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SURVEY OF TRIMETHYLALUMINUM-HYDRAZINE COMPLEXES

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FOREWORD

Synthesis of the methylhydrazine complexes of trimethylaluminum was performed at the Naval Ordnance Laboratory Corona to extend knowledge of the chemistry of trialkylaluminum complexes of nitrogen-containing Lewis bases. The experiments, which were started in July 1960 and completed in January 1961, were performed as part of the ARPA Solid-Propellant Research Program under WepTask RMMP-7A 032/211 7/F009-06-001.

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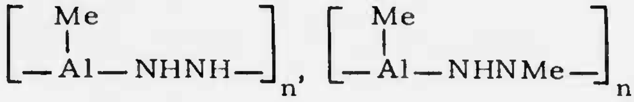
ABSTRACT

The complexing of trimethylaluminum and trimethylaluminum trimethylamine with hydrazine, methylhydrazine, 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, trimethylhydrazine, and tetramethylhydrazine has been carried out by means of two general reactions:

$$R_3Al + H_2NNR'_2 \longrightarrow R_3Al{:}NH_2NR'_2 \tag{1}$$

$$R_3Al{:}NH_2NR'_2 \longrightarrow R_2Al\text{—}NHNR'_2 + RH \tag{2}$$

The following complexes and polymers have been characterized:



$$\left[\text{—}\overset{\displaystyle Me}{\overset{|}{Al}}\text{—}NHNH\text{—}\right]_n, \left[\text{—}\overset{\displaystyle Me}{\overset{|}{Al}}\text{—}NHNMe\text{—}\right]_n,$$

$[Me_2Al\text{—}NHNMe_2]_2$,

$Me_2Al(NHNMe_2)(NH_2NMe_2)$, $[\text{—}Al(\text{—}NMeNMe\text{--})_{1.5}]_n$,

$Me_3Al{:}NHMeNMe_2$, $[Me_2Al\text{—}NMeNMe_2]_2$, and $Me_3Al{:}NMe_2NMe_2$

Elemental analyses, quantitative gas measurements, and infrared spectra are presented as supporting evidence for the formulas given above.

ACKNOWLEDGMENT

Several of the hydrazines used in this study were supplied by Dr. William R. McBride of the U. S. Naval Ordnance Test Station, China Lake, California. The authors also wish to thank Dr. Frederick E. Brinckman and Dr. Charles P. Haber of NOLC for their assistance in the conduct of this work.

INTRODUCTION

Until recently, only a few molecular addition compounds of aluminum ligands of Group V had been reported.[1] In some of the earliest work, Davidson and Brown[2] described methylaluminum-methylamine complexes. Later, Wiberg and May[3] reported some reactions of aluminum hydride with amines and ammonia, an area recently extended by Ruff and Hawthorne.[4, 5] Bonitz[6] isolated a triethylaluminum isoquinoline complex; and Ziegler, Gellert, and Neumann[7] based some analytical procedures on the reaction of alkylaluminum hydrides with amines. The compound diethylaluminum-dimethylamine was reported in the patent literature,[8] and a note on a new aluminum hydride adduct was presented by Davidson and Wartik.[9]

Most of the compounds described in the referenced publications contain a covalent aluminum-nitrogen bond which is formed by one of two general reactions:

1. Elimination of a hydrocarbon when an aluminumtrialkyl reacts with a secondary or primary amine:

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[1] F. G. A. Stone, Chem Revs., Vol. 58, p. 101 (1958).

[2] N. Davidson and H. C. Brown, J. Am. Chem. Soc., Vol. 64, p. 316 (1942).

[3] E. Wiberg and A. May, Z. Naturforschg., Vol. 10b, p. 232 and p. 234 (1955).

[4] J. K. Ruff and M. F. Hawthorne, J. Am. Chem. Soc., Vol. 82, p. 2141 (1960).

[5] J. K. Ruff and M. F. Hawthorne, J. Am. Chem. Soc., Vol. 83, p. 535 (1961).

[6] E. Bonitz, Ber., Vol. 88, p. 742 (1955).

[7] K. Ziegler and H. G. Gellert, Ann., Vol. 629, p. 20 (1960); and W. P. Neumann, Ann., Vol. 629, p. 23 (1960).

[8] K. Ziegler, British Patent 799,823, 13 August 1958.

[9] J. M. Davidson and T. Wartik, J. Am. Chem. Soc., Vol. 82, p. 5506 (1960).

$$R_3Al + NHR'_2 \longrightarrow [R_3Al{:}NHR'_2] \longrightarrow R_2Al-NR'_2 + RH$$

2. Elimination of hydrogen when an alkylaluminum hydride or an aluminum hydride reacts with ammonia, a primary amine, or a secondary amine:

$$R_2AlH + NH_3 \longrightarrow [R_2AlH{:}NH_3] \xrightarrow{\Delta} R_2Al-NH_2 + H_2$$

$$R_2AlH + NHR'_2 \longrightarrow [R_2AlH{:}NHR'_2] \xrightarrow{\Delta} R_2Al-NR'_2 + H_2$$

In both cases a stable covalent bond is formed via an intermediate with a dative bond, and in several instances the materials seems to react further to form polymeric substances, according to Laubengayer, Smith, and Ehrlich.[10]

The interactions of hydrazines with aluminum alkyls were of interest to this Laboratory, particularly those hydrazines with both N-H and N-C bonds. This report describes the reactions of trimethylaluminum and trimethylaluminum-trimethylamine with methylhydrazines.

EXPERIMENTAL DETAILS

APPARATUS

Most of the work described in this report was carried out in a conventional high-vacuum system.

The hydrazine was vacuum-distilled onto the frozen pentane solution of trimethylaluminum or trimethylaluminum trimethylamine by means of a two-armed adapter attached to a standard vacuum transfer line and fitted with 50-ml flasks. The resulting mixture was allowed to warm to room temperature, and the gas that evolved was expanded into the vacuum line. At the end of the reaction, the methane and trimethylamine were pumped into the calibrated portion of the system and the solvent was distilled off. The crude product was then sublimed, if possible. If no solvent was used, the crude material was transferred directly to the sublimation apparatus. In the few cases where preparations were not made on the vacuum line, the trimethylaluminum and solvent were placed in a 300-ml, one-necked, round-bottomed flask.

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[10] A. W. Laubengayer, J. D. Smith, and G. G. Ehrlich, J. Am. Chem. Soc., Vol. 83, p. 542 (1961).

In a typical experiment, approximately 1.5 grams of trimethylaluminum, 100 ml of pentane, and a magnetic stirring bar were introduced into the flask in the dry box. A pressure-equalizing dropping funnel with the appropriate hydrazine was placed in the neck of the flask, and the whole apparatus removed from the dry box. The reaction vessel was then placed in a cold bath, and the hydrazine was added dropwise with stirring. Any gas generated during the reaction was vented through a drying tube at the top of the dropping funnel.

In one case, the product obtained was a liquid at room temperature, but it sublimed very readily, so the special sublimation apparatus shown in Figure 1 was used. The cold finger is maintained at about -30°C, and the side arm flask contains the crude product. When the apparatus is evacuated the material sublimes onto the cold finger, and when the process is complete the pure product is allowed to melt and drop into the flask below.

