The Composition of Complex Metal Hydrides in Polar Solvents.
I. Tertiary Amines

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A study of the composition of complex metal hydrides of aluminum and boron in polar solvents reveals that although these compounds are stable in diethyl ether and tetrahydrofuran, in tertiary amine solvent, alane and borane extraction takes place with certain amines and complex metal hydrides. In general, alane and borane extraction takes place with the more covalently bonded complex metal hydrides whereas solvation or no interaction at all takes place with the more ionically bonded hydrides. Thus addition of trimethylamine to lithium aluminum hydride and chloromagnesium aluminum hydride resulted predominantly in alane extraction. On the other hand, ionic hydrides such as sodium aluminum hydride did not undergo alane extraction. Amines that were ineffective in alane extraction from lithium aluminum hydride proved successful in alane extraction with the more covalently bonded magnesium aluminum hydride compounds. Stable amine complexes of lithium aluminum hydride, sodium aluminum hydride, and lithium borohydride have been prepared and characterized. Attempts to extract amine boranes from magnesium borohydrides were unsuccessful. The structure of these amine complexes and possible mechanisms of alane extraction from complex aluminum hydrides are discussed. This and other evidence indicates that lithium aluminum hydride, unlike sodium aluminum hydride and other more ionic hydrides, does not exist in solution as ion aggregates but as covalently bonded species. Such a description of lithium aluminum hydride in solution is considered important in the mechanistic description of reduction reactions involving organic functional compounds.

Introduction

Early workers in the area of metal borohydride chemistry observed that borane could be extracted from beryllium borohydride by trimethylamine[1]

$$Be(BH_4)_2 + N(CH_3)_3 \longrightarrow HBeBH_4 + BH_3 \cdot N(CH_3)_3 \quad (1)$$
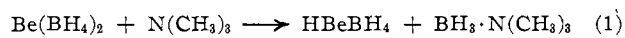
The symmetrical cleavage of metal borohydrides also has been employed in the preparation of transition metal hydrides. Recently bis(cyclopentadienyl)zirconium borohydride was shown to undergo borane extraction when allowed to react with trimethylamine[2]

$$(C_5H_5)_2Zr(BH_4)_2 + N(CH_3)_3 \longrightarrow$$
$$(C_5H_5)_2Zr(H)BH_4 + BH_3 \cdot N(CH_3)_3 \quad (2)$$
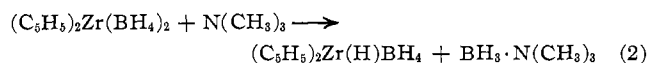
In addition to borane extraction, a complex borohydride can react with a tertiary amine to form simple solvates[3] of the borohydride as shown in eq 3.

$$LiBH_4 + nN(CH_3)_3 \longrightarrow LiBH_4 \cdot nN(CH_3)_3 \quad (n = 1 \text{ or } 2) \quad (3)$$
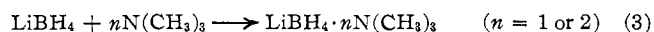
With transition metal compounds, the suggestion has been made that a cavalently bound BH_4 group is necessary for the borane extraction reaction[2].

The interaction of tertiary amines with complex aluminum hydrides has been investigated to a lesser extent. Wiberg has reported that the interaction of $LiAlH_4$ and trimethylamine results in solvate formation[4]. In this note, three complexes were isolated from ether solution

$$LiAlH_4 + nN(CH_3)_3 \longrightarrow LiAlH_4 \cdot nN(CH_3)_3 \quad (n = 1, 2, \text{ or } 3) \quad (4)$$
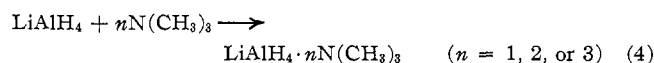
The bis and tris solvates were reported to be stable only at low temperatures, but the mono-trimethylamine solvate was said to be stable at room temperature.

More recently Peters[5] reported that the interaction of trimethylamine with $LiAlH_4$ in ether resulted in the formation of bis(trimethylamine)–alane. This reaction has been observed earlier by Heitsch[6] when drying tri-

$$LiAlH_4 + N(CH_3)_3 \longrightarrow LiH + AlH_3 \cdot N(CH_3)_3 \quad (5)$$

methylamine over lithium aluminum hydride. In neither case was the amine–alane formed in high yield nor the nonsublimable reaction product characterized. On the other hand, the work of Ehrlich[7] suggests that the insoluble product observed by Peters might be a mixture of Li_3AlH_6 and $LiAlH_4$ based on Ehrlich's successful preparation of Li_3AlH_6 from $LiAlH_4 \cdot N(C_2H_5)_3$ in diethyl ether. In this connection, Peters observed a curious dependence on the yield of the amine–alane as a function of the $N(CH_3)_3 : LiAlH_4$ ratio; a maximum yield of 44% was observed at a 0.5 amine : hydride ratio and decreased yields with decreasing amounts of amine.

The alane extraction reaction reported by Peters is in contrast to an earlier claim by Ruff and Hawthorne[8]. Using lithium hydride and trimethylamine–alane in ether, they were able to prepare $LiAlH_4$ in high yield

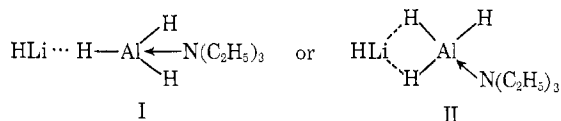$$LiH + AlH_3 \cdot N(CH_3)_3 \longrightarrow LiAlH_4 + N(CH_3)_3 \quad (6)$$
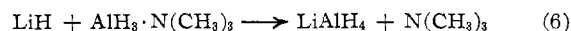
The only fully characterized amine adduct of lithium aluminum hydride was reported by Ehrlich and Rice[9]. The addition of triethylamine to a suspension of $LiAlH_4$ in benzene yielded a stable, soluble product of composition $LiAlH_4 \cdot N(C_2H_5)_3$ which was also iso-

(1) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **62**, 3425 (1940).

(2) B. D. James, R. N. Nanda, and M. G. G. Wallbridge, *Inorg. Chem.*, **6**, 1979 (1967).

(3) G. W. Schaeffer and D. J. Hunt, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p 28M.

(4) E. Wiberg, H. Noth, and R. Uson, *Z. Naturforsch.*, **11b**, 486 (1956).

(5) F. M. Peters, *Can. J. Chem.*, **42**, 1755 (1964).

(6) C. W. Heitsch, Ph.D. Thesis, University of Michigan, 1960.

(7) R. Ehrlich, A. R. Young, G. Rice, J. Dvorak, P. Shapiro, and H. F. Smith, *J. Am. Chem. Soc.*, **88**, 858 (1966).

(8) M. F. Hawthorne and J. K. Ruff, *ibid.*, **83**, 535 (1961).

