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A Study of the Reactions of Lithium Aluminum Hydride and Sodium Aluminum Hydride with Beryllium Chloride in Diethyl Ether and Tetrahydrofuran. A Report Questioning the Existence of $Be(AlH_4)_2$ in Solution

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The reactions of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ were studied in 1:1 and 2:1 ratios in both diethyl ether and THF as solvents. No evidence for the previously reported $Be(AlH_4)_2$ was found. In 2:1 ratio the reaction of $NaAlH_4$ and $BeCl_2$ in THF was found to be similar to the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether. Two surprising aspects of the latter reaction are that the AlH_3 formed is soluble in diethyl ether and the (2 LiCl)–BeH_2 formed is actually isolated as a complex ($Li_2BeH_2Cl_2$). The reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in THF results in complete solubilization of all products.

$$2NaAlH_4 + BeCl_2 \xrightarrow{THF} 2NaCl\downarrow + BeH_2\downarrow + 2AlH_3$$

$$2LiAlH_4 + BeCl_2 \xrightarrow{Et_2O} Li_2BeH_2Cl_2\downarrow + 2AlH_3$$

Once again $Li_2BeH_2Cl_2$ and AlH_3 are formed as in diethyl ether; however, in THF $Li_2BeH_2Cl_2$ is soluble. Evidence is presented to support the equilibrium $2LiAlH_4 + BeCl_2 \rightarrow Li_2BeH_2Cl_2 + 2AlH_3 \rightleftharpoons LiAlH_3Cl + LiBeH_2Cl + AlH_3$. The reaction of $LiAlH_4$ with $BeCl_2$ in 1:1 ratio in diethyl ether and that of $NaAlH_4$ with $BeCl_2$ in 1:1 ratio in THF present a similar picture since the by-products LiCl and NaCl are insoluble in diethyl ether and THF, respectively. Independent evidence has

$$2LiAlH_4 + 2BeCl_2 \xrightarrow{Et_2O} 2LiCl\downarrow + BeH_2\downarrow + HBeCl + H_2AlCl + AlH_3$$

$$2NaAlH_4 + 2BeCl_2 \xrightarrow{THF} 2NaCl\downarrow + BeH_2\downarrow + HBeCl + H_2AlCl + AlH_3$$

been obtained for the following reactions in order to establish the detailed nature of the above reactions

$$LiCl + AlH_3 \xrightarrow{THF} LiAlH_3Cl$$

$$2AlH_3 + BeCl_2 \xrightarrow{Et_2O} HBeCl + H_2AlCl + AlH_3$$

$$2LiCl + BeH_2 \xrightarrow[\substack{or\\Et_2O}]{THF} Li_2BeH_2Cl$$

$$LiAlH_4 + HBeCl \xrightarrow{THF} LiBeH_2Cl + AlH_3$$

$$LiCl + HBeCl \xrightarrow{THF} LiBeCl_2H$$

Introduction

In 1951 Wiberg and Bauer[1] reported that the reaction of $LiAlH_4$ with $BeCl_2$ in diethyl ether yields beryllium aluminum hydride $Be(AlH_4)_2$ and LiCl (eq 1). The insoluble LiCl was reported to precipitate from solution leaving dissolved $Be(AlH_4)_2$ which was recovered by removal of solvent.

$$2LiAlH_4 + BeCl_2 \rightarrow Be(AlH_4)_2 + 2LiCl \qquad (1)$$

Wood and Brenner[2] using the method of Wiberg and Bauer[1] reported that metastable solutions of $Be(AlH_4)_2$ could be prepared by combining $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether. It was reported that a white precipitate formed which was filtered from solution leaving a filtrate which exhibited a Be:Al:H ratio of 1.0:1.82:9.2, indicating the presence of $Be(AlH_4)_2$ in solution. The product was said to decompose within a few hours at the boiling point of ether; however, the decomposition products were not characterized. The product was reported to be stable for several days below 10°; however, the absence of data other than analysis leaves this product poorly described.

In other work,[3] the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether was reported to yield a precipitate of LiCl and BeH_2, leaving AlH_3 in solution.

Related to the work above is the reported preparation of $LiBe(AlH_4)_3$ which has been described in a recent patent.[4] This compound was prepared by the addition of $LiAlH_4$ in diethyl ether to a slurry of $BeCl_2$ in 2:1 ratio in a mixture of ether and hexane, at room temperature. Immediate precipitation resulted and the precipitated solid was removed as soon as the combination of reagents was completed. After addition of triethylamine to the filtrate, a solid having the empirical formula $LiBe(AlH_4)_3$ precipitated over a period of 7 days. The yield was *ca.* 5% based on $BeCl_2$. The compound was characterized by elemental and X-ray powder diffraction analysis. An explanation of the results obtained in this work was suggested (eq 2) based on prior art. If $Be(AlH_4)_2$ were formed initially and reacted preferentially with the $LiAlH_4$ reactant to form a stable adduct [$LiBe(AlH_4)_3$], the complex might be isolated after removal of the insoluble

$$4LiAlH_4 + 2BeCl_2 \rightarrow [Be(AlH_4)_2 + BeCl_2 + 2LiAlH_4 + 2LiCl] \rightarrow$$
$$LiBe(AlH_4)_3 + {}^1/_2BeH_2\downarrow + AlH_3 + {}^1/_2BeCl_2 + 3LiCl\downarrow \qquad (2)$$

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[1] E. Wiberg and R. Bauer, *Z. Naturforsch. B*, 6, 171 (1951).

[2] G. B. Wood and A. Brenner, *J. Electrochem. Soc.*, 104, 29 (1957).

[3] C. E. Holley and J. F. Lemons, "The Preparation of the Hydrides of Magnesium and Beryllium," Report IA-1660, Los Alamos Scientific Laboratory, Los Alamos, N. M., April 1, 1954.

[4] G. Rice and R. Ehrlich, U. S. Patent 3,383,187 (May 14, 1968).

products. The addition of triethylamine to the product solution may serve to induce precipitation of the complex.

Recently we found in a study of reactions[5] of $LiAlH_4$ and $NaAlH_4$ with magnesium halides (where the halogen is Cl, Br, or I) in diethyl ether and tetrahydrofuran that halogen atoms were replaced in a stepwise fashion in a simple metathetical exchange process to yield first $XMgAlH_4$ and then $Mg(AlH_4)_2$. The nature of the products was controlled by the choice of halogen and the solvent type. The reaction of $NaAlH_4$ and $CaCl_2$ in 2:1 ratio was reported to yield $Ca(AlH_4)_2$ and NaCl.[6] On the other hand, reaction of zinc,[7] cadmium,[8] and mercury[9] halides with $LiAlH_4$ in diethyl ether or tetrahydrofuran produced only the insoluble, unstable binary hydrides ZnH_2, CdH_2, and HgH_2 which decomposed to the metal and hydrogen at or below room temperature. It was postulated that $M(AlH_4)_2$ was initially formed which rapidly decomposed to the group IIb metal hydride which precipitated and to AlH_3 which remained in solution.

$$M(AlH_4)_2 \rightarrow MH_2 + 2AlH_3 \quad (M = Zn, Cd) \tag{3}$$

Recent Russian work[9] reported the preparation of $LiAl_2H_7$ and $LiAl_3H_{10}$ in diethyl ether according to eq 4 and 5. The

$$2LiAlH_4 + BeCl_2 \rightarrow LiAl_2H_7 + HBeCl + LiCl \tag{4}$$

$$3LiAlH_4 + BeCl_2 \rightarrow LiAl_3H_{10} + BeH_2 + 2LiCl \tag{5}$$

compounds $LiAl_2H_7$ and $LiAl_3H_{10}$ were reported to be very unstable in ether but somewhat more stable in the solid state.

Since there are conflicting reports concerning the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether, this reaction was reexamined in an attempt to resolve the conflicting reports. The reaction of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ in tetrahydrofuran solvent was also studied. Using elemental analysis, infrared spectroscopy, and X-ray powder diffraction techniques the above reactions were studied in detail.

Experimental Section

Reagents. Beryllium metal was obtained from the Brush Beryllium Co., Elmore, Ohio; the metal was in the form of high-purity electrorefined flake (99.4%). Chlorine gas was Matheson high purity, used without further purification. Bromine was obtained from Dow Chemical Co. and used without further purification. All solvents were distilled at atmospheric pressure from $LiAlH_4$ (diethyl ether) or $NaAlH_4$ (benzene, tetrahydrofuran) immediately before use. $LiAlH_4$ and $NaAlH_4$ were obtained as gray, lumpy solids from Ventron, Metal Hydrides Division.

Instrumentation. Infrared spectra were obtained using either a Perkin-Elmer Model 621 or a Model 257 infrared spectrophotometer. Potassium bromide cells were used. Spectra of solids were obtained in Nujol which had been dried over sodium wire and stored in a drybox.

X-Ray powder diffraction patterns were obtained using a Debye-Scherrer camera of 114.6-mm diameter using Cu Kα radiation with a nickel filter. Single-walled capillaries of 0.5-mm diameter were used.

