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# Concerning the Existence of Hydridomagnesium Aluminohydride ($HMgAlH_4$) and Hydridomagnesium Borohydride ($HMgBH_4$)

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Seven methods for the preparation of $HMgAlH_4$ and $HMgBH_4$ have been investigated

$$MH + XMgAlH_4 \longrightarrow MX + HMgAlH_4$$
$$RMgAlH_4 \xrightarrow{\Delta} HMgAlH_4 + \text{olefin}$$
$$RMgAlH_4 \xrightarrow[H_2]{\Delta} HMgAlH_4 + RH$$
$$RMgAlH_4 + MH \longrightarrow MR + HMgAlH_4$$
$$Mg(AlH_4)_2 + L \longrightarrow HMgAlH_4 + AlH_3 \cdot L$$
$$MgH_2 + AlH_3 \longrightarrow HMgAlH_4$$
$$MgH_2 + Mg(AlH_4)_2 \longrightarrow 2HMgAlH_4$$

In all of these reactions a mixture of $MgH_2$ and $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ was isolated rather than the expected $HMgAlH_4$ or $HMgBH_4$. The conclusion from this work is that $HMgAlH_4$ and $HMgBH_4$ disproportionate to $MgH_2$ and $MgAlH_4$ or $MgBH_4$. Borane and alane extraction of complex magnesium borohydrides and aluminohydrides with sodium and lithium hydride have been shown to be general reactions. Other important observations concerning fundamental transformations in hydride chemistry are reported.

## Introduction

The preparation of compounds of the types $HMgBH_4$ and $HMgAlH_4$ have been investigated previously. In 1940 Burg and Schlesinger[1] reported the preparation of $HBeBH_4 \cdot N(CH_3)_3$ by borane extraction of $Be(BH_4)_2$ with trimethylamine

$$Be(BH_4)_2 + 2N(CH_3)_3 \longrightarrow HBeBH_4 \cdot N(CH_3)_3 + BH_3N(CH_3)_3 \quad (1)$$

In 1951 Schlesinger[2] and coworkers reported that the addition of diethylmagnesium to a large excess of lithium aluminum hydride in diethyl ether followed by addition of benzene resulted in the precipitation of a solid with the empirical formula $HMgAlH_4$. Unfortunately, the compound was not characterized

$$LiAlH_4 + Mg(C_2H_5)_2 \longrightarrow HMgAlH_4 + \text{other products} \quad (2)$$

further. A recent reinvestigation[3] of reaction 2 has shown that $HMgAlH_4$ is not produced in this reaction.

In this paper we wish to report our attempts to prepare and characterize $HMgAlH_4$ and $HMgBH_4$.

## Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and water[4] or at the bench using typical Schlenk-tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

**Instrumentation.**—Infrared spectra were obtained in cesium iodide cells using a Perkin-Elmer Model 621 high-resolution infrared spectrophotometer. X-Ray powder diffraction patterns were obtained using a Debye–Scherrer camera of 114.6-mm diameter using Cu K$\alpha$ (1.540 Å) radiation with a nickel filter. Single-walled capillaries of 0.5-mm diameter were used. These were filled in the drybox and sealed with a microburner.

**Reagents.**—Tetrahydrofuran and benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride immediately prior to use. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium was obtained from the Dow Chemical Co. It was washed with diethyl ether and dried under vacuum prior to use.

Lithium and sodium aluminum hydride, sodium hydride (57% suspension in mineral oil), and sodium borohydride were obtained from Ventron Metal Hydrides Division.

Magnesium aluminum hydride, chloromagnesium aluminum hydride, iodomagnesium aluminum hydride, and magnesium halide were prepared as described previously.[5]

**Analytical Procedures.**—Halogen analysis was carried out by the Volhard method. Aluminum and magnesium analyses were carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanolamine. Lithium analysis was carried out by flame photometry. Hydridic hydrogen was analyzed by hydrolyzing a weighed sample of the compound on a high vacuum line and transferring the gas to a calibrated bulb *via* a Toepler pump after passing the gas through a liquid nitrogen trap.

**Preparation of Lithium Hydride.**—Lithium hydride was prepared as described previously.[6] The solid, obtained as a slurry in pentane, gave a lithium to hydrogen ratio of 1.00:1.00.

**Preparation of $(n\text{-}C_4H_9)_3SnH$.**—Tri-*n*-butyltin hydride was prepared as described previously.[7] The compound was distilled at 70° (6 mm). The infrared spectrum of the neat compound showed an absorption at 1810 $cm^{-1}$ characteristic of tri-*n*-butyltin hydride.

**Preparation of $ClMgBH_4$.**—Chloromagnesium borohydride was prepared as described previously.[8] Analysis of the product in solution showed a Mg:Cl ratio of 1.00:1.04. The infrared spectrum in THF showed B–H absorptions at 2380 and 2175 $cm^{-1}$.