(9) R. Ehrlich and G. Rice, *Inorg. Chem.*, **5**, 1284 (1966).

lated as a solid. On the basis of a comparison of the infrared spectrum of the product with that of triethyl-amine–alane, it was suggested that this compound was best formulated as a triethylamine–alane complex of lithium hydride

$$\text{HLi}\cdots\text{H}-\overset{\displaystyle H}{\underset{\displaystyle H}{\text{Al}}}\!\!\leftarrow\!\!\text{N(C}_2\text{H}_5)_3 \quad \text{or} \quad \text{HLi}\overset{\displaystyle H}{\underset{\displaystyle H}{\diagup\!\!\diagup}}\text{Al}\overset{\displaystyle H}{\underset{\displaystyle N(C_2H_5)_3}{\diagdown}}$$

I   II

The apparent discrepancy in the reports mentioned above led us into an investigation of the interactions of tertiary amines with lithium aluminum hydride and other complex metal hydrides in an attempt to more fully understand the process of alane extraction from complex aluminum hydrides. In this connection, the interaction of $LiAlH_4$, $ClMgAlH_4$, $NaAlH_4$, $[(n\text{-}C_8H_{17})_3(n\text{-}C_3H_7)N]AlH_4$, $Mg(AlH_4)_2$, $LiBH_4$, $ClMgBH_4$, and $Mg(BH_4)_2$ with several tertiary amines such as trimethylamine, triethylenediamine, and tetramethylethylenediamine was studied. It was also hoped that an understanding of the nature of complex alumino- and borohydrides in amine solution would be helpful in the understanding of the composition in less basic solvents such as diethyl ether and tetrahydrofuran. Hopefully a better understanding of the composition of complex metal hydrides in polar solvents will help in elucidation of the mechanisms of $LiAlH_4$ reduction of both organic and inorganic compounds.

Experimental Section

Purification of Compounds.—Air-sensitive compounds were handled in an inert-atmosphere box, Schlenk-type glassware, or on a standard high-vacuum line.[10] Solvents were distilled from lithium aluminum hydride or sodium aluminum hydride under an atmosphere of dry nitrogen prior to use. Triethylenediamine was purified by vacuum sublimation. Trimethylamine (Matheson) was stored over P_4O_{10} in a grease-free container on the vacuum line. N,N',N'',N'''-tetramethylethylenediamine was distilled from sodium aluminum hydride and stored over molecular sieve (Linde 4A).

Ether and tetrahydrofuran solutions of lithium aluminum hydride were prepared and filtered in a nitrogen filled drybox. Sodium aluminum hydride solutions were similarly prepared. Concentrations of the hydride solutions were determined by aluminum analysis (EDTA) of a known volume of hydrolyzed sample. Tri-n-octyl-n-propylammonium aluminum hydride was prepared by the method reported by Ehrlich and identified by its infrared spectrum.[11]

Analyses and Spectra.—Aluminum and magnesium were determined by EDTA titration. Lithium and sodium were determined by flame photometry. Potentiometric titrations were used to determine the total amine and alkali metal. Boron content was established by sodium hydroxide–mannitol titration using phenolphthalein as an indicator. The methyl borate distillation procedure was used with borohydride–amine compounds.

Infrared spectra were obtained on a Perkin-Elmer 621 grating instrument as Nujol mulls between KBr plates. X-Ray powder data were collected with a 114.6-mm camera using nickel-filtered Cu $K\alpha$ radiation. Samples were contained in thin-walled capillaries which were loaded in an inert atmosphere and sealed.

Tensimetric titrations with trimethylamine were performed

in the usual fashion[10] with correction being made for the amount of amine in the gas phase. The data are presented as a plot of the ratio of the total pressure in the tensimeter to the initial pressure of the solution before addition of any amine (pressure ratio) as a function of the ratio of amine to the hydride species in the condensed phase.

Reactions of LiAlH₄ and Triethylenediamine in Diethyl Ether.—When solutions of $LiAlH_4$ and triethylenediamine (TEDA) were mixed (1:1 molar ratio), an immediate precipitate was formed. No hydridic activity remained in the filtrate. The X-ray powder pattern and infrared spectrum of the precipitate indicated that the compound was unique and not a mixture of LiH and the insoluble TEDA–alane. *Anal.* Calcd for $LiAlH_4$·TEDA: Al, 17.97; Li, 4.62; TEDA, 74.74; H (hydridic), 2.67. Found: Al, 17.2; Li, 3.81; TEDA, 62.7; H, 2.65.

Preparation of Triethylenediamine–Alane.—Lithium aluminum hydride in diethyl ether was added to a suspension of TEDA·HBr also in diethyl ether. A moderately vigorous hydrogen evolution accompanied the addition of the hydride. The resulting suspension was stirred for 2 hr and the TEDA–alane isolated by filtration. *Anal.* Calcd for AlH_3·TEDA: Al, 18.97; H, 2.12. Found: Al, 17.97; H, 2.03.

Reaction of Lithium Hydride and AlH₃·TEDA in THF.—A suspension of the amine–alane (10 mmol) and LiH (12 mmol) in THF was stirred for 36 hr. The solid removed by filtration was identified as unreacted amine–alane. Evaporation of the filtrate yielded a white product which was identified as $LiAlH_4$·TEDA by infrared and X-ray powder diffraction.

Reaction of Tri-n-octyl-n-propylammonium Aluminum Hydride with Triethylenediamine.—A solution of the quaternary ammonium aluminum hydride and TEDA in THF gave no precipitate. The solvent was removed under a stream of nitrogen and the remaining white solid was shaken with 100 ml of dry ether. Not all the solid dissolved and the remaining white material was isolated by filtration and dried several hours at 60° under vacuum. The infrared spectrum and X-ray powder patterns of this material were identical with the quaternary ammonium aluminum hydride.

Reaction of NaAlH₄ with Triethylenediamine.—Addition of TEDA (36 mmol) to a THF solution of $NaAlH_4$ (36 mmol) in THF gave no apparent reaction. The THF was removed and replaced by dry ether and the resulting white suspension stirred for several hours. Following isolation by filtration, the white solid was dried under vacuum. *Anal.* Calcd for $NaAlH_4$·TEDA: Na, 13.84; Al, 16.26; H, 2.43; TEDA, 67.5. Found: Na, 14.27; Al, 15.90; H, 2.31; TEDA, 58.92.

Preparation of ClMgAlH₄·4THF.—The details of the preparation of $ClMgAlH_4$·4THF and $Mg(AlH_4)_2$·4THF are described elsewhere.[12] *Anal.* Calcd for $ClMgAlH_4$·4THF: Mg, 6.41; Al, 7.12; H, 1.05; Cl, 9.36. Found: Mg, 6.77; Al, 7.22; H, 1.03; Cl, 9.58. Calcd for $Mg(AlH_4)_2$·4THF: Mg, 6.49; Al, 14.41; H, 2.13. Found: Mg, 6.70; Al, 14.91; H, 2.1.

Reaction of ClMgAlH₄ and Triethylenediamine.—Addition of TEDA (36 mmol) to 200 ml of THF containing 35 mmol of $ClMgAlH_4$ gave an immediate precipitate. The X-ray powder pattern of the solid compound isolated by filtration showed the presence of TEDA–alane complex. Analysis of the residue indicated an atomic ratio of Cl:Mg:Al:H(hydridic) of 1.0: 2.8:6.2:26.1. Less than the theoretical amount of $MgCl_2$ was recovered in solution and the presence of species other than AlH_3·TEDA was indicated in the X-ray powder pattern, possibly $MgCl_2$·TEDA or $ClMgAlH_4$·n(TEDA).

Reaction of LiAlH₄ and Trimethylamine.—A tensimetric titration of lithium aluminum hydride in THF at -22.75 and 0° showed no interaction of trimethylamine with the hydride in this solvent (Figure 1).

