C_6H_5OH-quinuclidine, 36578-79-7; p-FC_6H_4OH-quinuclidine, 36578-80-0; p-ClC_6H_4OH-quinuclidine, 36578-81-1; p-Br-C_6H_4OH-quinuclidine, 36578-84-4; p-IC_6H_4OH-quinuclidine, 36578-83-3; p-t-BuC_6H_4OH-quinuclidine, 36578-78-6; $CHCl_3$-quinuclidine, 36578-76-4; CF_3CH_2OH-quinuclidine, 36578-82-2; HFIP-quinuclidine, 36578-85-5; $CF_3(CF_2)_5$-CF_2H-quinuclidine, 36578-86-6; I_2-quinuclidine, 23290-15-5; $B(CH_3)_3$-quinuclidine, 36578-88-8; quinuclidine, 100-76-5; pyrrole, 109-97-7; pyrrole-quinuclidine, 36578-77-5.

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The Nature of Trimethylamine-Dimethylalane

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The nature of trimethylamine-dimethylalane ($H(CH_3)_2Al{\cdot}N(CH_3)_3$) has been examined in detail in order to resolve a recent controversy. All of our data are consistent with the hypothesis that trimethylamine-dimethylalane is a discrete compound which exists as an equilibrium mixture of monomeric and more associated species. Tensimetric titrations between pure dimethylalane and $N(CH_3)_3$ establish the formation of only a 1:1 adduct. The reaction between $H(CH_3)_2Al{\cdot}N(CH_3)_3$ and $N(CH_3)_2H$ provides even more conclusive evidence that $H(CH_3)_2Al{\cdot}N(CH_3)_3$ is a discrete compound. The only aluminum-containing product from this reaction is $[(CH_3)_2Al{\cdot}N(CH_3)_2]_2$. Solution- and gas-phase molecular weight studies demonstrate that an equilibrium exists between monomeric and more associated species. Furthermore, the ^1H nmr data are also consistent with the existence of an equilibrium between monomeric and associated species.

The nature of trimethylamine-dimethylalane, $H(CH_3)_2$-$Al{\cdot}N(CH_3)_3$, has been the subject of recent controversy. Originally the compound[1] was believed to exist as a mixture of monomeric and dimeric species. More recently, the nmr spectrum of a benzene or cyclohexane solution of the material,[2] considered to be $H(CH_3)_2Al{\cdot}N(CH_3)_3$, has been interpreted in terms of a disproportionation equilibrium involving $H_3Al{\cdot}N(CH_3)_3$, $H_2(CH_3)Al{\cdot}N(CH_3)_3$, and $(CH_3)_3$-$Al{\cdot}N(CH_3)_3$ as products. If $H(CH_3)_2Al{\cdot}N(CH_3)_3$ does indeed readily disproportionate in solution, then much of the synthetic chemistry involving organoaluminum hydrides would have to be reconsidered and evaluated. Therefore, we felt that this controversy had to be resolved.

In order to understand the nature of $H(CH_3)_2Al{\cdot}N$-$(CH_3)_3$ we have examined its chemical, physical, and spectral properties. The compound was prepared directly from dimethylalane and trimethylamine. The previous workers[1,2] synthesized their samples of $H(CH_3)_2Al{\cdot}N$-$(CH_3)_3$ by an exchange reaction involving $(CH_3)_3Al{\cdot}N$-$(CH_3)_3$ and $H_3Al{\cdot}N(CH_3)_3$. This type of preparative reaction introduces ambiguities, which must be eliminated.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum line or a purified nitrogen atmosphere. All solvents were dried by conventional procedures. The dimethylalane was prepared from $LiAlH_4$ and $B(CH_3)_3$ in a sealed tube according to a previously published procedure.[3] The yields of dimethylalane, based on the $LiAlH_4$, were usually 70%. The physical properties of the dimethylalane were identical in every respect with those previously reported.[3] (Vapor pressure: 1.75 mm at 24.0°; lit.[3] 1.8 mm at 24.7°.) The trimethylboron was prepared by the reaction of methylmagnesium iodide with $BF_3{\cdot}O(C_4H_9)_2$ in n-butyl ether according to a previously published procedure.[4] The trimethylamine was dried with P_4O_{10} and distilled.

