

Figure 2.—The view of several unit cells down the  $c$  axis, showing the layered nature of the structure. The dotted lines indicate probable hydrogen bonds. The chloride ions are almost exactly midway in elevation between the N(1) atoms. The double dotted line between Cl and N(1) indicates probable hydrogen bonds to the nitrogen from chloride ions above and below.

different nitrogen atoms of three different cations. All three hydrogen atoms of the ammonia ligand and the lone hydrogen of the amine nitrogen appear to participate in hydrogen bonding. A careful study of a model of the structure showed that for one orientation of the ammonia ligand all of these hydrogen bonds have reasonable geometries. The Cl–N–Cl bond angles of the H-bonded system are given in Table III. Interlayer

TABLE IV  
ANGLES MADE BY Pt–N BONDS WITH THE CRYSTAL AXES<sup>a</sup>

Bond	Angle (deg) with		
	$a$ axis	$b$ axis	$c$ axis
Pt–N(1)	158.3 (8)	59.8 (8)	88.2 (8)
Pt–N(2)	75.6 (6)	36.8 (6)	121.6 (6)

<sup>a</sup> All angles are measured from positive axes.

interaction appears to be of the weaker van der Waals type. This description is substantiated by the observation that a cleavage plane lies parallel to the [010] face, which is usually the well-developed face of the crystal. The structure can be visualized by examining Figures 1 and 2 which present projections along the  $a$  and  $c$  axes respectively.

Finally, since the major purpose of this investigation is to provide information for the interpretation of oriented single-crystal experiments, the angles that the Pt–N bonds in the cation make with the respective crystal axes are presented in Table IV. The lack of significant intermolecular interactions along the axial direction of the square-planar cation would suggest that the molecular cation be treated as an “oriented-gas” ion in subsequent spectroscopic investigations.

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CONTRIBUTION FROM THE PROPELLANTS LABORATORY, FELTMAN RESEARCH LABORATORIES, PICATINNY ARSENAL, DOVER, NEW JERSEY 07801

## The Chemistry of Alane. XIV.<sup>1</sup> The Synthesis of Dimethylaminodichloroalane<sup>2</sup>

By ROBERT EHRLICH<sup>3</sup>

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Dimethylaminodichloroalane was prepared by a variety of methods. Careful purification of the product prepared by the reaction of (CH<sub>3</sub>)<sub>2</sub>NAIH<sub>2</sub> with HgCl<sub>2</sub> in diethyl ether showed that (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Cl was a by-product impurity. This suggests that the evolution of H<sub>2</sub> in this reaction is the result not of the decomposition of unstable HgH<sub>2</sub> but of the reaction of HCl, produced in the decomposition of an intermediate HHgCl, with the hydridic alane hydrogens.

During the course of the attempted synthesis of various alane derivatives it became necessary to prepare dimethylaminodichloroalane as an intermediate. Utilizing a variation of one of the two procedures reported in the literature,<sup>4</sup> however, did not produce material

with the reported properties. In order to clarify this situation, the synthesis of dimethylaminodichloroalane was reexamined in detail.

### Experimental Section

All reagents were handled and all filtrations were performed in a nitrogen-atmosphere vacuum drybox, and all reactions were conducted under dry nitrogen. All solvents were purified and dried by refluxing with LiAlH<sub>4</sub>, distilling, and storing over LiAlH<sub>4</sub> (benzene) or over LiH (diethyl ether and tetrahydrofuran). Dimethylamine and HCl were used directly from the cylinders. Lithium dimethylamide was obtained from K & K Laboratories, Plainview, N. Y. All melting points are uncorrected. Quanti-

(1) Paper XIII: R. Ehrlich and A. R. Young, II, *J. Inorg. Nucl. Chem.*, **30**, 53 (1968).

(2) (a) Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. (b) This investigation was supported under DA Project No. 1LO13001A91A, AMCMS 5016.11.844.

(3) Industrial Chemicals Research Laboratory, Allied Chemical Corp., Morristown, N. J. 07960.

(4) J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 1798 (1961).

tative hydrolyses were performed on a Toepler pump vacuum system with a calibrated collection section. Mass spectra were performed by Sadtler Research Laboratories, Inc., Philadelphia, Pa., on an AEI MS-902B double-focusing, high-resolution spectrometer at 70 eV and 100  $\mu$ A. Infrared spectra were obtained on a Perkin-Elmer Model 621 grating spectrophotometer. Differential thermal analyses (dta) were performed on a Du Pont Model 900 differential thermal analyzer.

