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## ALKYLALUMINUM HYDRIDE TRIMETHYLAMINE COMPLEXES

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#### ABSTRACT

Alkylaluminum hydride trimethylamine complexes have been obtained by several different methods: (a) reduction of an alkylaluminum halide trimethylamine complex with lithium hydride, (b) alkylation of aluminum hydride trimethylamine with dialkylmercury, (c) reaction of trialkylaluminum trimethylamine and aluminum hydride trimethylamine, and (d) reaction of dialkylaluminum chloride with lithium aluminum hydride and trimethylamine. Some physical properties of the compounds are reported, including the infrared and proton magnetic resonance spectra. Cryoscopic molecular weight determinations indicate that the compounds are associated in cyclohexane. Their possible structures are discussed.

#### INTRODUCTION

Trimethyldialuminum trihydride,  $(Me_3Al_2H_3)_n$ , and dimethylaluminum hydride,  $(Me_2AlH)_n$ , were originally prepared by subjecting a mixture of trimethylaluminum and hydrogen to an electric discharge (1). The latter compound was subsequently obtained from the reaction of trimethylaluminum and lithium aluminum hydride (2). Higher alkyl monohydrides have since been prepared (3, 4), but no uncomplexed dihydrides have been characterized. Since trivalent aluminum has empty 3p and 3d orbitals in addition to the three  $sp^2$  hybrid bonding orbitals, it can further hybridize to make one or two additional orbitals available for coordination with electron donor groups. There are many examples of coordination compounds of this type, among them  $AlH_3 \cdot NMe_3$ ,  $AlH_3 \cdot 2NMe_3$ , and  $Et_3Al \cdot OEt_2$ .

The coordinating power of aluminum suggested the possibility of stabilizing the alkylaluminum dihydrides by complex formation with a Lewis base. This was shown to be the case with the isolation of the stable trimethylamine complexes  $EtAlH_2 \cdot NMe_3$  and  $MeAlH_2 \cdot NMe_3$ . The methylaluminum and ethylaluminum monohydride trimethylamine complexes were also prepared (5). In the following equations, which summarize the methods of synthesis,  $R = CH_3$ — and  $C_2H_5$ —. The reaction between ethylaluminum dichloride trimethylamine and lithium hydride did not yield a product free of chlorine.

$$Et_{2}AlCl \cdot NMe_{3} + LiH \longrightarrow Et_{2}AlH \cdot NMe_{3} + LiCl$$

$$EtAlCl_{2} \cdot NMe_{3} + 2LiH \longrightarrow EtAlH_{2} \cdot NMe_{3} + 2LiCl$$
[A]

$$R_{2}Hg + AlH_{3} \cdot NMe_{3} \longrightarrow R_{2}AlH \cdot NMe_{3} + H_{2} + Hg$$
[B]

$$\frac{1}{2}R_2Hg + AlH_3 \cdot NMe_3 \longrightarrow RAlH_2 \cdot NMe_3 + \frac{1}{2}H_2 + \frac{1}{2}Hg$$

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#### CANADIAN JOURNAL OF CHEMISTRY. VOL. 41, 1963

## $AlH_3 \cdot NMe_3 + 2R_3Al \cdot NMe_3 \longrightarrow 3R_2AlH \cdot NMe_3$

 $2AlH_3 \cdot NMe_3 + R_3Al \cdot NMe_3 \longrightarrow 3RAlH_2 \cdot NMe_3$ 

$$R_{2}AICI + LiAIH_{4} \xrightarrow{\text{NMe}_{3}} 2RAIH_{2} \cdot \text{NMe}_{3} + LiCl \qquad [D]$$

[C]

#### EXPERIMENTAL

#### Apparatus

Because the alkylaluminum compounds are sensitive to air and moisture, all synthetic work was carried out either in a high-vacuum system or in a nitrogen atmosphere. Transfers were conducted in an inert atmosphere chamber.<sup>2</sup> For the vapor tension measurements of the triethylaluminum complex, a tensimeter was used (6).

