ligands (0.35 D.) compared to that of the adducts (0.22 D.) again suggests that there should be a larger lattice energy difference for the ligands.

Heats of Association.—In the temperature range indicated in Table III, the vapor pressures of $C_6H_9O_3P$ and the $B(CH_3)_3$ complex are less than 1 mm. Hence, it was assumed that the pressure was due to pure $B(CH_3)_3$. The data in Table III afforded a value of $\Delta H_{\text{assoc}} = -15.9 \pm 0.1$ kcal./mole for the reaction

$$B(CH_3)_3(g) + C_6H_9O_3P(s) = C_6H_9O_3PB(CH_3)_3(s)$$

It can be concluded, therefore, that $C_6H_9O_3P$ is a better donor toward $B(CH_3)_3$ than is $CH_3C(CH_2O)_3P$ since $\Delta H_{\text{assoc}} = -14.4 \pm 0.5$ kcal./mole for the reaction

$$B(CH_3)_3(g) + CH_3C(CH_2O)_3P(s) = CH_3C(CH_2O)_3PB(CH_3)_3(s)^3$$

However, $C_6H_9O_3P$ is still a weaker base toward $B(CH_3)_3$ than is $N(CH_3)_3$ in the reaction

$$N(CH_3)_3(s) + B(CH_3)_3(g) = (CH_3)_3NB(CH_3)_3(s)$$

where $\Delta H_{\text{assoc}} = -25.1$ kcal./mole.[3] It is probable that a comparison of $C_6H_9O_3P$ and $(CH_3)_3N$ in the gas phase would show them to be much more similar. The comparison made here in the solid phase reflects the differences in lattice energies; an effect which must enhance the apparent stability of the trimethylamine adduct.

Displacement Reactions.—Under the conditions employed in a previous investigation,[3] $CH_3C(CH_2O)_3P$ would not displace $N(CH_3)_3$ in the reaction

$$CH_3C(CH_2O)_3P + (CH_3)_3NBH_3 = CH_3C(CH_2O)_3PBH_3 + N(CH_3)_3$$

whereas the reverse reaction could be brought to completion. In contrast, $C_6H_9O_3P$ will substantially displace $N(CH_3)_3$ in the reaction

$$C_6H_9O_3P + (CH_3)_3NBH_3 = C_6H_9O_3PBH_3 + N(CH_3)_3$$

but the reaction is only partially reversed under the same conditions. Hence, $C_6H_9O_3P$ is a stronger base than $CH_3C(CH_2O)_3P$ with respect to BH_3 also.

If steric effects can be neglected in the comparison of $C_6H_9O_3P$ and $N(CH_3)_3$, then the use of either $B(CH_3)_3$ or BH_3 as reference acids should give similar results. Yet relative to $B(CH_3)_3$, solid $N(CH_3)_3$ is the stronger of the two bases by 9.2 kcal., while the liquid phase displacement reactions show that, relative to BH_3, the two ligands are much more comparable. This variation probably is due to lattice energy effects. The energies in these systems can be represented in a cyclic fashion

$$\begin{tikzcd}
L(s) + B(CH_3)_3(g) \arrow[r, "-\Delta H"] \arrow[d, "+\Delta H_v"'] & LB(CH_3)_3(s) \\
L(g) + B(CH_3)_3(g) \arrow[r, "\Delta H'"] & LB(CH_3)_3(g) \arrow[u, "-\Delta H_v'"']
\end{tikzcd}$$

where $L = N(CH_3)_3$ or $C_6H_9O_3P$. $\Delta H = \Delta H' + (\Delta H_v' - \Delta H_v)$.

The equilibria observed in the liquid phase displacement reactions indicate that the enthalpies of formation of the adducts are similar under these conditions. To a rough approximation the same should be true of the gas phase. Thus $\Delta H'$ for the $C_6H_9O_3P$–$B(CH_3)_3$ system is probably very close to that for the $N(CH_3)_3$–$B(CH_3)_3$ system. The differences in ΔH must be due to the difference in the quantities $(\Delta H_v' - \Delta H_v)$ for both systems. This difference in turn probably is due mainly to differences in ΔH_v, another manifestation of the high lattice energy of $C_6H_9O_3P$.