**Preparation of $C_2H_5MgBH_4$ and *sec*-$C_4H_9MgBH_4$.**—Ethylmagnesium borohydride was prepared as described previously.[5] *sec*-Butylmagnesium borohydride was prepared in a similar fashion. Analysis of the latter product in solution showed a Mg:Cl ratio of 1.0:0.02. The infrared spectrum of the solution showed bands at 2420, 2220, and 535 $cm^{-1}$.

**Preparation of $HMgAlH_3(C_2H_5)$ and $HMgAlH_3(n\text{-}C_4H_9)$.**—These compounds were prepared exactly as described previously.[9]

**Attempts to Prepare $HMgAlH_4$ and $HMgBH_4$.**—As indicated by the Results and Discussion section, numerous attempts were made to prepare $HMgAlH_4$ and $HMgBH_4$ by a variety of methods. Only a few examples are provided here in order to represent the type of experimental approach taken to evaluate the methods.

**Reaction of Sodium Hydride and $ClMgAlH_4$ in Tetrahydrofuran.**—To 50 ml of chloromagnesium aluminum hydride in

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

[2] G. B. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilbach, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **73**, 4585 (1951).

[3] E. C. Ashby and R. G. Beach, *Inorg. Chem.*, **9**, 2300 (1970).

[4] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, **33**, 491 (1962).

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

[6] E. C. Ashby and R. D. Schwartz, *ibid.*, **10**, 355 (1971).

[7] W. P. Neumann, *Angew. Chem., Int. Ed. Engl.*, **2**, 165 (1963).

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

[9] E. C. Ashby and R. D. Schwartz, *ibid.*, **11**, 919 (1972).

THF (0.2056 *M*) was added 454.5 mg of sodium hydride (57% dispersion in mineral oil). The solution was stirred for 2 days. The solution was then filtered and the filtrate gave on analysis a Cl:Mg:Al ratio of 0.0:1.0:1.88. From the filtration was isolated 1.96 g of solid. The infrared spectrum of the solid gave bands at 1725, 1025, 975, 790, and 745 cm$^{-1}$. The X-ray powder pattern of the solid gave lines corresponding to sodium chloride, magnesium aluminum hydride, and magnesium hydride.

**Reaction of Sodium Hydride and $ClMgBH_4$ in Tetrahydrofuran.**—To 45 ml of chloromagnesium borohydride in THF (0.4887 *M*) was added 1.925 g of sodium hydride (57% dispersion in mineral oil). The solution was stirred for 2 days and then filtered. The infrared spectrum of the filtrate showed no bands other than those assigned to THF. The X-ray powder pattern of the solid resulting from the filtration gave lines corresponding to sodium chloride, sodium borohydride, and magnesium hydride. The infrared spectrum of the solid gave bands corresponding to sodium borohydride and magnesium hydride.

**Reaction of $ClMgAlH_4$ and Sodium Hydride in Tetrahydrofuran in the Presence of *N,N,N',N'*-Tetramethylethylenediamine.**—To 75 ml of chloromagnesium aluminum hydride in tetrahydrofuran (0.2345 *M*) were added 11 ml of TMED and 739.6 mg of sodium hydride (57% in mineral oil). The solution was stirred for 2 days and then filtered. The analysis of the filtrate gave a Mg:Al:Cl ratio of 0.81:1.1:0.5. This represented about 70% reaction. The infrared spectrum of the solution after filtration had a band at 1715 cm$^{-1}$ corresponding to the Al–H stretching band in chloromagnesium aluminum hydride. The solid obtained from filtration exhibited bands at 1725, 1665, 1025, 1010, 940 (B), 870, 790, 760, and 590 cm$^{-1}$. The X-ray powder pattern of the solid showed lines corresponding to sodium chloride, magnesium aluminum hydride, and magnesium hydride.

**Reaction of $Mg(AlH_4)_2$ with $N(CH_3)_3$.**—Magnesium aluminum hydride (3.29 mmol) was added to 20 ml of benzene in a sealed tube reactor. Twenty millimoles of trimethylamine was added at −196°. The mixture was then sealed under vacuum and the mixture was allowed to stand at room temperature for 10 days. The resulting mixture was filtered and the analysis of the solid from filtration gave an Mg:H ratio of 1.0:1.98. The infrared spectrum and X-ray powder pattern of the solid corresponded to $MgH_2$. The analysis of the filtrate showed it to contain no magnesium but 95% of the original aluminum. The infrared spectrum of the filtrate was characteristic of $AlH_3 \cdot 2N(CH_3)_3$.