#### Preparation of Starting Materials

Commercially available lithium hydride (75% pure, based on hydrogen evolution) and lithium aluminum hydride (95% pure) were obtained from Metal Hydrides, Inc. Lecture bottles of the organoaluminum starting materials were supplied by the Ethyl Corporation and Texas Alkyls, Inc. Anhydrous aluminum trichloride was obtained from Matheson Company, Inc. All other starting materials were prepared in this laboratory

A method based on the procedure of Wiberg, Graf, and Uson (7) was used to prepare aluminum hydride trimethylamine. Lithium aluminum hydride, 32 g (0.8 mole), was refluxed in 500 ml of diethyl ether for 4 hours. After the insoluble material had settled to the bottom of the flask, the supernatant liquid was filtered into a 1-liter flask. An ether solution of 25 g (0.2 mole) of aluminum trichloride was added to the LiAlH<sub>4</sub> solution with continuous stirring. After 20 minutes, 50 ml (0.6 mole) of trimethylamine, dissolved in cold ether, was added to the reaction mixture. The product was collected by filtering the supernatant liquid of the reaction mixture, removing the ether under vacuum, and subliming the residue at 60° C (1 mm Hg). The pure AlH<sub>3</sub>·NMe<sub>3</sub> melted at 76° C and was free of chlorine. The yield was 65% based on AlCl<sub>3</sub>. Anal. Calc. for C<sub>3</sub>H<sub>12</sub>NAl: C, 40.44; H, 13.57; N, 15.72; Al, 30.28. Found: C, 40.42; H, 13.94; N, 15.49; Al, 30.53. Triethylaluminum trimethylamine was made on the vacuum line, by the reaction of a hexane solution of

Et<sub>3</sub>Al and gaseous trimethylamine. The product, after purification by vacuum distillation, boiled at 38–39° C (10<sup>-3</sup> mm Hg). Anal. Calc. for C<sub>9</sub>H<sub>24</sub>NAl: C, 62.38; H, 13.96; N, 8.09; Al, 15.57. Found: C, 62.68; H, 14.25; N, 8.30; Al, 16.03. Vapor pressure data and additional physical properties of triethylaluminum trimethylamine are shown in Tables I and II.

	TABLE I		
Vapor tensions of liquid	d triethylaluminun	n trimethylamin	ė

t (°C) P <sub>obs</sub> (mm Hg) P <sub>cale</sub> (mm Hg)	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$109.8 \\ 10.2 \\ 10.0$	$124.9 \\ 20.2 \\ 20.1$	$138.1 \\ 35.2 \\ 35.2$

TABLE II

D1 1	. •	
Physical	nronerfies of	triethvlaluminum
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M.p. (°C)	-41.0
B.p. $(C)^*$	-3017.0
$H_{\text{vap}}$ (kcal mole <sup>-1</sup> )	8.882 13.801
Mol. wt. <sup>‡</sup>	$\begin{array}{c} 27.4 \\ 180.0 \end{array}$
Mol. wt. (calc.)	173.3

\*By extrapolation of vapor pressure equation.  $t Log_{10} P (mm Hg) = A/T + B.$ \$In cyclohexane.

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Trimethylaluminum trimethylamine (8) was prepared in a manner analogous to that of the triethyl compound.

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<sup>2</sup>Model HE-43/HE-73, D. L. Herring Co., Inc., Sherman Oaks, California.

Ethylaluminum dichloride (9) was prepared by refluxing a mixture of aluminum trichloride (8.7 g, 0.065 mole) and Et<sub>2</sub>AlCl (7.8 g, 0.065 mole). The purified material boiled at 54–55° C (1 mm Hg) and melted at 32° C.

Dimethylmercury and diethylmercury were prepared by reaction of an excess of alkylmagnesium bromide with mercuric chloride in ethyl ether (10).

