

stituents than $\text{Co}(\text{CO})_4^-$. $\text{Mn}(\text{CO})_5^-$ and $(\pi\text{-C}_5\text{H}_5)\text{-Mo}(\text{CO})_3^-$ do not form complexes with $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ or $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ although $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$ reacts with $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and $\text{Hg}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$. Apparently, as the base strength of R in HgR_2 increases, mercury becomes such a weak Lewis acid that only the strongest Lewis bases will form adducts with it, while with weak bases as R, mercury is a sufficiently strong Lewis acid to add other weak bases. There seems to be a balancing of these effects such that three-coordinate mercury complexes HgR_3^- can be formed at both ends of the basicity scale of R but not with intermediate ligands.

A similar relationship between reactivity and the base strength of R^- in ZnR_2 , CdR_2 , HgR_2 , and $(\text{C}_6\text{H}_5)_3\text{-SnR}$ has been observed³⁴ for the displacement of R^- by dimethylformamide. The extent of dissociation of these compounds in DMF increased as the base strength of R^- decreased. Similarly, displacement of R^- by

(34) J. M. Burlitch, *J. Amer. Chem. Soc.*, **91**, 4562 (1969).

Br^- from ZnR_2 and $(\text{C}_6\text{H}_5)_3\text{SnR}$ increased as the base strength of R^- decreased.⁸

The effect of a strong Lewis base on the bonding of mercury to a weaker base is also apparent in the solid state. The Hg-Co bond distance of 2.573 (12) Å in $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{Hg}[\text{Co}(\text{CO})_4]^{35,36}$ is significantly longer than that of 2.499 (7) Å in $\text{Hg}[\text{Co}(\text{CO})_4]_2$.³⁷ There is no significant difference between the Hg-Co bond lengths in $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and $\text{BrHgCo}(\text{CO})_4$ ³⁶ in which the Br^- is of comparable base strength to $\text{Co}(\text{CO})_4^-$.

Acknowledgments.—This work was supported by the Advanced Research Projects Agency through the Purdue University Materials Science Council. H. L. Conder wishes to thank the Purdue Research Foundation for the award of a David Ross fellowship.

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Reactions of *cyclo*-1,5-Bis- μ -dimethylamino-3,7-di- μ -hydrido-2,4,6,8-tetrakis(dimethylaluminum) with Lewis Bases

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Treatment of $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$ with excess $\text{N}(\text{CH}_3)_3$ takes place in either of two ways. One reaction path leads to the formation of $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ and $2(\text{CH}_3)_2\text{AlHN}(\text{CH}_3)_3$, whereas the second affords $\text{Al}_3(\text{CH}_3)_6[\text{N}(\text{CH}_3)_2]_2\text{H}$ and $(\text{CH}_3)_2\text{-AlHN}(\text{CH}_3)_3$. Ammonia reacts to yield $[(\text{CH}_3)_2\text{AlNH}_2]$, $\text{HN}(\text{CH}_3)_2$, and $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$, while $(\text{CH}_3)_2\text{O}$ affords $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]$, CH_4 , and $[(\text{CH}_3)_2\text{AlO}(\text{CH}_3)_2]_2$. Treatment of $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$ with $\text{P}(\text{CH}_3)_3$ leads to partial decomposition as does solution formation in benzene.

Introduction

The preparation and characterization of $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$ (I) has been reported;² the bonding associated with this species involves both electron-sufficient (N) and -deficient bridges (H). A charge refinement of the crystallographic data indicates that the hydride of $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$ has a residual negative charge of $-0.45 e$, and the methide has $-0.39 e$ residual charge.³ Therefore, it was of interest to investigate the chemistry of I with nucleophiles of various strengths in order to ascertain the stability of H vs. N bridge bonds.

Experimental Section

Apparatus and Procedures.—Because of the pyrophoric nature of many of the reactants and products, materials were manipulated by standard techniques in a vacuum line equipped with mercury float and Kontes 4-mm Teflon valves. Transfer of nonvolatile material was performed in a metal Kewanee dry-box under a nitrogen atmosphere (Burdett high purity grade)

further dried with Linde 4A molecular sieve and P_2O_5 "granusic" Boher, reagent grade.

Infrared spectra of volatile materials were obtained in the gas phase using a 10-cm cell fitted with polished KBr plates. Low-volatile solids were milled in the drybox using Nujol or Fluorolube which had been dried and stored over Linde 4A molecular sieve. The mull spectra were run between KBr plates while liquids were run neat. Spectra were obtained on a Perkin-Elmer Model 457 grating spectrometer in the range 4000–400 cm^{-1} and calibrated by use of the 1376- cm^{-1} peak of Nujol or by superimposition of the 1601- cm^{-1} peak of a 0.05-mm polystyrene film. Band intensities are reported following the method of Durkin, DeHayes, and Gloré.⁴

Nuclear magnetic resonance spectra were obtained on solutions hermetically sealed in precision ground 5-mm o.d. Pyrex tubes, Yorde Mfg. Co. Spectra were run on a Varian A60-A spectrometer and were calibrated by using the solvent as an internal standard. All chemical shifts are reported with respect to tetramethylsilane. Analyses were performed as previously described.⁵

Reagents.—Solvents unless otherwise specified were obtained from J. T. Baker Chemical Co. as ACS analytical reagent grade and were dried and stored over sodium-potassium liquid alloy (Na/K) until use. Toluene- d_6 and benzene- d_6 , Diaprep Inc., 99 and 99.5% isotropic purity, were dried and stored over Na/K.

