69687-13-4; **9**, 69687-14-5; **10**, 69687-15-6; $[Me(Me_3Si)N]_2PMe$, 69687-16-7; $[Me(Me_3Si)N]_3P$, 69687-17-8; Me_3SiN_3, 4648-54-8; $(Me_3Si)_2NP(Ph)Me$, 68437-87-6; $(Me_3Si)_2NLi$, 4039-32-1; $F_2(Ph)PNSiMe_3$, 61701-83-5; $(t\text{-Bu})(Me_3Si)NPMe_2$, 68437-82-1; $Me(Me_3Si)NPMe_2$, 68437-84-3; $\overline{SiMe_2CH_2CH_2SiMe_2N}PMe_2$, 68437-96-7; $(Me_3Si)(t\text{-}BuMe_2Si)NPMe_2$, 68437-90-1; $Me(t\text{-}BuMe_2Si)NPMe_2$, 68437-93-4; $Me(Me_3Si)NLi$, 10568-44-2; PCl_3, 7719-12-2; $[Me(Me_3Si)N]_2PCl$, 69687-18-9.

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Preparation and Characterization of Magnesium Tetrahydridozincate, $MgZnH_4$

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Magnesium tetrahydridozincate, $MgZnH_4$, has been prepared by the following synthetic routes: (1) $2MgH_2 + 2Me_2Zn \xrightarrow{THF} MgZnH_4 + MgZnMe_4$; (2) $2Me_2Mg + 2ZnH_2 \xrightarrow{THF} MgZnH_4 + MgZnMe_4$; (3) $2MgH_2 + Me_2Zn \xrightarrow{THF} MgZnH_4 + Me_2Mg$; (4) $2MgH_2 + 4Me_2Zn \xrightarrow{THF} MgZnH_4 + [Mg(ZnMe_3)_2 + Me_2Zn]$; (5) $2MeMg + 4ZnH_2 \xrightarrow{THF} MgZnH_4 + MgZnMe_4 + 2ZnH_2$; (6) $Me_2Mg + Me_2Zn \xrightarrow{THF} MgZnMe_4 \xrightarrow{2LiAlH_4} MgZnH_4 + 2LiAlH_2Me_2$ (or $\xrightarrow{2MgH_2} MgZnH_4 + 2Me_2Mg$). Highly reactive magnesium hydride used in these reactions was prepared by the reaction of diethyl- or diphenylmagnesium with lithium aluminum hydride. Similarly, zinc hydride was prepared by the reaction of lithium aluminum hydride with either diphenylzinc, dimethylzinc, or zinc bromide in diethyl ether. Zinc hydride in active form was also prepared by the reaction of zinc bromide with magnesium hydride slurried in THF. Magnesium tetrahydridozincate was characterized by complete elemental analysis, X-ray powder diffraction, and DTA–TGA studies. The X-ray powder diffraction patterns of $MgZnH_4$, prepared by all of the above methods, were found to be identical.

Introduction

Since complex metal hydrides of aluminum and boron have become invaluable reagents in synthetic organic chemistry, it would seem important to evaluate complex metal hydrides of other main-group elements for possible usefulness as soluble chemical reducing agents. In this connection, we have reported the preparation of $KMgH_3$,[1] Li_2ZnH_4,[2] $LiCuH_2$,[3] and several other complex metal hydrides by the reaction of the corresponding "ate" complex with $LiAlH_4$. Very recently, we reported the preparation of magnesium zinc hydrides[4] by the reaction of magnesium zinc "ate" complexes with lithium aluminum hydride in diethyl ether. The product $MgZnH_4$ was reported to be prepared by two different methods (eq 1 and 2). In that report, we discussed a possible doubt about the existence of $MgZnH_4$ being a single and pure product or a physical mixture of MgH_2 and ZnH_2. The reason behind the doubt was that the so-called "ate" complex $MeZnMe_4$ was shown to exist in equilibrium with Me_2Mg and Me_2Zn. Therefore, the reaction of this product mixture with $LiAlH_4$ would probably give a mixture of products (eq 3). Furthermore, the X-ray powder diffraction patterns of the Mg/Zn products of reactions 1 and 2 were found to be different. Of course, if only $MgZnH_4$ was formed in each reaction, the Mg/Zn product should exhibit the same X-ray powder diffraction pattern.