It should be noted that dimethylalane is an extremely viscous liquid which is difficult to transfer quantitatively on a vacuum line. Thus, all quantitative transfers were accomplished by pumping the material into the appropriate vessel cooled to −196°.

Tensimetric Titrations between Dimethylalane and Trimethylamine. The nature and stoichiometry of the reaction between dimethylalane and $N(CH_3)_3$ were established by titrating samples of dimethylalane with $N(CH_3)_3$ tensimetrically. The titrations, which were conducted according to standard procedures,[5] were either run neat or run as n-heptane solutions at 25, −23, and −46°. In all titrations 1.00 ± 0.02 mol of $N(CH_3)_3$ reacted per mole of $(CH_3)_2$-AlH. All subsequent preparations of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ were accomplished by allowing the two reagents to react at −78° in a 1:1 mole ratio and then allowing the product to warm slowly to room temperature.

Physical Properties of $H(CH_3)_2Al{\cdot}N(CH_3)_3$. The compound $H(CH_3)_2Al{\cdot}N(CH_3)_3$ has a melting point of 17-25°. At room temperature one frequently observes the material to be a mixture of a liquid and solid. Above the melting point the material is a mobile liquid. The compound has a reproducible vapor pressure of 5.0 mm at 0° and is thermally stable at temperatures up to 100°. Thermal stability was monitored for the pure compound as well as a refluxing heptane solution, bp 98°. The vapor pressure of the compound as a function of temperature is given in Figure 1.

Analysis of $H(CH_3)_2Al{\cdot}N(CH_3)_3$. A sample of $H(CH_3)_2Al{\cdot}N$-$(CH_3)_3$ of sufficient size for analysis was prepared from dimethylalane and $N(CH_3)_3$. The entire sample was then divided into two parts by a vacuum distillation. Each part was then analyzed separately. Nitrogen was determined by the standard Kjeldahl method, whereas aluminum was measured by an EDTA titration.[6] *Anal.* Calcd. for $H(CH_3)_2Al{\cdot}N(CH_3)_3$: N, 12.0; Al, 23.1. Found (first fraction removed): N, 12.0; Al, 22.7. Found (second fraction): N, 12.0; Al, 23.1.

Molecular Weight Studies. The molecular weight of $H(CH_3)_2$-$Al{\cdot}N(CH_3)_3$ was measured in cyclopentane solution by vapor pressure depression and in the gas phase by vapor density. The results are given in Table I.

The molecular weight studies of the solution and gas phases require comment. The molecular weight studies of the solution were designed to provide data which would be directly comparable with the nmr data. Therefore, the measurements in cyclopentane at room temperature required vapor pressure depression as the mole-

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[1] F. M. Peters, B. Bartocha, and A. J. Bilbo, *Can. J. Chem.*, 41, 1051 (1962).

[2] A. Storr and V. G. Wiebe, *Can. J. Chem.*, 47, 673 (1969).

[3] T. Wartik and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 75, 835 (1953).

[4] H. C. Brown, *J. Amer. Chem. Soc.*, 67, 374 (1945).

[5] D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 61.

[6] G. E. Coates and J. Graham, *J. Chem. Soc.*, 233 (1963).

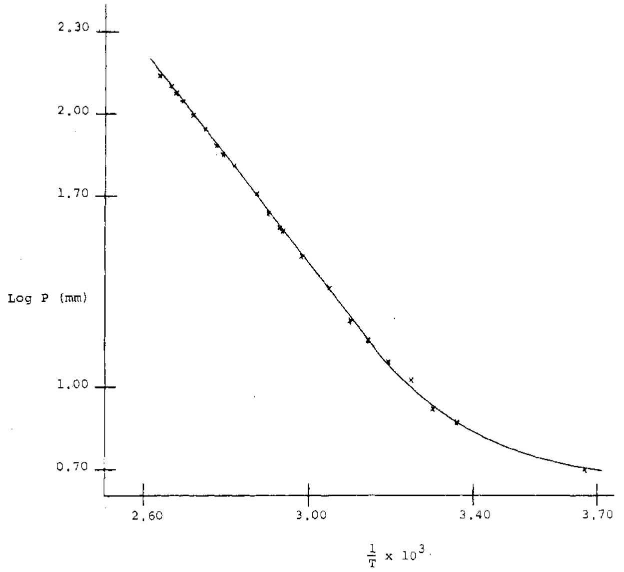

Figure 1. Vapor pressure of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ as a function of temperature.