(1) Work carried out in partial fulfillment of the Ph.D. degree, 1971.

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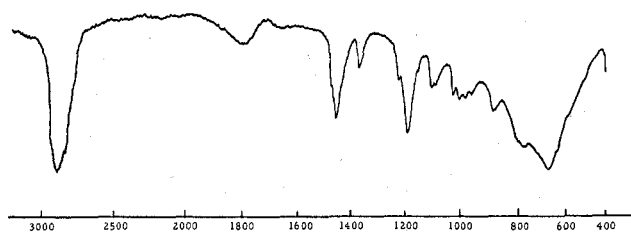


Figure 1.—Solid-state infrared spectrum of $\text{Al}_3(\text{CH}_3)_6[\text{N}(\text{CH}_3)_2]_2\text{H}$.

Aluminum trimethyl, Ethyl Corp., was vacuum fractionated through traps maintained at -22.9° (carbon tetrachloride slush) and -45.2° (chlorobenzene slush). The material retained in the -45.2° trap exhibited a vapor pressure of 9.5 Torr at 23° (lit.⁷ 8.8 Torr at 20° and 12.0 at 25°). Dimethylaminodimethylalane was obtained as a by-product in a reaction between dimethylaminodimethylborane and trimethylaluminum. The white solid was repeatedly fractionated through a 0° trap. The infrared spectrum of the material retained in the 0° trap was identical with that of an authentic sample.² Dimethylalane was prepared by the reaction of lithium aluminum hydride with boron trimethyl according to the procedure of Wartik and Schlesinger; the product had a vapor pressure of 1.9 Torr at 23° (lit.⁸ 1.8 Torr at 24.7°). Lithium aluminum hydride, Ventron, was extracted with diethyl ether prior to use. Trimethylamine, Matheson Co., Inc., was dried over lithium aluminum hydride at 0° with vigorous stirring. The vapor pressure at -78° was 6.3 Torr (lit.⁸ 6.6 Torr at -78°). Trimethylamine-dimethylalane was prepared by reaction of 0.3941 g (6.8 mmol) of dimethylalane with 11.0 mmol of trimethylamine at room temperature for 1 hr, following which 4.0 mmol of unchanged amine was recovered. Dimethyl ether, Baker reagent grade, was dried over LiAlH_4 prior to use. The infrared spectrum of the dried ether was identical with the literature spectrum.⁹ Trimethylphosphine, Ventron Inc., had a 0° vapor pressure of 159.8 Torr (lit.¹⁰ 158 Torr at 0°). The infrared spectrum showed no impurities by comparison with the literature spectrum.¹¹ Ammonia, Matheson anhydrous grade, was dried and stored over sodium at -78° until use. Bis- μ -dimethylamino-di- μ -hydrido-octamethyltetraalane (I) was prepared by the literature method.²

Reaction of I with $\text{N}(\text{CH}_3)_3$.—I, 0.351 mmol, mp range $<0.5^\circ$, was exposed to 1.053 mmol of $\text{N}(\text{CH}_3)_3$ at 0° for 3–5 min after which time the materials volatile at that temperature were removed, *in vacuo*, and separated by fractional distillation to yield a trace of white solid and 0.702 mmol of $\text{N}(\text{CH}_3)_3$. A white solid was then collected, *in vacuo*, in a trap maintained at -78° over the course of 2 days. The infrared spectrum of this material was identical with that of an authentic sample of $(\text{CH}_3)_2\text{AlH}\cdot\text{N}(\text{CH}_3)_3$. A portion of this solid was hydrolyzed with degassed hydrochloric acid for 18 hr to yield 0.253 mmol of H_2 and 0.508 mmol of CH_4 . The infrared spectrum of the non-volatile solid (mp 120 – 127° dec) is presented in Figure 1 and tabulated in Table I. The ^1H nmr spectrum of this nonvolatile white solid consists of signals at -2.17 and $+0.35$ ppm from TMS in the ratio, 1.5:1, respectively. A solution containing 0.0472 g of this material in 5.6338 g of benzene gave a freezing point depression of 0.169° which was reproduced after standing at 23° for 2 hr. The molecular weight calculated from these data is 252 ± 2 . It was necessary to take cooling curve data points well beyond the freezing point to obtain reproducible values for both the unknown and a standard naphthalene solution.

The second reaction course was followed whenever starting I had a melting point range of *ca.* 1° . Typically, 1.4889 g (4.69 mmol) of I and 12.30 mmol of trimethylamine were combined and allowed to warm to 0° briefly, as above, following which 2.46 mmol of unchanged amine was recovered. The white

TABLE I
INFRARED DATA FOR $\text{Al}_3(\text{CH}_3)_6[\text{N}(\text{CH}_3)_2]_2\text{H}$

Frequency $\pm 5 \text{ cm}^{-1}$	Tentative assignment	Frequency $\pm 5 \text{ cm}^{-1}$	Tentative assignment
2920 vs	Nujol	1044 m	$\nu_{\text{as}}(\text{NC}_2)$
2860 vs	$\nu(\text{C-H})$	1030 m	
1796 w	$\nu(\text{Al-H})$	998 m	
1462 s	Nujol	890 m	$\nu_s(\text{NC})_2$
1376 m	Nujol	790 s	$\nu_{\text{as}}(\text{AlC}_2)$
1237 m		690 vs	CH_3 wag
1202 s		581 m	$\nu_s(\text{AlC}_2)$
1177 m	$\rho(\text{CH}_3)$		
1119 m			
1105 m			

solid residue was completely sublimable and was shown to consist of $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ and $(\text{CH}_3)_2\text{AlH}\cdot\text{N}(\text{CH}_3)_3$ by comparative infrared spectroscopy.