When the titration was performed in ether solvent, an immediate precipitate formed on the addition of the first increment of amine. The titration curves for -22.75 and 0° show breaks

(10) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, pp 27–162.

(11) R. Ehrlich, A. R. Young, and D. D. Perry, *Inorg. Chem.*, **4**, 758 (1965).

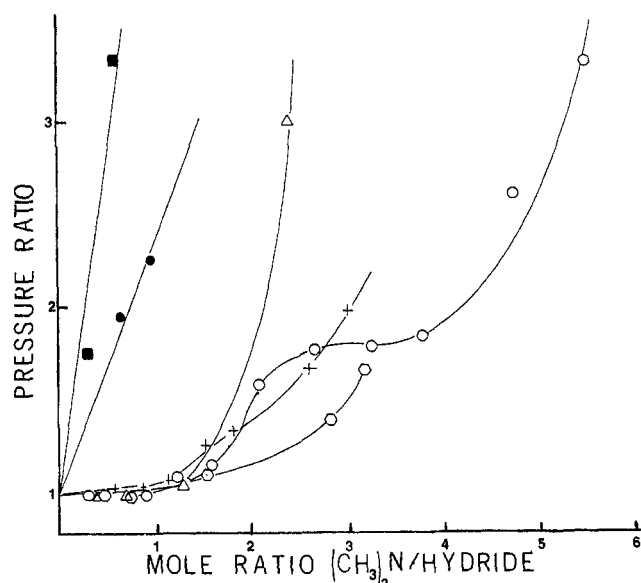(12) E. C. Ashby, R. D. Schwartz, and B. D. James, *ibid.*, **9**, 325 (1970).

Figure 1.—Tensimetric titrations of complex metal hydrides using trimethylamine: O, $Mg(AlH_4)$ in THF ($-22.75°$); ×, $LiAlH_4$ in ether ($-22.75°$); ●, $LiAlH_4$ in THF ($0°$); △, ClMg-$(AlH_4)\cdot2THF$ in toluene ($-22.75°$); ■, tri-*n*-octyl-*n*-propylammonium aluminum hydride in toluene at $0°$ (nominal amine to aluminohydride ratio); ⊙, $LiBH_4$ in ether ($-45.2°$).

at amine to $LiAlH_4$ stoichiometries of 1:1 (Figure 1). The amine adduct is not stable under vacuum at room temperature, for removal of volatiles under high vacuum resulted in the recovery of all the amine leaving $LiAlH_4$. If $LiAlH_4$ in diethyl ether is kept in the presence of trimethylamine for a few hours at $0°$, trace quantities of Li_3AlH_6 can be found in the nonsublimable residue and bis(trimethylamine)–alane can be isolated on sublimation. An 8% yield of the bis-amine–alane was obtained in 3–4 hr with an amine to hydride ratio of 4:1; 24 hr under comparable conditions gave a 27% yield of the amine–alane.

In another experiment, $LiAlH_4$ in diethyl ether (2 ml, 2.972 mmol) was outgassed by repeated freezing and thawing on a vacuum line in a tube equipped with a break-seal. Trimethylamine (4.694 mmol) was condensed on the frozen solution and the tube was sealed off under vacuum. The tube was opened after standing 1 month at room temperature and the volatile products were passed through a $-78°$ trap and collected at $-196°$. The material trapped at $-78°$, bis(trimethylamine)–alane, was transferred into a tared tube and weighed. The compound was identified by its infrared spectrum and melting point of 89–94° (lit. mp[13] 94–96°). The yield was 98%.

A similar experiment was performed except that the ether was removed from the lithium aluminum hydride (2.972 mmol) by heating to $60°$ at reduced pressure. The trimethylamine (4.69 mmol) was then condensed on the hydride and the tube sealed. After 1 month, this tube was opened and the bis(trimethylamine)–alane produced was weighed. The reaction was found to have gone to 30% completion in the absence of solvent.

X-Ray powder patterns confirmed the nonsublimable product from the first reaction was pure Li_3AlH_6. None of the lines for LiH was found in either of the sublimation residues but free $LiAlH_4$ could be detected in the reaction run without solvent.

Lithium aluminum hydride (20 mmol) which had been recrystallized from ether was suspended in benzene in a flask equipped with a Dry Ice cold finger condenser. Trimethylamine (25 mmol) was condensed into the reaction flask and the mixture was stirred for 3 days. The solid material isolated by filtration at the end of this time was determined to be pure Li_3AlH_6 from its X-ray powder pattern.

Reaction of NaAlH₄ and Trimethylamine.—A tensimetric titra-

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

tion of sodium aluminum hydride in THF with trimethylamine showed no interaction at $-22.75°$.

$NaAlH_4$ was suspended in benzene and stirred with excess trimethylamine for several days. No reaction had occurred after this time and the hydride was recovered unchanged.

Reaction of Tri-*n*-octyl-*n*-propylammonium Aluminum Hydride and Trimethylamine.—A tensimetric titration of a toluene solution of the quaternary ammonium aluminum hydride showed no interaction with trimethylamine at $-22.75°$ (Figure 1).

Reaction of ClMgAlH₄ and Trimethylamine.—Desolvation of $ClMgAlH_4\cdot4THF$ to $ClMgAlH_4\cdot2THF$ was accomplished by subjecting $ClMgAlH_4\cdot4THF$ to high vacuum overnight. The tensimetric titration performed on the bis solvate at $-22.75°$ indicates the formation of a complex containing 2 mol of amine (Figure 1). When totally desolvated this compound is not as stable as the $LiAlH_4–(CH_3)_3N$ complex toward loss of bis(trimethylamine)–alane, for in 6 hr it was possible to recover 55% of the aluminum from the compound as the amine–alane.

Reaction of Mg(AlH₄)₂ and Trimethylamine.—A tensimetric titration curve of a suspension of $Mg(AlH_4)_2$ in THF indicates the formation of two complexes at $-22.75°$. The more stable 2:1 complex $Mg(AlH_4)_2\cdot2N(CH_3)_3$ is consistent with the stable bis-THF solvate $(Mg(AlH_4)_2\cdot2THF)$, and a less stable tetrakis-trimethylamine solvate $(Mg(AlH_4)_2\cdot4N(CH_3)_3)$ is formed as well. The alane extraction reaction is slow for $Mg(AlH_4)_2$. Bis(trimethylamine)–alane was recovered in 42% yield after 10 days in the presence of excess amine (5.5:1 $N(CH_3)_3:Mg(AlH_4)_2$ ratio).

Reaction of NaAlH₄ and N,N′,N″,N‴-Tetramethylethylenediamine (TMED).—Addition of TMED to a THF solution containing $NaAlH_4$ gave no apparent reaction. On removal of solvent, the white crystalline compound obtained gave an analysis consistent with the formulation $NaAlH_4\cdot TMED$. *Anal.* Calcd for $NaAlH_4\cdot TMED$: Na, 13.51; Al, 15.86; H, 2.37. Found: Na, 13.86; Al, 15.73; H, 1.91.

Reaction of LiAlH₄ and TMED.—A $LiAlH_4$ solution in diethyl ether (71.8 mmol) was stirred vigorously while TMED (5.9 ml) was added. In the early stages of addition, a precipitate formed which redissolved. Finally a precipitate formed which did not dissolve. This was isolated and analyzed. *Anal.* Calcd for $LiAlH_4\cdot TMED$: Li, 4.50; Al, 17.51; H, 2.60. Found: Li, 4.80; Al, 16.17; H, 2.65.