Acknowledgments.—We wish to thank Mr. T. J. Huttemann for some of the dielectric constant measurements. J. G. V. also wishes to thank the National Science Foundation for a grant in support of this work. The contribution of the sample of $(CH_3)_3NBH_3$ by the Callery Chemical Company is greatly appreciated.

CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM AND HAAS COMPANY,
REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA

The Amine Complexes of Aluminum Hydride. V.[1] Hydrido Aluminum Borohydride Derivatives

BY JOHN K. RUFF

Received December 17, 1962

A series of compounds $H_{3-x}Al(BH_4)_x \cdot N(CH_3)_3$ (x = 1, 2, and 3) and $H_{2-x}Al(BH_4)_xN(CH_3)_2$ (x = 1 and 2) were prepared by a metathetical reaction between $LiBH_4$ and the corresponding chloro derivatives. Their properties and reactions with trimethylamine and mercuric chloride are discussed.

Aluminum borohydride was first prepared by the interaction of aluminum trimethyl and diborane.[2] The subsequent availability of lithium borohydride resulted in the development of a better preparative method[3]

$$3LiBH_4 + AlCl_3 \longrightarrow 3LiCl + Al(BH_4)_3$$

and this reaction has been extended to the preparation

---

(1) This work was performed under Contract No. DA-01-021 ORD 5135.

(2) H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *J. Am. Chem. Soc.*, **62**, 3421 (1940).

(3) H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *ibid.*, **75**, 209 (1953).

TABLE I

CHARACTERIZATION OF THE HYDRIDO ALUMINUM BOROHYDRIDE COMPLEXES

Compound	M.p. (b.p.), °C.	Yield, %	Calcd.			Found			Purification
			Al	B	Active H	Al	B	Active H	
$H_2AlBH_4 \cdot N(CH_3)_3$	19	77	26.24	10.52	5.84	26.00	11.04	5.86	Recrystn. from hexane at −78°
$HAl(BH_4)_2 \cdot N(CH_3)_3$	B.p. 59–60 (3 × 10^{-2} mm.)	60	23.14	18.52	7.72	23.24	18.31	7.62	Distillation under high vacuum
$Al(BH_4)_3 \cdot N(CH_3)_3$	78 (lit.[2] 79)	51	20.69	24.85	9.20	20.62	24.51	9.05	Vac. sublimation at 35°
$HAlBH_4N(CH_3)_2$	69	73	31.08	12.49	5.76	31.31	11.97	5.74	Vac. sublimation at 30°
$Al(BH_4)_2N(CH_3)_2$	156	53	26.82	21.47	7.95	26.70	20.91	7.79	Vac. sublimation at 60°

of the methyl-substituted aluminum borohydrides.[4]

No hydrido aluminum borohydride derivatives have been isolated but Ogg observed the formation of a new species which was believed to be $Al_2B_4H_{18}$ while investigating the n.m.r. spectrum of aluminum borohydride.[5]

$$2Al(BH_4)_3 \rightleftarrows B_2H_6 + Al_2B_4H_{18}$$

The system is apparently quite labile so that the isolation of such materials in the pure state might be difficult. It was felt that decreased lability could be achieved by the formation of complexes between the hydrido aluminum borohydrides and a suitable Lewis base. Aluminum borohydride itself was reported to form complexes with diethyl ether, ammonia, and trimethylamine which were less reactive than the borohydride.[2] Therefore the preparation of a series of hydrido aluminum borohydride amine complexes was attempted by reaction of the corresponding chloro derivatives with lithium borohydride.