Reaction of NH_3 with I and $[\text{Al}(\text{CH}_3)_3]_2$.—Ammonia (4.93 mmol, 0.0838 g) was condensed onto a 0.4706-g (1.48 mmol) sample of I in a 50-ml reaction bulb. The reactants were allowed to warm, and as the ammonia melted (mp -77.7°) some solution was observed. Somewhat below 0° the solution began to effervesce, and on reaching room temperature the gas evolution appeared to be complete. The mixture was cooled to -196° , and 3.02 mmol of hydrogen was collected. The mixture was warmed to room temperature and stirred for 15 min. No additional noncondensable gas was produced. The material, volatile at room temperature, was removed to a calibrated trap and expanded to yield 1.54 mmol of $\text{HN}(\text{CH}_3)_2$ characterized by infrared spectroscopy. The white solid reaction residue sublimed to the cold finger (*ca.* 15°) when heated to 45 – 55° ; its infrared spectrum was identical with that of $[(\text{CH}_3)_2\text{AlNH}_2]_n$. The ^1H nmr spectrum consisted of a broad absorption of low intensity centered at $+0.06$ ppm and a sharp singlet at $+0.71$ ppm.

A second reaction was carried out using 1.96 mmol (0.0333 g) of NH_3 and 0.2926 g (0.92 mmol) of I under conditions similar to those described above. The noncondensable gas from this reaction was characterized as 1.26 mmol of H_2 . The volatile materials were expanded to yield 0.68 mmol of slightly impure dimethylamine. The ^1H nmr spectrum of the residue contained all of the peaks present in the spectrum of the sublimed material from the reaction previously described. In addition, peaks were observed at -2.02 , -1.90 , and $+0.57$ ppm.

For purposes of comparison, 0.1421 g (1.97 mmol monomer) of aluminum trimethyl and 1.93 mmol of ammonia were condensed into a reaction vessel. On warming to room temperature, approximately 1 mmol of noncondensable gas formed and the residue was a white solid. Heating this solid to 70 – 80° resulted in additional noncondensable gas formation and melting of the solid to form a colorless liquid. At this point a total of 1.73 mmol of CH_4 was collected, and the reaction residue was sublimed to a 23° cold finger at 70 – 80° . The infrared data associated with this white crystalline solid are as follows: 3314 (m), 3254 (m), 2917 (m), 2883 (m), 2821 (m), 1610 (m), 1190 (m), 1056 (w), 969 (s), 946 (s), 930 (s), 890 (m), 786 (m, sh), 714 (vs), 608 (m), 578 (m, sh), and 479 cm^{-1} (w).

Reaction of I with $\text{P}(\text{CH}_3)_3$.—Trimethylphosphine, 4.78 mmol (0.3680 g), was condensed onto 0.4865 g (1.53 mmol) of I in a 50-ml reaction bulb which was then closed and warmed briefly to room temperature resulting in partial solution of the solid. The reactants were cooled to 0° , and the materials volatile at that temperature were condensed into a calibrated trap and expanded to yield 2.74 mmol of gas whose infrared spectrum matched that of the starting phosphine (2.74 mmol of $\text{P}(\text{CH}_3)_3$, 0.2110 g). This gas was returned to the flask and the reaction mixture stirred at room temperature for 2 days. The materials volatile at 0° were again removed and found identical in amount and infrared spectrum with the first gas sample. The reaction residue was found to have assimilated 181.1 mg of mass under those conditions (0.1811 g, 2.36 mmol of $\text{P}(\text{CH}_3)_3$). The reaction bulb was warmed to room temperature and pumped to constant weight. During this process, an additional 0.5853 g of matter was removed from the reaction mixture. This material retained by the reaction mixture at 0° but removed at room temperature (23 – 25°) was examined. The vapor pressure over this material was 31 Torr at 23° and was shown to be due to $\text{P}(\text{CH}_3)_3$ by examination of its infrared spectrum. This higher volatile material was removed *in vacuo* from the mixture, and a

(6) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, N. Y., 1948.

(7) D. F. Schriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

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

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crystalline material was sublimed into the gas cell. The infrared spectrum of this latter material was identical with that of $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ except for weak bands due to trimethylphosphine. The low-volatile residue consisted of a white solid and a viscous clear liquid at this point. The infrared spectrum of this white solid residue which remained in the reaction bulb was shown to be pure I by its infrared and proton spectra. The infrared spectrum of the viscous clear liquid contains no ν_{AlH} absorptions near 1800 cm^{-1} as are observed for $(\text{CH}_3)_2\text{AlHP}(\text{CH}_3)_2$ and $[(\text{CH}_3)_2\text{AlH}]_3$.