$$Me_2Mg + Me_2Zn \xrightarrow{Et_2O} MgZnMe_4 \xrightarrow{2LiAlH_4} MgZnH_4 + 2LiAlH_2Me_2 \quad (1)$$

$$Li_2ZnMe_4 + MgBr_2 \rightarrow 2LiBr + MgZnMe_4 \xrightarrow{2LiAlH_4} MgZnH_4 + 2LiAlH_2Me_2 \quad (2)$$

$$\begin{bmatrix} Me_2Mg \\ + \\ Me_2Zn \\ \uparrow\downarrow \\ MgZnMe_4 \end{bmatrix} \xrightarrow{2LiAlH_4} \begin{bmatrix} MgH_2 \\ + \\ ZnH_2 \\ + \\ MgZnH_4 \end{bmatrix} + 2LiAlMe_2H_2 \quad (3)$$

In order to resolve this discrepancy, it was decided to explore the preparation of $MgZnH_4$ by several other methods and to characterize the reaction products by X-ray powder diffraction and DTA–TGA studies. In this paper, we report several new synthetic routes to $MgZnH_4$ and attempts to prepare $Mg(ZnH_3)_2$.

Experimental Section

Apparatus. Reactions were performed under dry nitrogen by using Schlenk-tube techniques.[5] Filtration and other manipulations were carried out in a glovebox equipped with a recirculating system.[6]

X-ray powder diffraction data were obtained on a Philips-Norelco X-ray unit with a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 h. *d* spacings were read on a precalibrated scale

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equipped with viewing apparatus. Intensities were estimated visually. Infrared spectra were obtained by using a Perkin-Elmer 621 spectrophotometer. DTA-TGA studies were carried out under vacuum by using a Mettler Thermoanalyzer II with a high-vacuum attachment.[7]

Materials. Dimethylzinc was prepared from methyl iodide and Zn(Cu) coupled by a modification of the procedure of Noller.[8] Dimethylmagnesium was prepared from Me_2Hg and magnesium metal at room temperature.[7] Diethylmagnesium was prepared by the reaction of Et_2Hg with magnesium metal at 60–80 °C.[9] A THF solution of $ZnBr_2$ was prepared by dissolving sublimed $ZnBr_2$ in THF. Diethyl ether and THF (Fisher Certified reagent grade) were distilled under nitrogen over $LiAlH_4$ and $NaAlH_4$, respectively. Solutions of $LiAlH_4$ (Ventron, Metal Hydride Division) in ether and THF were prepared in the usual manner.

Analytical Methods. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[5] Zinc and magnesium, when present together, were determined at pH 10 by complexometric titration with EDTA. Zinc in the presence of magnesium was determined at pH 4 by adding excess EDTA and back-titrating with zinc acetate.

Preparation of Active Magnesium Hydride Slurry in THF. To a cool (0 °C) ether solution of either Ph_2Mg or Et_2Mg was added an equimolar amount of an ether solution of $LiAlH_4$ with continued stirring. An exothermic reaction resulted producing an insoluble white solid. The reaction mixture was stirred further at room temperature for $^1/_2$ h, and the white insoluble solid was washed several times with ether. Finally, the white solid was washed with THF and a slurry made in THF.

Analysis of the solid showed that it contained Mg and H in molar ratios of 1.00:1.90, and no aluminum was found in the slurry. X-ray pattern (Å units throughout): 3.90 (w), 3.19 (s), 2.51 (s), 2.26 (m), 1.68 (s), 1.51 (vw), 1.43 (w), 1.36 (w), 1.35 (w).

Preparation of Zinc Hydride Slurry in THF. (a) Reaction of Ph_2Zn with $LiAlH_4$ in Ether in 1:1 Molar Ratio. To a solution of Ph_2Zn in ether was added an equimolar amount of $LiAlH_4$ in ether at room temperature with constant stirring. An exothermic reaction resulted, and a precipitate formed. The reaction mixture was stirred further for $^1/_2$ h at room temperature, and the supernatant solution was removed by means of a syringe. The insoluble white solid was washed with ether several times and finally with THF. A THF slurry was made by adding THF to the insoluble solid. Analysis of the solid revealed that it contained Zn:H in the ratio of 1.00:1.96 and no aluminum. X-ray pattern: 4.50 (m), 3.79 (m), 3.26 (w), 3.12 (m), 2.96 (w), 2.82 (w), 2.50 (w), 2.40 (w), 2.29 (w), 2.23 (m), 2.18 (w), 2.08 (w).