Next, TMED and $LiAlH_4$ were mixed (10 ml of the amine and 2.0 g of the hydride). The pasty mixture was stirred for 24 hr and benzene added. Only some of the material dissolved in benzene. The analysis of the benzene soluble portion is consistent with the formation of $(LiAlH_4)_2TMED$ while the analysis of the insoluble portion is consistent with the formation of $LiAlH_4\cdot TMED$. *Anal.* Calcd for $(LiAlH_4)_2TMED$: Li, 7.22; Al, 28.08; H, 4.20. Found: Li, 8.35; Al, 29.15; H, 4.62. $(LiAlH_4)_2TMED$ could also be prepared by addition of the appropriate amount of amine to a solution of $LiAlH_4$ in diethyl ether. After filtration of a small amount of insoluble material which formed on addition of the amine, the solvent was removed to yield the 2:1 adduct.

The infrared spectra of these two compounds were identical although their X-ray powder patterns were different. No evidence for free $LiAlH_4$ was found in the $(LiAlH_4)_2TMED$ complex by either X-ray powder pattern or infrared data.

Regardless of the method of preparation, no evidence for the formation of TMED–alane was found. Treatment of the complexes with diethyl ether for several days did not produce even a trace amount of the amine–alane.

Reactions of LiBH₄ and Amines.—A tensimetric titration of $LiBH_4$ (recrystallized from diethyl ether) in diethyl ether showed the predominant species formed was a 1:1 adduct at -22.75 and $-45.2°$ (Figure 1). Though the relatively shallow curve indicates the probable formation of higher adducts, excess amine could be removed under vacuum at $-22.75°$. Because of the difficulty in effecting a quantitative separation of trimethylamine from ether, the amine was converted to the hydrochloride and weighed directly. The final amine to $LiBH_4$ ratio was 1.08:1 at

$-22.75°$. The sample lost all of the trimethylamine at room temperature. Infrared and X-ray powder diffraction data of the remaining product indicated it was unchanged LiBH₄. Solid LiBH₄ was treated with a 10% excess of 1:1 ratio with triethylamine in benzene. Although some solubilization of the hydride occurred, the soluble portion lost amine on isolation and was shown to be LiBH₄.

A precipitate is formed when TEDA is added to a solution of LiBH₄ in diethyl ether. This compound is resistant to hydrolysis; however complete hydrolysis was effected by incubation of the compound with 6 M HCl for 2 days at 100°. *Anal.* Calcd for LiBH₄·TEDA: Li, 5.17; B, 8.02; H, 3.01. Found: Li, 5.52; B, 8.60; H, 2.96.

Preparation of Chloromagnesium Borohydride and Reactions with Trimethylamine.—This compound was prepared by a published method.[14] *Anal.* Calcd for ClMgBH₄·3THF: Cl, 12.35; Mg, 8.47; H, 1.41. Found: Cl, 11.92; Mg, 8.13; H, 1.34.
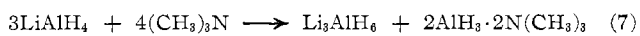
A tensimetric titration of chloromagnesium borohydride (as THF solvate) in toluene with trimethylamine indicated that no complex was formed at temperatures as low as $-22.75°$.

Attempts to desolvate ClMgBH₄·2THF lead to decomposition at 180° under high vacuum. The infrared spectrum of the volatile decomposition products showed the presence of boron–hydrogen bonds.

Reaction of NaBH₄ and MgCl₂ in Isopropylamine.—Magnesium chloride (prepared from ethylmagnesium chloride and anhydrous HCl in diethyl ether) and NaBH₄ were weighed into an O-joint tube under an inert atmosphere (MgCl₂: NaBH₄ molar ratio 1:2). The amine (dried over molecular sieve), 20 ml, was condensed in a reaction vessel under vacuum and the mixture was allowed to warm to room temperature. The reaction mixture was cooled with liquid nitrogen at the end of 2 hr and the system was opened to the Toepler pump; no hydrogen was detected. The X-ray powder pattern of the solid residue showed the presence of sodium chloride and presumably the isopropylamine solvate of magnesium borohydride.

Results and Discussion

On addition of the first increment of trimethylamine in the tensimetric titration of LiAlH₄ in diethyl ether, an immediate precipitation of the amine solvate occurs. Contrary to the report of Wiberg,[4] we found no evidence supporting more than 1 mol of the trimethylamine associating with LiAlH₄ in diethyl ether at temperatures as low as $-22.75°$. A 1:1 solvate was formed at this temperature and also at 0°. While Wiberg suggests that the 1:1 complex is stable at room temperature, we found that it was possible to remove all of the excess amine and solvent under vacuum leaving behind pure LiAlH₄ at 25°. When excess trimethylamine was allowed to stand in contact with LiAlH₄ in diethyl ether solution, small amounts (<10%) of bis(trimethylamine)–alane were detected after a few hours. The tensimetric titration was performed rapidly so that the effect of the alane extraction reaction on the titration curve would be minimal. In Peters' report of the alane extraction reaction involving LiAlH₄ and trimethylamine, the yield of the bis(trimethylamine)–alane was found to vary with a maximum (44%) being obtained at a 0.5:1 trimethylamine:LiAlH₄ ratio (based on the limiting reactant). We investigated this reaction in detail and found it to follow the stoichiometry

$$3LiAlH_4 + 4(CH_3)_3N \longrightarrow Li_3AlH_6 + 2AlH_3 \cdot 2N(CH_3)_3 \quad (7)$$

(14) W. E. Becker and E. C. Ashby, *Inorg. Chem.*, **4**, 1816 (1965).

The reaction is slow in ether but is complete in 1 month at room temperature. No lithium hydride or unreacted lithium aluminum hydride was found, and 98% of the theoretical amount of bis(trimethylamine)–alane was recovered at the end of this time. In benzene the reaction is more rapid and is complete in 3 days. Even in the absence of solvent, a 30% yield of the amine–alane is obtained at the end of a 1-month reaction period. In a more basic solvent like THF where complex formation does not occur as determined by tensimetric titration, LiAlH₄–trimethylamine mixtures are stable and no amine–alane is produced.

These results differ significantly from those reported by Ehrlich and Rice[7] for the system LiAlH₄–triethylamine. In this latter case a stable solvate (LiAlH₄·N(C₂H₅)₃) was formed in benzene; however in diethyl ether the alane extraction reaction occurred producing Li₃AlH₆ and triethylamine–alane. No details of this reaction as a route to Li₃AlH₆ were given. Because of the importance of this reaction, it was reexamined. The alane extraction reaction is even more sluggish than was found in the case of trimethylamine. A 1:1 molar mixture of LiAlH₄ and triethylamine in diethyl ether began to develop some turbidity after 1 hr of stirring at room temperature. In 3 days, the Li₃AlH₆ obtained (identified by X-ray powder pattern) corresponded to less than a 5% yield. The reaction filtrate continued to precipitate additional Li₃AlH₆ on standing.