Results and Discussion

The trimethylamine chloro alanes were found to react smoothly with a benzene suspension of lithium borohydride to produce the corresponding borohydride derivatives in good yield

$$H_2AlCl \cdot N(CH_3)_3 + LiBH_4 \longrightarrow \underset{\text{I}}{H_2AlBH_4 \cdot N(CH_3)_3} + LiCl$$

$$HAlCl_2 \cdot N(CH_3)_3 + 2LiBH_4 \longrightarrow \underset{\text{II}}{HAl(BH_4)_2 \cdot N(CH_3)_3} + 2LiCl$$

$$AlCl_3 \cdot N(CH_3)_3 + 3LiBH_4 \longrightarrow \underset{\text{III}}{Al(BH_4)_3 \cdot N(CH_3)_3} + 3LiCl$$

The dimethylamino chloro alanes underwent reaction in an analogous manner when treated with lithium borohydride

$$HAlClN(CH_3)_2 + LiBH_4 \longrightarrow \underset{\text{IV}}{HAlBH_4N(CH_3)_2} + LiCl$$

$$Cl_2AlN(CH_3)_2 + 2LiBH_4 \longrightarrow \underset{\text{V}}{(BH_4)_2AlN(CH_3)_2} + 2LiCl$$

The use of diethyl ether or tetrahydrofuran instead of benzene resulted in decreased purity of the crude trimethylamine complexes I, II, and III. This is felt to be attributable to the basicity of these solvents, since the borohydride group is susceptible to nucleophilic attack.[2]

The hydrido aluminum borohydride trimethylamine complexes that were prepared are listed in Table I. They were sufficiently volatile so that purification could be effected by sublimation or distillation. However, purification of $H_2AlBH_4 \cdot N(CH_3)_3$ was best accomplished by low temperature recrystallization, since the major impurity, trimethylamine borane, is also quite volatile. All of the compounds reacted violently with water and more slowly with oxygen. They are stable at ambient temperatures and $H_2AlBH_4 \cdot N(CH_3)_3$ could be heated at 55° for several hours without change as evidenced by its B^{11} n.m.r. spectrum. At 90° some decomposition occurred and hydrogen, a metallic mirror, and trimethylamine borane were produced. This suggests that the decomposition followed the equation

$$H_2AlBH_4 \cdot N(CH_3)_3 \xrightarrow{90^\circ} BH_3N(CH_3)_3 + Al + {}^3/_2H_2$$

The infrared spectra of the hydrido aluminum borohydride complexes are remarkably similar, in the 4 to 6 μ region, to that reported for aluminum borohydride,[6] with the exception that the spectra of those complexes which formally contain Al–H bonds have an additional band in the range of 5.3 to 5.4 μ. The bands present in the infrared spectra of the compounds are tabulated in Table II. The doublets occurring about 3.9 to 4.1 μ and the broad bands at 4.6 to 4.7 μ are assigned to the terminal B–H stretching modes and an asymmetric bridge stretching mode, respectively, after Price.[6] Assignment of the symmetric bridge stretching mode is complicated by the presence of absorptions due to the amine function in the region where it is to be expected.[7] The band at 5.3 to 5.4 9 is attributed to an Al–H bond.[8]

A quintuplet was observed in the B^{11} n.m.r. spectra of all of the hydrido aluminum borohydride complexes, indicating that four equivalent hydrogen atoms are bound to each boron and that in the derivatives containing two or more borohydride groups the borons are equivalent. The same equivalency of the hydrogens was observed in the B^{11} n.m.r. spectrum of aluminum borohydride[6] and it has been suggested that this is caused by a rapid internal exchange.[9] A typical spectrum is shown in Fig. 1. The field position of the quintuplets and the coupling constants for the complexes are also very close to those reported for alu-

---

[4] H. I. Schlesinger, *et. al.*, University of Chicago, Navy Contract N173S-9820, Final Report 1946–1947.

[5] R. A. Ogg and J. D. Ray, *Discussions Faraday Soc.*, **19**, 215 (1955).

