for both compounds. Since the hydride is thought to originate from rearrangement of hydrogen from the methyl group, one might expect to see larger hydride peaks from the dimethylaluminum chloride. In this spectrum, as well as the methylaluminum dichloride spectrum, the relative intensity of the hydrocarbon peaks, for example, the methane peak, was especially sensitive to the conditioning of the mass spectrometer. In general, the hydrocarbon peak was greatest after the original introduction and decreased with subsequent introductions.

Trimethylaluminum.—The monoisotopic spectrum for trimethylaluminum is shown in Table IV. The striking difference between this spectrum and the methylchloroaluminum compounds is the unimportance of the dimer peak. The spectrum is essentially that for monomeric trimethylaluminum. The peaks observed above the monomer parent ion are all less than 1% of the parent peak. The largest dimer species observed for aluminum chloride, methylaluminum dichloride, and dimethylaluminum chloride are Al₂Cl₅⁺, Al₂(CH₃)₂Cl₃⁺, and Al₂(CH₃)₃Cl₂⁺, respectively. The

TABLE IV

MONOISOTOPIC MASS SPECTRUM OF ALUMINUM TRIMETHYL

<i>m/e</i>	Species	Rel intens
12	C ⁺	0.1
13	CH ⁺	0.5
14	CH ₂ ⁺	1.3
15	CH ₃ ⁺	8.0
16	CH ₄ ⁺	9.7
27	Al ⁺	10.1
	C ₂ H ₃ ⁺	0.4
28	AlH ⁺	0.6
	C ₂ H ₄ ⁺	0.6
29	AlH ₂ ⁺	1.3
	C ₂ H ₅ ⁺	0.2
30	AlH ₃ ⁺	0.2
42	AlCH ₃ ⁺	5.6
43	HAICH ₃ ⁺	2.7
57	Al(CH ₃) ₂ ⁺	100.0
72	Al(CH ₃) ₃ ⁺	8.0
102	Al ₂ (CH ₃) ₃ H ₃ ⁺	0.2
115	Al ₂ (CH ₃) ₄ H ⁺	0.2
129	Al ₂ (CH ₃) ₅ ⁺	0.005
145	Al ₃ (CH ₃) ₄ H ₄ ⁺	0.2
203	Al ₄ (CH ₃) ₆ H ₅ ⁺	0.2

TABLE V
MONOISOTOPIC MASS SPECTRUM OF
DIMETHYLALUMINUM HYDRIDE

<i>m/e</i>	Species	Rel intens
12	C ⁺	0.3
13	CH ⁺	1.1
14	CH ₂ ⁺	2.9
15	CH ₃ ⁺	16.5
16	CH ₄ ⁺	17.4
26	C ₂ H ₂ ⁺	1.4
27	Al ⁺	33.2
	C ₂ H ₃ ⁺	2.9
28	AlH ⁺	1.7
	C ₂ H ₄ ⁺	0.8
29	AlH ₂ ⁺	2.6
	C ₂ H ₅ ⁺	2.4
30	AlH ₃ ⁺	0.3
	C ₂ H ₆ ⁺	1.3
41	AlCH ₂ ⁺	1.3
	C ₃ H ₅ ⁺	2.7
42	AlCH ₃ ⁺	13.7
	C ₃ H ₆ ⁺	0.9
43	HAICH ₃ ⁺	13.7
	C ₃ H ₇ ⁺	2.2
44	H ₂ AlCH ₃ ⁺	3.9
57	Al(CH ₃) ₂ ⁺	100.0
58	HAl(CH ₃) ₂ ⁺	5.3
59	Al ₂ H ₅ ⁺	11.9
72	Al(CH ₃) ₃ ⁺	2.9
73	Al ₂ CH ₃ H ₄ ⁺	7.1
83	Al ₂ CH ₃ CH ₂ ⁺	1.6
85	HAl ₂ (CH ₃) ₂ ⁺	1.3
87	Al ₂ (CH ₃) ₂ H ₃ ⁺	1.7
99	Al ₂ (CH ₃) ₃ ⁺ or Al ₂ H(CH ₃) ₂ CH ₂ ⁺	0.9
100	Al ₂ (CH ₃) ₃ H ⁺	1.1
101	Al ₂ (CH ₃) ₃ H ₂ ⁺	39.6
115	Al ₃ (CH ₃) ₄ H ⁺	3.2
116	Al ₂ (CH ₃) ₄ H ₂ ⁺	0.2
117	Al ₃ (CH ₃) ₂ H ₆ ⁺	0.8
131	Al ₃ (CH ₃) ₃ H ₅ ⁺	2.2
145	Al ₃ (CH ₃) ₄ H ₄ ⁺	0.2
159	Al ₃ (CH ₃) ₅ H ₃ ⁺	0.2
173	Al ₃ (CH ₃) ₆ H ₂ ⁺	0.3
175	Al ₄ (CH ₃) ₄ H ₇ ⁺	1.4
189	Al ₄ (CH ₃) ₅ H ₆ ⁺	1.9
205	Al ₅ (CH ₃) ₄ H ₁₀ ⁺	0.2
219	Al ₅ (CH ₃) ₅ H ₉ ⁺	0.3
233	Al ₅ (CH ₃) ₆ H ₈ ⁺	0.1
247	Al ₅ (CH ₃) ₇ H ₇ ⁺	0.1
249	Al ₆ (CH ₃) ₅ H ₁₂ ⁺	0.3
263	Al ₆ (CH ₃) ₆ H ₁₁ ⁺	0.3
277	Al ₆ (CH ₃) ₇ H ₁₀ ⁺	1.4