(b) Reaction of Zinc Bromide with $LiAlH_4$ in Ether. When an equimolar amount of $LiAlH_4$ in ether was added to an ether solution of zinc bromide at 0 °C, an exothermic reaction resulted with the formation of an insoluble solid. The reaction mixture was stirred for $^1/_2$ h, and the insoluble solid was separated and washed with ether and finally with THF. Anal. Calcd for ZnH_2: Zn:H = 1.00:2.00. Found: 1.00:1.92. The solid contained about 1–2% aluminum. X-ray pattern: 4.45 (s), 3.80 (w), 2.30 (m), 3.12 (m), 2.84 (w), 2.60 (w), 2.47 (w), 2.40 (w), 2.29 (w), 2.20 (w), 2.08.

(c) Reaction of Zinc Bromide with Magnesium Hydride Slurry in THF. To a THF slurry of active MgH_2 was added an equimolar amount of $ZnBr_2$ in THF. The reaction mixture was stirred for 1 h and the resulting insoluble solid separated and washed with THF.

Insoluble solid: Anal. Calcd for ZnH_2: Zn:H = 1.00:2.00. Found: 1.00:1.95. X-ray pattern: 4.60 (m, br), 3.79 (w), 3.25 (m, br), 2.82 (m), 2.60 (m), 2.46 (w), 2.29 (m), 2.08 (s, br), 1.93 (m).

Filtrate: Anal. Calcd for $MgBr_2$: Mg:Br = 1.00:2.00. Found: 1.00:2.00. X-ray pattern ($MgBr_2$·2.8THF): 9.2 (vs), 7.5 (w), 7.0 (w), 5.82 (w), 3.80 (vs), 3.75 (m), 3.47 (vs), 3.35 (m), 3.05 (vs), 2.80 (w), 2.70 (s), 2.53 (s), 2.35 (m), 2.28 (m), 2.18 (m), 2.12 (w), 2.00 (m), 1.96 (w), 1.80 (w), 1.78 (w), 1.665 (w), 1.50 (w).

Preparation of Magnesium Tetrahydridozincate, $MgZnH_4$. (a) Reaction of Dimethylzinc with Magnesium Hydride in THF in 1:1 Ratio. A THF solution of Me_2Zn (6.0 mmol) was added dropwise to a well-stirred slurry of MgH_2 (6.0 mmol) in THF. After the mixture was stirred for 4 h at room temperature, the insoluble white solid was separated by filtration, washed with THF, and dried under vacuum. The insoluble solid and the filtrate were analyzed.

Insoluble solid: Anal. Calcd for $MgZnH_4$·2THF: Mg:Zn:H:THF = 1.00:2.00:4.00:2.00. Found: 1.02:1.00:3.80:1.91. X-ray pattern: 9.20 (m), 7.70 (m), 7.24 (m), 5.65 (w), 5.45 (w), 4.55 (m), 4.25 (s), 4.15 (w), 4.00 (w), 3.61 (w), 3.43 (w), 3.22 (w), 2.65 (w), 2.45 (w), 2.40 (w), 2.30 (vw), 2.20 (vw), 2.01 (vw).

Filtrate: Anal. Calcd for $MgZnMe_4$: Mg:Zn:Me = 1.00:1.00:4.00. Found: 1.00:1.04:4.05. IR: ν(Mg–CH_3) 500 cm^{-1}; ν(Zn–CH_3) 576 cm^{-1}. NMR: singlet 2.82 ppm upfield from THF.

(b) Reaction of Dimethylmagnesium with Zinc Hydride Slurry in THF in 1:1 Ratio. To a well-stirred slurry of ZnH_2 in THF (5.5 mmol) was added a THF solution of Me_2Mg (5.5 mmol) dropwise at room temperature. The reaction mixture was stirred for 4 h and the insoluble white solid filtered, washed with dry THF, and dried under vacuum. The infrared and NMR spectra of the supernatant solution were recorded at room temperature. Both filtrate and insoluble solid were analyzed.

Insoluble solid: Anal. Calcd for $MgZnH_4$·2THF: Mg:Zn:H:THF = 1.00:1.00:4.00:2.00. Found: 1.00:1.03:4.01:1.92. X-ray pattern: 9.20 (m), 7.71 (m), 7.23 (m), 5.65 (m), 5.45 (w), 4.56 (m), 4.25 (s), 4.16 (w), 4.02 (w), 3.60 (w), 3.43 (w), 3.20 (w), 2.65 (w), 2.45 (w), 2.40 (w), 2.31 (vw), 2.20 (vw), 2.01 (vw).