## Results and Discussion

The reactions employed in the attempts to prepare $HMgAlH_4$ and $HMgBH_4$ can be divided into seven general categories (eq 3–9). The first reaction (eq 3)

$$Mg + XMgAlH_4 \longrightarrow MX + HMgAlH_4 \qquad (3)$$

$$RMgAlH_4 \xrightarrow{\Delta} HMgAlH_4 + \text{olefin} \qquad (4)$$

$$RMgAlH_4 \xrightarrow[H_2]{\Delta} RH + HMgAlH_4 \qquad (5)$$

$$RMgAlH_4 + MH \longrightarrow MR + HMgAlH_4 \qquad (6)$$

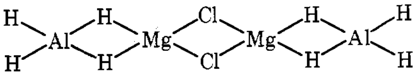
$$Mg(AlH_4)_2 + L \longrightarrow HMgAlH_4 + AlH_3 \cdot L \qquad (7)$$

$$MgH_2 + AlH_3 \longrightarrow HMgAlH_4 \qquad (8)$$

$$MgH_2 + Mg(AlH_4)_2 \longrightarrow 2HMgAlH_4 \qquad (9)$$

involves the reduction of a compound of empirical formula $XMgAlH_4$ or $XMgBH_4$ by a chemical source of hydride ion, *e.g.*, NaH. The second method (eq 4) involves the pyrolysis of a compound of empirical formula $RMgAlH_4$ or $RMgBH_4$. The third method (eq 5) involves the high-pressure hydrogenolysis of $RMgAlH_4$ or $RMgBH_4$ compounds. The fourth method (eq 6) involves the metathetical exchange between a metal–hydrogen compound and $RMgAlH_4$ or $RMgBH_4$. The fifth method (eq 7) involves extraction of aluminum hydride from $Mg(AlH_4)_2$. The sixth method (eq 8) involves the direct addition of aluminum hydride to $MgH_2$. The final method (eq 9) involves the redistribution of $MgH_2$ and $Mg(AlH_4)_2$.

**MH + $XMgAlH_4$.**—In an attempt to prepare $HMgAlH_4$ according to eq 3, sodium hydride was allowed to react with chloromagnesium aluminum hydride in THF at a molar ratio of 1:1. After several days the solution was filtered. Over 90% of the reaction product was insoluble in the solvent. Elemental analysis of the filtrate gave a Cl:Mg:Al ratio of 0.0:1.0:1.88. The filtrate consisted of a dilute solution of $Mg(AlH_4)_2$ as determined by infrared analysis. The solid isolated by filtration had an infrared spectrum exhibiting bands at 1725, 1025, 975, 790, and 745 cm$^{-1}$ characteristic of $Mg(AlH_4)_2 \cdot 4THF$. The X-ray powder pattern of the solid confirmed that it was a physical mixture of sodium chloride, magnesium hydride, and magnesium aluminum hydride. The conclusion to be drawn from this experiment depends on the structure of the reactant (dimer $ClMgAlH_4$). If $ClMgAlH_4$ has the structure indicated by I, then the conclusion is that $HMgAlH_4$ is produced in the above reaction but disproportionates to $MgH_2$ and $Mg(AlH_4)_2$. On the other hand, if $ClMgAlH_4$ has structure II, then the conclusion is that $MgH_2$ and $Mg(AlH_4)_2$ are produced in the above reaction without going through an intermediate $HMgAlH_4$.



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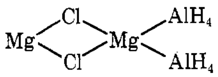

II

$$NaH + ClMgAlH_4 \longrightarrow NaCl + HMgAlH_4 \longrightarrow {}^1/_2MgH_2 + {}^1/_2Mg(AlH_4)_2 \qquad (10)$$

In an effort to stabilize $HMgAlH_4$ toward disproportionation, chloromagnesium aluminum hydride was allowed to react with sodium hydride in the presence of triethylamine and TMED. Since the possibility of $AlH_3$ extraction exists, weakly basic amines were used. In one experiment $ClMgAlH_4$ was first complexed with the chelating amine TMED; however, some aluminum hydride extraction did occur in addition to the formation of NaCl, $Mg(AlH_4)_2$, and $MgH_2$.