**Preparation of  $(\text{CH}_3)_2\text{NAlH}_2$ .**—Over a period of 3 hr 98.3 g of  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$  (1.2 mol) was added to a suspension of 75 g of powdered  $\text{LiAlH}_4$  in 1 l. of benzene with stirring and cooling. Stirring was continued at room temperature until hydrogen evolution ceased. The mixture was filtered, the filtrate was checked to ensure the absence of  $\text{Cl}^-$ , and then the clear benzene solution was freeze-dried. The white solid product was sublimed at 40–45° ( $10^{-4}$  mm), yielding 76.6 g (87% of theory), mp 93–94° (lit.<sup>5</sup> mp 89–90°). *Anal.* Calcd for  $(\text{CH}_3)_2\text{NAlH}_2$ : Al, 36.92; N, 19.17; active H, 2.76. Found: Al, 37.19; N, 19.20; active H, 2.70.

**Preparation of  $[(\text{CH}_3)_2\text{N}]_3\text{Al}$ .**—Dimethylamine was bubbled slowly through a solution of 3.1 g of  $(\text{CH}_3)_2\text{NAlH}_2$  (0.04 mol) in 100 ml of benzene at ambient temperature until no more hydrogen was evolved. The clear solution was freeze-dried and the white residue was sublimed at 90° ( $10^{-4}$  mm) to give 6.1 g (91%) of white, crystalline solid, mp 88–89° (lit.<sup>6</sup> mp 87–88°). *Anal.* Calcd for  $[(\text{CH}_3)_2\text{N}]_3\text{Al}$ : Al, 16.95; N, 26.39. Found: Al, 16.82; N, 26.50.

**Preparation of  $(\text{CH}_3)_2\text{NAlCl}_2$ . A. Reaction of  $(\text{CH}_3)_2\text{NAlH}_2$  with  $\text{HgCl}_2$  in Benzene.**—To a solution of 7.33 g of  $(\text{CH}_3)_2\text{NAlH}_2$  (0.10 mol) in 100 ml of benzene, cooled in an ice bath, was added 28.4 g of  $\text{HgCl}_2$  (0.10 mol) slowly from a side-arm dumper. Reaction was immediate but not too vigorous and gas evolution was not complete until after 16 hr; total evolved, 2.30 l. (STP, 103% of theory). During this period some white solid precipitated. The mercury was separated from the solid which was dried under vacuum at room temperature for 4 hr; weight, 6.62 g; mp 237–238°. Sublimation at 104–105° ( $5 \times 10^{-5}$  mm) did not change the melting point. *Anal.* Calcd for  $(\text{CH}_3)_2\text{NAlCl}_2$ : Al, 19.01; N, 9.87; Cl, 49.95. Found: Al, 19.36; N, 10.00; Cl, 49.53.

From the benzene solution was isolated 7.61 g of white solid, mp 210–222°. Sublimation at the usual conditions did not purify this material, but trituration with 5 ml of benzene raised the melting point to 230–235°. The infrared spectrum was identical with that of the benzene-insoluble portion. Total solid yield was 14.23 g (99% of theory).

The benzene-insoluble materials were soluble in THF, but precipitated on standing overnight at room temperature. The solid was dried under vacuum at room temperature for 4 hr. It started to decompose with foaming at 253°. *Anal.* Calcd for  $(\text{CH}_3)_2\text{NAlCl}_2 \cdot \text{THF}$ : Al, 12.60; N, 6.54; Cl, 33.12. Found: Al, 13.88; N, 6.88; Cl, 32.33.

**B. Reaction of  $(\text{CH}_3)_2\text{NAlH}_2$  with  $\text{HgCl}_2$  in  $(\text{C}_2\text{H}_5)_2\text{O}$ .**—Reaction A was repeated with the same quantities of reagents using 100 ml of ether as the solvent. Reaction was vigorous and gas evolution was complete after 8 hr. The mercury was removed by filtration and the solution was allowed to stand overnight. In the morning the solution had set up into a clear, colorless gel which was insoluble in more ether. It was broken up with 50 ml of THF, filtered, and dried at room temperature under vacuum for 72 hr; weight, 10.3 g of white, crystalline solid, mp 234–236°, identical with the material isolated from reaction A.

Evaporation of a THF solution of some of the solid and drying under vacuum for 8 hr at room temperature produced a white solid which melted with decomposition above 170°. *Anal.* Calcd for  $[(\text{CH}_3)_2\text{NAlCl}_2]_2 \cdot \text{THF}$ : Al, 15.16; N, 7.87; Cl, 39.83. Found: Al, 13.91; N, 6.49; Cl, 41.40. All of the THF was removed after pumping on the solid at room temperature for another 64 hr.