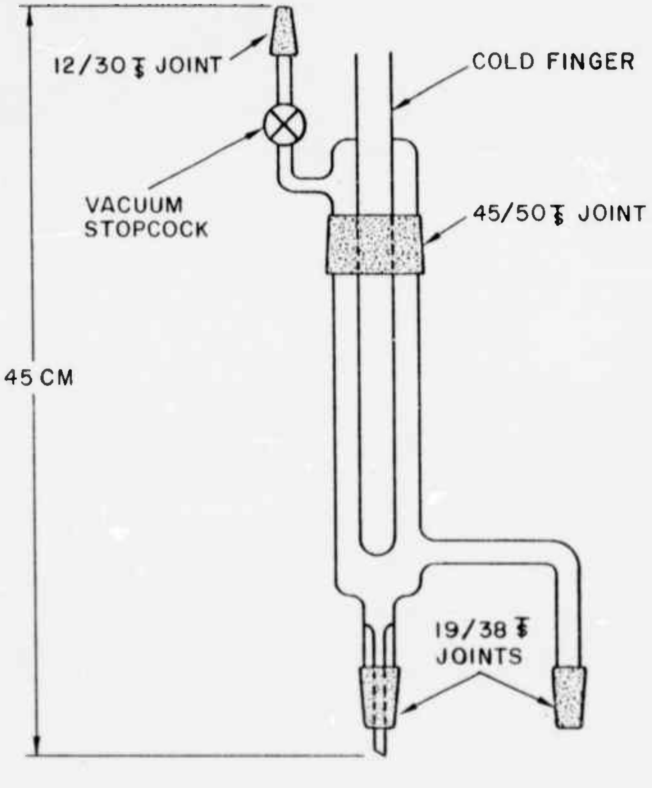

FIGURE 1. Special Sublimation Apparatus

REAGENTS

The trimethylaluminum used was purchased from the Ethyl Corporation of Baton Rouge, La., and vacuum-distilled before use. The trimethylaluminum trimethylamine[2] was prepared in this laboratory by the following method. Trimethylamine in excess of the 1:1 ratio required was condensed onto trimethylaluminum and pentane at -196 °C. The mixture was allowed to warm slowly to room temperature, the excess trimethylamine and solvent were then removed in vacuum, and the remaining crude trimethylaluminum trimethylamine was vacuum-sublimed at 50-55 °C. Its elemental analysis checked very well with the theoretical values.

Hydrazine (95%, Fairmount Chemical Co.), methylhydrazine (Commercial Solvents Corp.), 1, 1-dimethylhydrazine (Olin Matheson Corp.), 1, 2-dimethylhydrazine (Metalectro Corp.), and tetramethylhydrazine (Metalectro Corp.) were distilled from calcium hydride before use. The trimethylhydrazine was prepared by the method of Class, Aston, and Oakwood.[11] All solvents were of reagent grade quality and were distilled from calcium hydride before use.

MOLECULAR WEIGHTS

Molecular weights of the products were measured in cyclohexane with a standard freezing point apparatus shown in Figure 2. This device was fitted with an electrical stirring motor for use in a dry box.

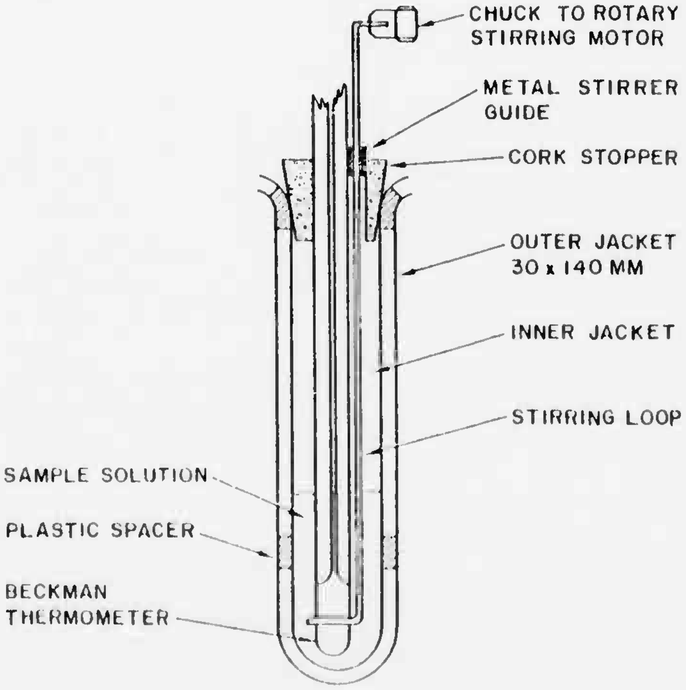

FIGURE 2. Molecular Weight Apparatus

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[11] J. B. Class, J. G. Aston, and T. S. Oakwood, J. Am. Chem. Soc., Vol. 75, p. 2937 (1953).

METHANE AND ALUMINUM ASSAY

Approximately 0.5 gram of each sublimed sample was hydrolyzed on the vacuum system with methanol. The methane evolved was pumped through a -196°C trap into the calibrated part of the vacuum line. The hydrolyzed material was treated with water and dilute hydrochloric acid until the solid dissolved, then transferred to a beaker and made basic to litmus with dilute ammonia. The precipitate was filtered and then converted to aluminum oxide in the standard manner for aluminum determinations.

PURIFICATION

Most of the nonpolymeric materials were purified by vacuum sublimation at a temperature range between 50 and 60°C. The apparatus has a path of about 45 mm and the cold surface was kept at -15°C except when the special sublimation apparatus described above was used. The polymeric materials could not be sublimed, nor were they soluble in solvents that did not react with them; they were, therefore, not purified after removal of the solvents and excess hydrazine.

INFRARED SPECTRA

The infrared spectra were made on a Beckman IR-5 spectrophotometer. A sodium chloride cell with a 0.0025 mm lead spacer was employed, and solid materials were suspended in Nujol.

RESULTS

Me_3Al AND HYDRAZINE

Attempts to prepare a complex on the vacuum line proved unsuccessful because of the high melting point of hydrazine. Since an explosion occurred whenever the hydrazine thawed, the alternate technique of running the experiment at atmospheric pressure had to be employed.

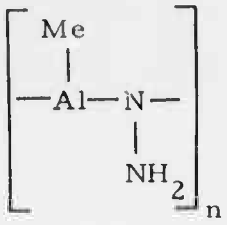
A white, fluffy solid was obtained after removal of the pentane solvent. Two preparations were made and an elemental analysis was performed for each product. The results are given below:

Calcd. for CH_5N_2Al: C, 16.44; H, 8.28; N, 38.36; Al, 36.93.

Found (Prep. 1): C, 18.05; H, 7.77; N, 34.62; Al, 32.25.

Found (Prep. 2): C, 24.03; H, 9.14; N, 27.91; Al, 33.48.

These data suggest a polymeric structure with the following formula:

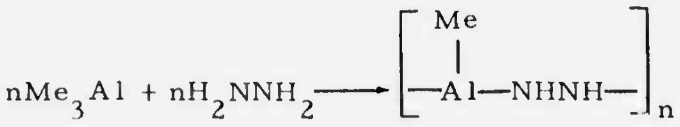


$$\left[-\overset{Me}{\overset{|}{Al}}-\underset{\underset{NH_2}{|}}{N}-\right]_n$$

and/or

$$\left[-\overset{Me}{\overset{|}{Al}}NHNH-\right]_n$$

Hydrolysis of 0.4270 gram of the product from Preparation 1 yielded 0.0993 gram of methane. Based on the formula above, this amount of methane corresponds to a molar ratio of methane to compound of 1.04. The infrared spectrum shown in Figure 3 has a N-H absorption at 3.08 μ. The reaction may be written:



$$nMe_3Al + nH_2NNH_2 \longrightarrow \left[-\overset{Me}{\overset{|}{Al}}-NHNH-\right]_n$$

$Me_3Al:NMe_3$ AND HYDRAZINE

One attempt was made to prepare a complex of $Me_3Al:NMe_3$ and hydrazine using the vacuum technique, but the mixture exploded; and no attempt has been made using the atmospheric method.

Me_3Al AND METHYLHYDRAZINE

As with hydrazine, the vacuum method produced only explosions when methylhydrazine was allowed to react with Me_3Al. However, the alternate procedure of carrying out the reaction of trimethylaluminum with methylhydrazine at atmospheric pressure was successful, and a powdery white solid was obtained after the pentane had been removed in vacuum. An elemental analysis gave the following results:

Calcd. for $C_2H_7N_2Al$: C, 27.90; H, 8.19; N, 32.55[12]; Al, 31.35.
Found: C, 28.18; H, 8.05; N, 30.37; Al, 30.40.