#### Preparation of Reaction Intermediates

In order to understand the nature of the intermediates in the reactions of lithium hydride and alkylaluminum chlorides, the trimethylamine adducts of the alkylaluminum chlorides were prepared. Two methods led to the same products: (a) direct union of the reactants, and (b) their reaction in ethyl ether. In the presence of excess trimethylamine only the monoamine adducts were formed. The diethyl compound melted at -33 to  $-32^{\circ}$  C. Anal. Calc. for C<sub>7</sub>H<sub>19</sub>ClNA1: Cl, 19.74; Al, 15.02. Found: Cl, 20.23; Al, 15.52. Ethylaluminum dichloride trimethylamine melted at 50–52° C. Anal. Calc. for C<sub>5</sub>H<sub>14</sub>Cl<sub>2</sub>NA1: C, 32.27; H, 7.58; Cl, 38.11; N, 7.53; Al, 14.50. Found: C, 31.76; H, 7.74; Cl, 38.02; N, 7.58; Al, 14.04.

#### Preparation of Diethylaluminum Hydride Trimethylamine

#### Method A

Diethylaluminum chloride, 19.0 g (0.16 mole), was placed in 250 ml of diethyl ether in a three-necked, 500-ml flask equipped with reflux condenser and drying tube, N<sub>2</sub> gas inlet, and NMe<sub>3</sub> gas inlet. Excess trimethylamine was bubbled into the solution, which was kept at  $-20^{\circ}$  C for 1 hour. After the ether solution of Et<sub>2</sub>AlCl·NMe<sub>3</sub> had reached room temperature, 1.7 g of powdered 75% LiH (0.16 mole pure LiH) was added. The reaction mixture was then maintained at reflux temperature for 9 hours. The solids were allowed to settle overnight. The clear supernatant liquid was filtered into a distilling flask, and the ether was removed in vacuum. During the slow, high-vacuum distillation that followed, the distillation flask was kept at 40° and the receiving trap at  $-196^{\circ}$  C. A sample of the distillate redistilled at 63–65° C (1 mm Hg). The melting point was  $-28^{\circ}$  C. Methanolysis of a 0.2643 g sample gave the following results: calc. for H<sub>2</sub>: 40.8 ml at S.T.P., found: 39.6 ml; calc. for Al: 18.58%, found: 18.86%. The analytical data are summarized in Table III.

		$\mathbf{D} = \langle \mathbf{C} \rangle$		Anal. found			
Compound -	M.p. (°C)	(1 mm Hg)	Anal. calc.	А	В	С	D
Et <sub>2</sub> AlH · NMe <sub>3</sub>	-28	63-65	C, 57.89 H, 13.88 N, 9.65 Al. 18.58	57.92 13.70 9.62 18.34	$57.66 \\ 13.84 \\ 10.03 \\ 18.39$	$56.98 \\ 13.52 \\ -8.84 \\ 18.03$	
EtAlH <sub>2</sub> ·NMe <sub>3</sub>		39-40	C, 51.25 H, 13.76 N, 11.96 Al, 23.03	_ 10,101	$51.29 \\ 13.93 \\ 11.95 \\ 22.72$	51.18 14.06 11.94 22.73	$50.97 \\ 13.64 \\ 12.13 \\ 22.77$
Me₂AlH · NMe₃	33–35	42-43	C, 51.25 H, 13.76 N, 11.96 Al, 23.03		$51.43 \\ 13.60 \\ 11.83 \\ 22.77$	$51.50 \\ 12.97 \\ 12.10 \\ 23.20$	
MeAlH₂∙NMe₃	-35	25–26	C, 46.58 H, 13.68 N, 13.58 Al, 26.16		$\begin{array}{c} 46.26 \\ 13.67 \\ 13.30 \\ 25.83 \end{array}$	$\begin{array}{c} 47.04 \\ 12.88 \\ 13.77 \\ 26.66 \end{array}$	$\begin{array}{c} 46.71 \\ 13.61 \\ 13.59 \\ 26.03 \end{array}$