Filtrate: Anal. Calcd for $MgZnMe_4$: Mg:Zn:Me = 1.00:1.00:4.00. Found: 1.04:1.00:3.65. IR: ν(Mg–CH_3) 502 cm^{-1}; ν(Zn–CH_3) 575 cm^{-1}. NMR: singlet at 2.80 ppm upfield from THF.

(c) Reaction of Dimethylzinc with Magnesium Hydride in THF in 1:2 Ratio. The reaction between Me_2Zn (4.0 mmol) and MgH_2 (8.0 mmol) in THF was carried out similarly to (a). The insoluble solid was filtered, washed with THF, and dried under vacuum. Analysis of the solid and the filtrate provided the following results.

Insoluble solid: Anal. Calcd for $MgZnH_4$·2THF: Mg:Zn:H:THF = 1.00:1.00:4.00:2.00. Found: 1.06:1.00:4.00:1.96. X-ray pattern: 9.20 (m), 7.70 (m), 7.20 (m), 5.65 (w), 5.45 (w), 4.55 (m), 4.25 (s), 4.15 (w), 4.00 (w), 3.6 (w), 3.43 (w), 3.20 (w), 2.65 (w), 2.45 (w), 2.40.

Filtrate: Anal. Calcd for Me_2Mg: Mg:Me = 1.00:2.00. Found: 1.00:1.95. IR: ν(Mg–CH_3) 418 cm^{-1}. NMR: singlet at 3.56 ppm upfield from THF.

(d) Reaction of Magnesium Hydride with Dimethylzinc in THF in 1:2 Ratio. Magnesium hydride (4.0 mmol) and Me_2Zn (8.0 mmol) were allowed to react similarly to (a). The insoluble solid formed, and the supernatant solution was analyzed.

Insoluble solid: Anal. Calcd for $MgZnH_4$·2THF: Mg:Zn:H:THF = 1.00:1.00:4.00:2.00. Found: 1.00:1.06:4.03:1.98. X-ray pattern: same as in the case of reaction (c).

Filtrate: Anal. Calcd for [$Mg(ZnMe_3)_2$ + Me_2Zn]: Mg:Zn:Me = 1.00:3.00:8.00. Found: 1.00:2.89:7.89. IR: ν(Mg–CH_3) 520 cm^{-1}; ν(Zn–CH_3) 580 cm^{-1}. NMR: singlet at 2.70 ppm upfield from THF.

(e) Reaction of Dimethylmagnesium with Zinc Hydride in THF in 1:2 Ratio. Dimethylmagnesium (5.0 mmol) in THF was added dropwise to a well-stirred slurry of ZnH_2 (10.0 mmol) in THF. The reaction mixture was stirred for 5 h and the insoluble solid filtered, washed with THF, and dried under vacuum.

Insoluble solid: Anal. Calcd for $MgZnH_4$ + $2ZnH_2$: Mg:Zn:H = 1.00:3.00:8.00. Found: 1.00:2.95:7.91. X-ray pattern: same as that for $MgZnH_4$·2THF.

Filtrate: Anal. Calcd for $MgZnMe_4$: Mg:Zn:Me = 1.00:1.00:4.00. Found: 1.00:1.04:4.04. IR: ν(Mg–CH_3) 508 cm^{-1}; ν(Zn–CH_3) 572 cm^{-1}. NMR: singlet at 2.80 ppm upfield from THF.

(f) Preparation and Reactions of $MgZnMe_4$ in THF with (i) $LiAlH_4$ or (ii) MgH_2 in 1:2 Ratio. Magnesium tetramethylzincate, $MgZnMe_4$, was prepared in THF by the reaction of Me_2Mg (6.0 mmol) in THF with a THF solution of Me_2Zn (6.0 mmol). The reaction mixture was stirred for 2 h.

(i) To 3.0 mmol of $MgZnMe_4$ in THF was added, dropwise with constant stirring at room temperature, a THF solution of $LiAlH_4$ (6.0 mmol). An exothermic reaction occurred, and a white precipitate appeared immediately. This mixture was then stirred for an additional hour and filtered. The solid was washed with THF and dried under vacuum at room temperature.