Using conditions somewhat different from those employed to achieve the alane extraction reaction, Ruff and Hawthorne were able to prepare LiAlH₄ by displacement of trimethylamine from the trimethylamine–alane with LiH (eq 6). Working in refluxing ether, LiAlH₄·amine formation was minimized and, though it was not strictly stated, the liberated amine may have been removed from the system. At any rate, the formation of LiAlH₄ is more rapid than that of Li₃AlH₆ and in the reaction time allotted (2 hr), it is reasonable that a detectable amount of Li₃AlH₆ would not be obtained. Thus the displacement of amine from an amine–alane by lithium hydride does appear to be a valid reaction when conditions are chosen such that the alane extraction or solvation reactions with the LiAlH₄ produced do not occur.
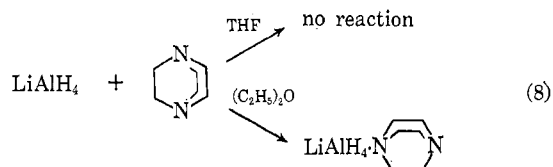
The infrared spectrum of LiAlH₄ in THF is unchanged by the addition of triethylenediamine (TEDA) suggesting that no reaction takes place. A stirred suspension of lithium hydride and TEDA–alane in THF results in a solution whose infrared spectrum is identical with that of a 1:1 mixture of LiAlH₄ and TEDA. The displacement reaction proceeds in spite of the low solubilities of both reactants. Free LiAlH₄ could not be isolated from this reaction mixture because of the nonvolatile nature of the amine. The solutions described above are stable for months without the formation of a precipitate indicating that an alane extraction reaction has not occurred.

Similarly, a tensimetric titration of LiAlH₄ in THF with trimethylamine indicated that THF is so basic a
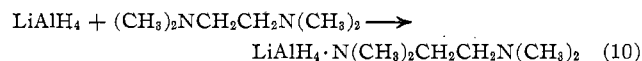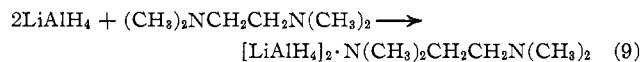
solvent that no interaction between LiAlH$_4$ and trimethylamine occurred. Trimethylamine as well as TEDA added to THF solutions of LiAlH$_4$ does not give rise to alane extraction.

The addition of TEDA to a diethyl ether solution of LiAlH$_4$ results in the formation of the insoluble LiAlH$_4$·TEDA solvate. No evidence for alane extraction was found and the probable reason for this is the low solubility of the amine solvate.

$$LiAlH_4 \ + \ \underset{(C_2H_5)_2O}{\overset{THF}{\underset{\longrightarrow}{\longrightarrow}}} \ \begin{matrix} \text{no reaction} \\ \\ LiAlH_4 \cdot N \diamond N \end{matrix} \qquad (8)$$

With the bidentate ligand N,N′,N″,N‴-tetramethylethylenediamine (TMED), two solvates of LiAlH$_4$ could be prepared in diethyl ether. The insoluble LiAlH$_4$·TMED is isolated in quantitative yield by adding the amine in 1:1 ratio to an ether solution of LiAlH$_4$. When 0.5 mol of amine is used for each mole of LiAlH$_4$, the soluble (LiAlH$_4$)$_2$·TMED is isolated by removing the solvent. The compound does not contain unsolvated LiAlH$_4$ as indicated by X-ray powder pattern and infrared analysis. Although the infrared spectra of these two TMED complexes are the same (Table I), their X-ray powder patterns and solubilities are different. Like the triethylamine complex of LiAlH$_4$, (LiAlH$_4$)$_2$·TMED is soluble in benzene. Stirring either of the TMED complexes with ether for several days did not give rise to a detectable amount of TMED–alane.

2LiAlH$_3$ + (CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$ ⟶

[LiAlH$_4$]$_2$·N(CH$_3$)$_2$CH$_2$CH$_2$N(CH$_3$)$_2$ (9)

LiAlH$_4$ + (CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$ ⟶

LiAlH$_4$·N(CH$_3$)$_2$CH$_2$CH$_2$N(CH$_3$)$_2$ (10)

The reaction between NaAlH$_4$ and trimethylamine in benzene was carried out under the most favorable conditions found for alane extraction from LiAlH$_4$. After several days, no alane extraction was detected and the NaAlH$_4$ was recovered unchanged. No conditions were found for the alane extraction reaction using NaAlH$_4$ although a number of new amine complexes were isolated.

The TEDA solvate of NaAlH$_4$ is best prepared by treatment of a THF solution of the complex metal hydride with the amine in 1:1 ratio. Although the product does not precipitate from THF, evaporation of the solvent followed by washing of the resulting solid with diethyl ether afforded a quantitative yield of the NaAlH$_4$·TEDA. The TMED solvate was prepared in a similar fashion. Both the TEDA and TMED solvates of NaAlH$_4$ showed no tendency to undergo the alane extraction reaction in diethyl ether or hydrocarbon solvents.
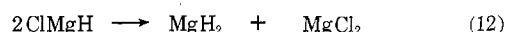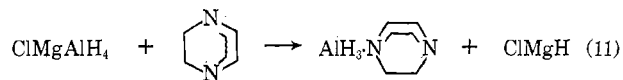
Alane extraction from magnesium aluminum hydride compounds is far more facile than that observed for LiAlH$_4$. TEDA reacts rapidly with a solution

TABLE I

INFRARED SPECTRA OF ALUMINUM HYDRIDE SPECIES

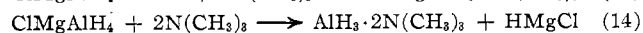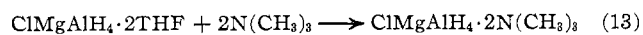| Compound	ν(Al–H), cm^{-1}	δ(Al–H), cm^{-1}
LiAlH$_4$	1780 (1810 sh), 1650	
LiAlH$_4$ (in THF)	1694	765
LiAlH$_4$·TEDA	1730	758
LiAlH$_4$·TMED	1685	750
(LiAlH$_4$)$_2$·TMED	1685	750
LiAlH$_4$ (in ether)	1740	760
Mg(AlH$_4$)$_2$[a]	1855, 1830	
Mg(AlH$_4$)$_2$·2THF[a]	1785, 1730	
Mg(AlH$_4$)$_2$·4THF[a]	1725	
Mg(AlH$_4$)$_2$·2(C$_2$H$_5$)$_2$O[a]	1800	
ClMgAlH$_4$[a]	1850, 1830	
ClMgAlH$_4$·2THF[a]	1775	
ClMgAlH$_4$·4THF[a]	1730	
NaAlH$_4$	1650	895
NaAlH$_4$ (in THF)	1680	772
NaAlH$_4$·TEDA	1630	750
NaAlH$_4$·TMED	1660	
AlH$_4$·N(C$_8$H$_{17}$)C$_8$H$_7$	1660	
AlH$_3$·TMED	1680	
AlH$_3$·TEDA	1713	
AlH$_3$·N(CH$_3$)$_3$[b]	1783	
AlH$_3$·[N(CH$_3$)$_3$]$_2$[b]	1692	

[a] Reference 11.   [b] Reference 18.

of ClMgAlH$_4$ in THF to give an immediate precipitate. X-Ray powder diffraction and infrared analyses indicated the presence of TEDA–alane in addition to other components. The observation of soluble chloride is consistent with the intermediate formation of HMgCl which is expected to disproportionate in THF as suggested earlier[15]

$$ClMgAlH_4 \ + \ \langle N \ N \rangle \ \longrightarrow \ AlH_3 \cdot N \diamond N \ + \ ClMgH \quad (11)$$

$$2ClMgH \ \longrightarrow \ MgH_2 \ + \ MgCl_2 \qquad (12)$$

The total chloride content of the solution was low; however the TEDA complex of MgCl$_2$ is insoluble in THF and is undoubtedly one of the components of the precipitate.