**C. Reaction of  $(\text{CH}_3)_2\text{NAlH}_2$  with  $\text{HCl}$ .**—A solution of 1.46 g of  $(\text{CH}_3)_2\text{NAlH}_2$  (0.020 mol) in 75 ml of benzene was prepared in

a round-bottom flask attached to the vacuum rack. The solution was frozen with liquid  $\text{N}_2$  and evacuated, and 0.040 mol of  $\text{HCl}$  was condensed into the flask. The mixture was allowed to warm to room temperature, stirred for about 30 min, and then refrozen to condense unreacted  $\text{HCl}$  back onto the reaction mixture. This process was repeated until no more hydrogen was evolved. The hydrogen was pumped by a Toepler pump through three liquid  $\text{N}_2$  traps into a calibrated collection system, measured, and identified as  $\text{H}_2$  by spectroscopy. Total evolution was 0.039 mol.

The benzene solution was freeze-dried to produce 2.80 g of white solid, melting over a wide range to 205°. Part of this material (1.11 g) was sublimed at 51° ( $10^{-3}$  mm) to give 0.74 g of material, mp 183–220°. A second fraction (0.28 g) was obtained at 99° ( $10^{-3}$  mm) but the melting range was similar to that of the first fraction. The ir spectra of both fractions were very similar to that of pure  $(\text{CH}_3)_2\text{NAlCl}_2$ . Trituration of the combined fractions with 5 ml of benzene gave 0.38 g of white solid, mp 236–238°, identical with pure  $(\text{CH}_3)_2\text{NAlCl}_2$ . *Anal.* Found: Al, 19.50; N, 9.69; Cl, 50.11.

The sublimation residue gave on heating to 110° ( $10^{-3}$  mm) a small amount of crystals, mp 169–172°, which contained chlorine but not aluminum. The ir spectrum was that of  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$  but not enough material was isolated for a quantitative analysis.

**D. Reaction of  $[(\text{CH}_3)_2\text{N}]_3\text{Al}$  with  $\text{AlCl}_3$ .**—A solid mixture of 1.59 g of  $[(\text{CH}_3)_2\text{N}]_3\text{Al}$  (0.01 mol) and 2.66 g of  $\text{AlCl}_3$  (0.02 mol) was heated at 90°, under  $\text{N}_2$ , in a sublimation apparatus. (The mixing of the two solids was exothermic.) Then the pressure was reduced to  $4 \times 10^{-5}$  mm and the solid was sublimed at 92–93°. The white, crystalline sublimate (3.63 g, 85% of theory) melted from 205 to 221°. Trituration with 6 ml of benzene produced 3.05 g of product, mp 232–235°, identical with  $(\text{CH}_3)_2\text{NAlCl}_2$ . *Anal.* Found: Al, 19.37; N, 9.96; Cl, 49.36.

**E. Reaction of  $\text{LiN}(\text{CH}_3)_2$  with  $\text{AlCl}_3$ . 1. In  $(\text{C}_2\text{H}_5)_2\text{O}$ .**—To a solution of 3.87 g of  $\text{AlCl}_3$  (0.029 mol) in 100 ml of ether was added 1.29 g of  $\text{LiN}(\text{CH}_3)_2$  (0.025 mol). Heat was evolved during the addition. Then the mustard-colored suspension was stirred 48 hr at ambient temperature and filtered; the solvent was removed from the filtrate leaving a red, viscous oil. The oil was dissolved in THF and allowed to stand overnight at room temperature. Obtained was 0.42 g (12%) of white precipitate, mp 257–259° dec, which was identified as  $(\text{CH}_3)_2\text{NAlCl}_2 \cdot \text{THF}$  by comparison.

**2. In THF.**—The reaction was repeated with 3.33 g of  $\text{AlCl}_3$  (0.025 mol), 1.28 g of  $\text{LiN}(\text{CH}_3)_2$  (0.025 mol), and 100 ml of THF. A clear solution resulted which yielded a yellow-orange residue. Sublimation at  $5 \times 10^{-5}$  mm and temperatures from 51 to 153° produced only 0.29 g of white, solid  $(\text{CH}_3)_2\text{NAlCl}_2$ .