From the empirical formula for $C_2H_7N_2Al$ two structures can be written:

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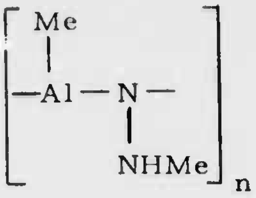
[12] Low nitrogen analyses seem characteristic of the polymeric trimethylaluminum-hydrazine materials. No explanation for this phenomenon has been found as yet.

$$\left[\begin{array}{l}\mathrm{Me}\\ \mid\\ -\mathrm{Al}-\mathrm{NHNMe}-\end{array}\right]_n$$

and

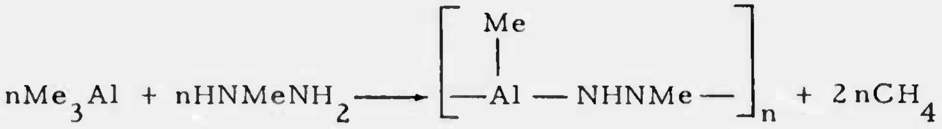


$$\left[\begin{array}{l}\mathrm{Me}\\ \mid\\ -\mathrm{Al}-\mathrm{N}-\\ \qquad\quad \mid\\ \qquad\ \mathrm{NHMe}\end{array}\right]_n$$

(I) (II)

The product was assumed to be a polymer, and, like the hydrazine polymer, it was not soluble in hydrocarbons and a molecular weight determination could not be made. The material did not have a sharp melting point, but it decomposed slowly on heating to 200°C and could not be sublimed.

Hydrolysis of 0.723 gram of the product with methanol produced 0.089 gram of methane, which, assuming the formula above, corresponds to a molar ratio of methane to product of 0.785. The infrared spectrum (Figure 4) of the polymer showed a N-H absorption at 3.10 μ, but no NH_2 absorption at 6.2 μ. The reaction may be written thus:



$$n\mathrm{Me_3Al} + n\mathrm{HNMeNH_2} \longrightarrow \left[\begin{array}{l}\mathrm{Me}\\ \mid\\ -\mathrm{Al}-\mathrm{NHNMe}-\end{array}\right]_n + 2n\mathrm{CH_4}$$

$Me_3Al:NMe_3$ AND METHYLHYDRAZINE

The reaction of $Me_3Al:NMe_3$ with methylhydrazine was also carried out in pentane at atmospheric pressure because an attempt to use the vacuum technique resulted in an explosion. The product looked exactly like the one obtained from Me_3Al and methylhydrazine, and the infrared spectra of the two materials were essentially the same. An aluminum assay of the crude product gave 30.55% (calcd. 31.35%), and a methane measurement resulted in a molar ratio of methane to compound I or II of 0.775. From this evidence it seems certain that the two materials are identical.

Me_3Al AND 1,1-DIMETHYLHYDRAZINE

The reaction of Me_3Al with 1,1-dimethylhydrazine may be carried out in pentane or without a solvent. The latter method is preferable because the reaction mixture can be sublimed directly without the trouble of removing the pentane. In a typical experiment, 0.680 gram (9.45 mmoles) of Me_3Al reacted with 0.632 gram (10.5 mmoles) of 1,1-dimethylhydrazine. Methane was evolved and 0.143 gram (8.95 mmoles)

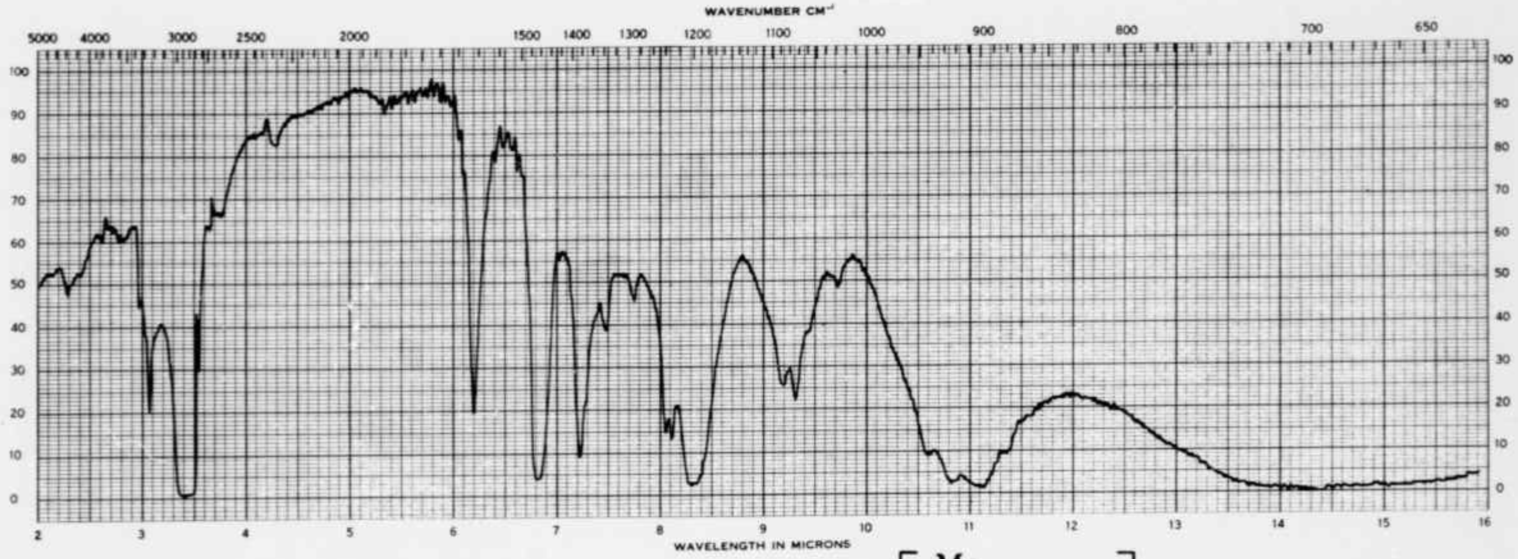


FIGURE 3. Infrared Spectrum of $\left[-\overset{\text{Me}}{\overset{|}{\text{Al}}}-\text{NHNH}-\right]_n$

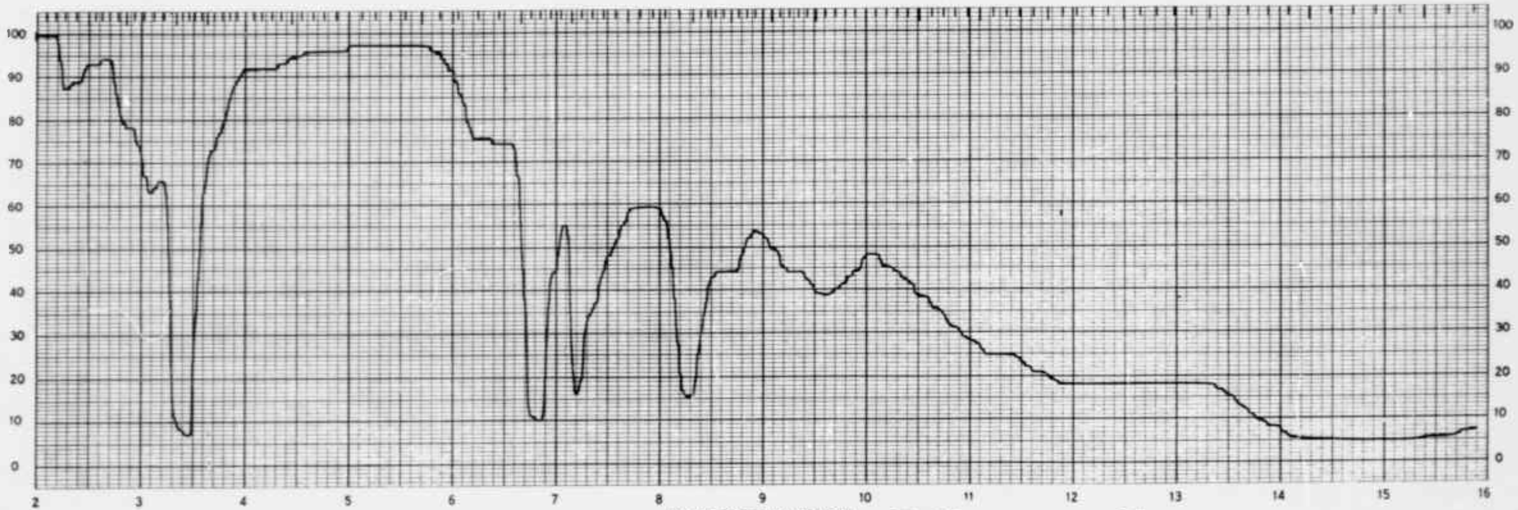


FIGURE 4. Infrared Spectrum of $\left[-\overset{\text{Me}}{\overset{|}{\text{Al}}}-\text{NHNMe}-\right]_n$