The degree of solvation of ClMgAlH$_4$ also appears to influence the alane extraction reaction. The bis-THF solvate (ClMgAlH$_4$·2THF) in the presence of excess trimethylamine formed only a trace of the amine–alane in 3 days. Totally desolvated ClMgAlH$_4$ underwent the alane extraction reaction to 50% completion in 5 hr at 0°. A tensimetric titration of ClMgAlH$_4$·2THF in toluene indicated the formation of the bis-trimethylamine solvate. The totally desolvated species could not be used for such titration because of the facile alane extraction.

ClMgAlH$_4$·2THF + 2N(CH$_3$)$_3$ ⟶ ClMgAlH$_4$·2N(CH$_3$)$_3$ (13)

ClMgAlH$_4$ + 2N(CH$_3$)$_3$ ⟶ AlH$_3$·2N(CH$_3$)$_3$ + HMgCl (14)

The tensimetric titration curve involving trimethylamine and a suspension of Mg(AlH$_4$)$_2$ in THF showed the formation of a stable bis-trimethylamine solvate at −22.75°. Two additional moles of trimethylamine can be bound to this species at −22.75° though they are held less strongly. In contrast to the case of

(15) E. C. Ashby, R. A. Kovar, and K. Kawakami, *Inorg. Chem.*, 9, 317 (1970).

LiAlH$_4$, alane extraction occurs with Mg(AlH$_4$)$_2$ even in THF. The amine–alane was recovered in 42% yield from Mg(AlH$_4$)$_2$ in THF in 19 days at room temperature.

Lithium borohydride was found to form only a monosolvate with trimethylamine at $-22.75°$. The excess amine over the 1:1 stoichiometry could be removed at $-22.75°$ and all of the amine could be

$$\text{LiBH}_4 + n\text{N(CH}_3)_3 \longrightarrow$$
$$\text{LiBH}_4 \cdot \text{N(CH}_3)_3 + (n - 1)\text{N(CH}_3)_3 \quad (15)$$
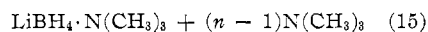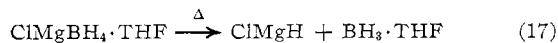
removed at room temperature (see eq 15). No evidence for higher solvates was found although higher solvates were reported as determined by pressure composition studies on the solid borohydride in the absence of solvent.[3] We were unable to investigate this system at temperatures where the bis solvate was observed[16] in ether due to the low vapor pressure of trimethylamine at $-80°$.

While LiBH$_4$ is solubilized in benzene by triethylamine, no stable complex could be isolated. Unsolvated lithium borohydride was recovered from benzene solution on evaporation of the solvent and amine. The stable TEDA solvate could be prepared in diethyl ether and is stable under vacuum. Like the corresponding LiAlH$_4$ solvate, it is insoluble in ether.

 (16)
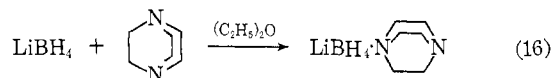
It has been reported that attempts to desolvate Mg(BH$_4$)$_2 \cdot$THF lead to the loss of boron from the compound.[17] Finding that the THF solvate of ClMg-BH$_4$ in toluene failed to show an interaction with trimethylamine, desolvation of this compound was attempted. At a temperature of 180°, the compound seemed to melt and a condensable material was collected at $-196°$; however no hydrogen was detected. The gas-phase infrared spectrum of the volatile species produced indicated the presence of boron–hydrogen as well as boron–oxygen bonds. Presumably compounds of the type H$_n$B(OC$_4$H$_9$)$_{3-n}$ were formed due to the suspected[18,19] THF cleavage of the borane at such a high temperature. Based on weight loss, about 60% of the boron was removed from the parent borohydride at 180°. X-Ray powder diffraction of the remaining solid showed the presence of MgCl$_2$ and MgH$_2$. The suggested course of the reaction is

$$\text{ClMgBH}_4 \cdot \text{THF} \xrightarrow{\Delta} \text{ClMgH} + \text{BH}_3 \cdot \text{THF} \quad (17)$$
$$2\text{ClMgH} \longrightarrow \text{MgCl}_2 + \text{MgH}_2 \quad (18)$$
$$\text{BH}_3 \cdot \text{THF} \longrightarrow \text{H}_n\text{B(OC}_4\text{H}_9)_{3-n} \quad (19)$$

The report that attempts to prepare Mg(BH$_4$)$_2$ in i-C$_3$H$_7$NH$_2$ from NaBH$_4$ and magnesium chloride led to hydrogen evolution[17] could not be substantiated. When the primary amine was condensed on a mixture of NaBH$_4$ and magnesium chloride (prepared from

i-C$_3$H$_7$MgCl and HCl in ether), no hydrogen evolution was observed over a period of several hours at room temperature. Removal of the solvent followed by vacuum sublimation did not give any of the amine-borane. Sodium chloride was shown to be present in the solid residue.

The structural nature of amine solvates of complex aluminum hydrides is of interest in light of the alane extraction reaction. Proposed structures for the only previously fully characterized LiAlH$_4 \cdot$(amine) solvate involved coordination of the aluminum atom with partial displacement of LiH from the compound. These structures (I and II) were proposed because the infrared spectrum of the LiAlH$_4 \cdot$(C$_2$H$_5$)$_3$N solvate was identical with that of triethylamine–alane. It has long been recognized[20–22] that the aluminum–hydrogen stretching frequency is strongly dependent on the coordination number of the aluminum hydride species; that is, as the number of ligands on the aluminum atom increases, the ν(Al–H) decreases. For example, pentacoordinate aluminum generally exhibits an Al–H stretching vibration in the region <1750 cm^{-1} while tetracoordinate species are characterized by frequencies in the region >1750 cm^{-1}.

Lack of specific structural information on many of the complex metal hydride–amine solvates reported here does not permit an unambiguous interpretation of the infrared spectra of these compounds. The infrared spectrum of LiAlH$_4$ as a solid shows several bands in the infrared region normally associated with aluminum–hydrogen vibrations. This suggests a change in selection rules due to a low site symmetry for the AlH$_4^-$ group which allows the normally Raman-only active ν_1 to be seen in the infrared spectrum.

Field effects may also be important in exerting a significant influence on the aluminum–hydrogen vibrations in the infrared spectrum. The dependence of asymmetric metal–halogen vibrations in tetrahedral complexes on cation size has been noted, but lack of structural information again provides no clear-cut explanation.[23] The infrared spectrum of LiAlH$_4$ is influenced by solvents (ν(Al–H) in ether is 1740 cm^{-1} while in THF it is found at 1694 cm^{-1}). This is suggestive that the degree of solvation of the Li cation influences the infrared spectrum of LiAlH$_4$ even in solution. It is not unreasonable to postulate that amine adducts of complex metal hydrides involve solvation of the cation and that the infrared spectral data of such complexes in the solid state reflect the change in ionic potential as a decrease in ν(AlH). A similar effect, presumably due to differing ionic potentials, has been observed in the alkali metal hexahydridoaluminates[24] (ν(Al–H) in Li$_3$AlH$_6$ is at 1720 cm^{-1} while ν(Al–H) in K$_3$AlH$_6$ is at 1300 cm^{-1}) and magnesium aluminum hydride.