In another reaction lithium hydride was added in excess as a pentane slurry to iodomagnesium aluminum hydride in diethyl ether. The rationale behind this experiment lies in the fact that LiI is soluble in diethyl ether, and, hence, if $HMgAlH_4$ is formed, it should precipitate clearly from the reaction mixture. The solution was filtered after several days and the elemental analysis of the filtrate gave a I:Mg:Al ratio of 1.52:0.0:1.0. The infrared spectrum of the filtrate corresponded to lithium aluminum hydride. The solid obtained from the filtration of the reaction mixture gave an infrared spectrum and an X-ray powder pattern characteristic of magnesium hydride. When the lithium hydride was added to iodomagnesium aluminum hydride in a 1:1 ratio, the infrared spectrum of the solution after stirring for several days corresponded to lithium aluminum hydride. The infrared spectrum and X-ray powder pattern of the solid obtained by filtration of the reaction mixture corresponded to a mixture of lithium iodide, magnesium hydride, and unreacted iodomagnesium aluminum hydride. Thus, the reaction seems to proceed both by aluminum hydride extraction (eq 11

$$LiH + IMgAlH_4 \longrightarrow LiAlH_4 + IMgH \qquad (11)$$

and 12) and by metathetical exchange followed by

$$2IMgH \longrightarrow MgH_2 + MgI_2 \tag{12}$$

disproportionation (eq 13 and 14). Another possibility is that the products of eq 11 ($LiAlH_4$ and IMgH) react directly to produce the products of eq 13 (LiI and $HMgAlH_4$). By this pathway, eq 12 and 13 are circumvented.

$$LiH + IMgAlH_4 \longrightarrow LiI + HMgAlH_4 \tag{13}$$

$$2HMgAlH_4 \longrightarrow MgH_2 + Mg(AlH_4)_2 \tag{14}$$

**MH + $XMgBH_4$.**—When sodium hydride (in excess) was allowed to react with chloromagnesium borohydride in THF, the resulting solid was shown by X-ray powder pattern analysis to be a mixture of sodium chloride, sodium borohydride, and magnesium hydride. This reaction also presumably proceeds *via* $BH_3$ extraction (eq 15–17) in the presence of excess

$$NaH + ClMgBH_4 \longrightarrow NaBH_4 + HMgCl \tag{15}$$

$$2HMgCl \longrightarrow MgH_2 + MgCl_2 \tag{16}$$

$$MgCl_2 + 2NaH \longrightarrow MgH_2 + 2NaCl^{8} \tag{17}$$

NaH and/or *via* metathetical exchange (eq 18–20).

$$NaH + ClMgBH_4 \longrightarrow NaCl + HMgBH_4 \tag{18}$$

$$2HMgBH_4 \longrightarrow MgH_2 + Mg(BH_4)_2 \tag{19}$$

$$Mg(BH_4)_2 + 2NaH \longrightarrow 2NaBH_4 + MgH_2 \tag{20}$$

However, the overall reaction results in the formation of only NaCl, $MgH_2$, and $NaBH_4$.

As in the above case using $ClMgAlH_4$, it is also possible that the products of eq 15 ($NaBH_4$ + HMgCl) react directly to produce the products of eq 18 (NaCl and $HMgBH_4$), thus circumventing eq 16–18.

Chloromagnesium borohydride is monomeric in THF,[8] but its composition in solution is not known with certainty. Therefore, the conclusions to be drawn from these results are similar to those of the reaction of NaH and $ClMgAlH_4$. If $ClMgBH_4$ exists in solution as monomeric $ClMgBH_4$, then we can conclude that the intermediate $HMgBH_4$ disproportionates. However, if $ClMgBH_4$ exists in solution as an equilibrium mixture containing $MgCl_2$ and $Mg(BH_4)_2$, then the normal course of reaction might produce a mixture of $MgH_2$ and $Mg(BH_4)_2$ without going through the intermediate $HMgBH_4$.

When lithium hydride was stirred with chloromagnesium borohydride, no reaction was detected after several days

$$LiH + ClMgBH_4 \xrightarrow{\text{THF}} \text{no reaction} \tag{21}$$

**$HMgAlH_3R$ Pyrolysis.**—In the pyrolysis experiments, hydridomagnesium *n*-butyltrihydridoaluminate [$HMgAlH_3(n\text{-}C_4H_9)$] was suspended in light mineral oil. The slurry was heated under vacuum at 80° for several hours; however, elemental and infrared analyses of the resulting solid product showed it to be recovered starting material. Similar results were obtained in octane solution.

In the compounds represented empirically as $RMgAlH_4$, the alkyl group is actually bonded to aluminum[9] ($HMgAlH_3R$) and is much more stable than if it were bonded to magnesium. With this in mind, higher pyrolysis temperatures were studied. When the solvent was removed under vacuum from an ether solution of $HMgAlH_3(n\text{-}C_4H_9)$, a white solid resulted which was then heated under vacuum. When the temperature reached 150°, drops of liquid began collecting on the upper reaches of the flask and the solid began to turn gray. The sample was then cooled, hexane was added, and the mixture was filtered. The filtrate gave an Al:Mg:H ratio of 1.45:0.0:1.0. The X-ray powder pattern of the resulting solid showed lines corresponding to magnesium hydride, aluminum metal, and unreacted $HMgAlH_3(n\text{-}C_4H_9)$. These results indicate that before the alkyl group is removed by pyrolysis, the compound $HMgAlH_3R$ decomposes to $MgH_2$ and $RAlH_2$. However, $RAlH_2$ compounds are known to disproportionate to the more stable $R_2AlH$ compounds and $AlH_3$ followed by decomposition of $AlH_3$ to Al, $H_2$, and intermediate Al–H compounds at 150°.