Treatment of the residue with diethyl ether in a Soxhlet extractor did not remove any  $\text{LiCl}$ . The elemental analysis of the residue was poor, but the Li:Al:Cl:N ratio was 0.93:1.00:2.87:1.09 indicating the presence of the complex salt  $\text{LiAlCl}_3\text{N}(\text{CH}_3)_2$ .

**Preparation of  $[(\text{CH}_3)_2\text{N}]_2\text{AlCl}$ .**—Solid  $[(\text{CH}_3)_2\text{N}]_3\text{Al}$  (3.18 g, 0.02 mol) was mixed with 1.34 g of  $\text{AlCl}_3$  (0.01 mol) in a sublimator. There was an immediate exothermic reaction resulting in a brownish red liquid. The mixture was heated under  $\text{N}_2$  at 89–93° for 1 hr. Then the temperature was reduced to 55° and the  $[(\text{CH}_3)_2\text{N}]_2\text{AlCl}$  was sublimed at  $3 \times 10^{-5}$  mm for 4.5 hr. A total of 2.08 g (46%) of white solid was obtained, mp 59–60° (lit.<sup>6</sup> mp 55–57°). *Anal.* Calcd for  $[(\text{CH}_3)_2\text{N}]_2\text{AlCl}$ : Al, 17.92; N, 18.60; Cl, 23.54. Found: Al, 17.43; N, 18.19; Cl, 23.77.

**Preparation of  $[(\text{CH}_3)_2\text{N}]_3\text{Al}_2\text{Cl}_3$ . A. From  $[(\text{CH}_3)_2\text{N}]_3\text{Al}$  and  $\text{AlCl}_3$ .**—1. A mixture of 1.18 g of  $[(\text{CH}_3)_2\text{N}]_3\text{Al}$  (7.4 mmol) and 1.00 g of  $\text{AlCl}_3$  (7.5 mmol), which reacted exothermically with liquefaction, was heated at 90–100° for 1 hr. Sublimation at 101° ( $10^{-4}$  mm) for 4.5 hr gave 1.62 g of white crystals which melted partially at 85° and decomposed slowly above 144°. Re-sublimation at 63° ( $10^{-5}$  mm) for 6 hr did not change the melting behavior. A powder X-ray diffraction pattern showed no  $(\text{CH}_3)_2$

(5) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960).

(6) J. K. Ruff, *ibid.*, **83**, 2835 (1961).

TABLE I  
 MASS SPECTRUM OF  $(\text{CH}_3)_2\text{NAlCl}_2$ 

<i>m/e</i>	Fragment	<i>m/e</i>	Fragment
282	$\text{C}_4\text{H}_{12}\text{N}_2\text{Al}_2\text{Cl}_4^+$	140	$\text{C}_2\text{H}_6\text{NAlCl}_2^+$
267	$\text{C}_3\text{H}_9\text{N}_2\text{Al}_2\text{Cl}_4^+$	106	$\text{C}_2\text{H}_6\text{NAlCl}^+$
247	$\text{C}_4\text{H}_{12}\text{N}_2\text{Al}_2\text{Cl}_3^+$	97	$\text{AlCl}_2^+$
185	$\text{C}_4\text{H}_{12}\text{N}_2\text{AlCl}_2^+$	44	$\text{C}_2\text{H}_6\text{N}^+$

$\text{NAlCl}_2$ ,  $[(\text{CH}_3)_2\text{N}]_2\text{AlCl}$ ,  $[(\text{CH}_3)_2\text{N}]_3\text{Al}$ , or  $\text{AlCl}_3$ . Solution of the solid in THF and standing for 24 hr at room temperature gave no precipitate and solvent removal gave unchanged starting material. *Anal.* Calcd for  $[(\text{CH}_3)_2\text{N}]_3\text{Al}_2\text{Cl}_3$ : Al, 18.45; N, 14.36; Cl, 36.36. Found: Al, 19.23; N, 13.10; Cl, 39.61.

2. Reaction 1 was repeated with 1.60 g of the alane and 1.34 g of  $\text{AlCl}_3$  (both 0.01 mol) in 50 ml of THF. The clear solution was stirred for 16 hr at ambient temperature. Solvent removal gave 2.91 g of white solid, mp 80–83° dec. The ir spectrum and powder X-ray diffraction pattern were identical with those of the product of reaction 1.