TABLE III

The ethylaluminum and methylaluminum hydride trimethylamine complexes

#### Method B

Aluminum hydride trimethylamine, 4.0 g (0.045 mole), was placed in a three-necked, 500-ml flask, and 250 ml of hexane was added. A hexane solution of diethylmercury, 11.6 g (0.045 mole), was added dropwise to the AlH<sub>3</sub> · NMe<sub>3</sub> with stirring and heating. A grey precipitate of mercury was visible after 10 minutes of reaction. The system was kept at 60° C for 4 hours and then permitted to stand for 5 days at room temperature. The supernatant liquid was filtered into a distilling flask, and the solvent was removed in vacuum. Purification of the residue by high-vacuum distillation produced a liquid that boiled at  $63-65^{\circ}$  C (1 mm Hg). Methanolysis of a 0.4363-g sample gave the following results: calc. for H<sub>2</sub>: 67.2 ml at S.T.P., found: 61.2 ml; calc. for Al: 18.58%, found: 19.19%.

#### Method C

Triethylaluminum trimethylamine, 4.0 g (0.023 mole), and 1.0 g (0.011 mole) of  $AlH_3 \cdot NMe_3$  were placed in a flask and heated with stirring for 30 minutes at 40°. Stirring was continued for 2 hours at room temperature. Distillation yielded a compound boiling at 63–64° C (1 mm Hg).

#### Preparation of Ethylaluminum Dihydride Trimethylamine

#### Method A

Several attempts to synthesize the ethylaluminum dihydride amine complex by using lithium hydride in ethyl ether were only partially successful. Although reduction took place, as indicated by the presence of an Al—H band in the infrared spectrum of the reaction mixture, no compound free of chlorine could be obtained.

#### Method B

The compound was prepared by Method B and gave the following hydrolytic results for a 0.4828-g sample: calc. for H<sub>2</sub>: 184.7 ml at S.T.P., found: 181.0 ml; calc. for Al: 23.03%, found: 22.93%.

#### Method C

The compound was also prepared by Method C given above.

#### Method D

A solution of 5.9 g (0.155 mole) LiAlH<sub>4</sub> in 300 ml of ether was prepared. To this was added dropwise 18.6 g (0.155 mole) of Et<sub>2</sub>AlCl in ether. White solids began to precipitate immediately. After the mixture had been refluxed for 20 minutes the solids were allowed to settle, the liquid was filtered into a flask, and the ether was removed in vacuum. A gelatinous material remained. A portion of the gelatinous residue was allowed to react with gaseous trimethylamine. The mixture became quite warm and liquefied while ether and some hydrogen were evolved. A grey solid, presumably metallic aluminum, also formed. When the reaction mixture was subjected to vacuum in a sublimation apparatus, a small amount of white solid collected on the cold finger. According to the melting point (88–92° C) it was  $AlH_3 \cdot 2NMe_3$  (7). Fractionation under vacuum of the liquid residue yielded  $EtAlH_2 \cdot NMe_3$  as well as some  $Et_2AlH \cdot NMe_3$  (the latter was identified by its infrared spectrum and boiling point).

## Preparation of Dimethylaluminum Hydride Trimethylamine

Dimethylaluminum hydride trimethylamine was prepared according to Methods B and C. It is interesting that dimethylaluminum chloride, following treatment with trimethylamine in ether solution, was found unreactive toward lithium hydride at 36° C.

#### Preparation of Methylaluminum Dihydride Trimethylamine

Successful preparation was effected by Methods B, C, and D. A variation of Method D, where the hydride was not isolated from solution prior to addition of trimethylamine, yielded only  $MeAlH_2 \cdot NMe_3$ . This behavior is in contrast to the corresponding ethyl reaction, where both the monohydride and dihydride were found among the reaction products.

## Analytical Results

The alkylaluminum hydride trimethylamine complexes were purified by vacuum distillation and were analyzed for the elements. The analytical results,<sup>3</sup> melting points,<sup>4</sup> and boiling points of the compounds are shown in Table III. The capital-letter designations under the column heading "Anal. found" refer to the methods of synthesis used.