Solid: Anal. Calcd for $MgZnH_4$·2THF: Mg:Zn:H:THF = 1.00:1.00:4.00:2.00. Found: 1.02:1.00:3.96:1.97. X-ray pattern: 8.50 (w), 7.29 (s), 5.45 (w), 4.55 (m), 4.42 (w), 4.25 (s), 3.92 (m), 3.60 (m), 3.45 (w), 2.93 (w), 2.85 (w), 2.62 (w), 2.15 (w), 2.00 (vw).

(ii) Magnesium tetramethylzincate (3.0 mmol) in THF was added to a slurry of MgH_2 (6.0 mmol) in THF. The reaction mixture was stirred for 5 h at room temperature. A solid was always present during the reaction. The white solid was filtered, washed with THF, and dried under vacuum. The filtrate was shown to be Me_2Mg by elemental analysis and infrared and NMR spectroscopy.

Filtrate: Anal. Calcd for Me_2Mg: Mg:Zn:Me = 1.00:0.0:2.00. Found: 1.00:0.5:2.04. NMR: singlet at 3.55 ppm upfield from THF. IR: ν(Mg–CH_3) 519 cm^{-1}.

Solid: Anal. Calcd for $MgZnH_4 \cdot 2THF$: Mg:Zn:H:THF = 1.00:1.00:4.00:2.00. Found: 1.04:1.00:3.98:1.93. X-ray pattern: similar to that for $MgZnH_4 \cdot 2THF$.

Reaction of Magnesium Hydride with Zinc Bromide in 1:2 Ratio in THF. To a well-stirred slurry of MgH_2 (4.5 mmol) in THF was added dropwise a THF solution of 9.0 mmol of $ZnBr_2$. The reaction was exothermic, and a large amount of precipitate formed. The reaction mixture was stirred at room temperature for 2 h, and the solid was filtered, washed with THF, and dried under vacuum. The filtrate contained 2–3% magnesium, zinc, and bromine.

Solid: Anal. Calcd for $ZnH_2 + MgZnBr_4$: Mg:Zn:H:Br = 1.00:2.00:2.00:4.00. Found: 1.00:2.07:1.97:4.05. X-ray pattern: 8.40 (m), 7.70 (s), 7.00 (m), 5.17 (w), 4.60 (vw), 4.20 (vw), 4.10 (vw), 3.75 (w), 3.60 (vw), 3.45 (vw), 3.30. IR (Nujol): 1615 (w), 1458 (vs), 1378 (vs), 1370 (sh), 1346 (m), 1320 (w), 1296 (m), 1246 (m), 1173 (m), 1073 (w), 1011 (s), 921 (m), 850 (s), 720 (w), 670 (m), 570 (w), 315 (s), 309 (s), 295 (s), 271 (w), 240 (s) cm^{-1}.

Reaction of Magnesium Bromide with Zinc Bromide in 1:1 Ratio in THF. A THF solution of $ZnBr_2$ (3.0 mmol) was added dropwise to a THF solution of 3.0 mmol of $MgBr_2$. A white crystalline solid appeared immediately. The reaction mixture was stirred at room temperature for 1 h, and the solid was filtered, washed with THF, and dried under vacuum at 25 °C (0.1 mmHg) for 1 h. Anal. Calcd for $MgZnBr_4 \cdot 5THF$: Mg:Zn:Br:THF = 1.00:1.00:4.00:5.00. Found: 1.00:1.03:4.03:4.95. X-ray pattern: 8.40 (m), 7.70 (s), 7.01 (m), 5.17 (w), 4.60 (vw), 4.21 (vs), 4.10 (vw), 3.75 (w), 3.60 (vw), 3.45 (vw), 3.31 (vw). IR (Nujol): 1615 (w), 1456 (vs), 1377 (vs), 1370 (m), 1346 (m), 1296 (m), 1245 (m), 1173 (m), 1073 (w), 1101 (s), 921 (m), 850 (s), 720 (w), 670 (m), 570 (w), 315 (s), 308 (s), 295 (s), 271 (w), 240 (s) cm^{-1}.