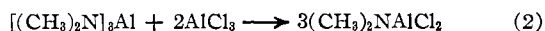
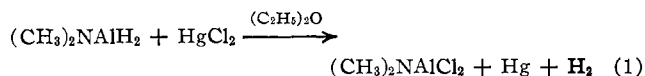
**B. From  $(\text{CH}_3)_2\text{NAlCl}_2$  and  $[(\text{CH}_3)_2\text{N}]_2\text{AlCl}$ .**—The clear, colorless solution of 1.14 g of  $[(\text{CH}_3)_2\text{N}]_2\text{AlCl}$  and 1.08 g of  $(\text{CH}_3)_2\text{NAlCl}_2$  (both 7.6 mmol) in 50 ml of THF was stirred 24 hr at ambient conditions. A small amount of gelatinous material was removed by filtration and the solvent was removed from the filtrate leaving 1.78 g of white solid, mp 73–77° dec, identical with the products from part A.

**Isolation of  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ .**—A total of 27.2 g of  $\text{HgCl}_2$  (0.1 mol) was added slowly to a solution of 7.3 g of  $(\text{CH}_3)_2\text{NAlH}_2$  (0.1 mol) in 100 ml of diethyl ether. Hydrogen evolution over a 16-hr period totaled 2.16 l. (STP, 96% of theory). Filtration produced 29.0 g of gray solid which on treatment with THF gave 20.0 g of Hg (99%) and 10.9 g of  $(\text{CH}_3)_2\text{NAlCl}_2 \cdot \text{THF}$ .

Removal of diethyl ether from the filtrate produced 5.0 g of white waxy solid. Trituration with benzene gave a total of 1.7 g of  $(\text{CH}_3)_2\text{NAlCl}_2$ , mp 232–235°. From the residue was isolated 1.9 g of white solid, mp 109–140°. Sublimation at 108° (10<sup>-3</sup> mm) for 6 hr gave 0.84 g of white crystals, mp 171–173°. *Anal.* Calcd for  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ : C, 29.46; H, 9.89; N, 17.18; Cl, 43.48. Found:<sup>7</sup> C, 29.78; H, 10.32; N, 17.70; Cl, 41.78; Al, <0.7. The ir and mass spectra and the powder X-ray diffraction pattern confirmed that the solid was  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ .

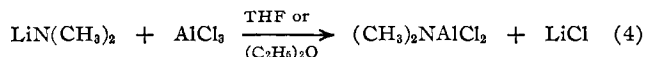
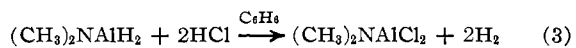
### Results and Discussion

The synthesis of dimethylaminodichloroalane, utilizing the two procedures, (1) and (2), reported in the



literature,<sup>4,6</sup> did not produce a material with the physical properties listed for the desired compound. Pure  $(\text{CH}_3)_2\text{NAlCl}_2$  could not be obtained from the crude products by sublimation, the sublimes still showing the presence of impurities by their broad melting ranges. Repeating reaction 1 with benzene as the solvent instead of diethyl ether produced pure  $(\text{CH}_3)_2\text{NAlCl}_2$ , but with a melting point 86° higher than that reported.

In order to verify the preparation of the dichloride the reactions shown in (3) and (4) were also run. After the



necessary purifications, they produced the high-melting  $(\text{CH}_3)_2\text{NAlCl}_2$ . The reactions with  $\text{LiN}(\text{CH}_3)_2$  were

(7) Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

complicated by complex salt formation and almost no  $(\text{CH}_3)_2\text{NAlCl}_2$  was isolated in THF.

The  $(\text{CH}_3)_2\text{NAlCl}_2$  prepared in this study melted at 237–238° (*vs.* 151° reported<sup>4,6</sup>). A differential thermal analysis showed no evidence of any exothermic decomposition but did show the melting endotherm at 236° and a very large endotherm doublet centered at 267°. An examination of the chloride above its melting point in a capillary tube indicated that this endotherm was associated primarily with a boiling point although some decomposition was also occurring.

A mass spectrometric examination showed that the dichloride was dimeric in the vapor state, and no fragments larger than the dimer molecular ion were observed. (The major fragment ions of the mass spectrum are listed in Table I.<sup>8</sup>) It is probable that the dimer is formed by bridging through the dimethylamino groups, as in  $(\text{CH}_3)_2\text{N}(\text{BCl}_2)_2$ ,<sup>9</sup> rather than the chlorines.

The similarities of the sections between 850 and 1500  $\text{cm}^{-1}$  (due to the dimethylamino groups) in the infrared spectra of all of the dimethylaminoalane compounds (Table II) and the differences in the region below 600  $\text{cm}^{-1}$  from that of  $\text{AlCl}_3$  support this conclusion.