(16) E. Wiberg and A. Jahn, *Z. Naturforsch.*, **11b**, 489 (1956).

(17) J. Plesek and S. Hermanek, *Collection Czech. Chem. Commun.*, **31**, 3845 (1966).

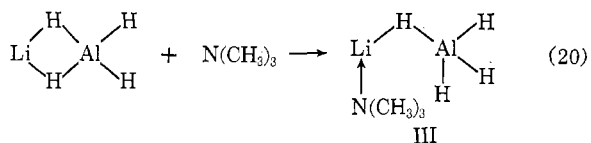(18) E. C. Ashby and W. E. Foster, *J. Am. Chem. Soc.*, **88**, 3248 (1966).

(19) E. Wiberg and W. Gosele, *Z. Naturforsch.*, **10b**, 236 (1955).

(20) R. Ehrlich, A. R. Young, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, **2**, 650 (1963).

(21) R. Dautel and W. Zeil, *Z. Elektrochem.*, **64**, 1234 (1960).

(22) H. Roszinski and R. Dautel, *Z. Physik. Chem.*, **36**, 26 (1963).

(23) D. M. Adams, "Metal Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968, pp 42–43, and references cited therein.

(24) E. C. Ashby and B. D. James, *Inorg. Chem.*, **8**, 2468 (1969).

The solubility of amine complexes of alkali metal aluminum hydrides in hydrocarbons is also suggestive of cation solvation for it is a commonly observed phenomenon that increasing cation size enhances solubility in noncoordinating solvents.

Additional evidence consistent with a lack of aluminum coordination in alkali metal aluminum hydrides was obtained by an examination of amine interactions with tri-n-octyl-n-propylammonium aluminum hydride. Even under the most favorable conditions of a hydrocarbon solvent, the tetrahydridoaluminate anion (AlH_4^-) demonstrated no acidity toward trimethylamine.

As Ehrlich and Rice have observed in the case of $LiAlH_4 \cdot N(C_2H_5)_3$, we also find that on formation of an amine complex, the $\nu(Al–H)$ of $LiAlH_4$ does decrease. We do not observe the fortuitous agreement in the infrared spectra of other amine adducts with the corresponding amine–alane (Table I).

The failure of the alane extraction reaction to occur in strong donor solvents where amine solvation does not occur suggests that the formation of the amine complex is the first process to occur in the alane extraction reaction. The solvation could take place to the alkali metal as well as at aluminum (eq 20). There seem to be no data at this time which would allow one to make a clear-cut choice between the intermediates I or II and III. On formation of the amine complex

$$Li\underset{H}{\overset{H}{\diagup}}Al\underset{H}{\overset{H}{\diagdown}} + N(CH_3)_3 \longrightarrow Li\overset{H}{\underset{\underset{N(CH_3)_3}{\uparrow}}{\diagup}}Al\overset{H}{\underset{H}{\diagdown}} \quad (20)$$

III

III, the aluminum hydride residue is partially displaced from the LiH fraction. This sort of intermediate has been proposed for the cleavage of diborane and evidence has been obtained for the existence of such an intermediate using nmr and infrared spectroscopy.[25]

Another possibility involves the equilibrium

$$LiAlH_4 \rightleftarrows LiH + AlH_3 \quad (21)$$

Although this equilibrium lies predominantly to the left if it exists at all, driving it to the right by removal of the alane as the amine–alane would produce LiH in a highly reactive state (as would the first case considered) which would favor reaction with $LiAlH_4$ to give Li_3AlH_6. The reaction between $LiAlH_4$ and lithium hydride to give Li_3AlH_6 (eq 22) has been observed

$$2LiH + LiAlH_4 \longrightarrow Li_3AlH_6 \quad (22)$$
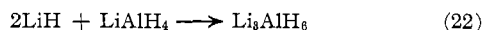
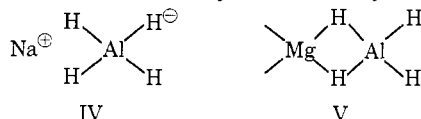in the presence of triethylaluminum catalyst.[26]

The inability of the more ionic hydrides such as $NaAlH_4$ to undergo the alane extraction reaction can be explained by the lack of covalent interaction in these compounds and consequently the impossibility

of forming such intermediates as I, II, or III. Consistent with this model is the relative ease of complex magnesium aluminum hydride compounds to undergo the alane extraction reactions.
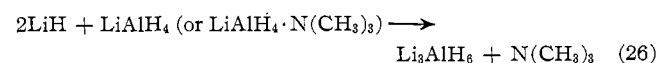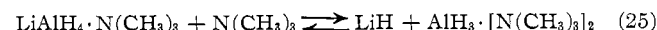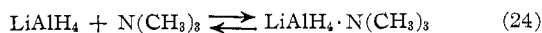
The nature of the products of the alane extraction reaction are of prime importance in determining if this reaction will occur. This was inferred in the earlier discussion of amine displacement by metal hydrides. For example, $LiBH_4$ is not expected to undergo the alane extraction reaction simply on the basis of the known reaction of lithium hydride with amine–boranes

$$LiH + BH_3NR_3 \rightleftarrows LiBH_4 + R_3N \quad (23)$$
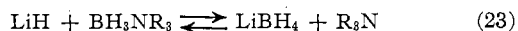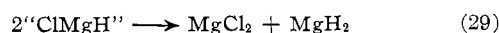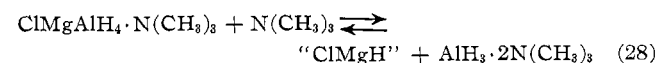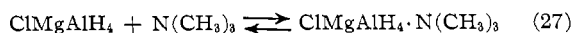
In one case (IV) the tetrahydridoaluminate ion is hardly susceptible to hydride ion displacement by a tertiary amine. On the other hand, as the covalent character of the complex metal hydride increases *via* hydrogen bridge bonding, the central metal atom becomes more susceptible to bridge cleavage since the energy lost by breaking the bridge bond ($\sim$10 kcal) is more than compensated for by the solvation of the central metal atom by the tertiary amine. On

$$Na^{\oplus} \quad \underset{H}{\overset{H}{\diagup}}Al\underset{H}{\overset{H^{\ominus}}{\diagdown}} \qquad \underset{}{\overset{H}{\diagup}}Mg\underset{H}{\overset{H}{\diagdown}}Al\underset{H}{\overset{H}{\diagdown}}$$