corresponding dimer peak Al₂(CH₃)₃⁺ was estimated to be of the order of 0.005% of the base peak for trimethylaluminum. There were two other dimer peaks which could be assigned to Al₂(CH₃)₃H₃⁺ and Al₂(CH₃)₄H⁺. Small peaks at *m/e* 145 and 203 were ascribed to Al₃(CH₃)₄H⁺ and Al₄(CH₃)₆H₅⁺. There is good evidence to believe that these latter two are a function of the pressure. None of the peaks above the monomer peak was more than 0.2% of the base peak.

Dimethylaluminum Hydride.—The monoisotopic spectrum for dimethylaluminum hydride is shown in Table V. The important dimer peak is identified as

TABLE VI
METASTABLE REACTIONS

Aluminum Chloride (Monoisotopic Metastables Cl ³⁵)			
		Obsd	Calcd
Al ₂ Cl ₆ ⁺ → Al ₂ Cl ₅ ⁺ + Cl		198.5	198.6
Methylaluminum Dichloride (Monoisotopic Metastables Cl ³⁵)			
		Obsd	Calcd
Al ₂ CH ₃ Cl ₄ ⁺ → AlCH ₃ Cl ⁺ + AlCl ₃		28.5	28.4
Dimethylaluminum Chloride (Monoisotopic Metastables Cl ³⁵)			
		Obsd	Calcd
Al ₂ (CH ₃) ₃ Cl ₂ ⁺ → Al(CH ₃) ₂ ⁺ + AlCH ₃ Cl ₂		19.2	19.2
Al(CH ₃) ₂ ⁺ → AlCH ₃ ⁺ + CH ₃		30.9	30.9
Al(CH ₃) ₂ ⁺ → AlCH ₂ ⁺ + CH ₄		29.5	29.5
Trimethylaluminum			
		Obsd	Calcd
Al(CH ₃) ₂ ⁺ → Al ⁺ + (CH ₃) ₂		12.8	12.8
Al(CH ₃) ₂ ⁺ → AlH ₂ ⁺ + C ₂ H ₄		14.7	14.8
Al(CH ₃) ₂ ⁺ → AlCH ₃ ⁺ + CH ₃		30.9	30.9
(weak) HAl(CH ₃) ₃ ⁺ → Al ⁺ + CH ₄		16.9	17.0
(weak) AlH ₂ ⁺ → Al ⁺ + H ₂		25.2	25.1
(weak) AlH ⁺ → Al ⁺ + H		26.1	26.0
Dimethylaluminum Hydride			
		Obsd	Calcd
(weak) Al(CH ₃) ₂ ⁺ → AlH ₂ ⁺ + C ₂ H ₄		14.7	14.8
(weak) Al ₂ (CH ₃) ₄ H ⁺ → Al(CH ₃) ₂ ⁺ + Al(CH ₃) ₂ H		28.2	28.3
(weak) Al(CH ₃) ₂ ⁺ → AlCH ₃ ⁺ + CH ₃		30.9	30.9
Al(CH ₃) ₂ ⁺ → HCH ₃ Al ⁺ + CH ₂		32.2	32.4
Al ₂ (CH ₃) ₄ H ⁺ → Al(CH ₃) ₃ ⁺ + AlCH ₃ H		45.1	45.1
Al ₃ (CH ₃) ₅ H ₅ ⁺ → Al ₃ (CH ₃) ₃ H ₃ ⁺ + H ₂		126.8	127

Al₂(CH₃)₃H₂⁺. As in the case with aluminum chloride, groups of peaks were found above the dimer peak. Unlike the aluminum chloride spectrum, assignments could be made for many of these peaks and identified as trimer, tetramer, pentamer, and hexamer species. The region above the hexamer peaks was clean. This contrasted with the aluminum chloride spectrum which showed smaller and smaller peaks extending on out with no clear-cut termination.