Thermal analysis was performed on a Mettler Thermoanalyzer II modified for differential pressure recording at reduced pressure. Samples of approximately 50-mg size were run in an aluminum crucible at a heating rate of 2°/min. Alumina (60 mesh) was used as the reference material. In the part labeled ΔP on the dta-tga tracer, the shaded area indicates that a condensable gas only is being evolved. A more detailed description of the apparatus has been described elsewhere.[10]

Analytical Work. Aluminum was determined by standard EDTA titration. Beryllium was determined gravimetrically by precipitation as the hydroxide, followed by ignition to the oxide at 1000° for 1 hr. Aluminum interference was prevented by the addition of an excess of EDTA which complexes the aluminum and prevents its precipitation as the hydroxide. An alternative method used for determining beryllium and aluminum was to adjust the pH of the sample to 7.8 and then add NaF. This sample was heated to dissolve the NaF. When the sample was cooled, the NaOH formed was titrated to pH 7.8 with standard HCl.

Analysis for chloride and bromide was carried out using a modified Volhard procedure.

Hydrogen analysis was accomplished by acid hydrolysis of a weighed amount of sample on a standard vacuum line equipped with a Toepler pump.[11]

Preparative Methods. All operations were carried out under an atmosphere of dry, oxygen-free nitrogen in a glove box or by use of bench-top inert-atmosphere techniques.[11]

Standard Solutions of Complex Aluminum Hydrides. Solutions of $LiAlH_4$ in diethyl ether and tetrahydrofuran and solutions of $NaAlH_4$ in tetrahydrofuran were prepared by stirring the solid hydride for 24 hr with freshly distilled solvent, followed by filtration, to yield a clear, colorless solution. These reactant solutions were standardized by aluminum analysis and transferred volumetrically.

Beryllium Chloride Solvates. Beryllium chloride was prepared according to the method of Wood and Brenner.[2] Argon was used as a carrier gas instead of nitrogen, resulting in an almost quantitative yield of $BeCl_2$. To prepare the etherates of $BeCl_2$, a quantity of the unsolvated halide was suspended in dry benzene and the mixture cooled in an ice-water bath. A quantity (50% excess based on the bis solvate) of dry diethyl ether or tetrahydrofuran was added slowly as the mixture was stirred. The solvated $BeCl_2$ which is soluble in benzene was isolated by removal of benzene under vacuum. *Anal.* Calcd for $BeCl_2 \cdot 2THF$: Be, 4.02; Cl, 31.6. Found: Be, 3.93; Cl, 30.9. Calcd for $BeCl_2 \cdot 2Et_2O$: Be, 3.95; Cl, 31.1. Found: Be, 3.86; Cl, 30.5. Infrared and X-ray powder diffraction data were recorded for the solvates.

Reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 Ratio in Ether. To 32.29 mmol of $BeCl_2$ in 250 ml of diethyl ether was added 64.58 mmol of $LiAlH_4$ solution at 0°. A white precipitate formed at once and increased in volume as the $LiAlH_4$ was added. The mixture was stirred for 15 hr and filtered through a glass frit, yielding a white residue and a colorless, clear filtrate. *Anal.* Found for the insoluble residue: H, 2.64; Be, 7.72; Al, 6.43; Cl, 60.6. The X-ray powder diffraction pattern contained only lines arising from LiCl. The infrared spectrum (Nujol mull) exhibited very broad absorptions at 1755, *ca.* 1350, and 768 cm^{-1}. *Anal.* Found for the ether-soluble fraction: H, 5.99; Li, 0.73; Al, 50.2. No beryllium or chloride was detected. The solvent was removed under vacuum and the resulting solid was shown to contain no powder diffraction lines attributable to LiCl or starting materials. The infrared spectrum of a Nujol mull of this material showed the following absorptions: 1755 (s, vb), 1660 (s, vb), 1022 (s), 720 (s, b), and 605 (m) cm^{-1}.

A similar experiment was performed at −78°; the mixture was stirred at this temperature for 60 min and then filtered while cold. Again, a white residue was recovered, leaving a clear, colorless filtrate. *Anal.* Found for the insoluble residue: H, 2.40; Be, 7.50; Al, 8.55; Cl, 60.6. The infrared spectrum of a Nujol mull of the insoluble residue gave the following absorptions: 1750 (s, vb), 1350 (s, vb), 765 (m, vb), and 316 (s, b) cm^{-1}. The X-ray powder diffraction pattern indicated no lines other than those arising from LiCl. *Anal.* Found for the solid isolated by removing solvent from the ether-soluble fraction of this reaction: H, 5.98; Li, 0.78; Al, 50.2. Again, no beryllium or halogen was found. The infrared spectrum showed absorption bands at 1778 (s, vb), 1600 (s, vb), 1020 (s, b), 720 (s, b), and 597 (s, b) cm^{-1}. The X-ray powder diffraction pattern showed no lines attributable to LiCl or starting materials. Material balances in these reactions averaged 85-90%.

In a similar experiment in which the reaction temperature and time were different, 10 mmol of $BeCl_2$ was added to 20 mmol of $LiAlH_4$ in 150 ml of ether at room temperature. A white precipitate appeared immediately. The mixture was stirred for 2 hr and then filtered, yielding a white residue and a colorless clear filtrate. Removal of the solvent from the filtrate yielded a white powder. Analysis of the precipitate gave Be:Al:Li:H:Cl = 1.00:0.078:1.90:2.0:1.90. X-Ray analysis showed lines for LiCl plus another pattern (see Table III). The analysis of the soluble compound gave Be:Al:H:Li:Cl = 0.0:1.0:3.3:0.023:0.023.

The above reaction was repeated except the filtration was carried

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(5) E. C. Ashby, R. D. Schwartz, and B. D. James, *Inorg. Chem.*, 9, 325 (1970).

(6) British Patent 905,985 (1962).

(7) E. Wiberg, W. Henle, and R. Bauer, *Z. Naturforsch. B*, 6, 393 (1951); 7, 249 (1952).

(8) E. Wiberg and W. Henle, *Z. Naturforsch. B*, **6**, 461 (1951).

(9) T. N. Dymova, *et al.*, *Dokl. Akad. Nauk SSSR*, **184**, 1338 (1969).

(10) (a) E. C. Ashby and J. Watkins, *Inorg. Chem.*, in press; (b) E. C. Ashby and P. Claudy, *J. Chem. Educ.*, in press.

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

out 2-3 min after the mixing of the reactants. The analysis of the precipitate gave Be:Al:H:Li:Cl = 1.0:0.109:2.1:2.2:2.2. X-Ray analysis gave two fine lines characteristic of LiCl plus another pattern which corresponds to that found in the precipitate above except with more lines. The dta-tga is shown in Figure 1. The analysis of the soluble compound gave Al:H:Li:Be = 1.0:2.97:0.002:0.0. The dta-tga is shown in Figure 2. The precipitate was stirred in diethyl ether for 3 days at room temperature. At the end of this time the ether was removed under vacuum. The X-ray powder pattern showed only lines characteristic of LiCl. The dta-tga is shown in Figure 3 (compare it to Figure 1).

Equilibration of a 2:1 mixture of $LiAlH_4$ and $BeCl_2$ in diethyl ether for 135 hr at 25° yielded products with infrared spectra identical with those of the products isolated when the reaction mixture was worked up immediately. The X-ray powder pattern of the insoluble product exhibited only lines characteristic of LiCl.

Reaction of $NaAlH_4$ and $BeCl_2$ in 2:1 Ratio in Tetrahydrofuran. To a stirred suspension of 20.87 mmol of $BeCl_2 \cdot 2THF$ in 150 ml of THF, cooled to 0° in an ice-water bath, was added 41.74 mmol of $NaAlH_4$ in THF. Immediate precipitation resulted. After stirring for 30 min at 0°, the mixture was filtered while cold yielding a white residue and a clear, colorless filtrate. Removal of the THF from the filtrate at reduced pressure produced a white solid. *Anal.* Found for the insoluble fraction: H, 1.36; Be, 5.16; Al, 1.91; Cl, 46.9. The X-ray powder diffraction pattern contains five unidentified lines in addition to those arising from NaCl. The infrared spectrum of a Nujol mull of this sample exhibits the following absorptions: 1710 (s, vb), 1350 (s, vb), 1020 (w), and 815 (s, vb) cm^{-1}. *Anal.* Found for the residue from the soluble fraction: H, 3.05; Be, 0.309; Al, 26.2; Cl, 0.763. The X-ray powder diffraction pattern of this sample had many lines, but none due to $BeCl_2 \cdot 2THF$. The infrared spectrum of a Nujol mull shows absorptions at the following positions: 1800 (s, b), 1625 (m, vb), and 1015 (s, b) cm^{-1}.