$$HMgAlH_3R \xrightarrow{\Delta} MgH_2 + RAlH_2 \tag{22}$$

$$2RAlH_2 \longrightarrow R_2AlH + AlH_3 \tag{23}$$

$$AlH_3 \longrightarrow Al + {}^3/_2H_2 \tag{24}$$

The decomposition of $HMgAlH_3R$ in the above manner is not surprising in view of the results of Ziegler and Holzkamp.[10] These workers attempted to distil $Mg[Al(C_2H_5)_4]_2$ but instead obtained $Al(C_2H_5)_3$ leaving behind the involatile $Mg(C_2H_5)_2$ (eq 25).

$$Mg[Al(C_2H_5)_4]_2 \xrightarrow{\Delta} Al(C_2H_5)_3 + Mg(C_2H_5)_2 \tag{25}$$

**$RMgBH_4$ Pyrolysis.**—Ethylmagnesium borohydride was obtained as the THF solvate and was dissolved in 100 ml of heavy mineral oil. This solution was heated slowly to 170°. At this point a gas was evolved and a solid formed. The solid obtained was filtered and washed with benzene. Elemental analysis of this solid gave a Mg:H ratio of 1.0:3.74 with no ethane present. The infrared spectrum of the solid exhibited absorption bands at 2270 and 2380 $cm^{-1}$ characteristic of $Mg(BH_4)_2$ as the THF solvate. X-Ray powder pattern analysis of the solid exhibited strong lines characteristic of magnesium hydride.

The pyrolysis of *sec*-butylmagnesium borohydride was attempted since the *sec*-butyl group is more susceptible to olefin elimination at a lower temperature. *sec*-Butylmagnesium borohydride as the diethyl ether solvate was dissolved in octane and heated to 80° under vacuum. A solid was obtained that exhibited lines in its X-ray powder pattern characteristic of a mixture of magnesium hydride and $Mg(BH_4)_2$. Magnesium aluminum hydride as the monotetrahydrofuran solvate was heated to 145° until weight loss was constant. The resulting solid was gray and its X-ray powder pattern showed lines for $MgH_2$ and aluminum metal only.

**$HMgAlH_3R$ Hydrogenolysis.**—The hydrogenolysis of $HMgAlH_3(n\text{-}C_4H_9)$ in diethyl ether was carried out at 3000 psi hydrogen at 50°. The solution was filtered and the elemental analysis of the filtrate gave a Mg:Al ratio of 1.0:2.33. The infrared spectrum of the filtrate gave bands in the Al–C stretching region at 670 $cm^{-1}$, a shoulder at 700 $cm^{-1}$, and also a band at 1680 $cm^{-1}$. This combination of absorption bands is characteristic of $AlR_2H_2^-$ compounds. The solid obtained from this filtration gave on analysis a Mg:Al:H ratio of 1.0:0.3:2.63. The infrared spectrum of the solid corresponded to magnesium hydride; however, no bands in the Al–H stretching region were observed. The X-ray powder pattern corresponded to magnesium hydride and aluminum metal. Although hydrogenolysis of an $RMgAlH_4$ compound would be expected to produce $HMgAlH_4$ or a mixture of $MgH_2$ and $Mg(AlH_4)_2$, only $MgH_2$ was detected.

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[10] K. Ziegler and E. Holzkamp, *Ann.*, **605**, 93 (1957).

The hydrogenolysis of $HMgAlH_3R$ compounds appears to follow a course similar to the pyrolysis of this class of compounds, that is, the formation of $MgH_2$ and $RAlH_2$ followed by disproportionation of the $RAlH_2$ to $R_2AlH$ and $AlH_3$ (eq 26 and 27). $R_2AlH$ could then

$$HMgAlH_3 \xrightarrow{\Delta} MgH_2 + RAlH_2 \qquad (26)$$

$$2RAlH_2 \longrightarrow R_2AlH + AlH_3 \qquad (27)$$

react with the $MgH_2$ formed to give $Mg(AlR_2H_2)_2$ (eq 28). $AlH_3$ would decompose to hydrogen and

$$2R_2AlH + MgH_2 \longrightarrow Mg(AlR_2H_2)_2 \qquad (28)$$

aluminum metal as indicated by the powder pattern of the solid (eq 29).