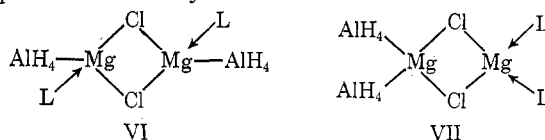IV   V

the other hand the borane extraction reaction is not expected to occur if the hydride product (LiH) from borane extraction is incapable of redistribution with the complex metal hydride ($LiBH_4$) as is the case for Li_3AlH_6 and MgH_2.[27] In some cases failure of the hydride-containing product to redistribute may be a function of a reaction subsequent to alane extraction. For example

$$LiAlH_4 + N(CH_3)_3 \rightleftarrows LiAlH_4 \cdot N(CH_3)_3 \quad (24)$$
$$LiAlH_4 \cdot N(CH_3)_3 + N(CH_3)_3 \rightleftarrows LiH + AlH_3 \cdot [N(CH_3)_3]_2 \quad (25)$$
$$2LiH + LiAlH_4 \text{ (or } LiAlH_4 \cdot N(CH_3)_3) \longrightarrow$$
$$Li_3AlH_6 + N(CH_3)_3 \quad (26)$$

or

$$ClMgAlH_4 + N(CH_3)_3 \rightleftarrows ClMgAlH_4 \cdot N(CH_3)_3 \quad (27)$$
$$ClMgAlH_4 \cdot N(CH_3)_3 + N(CH_3)_3 \rightleftarrows$$
$$\text{"ClMgH"} + AlH_3 \cdot 2N(CH_3)_3 \quad (28)$$
$$2\text{"ClMgH"} \longrightarrow MgCl_2 + MgH_2 \quad (29)$$

The structure of $ClMgAlH_4$ in solution is unknown but is probably either a covalently bonded symmetric or asymmetric dimer (VI, VII).[12] In the first case (VI), alane extraction would produce ClMgH which could disproportionate to MgH_2 and $MgCl_2$, whereas in the second case (VII), magnesium hydride would be produced directly.

$$AlH_4–Mg\underset{L}{\overset{Cl}{\diagup}}\underset{Cl}{\overset{L}{\diagdown}}Mg–AlH_4 \qquad \underset{AlH_4}{\overset{AlH_4}{\diagup}}Mg\underset{Cl}{\overset{Cl}{\diagup}}\underset{L}{\overset{L}{\diagdown}}Mg\underset{L}{\overset{}{\diagdown}}$$

VI   VII

(25) (a) S. G. Shore and C. L. Hull, *J. Am. Chem. Soc.*, **88**, 5346 (1966); S. G. Shore and C. L. Hull, *ibid.*, **89**, 3947 (1967); (b) Y. Matsui and R. C. Taylor, *ibid.*, **90**, 1363 (1968).

(26) P. Chini, A. Baradel, and C. Vacca, *Chim. Ind.* (Milan), **48**, 596 (1966).

(27) Although Hawthorne and Ruff have reported that commercial grade MgH_2 does not react with trimethylamine–alane, we have found evidence that this reaction will occur with MgH_2 prepared from diethylmagnesium and $LiAlH_4$ and that the formation of magnesium aluminum hydride seems to be an equilibrium process in hydrocarbon solvents.

Although this criterion for alane extraction from tetrahydridoaluminates and borane extraction from tetrahydridoborates has not been widely investigated in transition metal compounds, it probably applies here as well. For example, contrary to published reports, bis(triphenylphosphine)tetrahydridoboratocopper(I) is unstable in pyridine and decomposes to copper metal, hydrogen, and pyridine–borane. Also attempts to prepare the very stable [(C₆H₅)₃P]₂CuBH₄ complex from copper hydride and pyridine–borane in the presence of phosphine were not successful.[28]

While the nature of the hydride species as a result of alane extraction is important, it is probably not

the sole determining factor. If it were, the reaction of trimethylamine with NaAlH₄ might be expected to yield Na₃AlH₆.[29] The lack of reaction is probably best explained in terms of the ionic model for NaAlH₄ mentioned earlier.

(28) J. A. Dilts, Ph.D. Thesis, Northwestern University, 1969.

(29) L. I. Zakharkin and V. V. Gavrilenko, *Dokl. Akad. Nauk SSSR*, **145**, 145, 793 (1962).

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Reactions of Some Trialkyls of Phosphorus, Arsenic, or Antimony with Some Organohalophosphines, -arsines, or -stibines

BY JACK C. SUMMERS AND HARRY H. SISLER

The reactions of a series of alkyl- and arylphosphines, -arsines, or -stibines with a variety of halo- and haloalkyl- (or haloaryl-) phosphines, -arsines, or -stibines have been studied. It has been shown that in most instances the formation of adducts of the general formula $R_nMX_{3-n} \cdot yM'R'_3$ occurs and that in many instances these adducts decompose to give M–M bonded compounds plus $R'_3M'X_2$. It was further shown by electrical conductance and proton magnetic resonance data that a number of these adducts are ionic in solution.
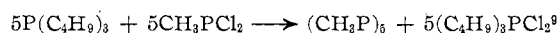
Introduction

Reactions of the trialkyls of phosphorus, arsenic, and antimony with organohalophosphines, -arsines, and -stibines have been studied by several investigators.[1-10] In some of the reactions, adducts of the type $R_nMX_{3-n} \cdot yM'R'_3$, where $y = 1$ or 2, were obtained. In others, compounds containing M–M bonds and compounds of the type $R'_3M'X_2$ were obtained. The nature of the bonding and structure of these adducts have not been determined nor have the parameters which influence the type of product obtained.
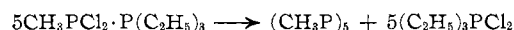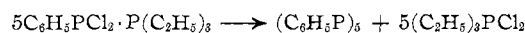
In most instances, reactions of trialkylphosphines with diorganohalophosphines and -arsines yield stable phosphino- and arsinophosphonium salts of the type $[R_2MPR'_3]X$.[5,6,10] The reaction of triethylphosphine with diphenylchlorophosphine yields the adduct [(C₆H₅)₂PP(C₂H₅)₃]Cl.[6] Tri-*n*-butylphosphine, however,

brings about oxidative coupling as it reacts with diphenylchlorophosphine to give tetraphenylbiphosphine and tri-*n*-butyldichlorophosphorane.[7]

Studies from this laboratory have shown that tri-*n*-butylphosphine reacts with phenyldichlorophosphine and methyldichlorophosphine to abstract chlorine and give oxidative coupling according to

$$5P(C_4H_9)_3 + 5C_6H_5PCl_2 \longrightarrow (C_6H_5P)_5 + 5(C_4H_9)_3PCl_2^{[7,11]}$$

$$5P(C_4H_9)_3 + 5CH_3PCl_2 \longrightarrow (CH_3P)_5 + 5(C_4H_9)_3PCl_2^{[9]}$$

However, the reactions of triethylphosphine with phenyldichlorophosphine and methyldichlorophosphine at −20° give the adducts C₆H₅PCl₂·P(C₂H₅)₃ and CH₃PCl₂·P(C₂H₅)₃, respectively; upon warming to room temperature, these adducts decompose according to[9]

$$5C_6H_5PCl_2 \cdot P(C_2H_5)_3 \longrightarrow (C_6H_5P)_5 + 5(C_2H_5)_3PCl_2$$

$$5CH_3PCl_2 \cdot P(C_2H_5)_3 \longrightarrow (CH_3P)_5 + 5(C_2H_5)_3PCl_2$$

Reactions of tri-*n*-butylphosphine with organodihaloarsines yield only 1:1 adducts.[8] Attempts to convert these adducts to products containing As–As bonds by heating failed. Conductance measurements in nitromethane indicate that these adducts can best be written as [R(X)AsP(C₄H₉)₃]X.[8] However, in deu-

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