The dichloride possessed a novel powder X-ray diffraction pattern (Table III) which showed that none of the other dimethylaminoalane derivatives nor  $\text{AlCl}_3$  was present.

It was possible to isolate two stable, but weak, THF adducts of  $(\text{CH}_3)_2\text{NAlCl}_2$  by dissolving the pure dichloride in THF. The 1:1 complex precipitated from solution on standing at room temperature overnight, but the THF could be removed readily by pumping on the complex at room temperature. After 8 hr the composition of the adduct approached that of  $[(\text{CH}_3)_2\text{NAlCl}_2]_2 \cdot \text{THF}$ , and after 72 hr the solvent-free dichloride was recovered. In contrast,  $(\text{CH}_3)_2\text{NAlH}_2$  does not form a complex even with as strong a Lewis base as trimethylamine,<sup>10</sup> although reaction with  $\text{NaH}$  was reported to lead to  $\text{NaAlH}_4$  and  $[(\text{CH}_3)_2\text{N}]_2\text{AlH}$ .<sup>11</sup>

The identity of the high-melting material (mp 237–238°) thus was definitely established as  $[(\text{CH}_3)_2\text{NAlCl}_2]_2$ . The large discrepancy between the melting point found and that reported previously,<sup>4,6</sup> however, could not be rationalized adequately except by the assumption that the low melting point was due to a mixture rather than pure  $(\text{CH}_3)_2\text{NAlCl}_2$ . In all of the preparations (except that of eq 1 in benzene) the products invariably had a wide melting range, usually starting near 140°. Sublimation never led to the pure dichloride, indicating that the impurity, or impurities, possessed substantial volatility at the temperatures and pressures used for sublimation. However, sublimation of the pure  $(\text{CH}_3)_2\text{NAlCl}_2$

(8) A solution molecular weight determination was not possible because of the insolubility of the compound in inert solvents such as benzene.

(9) H. Hess, *Z. Krist.*, **118**, 361 (1963).

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

(11) The difference between  $(\text{CH}_3)_2\text{NAlCl}_2$  and  $(\text{CH}_3)_2\text{NAlH}_2$  in their ability to form Lewis base complexes can be ascribed to the change in electronegativity of the nitrogen and aluminum atoms due to the inductive effect of the chlorines. This would decrease the differences in electronegativity between the nitrogen and aluminum atoms and increase the tendency for complex formation.

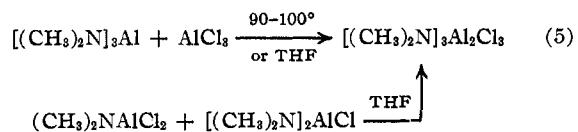
TABLE II  
 INFRARED SPECTRA OF DIMETHYLAMINOALANES

$[(\text{CH}_3)_2\text{N}]_3\text{Al}^a$	$[(\text{CH}_3)_2\text{N}]_3\text{AlCl}^a$	$(\text{CH}_3)_2\text{NAlCl}_2^a$	$[(\text{CH}_3)_2\text{N}]_3\text{Al}_2\text{Cl}_3^a$	$\text{AlCl}_3^b$	$(\text{CH}_3)_2\text{NAlH}_2^c$
2915 m <sup>d</sup>	2915 m	3250	2910 m		2920 wm
2800 ms	2830 m	3235 } d, m	2840 w		2870 wm
2754 ms	2770 m	2990 m	2760 mw		2800 w
1457 ms	1458 ms	2965 m	1460 ms		1825 } d, vs
1440 sh	1440 sh	2940 wm	1435 sh		1812
1405 w	1406 w	2860 w	1404 w		1458 m
1260 s	1270 m	2820 mw	1268 m		1437 w
1228 wm	1229 wm	1465 sh	1229 wm		1265 w
1150 s	1155 m	1457 m	1158 ms		1220 m
1106 wm	1105 wm	1440 vw	1104 m		1165 m
1062 wm	1065 wm	1395 vw	1065 m		1120 w
1030 m	1026 m	1270 w	1023 s		1103 ms
965 vs	1016 sh	1231 m	980 s		1070 vw
890 vs	976 ms	1172 wm	885 vs		1038 w
818 mw	885 s	1105 m	816 m		1019 s
785 sh	818 m	1047 m	762 mw		980 w
662 vvs	790 w	1028 sh	658 m	625 s	900 m
600 vs	657 vs	1018 ms	587 m	606 m	880 vs
540 m	615 vs	935 vw	555 ms	506 m	761 vvs
518 m	590 vvs	883 s	545 m	484 s	748 vvs
420 sh	558 vvs	780 vvw	440 mw	438 w	
397 wm	500 sh	645 s, sh	415 mw	420 m	
355 vw	470 sh	625 s	370 wm	340 vs	
327 vw	368 wm	580 ms	340 w		
		555 s			
		490 mw			
		468 w			
		416 wm			
		358 mw			
		320 w			
		270 w			