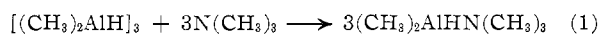
Reaction of I and $[(\text{CH}_3)_2\text{AlH}]_3$ with $\text{O}(\text{CH}_3)_2$.—Dimethyl ether, 5.02 mmol (0.2309 g), was condensed onto a 0.5342-g (1.68 mmol) sample of I in a 50-ml bulb which was closed and allowed to warm to room temperature briefly. The volatile material was removed at this time and proved to be 5.02 mmol of the starting ether which was returned to the reaction flask stirred at room temperature. After 1 day CH_4 (1.26 mmol) was collected and only 4.42 mmol of ether recovered. All condensable phases were returned to the flask and the reaction continued at room temperature with periodic CH_4 collection as follows [time (days)/mmol of CH_4]: 0.54/0.69, 1.25/1.18, 2/2.26, 3/3.02, 5/3.32, 12/3.90, 14/4.04, 17/4.06. After 17 days the reaction vessel was cooled to 0° , and the volatile materials were removed *in vacuo* and fractionated through a -78° trap into a -196° trap. The material passing the -78° trap was shown by its -78° vapor pressure of 3.0 Torr (lit. 35.3 Torr¹²) and infrared spectrum to be $\text{O}(\text{CH}_3)_2$ and was expanded to produce 2.40 mmol. The trace of material retained in the -78° trap appeared to be a mixture of $\text{O}(\text{CH}_3)_2$ and $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ as judged by its infrared spectrum and was not characterized further. Colorless crystals were removed at this point; their infrared and proton spectra were identical with $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$. The infrared spectrum of the colorless liquid residue contained a broad absorption at 1790 cm^{-1} .

A second reaction between 0.1499 g (0.47 mmol) of I and 1.61 mmol of $\text{O}(\text{CH}_3)_2$ was carried out under conditions identical with those above except that the reaction was stopped by removal of the ether after 2 days. At that time, 0.46 mmol of CH_4 and 0.68 mmol of unchanged ether were recovered from the reaction mixture maintained at 0° . Over a period of 3–4 days this mixture separated into a colorless liquid, retained in the lower portion of the bulb, and a colorless crystalline solid which sublimed to the upper portion of the bulb. The infrared spectrum of the liquid contained a broad absorption at 1800 cm^{-1} while the spectrum of the solid was identical with that of $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$.

For purposes of comparison, dimethylalane, *ca.* 0.1500 g ($\pm 0.02\text{ g}$; $\sim ca.$ 3 mmol of monomer) was combined with 1.97 mmol of dimethyl and stored at room temperature for 2.5 days. These two substances reacted to form 1.70 mmol of methane during that time. This reaction was not investigated further because the evolution of methane was the commodity of interest.

Results and Discussion

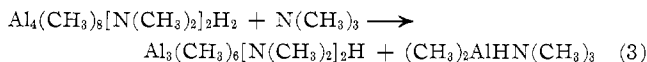
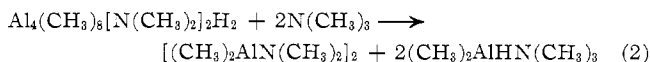
Covalent compounds of aluminum are very strong Lewis acids and as such are capable of forming adducts, even with weak Lewis bases. The oligomerization of $(\text{CH}_3)_2\text{AlH}$ and $(\text{CH}_3)_3\text{Al}$ are examples of this type of behavior where the methide and hydride moieties are considered the weak bases. In principle, a weak base may be displaced by a stronger base and this type of reaction is exemplified by the reaction represented by eq 1, where the weak base, hydride, is displaced by the



strong base, N. This reaction is aided by the ease with which a five-coordinate transition state is reached around the aluminum. One can envisage a nucleophilic attack by the base on a four-coordinate aluminum atom in an oligomer to form a five-coordinate transition state followed by rupture of the weaker coordinate covalent bond resulting in the formation of a new adduct. The molecular formulation of I has been interpreted to contain two different kinds of bridge

bonds, one containing a nitrogen atom and the other containing a hydrogen atom.² Reactions of I with a series of Lewis bases were undertaken as part of the development of the general chemistry of this new species, and to determine the relative stability of this aluminum heterocycle toward ring cleavage.

Reaction of I with $\text{N}(\text{CH}_3)_3$.—The reaction of I in the presence of 3 molar equiv of trimethylamine was found to follow two separate paths, summarized by eq 2 and 3. The reaction represented by eq 2 repre-



sents complete degradation of I into its molecular components in their most stable form in the reaction environment. The reaction of I with 1 molar equiv of $\text{N}(\text{CH}_3)_3$, eq 3, takes place when I is ultrapure, *i.e.*, when the melting point range is $\leq 0.5^\circ$. The former reaction occurs with samples whose melting point ranges are *ca.* 1° . The 1:1 stoichiometry represented in eq 3 is verified by recovery of all but 0.95 molar equiv of the trimethylamine and recovery of a low-volatile white solid which sublimes *in vacuo* from the reaction bulb at room temperature to a trap maintained at -78° . This solid is identified as $(\text{CH}_3)_2\text{AlHN}(\text{CH}_3)_3$ by comparison of its infrared spectrum with that of an authentic sample. In addition, the mass of sublimed material corresponds to loss of 0.91 molar equiv of $(\text{CH}_3)_2\text{AlH}$.