Metastable Peaks.—The ion decompositions leading to the metastable peaks observed in the spectra are listed in Table VI. These peaks are consistent with the species listed in Table I–V.

The only metastable transition observed in the aluminum trichloride spectrum is the decomposition of the parent dimer ion to Al₂Cl₅⁺, the ion which also gives the most intense peak in the spectrum.

Methylaluminum dichloride also exhibits one metastable peak. It is due to the decomposition of the dimer ion Al₂CH₃Cl₄⁺ to AlCH₃Cl⁺ and AlCl₃. In the normal spectrum, the ion AlCH₃Cl⁺ is intense. Some of the AlCl₂⁺ may arise from this rearrangement to AlCl₃ followed by a loss of chlorine as well as from the direct loss of a methyl group.

The dimethylaluminum chloride spectrum shows three metastable transitions. One of these, the

$\text{Al}(\text{CH}_3)_2^+$ decomposition to AlCH_3^+ and CH_3 , is observed in all three compounds of this series containing at least two methyl groups. However, the metastable peak due to the $\text{Al}(\text{CH}_3)_2^+$ decomposition to form AlCH_2^+ and methane is not observed in the trimethylaluminum and dimethylaluminum hydride spectra. The third metastable peak is due to the decomposition of the dimer ion $\text{Al}_2(\text{CH}_3)_3\text{Cl}_2^+$ to $\text{Al}(\text{CH}_3)_2^+$, the most intense ion observed in the spectrum, and AlCH_3Cl_2 whose counterpart ion is interestingly not observed.

The only metastable peaks observed for trimethylaluminum originate from monomer ions. This is consistent with the spectrum which indicates a virtual absence of dimer ions. One of the strong metastable transitions and three of the weak transitions produce Al^+ ions. Thus there are several paths for the formation of the strong Al^+ peak in the spectra. The metastable transition in which $\text{Al}(\text{CH}_3)_2^+$ decomposes to AlH_2^+ and C_2H_4 indicates one pathway for hydride and C_2 ion fragment formation. Various ions of both types are found in the spectra.

The dimethylaluminum hydride spectrum shows many of the same metastable peaks as trimethylaluminum. These metastables which are found in both spectra involve the decomposition of the $\text{Al}(\text{CH}_3)_2^+$ ion. It is noted that the AlH_2^+ ion is formed from $\text{Al}(\text{CH}_3)_2^+$ ion as in trimethylaluminum and that no metastable transition could be found in which AlH_2^+ is formed from an ion containing the original hydridic hydrogen in the molecule. One of the two dimer ion metastables forms $\text{Al}(\text{CH}_3)_3^+$. The observation of this transition points to a pathway for the formation of $\text{Al}(\text{CH}_3)_3^+$ and removes most of the apprehensions regarding the possibility that the relatively small $\text{Al}(\text{CH}_3)_3^+$ peak in the spectrum is due to trimethylaluminum impurities.

Discussion

Mass spectral evidence indicates that hydrogen bridge bonds are present in a greater variety of ion species than chlorine or methyl bridge bonds. The methyl bridge is either extremely weak or particularly susceptible to electron impact. In the trimethylaluminum spectrum there were only a few small peaks above the m/e corresponding to the monomer. None of these small peaks could be assigned to species arising from simple fragmentation of the dimer. All of the peaks for which assignment could be made were for species which contained hydridic hydrogen from rearrangement reactions. This would seem to indicate that when more than one aluminum is found in a species it is held together by hydrogen bridges rather than by methyl bridges. Unlike the molecular weight and spectroscopic techniques, the mass spectrometric method is not capable of detecting the presence of methyl bridging in the gas phase. The two methylaluminum chloride spectra, on the other hand, indicate that chlorine forms a simple dimeric bridged structure in the gas phase. The high molecular weight species observed in the aluminum trichloride spectrum is very

likely due to the very short path length between the solid probe and the source. It is to be noted again that this is the only compound of the series whose spectrum was determined using the solid probe. Apparently a large number of different species were formed from the sublimate because the chlorine-35 and -37 patterns could not be identified easily beyond the dimer and species assignment could not be made. That there might be fragmentation from a polymer was indicated by the grouping of peaks in families going toward higher mass numbers. Another anomaly in the aluminum trichloride spectrum is the low intensity of the parent Al_2Cl_6^+ peak. That the intensity of this peak is so very much less than the corresponding dimeric peaks for the methylaluminum chlorides would seem to indicate that the differences in sample introduction make comparisons of bridge bonding on the basis of mass spectra not too meaningful. The species ascribable to hydrogen bridging observed primarily in dimethylaluminum hydride could be clearly assigned to dimer, trimer, tetramer, pentamer, and hexamer species. Of the three bridge-forming moieties studied, hydrogen appears to be involved in the largest variety of structures.