#### Molecular Weights

Molecular weights were determined cryoscopically in an airtight glass apparatus fitted with a magnetically driven stirrer.<sup>5</sup> The alkylaluminum hydride trimethylamine solutions in cyclohexane were prepared in the dry box. Outside the dry box the charged airtight glass vessel was placed in the ice-cooled glass jacket of the cryoscopic molecular weight apparatus and the electromagnet that drives the stirrer was attached. The freezing point of pure solvent was determined immediately prior to each solution determination. The apparent molecular weights of the alkylaluminum hydride trimethylamine complexes are given in Table IV.

#### Spectral Data

A model IR-5 Beckman double-beam infrared spectrophotometer with sodium chloride optics was used to record spectra. A NaCl cell with a 0.001-in. lead spacer was used for the samples. The major absorptions in the infrared of the new alkylaluminum complexes are summarized in Table V.

Proton magnetic resonance spectra of the alkylaluminum hydride trimethylamine complexes in cyclohexane solution, tabulated in Table VI, were obtained at 60 Mc, using a Varian model V-4302 nuclear magnetic resonance spectrometer.

<sup>3</sup>Elemental analyses were conducted by the Schwarzkopf Microanalytical Laboratory, Woodside, New York. <sup>4</sup>Melting points are uncorrected and were determined by the capillary method or the Stock magnetic plunger technique, depending upon the physical state of the material at room temperature. <sup>5</sup>Bender and Hobein, G.m.b.H., Munich, Germany.

#### PETERS ET AL.: COMPLEXES

TABLE IV
Molecular weights of ethylaluminum and methylaluminum hydride trimethylamine
complexes*

Compound	Form. wt.	Molal concn.	Mol. wt.	Av. deg. of assoc.
$Et_2AlH \cdot NMe_3$	145.2	$\begin{array}{c} 0.053 \\ 0.063 \\ 0.072 \end{array}$	169 172 173	1.18
EtAlH <sub>2</sub> ·NMe <sub>3</sub>	117.2	$\begin{array}{c} 0.080 \\ 0.082 \\ 0.083 \end{array}$	187 189 186	1.60
Me₂AlH · NMe₃	117.2	$\begin{array}{c} 0.071 \\ 0.074 \\ 0.076 \\ 0.078 \end{array}$	$157 \\ 157 \\ 157 \\ 157 \\ 159$	1.34
MeAlH <sub>2</sub> ·NMe <sub>3</sub>	103.1	$\begin{array}{c} 0.091 \\ 0.105 \\ 0.110 \\ 0.118 \end{array}$	$204 \\198 \\199 \\203$	1.95

\*Molecular weight measurements were taken cryoscopically in cyclohexane.

## TABLE V

Major absorptions in the infrared spectra of the ethylaluminum and methylaluminum hydride trimethylamine complexes

- Compound	Absorption (cm <sup>-1</sup> )*†
Et₂AlH · NMe₃	2980 (sh, m); 2960 (sh, s); 2880 (vs); 2760 (m); 2700 (w); 1730 (vs); 1480, 1465 (d, vs); 1410 (m); 1370 (w); 1245, 1233 (d, m); 1190 (m); 1103 (m); 997 (vs, b, u); 950 (m); 918 (m); 897 (m); 818 (s); 770 (vs, b)
$EtAlH_2 \cdot NMe_3$	2970 (s); 2900 (vs); 2880 (m); 2710 (w); 1750 (vs, b); 1487, 1470 (d, vs); 1410 (s); 1370 (w); 1250 (s); 1190 (m); 1107 (s); 1000 (vs, b); 952 (s); 920 (s); -898 (s, b); 822 (vs)
Me <sub>2</sub> AlH·NMe <sub>3</sub>	$\begin{array}{l} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array} \\ & 3000 \ (\text{sh, s}); \ 2970 \ (\text{s}); \ 2900 \ (\text{vs}); \ 2800 \ (\text{sh, s}); \ 1750 \ (\text{vs}); \ 1480, \ 1470 \ (\text{d, vs}); \ 1410 \\ (\text{m}); \ 1250 \ (\text{s}); \ 1190 \ (\text{vs}); \ 1108 \ (\text{s}); \ 1002 \ (\text{vs}); \ 823 \ (\text{s}) \end{array}$
MeAlH <sub>2</sub> ·NMe <sub>3</sub>	2970 (ms); 2900 (s); 1750 (vs); 1480, 1470 (d, vs); 1410 (m); 1250 (ms); 1192 (ms); 1108 (m); 1002 (vs); 823 (m)
*Spectra were calibr	ated against the standard spectrum of polystyrene