This reaction was repeated and the products were stirred at room temperature for a period of time to allow possible product redistribution. To 10.39 mmol of $BeCl_2 \cdot 2THF$ in 75 ml of THF was added 20.77 mmol of $NaAlH_4$. The reaction was carried out at room temperature producing an immediate white precipitate. After stirring for 92 hr no obvious further solubilization of the precipitate had occurred. Filtration of this mixture produced a white solid and a colorless filtrate. Infrared examination of the filtrate showed the following absorptions (THF bands deleted): 1640 (s), 793 (s), and 726 (s) cm^{-1}. Nmr spectra of the filtrate indicated nothing other than solvent over a 950-Hz sweep width. Removal of solvent from this filtrate yielded a white solid. *Anal.* Found: H, 3.39; Be, 3.70; Al, 25.6; Cl, 2.59. A Nujol mull of this solid showed infrared absorption bands at 1816 (s, b), 1606 (s, vb), 1350 (m, b), 1170 (w), 1120 (w), 1017 (w), 969 (w), 846 (w), 740 (m, b), and 671 (w) cm^{-1}. The X-ray powder diffraction pattern of this solid consists of four lines also found in the product resulting by removing solvent from the reaction mixture of 2 $LiAlH_4$ + $BeCl_2$ in THF. *Anal.* Found for the insoluble residue obtained from this reaction: H, 0.649; Be, 2.77; Al, 1.80; Cl, 44.2. The infrared spectrum of a Nujol mull of this solid had the following absorptions: 1805 (s, b), 1683 (s, b), 1544 (s, b), 1322 (m, sh), 1238 (w), 1150 (m), 1058 (m, sh), 1029 (s), 986 (m), 967 (m), 855 (s, b), 764 (s, b), and 723 (s, b) cm^{-1}. The X-ray powder diffraction pattern contains the NaCl pattern plus a faint, indistinct line found in the pattern observed above for the soluble portion.

An attempt was made to detect the presence of butoxyalane species (produced by AlH_3 cleavage of THF) in the soluble 2:1 product which had been equilibrated for 92 hr. Acid hydrolysis of the solid, followed by benzene extraction of the hydrolysate, confirmed the presence of 1-butanol when the extract was examined by vapor-phase chromatography. The estimated aluminum:butanol ratio was slightly greater than 1.

The above reaction was repeated for a shorter reaction period in order to minimize THF cleavage. To 9.95 mmol of $BeCl_2$ as a suspension in THF was added 19.9 mmol of $NaAlH_4$ in THF. The mixture was stirred for 1.5 hr and filtered. A white precipitate and slightly turbid solution were obtained. The solvent was removed from the filtrate under vacuum producing a white powder. Analysis of the precipitate gave a Be:H:Cl:Na:Al ratio of 1.2:1.96:2.93:2.30:0.04. The X-ray powder pattern of this solid showed lines for NaCl plus two lines which do not match $BeCl_2 \cdot 2THF$. The analysis of the THF-soluble portion gave a Na:Al:H:Be:Cl ratio of 0.15:1.00:2.98:0.0:0.0.

Reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 Ratio in THF. To 32.1 mmol of $BeCl_2 \cdot 2THF$ suspended in 200 ml of dry THF was added 64.2 mmol of $LiAlH_4$. No heat of reaction was noted, but most of the suspended halide dissolved immediately leaving a slightly turbid solution. Stirring at 25° for 48 hr produced a completely clear, colorless, homogeneous solution. Removal of solvent until the volume was 100 ml caused no change. Approximately 100 ml of dry benzene was distilled into the solution, causing the appearance of a white precipitate. After removal of 50 ml of solvent by reduced pressure distillation, the solution was filtered to separate the white

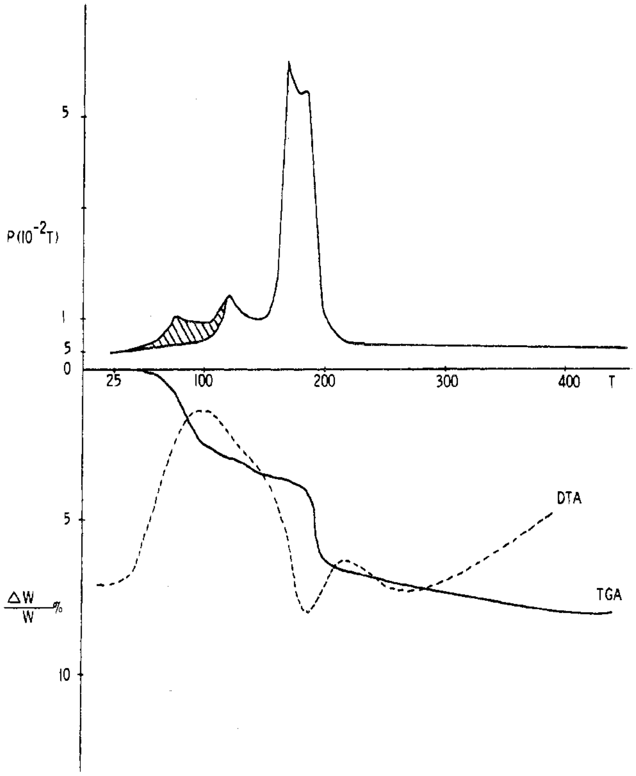


Figure 1. Vacuum dta-tga of $BeH_2 \cdot 2LiCl$.

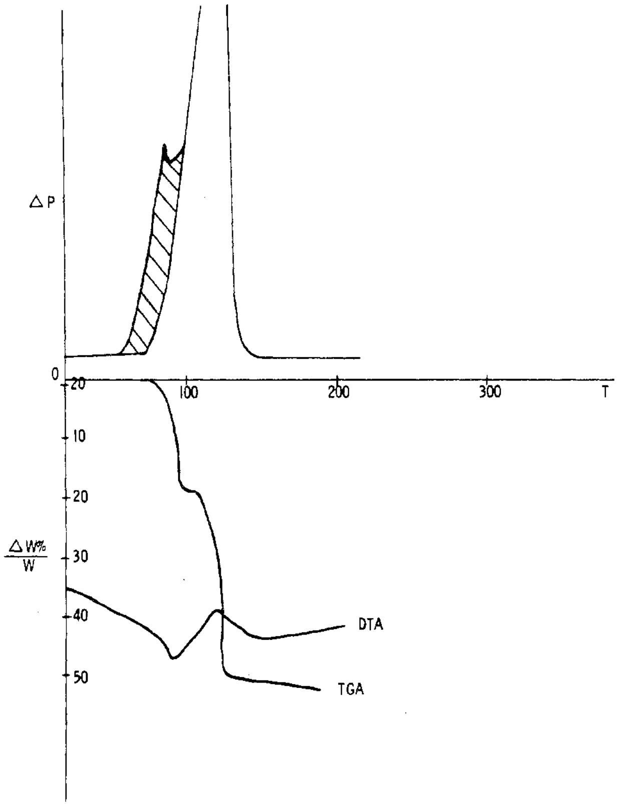


Figure 2. Vacuum dta-tga of $AlH_3 \cdot 0.25OEt_2$.

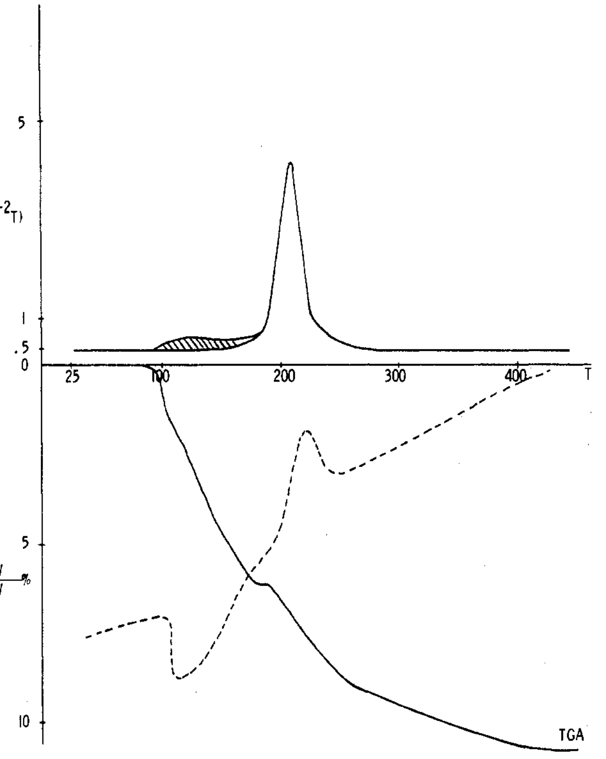


Figure 3. Vacuum dta–tga of a mixture of 2 LiCl + BeH_2.

insoluble residue from the clear filtrate. The residue was shown to be pure LiCl (26 mmol, 40%) by infrared and powder diffraction examination. Evaporation of the remainder of the solvent produced a gummy residue which solidified. The X-ray powder diffraction pattern of this solid showed the presence of additional LiCl plus nine other weak lines which could have arisen from a trace of $BeCl_2 \cdot 2THF$ or $LiAlH_4 \cdot n THF$. The infrared spectrum of a Nujol mull of this material showed the following absorption pattern: 1802 (s), 1023 (m), 842 (m), 752 (s), 725 (s), 623 (w), and 528 (w) cm^{-1}. Readdition of 100 ml of benzene to the product, followed by vigorous stirring, caused dissolution of some of the solid material. Filtration yielded a white residue and a colorless filtrate. The X-ray powder diffraction pattern of the white solid indicated the presence of LiCl plus lines found in the original sample before benzene addition. The infrared spectrum of this solid showed the following absorptions: 1812 (s, b), 1616 (s, vb), 1236 (m, b), 1071 (m), 1028 (m), 859 (m), 843 (m), 753 (s), 605 (s), and 534 (s) cm^{-1}. Removal of benzene solvent from the filtrate produced a gummy solid which would not solidify after prolonged pumping at 10^{-5} mm pressure, and for which no diffraction data could be obtained. The infrared spectrum of a Nujol mull of this material was the same as that found for the original material before benzene addition, with the appearance of a broad band of low intensity at 1619 cm^{-1}. *Anal.* Found for the benzene-insoluble portion of this reaction: H, 1.86; Al, 17.0; Cl, 37.4. Found for the benzene-soluble product: H, 1.68; Be, 4.47; Al, 16.6; Cl, 1.88.