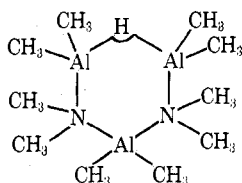
The white solid residue exhibits a cryoscopic molecular weight of 252 ± 3 in benzene which does not change when the solution is warmed to 25° for 2 hr and the molecular weight is then redetermined. The reaction stoichiometry and the molecular weight are consistent with the molecular formulation, $\text{Al}_3(\text{CH}_3)_6[\text{N}(\text{CH}_3)_2]_2\text{H}$ (260). The proton spectrum of this species contains absorbances at -2.17 ppm and a broader singlet at $+0.35\text{ ppm}$ in the ratio *ca.* 1.5. The absorbance at -2.17 ppm is in the proper region for assignment to a methyl group on nitrogen (*cf.* -2.11 ppm for I), and the absorbance at $+0.35\text{ ppm}$ is assigned to methyl groups on aluminum (*cf.* $+0.40\text{ ppm}$ for I). The infrared spectrum of the white residue, Figure 1 and Table I, also supports the proposed formulation. Of particular importance is the presence of the Al–H stretch at 1796 cm^{-1} , indicating the presence of an aluminum hydride, and the absence of bands due to I at 474, 581, 876, and 1098 cm^{-1} and the absence of bands due to $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ at 476 and 576 cm^{-1} , indicating that the solid is not an admixture of I and $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$.^{2,5}

The bands in the infrared spectrum can be tentatively assigned based on comparison with previous reports. As mentioned above, the 1796-cm^{-1} band is assigned to the Al–H stretch. The relatively low energy of this band is consistent with a relatively high electron density about aluminum, and the breadth of this absorbance is consistent with a bridging hydride.¹³ The bands at 1237, 1202, 1177, 1119, and 1105 cm^{-1} are assigned to methyl rocking motions by comparison with bands at 1258, 1202, 1172, and 1128 cm^{-1} in $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_3$.⁵ The lack of strong bands be-

(12) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

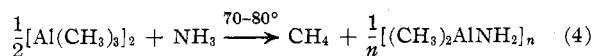
(13) G. Schomburg and E. G. Hoffman, *Z. Elektrochem.*, **61**, 1110 (1957).

tween 1160–1170 and 980–990 cm^{-1} indicates that no terminal NC_2 groups are present.⁵ The bands at 1044 and 890 cm^{-1} are assigned to the antisymmetric and symmetric NC_2 modes for bridging NC_2 groups by reference to the same modes which appear at 1043 and 901 cm^{-1} in $\text{Al}[\text{N}(\text{CH}_3)_2]_3$.⁵ The bands at 790 and 595 cm^{-1} are assigned to the asymmetric and symmetric AlC_2 modes by comparison with the values of 775 and 581 cm^{-1} for these modes in I. The strong band at 690 cm^{-1} is assigned to a methyl wag by reference to the 714- cm^{-1} band in $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ and the 670- cm^{-1} band in I.⁵ The infrared spectrum allows the following conclusions to be drawn about the structure of the compound: NC_2 groups are present but only in bridging positions; Al–H groups are present, probably in bridging positions; AlC_2 groups are present and are in terminal positions. The molecular structure most consistent with the ir, ^1H nmr, molecular weight, and reaction stoichiometry data is



When very slightly impure I is exposed to excess trimethylamine, reaction occurs according to eq 2 wherein all but 2.0 molar equiv of the amine is recovered unchanged. The white solid products sublime slowly, *in vacuo*, leaving no residue. The higher volatile solid is identified as $(\text{CH}_3)_2\text{AlHN}(\text{CH}_3)_2$ and the lower volatile solid as $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ by the exact match of their infrared spectra with authentic samples of these two solids. The reaction with 2 molar equiv of amine was verified in detail for the first three times and subsequently by amine uptake only. It is probable that small amounts of impurities catalytically cause addition of a second molar equivalent of amine.

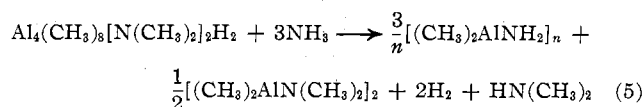
Reaction of I with NH_3 .—Treatment of I with ammonia can best be understood by comparison of this reaction with that of $[\text{Al}(\text{CH}_3)_3]_2$ and NH_3 . Aluminum trimethyl and NH_3 react according to eq 4. The



low-volatile material from this reaction sublimates at 70–80° to form white crystals. The infrared spectrum of $[(\text{CH}_3)_2\text{AlNH}_2]_n$ contains a sharp doublet at 3314 and 3254 cm^{-1} which is assigned to $\nu(\text{NH}_2)$ and a sharp singlet at 1610 cm^{-1} to $\delta(\text{NH}_2)$. The band centered around 1190 cm^{-1} is assigned to methyl rocking modes for aluminum methyl groups (*cf.* 1212, 1194, and 1164 cm^{-1} for I). The bands at 787 and 578 cm^{-1} are assigned to ν_{as} - and $\nu_{\text{s}}(\text{AlC}_2)$, respectively (*cf.* 775 and 581 cm^{-1} for I). The 608- and 714- cm^{-1} bands are assigned to an aluminum methyl deformation (*cf.* 670 and 618 cm^{-1} for I). The bands at 969, 946, 930, and 890 cm^{-1} remain to be assigned. Two of these may represent the torsional oscillation of the NH_2 group. Although this mode usually occurs 100–150 cm^{-1} lower in frequency, it is possible that strong coupling with the AlC_2 torsional mode raises the energy of this band. Comparison with the literature properties is not possible for $[(\text{CH}_3)_2\text{AlNH}_2]_n$ because the only mention

of this compound is in an article dealing with reactions of $(\text{CH}_3)_2\text{Al-X}$ molecules, and no details of preparation or spectral properties were presented.¹⁴