Reaction of $MgZnBr_4$ with $LiAlH_4$ in Ether in 1:2 Ratio. Attempted Preparation of $MgZnH_4$. To a slurry of $MgZnBr_4$ (4.00 mmol) in THF at 0 °C was added $LiAlH_4$ (8.0 mmol) in THF dropwise with constant stirring. The crystalline nature of the solid was changed to a fine precipitate. The reaction mixture was stirred for 2 h, and the white insoluble solid was filtered, washed with ether, and dried under vacuum. Anal. Calcd for ZnH_2: Mg:Zn:H = 0.0:1.00:2.00. Found: 0.05:1.00:1.98. The X-ray pattern corresponded to zinc hydride. The filtrate showed Al–H stretching at 1780 cm^{-1}. The X-ray powder diffraction pattern of the filtrate gave lines due to $MgBr_2 \cdot 3THF$ and LiBr.

Results and Discussion

Recently, we have been able to prepare HMgX compounds (where X = Cl or Br)[10] in THF solution by the reaction of magnesium halides with an active form of MgH_2 (eq 4). This

$$MgH_2 + MgX_2 \rightarrow 2HMgX \qquad (4)$$

$$MgR_2 + LiAlH_4 \rightarrow MgH_2 + LiAlR_2H_2 \qquad (5)$$

$$MgH_2 + ZnX_2 \nrightarrow HZnX + HMgX \qquad (6)$$

active MgH_2 was prepared by the reaction of diphenyl- or diethylmagnesium with $LiAlH_4$ in ether (eq 5). Since MgH_2 reacts very rapidly with magnesium halides in THF, it was considered worthwhile to react magnesium hydride with zinc halides in order to prepare HZnX compounds (eq 6). When an equimolar amount of $ZnBr_2$ was allowed to react with MgH_2 slurry in THF, an exothermic reaction resulted, and a crystalline white solid was formed. This solid was characterized and found to be ZnH_2 indicating the reaction course shown by eq 7. Another attempt was made to prepare HZnBr

$$MgH_2 + ZnBr_2 \xrightarrow{THF} ZnH_2 + MgBr_2 \qquad (7)$$

by the reaction of MgH_2 with $ZnBr_2$ in 1:2 ratio. It was thought that initially reactive ZnH_2 would be formed which would react with more $ZnBr_2$ to give the desired product, HZnBr. When this reaction was carried out, an insoluble solid formed which was characterized to be a mixture of $MgZnBr_4$ and ZnH_2 by X-ray powder diffraction and elemental analyses. These results suggested that MgH_2 reacted with 1 mole equiv of $ZnBr_2$ to produce ZnH_2 and $MgBr_2$ according to eq 7. The $MgBr_2$ formed then reacted further with another mole equivalent of $ZnBr_2$ to give $MgZnBr_4$. In order to support our conclusion, $MgBr_2$ and $ZnBr_2$ in THF were allowed to react at room temperature. Immediate precipitation of a crystalline solid took place, and the solid was characterized by elemental analysis to be $MgZnBr_4 \cdot 5THF$ (eq 8). The

$$MgBr_2 + ZnBr_2 \xrightarrow{THF} MgZnBr_4 \qquad (8)$$

X-ray powder diffraction pattern showed it to be a single compound and not a mixture of $MgBr_2 \cdot 3THF$ and $ZnBr_2 \cdot 2THF$.

We have shown previously that the reaction of mixed-metal "ate" complexes ($M_mM'_nR_{2n+m}$) with $LiAlH_4$ results in the formation of the corresponding complex metal hydride.[1-3] For example, the reaction of Li_2ZnMe_4 with $LiAlH_4$ results in the formation of Li_2ZnH_4 (eq 9). We have also shown that the

$$Li_2ZnMe_4 + 2LiAlH_4 \rightarrow Li_2ZnH_4\downarrow + 2LiAlMe_2H_2 \qquad (9)$$

reaction of $ZnBr_2$ with $LiAlH_4$ in ether produces ZnH_2. Preparation of ZnH_2 from $ZnBr_2$ is much less expensive than preparing it from R_2Zn compounds. Since we prepared $MgZnBr_4$ as a stable complex, we thought it would be worthwhile to react this compound with $LiAlH_4$ in order to prepare $MgZnH_4$. When $MgZnBr_4$ in THF was allowed to react with 2 mole equiv of $LiAlH_4$ in ether, an insoluble solid resulted. The infrared spectrum of the supernatant solution showed Al–H stretching at 1780 cm^{-1} characteristic of AlH_3 in ether. The insoluble solid was shown to be ZnH_2 by elemental analysis. The reaction probably proceeds according to eq 10. Magnesium bromide in solution does not react with AlH_3 as reported previously.[11]

$$MgZnBr_4 + 2LiAlH_4 \xrightarrow{Et_2O} 2LiBr + MgBr_2 + 2AlH_3 + ZnH_2\downarrow \qquad (10)$$