[6] W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

[7] The methyl absorptions for $AlD_3 \cdot N(CH_3)_3$ and $AlH_3 \cdot N(CH_3)_3$ in benzene solution occur at 6.85 and 7.13 μ, and the symmetric bridge stretching mode in $Al(BH_4)_3$ occurs at 6.76 μ.[5]

[8] G. Schomburg and E. G. Hoffmann, *Z. Elektrochem.*, **61**, 110 (1957).

[9] W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 132 (1959).

TABLE II

THE INFRARED SPECTRA (IN μ) OF THE HYDRIDO ALUMINUM BOROHYDRIDE COMPLEXES[a]

$Al(BH_4)_2N(CH_3)_2$[b]		$HAlBH_4N(CH_3)_2$[b]		$H_2AlBH_4 \cdot N(CH_3)_3$		$HAl(BH_4)_2 \cdot N(CH_3)_3$		$Al(BH_4)_3 \cdot N(CH_3)_3$[b]	
3.39	vs	3.45	s	3.40	s	3.38	m	3.40	ms, br.
3.94	s, dbt.	4.02	m	3.56	dbt.	3.46	dbt.	4.05	s
4.06		4.13	dbt.	4.08	s	4.07	s	4.15	dbt.
4.71	s, br.	4.65	ms	4.16	dbt.	4.16	dbt.	4.70	s
6.80	s, br.	5.35	s	4.57	s	4.67	s	6.85	s, br.
7.27	w	6.83	s	5.45	vs	5.46	vs	7.10	vw
7.65	vw	7.62	m	6.76	s	6.78	s	7.75	vw
8.13	w	8.10	w	6.84	dbt.	6.85	dbt.	8.12	w
8.54	vw	8.55	vw	7.10	vw	8.10	w	8.60	vw
8.93	m	8.95	m, br.	8.04	m	8.33	m	8.95	s, br.
9.06	dbt.	9.62	m	8.54	vw	8.94	m	10.23	s
7.79	m	11.13	ms, br.	8.94	m	9.10	w	12.30	s
10.13	w			9.05	m	10.14	s		
11.30	m, br.			10.02	vs	13.85	vs, br.		
				11.45	w, br.				
				12.45	vs, br.				

[a] w, weak; m, medium; s, strong; v, very; br., broad; dbt., doublet. [b] Spectra obtained in Nujol mull; Nujol bands included in tabulation.

TABLE III

B^{11} N.M.R. SPECTRA OF THE HYDRIDO ALUMINUM BOROHYDRIDES

	$\delta \times 10^6$	J_{BH}
$Al(BH_4)_3$[a]	55.1	86
$Al(BH_4)_3 \cdot N(CH_3)_3$	56.7	84
$HAl(BH_4)_2 \cdot N(CH_3)_3$	56.3	85
$H_2AlBH_4 \cdot N(CH_3)_3$	56.5	85
$HAlBH_4N(CH_3)_2$	55.5	86
$Al(BH_4)_2N(CH_3)_2$	55.9	85

[a] Reference 5.

minum borohydride[5] (see Table III). Furthermore the presence of four equivalent hydrogen atoms bound to each boron eliminates numerous possible structural configurations (involving B–N bonds and Al–N–B bridge bonds) for the various complexes and demonstrates that the Al–N bond remained intact during their preparation.

Both the infrared and n.m.r. data support the view that the bonding of the borohydride group in the complexes is essentially the same as in aluminum borohydride. If the double hydride bridge structure proposed for aluminum borohydride[6] is assumed to apply to the complexes then the nature of the orbitals involved in the bridge bonds becomes important. It is immediately apparent that a static double hydride bridge model involving six bonding aluminum orbitals (as in the AlF_6^{-3} ion) cannot be entirely correct since it would require aluminum in $Al(BH_4)_3 \cdot N(CH_3)_2$ to have a coördination number of seven. An alternate proposal which utilizes only one bonding orbital on aluminum per borohydride group is perhaps more compatible with the chemistry of these materials and on this basis the Lewis acidity of the aluminum in aluminum borohydride would be predicted. The exact geometric arrangement of the hydrogen atoms between the boron and aluminum is not known and it is not uniquely determined by employing only a single bonding orbital from the aluminum, since geometric configurations expected for both single or double hydride bridge structures are possible.[10] The internal exchange occurring in the borohydride group as indicated by the B^{11} n.m.r. suggests a labile system so that it may be difficult to determine the position of the hydrogen atoms.