The above reaction was repeated under conditions designed to minimize solvent cleavage. To 12.37 mmol of $BeCl_2 \cdot 2THF$ was added 24.74 mmol of $LiAlH_4$ in 225 ml of tetrahydrofuran. The reaction mixture temperature was maintained at 0° with vigorous stirring for 15 hr, producing a slightly turbid solution. The turbidity vanished when the mixture was stirred at room temperature for 2 hr. Solvent was removed by reduced pressure distillation at low temperature. The solution remained clear until a volume of 30 ml was reached, where a steadily increasing amount of solid began to precipitate. The final product was a white solid which was evacuated for 12 hr to remove excess solvent. The infrared spectrum of a Nujol mull of this material had the following absorptions: 1808 (s, b), 1616 (m, vb), 1017 (s), 852 (m), 730 (m), and 621 (m) cm^{-1}. The X-ray powder pattern of this solid contains LiCl lines plus other well-defined lines which match the corresponding sample from the previous reaction, with the exception of four weak lines.

The above reaction was repeated so that the residue isolated by solvent removal could be extracted with benzene. A white suspension resulted and filtration produced a white residue and a clear filtrate. The infrared spectrum of the insoluble residue exhibited the following absorptions: 1765 (s, b), 1350 (m, b), 1007 (w), 841 (w, b), 1718 (w), 669 (s), and 400–200 (s, b) cm^{-1}. Evaporation of benzene from the filtrate produced a white solid. *Anal.* Found: H, 3.19; Al, 28.5; Cl, 5.22. The beryllium concentration was too small to measure accurately and no lithium was found by flame photometric analysis. The infrared spectrum of this product had the following absorptions: 2000–1300 (b, s), 1169 (w), 1079 (m), 910 (w), 716 (w), 669 (w), and 246 (m) cm^{-1}.

In a separate experiment the solid obtained from the 2:1 reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether was added to a solution of AlH_3 in THF, such that the Be:Al ratio was 1.0:2.0. The solid dissolved and the infrared spectrum of the solution showed bands at 1740 (sh), 1700, 775, and 745 (sh) cm^{-1}. This corresponds to the spectrum of the reaction mixture from $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in THF. The infrared spectrum of $Li_2BeCl_2H_2$ in THF shows broad bands at 1825 (m) and 1650 (m) cm^{-1} and a sharper band at 775 cm^{-1}. If LiCl in THF is added to AlH_3 in THF in a 1:1 ratio, the infrared spectrum shows bands at 1740 (sh), 1700, 775, and 750 cm^{-1}.

Reaction of HBeCl and AlH_3 in THF. An equimolar mixture of BeH_2 and $BeCl_2$ in ether produced a clear solution from which HBeCl was produced on solvent removal. To the HBeCl was added AlH_3 in THF in a 1:1 ratio. No solid was formed. Analysis of the solution gave a Be:Al:H ratio of 1.15:1.00:4.14. The infrared spectrum of the solution gave bands at 1740, 800, and 740 cm^{-1}.

Reaction of $LiAlH_4$ and HBeCl in THF. To an ether solution of HBeCl was added $LiAlH_4$ in ether in a 1:1 ratio. A solid was formed and the infrared spectrum of the solution corresponded to AlH_3 in ether. When the solvent was removed under vacuum, a solid was produced which redissolved in THF. The infrared spectrum of the resulting solution showed bands at 1730 (sh), 1700, 775, and 740 cm^{-1}.

Reaction of $LiAlH_4$ and $BeCl_2$ in 1:1 Ratio in THF. $LiAlH_4$ (28.9 mmol) was added dropwise to a stirred suspension of 28.9 mmol of $BeCl_2$ in 200 ml of tetrahydrofuran at 25°. The suspended crystals of $BeCl_2 \cdot 2THF$ dissolved immediately, leaving a slightly turbid solution. Stirring for 15 hr yielded a perfectly clear, homogeneous solution. Distillation of 150 ml of benzene into the reaction mixture left it unchanged. Removal of solvent at reduced pressure until the total volume was approximately 20 ml caused the appearance of a precipitate which upon isolation was identified as LiCl. The filtrate precipitated more LiCl on standing. Removal of the remainder of the solvent yielded a gummy solid which solidified after prolonged pumping at 0.5 mm pressure. The infrared spectrum of this solid showed absorption bands at 1877 (m), 1802 (s), 1781 (s), 1618 (m, vb), 1238 (w), 1170 (w), 1115 (w), 1060 (m), 1028 (s), 967 (s), 916 (w), 875 (w), 754 (m), 657 (m), 580 (w), and 460 (m) cm^{-1}. The X-ray powder pattern indicated the presence of LiCl plus many additional lines which do not match $BeCl_2 \cdot 2THF$. Addition of 60 ml of dry benzene to this solid produced a white slurry which was stirred for several hours and filtered. The white residue obtained had the following infrared spectrum: 1880 (w, b), 1830 (w, b), 1539 (s, b), 1189 (m, b), 1122 (w), 1062 (m), 998 (w), 972 (w), 898 (m), 803 (w), 724 (s), 563 (s), and 338 (w) cm^{-1}. The X-ray powder diffraction pattern indicated the presence of LiCl plus seven unidentified lines. *Anal.* Found for the solid: H, 1.26; Be, 0.764; Al, 13.4; Cl, 35.42. Removal of benzene from the filtrate yielded a gummy solid that did not solidify on prolonged pumping at reduced pressure with heating (65°, 24 hr). Slight discoloration of the material was noted along with some gas evolution, and the product was finally characterized as a plastic mass. *Anal.* Found for the product: H, 0.716; Be, 4.70; Al, 10.2; Cl, 16.1. The infrared spectrum of a Nujol mull of this product before heating at reduced pressure showed absorption bands at 1876 (s), 1810 (s), 1780 (sh), 1312 (w), 1267 (w), 1240 (w), 1169 (m), 1153 (w), 1116 (m), 1060 (s), 1028 (s), 965 (w), 948 (w), 901 (w), 843 (w), 760 (w, b), 722 (w, b), 664 (w), 570 (w, sh), and 463 (s) cm^{-1}. The infrared spectrum of a Nujol mull of the same sample after heating under vacuum showed absorption bands at 1876 (s, b), 1803 (s, sh), 1348 (w), 1306 (w), 1258 (m), 1238 (m), 1166 (s), 1114 (m), 1056 (s), 1023 (s, b), 959 (s, b), 898 (m), 826 (s, b), 642 (s, b), 573 (m, sh), 525 (m), and 458 (s) cm^{-1}.

The reaction was repeated in tetrahydrofuran at 0° using 8.46 mmol of $BeCl_2$ and 8.46 mmol of $LiAlH_4$ in 150 ml of tetrahydrofuran. The mixture was stirred for 15 hr at 0° yielding a slightly turbid solution. Removal of solvent at reduced pressure caused no solid precipitation until approximately 50% of the solvent had been removed. The final product of solvent removal was a gummy solid. Thirty-nine hours of pumping at reduced pressure (0.1 mm, 25°) yielded a plastic solid whose infrared spectrum showed absorption bands at 1778 (vs, b), 1575 (sh), 1237 (m), 1170 (s), 1110 (w), 1005 (s), 960 (m), 920 (s), and 840 (s, b) cm^{-1}. Continued pumping (24 hr) finally yielded a white powder whose infrared spectrum as a Nujol mull showed absorption bands at 1802 (s, b), 1619 (s, b), and 457 (w) cm^{-1}, plus an irregular base line which showed no definite absorption bands. The powder diffraction pattern of this solid indicated the presence of LiCl plus 11 additional lines which do not match $BeCl_2 \cdot 2THF$.

Reaction of $NaAlH_4$ and $BeCl_2$ in 1:1 Ratio in THF. To a stirred suspension of 15.6 mmol of $BeCl_2 \cdot 2THF$ in 150 ml of THF at 0° was added 15.6 mmol of $NaAlH_4$. A white precipitate formed and the reaction mixture was stirred for an additional 30 min prior to filtration. Filtration produced a white solid residue and a clear filtrate. Removal of solvent from the filtrate by reduced pressure distillation, in the cold, gave a white solid. *Anal.* Found for the insoluble product: H, 0.806; Be, 2.94; Al, 1.28; Cl, 43.4. The infrared spectrum of a Nujol mull of the solid showed absorption bands at 1729 (s, b), 1350 (m, vb), 1011 (s), 955 (w), 912 (w), 863 (s), 730 (m, b), and 542 (m, b) cm^{-1}. The X-ray powder diffraction pattern showed the presence of $BeCl_2 \cdot 2THF$ and NaCl with three unidentified weak lines. *Anal.* Found for the solid isolated from the soluble portion of the reaction mixture: H, 2.72; Be, 4.08; Al, 21.2; Cl, 15.8. The infrared spectrum of a Nujol mull of this solid showed absorption bands at 1874 (s, b), 1573 (s, vb), 1160 (m, b), 1019 (s, b), 950 (s, b), 829 (s, b), 712 (s, b), 649 (s, b), 452 (m, b), 369 (w), and 343 (w) cm^{-1}. The X-ray powder diffraction pattern of this solid shows numerous lines, however it does not confirm the presence of $BeCl_2 \cdot 2THF$ or NaCl.