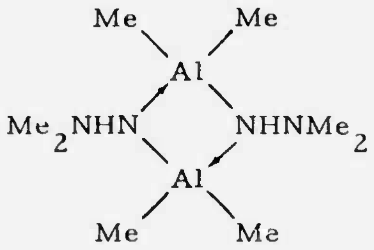
was recovered, which represented a molar ratio of methane to Me_3Al of 0.945. After one sublimation of the white crystalline product, the following elemental analysis was obtained:

Calcd. for $C_4H_{13}N_2Al$: C, 41.36; H, 11.28; N, 24.13; Al, 23.23.
Found: C, 41.12; H, 11.04; N, 24.21; Al, 23.82.

The melting point of the sublimed product was 77-78.5°C,[13] and its infrared spectrum is shown in Figure 5. There was an absorption at 3.17 μ for the N-H bond, but none at 6.2 μ for the NH_2 group.

Two molecular weight determinations gave the values 238 and 240 for the compound.

From the above data, it appears certain that the complex has the structural formula $Me_2AlNHNMe_2$ and that it is a dimer with a molecular weight of 232.3. This dimer probably has the configuration shown below:



$Me_3Al:NMe_3$ AND 1,1-DIMETHYLHYDRAZINE

The reaction of $Me_3Al:NMe_3$ with 1,1-dimethylhydrazine produced a compound different from the one obtained with the uncomplexed Me_3Al.

From the reaction mixture of 1.36 grams (10.4 mmoles) of $Me_3Al:NMe_3$ and 1.62 grams (27.1 mmoles) of 1,1-dimethylhydrazine, 0.142 gram (8.86 mmoles) of methane and 0.451 gram (7.75 mmoles) of trimethylamine were recovered. Since the reaction required no solvent, the crude material was sublimed directly to yield a white crystalline solid (m.p. 81-82°C). Elemental analysis of this product gave the following results:

Calcd. for $C_6H_{21}N_4Al$: C, 40.89; H, 12.01; N, 31.78; Al, 15.30.
Found: C, 40.60; H, 11.77; N, 31.58; Al, 15.95.

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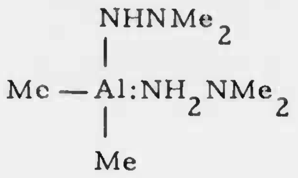
[13] All melting points reported are uncorrected.

The structural formula corresponds to that for a 2:1 complex of the hydrazine and trimethylaluminum:



$$\mathrm{Me-\overset{\overset{\displaystyle NHNMe_2}{|}}{\underset{\underset{\displaystyle Me}{|}}{Al}}:NH_2NMe_2}$$

A molecular weight determination in cyclohexane y[illegible] the value 178.7 (calcd. 176.1). Hydrolysis of 0.275 gram (2.08 mmoles) of the product with methanol produced 0.068 gram of methane (4.28 mmoles), thus giving the expected 2:1 molar ratio of methane to compound. The infrared spectrum of this complex is shown in Figure 6. One notable feature of this spectrum is that a small peak appears at 3.07 μ for the N-H bond, but there is not a peak at 6.2 μ for the NH_2 group as expected from the structure given above, despite the analytical and hydrolytical evidence for this compound.

Me_3Al, $Me_3Al:NMe_3$, AND 1,2-DIMETHYLHYDRAZINE

Five attempts were made with Me_3Al and $Me_3Al:NMe_3$ to prepare a compound with 1,2-dimethylhydrazine, but only one produced a material that could be characterized. All the other experiments yielded clear viscous polymeric materials of indefinite composition. The only difference in procedure was an extended reaction time in the one successful run.

A mixture of 0.812 gram (6.20 mmoles) of $Me_3Al:NMe_3$ and 0.530 gram (8.83 mmoles) of 1,2-dimethylhydrazine was allowed to stand at room temperature overnight. The reaction produced 0.293 gram of CH_4 (18.3 mmoles), 0.427 gram of NMe_3 (5.77 mmoles), and a powdery white solid. Elemental analysis of the solid gave the following results:

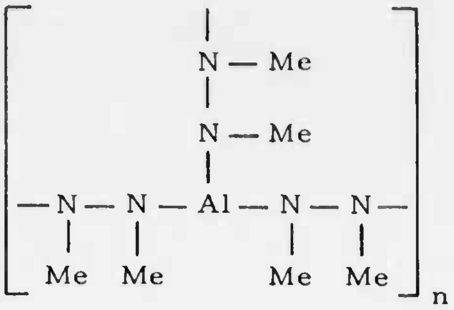
Calcd. for $C_3H_9N_3Al$: C, 31.58; H, 7.94; Al, 23.65.
Found: C, 30.34; H, 7.94; Al, 24.09.

As expected, hydrolysis of the product with methanol yielded no methane.

From the above data, it appears that the following reaction takes place if the reaction mixture is allowed to stand long enough:

$$\mathrm{nMe_3Al:NMe_3 + 1.5\,nHNMeNMeH \longrightarrow \left[Al(NMeNMe)_{1.5}\right]_n + 3\,nCH_4 + nNMe_3}$$

The product is a completely cross-linked polymer of the structure



with each aluminum atom sharing one half of three [—NMe—NMe—] units. The other glassy materials obtained appear to be incompletely polymerized. The infrared spectrum (Figure 7) has only a very small peak at 3.07 μ, which gives more evidence for the formula written above. No monomeric intermediate could be isolated under the conditions employed, but there is a possibility that one does exist, and an attempt may be made to isolate it in future experiments.

Although the solid polymer was not soluble in hydrocarbon solvents, the viscous fluids could be dissolved, and an estimate of the molecular weight of one sample was made. A value of 630 was found in the determination.

Me_3Al AND TRIMETHYLHYDRAZINE

In all the reactions discussed previously, the elimination of methane accompanied the complex formation, but in the following reaction it was possible to isolate the adduct intermediate before the methane was evolved. In fact, the intermediate appears to fairly stable, and heating at 60°C for about 20 hours is required to form the calculated quantity of methane.

In a typical example, 3.54 grams (49.1 mmoles) of Me_3Al and 9.62 grams (130 mmoles) of trimethylhydrazine reacted in pentane to produce a clear liquid material after the solvent and excess trimethylhydrazine were removed by vacuum. A sublimation at room temperature produced a crystalline solid (m.p. 80-83°C) from which the following elemental analysis was made:

Calcd. for $Me_3Al{:}NHMeNMe_2$: C, 49.29; H, 13.10; N, 19.16; Al, 18.45.
Found: C, 51.14; H, 12.60; N, 18.92; Al, 18.58.