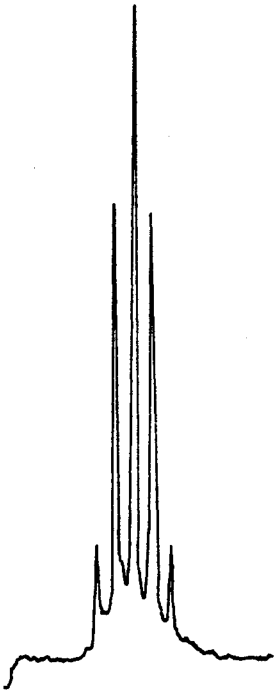

Fig. 1.—The B^{11} N.m.r. spectra of $AlBH_6 \cdot N(CH_3)_3$.

The dimethylamino aluminum borohydrides, IV and V, were found to be associated in benzene; $HAlBH_4N(CH_3)_2$, $\bar{n}$ = 2.84, and $Al(BH_4)_2N(CH_3)_2$, $\bar{n}$ = 2.31. The same decrease in the degree of association upon substitution which was noted previously for the dimethylamino chloro and dichloro alanes and tris- and bis-dimethylamino alanes[11] again was apparent. Although association could occur *via* hydride bridging, it is more likely that it involves bridging dimethylamino groups. The dimethylamino group, if free, probably would attack the borohydride group since

---

[10] The author wishes to thank one of the reviewers for pointing out that two equivalent forms of the double bridge structure may be written in which there is only one three center Al–H–B bond.

[11] J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2835 (1961).

trimethylamine, in excess, is known to cleave the hydride bridges in aluminum borohydride to produce trimethylamine borane.[2]

Dimethylamino hydrido aluminum borohydride and dimethylamino aluminum diborohydride also were found to react rapidly with trimethylamine and the stoichiometry of the reaction could easily be determined by a tensiometric titration. Reactions with excess amine in sealed bulbs produced the same stoichiometry.

$$HAlBH_4N(CH_3)_2 + N(CH_3)_3 \longrightarrow H_2AlN(CH_3)_2 + BH_3N(CH_3)_3$$

$$Al(BH_4)_2N(CH_3)_2 + 2N(CH_3)_3 \longrightarrow H_2AlN(CH_3)_2 + 2BH_3N(CH_3)_2$$

The B^{11} n.m.r. spectra of the crude product mixtures consisted of a quadruplet, indicating that complete conversion of BH_4 groups to BH_3 groups had occurred. The isolation of trimethylamine borane although in moderate yield further supports the above equations.

An attempt was made to prepare bis-dimethylamino aluminum borohydride by reaction of lithium borohydride with bis-dimethylamino chloro alane

$$[(CH_3)_2N]_2AlCl + LiBH_4 \longrightarrow \underset{\text{VI}}{[(CH_3)_2N]_2AlBH_4} + LiBH_4$$

When the reaction was run at low temperatures a crude product apparently contaminated with lithium chloride and lithium borohydride was isolated. The infrared spectrum of this material was very like that observed for dimethylamino aluminum diborohydride (V). The B^{11} n.m.r. spectrum of the cold reaction mixture (after filtration of the precipitated lithium chloride) consisted predominantly of a quintuplet. However, upon attempted purification, either by recrystallization or sublimation, the material underwent a rearrangement and bis-(dimethylamino borane)-bis-dimethylamino alane was isolated in moderate yield.[12] The exact course of the rearrangement

$$2[(CH_3)_2N]_2AlBH_4 \longrightarrow HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2 + \ldots$$

is not known since the co-products could not be separated and identified. The instability of bis-dimethylamino aluminum borohydride, VI, is felt to arise from a nucleophilic attack by one of the free dimethylamino groups on the borohydride group.