Table I. Molecular Weight Studies

Vapor pressure lowering–Cyclopentane Solution (20°)			Vapor density–gas phase		
Concn, *m*	Mol wt	Deg of assocn	Temp, °C	Mol wt	Deg of assocn
0.101	117	1.00	27.0	138	1.18
0.150	130	1.11	90.0	113	0.965
0.192	155	1.33			
0.416	186	1.59			

cular weight method. This method involves a tedious procedure which has more systematic errors than the other methods. The gas-phase molecular weight measurements at 27° were made by attaching a sample tube containing $H(CH_3)_2Al{\cdot}N(CH_3)_3$ to a large (3.05 l.) evacuated bulb having an attached manometer. The sample of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ was expanded into the large bulb, the pressure in the bulb was measured, and then the mass of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ which expanded into the bulb from the sample tube was determined. Pressures of 1–2 mm generated by 40–50 mg of material were typical data. The value given in Table I is the average of six sets of measurements. The molecular weights differed by a maximum of 15 units. The significance of the molecular weight data is the apparent association behavior of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ in both the solution and gas phases. The comparison of the degrees of association between the solution and gas phases can only be meaningful if the effects of the influence of solvation energy are considered.

Reaction of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ with $N(CH_3)_2H$. The compound $H(CH_3)_2Al{\cdot}N(CH_3)_3$ was allowed to react with $N(CH_3)_2H$ in order to establish the chemical nature of the adduct. Dimethylalane was also treated with $N(CH_3)_2H$ in order to establish product comparisons. All reactions were carried out similarly. The experiments, conditions, and results are given in Table II.

In a typical reaction, 1.92 mmol (0.225 g) of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ was prepared in a flask. Dimethylamine (1.92 mmol) was condensed into the flask at −196°. As the flask was warmed slowly to room temperature, gas evolution occurred. After the reaction was complete, the noncondensable gas (1.89 mmol of H_2) was removed and measured with a Toepler pump-gas buret assembly. Subsequently, a condensable gas (1.85 mmol of $N(CH_3)_3$) was removed. The material (0.188 g) remaining in the reaction flask was a volatile white solid which was identified as $[(CH_3)_2Al{\cdot}N(CH_3)_2]_2$ according to its melting point and infrared spectrum[7] (mp 152–153°, lit.[7] mp 153–154°).

Nuclear Magnetic Resonance Spectra. All ^1H nmr spectra were recorded at 100 MHz by means of a Jeolco Model MH-100 spectrometer. The chemical shifts, referred to cyclopentane as standard (0.00 ppm), are given in Table III. The temperature of these measurements was the operating temperature of the instrument, 24°. Our data are in agreement with those of the earlier workers.[1,2] The dependence of the observed spectrum of the methylaluminum lines on the concentration of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ is shown in Figure 2. The temperature dependence of the spectrum was observed for the 0.683 and 1.355 *m* samples. As the temperature was lowered from 24 to −50°, the high-field $Al\text{-}CH_3$ line decreased in intensity whereas the lower field $Al\text{-}CH_3$ lines increased in intensity. It must be noted that these changes were very small but clear. Furthermore, the appearance of the entire spectrum at 24° was very similar to that at −50°. The $N\text{-}CH_3$ line remained a singlet at −50°.

Infrared Spectra. The infrared spectra were recorded in the range 4000–400 cm^{-1} by means of a Perkin-Elmer 457 spectrometer. Spectra were recorded of the gas, the liquid at room temperature, and the solid at temperatures below −78°. Furthermore, it should be noted that spectra of samples of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ before being dissolved in cyclopentane and after the cyclopentane was removed were identical in every respect.