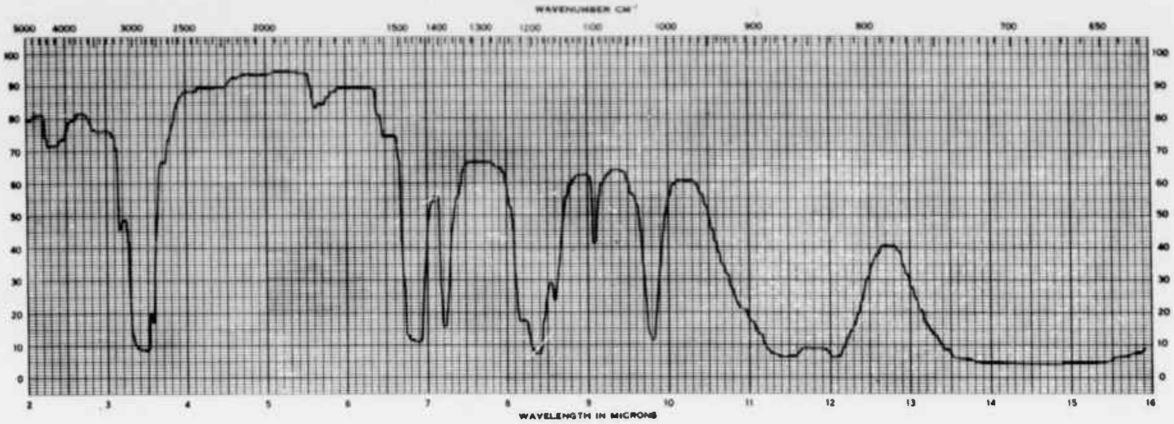


FIGURE 5. Infrared Spectrum of $\left[Me_2Al{-}NHNMe_2\right]_2$

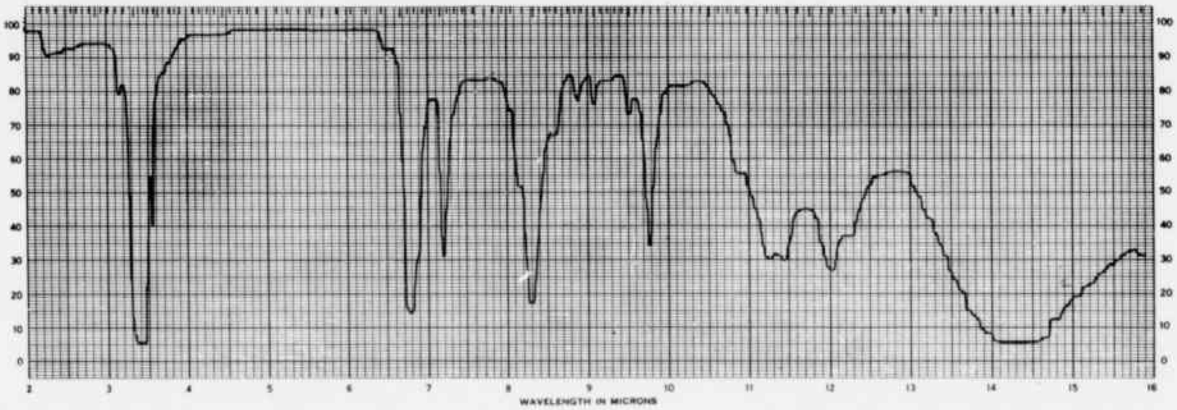


FIGURE 6. Infrared Spectrum of $Me_2Al(NHNMe_2)(NH_2NMe_2)$

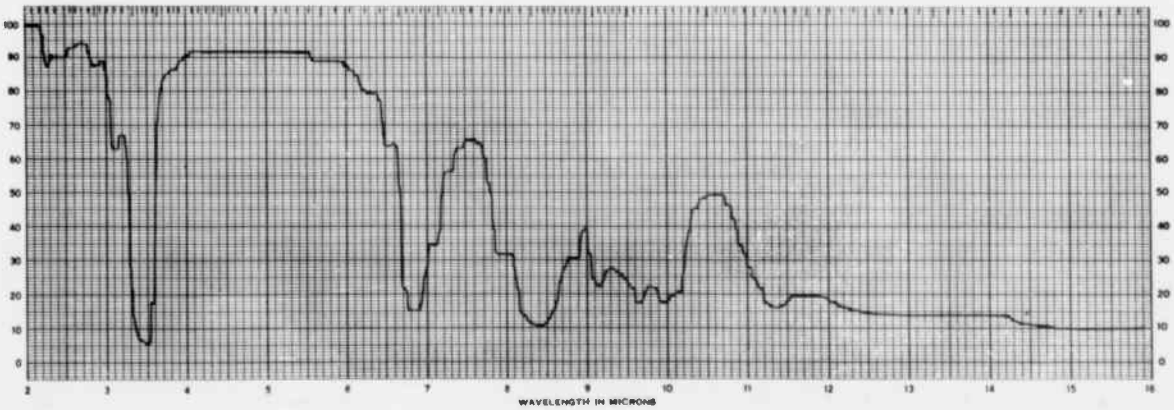


FIGURE 7. Infrared Spectrum of $\left[{-}Al({-}NMeNMe{-})_{\overline{1.5}}\right]_n$

The initial reaction would then be written:

$$Me_3Al + MeNHNMe_2 \longrightarrow \underset{(III)}{Me_3Al{:}NHMeNMe_2} \qquad (1)$$

The molecular weight (freezing point depression) of compound III was found to be 141.6; and the calculated formula weight for $Me_3Al{:}NHMeNMe_2$ is 146.2.

The product was slowly resublimed at 60°C over a period of 20 hours and a white solid (m.p. 125.0-126.5°C) deposited on the cold finger of the sublimation apparatus. The elemental analysis of this material gave the following values:

Calcd. for $Me_2Al\text{-}NMeNMe_2$: C, 46.13; H, 11.61; N, 21.52; Al, 20.73.

Found: C, 44.82; H, 11.77; N, 22.82; Al, 20.34.

Upon heating, compound III loses a molecule of methane to become IV in the reaction:

$$Me_3Al{:}NHMeNMe_2 \xrightarrow{60^\circ C} \underset{(IV)}{Me_2Al\text{—}NMeNMe_2} + CH_4 \qquad (2)$$

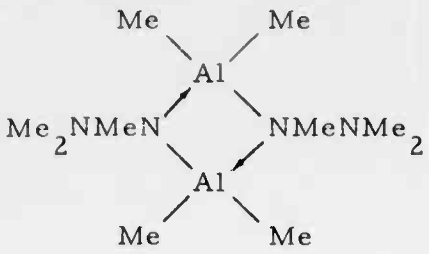
In another experiment, 1.24 grams (17.3 mmoles) of Me_3Al and 1.27 grams (17.1 mmoles) of trimethylhydrazine reacted in the absence of solvent. The mixture was heated at 55°C for 20 hours and 0.270 gram (16.8 mmoles) of methane was recovered. This corresponds to a molar ratio of methane to Me_3Al of 0.975. A white solid was obtained and sublimed once at 60°C; it melted at 125-126°C. The results of an elemental analysis of this material are given below:

Calcd.: C, 46.13; H, 11.61; N, 21.52; Al, 20.73.

Found: C, 45.59; H, 11.52; N, 23.49; Al, 20.42.

The calculated percentages correspond to compound IV, thus indicating that $Me_2Al\text{-}NMeNMe_2$ can be prepared directly by immediately warming the reaction mixture to about 60°C until methane evolution ceases.

Two molecular weight determinations were made; the values obtained were 250.2 and 258.4. These results indicate that compound IV exists as a dimer with the probable structural formula:



The calculated molecular weight of the dimer is 260.4. The infrared spectra of compounds III and IV are shown in Figure 8.

$Me_3Al:NMe_3$ AND TRIMETHYLHYDRAZINE

In its initial stages, the reaction of trimethylaluminum trimethylamine with trimethylhydrazine appears to be very much like the reaction with uncomplexed Me_3Al, except in this case trimethylamine is displaced by trimethylhydrazine to form a 1:1 adduct:

$$Me_3Al{:}NMe_3 + HNMeNMe_2 \longrightarrow Me_3Al{:}NHMeNMe_2 + NMe_3$$

In a typical reaction, 1.34 grams (10.2 mmoles) of $Me_3Al:NMe_3$ reacted with 0.813 gram (11.0 mmoles) of trimethylhydrazine without solvent. The mixture was heated to 60°C until gas evolution ceased (18 hours). The white solid obtained was sublimed at room temperature onto a -15°C cold finger. An elemental analysis agreed with the values for the 1:1 adduct, $Me_3Al:NHMeNMe_2$.