$$AlH_3 \longrightarrow Al + {}^3/_2H \qquad (29)$$

**$RMgBH_4$ Hydrogenolysis.**—The results of the hydrogenolysis of *sec*-butylmagnesium borohydride in both diethyl ether and benzene are straightforward. Reaction at 2000 psi hydrogen at 50° (eq 30) produced a

$$2sec\text{-}C_4H_9MgBH_4 \xrightarrow{H_2} MgH_2 + Mg(BH_4)_2 + C_4H_{10} \qquad (30)$$

white solid that had an infrared spectrum corresponding to magnesium hydride; however, no bands in the boron–hydrogen stretching region were observed. The X-ray powder pattern gave strong lines corresponding to pure magnesium hydride. The weight of the solid obtained corresponded to a quantitative yield of magnesium hydride. The filtrate from this reaction exhibited infrared bands at 2450 and 2220 $cm^{-1}$ characteristic of $Mg(BH_4)_2$ as the diethyl ether solvate. When the reaction was carried out in benzene, similar results were obtained; *i.e.*, a solid consisting of magnesium hydride and magnesium borohydride (as the ether solvate) in solution was formed.

In an attempt to learn something of the nature of *sec*-butylmagnesium borohydride in solution, molecular association measurements in diethyl ether were carried out. The association was found to increase steadily from $i = 1.23$ at 0.066 *m* to $i = 1.45$ at 0.31 *m*. It is clear that hydrogenolysis of this compound does not produce hydridomagnesium borohydride but instead a mixture of magnesium hydride and magnesium borohydride. This result also establishes the point that magnesium hydride and magnesium borohydride will not redistribute in solution to yield hydridomagnesium borohydride.

**$RMgBH_4$ + MH.**—Ethylmagnesium borohydride in diethyl ether was allowed to react with tri-*n*-butyltin hydride in a 1:1 mole ratio for several days. At the end of this time, the mixture was filtered. The infrared spectrum of the solution showed bands characteristic of unreacted $EtMgBH_4$ and $Bu_3SnH$. The analysis of the resulting solid gave a Mg:H ratio of 1.0:2.3. The X-ray powder pattern of this solid corresponded to that of magnesium hydride.

In another experiment *sec*-butylmagnesium borohydride in diethyl ether was also allowed to react with tri-*n*-butyltin hydride in a 1:1 mole ratio (eq 31).

$$sec\text{-}C_4H_9MgBH_4 + (n\text{-}C_4H_9)_3SnH \longrightarrow {}^1/_2MgH_2 + {}^1/_2Mg(BH_4)_2 + (n\text{-}C_4H_9)_3Sn(sec\text{-}C_4H_9) \qquad (31)$$

Infrared spectra of the supernatant solution were taken at various intervals. The spectra indicated the disappearance of the Sn–H band at 1800 $cm^{-1}$ and the Mg–C stretching band at 535 $cm^{-1}$. When these bands had disappeared completely, the solution was filtered. The solid obtained by this filtration gave a Mg:H ratio of 1.0:1.89. Its infrared spectrum showed no bands due to B–H stretching but did show bands characteristic of magnesium hydride. Infrared analysis of the reaction filtrate indicated the presence of $Mg(BH_4)_2$.

**$HMgAlH_3R$ + MH.**—Tri-*n*-butyltin hydride was allowed to react in a 1:1 mole ratio with $HMgAlH_3(C_2H_5)$ in ether and in a separate experiment with $HMgAlH_3(n\text{-}C_4H_9)$. In both cases a trace amount of solid of indefinite composition was formed within a few minutes of initiation of the reaction. However, the amount of this solid did not increase even after stirring for several days. The infrared spectrum of the solution showed a mixture of unreacted $Bu_3SnH$ and $HMgAlH_3(C_2H_5)$. The infrared spectrum of the solution did not change even after stirring for several days. The conclusion is that the $(C_4H_9)SnH$ does not react with $HMgAlH_3(C_2H_5)$ or $HMgAlH_3(n\text{-}C_4H_9)$.

Neuman and coworkers[11] in the examination of the reaction of trialkyltin hydrides with aluminum alkyls found that ethers and tertiary amines inhibit the reaction. They concluded that the electron-deficient state of the aluminum is important in the exchange. Since in the tetrahydridoaluminate compounds the aluminum is no longer electron deficient, it is perhaps not surprising that the reaction between $(C_4H_9)_3SnH$ and $HMgAlH_3R$ compounds does not proceed. Van Der Kerk and coworkers[12] in their examination of the reaction between $(C_6H_5)_3SnH$ and $(C_2H_5)MgBr\cdot N(C_2H_5)_3$ reported that instead of getting hydrogen–alkyl exchange, ethane was evolved and a compound with a tin–magnesium bond was formed. It should be emphasized that in none of the reactions between $R_3SnH$ and either $HMgAlH_3R$ or $RMgBH_4$ compounds was any gas evolved.