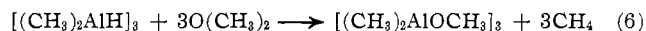
Treatment of $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$ with 3 mol of NH_3 affords the reaction described by eq 5. The ex-



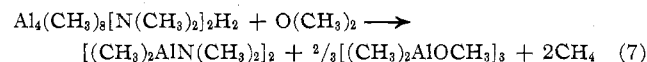
perimentally found ratios of NH_3 consumed to H_2 and $\text{HN}(\text{CH}_3)_2$ evolved were 3:2:1. It is clear that ammonia is protonic toward I as well as a transaminating reagent. In order to determine which of these reactions are preferred, I was treated with 2 molar equiv of NH_3 in the hope that either H_2 or $\text{HN}(\text{CH}_3)_2$ would be evolved exclusively. In this latter case, again both were evolved and in the *ca.* ratio $2\text{H}_2:1\text{HN}(\text{CH}_3)_2$. It may safely be concluded that transamination and hydride abstraction from I are simultaneous reactions of equal importance.

Reaction of I with $\text{P}(\text{CH}_3)_3$.—When a solution of I in $\text{P}(\text{CH}_3)_3$ is cooled to 0° and the $\text{P}(\text{CH}_3)_3$ removed, *in vacuo*, *ca.* 1 molar equiv of $\text{P}(\text{CH}_3)_3$ is retained. The majority of this $\text{P}(\text{CH}_3)_3$ is subsequently evolved at *ca.* 25°. Pumping on the residue affords trace quantities of $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$, identified by its ir spectrum, and an unidentified low volatile liquid which does not contain Al–H bonds based on the fact that no ir absorptions were present in the 1800- cm^{-1} range. It appears that $\text{P}(\text{CH}_3)_3$ serves principally as a solvent for I because if it behaved as a nucleophile, one would expect formation of $(\text{CH}_3)_2\text{AlHP}(\text{CH}_3)_3$ and the latter was definitely not present based on comparative infrared studies with the simple adduct.

Reaction of $(\text{CH}_3)_2\text{AlH}$ and I with $\text{O}(\text{CH}_3)_2$.—Dimethylalane reacts relatively fast with $\text{O}(\text{CH}_3)_2$ according to eq 6. This reaction may be viewed as



nucleophilic attack on the alane ring affording the intermediate $(\text{CH}_3)_2\text{AlHO}(\text{CH}_3)_2$, followed by elimination of CH_4 . The principal reaction of $\text{O}(\text{CH}_3)_2$ with I appears to be identical with that with $[(\text{CH}_3)_2\text{AlH}]_3$ but at a much slower rate indicating the eight-membered ring of I is more stable to $\text{O}(\text{CH}_3)_2$ than the six-membered dimethylalane ring. This reaction is summarized by eq 7. In both reactions the methoxy prod-



uct was characterized by its infrared and ^1H nmr spectrum: σ –3.11 and +0.62 ppm (*lit.*¹⁵ –3.16 and +0.60 ppm). The $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ was identified by its infrared spectrum.

Correlation of Physical and Chemical Properties of I.—I is stable as a solid at 25° in the absence of O_2 and H_2O as demonstrated by the successful completion of an X-ray crystal structure, on a single crystal, which spanned a 6-week period.³ Even under X-ray bombardment, decomposition is less than 5%. In solution, however, decomposition is much more rapid as indicated by the ^1H nmr spectrum of I as a function of time

(14) M. I. Prince and K. Weiss, *J. Organometal. Chem.*, **2**, 166 (1964).
 (15) T. Mole, *Aust. J. Chem.*, **19**, 373 (1966).

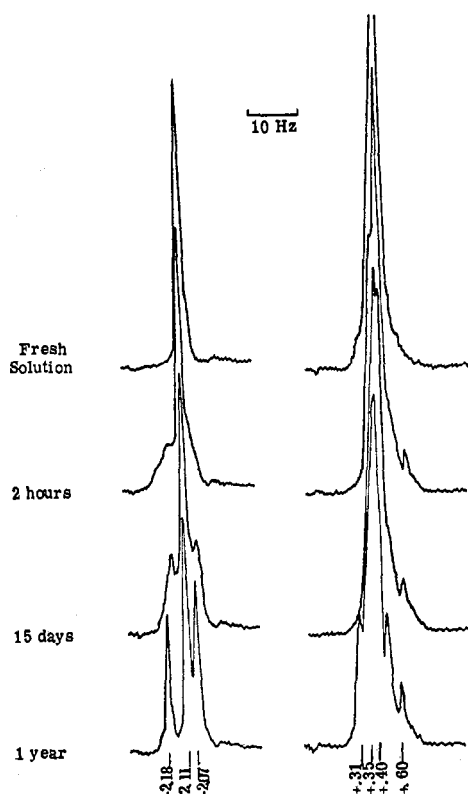


Figure 2.—Proton nmr spectrum of $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$ as a function of time.