The following give the spectra of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ [frequency, cm^{-1} (intensity: s, strong; m, medium; w, weak; sh, shoulder)]. **Gas phase, +30°:** 3010 (w), 2982 (w), 2922 (m), 2864 (w), 1775 (s), 1767 (s), 1480 (m), 1200 (m), 1101 (w), 1008 (m), 918 (w), 828 (w), 743 (s), 718 (s), 584 (w), 493 (w). **Gas phase, +90°:** 2980 (s, sh), 2917 (s), 1760 (s), 1480 (s), 1467 (s), 1410 (w), 1245 (m), 1188 (m), 1101 (w), 998 (s), 823 (m), 705 (s), 620 (w), 590 (w), 505 (m). **Liquid phase, +30°:** 3005 (m), 2980 (m), 2916 (s), 2894 (s), 1732 (m), 1475 (s), 1460 (m), 1445 (m), 1404 (w), 1240 (m), 1180 (s), 1097 (m), 992 (s), 815 (m), 770 (m, sh), 685 (s), 617 (m), 581 (m), 515 (m), 500 (m). **Solid phase, <−78°:** 3005 (w), 2982 (w), 2925 (s), 2890 (w), 1735 (s), 1477 (s), 1455 (m), 1442 (w), 1245 (w), 1182 (m), 1095 (w), 995 (s), 821 (w), 772 (m), 736 (s), 705 (s), 636 (w), 620 (w), 586 (w), 509 (w).

Results and Discussion

A great variety of experiments designed to elucidate the nature of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ have been performed. All of our data are consistent with the hypothesis that $H(CH_3)_2Al{\cdot}N(CH_3)_3$ is a discrete compound which exists as a mixture of monomeric and more associated species at room temperature. The nature of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ is not changed significantly by the process of dissolution. We have no evidence to support the hypothesis[2] that $H(CH_3)_2Al{\cdot}N(CH_3)_3$ disproportionates in solution.

The tensimetric titration data are consistent with the hypothesis that $H(CH_3)_2Al{\cdot}N(CH_3)_3$ is a discrete compound. Only 1 mol of $N(CH_3)_3$ is consumed per mole of $(CH_3)_2AlH$ and there is no dependence of the data on temperature or solvent. Thus, dimethylalane reacts with $N(CH_3)_3$ to form only $H(CH_3)_2Al{\cdot}N(CH_3)_3$. There is no evidence for a bis-amine adduct, $H(CH_3)_2Al{\cdot}2N(CH_3)_3$, or the disproportionation equilibrium given by eq 1.

$$5H(CH_3)_2Al{\cdot}N(CH_3)_3 \rightleftarrows H_3Al{\cdot}N(CH_3)_3 + H_2(CH_3)Al{\cdot}N(CH_3)_3 + 3(CH_3)_3Al{\cdot}N(CH_3)_3 \quad (1)$$

If $H(CH_3)_2Al{\cdot}N(CH_3)_3$ did disproportionate to form $H_3Al{\cdot}N(CH_3)_3$ as a product, more than 1 mol of $N(CH_3)_3$ would have been consumed per initial mole of $H(CH_3)_2Al$, because $H_3Al{\cdot}N(CH_3)_3$ reacts with $N(CH_3)_3$ to form $H_3Al{\cdot}2N(CH_3)_3$.[8] Storr and Wiebe[2] suggested the presence of 11.2% $H_3Al{\cdot}N(CH_3)_3$ according to their interpretation of the nmr data.

The reaction of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ with $N(CH_3)_2H$ provides even more convincing evidence that $H(CH_3)_2Al{\cdot}N(CH_3)_3$ is a discrete compound. Dialkylamines[9,10] are known to react readily with aluminum hydrides to form H_2 and the corresponding dialkylamino derivative. According to our data, the only aluminum-containing product formed when a pure sample or a cyclopentane solution of $H(CH_3)_2$-

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(7) O. T. Beachley, Jr., G. E. Coates, and G. Kohnstan, *J. Chem. Soc.*, 3248 (1965).

(8) C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, **2**, 508 (1963).

(9) J. K. Ruff and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **83**, 535 (1961).

(10) J. K. Ruff, *J. Amer. Chem. Soc.*, **83**, 2835 (1961).

Table II. Reactions of Methylalane Compounds with Dimethylamine

Amt, mmol				Amt, mmol	
$H(CH_3)_2Al{\cdot}N(CH_3)_3$	$N(CH_3)_2H$	T, °C	Solvent	H_2	$(CH_3)_2Al{\cdot}N(CH_3)_2$[a]
1.92	1.92	25		1.89	1.86
1.72	1.72	−8	C_5H_{10}	1.70	1.56
$H(CH_3)_2Al$					
2.24	2.24	25		2.22	2.22
2.20	2.24	−8	C_6H_{12}	2.19	2.08

[a] There were unavoidable mechanical losses of the product during transfer in the drybox.