<sup>a</sup> KBr pellet between CsI windows vs. a KBr pellet blank between CsI windows. <sup>b</sup> E. G. Hoffmann, *Z. Elektrochem.*, **64**, 616 (1960); W. Klemperer, *J. Chem. Phys.*, **24**, 353 (1956). <sup>c</sup> Benzene solution differentially against benzene. <sup>d</sup> Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; d, doublet.

$\text{NAlCl}_2$  produced no change in the compound, showing that no disproportionation or thermal equilibration of oligomers had taken place, such as is known to occur with  $(\text{CH}_3)_2\text{NBCl}_2$ .<sup>12</sup> The possibility of the impurity being a diethyl ether complex of the dichloride was ruled out by the failure to change the impure material under conditions which readily removed complexed THF.

Since one of the reported methods of preparing  $(\text{CH}_3)_2\text{NAlCl}_2$  was a disproportionation (eq 2), the possibility that the impurity was the dimethylaminoaluminum sesquichloride,  $[(\text{CH}_3)_2\text{N}]_3\text{Al}_2\text{Cl}_3$ , had to be considered. In order to check this, the sesquichloride was prepared in several ways (eq 5). In the absence of



solvent the mixing of reagents was exothermic and the product was the sesquichloride. In THF the same compound was obtained and was found to be stable to cleavage by THF (no  $(\text{CH}_3)_2\text{NAlCl}_2 \cdot \text{THF}$  precipitated on long-term standing). The powder X-ray diffraction pattern demonstrated that this sesquichloride was not

the contaminating substance in the impure  $(\text{CH}_3)_2\text{NAlCl}_2$ .

Repetition of the preparation of  $(\text{CH}_3)_2\text{NAlCl}_2$  in diethyl ether on a larger scale, followed by differential solvent treatment and careful sublimation finally resulted in the isolation of a white solid, mp 171–173°, which was identified by analysis, infrared and mass spectrometry, and the powder X-ray diffraction pattern to be  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ . Addition of a little of this material to pure  $(\text{CH}_3)_2\text{NAlCl}_2$  produced mixtures which started to soften at about 125° and melted slowly from about 145° up. Thus, it appears likely that the  $(\text{CH}_3)_2\text{NAlCl}_2$ , mp 151°, was contaminated with a small quantity of  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ .

Rigorous drying of both diethyl ether and THF by distillation from  $\text{LiAlH}_4$ , as well as prior solution of the hydrolytically very sensitive  $(\text{CH}_3)_2\text{NAlH}_2$  in the solvent, rules out the formation of  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$  by subsequent hydrolysis. Thus, the formation of  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$  in the preparation of  $(\text{CH}_3)_2\text{NAlCl}_2$  is very significant and must have a bearing on the mechanism of the reaction of hydrides with  $\text{HgCl}_2$ . It has been suggested that the formation of mercury and hydrogen in this reaction was due to either the decomposition of unstable  $\text{HgH}_2$  or the disproportionation of a substituted mercuric hydride,<sup>4</sup> especially in the reactions where



(12) E. Wiberg and K. Schuster, *Z. Anorg. Allgem. Chem.*, **213**, 89 (1933).