(Figure 2). A fresh solution of I in benzene exhibits two ^1H singlets; one of area 1, σ -2.11 ppm, due to the amino methyls, and one of area 2 at $+0.40$ ppm due to the aluminum methyls. Axial and equatorial methyl groups which are expected if the ring has a static conformation in solution are not resolved. There are two possible explanations for the lack of such resolution: a rapid conformation inversion of the ring or very nearly identical chemical shifts for the axial and equatorial groups. If the equivalence of the methyl groups is due to rapid inversion, it would be possible, in principle, to lower the temperature and stop the inversion process. However, the temperature at which inversion ceases depends on the energy barrier surmounted in that process. For cyclohexane systems, the barrier to inversion is 6.4 kcal/mol and the temperature at which peak broadening occurs is -60° .¹⁶ Because the ring size of I is larger than cyclohexane and because the hydrogen bridge has no directional preference, it is felt that the energy barrier to ring inversion in I is smaller than 6.4 kcal/mol; consequently, the nmr spectrum should not show peak broadening until temperatures below -60° are reached. Experimentally the peak widths of a toluene- d_3 solution of I are independent of temperature over the range studied, $+38$ to -63° . There is a small dependence of the amine methyl chemical shift on the temperature, causing that resonance to move to higher field at lower temperatures; *i.e.*, the apparent-chemical shift at -63° is -1.86 ppm. While the alternate possibility of coincident chemical shifts cannot be unequivocally excluded, it seems very unlikely that the axial and equatorial methyls on the nitrogen atom and on each of the two nonequivalent aluminum atoms would all have accidentally identical chemical shifts.

(16) W. B. Moniz and J. A. Dixon, *J. Amer. Chem. Soc.*, **83**, 1670 (1961).

The nmr spectrum of I as a function of time indicates decomposition in solution. The first new absorptions appear within an hour if the sample is maintained at room temperature. The amine methyl absorbance broadens on the low-field side, at *ca.* -2.18 ppm, as does the aluminum methyl absorbance, at *ca.* $+0.35$ ppm, and a high-field peak appears at 0.60 ppm above TMS. These absorbances can be assigned as follows: the amine shoulder and the 0.60 -ppm peak are attributed to $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ (lit.¹⁷ -2.16 and $+0.59$ ppm), and the aluminum alkyl shoulder is attributed to $[(\text{CH}_3)_2\text{AlH}]_3$ whose chemical shift was determined to be $+0.35$.¹⁷ The decomposition process continues to increase the intensity of the new peaks at the expense of the parent for a period of 10–14 days at which time new absorbances at -2.07 and $+0.35$ ppm begin to appear. The latter absorbance can be attributed to methyl protons on aluminum trimethyl which are known to exchange terminal and bridging groups rapidly at ambient temperatures (lit.¹⁵ $+0.34$ ppm). The presence of aluminum trimethyl requires an exchange of either hydrido or dimethylamino groups with an alkyl group to have taken place, and hence the -2.07 ppm absorbance is assigned to the exchanged species, either $\text{CH}_3\text{Al}[\text{N}(\text{CH}_3)_2]_2$ or $\text{CH}_3\text{Al}(\text{H})\text{N}(\text{CH}_3)_2$. Finally, after 1 to 1.5 months the spectrum reaches its final form with the appearance of a very small absorbance at $+0.31$ ppm.

The proposed scheme of decomposition is supported by the fact that when an nmr tube, which contained decomposed I, was broken open on the vacuum line and the solvent removed, the infrared spectrum of the products of decomposition clearly showed the presence of the more highly volatile $[(\text{CH}_3)_2\text{AlH}]_3$. The infrared cell was cooled to 0° and pumped on for several hours to remove this material following which an infrared spectrum of the residual white solid was obtained. This product had a spectrum very similar to $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ with traces of residual $[(\text{CH}_3)_2\text{AlH}]_3$. No infrared evidence of the presence of $[(\text{CH}_3)_3\text{Al}]_2$ was observed. Further credence is lent the decomposition scheme by low-temperature nmr study of the decomposed solution of I. The exchange of bridge and terminal methyl groups of the aluminum trimethyl proposed to be present can be stopped at low temperature, resulting in two separate resonances for these groups.¹⁸ When a toluene- d_3 solution of I which had reached the terminal phase of decomposition is cooled to -63° , the absorbance at $+0.36$ begins to broaden and decrease in intensity. Lower temperatures could not be reached owing to the freezing of the chloroform external standard. At -63° , however, the spectrum of $[(\text{CH}_3)_3\text{Al}]_2$ broadens also and is finally resolved into terminal and bridging resonances at -75° .¹⁸ It is interesting to note that the final solution spectrum of I and its decomposition products still shows the two absorbances due to I, even in samples which are 1.5 years old. The presence of I suggests that it may exist in equilibrium with its decomposition products and, conversely, that a mixture of $[(\text{CH}_3)_3\text{Al}]_2$, $[(\text{CH}_3)_2\text{AlH}]_3$, $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$, and either $[\text{CH}_3\text{Al}(\text{H})\text{N}(\text{CH}_3)_2]_x$ or $\{\text{CH}_3\text{Al}[\text{N}(\text{CH}_3)_2]_2\}_2$ should produce I after the system attains equilibrium. A similar system, $[(\text{CH}_3)_2\text{AlH}]_3$, $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$, and $[(\text{CH}_3)_3\text{Al}]_2$, was studied but after 1.5 months the

(17) E. P. Schram, *Inorg. Chem.*, **5**, 1291 (1966).