Table III. Nuclear Magnetic Resonance Data[a]

Compd	δ(N–CH_3), ppm	δ(Al–CH_3), ppm	Solvent	Concn
$H(CH_3)_2Al{\cdot}N(CH_3)_3$	−0.89	+2.35, 2.40, 2.44	C_5H_{10}	0.202 *m*
$H(CH_3)_2Al{\cdot}N(CH_3)_3$	−0.85	+2.36, 2.40, 2.44	C_5H_{10}	0.683 *m*
$H(CH_3)_2Al{\cdot}N(CH_3)_3$	−0.89	+2.33, 2.39, 2.45	C_5H_{10}	1.355 *m*
$H(CH_3)_2Al{\cdot}N(CH_3)_3$	−0.95	+2.32, 2.39, 2.45	C_5H_{10}	>95%
$H(CH_3)_2Al{\cdot}N(CH_3)_3$	−0.37	+2.07, 2.13, 2.18	C_6H_6	10%
$(CH_3)_3Al{\cdot}N(CH_3)_3$	−0.87	+2.42	C_5H_{10}	10%
$H_3Al{\cdot}N(CH_3)_3$	−0.54[b]		C_6H_6	
$[(CH_3)_2Al{\cdot}N(CH_3)_2]_2$	−0.85	+2.25	C_5H_{10}	10%
$H(CH_3)_2Al$		+2.08	C_5H_{10}	75%
$N(CH_3)_3$	−0.59		C_5H_{10}	10%

[a] The chemical shifts in all spectra are referenced to cyclopentane as standard (0.00 ppm). [b] R. A. Kovar and E. C. Ashby, *Inorg. Chem.*, 10, 893 (1971).

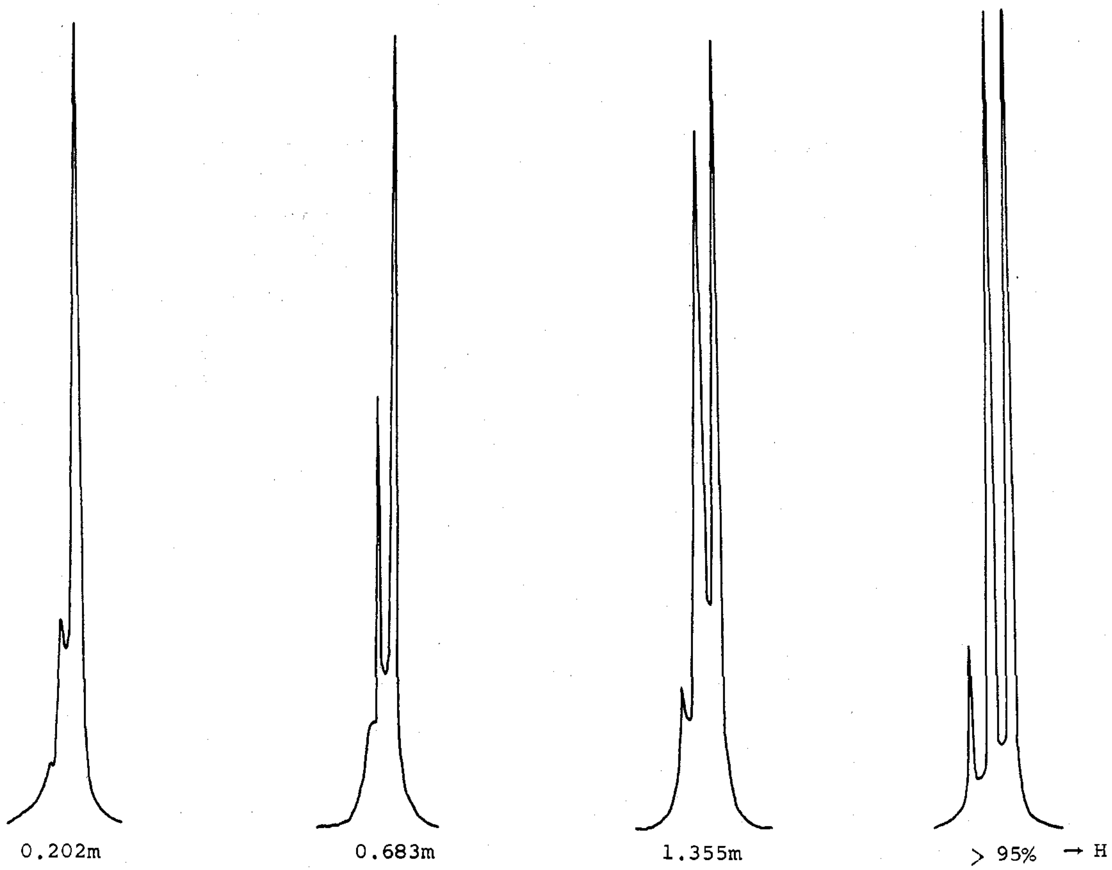

Figure 2. Concentration dependence of the nmr spectrum of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ (lines due to methyl groups bound to aluminum).