Spectra weak, m = medium, s = strong, v = very, sh = shoulder, d = doublet, b = broad, u = unsymmetrical.

Nuclear magnetic resonance spectra of the ethylaluminum and methylaluminum hydride trimethylamine complexes\*

TABLE VI

	δ†			
Compound	Н	N—CH <sub>3</sub>	CH3	CH <sub>2</sub>
Et <sub>2</sub> AlH · NMe <sub>3</sub> EtAlH <sub>2</sub> · NMe <sub>3</sub> Me <sub>2</sub> AlH · NMe <sub>3</sub> MeAlH <sub>2</sub> · NMe <sub>3</sub>	-2.10 -2.10 -2.10	$-0.94 \\ -1.04 \\ -0.95 \\ -1.02$	$0.35 \\ 0.47 \\ 2.27, 2.32 \\ 2.24, 2.34 \\ 8$	$\begin{array}{c}1.59\\1.64\end{array}$

\*Cyclohexane, as the standard, is arbitrarily given the value of  $\delta = 0$ . Solutions are approximately 10% by weight. † $\delta$  (the chemical shift) =  $[(Hr-H)/Hr] \times 10^6$ . ‡Not observed. \$Doublet. [Some splitting observed.

#### CANADIAN JOURNAL OF CHEMISTRY. VOL. 41, 1963

#### DISCUSSION

## Synthetic Methods

The reduction of  $Et_2AlCl \cdot NMe_3$  to  $Et_2AlH \cdot NMe_3$  with lithium hydride was found to be more sluggish than the corresponding reaction using  $Et_2AlCl$ -etherate (3). Approximately half the calculated amount of hydride was collected after 9 hours of refluxing of the reactants in ether solution. Times up to 24 hours were used to attempt the lithium hydride conversion of  $EtAlCl_2 \cdot NMe_3$  to  $EtAlH_2 \cdot NMe_3$ . Partial conversion was attained in numerous instances; a strong Al—H absorption repeatedly appeared in the infrared spectra of the ether-soluble fractions of the reaction mixtures. The pure dihydride, free of chlorine, was never obtained, however. In contrast to the diethyl compound, dimethylaluminum chloride trimethylamine did not react with lithium hydride in refluxing ether. Consequently, reduction of methylaluminum dichloride trimethylamine was not attempted.

Replacement of the hydrogen atoms in  $AlH_3 \cdot NMe_3$  and  $LiAlH_4$  by alkylmercury and arylmercury compounds has been shown to be a general reaction. A mechanism for the reaction has been proposed (11,12). Divinylmercury (13) and bisperfluorovinylmercury (14) react analogously with aluminum hydride trimethylamine, the latter reaction being violent at room temperature in ethyl ether. The partial substitution of alkyl groups for hydrogen on  $AlH_3 \cdot NMe_3$  was accomplished by carefully controlling the stoichiometry of the reactants. Diethylmercury was found slightly more reactive towards  $AlH_3 \cdot NMe_3$  than dimethylmercury. Hexane was found to be a better reaction medium than ether, even though the  $AlH_3 \cdot NMe_3$  is insoluble in hexane, because a higher reaction temperature could be employed. A temperature of 60° C for several hours was usually required to complete the reaction. The yields of products were high since the evolution of hydrogen and the precipitation of mercury cause the equilibrium to shift continually to the right.