Calcd.: C, 49.29; H, 13.10; N, 19.16; Al, 18.45.

Found: C, 50.99; H, 13.33; N, 18.57; Al, 18.27.

The melting point of this material, 80-83°C, is identical with that of compound III of the previous reaction.

To see if another complex could be prepared from this reaction, the $Me_3Al:NMe_3$ and $NHMeNMe_2$ reacted in a 1:2 molar ratio. A mixture of 1.96 grams (14.9 mmoles) of $Me_3Al:NMe_3$ and 2.31 grams (31.1 mmoles) of trimethylhydrazine was allowed to react at 75°C for two days until the gas evolution stopped. A clear liquid remained, and 0.192 gram (12.0 mmoles) of methane and 0.576 gram (9.77 mmoles) of trimethylamine were recovered. Since the product was a liquid, it was sublimed at room temperature onto a -30°C cold finger in the apparatus shown in Figure 1. The sublimed material had a melting point of 13.5-15.0°C. The elemental analysis of the sublimed product, however, gave results which show that the compound has the same

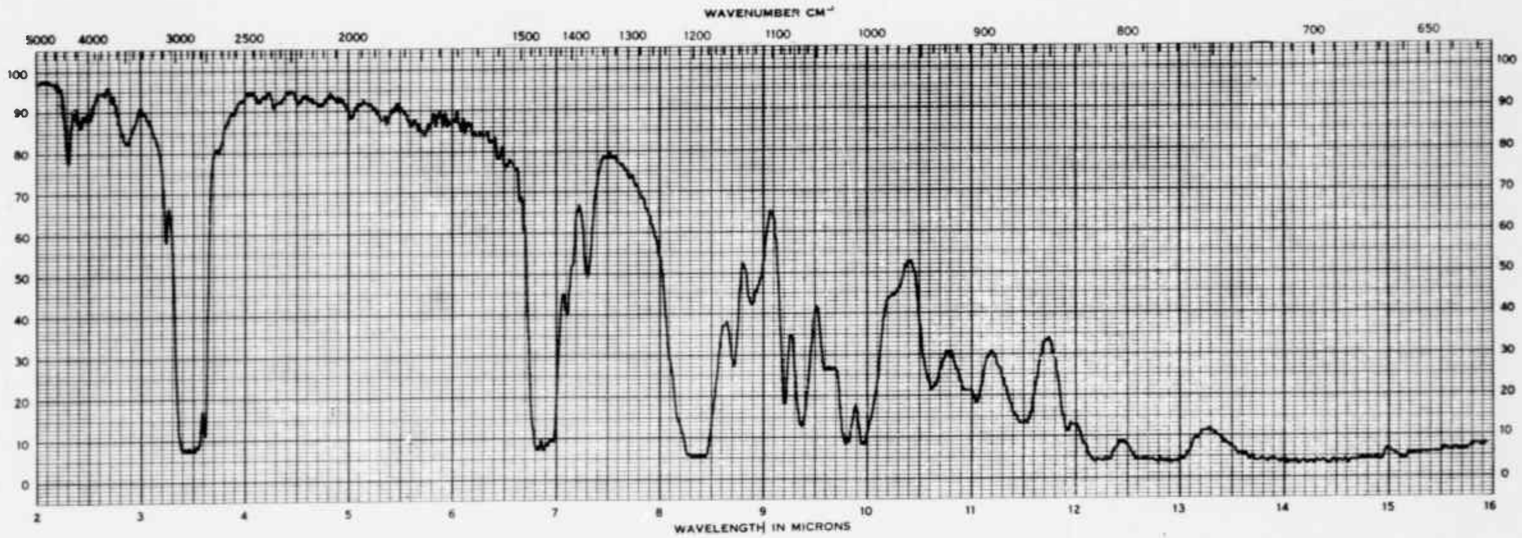


FIGURE 8a. Infrared Spectrum of $Me_3Al:NHMeNMe_2$

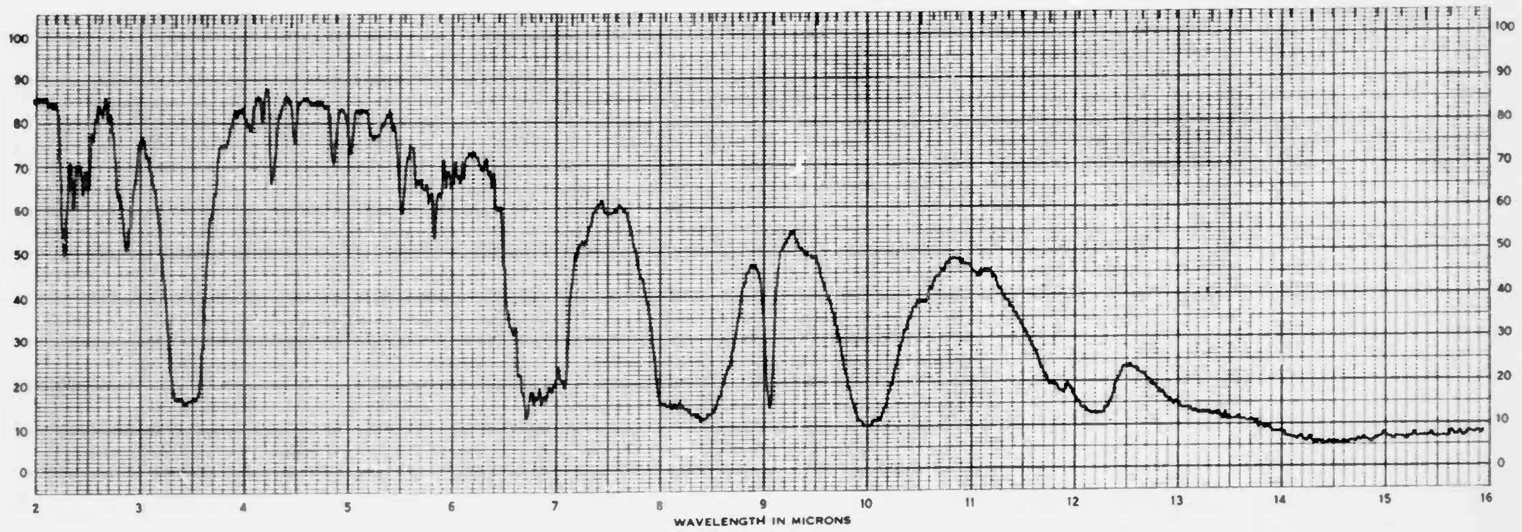


FIGURE 8b. Infrared Spectrum of $\left[Me_2Al{-}NMeNMe_2\right]_2$

empirical formula as the $C_5H_{15}N_2Al$ synthesized in the reaction between Me_3Al and trimethylhydrazine.

Calcd.: C, 46.13; H, 11.61; N, 21.52; Al, 20.73.

Found: C, 44.09; H, 11.63; N, 23.11; Al, 21.94.

The reaction may be written thus:

$$Me_3Al{:}NMe_3 + NHMeNMe_2 \xrightarrow{75^\circ} C_5H_{15}N_2Al + CH_4 + NMe_3$$

Two molecular weight determinations gave the values 189 and 195 for this compound. Since the formula weight for the monomer $C_5H_{15}N_2Al$ is 130.2 and for the dimer is 260.4, the compound appears to be partially associated in cyclohexane. The infrared spectrum of the complex is shown in Figure 9. A hydrolysis of 0.229 gram (17.6 mmoles based on the formula $C_5H_{15}N_2Al$) with methanol yielded 0.0483 gram (30.2 mmoles) of methane.