Reaction of $LiAlH_4$ and $BeCl_2$ in 1:1 Ratio in Ether. $LiAlH_4$ (25.03 mmol) was added dropwise to 25.03 mmol of $BeCl_2$ in 250 ml of ether at 0° producing a white precipitate. Filtration yielded a white solid and a clear filtrate. Removal of the solvent from the filtrate produced a clear glass puddle which disintegrated upon further evacuation to a powder having a crystalline appearance. *Anal.* Found for the insoluble material: H, 2.46; Be, 8.37; Al, 3.25; Cl, 62.2. The powder diffraction pattern showed LiCl plus three additional weak lines. The infrared spectrum of a Nujol mull of this solid had the following absorptions: 1758 (s, vb), 1350 (m, vb), 1022 (w), and 778 (m, vb) cm^{-1}. *Anal.* Found for the soluble product: H, 265; Be, 3.58; Al, 23.0; Cl, 26.1. The infrared spectrum of a Nujol mull of this product exhibits absorptions at 2200–1200 (s, b), 1190 (w), 1150 (w), 1091 (w), 1023 (w), 973 (w), 890 (w), 844 (w), 760 (w), 600 (w, b), and 444 (w) cm^{-1}. The X-ray powder pattern consisted of four diffused lines which match those found for the soluble species in the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio.

The reaction was repeated at −78° using 22.7 mmol of $BeCl_2 \cdot 2Et_2O$ and 22.7 mmol of $LiAlH_4$ in 200 ml of diethyl ether. Again a precipitate formed immediately. After stirring for 45 min, filtration in the cold produced a white solid and a clear filtrate. Removal of the solvent from the filtrate produced a white solid. *Anal.* Found for the insoluble residue: H, 2.08; Be, 9.02; Al, 3.46; Cl, 58.1. The infrared spectrum of a Nujol mull of the insoluble solid had the following absorptions: 1765 (s, vb), 1350 (m, vb), 1190 (w), 1150 (w), 1085 (w), 1017 (m), 890 (w), 883 (m), and 841 (w) cm^{-1}. The X-ray powder pattern showed the LiCl pattern plus one weak, unidentified line. *Anal.* Found for the solid isolated from the soluble portion of this reaction mixture: H, 3.25; Be, 1.08; Al, 28.2; Cl, 34.0. The infrared spectrum of a Nujol mull of this solid exhibited absorptions at 1851 (m, vb), 1615 (m, vb), 1257 (w), 1187 (w), 1145 (w), 1086 (w), 1014 (w), 968 (w), 888 (w), 730 (m, b), 620 (w), and 443 (w) cm^{-1}. The X-ray powder diffraction pattern contained four weak lines.

The above reaction was repeated at room temperature in order to compare the results obtained at the lower temperature. To 100 ml of $BeCl_2$ in diethyl ether (0.2325 *M*) was added 19.5 ml of $LiAlH_4$ in ether (1.119 *M*). The solution was stirred overnight and then filtered producing a white solid and a clear solution. Analysis of the solid gave an Al:Be:H:Cl ratio of 0.0:1.00:2.18:1.85. The solid contained 52% of the original beryllium. Analysis of the solution gave an Al:Be:H:Cl ratio of 1.0:0.44:2.99:1.07. The infrared spectrum of the solution showed bands at 1840, 1795, 972, 908, 772, and 725 cm^{-1}.

Reaction of BeH_2 and AlH_3 in 1:2 Ratio in THF and Diethyl Ether. To 7.6 mmol of BeH_2 was added 15.0 mmol of AlH_3 in THF. The solution was stirred 2 days and then filtered. Analysis of the filtrate showed no beryllium in solution. The infrared spectrum of the solution corresponded to AlH_3 and the intensity had not changed. Similar results were obtained in diethyl ether.

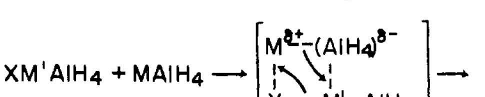
Infrared Spectra of Reaction Solutions of $LiAlH_4$ and $BeCl_2$ in Diethyl Ether. Molar increments of $LiAlH_4$ in ether were added to 9.23 mmol of $BeCl_2$ dissolved in 50 ml of diethyl ether. After the hydride addition, the mixture was stirred for 30 min to 1 hr, the precipitate was allowed to settle, and samples (1 ml) of the clear supernatant were withdrawn by syringe for infrared examination. Absorptions at a 1:1 hydride:halide ratio were (solvent bands omitted) 1848 (s), 1787 (s), 1638 (w), 964 (m), 904 (m), 764 (s), 712 (s), 569 (w), and 502 (w) cm^{-1}. These bands were unchanged on stirring for 16 hr. Absorptions at a 2:1 ratio were 1811 (s, sh), 1787 (s), 1638 (w), 900 (w), 753 (s), 675 (m), and 540 (w) cm^{-1}. Absorptions at a 3:1 ratio were 1812 (s, sh), 1785 (s), 1747 (s), 900 (w), 754 (s), 685 (m), and 540 (w) cm^{-1}. Filtration of the mixture produced a white residue which had the following spectrum after drying at reduced pressure: 1754 (s, b), 1350 (m, b), 1025 (w), and 752 (s, b) cm^{-1}. The powder diffraction pattern of this solid showed only LiCl and a single additional, indistinct line. Removal of ether from the clear, colorless filtrate produced a white solid having the following infrared spectrum: 1778 (s, b), 1618 (s, b), 1147 (w), 1026 (s), 891 (m, sh), 802 (w, sh), 720 (s, b), and 600 (s) cm^{-1}. The X-ray powder diffraction pattern of this solid contained eight lines. A sample of $LiAlH_4$ solution was stripped of solvent at 25° to yield a white solid whose infrared spectrum was 1778 (s, b), 1666 (s, b), 1148 (w), 867 (s, b), and 714 (s, b) cm^{-1}. The X-ray powder pattern of this partially desolvated hydride did not match the pattern for the ether-soluble product described above. The soluble reaction product was unstable and decomposed to a dark gray solid with gas evolution.

Infrared Spectra of Reaction Solutions of $LiAlH_4$ and $BeCl_2$ in THF. $LiAlH_4$ in THF was added to 4.54 mmol of $BeCl_2$ in 50 ml of tetrahydrofuran. Spectra were recorded for samples of the clear, homogeneous solution. Absorptions at 0:1 ratio: 665 (s, sh), 574 (m), and 524 (w) cm^{-1}. Absorptions at 1:1 ratio: 1730 (s, b), 773 (m), 729 (m), 670 (s, sh), and 378 (w) cm^{-1}. Absorptions at 2:1 ratio: 1730 (s, sh), 1701 (s), 776 (s), 731 (w), 680 (m, sh), and 370 (m, b) cm^{-1}. Absorptions at 3:1 ratio: 1730 (s, sh), 1695 (s), 1646 (m, sh), 774 (s), 731 (w), 680 (m, sh), and 370 (m, b) cm^{-1}. Absorptions at 7:1 ratio: 1691 (s), 1646 (s, sh), 763 (s), 733 (m, sh), 679 (m), 530 (w), and 384 (s) cm^{-1}. Absorptions of $LiAlH_4$ solution: 1691 (s), 763 (s), and 390 (m) cm^{-1}.

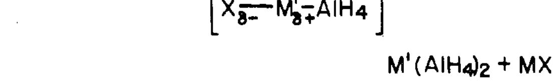
Infrared Spectra of Reaction Solutions of $NaAlH_4$ and $BeCl_2$ in THF. The procedure was the same as above except that the precipitate formed would not settle on standing for 1 hr. At a 2:1 ratio, the mixture was filtered and the infrared spectrum of the filtrate examined. Absorptions were found at 1736 (s), 1269 (w, sh), 797 (w), and 724 (m) cm^{-1}. $NaAlH_4$ in THF has absorptions at 1680 and 772 cm^{-1}.