It was hoped that by allowing $HMgAlH_3R$ compounds to react with a large excess of $LiAlH_4$ or $NaAlH_4$, alkyl–hydrogen exchange would take place resulting in the precipitation of $HMgAlH_4$ from solution. However, in a series of experiments it was shown that little reaction occurs and that most of the starting materials are recovered unreacted

$$LiAlH_4 + HMgAlH_3(C_2H_5) \not\longrightarrow HMgAlH_4 + LiAlH_3(C_2H_5) \qquad (32)$$

A further attempt to prepare $HMgAlH_4$ by alkyl–hydrogen exchange involves the reaction of diethylaluminum hydride with $HMgAlH_3(n\text{-}C_4H_9)$ in a 1:1 mole ratio in diethyl ether. No solid was formed after stirring the solution for several days. The diethyl ether was then removed under vacuum and the solid obtained was heated under vacuum to 80°. At this point a clear, colorless liquid distilled. The analysis of this distillate after diethyl ether was added gave an Al:H ratio of 1.1:1.0. The infrared spectrum of the solution gave a sharp band at 1755 $cm^{-1}$ indicating the presence of $(C_2H_5)_2AlH$. The solid remaining after the distillation was complete gave a Mg:Al:H ratio of 1.5:1.0:4.5. The X-ray powder pattern of the solid showed lines characteristic of $HMgAlH_3(n\text{-}C_4H_9)$, $MgH_2$, and aluminum metal.

In this reaction a complex may have been formed

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(11) W. P. Neuman, H. Niermann, and B. Schneider, *Angew. Chem., Int. Ed. Engl.*, **2**, 547 (1963).

(12) H. M. J. C. Creemers, J. G. Noltes, and G. J. M. Van Der Kerk, *J. Organometal. Chem.*, **14**, 217 (1968).

between $(C_2H_5)_2AlH$ and $HMgAlH_3(n\text{-}C_4H_9)$ which upon heating decomposed again to $(C_2H_5)_2AlH$ and $HMgAlH_3(n\text{-}C_4H_9)$ (eq 33). The low aluminum

$$(C_2H_5)AlH + HMgAlH_3(n\text{-}C_4H_9) \longrightarrow (C_2H_5)_2AlH \cdot HMgAlH_3(n\text{-}C_4H_9) \xrightarrow{\Delta} (C_2H_5)_2AlH + HMgAlH_3(n\text{-}C_4H_9) \quad (33)$$

analysis of the solid as well as the presence of aluminum metal and $MgH_2$ in the powder pattern may be due to a decomposition of $HMgAlH_3(n\text{-}C_4H_9)$ similar to that seen in the pyrolysis experiments.

Diethylmagnesium was allowed to react with aluminum hydride in THF in a mole ratio of 3:5. It was expected that $Al(C_2H_5)_3$ and $HMgAlH_4$ would be formed according to eq 34. However, no solid formed initially. The tetrahydrofuran solvent was removed under vacuum and hexane was added. The hexane solution was then filtered and the analysis of the filtrate gave an Al:H ratio of 1.0:2.04. The analysis of the resulting solid gave an Al:H ratio of 1.0:3.5. This indicates that eq 34 is not followed but that the alkyl groups are statistically distributed between the two aluminum compounds.

$$\begin{array}{l} 3Mg(C_2H_5)_2 + 5AlH_3 \not\longrightarrow 2Al(C_2H_5)_3 + 3HMgAlH_4 \\ 2Mg(C_2H_5)_2 + 3AlH_3 \longrightarrow (C_2H_5)_2AlH + 2HMgAlH_3(C_2H_5) \end{array} \quad (34)$$

When hydridomagnesium tetraethylaluminate in THF was allowed to react with an excess of sodium aluminum hydride, no precipitate formed after stirring for several days (eq 35). Here again, there is probably a statistical redistribution of the alkyl groups among the aluminum atoms.

$$HMgAl(C_2H_5)_4 + NaAlH_4 \not\longrightarrow HMgAlH_4 + NaAl(C_2H_5)_4 \quad (35)$$

**$Mg(AlH_4)_2$ + L.**—Sodium hydride was allowed to react with $Mg(AlH_4)_2 \cdot 4THF$ in THF solution. The solution was stirred for several days and then filtered. The infrared spectrum of the filtrate was identical with that of an independent sample of $NaAlH_4$. The infrared spectrum of the solid showed it to be a mixture of $MgH_2$ and $Mg(AlH_4)_2 \cdot 4THF$. Equations 36 and 37 are presented to describe the most probable reaction path.