TABLE III  
 POWDER X-RAY DIFFRACTION PATTERNS<sup>a</sup>

[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> Al		[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> AlCl		(CH <sub>3</sub> ) <sub>2</sub> AlCl <sub>2</sub>		[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> Al <sub>2</sub> Cl <sub>3</sub>		AlCl <sub>3</sub>		(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl	
d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>
8.45	f	10.28	f	4.74	f	13.67	m	5.86	s	7.30	vf
7.50	vvs	9.12	f	4.19	vvs	8.51	f	2.94	s	5.99	vf
6.12	vf	8.45	m	3.94	m	7.72	m	2.82	m	5.56	f
5.59	vs	7.67	vvs	3.48	s	6.99	vs	2.47	vvs	4.98	s
5.28	m	7.32	f	3.28	vf	6.82	vvs	1.92	mw	4.13	f
5.10	vf	6.95	f	3.08	vvf	6.56	ms	1.76	m	4.06	w
4.37	s	6.15	f	2.75	s	5.65	ms	1.71	s	3.99	w
4.13	vf	5.26	w	2.51	wm	5.28	ms	1.64	mw	3.66	vvs
3.72	s	4.67	mw	2.42	ms	4.95	w	1.51	w	3.36	mw
3.54	w	4.17	f	2.25	w	4.51	s	1.48	mw	3.27	f
3.34	mw	3.92	f	2.18	s	4.31	ms	1.46	m	3.15	w
3.23	mw	3.59	m	2.13	s	3.95	m	1.40	m	3.11	w
3.00	mw	3.29	f	2.09	w	3.86	s	1.28	w	2.95	ms
2.91	m	3.17	f	2.05	w	3.39	ms	1.23	mw	2.80	ms
2.78	w	2.94	f	1.98	f	3.30	s	1.17	mw	2.58	ms
2.66	w	2.78	m	1.94	w	3.18	w	1.11	w	2.50	vf
2.36	w	2.48	mw	1.90	mw	3.10	w	1.08	m	2.30	m
2.27	w	2.24	w	1.74	mw	3.01	m	1.03	w	2.18	mw
				1.70	f	2.91	mw	1.02	mw	2.06	w
				1.68	w	2.88	w	0.997	mw	2.00	w
				1.63	f	2.83	mw	0.986	mw	1.90	f
				1.57	vvf	2.64	m	0.972	f	1.86	f
				1.51	s	2.48	m	0.968	m	1.80	f
				1.47	m	2.36	m	0.944	f	1.74	f
				1.44	m	2.33	m	0.937	w	1.64	vf
				1.40	m			0.916	w	1.51	w
				1.34	w			0.882	mw		
				1.31	w			0.855	mw		
				1.25	vvf			0.845	mw		
				1.22	vvf			0.836	w		
								0.818	vs		
								0.807	s		

<sup>a</sup> Cu K $\alpha$  radiation; Debye-Scherrer camera with radius of 1 radian. Abbreviations: s, strong; m, medium; w, weak; f, faint; v, very.

organomercury compounds react with alanes to form organoalanes. However, neither of these suggestions can account for the formation of (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Cl which requires the breaking of a strong Al-N bond. Mercuric chloride, which would be the disproportionation product from the ClHgH intermediate, is not capable of breaking this bond. However, if the intermediate ClHgH were to decompose with the formation of HCl, this would provide a pathway to (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Cl.

Some substantiation of the involvement of HCl was provided by the reaction of (CH<sub>3</sub>)<sub>2</sub>NAlH<sub>2</sub> and HCl and by one reaction of (CH<sub>3</sub>)<sub>2</sub>NAlH<sub>2</sub> and HgCl<sub>2</sub> in a THF-benzene mixture. The former produced a small amount of (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Cl. The latter, on sublimation, gave a few drops of liquid which was very sensitive to hydrolysis, evolving hydrogen, and which contained chlorine and aluminum. An infrared spectrum showed an Al-H absorption but no C-H absorptions and this material probably was dichloroalane.<sup>13-15</sup>

The presence of a Lewis base favors the formation of

(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Cl during the reaction with HgCl<sub>2</sub>. This is to be expected as a consequence of the increased effective concentration of HCl in the reaction mixture by virtue of the formation of a stable Lewis base-HCl complex. In the absence of a Lewis base a large excess of HCl must be present before any evidence of (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Cl formation is found. This was the case in the reaction of (CH<sub>3</sub>)<sub>2</sub>NAlH<sub>2</sub> with HCl.

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(13) Although the reaction was run in the presence of THF and the Cl<sub>2</sub>-AlH. THF adducts are solids,<sup>14</sup> the sublimation was carried out at 117° (10<sup>-3</sup> mm), well above the melting points of these adducts and at a pressure which would tend to break up these complexes. (Cl<sub>2</sub>AlH)<sub>2</sub> is a liquid and stable as such, but ClAlH<sub>2</sub>, stable only as the adduct, disproportionates to Cl-AlH + (AlH<sub>3</sub>)<sub>2</sub>.<sup>15</sup>

(14) D. L. Schmidt and E. E. Flagg, *Inorg. Chem.*, **6**, 1262 (1967).

(15) E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6b**, 460 (1951); E. Wiberg and R. Úson Lacal, *Rev. Acad. Cienc. Exact. Fis. Quim. y Nat. Zaragoza*, **9** (2), 91 (1954).