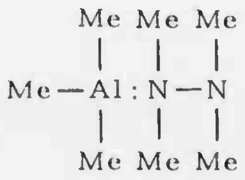
Me_3Al AND TETRAMETHYLHYDRAZINE

By the reaction of 1.10 grams (15.3 mmoles) of Me_3Al with 1.51 grams (17.0 mmoles) of tetramethylhydrazine in pentane, a white crystalline substance was obtained. The mixture was allowed to warm to room temperature and to stand for 2 hours. When no gas evolution was observed after this time, the pentane solvent was removed as quickly as possible in vacuum, and the product was sublimed once at 60°C onto a -15°C cold finger. Elemental analysis of the crystalline compound (m.p. 65.5-66.0°C) gave the following results:

Calcd.: C, 52.47; H, 13.21; N, 17.48; Al, 16.84.

Found: C, 52.48; H, 13.03; N, 17.40; Al, 16.87.

The calculated values agree closely with those for the 1:1 complex:



$$\begin{array}{ccccccc} & & \mathrm{Me} & & \mathrm{Me} & & \mathrm{Me} \\ & & | & & | & & | \\ \mathrm{Me} & - & \mathrm{Al} & : & \mathrm{N} & - & \mathrm{N} \\ & & | & & | & & | \\ & & \mathrm{Me} & & \mathrm{Me} & & \mathrm{Me} \end{array}$$

A molecular weight measurement gave the value 163.5 (calcd. 160.3). The infrared spectrum is shown in Figure 10.

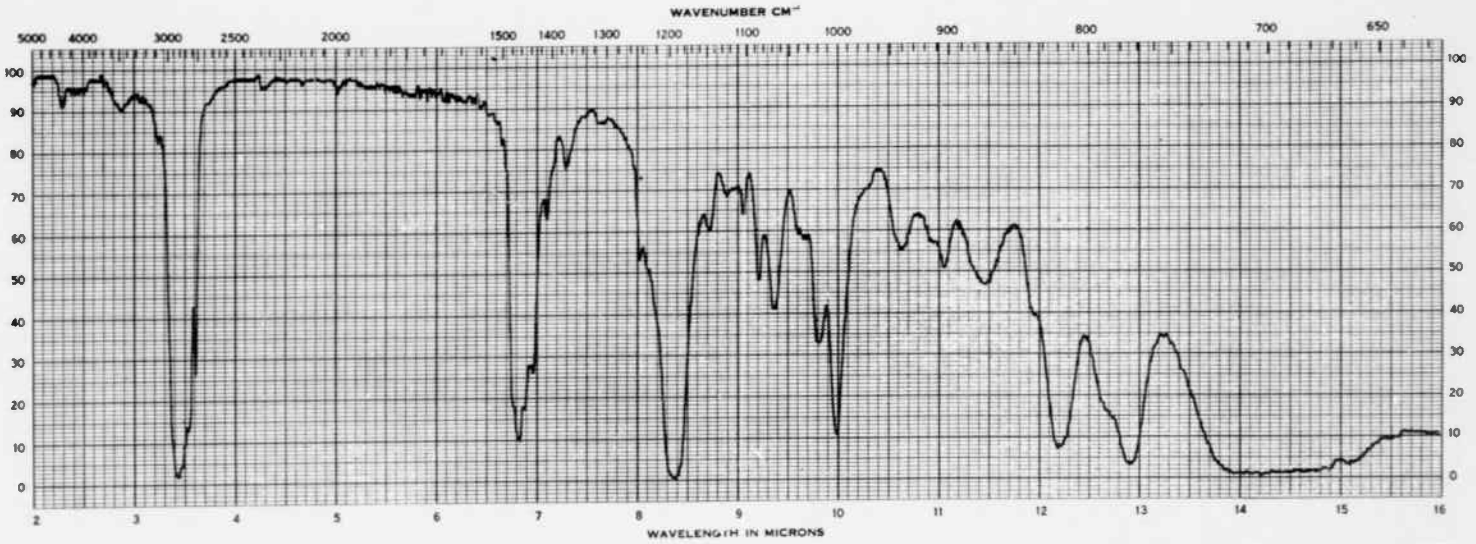


FIGURE 9. Infrared Spectrum of complex of $Me_3Al:NMe_3$ and $NHMeNMe_2$ ($C_5H_{15}N_2Al$)

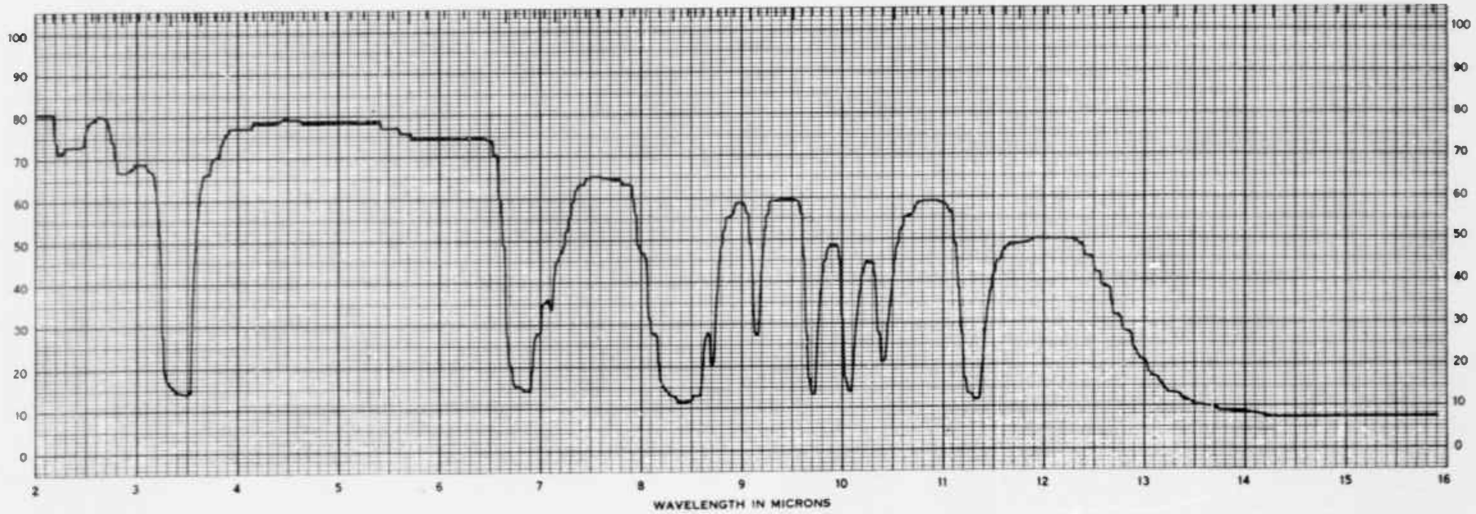


FIGURE 10. Infrared Spectrum of $Me_3Al:NMe_2NMe_2$

DISCUSSION

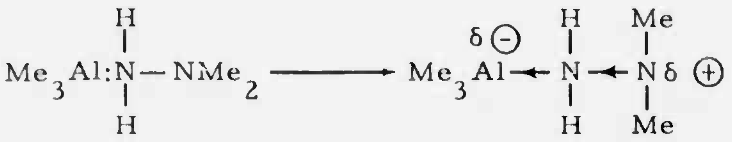
All the reactions studied occur in a sequence shown by the following equations:

$$\mathrm{Me_3Al + HRNNR_2 \longrightarrow Me_3Al{:}NRHNR_2} \qquad (1)$$

$$\mathrm{Me_3Al{:}NRHNR_2 \longrightarrow Me_2Al{-}NRNR_2 + CH_4} \qquad (2)$$

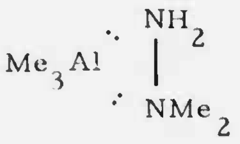
Reaction (1) represents the formation of a complex with a dative Al:N bond, and reaction (2) represents the subsequent formation of a covalent Al-N bond in the complex.