$$NaH + Mg(AlH_4)_2 \longrightarrow NaAlH_4 + HMgAlH_4 \quad (36)$$

$$2HMgAlH_4 \longrightarrow MgH_2 + Mg(AlH_4)_2 \quad (37)$$

We have previously found[13] that trimethylamine abstracts $AlH_3$ from $Mg(AlH_4)_2$ in 42% yield after 10 days in a sealed tube. In an attempt to determine if the $AlH_3$ abstraction produces $HMgAlH_4$ as an intermediate product, we allowed trimethylamine to react with $Mg(AlH_4)_2$ in a sealed tube for 10 days (eq 38).

$$Mg(AlH_4)_2 + N(CH_3)_3 \begin{array}{l} \not\nearrow HMgAlH_4 + AlH_3 \cdot N(CH_3)_3 \\ \searrow MgH_2 + 2AlH_3 \cdot 2N(CH_3)_3 \end{array} \quad (38)$$

At the end of this time we recovered $AlH_3 \cdot 2NMe_3$ in 95% yield. The solid remaining was shown by elemental, infrared, and X-ray powder pattern analyses to be $MgH_2$.

In an attempt to desolvate $Mg(AlH_4)_2 \cdot THF$, this compound was heated to 140° until all the THF had been removed. Desolvated $Mg(AlH_4)_2$ was desired so that the thermal decomposition of this compound could be studied in an effort to effect partial pyrolysis of $Mg(AlH_4)_2$ to $HMgAlH_4$, aluminum, and hydrogen. However, the solid obtained from the desolvation was shown by X-ray powder diffraction to contain $MgH_2$ and aluminum metal (eq 39).

$$Mg(AlH_4)_2 \begin{array}{l} \overset{\Delta}{\not\nearrow} HMgAlH_4 + Al + \tfrac{3}{2}H_2 \\ \searrow MgH_2 + 2Al + 3H_2 \end{array} \quad (39)$$

**$Mg(BH_4)_2$ + L.**—Sodium hydride was allowed to react with $Mg(BH_4)_2$ in diethyl ether in a mole ratio of 1:1 (eq 40). After stirring for several days the solution was filtered. The infrared spectrum of the filtrate was identical with that of an independent sample of $Mg(BH_4)_2$. The X-ray powder pattern showed lines corresponding to sodium borohydride and magnesium hydride. This indicates that any $HMgBH_4$ formed *via* borane extraction disproportionated to $MgH_2$ and $Mg(BH_4)_2$ (eq 41).

$$NaH + Mg(BH_4)_2 \longrightarrow NaBH_4 + HMgBH_4 \quad (40)$$

$$2HMgBH_4 \longrightarrow MgH_2 + Mg(BH_4)_2 \quad (41)$$

**$MgH_2$ + $AlH_3$.**—Magnesium hydride was allowed to react with $AlH_3 \cdot 2THF$ in benzene. The resulting solution was filtered and the filtrate showed weak bands at 1735, 910, and 750 $cm^{-1}$. These bands are characteristic of $Mg(AlH_4)_2 \cdot 4THF$ which is slightly soluble in tetrahydrofuran. The infrared spectrum of the solid obtained from this filtration showed bands corresponding to $Mg(AlH_4)_2 \cdot 4THF$ and $MgH_2$. The X-ray powder pattern of the solid showed lines corresponding to $Mg(AlH_4)_2 \cdot 4THF$. It is very probable that in this case $HMgAlH_4$ is formed. However, it is not clear whether the $Mg(AlH_4)_2$ actually isolated in this reaction is a result of the disproportionation of $HMgAlH_4$ or simply a result of the further reaction of $HMgAlH_4$ with $AlH_3 \cdot 2THF$ (eq 42). Magnesium hydride was found not to react with bis(trimethylamine)–alane in benzene solution.

$$MgH_2 + AlH_3 \longrightarrow HMgAlH_4 \xrightarrow{AlH_3} Mg(AlH_4)_2 \quad (42)$$

Although no specific reaction between $MgH_2$ and either $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ was studied, it is clear from the results of a number of the reactions described in this paper that $MgH_2$ does not redistribute either with $Mg(AlH_4)_2$ to give $HMgAlH_4$ or with $Mg(BH_4)_2$ to give $HMgBH_4$.

To summarize, we have investigated seven general methods for preparing $HMgAlH_4$ (eq 3–9). In none of these cases was $HMgAlH_4$ or $HMgBH_4$ isolated. Instead, a physical mixture of $MgH_2$ and either $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ was obtained.

In all probability, if $HMgAlH_4$ or $HMgBH_4$ were stable compounds, some of the reactions carried out in this study should have produced these compounds. We have concluded, therefore, that $HMgAlH_4$ and $HMgBH_4$ are unstable and disproportionate to $MgH_2$ and $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ in ether solvents.

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[13] J. A. Dilts and E. C. Ashby, *Inorg. Chem.*, **9**, 855 (1970).