Results and Discussion

The reaction of complex aluminum hydrides, $MAlH_4$ (where M = Li, Na, K), and metal halides of group II, $M'X_2$ (where M′ = Be, Mg, Zn, Cd, Hg), can be visualized in either of two ways, depending on whether one considers the structure of an alkali metal aluminum hydride to be best represented by $M^{\delta+}\cdots(AlH_4)^{\delta-}$ or $M^{\delta+}\cdots H^{\delta-}{-}AlH_3$. If the alkali metal aluminum hydride is represented as an undissociated ion pair ($M^{\delta+}\cdots(AlH_4)^{\delta-}$), then the reaction can be represented as a simple metathetical exchange reaction in which the dipoles of polar bonds align in the appropriate way for exchange to take place



(6)



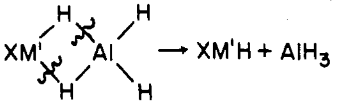
(7)

When M = Li or Na, M′ = Mg, and X = Cl, Br, or I, the above reactions are observed.[5] Reaction 6 is observed when the ratio of $MAlH_4$ to MgX_2 is 1:1 and reaction 7 is observed when 1 additional mol of $MAlH_4$ is added (when M = Na). When M′ is a less electropositive metal than aluminum, compounds such as $XM'AlH_4$ and $M'(AlH_4)_2$ are not stable. Hence, although the reaction may proceed through pathways 6 and 7, disproportionation of these compounds to more stable products takes place

$$XM'AlH_4 \rightarrow XM'H + AlH_3 \quad (8)$$

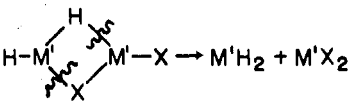
$$M'(AlH_4)_2 \rightarrow M'H_2 + 2AlH_3 \quad (9)$$

The disproportionation of $XM'AlH_4$ could be represented by a simple dissociation of metal-hydrogen bridge bonds



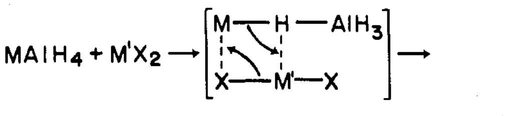
(10)

The compound $XM'H$ is not stable when $M' = Mg$ and has been shown to disproportionate further to $M'H_2$ and $M'X_2$.[12]

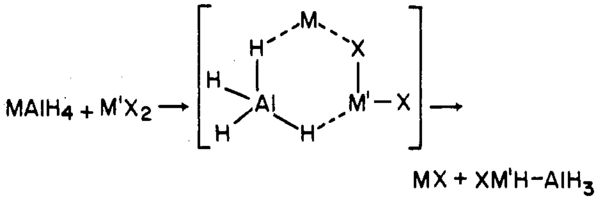


(11)

As stated earlier, another possible reaction pathway involves the visualization of a complex metal hydride as a hydrogen-bridged species reacting through either a four- or a six-center transition state (eq 12 and 13). Of course, $XM'H$-AlH_3 ($XM'AlH_4$) can disproportionate by hydrogen bridge dissociation to $XM'H$ and AlH_3. It is not necessary that MX and HM'X be separate species; thus it should be possible to isolate $MX \cdot M'HX$ (or $MM'X_2H$) as a single compound depending on the nature of M and M'. Furthermore, reaction of $MX \cdot M'XH$ with another molecule of $MAlH_4$ could result in the substitution of H for X with the resultant formation of $M'H_2$ (eq 14). Which of these pathways is actually taking place and to what extent should depend on the nature of M, M', and X. Although pathways 6 and 7 describe the reaction of $NaAlH_4$ with MgX_2, it appears that the pathways described by eq 8-14 are in operation when the electropositivity of M' is less than or equal to that of aluminum as in the case of beryllium.



(12)



(13)

$$MX \cdot M'XH + MAlH_4 \rightarrow 2MX + M'H_2 + AlH_3 \quad (14)$$

The approach taken to study the reactions of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ in diethyl ether and THF was to mix solutions of the $MAlH_4$ and BeX_2 compounds in 1:1 and 2:1 ratios and carry out complete elemental analysis on the resulting solution and on any precipitate that formed. In addition all precipitates were subjected to dta-tga, powder diffraction, and infrared analysis, and all solutions were further investigated by infrared spectroscopy. Because infrared analysis is so important in these studies, the reader might find the following generalizations useful in the interpretation of the data that follows. Terminal Al-H stretching frequencies occur between 1912 and 1660 cm^{-1} and may be lower in bridging situations (1550 cm^{-1}). Deformation modes of AlH_4^- are observed at *ca.* 750 cm^{-1}. Shifts in Al-H stretching frequencies have been correlated with the increase or decrease of the coordination number of aluminum. In general, increasing the coordination number of aluminum will cause the Al-H stretching frequency to decrease.[13] We[14] have discussed the shift in the Al-H stretching frequency in terms of covalent interactions for selected derivatives of complex aluminum hydrides.

Reactions in Diethyl Ether. Since $NaAlH_4$ is not soluble in ether, $LiAlH_4$ was the only hydride studied in this solvent involving the reactions of $MAlH_4$ compounds with beryllium chloride. The results of reactions of $LiAlH_4$ with $BeCl_2$ in ether at 1:1 and 2:1 ratios at +25 and −78° are recorded in Tables I and II.

$LiAlH_4$ and $BeCl_2$ in 2:1 Ratio. The reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio is rapid and complete within 1 hr even at −78°. At this stoichiometric ratio aluminum hydride is recovered virtually uncontaminated, except by residual solvent, from the soluble portion of the reaction mixture. The infrared spectrum of the reaction solution has a strong absorption at 1787 cm^{-1}, which does not agree closely with the value of 1801 cm^{-1} observed by Ehrlich[15] for a metastable solution of AlH_3 prepared from $LiAlH_4$ and $AlCl_3$ using the method of Finholt.[16] Aluminum hydride prepared in diethyl ether by this latter reaction precipitates from solution within minutes after its separation from the LiCl by-product. In contrast, the AlH_3 generated by $LiAlH_4$-$BeCl_2$ interaction is stable in ether solution over a period of at least 135 hr at room temperature. A slight precipitate does appear after 24 hr. However, the AlH_3 concentration drops only 4% after 1 week. The dta-tga for $AlH_3 \cdot 0.25OEt_2$ shown in Figure 2 indicates that the AlH_3 begins to lose ether at about 50°. Hydrogen evolution begins at 90° and is centered at 110°.

The ether-insoluble product of this reaction gave an analysis which indicated the product to be a mixture of LiCl and BeH_2 in 2:1 ratio. However, when the reaction mixture is worked up rapidly, the X-ray powder pattern data (Table III) indicate that the product is not a physical mixture of LiCl and BeH_2. The only other possibility appears to be that it is a complex as shown in eq 15. When this solid was stirred in ether for several days, the X-ray powder pattern of the product was consistent with a physical mixture of LiCl and BeH_2. The dta curve for the complex ($Li_2BeCl_2H_2$) (Figure 1) shows that it decomposes endothermally at 160°, whereas the same product, stirred for 3 days in ether, shows an exothermal decomposition at 185° (Figure 3). Further evidence supporting complex formation rests on the fact that BeH_2 is insoluble in THF, yet a mixture of BeH_2 + 2 LiCl dissolves in THF after stirring overnight. The infrared spectrum of the resulting solution shows bands at 1825, 1650, and 775 cm^{-1}.

$$2LiAlH_4 + BeCl_2 \rightarrow Li_2BeCl_2H_2 + 2AlH_3 \quad (15)$$

Thus, neither the original report of the preparation of $Be(AlH_4)_2$ by Wiberg[1] or the later report by Wood and Brenner[2] could be substantiated although the report by

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

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

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Table I. Reactions of $LiAlH_4$ and $BeCl_2$ in Diethyl Ether at 25°

$LiAlH_4$: $BeCl_2$	Solubility of product	H:Al	(Total H^- less AlH_3): Be	Be:Cl
1:1	Sol	3.08:1.0	1.0:5.22	1.0:1.85
1:1	Insol	20.2:1.0	2.24:1.0	1.0:1.89
2:1	Sol	3.12:1.0	No Be	No Be
2:1	Insol	11.0:1.0	2.22:1.0	1.0:2.0

Table II. Reactions of $LiAlH_4$ and $BeCl_2$ in Diethyl Ether at −78°

$LiAlH_4$: $BeCl_2$	Solubility of product	H:Al	(Total H^- less AlH_3): Be	Be:Cl
1:1	Sol	3.09:1.0	1.0:2.22	1.0:2.84
1:1	Insol	16.2:1.0	1.69:1.0	1.0:1.64
2:1	Sol	3.18:1.0	No Be	No Be
2:1	Insol	10.5:1.0	2.06:1.0	1.0:2.05

Table III. X-Ray Powder Diffraction Data for $Li_2BeCl_2H_2$[a]

1		2		3		4	
d, Å	*I*[b]	*d*, Å	*I*	*d*, Å	*I*	*d*, Å	*I*
3.96	s	3.96	w	3.30	w	2.967	100
3.42	w			2.96	s		
2.98	w	2.95	s	2.85	vvw		
2.70	vs	2.70	s	2.70	vw		
2.56	w	2.56	s	2.56	s	2.57	85
2.42	w						
2.30	vw						
2.21	m	2.20	vw				
2.11	vw						
2.04	vw			2.00	vw		
1.93	s						
1.90	s	1.91	w				
1.86	w						
1.71	w	1.80	m				
1.615	w			1.81	s	1.817	58
1.64	vw						

[a] Species: **1**, precipitate of 2 $LiAlH_4$ + $BeCl_2$ obtained immediately after mixing; **2**, precipitate of 2 $LiAlH_4$ + $BeCl_2$ obtained 2 hr after mixing; **3**, product **1** stirred 3 days in Et_2O; 4, LiCl (ASTM). [b] Key: w, weak; m, medium; s, strong; v, very.