(18) N. Müller and D. E. Pritchard, *J. Amer. Chem. Soc.*, **82**, 248 (1960).

spectrum had not changed from its original appearance.²

The thermodynamic instability and low barrier to dissociation have important influences on the chemistry of I. If the interaction of unreactive solvent molecules with I provides sufficient perturbation to bring about slow dissociation, then the action of a strongly coordinating base would probably achieve similar results in a shorter time. This result is in fact what is observed. The generally accepted order of Lewis base strengths toward Al is $N > O > P$. Trimethylamine reacts rapidly with I to either partly or completely degrade I into its molecular components. Dimethyl ether behaves similarly followed by further chemical reaction affording CH_4 . The relative carbonium character of CH_3 associated with $\text{O}(\text{CH}_3)_2$ and $\text{N}(\text{CH}_3)_3$ is in the expected order with respect to the relative ionic character of $\delta^-\text{O}-\text{C}^{\delta+}$ vs. $\delta^-\text{N}-\text{C}^{\delta+}$, 22 and 12%, respectively, as calculated by the Pauling method.¹⁹ Trimethylphosphine serves principally as a solvent for the solution decomposition of I, similar in behavior to benzene. A charge refinement of the crystallographic data indicates that the hydride of I has a large residual negative charge of $-0.45 e$ and the methide has $-0.39 e$ residual charge.³ These values imply that these moieties would make I a very good reducing agent. If the fact that I is thermodynamically unstable is superimposed on these values, one would conclude that I should be one of the strongest reducing agents known owing to the additional release of free

energy in forming the more stable dissociation products.

It is interesting to compare the relative stabilities of $[(\text{CH}_3)_2\text{AlH}]_3$, $\text{Al}_4(\text{CH}_3)_8[\text{N}(\text{CH}_3)_2]_2\text{H}_2$, $\text{Al}_3(\text{CH}_3)_6[\text{N}(\text{CH}_3)_2]_2\text{H}$, and $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ toward nucleophilic attack. Dimethylaminodimethylaluminum, $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$, is a four-membered ring containing two nitrogen bridges and is unreactive toward $\text{N}(\text{CH}_3)_3$. As a rationale for this behavior, it is noted that hydride bridges and alkyl or aryl bridges are inherently "electron deficient"; *i.e.*, a closed-shell electron configuration cannot be simultaneously accomplished for all atoms in the molecule. Amine bridges, on the other hand, do not suffer from electron deficiency because the nitrogen atom has a lone pair of electrons which it may use to form a dative bond to aluminum. The result of such a bond is polarization of the electron cloud about nitrogen, not deficiency. Thus, in the series at hand, reaction by nucleophilic attack on the ring produces fissure of the ring until a certain amount of deficiency is lost; *i.e.*, the framework of $[(\text{CH}_3)_2\text{AlH}]_3$ contains 6 electrons spread over 6 bonds (1.0 electron/bond), I contains 12 electrons in 8 bonds (1.5 e/bond), $\text{Al}_3(\text{CH}_3)_6[\text{N}(\text{CH}_3)_2]_2\text{H}$ is proposed to contain 10 electrons for 6 bonds (1.67 e/bond), and $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ 8 electrons and 4 bonds (2.0 e/bond). It would be interesting to compare molecular orbital calculations for each of these heterocyclic rings with the observed order of stability.

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Far-Infrared and Tin-119m Mössbauer Study of Complexes of Phosphorus- and Arsenic-Containing Ligands with Tin(IV) Halides

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Twenty-five complexes of the type SnX_4B_2 , where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$, $\text{B} = \text{R}_3\text{PO}$ ($\text{R} = \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{C}_6\text{H}_5$), $(\text{C}_6\text{H}_5)_3\text{AsO}$, $(\text{CH}_3)_2\text{SO}$, $(\text{C}_6\text{H}_5)_3\text{As}$, R_3P ($\text{R} = \text{C}_4\text{H}_9, \text{C}_6\text{H}_5, \text{C}_8\text{H}_{17}$), or $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{P}$, and $\text{B}_2 = o\text{-}[(\text{C}_6\text{H}_5)_2\text{P}]\text{C}_6\text{H}_4$, $o\text{-}(\text{CH}_3)_2\text{N}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2$, or $[o\text{-}(\text{CH}_3)_2\text{N}(\text{C}_6\text{H}_4)]_2\text{P}(\text{C}_6\text{H}_5)$, fifteen of them previously unreported, have been synthesized and studied by $^{119\text{m}}\text{Sn}$ Mössbauer and far-infrared techniques. Cis and trans isomers have been distinguished by the number of $\nu(\text{Sn}-\text{X})$ and $\delta(\text{Sn}-\text{X})$ bands they exhibit; those assigned trans on this basis are found to exhibit Mössbauer quadrupole splittings of *ca.* 1 mm/sec. The point-charge model predicts that the QS for cis isomers should be half that for the trans, and the QS for these isomers is barely resolvable as expected. In one case, $\text{SnCl}_4 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$, the infrared and Mössbauer evidence leads to opposite stereochemical assignments. In general, the oxygen donor ligands give cis complexes while all the fifth-group donor ligands but triphenylarsine give the trans isomers except when bidentate. These differences are rationalized on steric arguments.

The quadrupole splitting (QS) parameter in $^{119\text{m}}\text{Sn}$ Mössbauer spectroscopy has, with the application of the results of point-charge calculations,² proved useful in distinguishing cis and trans isomers in octahedral organotin complexes. The extension of the point-charge

model to other geometries^{3,4} is proving useful as well, but the further application of QS data to the elucidation of molecular symmetries is limited by the apparently large number of cases of asymmetric tin(IV) compounds for which the QS is small compared with the relatively

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