The preparation of the trimethylamine complex of dichloro aluminum borohydride by the chlorination of the corresponding hydrido aluminum borohydride with mercuric chloride was attempted.[13] The reaction occurred smoothly at 0°. Analyses of the crude product agreed fairly well with expected composition and

$$H_2AlBH_4 \cdot N(CH_3)_3 + HgCl_2 \xrightarrow{0°} Cl_2AlBH_4 \cdot N(CH_3)_3 + Hg + H_2$$

the infrared spectrum contained no bands in the Al–H stretching region. However B^{11} n.m.r. analysis showed the crude product to be contaminated with a material containing a BH_3 group. Upon recrystallization the purity of the sample decreased and a larger quadruplet relative to the quintuplet was observed in the B^{11} n.m.r. spectrum. Elemental analyses also reflected its decreased purity. Other attempts to isolate a pure sample of trimethylamine dichloro aluminum borohydride were equally unsuccessful. However, when an excess of lithium borohydride was allowed to react with the cold chlorination reaction mixture a moderate yield of trimethylamine aluminum borohydride (III) was obtained. The reaction occurring is believed to be

$$Cl_2AlBH_4 \cdot N(CH_3)_3 + 2LiBH_4 \longrightarrow Al(BH_4)_3 \cdot N(CH_3)_3 + 2LiCl$$

Experimental

Since the products as well as the starting materials react with oxygen and moisture all operations were performed in an inert atmosphere or in a conventional vacuum line.

Materials.—The preparation of the amine complexes of the chloro alanes and the amino chloro alanes is reported elsewhere.[11,13] Lithium borohydride was used as obtained from Metal Hydrides, Inc., and the Matheson Company supplied the trimethylamine.

Preparation of the Hydrido Aluminum Borohydride Trimethylamine Complexes.—The preparation was performed in a similar manner for all of the compounds. The appropriate chloro alane amine compound (50 mmoles) was allowed to react with 100% excess lithium borohydride in 100 to 150 ml. of benzene for 4 to 6 hr. at ambient temperature. The reaction mixture was filtered in a vacuum filtration apparatus and the benzene was removed from the filtrate under reduced pressure. The residue was purified as described in Table I. Yields are based on the purified product.

Reaction of $[(CH_3)_2N]_2AlCl$ with $LiBH_4$.—Diethyl ether, 75 ml., was condensed onto a mixture of 6.03 g. (39.9 mmoles) of $[(CH_3)_2N]_2AlCl$ and 0.53 g. (41.0 mmoles) of lithium borohydride. The mixture was brought to −35° and stirred at this temperature for 0.5 hr. Then it was filtered rapidly with a −45° bath around the filter plate. The filtrate was warmed to −35° again and the solvent was removed under vacuum. A white solid remained.

Anal. Calcd. for $[(CH_3)_2N]AlBH_4$: Al, 20.78; B, 8.32; Li, 0; active H, 3.08; Cl, 0. Found: Al, 18.12; B, 8.11; Li, 0.4; active H, 2.85; Cl, 1.3.

The infrared spectrum contained a doublet at 4.0 and 4.10 μ and a broad band centered at 4.72 μ. No bands were observed in the 5 to 6 μ region. The B^{11} n.m.r. of the white solid in cold ether consisted primarily of quintuplet; however, several smaller bands were present.

The solid obtained above was added to 100 ml. of hexane and refluxed for 1 hr. The mixture was filtered hot and allowed to stand. A 1.81-g. (12.7 mmoles) yield of bis-(dimethylamino borane)-bis-dimethylamino alane was obtained, m.p. 119–120°. Its identity was confirmed by mixture melting points and a comparison of its infrared spectrum with that of an authentic sample.