Holley and Lemons[3] was found to be substantially correct. Also, no evidence was found for the formation of $LiBe(AlH_4)_3$ in reactions between $LiAlH_4$ and $BeCl_2$ in diethyl ether, under the conditions reported herein.[4]

Contrary to reports by Dymova,[9] $LiAl_2H_7$ is not the product in solution upon reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio (eq 16). We have prepared HBeCl by an independent

$$2LiAlH_4 + BeCl_2 \rightarrow LiAl_2H_7 + HBeCl + LiCl \qquad (16)$$

method and have found that it is soluble in ether. We have found less than 0.8% lithium in the soluble products of the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether and an Al:Li ratio of approximately 17. X-Ray powder diffraction data for these soluble products do not match those of the Russian report. The powder pattern of $AlH_3 \cdot 0.25OEt_2$ which we have isolated from the 2:1 reaction at 25° does agree well with the powder pattern of $AlH_3 \cdot 0.25OEt_2$ reported by French workers.[17]

$LiAlH_4$ and $BeCl_2$ in 1:1 Ratio. For the reactions where the $LiAlH_4$:$BeCl_2$ ratio is 1:1, the reaction is more complex. Infrared data, elemental analysis, and X-ray powder diffraction data of the insoluble reaction product show that the major constituents are LiCl and BeH_2. Elemental analysis of the soluble portion of the reaction indicates empirically a mixture of 2 AlH_3 and $BeCl_2$. However, studies of the reaction of AlH_3 and $BeCl_2$ in ether[18] show that redistribution between AlH_3 and $BeCl_2$ takes place according to eq 17 and

$$AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl \qquad (17)$$

18. Thus, the reaction of $LiAlH_4$ and $BeCl_2$ in ether in 1:1

$$2AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl + AlH_3 \qquad (18)$$

ratio can be represented by eq 19.

$$2LiAlH_4 + 2BeCl_2 \rightarrow 2LiCl\downarrow + BeH_2\downarrow + HBeCl + AlH_2Cl + AlH_3 \qquad (19)$$

Reactions in Tetrahydrofuran. Both $NaAlH_4$ and $LiAlH_4$ were allowed to react with $BeCl_2$ in THF. Of the alkali metal halide by-products, NaCl is insoluble while LiCl is soluble in THF. Because of the solubility of LiCl in THF the reaction course is more complicated when $LiAlH_4$ is involved since LiCl can then interact with other products in solution such as AlH_3 and BeH_2. However, NaCl eliminates the above possibilities and hence the reaction course is not as complicated. A summary of results of reactions of $NaAlH_4$ with $BeCl_2$ in 1:1 and 2:1 ratio at 25 and 0° are recorded in Tables IV and V.

$NaAlH_4$ and $BeCl_2$ in 2:1 Ratio. When $NaAlH_4$ was allowed to react with $BeCl_2$ in a 2:1 ratio in THF, the results were found to be very similar to the results obtained for the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether. The soluble reaction product is AlH_3 which was identified by elemental and infrared analyses (strong absorption at 1800 and 1625 cm^{-1} (Nujol)). The insoluble reaction products are NaCl and BeH_2 (the terminal Be-H stretching frequency occurs at 1710 cm^{-1} when the product is isolated from THF). X-Ray powder diffraction studies on the solid product show it to be a physical mixture of BeH_2 and NaCl and not a complex as had been observed in the case of LiCl and BeH_2 (*i.e.*, $Li_2BeH_2Cl_2$).

$$2NaAlH_4 + BeCl_2 \rightarrow 2AlH_3 + 2NaCl\downarrow + BeH_2\downarrow \qquad (20)$$

$NaAlH_4$ and $BeCl_2$ in 1:1 Ratio. The reaction of $NaAlH_4$ and $BeCl_2$ in 1:1 ratio in THF is more complex than the same reaction carried out in 2:1 mole ratio. The insoluble product mixture was shown by elemental analysis and X-ray powder diffraction data to contain NaCl, BeH_2, and a small amount of $BeCl_2 \cdot 2THF$ as the principal components. Analytical data suggest that the soluble species are AlH_3, H_2AlCl, and HBeCl. Although HBeCl has only limited solubility in THF, the addition of AlH_3 to a slurry of HBeCl in THF causes all the HBeCl to dissolve. The solution spectrum of this mixture is unchanged from that of AlH_3; however, due to the increased solubility of HBeCl, it is concluded that a weak interaction to produce a compound of empirical formula $ClBeAlH_4$ is possible

$$AlH_3 + HBeCl \rightleftharpoons ClBeAlH_4 \qquad (21)$$

Thus, the products of this reaction in 1:1 ratio (NaCl, BeH_2, and AlH_3) are the same as the products produced when the ratio is 2:1 except that the AlH_3 formed reacts further with the additional amount of $BeCl_2$ present in 1:1 ratio. Thus, one could look at the reaction sequence in the following way

$$2NaAlH_4 + BeCl_2 \rightarrow 2NaCl + BeH_2 + 2AlH_3 \qquad (22)$$

$$2AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl + AlH_3 \qquad (23)$$

$$2NaAlH_4 + 2BeCl_2 \rightarrow 2NaCl\downarrow + BeH_2\downarrow + H_2AlCl + HBeCl + AlH_3$$

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Table IV. Reactions of NaAlH$_4$ and BeCl$_2$ in THF at 0°

NaAlH$_4$: BeCl$_2$	Solubility of product	H:Al	(Total H$^-$ less AlH$_3$): Be	Be:Cl
1:1	Sol	3.47:1.0	1.0:1.23	1.02:1.0
1:1	Insol	16.9:1.0	1.0:1.23	1.0:1.52
2:1	Sol	3.14:1.0	1.0:1.23	8.40:1.0
2:1	Insol	19.2:1.0	1.84:1.0	1.0:2.13

Table V. Reactions of NaAlH$_4$ and BeCl$_2$ in THF at 25°

NaAlH$_4$: BeCl$_2$	Solubility of product	H:Al	(Total H$^-$ less AlH$_3$): Be	Be:Cl
2:1	Sol	3.57:1.0	1.32:1.0	5.62:1.0
2:1	Insol	9.37:1.0	1.46:1.0	1.0:4.05

As mentioned earlier, we have studied the reaction of AlH$_3$ and BeCl$_2$ in diethyl ether[18] and have found that the reaction proceeds as shown in eq 23.

LiAlH$_4$ and BeCl$_2$. As was mentioned earlier, LiCl, the alkali metal halide by-product of the reaction of LiAlH$_4$ and BeCl$_2$ in THF, is soluble in THF. Since this is the only case studied where the alkali metal halide by-product is soluble in the reaction solvent, it is interesting to observe the effect that this solubility has on the reaction products. In order to simplify the interpretation of the results of the reaction between LiAlH$_4$ and BeCl$_2$, we shall consider first the independent interaction of the probable products of this reaction, *i.e.*, LiCl, BeH$_2$, AlH$_3$, and HBeCl.

When LiCl was added to a solution of AlH$_3$ in THF, complex formation was indicated by the change in the infrared spectrum of the solution. AlH$_3$ in THF absorbs at 1739 cm^{-1}; however, when LiCl is added, the infrared spectrum shows a band at 1705 cm^{-1} with a shoulder at 1745 cm^{-1}. This observation indicates an equilibrium of the type shown in eq 24. Earlier we observed the formation of this complex in diethyl ether.[19] Whereas LiCl is insoluble in ether, in the presence of an equimolar amount of AlH$_3$, it is soluble.

$$\mathrm{LiCl + AlH_3 \rightleftharpoons LiAlH_3Cl} \qquad (24)$$

The complex Li$_2$BeH$_2$Cl$_2$ formed in ether was found to be soluble in THF and the infrared spectrum showed weak lines at 1825 and 1650 cm^{-1}. The fact that the complex Li$_2$BeH$_2$Cl$_2$ is soluble in THF and BeH$_2$ is insoluble indicates that the complex is stable in THF and therefore some interaction between LiCl and BeH$_2$ in THF takes place

$$\mathrm{2LiCl + BeH_2 \rightarrow Li_2BeH_2Cl_2} \qquad (25)$$

It was also found that when a THF solution of LiCl was added to preformed BeH$_2$ and stirred overnight, 20% of the beryllium was found in solution.

When LiAlH$_4$ was allowed to react with HBeCl in THF, the resulting clear solution showed ir bands at 1730 (sh), 1700, 775, and 740 cm^{-1}. If the shoulder at 1730 cm^{-1} is assigned to AlH$_3$, then the band at 1700 cm^{-1} could be assigned to a terminal Be-H stretching vibration in LiBeH$_2$Cl (eq 26).

$$\mathrm{LiAlH_4 + HBeCl \xrightleftharpoons{THF} LiBeH_2Cl + AlH_3} \qquad (26)$$

This band could not be assigned to LiAlH$_3$Cl since, if this were formed, then BeH$_2$ would also be formed and would precipitate from solution (eq 27).

$$\mathrm{LiAlH_4 + HBeCl \not\rightarrow LiAlH_3Cl + BeH_2} \qquad (27)$$

Interactions between Be-H and Al-H compounds appear to be very weak or nonexistent. In the reaction of LiAlH$_4$ and BeCl$_2$ in diethyl ether no evidence for Be(AlH$_4$)$_2$ was found. No reaction was observed between BeH$_2$ and AlH$_3$ in diethyl ether or in THF. Beryllium was found in solution only in cases where cleavage of the THF solvent had occurred. As was pointed out earlier, when AlH$_3$ was allowed to react with HBeCl in THF, the spectrum corresponded to that of a solution of AlH$_3$ in THF.

$$\mathrm{BeH_2 + 2AlH_3 \xrightarrow[or\ Et_2O]{THF} Be(AlH_4)_2} \qquad (28)$$

LiAlH$_4$ and BeCl$_2$ in 2:1 Ratio. When LiAlH$_4$ was allowed to react with BeCl$_2$ in 2:1 ratio in THF, the ir spectrum of the solution exhibited bands at 1730 (sh) and 1701 cm^{-1}. This is similar to the spectrum obtained from the mixture of LiCl and AlH$_3$ which is attributed to LiAlH$_3$Cl. It is also similar to that obtained from the reaction of LiAlH$_4$ and HBeCl in THF which is postulated to yield AlH$_3$ and LiBeH$_2$Cl. If the solvent is removed from the 2:1 mixture of LiAlH$_4$ and BeCl$_2$ and benzene is added, a solid is obtained which was identified as LiCl (40% of theoretical). Since the interaction of LiCl and AlH$_3$ is described by an equilibrium as indicated by the infrared spectrum of the mixture, the removal of solvent and addition of benzene could cause the removal of LiCl from this equilibrium. This would leave AlH$_3$ in solution and the beryllium could continue to be solubilized as LiBeH$_2$Cl. When all the solvent was removed from the reaction product and the resulting solid was extracted with benzene, 56% of the theoretical amount of AlH$_3$ was extracted into the benzene solution.