The mixing of stoichiometric quantities of  $R_3Al \cdot NMe_3$  and  $AlH_3 \cdot NMe_3$  has led to nearly quantitative yields of the alkylaluminum hydride compounds. Nuclear magnetic resonance spectra, boiling points, and cryoscopic molecular weight determinations have indicated that single compounds are formed in each case and not equilibrium mixtures containing the reactants.

Whereas reaction of Groups I and II metal alkyls with lithium aluminum hydride leads to the formation of the corresponding metal hydrides (15), the trialkyls of boron, aluminum, and gallium react according to the equation (2)

## $LiAlH_4 + R_3M \rightarrow R_2AlH + LiMRH_3.$

It must be pointed out, however, that the reactions of Groups I and II metal alkyls with lithium aluminum hydride were carried out in diethyl ether whereas those of Group III were accomplished in the absence of solvent. To check the possibility of further exchange in the reaction of trialkylaluminum and lithium aluminum hydride, the reaction was conducted in diethyl ether using a 3:1 molar ratio of LiAlH<sub>4</sub> to Me<sub>3</sub>Al. The product was first isolated as the etherate, and was subsequently treated with trimethylamine for easy identification. Only the monohydride was found, indicating that  $R_2AlH$  is the reaction product in the absence of or in the presence of diethyl ether. Thus, the formation of the alkylaluminum dihydride trimethylamine complexes by reaction of lithium aluminum hydride and dialkylaluminum halide with subsequent addition of trimethylamine may proceed by the following route:

$$LiAlH_4 + R_2AlX \xrightarrow{Et_2O} R_2AlH + [LiAlH_3X]$$

 $LiX + AlH_3$ 

## $AlH_3 + R_2AlH \rightarrow 2RAlH_2 \xrightarrow{NMe_3} 2RAlH_2 \cdot NMe_3.$

In the case of R = methyl, the reaction product is all MeAlH<sub>2</sub>·NMe<sub>3</sub>. The corresponding reaction where R = ethyl yields a mixture of EtAlH<sub>2</sub>·NMe<sub>3</sub>, Et<sub>2</sub>AlH·NMe<sub>3</sub>, and AlH<sub>3</sub>·2NMe<sub>3</sub>, possibly indicating that the combination of AlH<sub>3</sub> and Et<sub>2</sub>AlH did not proceed to completion before trimethylamine was introduced into the system. Since excess trimethylamine was used, the very stable AlH<sub>3</sub>·2NMe<sub>3</sub> was formed. This compound does not appear to react with either R<sub>3</sub>Al·NMe<sub>3</sub> or R<sub>2</sub>AlH·NMe<sub>3</sub>.

#### Physical Properties

At room temperature the ethylaluminum and the monomethylaluminum hydride trimethylamine complexes are mobile liquids that can be distilled without disproportionation or dissociation under high vacuum. The dimethylaluminum complex is a lowmelting solid which sublimes readily under vacuum at room temperature without change. However, the evolution of trimethylamine from each of the complexes was observed during the attempt to obtain their mass spectra at a pressure of  $10^{-7}$  mm Hg. The complexes appear to be unstable at temperatures above 80° C.