Reaction of the Dimethylamino Hydrido Aluminum Borohydrides with Trimethylamine. (A) Sealed Bulb Experiments.—A similar procedure was followed for both the dimethylamino aluminum borohydrides. Duplicate experiments were run on each compound. Dimethylamino aluminum diborohydride (V), 1.105 g. (10.10 mmoles), was placed in a 1-l. seal-off bulb together with 105.1 mmoles of trimethylamine and 15 ml. of paraffin oil. The bulb was sealed off and allowed to stand 24 hr. at 25°. Trimethylamine, 84.1 mmoles, was recovered by fractionation. A sample of the reaction mixture was taken for a B^{11} n.m.r. spectrum and 0.61 g. (8.38 mmoles) of trimethylamine borane, m.p. 92°, was obtained from the mixture by fractionation. The same procedure was followed when dimethylamino hydrido aluminum borohydride (IV) was employed. A 0.865-g. (9.97 mmoles) sample of the compound consumed 10.25 mmoles

---

(12) J. K. Ruff, *Inorg. Chem.*, **1**, 612 (1962).

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

of trimethylamine and 0.33 g. (4.53 mmoles) of trimethylamine borane was obtained from the reaction mixture. The B^{11} n.m.r. of both reaction mixtures consisted solely of a quadruplet.

(B) **Tensiometric Titrations.**—The tensiometric titrations of dimethylamino hydrido aluminum borohydride and dimethylamino aluminum diborohydride with trimethylamine were performed as described previously.[11] A ratio of amine to hydride of 1.04 was found for the former and 1.96 for the latter. Equilibrium was attained in the system shortly after reaching ambient temperature (see Fig. 2).

Attempted Preparation of $Cl_2AlBH_4 \cdot N(CH_3)_3$.—A 5.51-g. (21.8 mmoles) sample of mercuric chloride was added slowly to a solution of 2.18 g. (19.9 mmoles) of I in 10 ml. of benzene at 0°. After the gas evolution had ceased, the mixture was filtered cold and the benzene was removed from the filtrate at 0°. The solid residue was dried for 6 hr. at 0° under vacuum.

Anal. Calcd. for $Cl_2AlBH_4 \cdot N(CH_3)_3$: Al, 15.72; Cl, 41.3; B, 6.30; active H, 2.33. Found: Al, 16.04; Cl, 41.6; B, 5.61; active H, 2.36.

In another run 1.02 g. (10.2 mmoles) of I in 2.61 g. (9.64 mmoles) of mercuric chloride were allowed to react in 50 ml. of toluene at −10° for 1 hr. Then 1.07 g. (48.6 mmoles) of lithium borohydride was added and the mixture was stirred 2 hr. at −10° and 4 hr. at 0°. After filtration, the toluene was removed at 25° under vacuum and a white solid residue was obtained. Sublimation of the residue at 35° afforded 0.76 g. (5.8 mmoles) of III, m.p. 78°.

Analysis.—The active hydrogen content was determined by hydrolysis with a 1:1 methanol–trifluoroacetic acid mixture in sealed bulbs. The bulbs were allowed to stand overnight and then heated for 3 hr. at 50° before being opened. The amount of hydrogen evolved was measured by means of a Toepler pump and a calibrated storage bulb system. The remaining solution was treated as previously described in order to determine the aluminum content.[14] An aliquot was titrated for boric acid by the conventional mannitol titration procedure.