$Al{\cdot}N(CH_3)_3$ reacted with $N(CH_3)_2H$ is $[(CH_3)_2Al{\cdot}N(CH_3)_2]_2$ (Table II). Equation 2 summarizes the observed

$$H(CH_3)_2Al{\cdot}N(CH_3)_3 + N(CH_3)_2H \rightarrow {}^1/_2[(CH_3)_2Al{\cdot}N(CH_3)_2]_2 + N(CH_3)_3 + H_2 \quad (2)$$

reaction. If $H(CH_3)_2Al{\cdot}N(CH_3)_3$ had disproportionated according to eq 1, a variety of products, including $Al[N(CH_3)_2]_3$, $CH_3Al[N(CH_3)_2]_2$, $(CH_3)_3Al{\cdot}N(CH_3)_2H$, and $[(CH_3)_2Al{\cdot}N(CH_3)_2]_2$, would have been observed.[9,10]

The chemistry of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ establishes the material as a discrete compound. Molecular weight studies (Table I) indicate that there is an equilibrium between monomeric and more associated species in solution and in the gas phase. Earlier workers[1] made similar observations for cyclohexane solution. The physical properties of the pure compound also suggest the presence of a variety of species, monomeric and associated. The compound has a wide melting point range, 17-25°, indicating a mixture of species. However, the reproducible vapor pressure of the compound suggests these species have identical simplest formulas, but different molecular formulas. The shape of the graph log P *vs.* $1/T$ (Figure 1) and the gas-phase molecular weight data (Table I) suggest the presence of a variety of species in the condensed phase and in the gas phase below 40°, whereas only monomeric species are probably present above 40°. The infrared spectral data for the compound also suggest the existence of more than one species. In the gas phase there are two Al-H stretching bands at 1775 and 1767 cm^{-1}. It is of interest to note that neither of these bands correspond to the Al-H stretching frequency in $H_3Al{\cdot}N(CH_3)_3$,[11] 1792 cm^{-1}.

The ^1H nmr spectra of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ are consistent with all of our previous observations. The spectrum of the essentially pure material has one line due to the $N\text{-}CH_3$ group and three lines assigned to methyl groups bound to aluminum. This spectrum is similar to that observed by Storr and Wiebe.[2] However, we interpret the three $Al\text{-}CH_3$ lines in terms of three species of different degrees of association. As the sample is diluted, the relative intensities of the $Al\text{-}CH_3$ lines change (Figure 2). The high-field line increases in intensity whereas the lower field lines decrease. Therefore, the high-field line is probably due to the monomeric species, whereas the lower field lines are assigned to more associated species, such as a dimer and trimer. Similar assignments have been made for monomeric and the associated species in another system.[12] The relative intensities of these lines, their assignments according to monomeric, dimeric, and trimeric species, and their concentration dependencies are consistent with our molecular weight measurements in the identical solvent.

The fundamental use of a balanced chemical equation provides additional support for our conclusion that the three $Al\text{-}CH_3$ lines are due to at least three species of different degrees of association. The balanced equations for an association equilibrium and the disproportionation equilibrium[2] are

$$5H(CH_3)_2Al{\cdot}N(CH_3)_3 \rightleftarrows [H(CH_3)_2Al{\cdot}N(CH_3)_3]_2 + [H(CH_3)_2Al{\cdot}N(CH_3)_3]_3 \quad (3)$$

$$5H(CH_3)_2Al{\cdot}N(CH_3)_3 \rightleftarrows 3(CH_3)_3Al{\cdot}N(CH_3)_3 + H_2(CH_3)Al{\cdot}N(CH_3)_3 + H_3Al{\cdot}N(CH_3)_3 \quad (4)$$