If the complex Li$_2$BeH$_2$Cl$_2$ is allowed to react with 2 mol of AlH$_3$ in THF, a clear solution results. The infrared spectrum of this solution is identical with the spectrum from the reaction of LiAlH$_4$ and BeCl$_2$ in 2:1 ratio. This observation is best explained by the displacement of one of the LiCl molecules of the complex (Li$_2$BeH$_2$Cl$_2$) by AlH$_3$ to yield LiAlH$_3$Cl and LiBeH$_2$Cl. The reaction of LiAlH$_4$ and BeCl$_2$ in 2:1 ratio and of Li$_2$BeH$_2$Cl$_2$ in admixture with 2 mol of AlH$_3$ can then be understood as an equilibrium mixture described by

$$\mathrm{2LiAlH_4 + BeCl_2 \rightarrow LiAlH_3Cl + LiBeH_2Cl + AlH_3 \rightleftharpoons Li_2BeH_2Cl_2 + 2AlH_3} \qquad (29)$$

As LiAlH$_4$ was added to BeCl$_2$ in THF in ratios greater than 2:1, the only changes observed in the spectrum were due to the appearance of a band at 1691 cm^{-1} due to excess LiAlH$_4$.

When LiAlH$_4$ was allowed to react with BeCl$_2$ in a 1:1 ratio in THF, the ir spectrum of the solution exhibited a broad band centered at 1730 cm^{-1}. If one assumes that the products are identical with those observed in the 1:1 case in diethyl ether (eq 30), then one would expect bands at 1836 and 1755 cm^{-1} due to AlH$_2$Cl.[20] However, these bands are not observed in the 1:1 reaction of LiAlH$_4$ and BeCl$_2$ in THF; therefore, AlH$_2$Cl cannot be present in the reaction mixture. The products of this reaction can be satisfactorily explained if one assumes that the LiCl generated in the reaction complexes with other products of the reaction (*e.g.*, HBeCl) in a manner similar to the 2:1 case in THF which is discussed above. The reaction could therefore be described by eq 31.

$$\mathrm{2LiAlH_4 + 2BeCl_2 \rightarrow HBeCl + AlH_2Cl + AlH_3 + Li_2BeCl_2H_2} \qquad (30)$$

$$\mathrm{LiAlH_4 + BeCl_2 \rightarrow LiCl + HBeCl + AlH_3 \rightarrow LiBeCl_2H + AlH_3} \qquad (31)$$

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In a separate experiment LiCl in THF was added to HBeCl. The ir spectrum of the resulting clear solution showed a very weak broad band at 1700 cm^{-1}. At the same concentration AlH_3 in THF shows a very intense band at 1739 cm^{-1}. One might, therefore, expect that a 1:1 mixture of $LiBeCl_2H$ and AlH_3 would give an ir spectrum with a broad band centered at approximately 1730 cm^{-1} as we indeed found for the reaction product of $LiAlH_4$ and $BeCl_2$ in THF. The predicted spectra of other possible products are not consistent with the observed spectrum of the reaction product of $LiAlH_4$ and $BeCl_2$ in 1:1 ratio in THF. The only difference between the reaction of $LiAlH_4$ and $BeCl_2$ in 1:1 ratio in ether and THF (eq 30 and 31) is the fact that in THF (eq 31) the AlH_3 formed does not react with HBeCl to form BeH_2 and H_2AlCl. This observation is not inconsistent with known reactivity differences of AlH_3 or other aluminum compounds in THF compared to ether.

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Registry No. $BeCl_2 \cdot 2THF$, 15663-55-5; $BeCl_2 \cdot 2Et_2O$, 14267-69-7; $LiAlH_4$, 16853-85-3; $BeCl_2$, 7787-47-5; $NaAlH_4$, 13770-96-2; HBeCl, 42016-55-7; AlH_3, 7784-21-6; BeH_2, 7787-52-2; $Li_2BeCl_2H_2$, 39405-85-1; $AlH_3 \cdot 0.25OEt_2$, 2835-71-1.

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Phosphine-Borane Derivatives. VI.[1] Hydrogen-1, Boron-11, Fluorine-19, and Phosphorus-31 Nuclear Magnetic Resonance Investigation of Some Alkyl- and Arylphosphine Adducts

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The ^{1}H and ^{11}B nmr parameters for the adduct series $R_nPH_{3-n} \cdot BX_3$ (R = Me, Ph; $n = 0, 1, 2$; X = H, F, Cl, Br, I) are reported. ^{1}H, ^{11}B, and ^{31}P nmr parameters are reported for the BX_nH_{3-n} ($n = 0, 1, 2$; X = Cl, Br, I) adducts of all R_nPH_{3-n} Lewis bases. ^{19}F nmr parameters are reported for all $R_nPH_{3-n} \cdot BF_3$ adducts except for PH_3BF_3. Chemical shift and coupling constant data are examined in the light of their utility as indicators of acid–base strength or complex stability. Internal consistency between the nmr parameters of the various nuclei is to be expected only where large changes in trend occur.

Introduction

Recent ^{11}B nmr investigations[2-5] of the properties of the phosphorus-boron bond have indicated that while coupling constant and chemical shift data can, within narrow limits, be correlated with bond strength, no unrestricted application can be made of these parameters as measures of compound stability or of relative orders of Lewis acidity and basicity. In our previous ^{1}H nmr study[1] of the phosphine-boron trihalide adducts attention was called to the apparent correlation between the value of the direct J_{PH} coupling constant and the Lewis acidity of the BX_3 species. We present here an extension of that investigation to the ^{1}H nmr parameters of boron trihalide adducts of dimethyl-, phenyl-, and diphenylphosphine. In addition ^{11}B chemical shifts and coupling constants have been obtained for all five series. ^{31}P data are presented for all systems sufficiently soluble to permit investigation. ^{19}F nmr determinations are reported where applicable. The various ^{1}H, ^{31}P, ^{11}B, and ^{19}F parameters are examined for their utility as predictive indicators and for their mutual internal consistency within a given adduct series.

Experimental Section

All adducts except for $PhPH_2 \cdot BI_3$ and $Ph_2PH \cdot BI_3$ were prepared by direct combination of reactants in standard nmr tubes (4-mm o.d.) on a vacuum line in a manner described previously.[1] The adducts $PH_3 \cdot BH_2X$ and $PH_3 \cdot BHX_2$ (X = Cl, Br) were prepared following the method of Drake and Simpson[6] while a procedure analogous to theirs was used to prepare the new adducts $PH_3 \cdot BH_2I$ and $PH_3 \cdot BHI_2$. The solvents employed, CD_3I (Stohler Isotope Chemicals, Montreal; 1% ^{1}H impurity) CH_3I, and CH_2Cl_2, were checked for spectroscopic purity prior to use.

^{1}H Nmr Spectra. CD_3I was used as solvent for all adducts except those of the $(CD_3)_2PH \cdot BX_3$ system where CH_2Cl_2 was found to be necessary for reasons previously given.[1] Spectra were recorded in sealed tubes over a carefully varied temperature range from −70 to +75° on a JEOL C60HL high-resolution spectrometer. Tetramethylsilane and solvent were distilled onto the adduct which was contained in an nmr tube attached to the vacuum line. The tube was then drawn off the line and sealed with a torch, with the contents held at −196°.

^{31}P Nmr Spectra. CH_3I was used as solvent for all adducts investigated. Spectra were recorded at 24.29 MHz in sealed tubes identical with those used in the ^{1}H nmr work. Temperatures were maintained between −10 and 0°. $POCl_3$ in small capillary tubes was used as external standard. The low solubility of the adducts severely reduced the intensity of the resonance peaks. Removal of the reference capillary when not needed by inverting the sample tube overcame this difficulty and allowed for a more precise measurement of coupling constants. Nevertheless, solubility limitations reduced the number of adducts studied to 11.

^{11}B Nmr Spectra. CH_3I was employed as solvent for all adduct systems. Spectra were recorded at 19.25 MHz with $BF_3 \cdot OEt_2$ serving as external reference. Temperatures were varied in *ca.* 10° intervals from −30° (where peak broadening became significant) to +25°. Manipulation of the reference capillary was identical with the ^{31}P procedure.

^{19}F Nmr Spectra. CH_2Cl_2 was employed as solvent for all BF_3 adducts. Spectra were recorded at 56.45 MHz using CCl_3F as internal standard. Temperatures were varied from −90 to +25° as the stability of the adduct warranted.

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