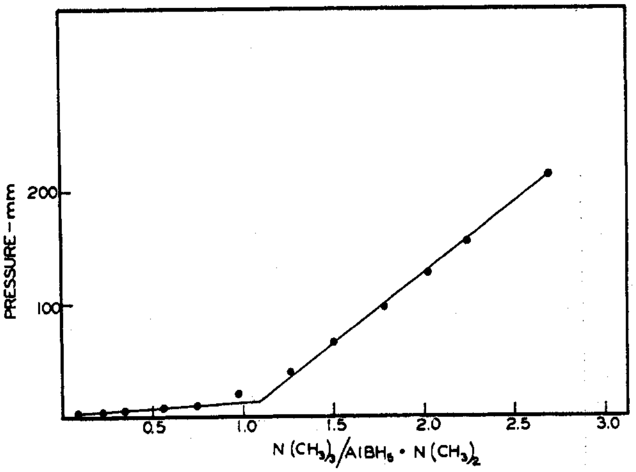

Fig. 2.—Titration of $HAlBH_4 \cdot N(CH_3)_2$ with $N(CH_3)_3$ in decane solution.

Molecular Weight Determination.—The apparent molecular weights of dimethylamino hydrido aluminum borohydride and dimethylamino aluminum borohydride were determined cryoscopically in benzene.[14] Mol. wt. of $HAlBH_4N(CH)_3)_2$: Calcd. 87; Found 245, 250. Mol. wt. of $Al(BH_4)_2N(CH_3)_2$: Calcd. 101; Found 231, 235.

Infrared Spectra.—The infrared spectra of the hydrido aluminum borohydride complexes were obtained on Nujol mulls (for the solid products) or on capillary layers (liquid samples) with a Perkin-Elmer Model 21 spectrophotometer. All samples were prepared and handled in the drybox prior to obtaining the spectra.

N.m.r. Spectra.—The B^{11} n.m.r. spectra were obtained on 10–15% solutions of the complexes in benzene, with a Varian Model V-4300B spectrometer operating at 12.8 Mc. Trimethylborate was used as an external standard. The chemical shifts and coupling constants are presented in Table III.

---

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

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

The Synthesis and Spectra of B-Trifluoroborazine

BY A. W. LAUBENGAYER, K. WATTERSON, D. R. BIDINOSTI, AND RICHARD F. PORTER[1]

Received October 18, 1962

The reaction of B-trichloroborazine, $Cl_3B_3N_3H_3$, vapor with potassium fluoroborate produces B-trifluoroborazine, $F_3B_3N_3H_3$, together with $F_2ClB_3N_3H_3$ and $FCl_2B_3N_3H_3$. Pure B-trifluoroborazine has been prepared by the reaction of B-trichloroborazine with excess antimony trifluoride. Its mass and infrared spectra are compared with those of B-trichloroborazine and trifluoroboroxine. The tendency for ring cleavage *vs.* breaking of boron–halogen bonds in these isoelectronic heterocyclic ring compounds is discussed.

Introduction

Although numerous B-chloro- and B-bromo-derivatives of borazine have been known for some time there is little information about the fluoroborazines.[2] Wiberg and Horeld[3] have reported that B-trifluoro N-trimethylborazine is formed from dimethylfluoroborane and methylamine. Pearson and Frazer[4] prepared mixtures of fluoroborazines from the reaction of diborane with tetrafluorohydrazine. They obtained mass spectral and infrared evidence for $FH_2B_3N_3H_3$, $F_2HB_3N_3H_3$, and $F_3B_3N_3H_3$ in the mixtures but did not isolate the pure compounds. They suggested that the mixtures might have isomeric molecules present, rendering separation difficult. Reaction of ammonia with boron trifluoride gives the crystalline adduct $H_3N{:}BF_3$, which, when heated, decomposes to NH_4BF_4 and boron nitride with no evidence for the intermediate formation of fluoroborazines.[5] Efforts to prepare

---

[1] Alfred P. Sloan Fellow.

[2] J. C. Sheldon and B. C. Smith, *Quart. Rev.* (London), **14**, 200 (1960).

[3] E. Wiberg and G. Horeld, *Z. Naturforsch.*, **6B**, 338 (1951).

[4] R. K. Pearson and J. W. Frazer, *J. Inorg. Nucl. Chem.*, **21**, 188 (1961).

[5] A. W. Laubengayer and G. Condike, *J. Am. Chem. Soc.*, **70**, 2274 (1948).