The nmr data show that the relative intensities of the lines, hence the concentrations of the three observed species, depend upon the concentration of the sample. This can only be consistent with the association equilibrium (eq 3). The equation for the disproportionation equilibrium (eq 4) requires that the relative concentrations of the possible species be independent of the concentration of the solution, as 5 mol of reactant form 5 mol of product. Furthermore, the balanced equation for the disproportionation equilibrium requires that the concentrations of $(CH_3)_3Al{\cdot}N(CH_3)_3$ and $H_2(CH_3)Al{\cdot}N(CH_3)_3$ be in a ratio of 3:1, if the equilibrium is established by starting with $H(CH_3)_2Al{\cdot}N(CH_3)_3$. Storr and Wiebe[2] reported 29.3% $(CH_3)_3Al{\cdot}N(CH_3)_3$ and 21.2% $H_2(CH_3)Al{\cdot}N(CH_3)_3$. This is not a ratio of 3:1. As they contended that their samples have the appropriate composition for $H(CH_3)_2Al{\cdot}N(CH_3)_3$, material could not have been lost to account for the difference between the observed data and that required by the balanced chemical equation. Furthermore, the lines in the spectra of our samples which are prepared from pure dimethylalane are not consistent with this required 3:1 ratio either. Hence, the nmr spectra are not consistent with a disproportionation equilibrium.

In order further to dismiss the hypothesis of disproportionation, we have attempted to show that the high-field $Al\text{-}CH_3$ line in the nmr spectrum cannot be due to $(CH_3)_3AlN(CH_3)_3$, the suggestion of Storr and Wiebe.[2] The chemical shift (Table III) of the high-field line is +2.44 ppm whereas that of $(CH_3)_3Al{\cdot}N(CH_3)_3$ is +2.42 ppm. These values are essentially within the experimental error of our instrument and are not conclusive for eliminating the presence $(CH_3)_3\text{-}Al{\cdot}N(CH_3)_3$. Therefore, we observed the nmr spectrum of a sample which contained 1.355 *m* $H(CH_3)_2Al{\cdot}N(CH_3)_3$ and 1.355 *m* $(CH_3)_3Al{\cdot}N(CH_3)_3$. The high-field $Al\text{-}CH_3$ line in the spectrum of this sample was different from that observed for the solution of pure $H(CH_3)_2Al{\cdot}N(CH_3)_3$. The high-field line was asymmetrical (a bump on the low-field side) for the mixture whereas it was symmetrical for the solution of pure $H(CH_3)_2Al{\cdot}N(CH_3)_3$. This observation would indicate that the high-field line in the spectrum of the mixture was due to the partial superposition of the line from $(CH_3)_3Al{\cdot}N(CH_3)_3$ and the line of the proposed monomeric form of $H(CH_3)_2Al{\cdot}N(CH_3)_3$. Furthermore, the relative intensities of the two lower field $Al\text{-}CH_3$ lines did not change from that observed for the solution of pure $H(CH_3)_2Al{\cdot}N(CH_3)_3$. If the disproportionation equilibrium described the system, the relative intensities of the two lower field $Al\text{-}CH_3$ lines must change.

In conclusion, $H(CH_3)_2Al{\cdot}N(CH_3)_3$ is a discrete compound which exists as a mixture of monomeric and associated species. The associated species probably have five-coordinate aluminum which involves hydrogen-bridge bonding. Hydrogen bridges[13] are more energetically favorable than methyl bridges. The hydrogen bridges in these five-coordinate species are probably not very strong. The association reaction probably has a relatively small ΔH as the relative intensities of the methylaluminum resonances do not change dramatically with temperature.

Registry No. $H(CH_3)_2Al{\cdot}N(CH_3)_3$, 19582-11-7; $[(CH_3)_2\text{-}Al{\cdot}N(CH_3)_2]_2$, 2245-08-13; $H(CH_3)_2Al$, 865-37-2; $N(CH_3)_3$, 75-50-3; $(CH_3)_3Al{\cdot}N(CH_3)_3$, 19553-62-9.

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(11) G. W. Fraser, N. N. Greenwood, and B. P. Straughan, *J. Chem. Soc.*, 3742 (1963).

(12) B. Y. Kimura and T. L. Brown, *J. Organometal. Chem.*, 26, 57 (1971).

(13) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I, 3rd ed, Methuen, London, 1967, p 340.