It is noteworthy that in the two examples of dative bonded complexes that have been isolated, i.e., the reaction of trimethylaluminum with trimethylhydrazine and with tetramethylhydrazine, the complex forms in a 1:1 ratio, and no further reaction with trimethylaluminum is observed. The structure of these complexes must be such that further reaction is inhibited. The charge distribution of a tetracoordinated aluminum complex with an unsymmetrical hydrazine



$$\mathrm{Me_3Al{:}\overset{H}{\underset{H}{N}}{-}NMe_2 \longrightarrow Me_3\overset{\delta\ominus}{Al} \leftarrow \overset{H}{\underset{H}{N}} \leftarrow \overset{Me}{\underset{Me}{N}}\,\delta\oplus}$$

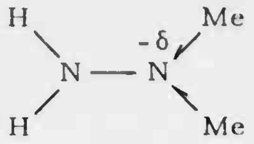
or an intermediate involving a pentacoordinated aluminum atom



$$\mathrm{Me_3Al \begin{matrix} \cdot\cdot\; NH_2 \\ | \\ \cdot\cdot\; NMe_2 \end{matrix}}$$

would inhibit further reaction with trimethylaluminum.

One of the striking features of <u>all</u> the reactions studied is the fact that methane is the only gas evolved. According to current theory, the inductive effect of methyl groups should increase the electron density around that nitrogen atom of an unsymmetrical hydrazine that has the most methyl groups. For example, in 1,1-dimethylhydrazine the nitrogen atom with the two methyl groups should have a higher electron density than the one with the two hydrogen atoms,



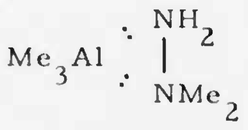
and electrophilic reagents should bond initially to the most highly methylated nitrogen atom. Therefore, treatment with trimethylaluminum should produce ethane or no gas at all, as shown in the hypothetical reaction with 1,1-dimethylhydrazine:

$$Me_3Al + Me_2NNH_2 \longrightarrow Me_2Al\text{-}NMeNH_2 + C_2H_6$$

However, since methane is evolved, the least alkylated nitrogen atom forms the covalent bond with aluminum, and it appears that a simple description of inductive effects does not apply to these reactions.

The formation of the covalent Al-N bond may, however, be controlled by steric effects which enable the aluminum atom to approach more closely the nitrogen atom with the least number of bulky (methyl) groups bonded to it.

If the formula $Me_3Al{:}NH_2NMe_2$ with a tetracoordinated aluminum atom represents an intermediate, then the steric effect will establish the dative Al-N bond at the least methylated nitrogen atom. If the complex with pentacoordinated aluminum

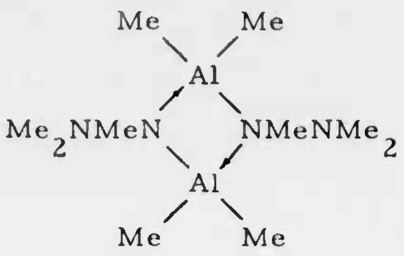


$$Me_3Al \begin{matrix} \therefore NH_2 \\ \quad | \\ \because NMe_2 \end{matrix}$$

is the intermediate, then the aluminum atom may be forced nearer the nitrogen atom with fewer methyl groups, and a covalent bond will form preferentially with this atom.

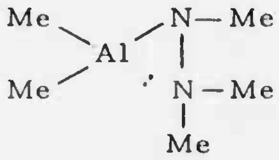
In summary, although the data are not sufficient to determine the structure of the dative bonded intermediate, the covalent bonded complexes are formed by a 1,2 elimination of methane with the aluminum atom bonded to the least alkylated nitrogen atom. The formation of this complex appears to be controlled by steric rather than inductive effects on unsymmetrical hydrazines.

As indicated earlier, the reaction between trimethylaluminum and trimethylhydrazine yields the adduct $Me_3Al{:}NHMeNMe_2$, which, upon heating to 65-70°C for several hours, forms a dimer which may have the structure[14]



The dimerization is accompanied by methane evolution. This product is very similar to one produced in the 1,1-dimethylhydrazine reaction; and an attempt may be made in future work to isolate an intermediate at a lower temperature.

The reaction of trimethylaluminum trimethylamine with trimethylhydrazine also produced the 1:1 condensation complex described above. A separate reaction under more vigorous conditions resulted in a complex with the chemical composition of compound IV ($C_5H_{15}N_2Al$), but with physical properties radically different from those of the complex prepared by the reaction of trimethylaluminum and trimethylhydrazine. The molecular weight data suggest a complex that is only partially associated to the dimeric state. The hydrolysis of the complex yields two moles of methane for each mole of material with the empirical formula $C_5H_{15}N_2Al$, hence this substance contains a Me_2Al-group. It should also be noted that the complex was prepared under the most rigorous temperature conditions employed in this series of reactions; therefore, it should be a stable configuration, perhaps more stable than either compound III or compound IV. Although no proof is available, the structure is not inconsistent with the data obtained so far.



This structure has the correct empirical formula, contains a Me_2Al function, may be a liquid at room temperature, and may be partly associated in cyclohexane solution to give an intermediate molecular weight.

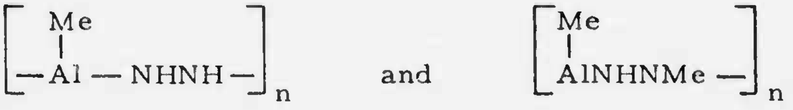
---

[14] Nitrogen bridged structures for similar borane amine compounds have been described by K. Hedberg and A. J. Stosick, J. Am. Chem. Soc., Vol. 74, p. 954 (1952); and by L. M. Trefonas and W. M. Lipscomb, J. Am. Chem. Soc., Vol. 81, p. 4435 (1959).

Since this low melting compound should be the most stable of the complexes formed in the reaction between trimethylaluminum or trimethylaluminum trimethylamine and trimethylhydrazine, an attempt was made to convert compound IV, $[\text{Me}_2\text{Al-NMeNMe}_2]_2$, into its low melting isomer by heating a quantity of it with an equimolar amount of trimethylhydrazine at 75°C for 2 days. A quantity of IV without any trimethylhydrazine present was similarly heated for the same period. No trace of the low melting complex was obtained from either treatment; hence the reaction route with trimethylaluminum trimethylamine and trimethylhydrazine at 70°C may be unique.

Two more points are worth noting. The reaction between trimethylaluminum trimethylamine and 1,1-dimethylhydrazine forms a complex that contains both a covalent and a dative Al:N bond. This compound is the only example of such a bonding configuration among the complexes obtained from this work.

Aside from the infrared evidence, the work of Ziegler and Gellert[7] also confirms the results obtained here, namely, the same nitrogen is never bonded more than once to an aluminum atom. Thus it is fairly certain that the polymers formed from the reaction of trimethylaluminum with hydrazine and methylhydrazine have the respective structural formulas



$$\left[-\overset{\text{Me}}{\overset{|}{\text{Al}}}-\text{NHNH}-\right]_n \quad \text{and} \quad \left[\overset{\text{Me}}{\overset{|}{\text{Al}}}\text{NHNMe}-\right]_n$$

Further study of these complexes is planned to elucidate the structures of those complexes for which there are now insufficient data. The work undertaken also suggests that some interconversions such as

$$\text{Me}_2\text{Al(NHNMe}_2\text{)}\,(\text{H}_2\text{NNMe}_2) + \text{Me}_3\text{Al} \longrightarrow (\text{Me}_2\text{AlNHNMe}_2)_2 + \text{CH}_4$$

may be possible; and more work on such reactions is planned.

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The complexing of Me_3Al and $Me_3Al{:}NMe_3$ with hydrazine, methylhydrazine, 1,1- and 1,2-dimethylhydrazine, trimethylhydrazine, and tetramethylhydrazine was carried out by means of two general reactions: $R_3Al + H_2NNR'_2 \longrightarrow R_3Al{:}NH_2NR'_2$ and $R_3Al{:}NH_2NR'_2 \longrightarrow R_2Al\text{-}NHNR'_2 + RH$. Elemental analyses, quantitative gas measurements, and infrared spectra are given for several complexes and polymers that were characterized.

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1. Trimethylaluminum-hydrazine complexes
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WepTask: RMMP-7A 032/211
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