Because the spectrum of dimethylaluminum hydride cuts off rather abruptly after the hexameric species, one can conclude that these species are primarily ring or cluster arrangements rather than linear fragments. Under this assumption the dimeric species is postulated to have the tetramethyldiborane structure. The trimeric species is an arrangement wherein the aluminums are located at the corners of a triangle. This means that the hydrogen bridge bonds are getting more linear in that the aluminum orbitals contributing to the three-center bond are more nearly along the aluminum-aluminum axis, thus forcing the hydrogen s orbital to move closer in order to maintain the same amount of orbital overlap. This, however, is believable in that the boron-hydrogen-boron bond angles in boron hydrides are found to vary over wide limits,³⁶ a result consistent with the geometry of the hydrogen s orbital. If the cyclic structure is extended, the aluminum orbitals get closer and closer to the aluminum-aluminum axis. Indeed, for the five- and six-membered rings, the orbitals can be exactly on the axis. This would lead to a hydrogen bridge bond more linear than any previously observed. An alternate possibility is to place the aluminums at the corners of polyhedra. For example, a tetramer may have a tetrahedral arrangement, a pentamer, a trigonal-bipyramidal or square-pyramidal arrangement, and a hexamer, a trigonal-prismatic or octahedral arrangement. An interesting observation regarding polyhedral geometry is that the number of hydrogens observed in the species suggests the assignment of a hydrogen bridge bond at each edge of the polyhedron. This leads to a number of considerations such as con-

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nectedness of the polyhedra, number of formal bonds, and extent of d-orbital participation. The evidence presented here, however, is not sufficient to remove these considerations from the purely speculative classification.

Whatever the structure of the aggregate species, the results are in agreement with Wartik's molecular weight observation for dimethylaluminum hydride.³³ The principal species in the gas phase is most probably the dimer. Trimers, however, are possible and exist in the vapor phase and most certainly in solution. The tetramers and hexamers would not be expected with unrearranged dimethylaluminum hydride because there would be insufficient hydrogen bridge bonds. They are observed when the electron impact causes rearrangements producing an average of more than one hydride per aluminum. They should also be observed if methylaluminum dihydride were to be prepared. So far this compound has not been characterized. The results presented not only suggest a possible approach to the synthesis of the dihydride but also suggest that the structural studies of the dihydride may be quite interesting.

An interesting generalization that we have observed is that most of the ion species obey the rule that the number of substituents is $3n - 1$, where n is the number of aluminum atoms in the species. This rule holds true for rearranged species as well as for species which can be formed without rearrangement. Calculations on the basis of this rule are very valuable in identifying the ion species, in particular those of the polymeric species. These identifications confirm the observation that the C-Al bond is more easily broken than the C-H bond of the methyl group attached to the central

aluminum atom. This observation is in accord with the results reported for the group IVa metal alkyls.³⁷⁻⁴³ The rule is also an indication that ions of the type $Al_xA_xB_y$, where $x + y = 3n - 1$, are ions which have a high probability of being observed in the mass spectra.

The cause for the high hydrocarbon peaks on first introducing the sample is most probably hydrolysis. The hydrocarbons found in studying other organometallic compounds substituted with ethyl and higher alkyls indicate that the hydrocarbon is an alkane rather than an alkene. The former is a hydrolysis product whereas the latter is formed by thermal decompositions. The hydrolysis probably takes place on the walls of the sample introduction system even though the sample system is maintained at a high vacuum. Partially hydrolyzed material might also exist in the sample itself. The sample is carefully fractionated in a vacuum system, but hydrolysis could conceivably take place upon transfer to the sample container.

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Preparation of Trialuminum Triboron Heptakis(dimethylamino)pentahydride^{1a}

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Treatment of bis(trimethylamine)-alane, $[(CH_3)_3N]_2AlH_3$, with tetrakis(dimethylamino)diborane(4), $[(CH_3)_2N]_4B_2$, results in the formation of the following known compounds: H_2 , $(CH_3)_3N$, $[(CH_3)_2NBH_2]_2$, $[(CH_3)_2N]_2BH$, and $(CH_3)_3NBH_3$. In addition, a new species was prepared, $Al_3B_3[N(CH_3)_2]_7H_5$, which most likely contains three B-Al bonds. Characterization of this new compound is discussed.

Introduction

As part of a continuing effort to prepare metal-metal or metal-metalloid bonds,^{2,3} the reduction of bis-

(trimethylamine)-alane, $[(CH_3)_3N]_2AlH_3$, by tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, was investigated.

Experimental Section

Apparatus and Procedures.—All reactions were carried out in a standard vacuum line equipped with mercury float valves and stopcocks lubricated with Apiezon N grease. Experimental equipment was attached to the vacuum line with Viton A O-ring

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