The molecular weight determinations show that the methylaluminum and ethylaluminum hydride trimethylamine complexes are associated in cyclohexane. The degree of association appears to be a function of the number and the size of the alkyl groups attached to aluminum (Table IV). Thus, steric hindrance seems to offset the tendency for aluminum to increase its coordination number to 5 by using 3d orbitals in its hybridization. If the association is occurring by way of hydrogen bridges, then the hybridization of pentacoordinated aluminum must be considered. If two symmetrical bipyramids are joined on an edge by two hydrogen atoms, each aluminum atom will exhibit the  $sp^3d$ state. However, according to the estimate of the Al-H bridge distance in the aluminum hydride trimethylamine dimer by Ruff and Hawthorne (16), the Al-Al bond distance will be less than twice the normal covalent radius of aluminum in the  $s\rho^3 d$  structure. Gillespie (17) has proposed an  $sp^3spd$  hybridization for the carbon atom which utilizes three normal  $sp^3$  orbitals and two equivalent spd orbitals which are formed from the remaining  $sp^3$  orbital and a 3d orbital. Ruff and Hawthorne find that a reasonable Al—Al bond distance can be calculated from the  $sp^3spd$  interpretation of the aluminum atom and their estimated Al—H bridge distance. A similar interpretation appears reasonable in the case of the analogous alkyl dimers. If the double hydrogen bridge is considered to be rigid, several isomers of each compound in the dimeric state are expected. The resulting nonequivalent alkyl groups may contribute to the methyl and methylene splitting observed in the nuclear magnetic resonance spectra of the alkylaluminum hydride amines (Table VI).<sup>6</sup> It must be pointed out, however, that a number of species may be present in a solution of each of the compounds in cyclohexane, since cryoscopy gives only an average molecular weight value of the species under consideration. Hence, the existence of the dimer is only postulated. The phenomenon of association may even be the result

<sup>6</sup>A referee has suggested that the splitting observed may be explained in terms of an alternate structure for the dimer which involves bridging methyl or ethyl groups. Low-temperature n.m.r. studies will be required to determine the cause of the splitting.

## CANADIAN JOURNAL OF CHEMISTRY. VOL. 41, 1963

of dipole-dipole interactions rather than hydrogen bridging. Further studies are required to elucidate the structures and the modes of association in these electron-deficient aluminum compounds.

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#### REFERENCES

- REFERENCES
  1. O. STECKER and E. WIBERG. Chem. Ber. 75, 2003 (1942).
  2. T. WARTIK and H. I. SCHLESINGER. J. Am. Chem. Soc. 75, 835 (1953).
  3. K. ZIEGLER, H. GELLERT, H. MARTIN, K. NAGEL, and T. SCHNEIDER. Ann. Chem. 589, 91 (1954).
  4. K. ZIEGLER, K. SCHNEIDER, and J. SCHNEIDER. Ann. Chem. 623, 9 (1959).
  5. F. M. PETERS and B. BARTOCHA. Chem. Ind. (London), 1271 (1961).
  6. A. B. BURG and H. I. SCHLESINGER. J. Am. Chem. Soc. 59, 780 (1937).
  7. E. WIBERG, H. GRAF, and R. USÓN. Z. Anorg. Allgem. Chem. 272, 221 (1953).
  8. N. DAVIDSON and H. C. BROWN. J. Am. Chem. Soc. 64, 316 (1942).
  9. A. VON GROSSE and J. M. MAVITY. J. Org. Chem. 5, 106 (1940).
  10. H. GILMAN and R. E. BROWN. J. Am. Chem. Soc. 52, 3314 (1930).
  11. T. G. TRAVLOR. Chem. Ind. (London), 1223 (1959).
  12. J. K. RUFF. J. Am. Chem. Soc. 83, 1798 (1961).
  13. B. BARTOCHA, A. J. BILBO, and M. Y. GRAY. Angew. Chem. 72, 36 (1960).
  14. B. BARTOCHA and A. J. BILBO. J. Am. Chem. Soc. 83, 2202 (1961).
  15. G. D. BARBARAS, C. DILLARD, A. E. FINHOLT, T. WARTIK, K. E. WILZBACH, and H. I. SCHLESINGER. J. Am. Chem. Soc. 73, 4585 (1951).
  16. J. K. RUFF and M. F. HAWTHORNE. J. Am. Chem. Soc. 82, 2141 (1960).
  17. R. J. GILLESPIE. J. Chem. Soc. 1002 (1952).
- 16. J. K. RUFF and M. F. HAWTHORNE. J. Am. Chem. Soc. 82, 2141 (1960). 17. R. J. GILLESPIE. J. Chem. Soc. 1002 (1952).