Recently, we have prepared a series of alkylmagnesium hydrides[12] by the reaction of R_2Mg compounds with MgH_2. Since R_2Zn compounds react with R_2Mg compounds to form $MgZnR_4$, it was concluded that R_2Zn compounds would probably react with MgH_2 to form mixed-hydrido "ate" complexes of magnesium and zinc. Similarly, it should be possible for R_2Mg compounds to react with ZnH_2 to form the same mixed-hydrido "ate" complexes of magnesium and zinc. Thus, when a THF solution of Me_2Zn was added to an equimolar amount of a THF slurry of MgH_2, it was no surprise to find that $MgZnH_4 \cdot 2THF$ was formed as an insoluble solid and that the supernatant solution contained $MgZnMe_4$. It was observed during the course of this reaction that a clear solution existed just after the addition of MeZn to MgH_2; however, when the mixture was further stirred (~5 min), an insoluble white solid was formed. NMR analysis of the clear solution showed a singlet at 2.85 ppm which was close to the singlet observed for $MgZnMe_4$. These observations suggested that probably a mixed complex, $MgZnH_2Me_2$, formed which then disproportionates to $MgZnMe_4$ and $MgZnH_4$ (eq 11). On

$$MgH_2 + Me_2Zn \xrightarrow{THF} [MgZnMe_2H_2] \rightarrow {}^1/_2MgZnH_4\downarrow + {}^1/_2MgZnMe_4 \qquad (11)$$

the other hand, when the reaction of Me_2Zn with MgH_2 was carried out in 1:2 ratio, a somewhat different result was observed. In this case the supernatant solution showed a singlet at 3.56 ppm upfield from THF in its NMR spectrum and a band at 518 cm^{-1} in its infrared spectrum indicative of the Mg–CH_3 group in Me_2Mg. The insoluble solid was characterized to be $MgZnH_4 \cdot 2THF$ by both elemental analysis and

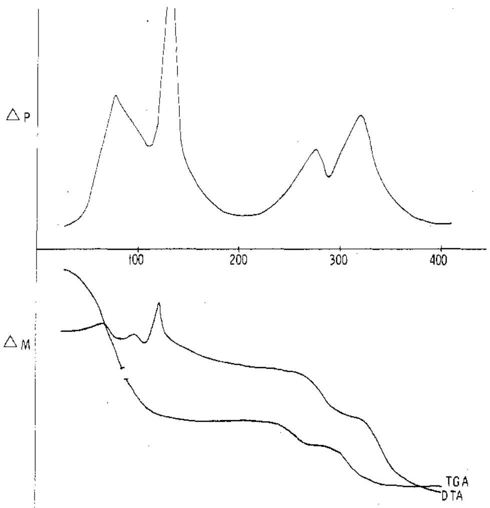

Figure 1. DTA–TGA of $MgZnH_4{\cdot}2THF$ prepared by the reaction of Me_2Zn with MgH_2.

X-ray powder diffraction pattern comparison with an authentic sample (eq 12). It is interesting to note that the reaction of

$$Me_2Zn + 2MgH_2 \xrightarrow{THF} MgZnH_4 + Me_2Mg \quad (12)$$

Me_2Zn with MgH_2 in 1:1 ratio gave $MgZnMe_4$; therefore, there should be a reaction between $MgZnMe_4$ and MgH_2 in the case of the reaction of Me_2Zn with MgH_2 in 1:2 ratio. In order to test this postulate, $MgZnMe_4$ was prepared by the reaction of Me_2Mg with Me_2Zn in a 1:1 ratio and then allowed to react with a slurry of MeH_2 in THF. In this reaction, the supernatant solution was observed to contain Me_2Mg while the insoluble solid formed was determined to be $MgZnH_4{\cdot}2THF$ (eq 13).

$$MgZnMe_4 + MgH_2 \xrightarrow{THF} MgZnH_4 + Me_2Mg \quad (13)$$

When Me_2Mg was allowed to react with ZnH_2 slurry in 1:1 ratio in THF, a clear solution was not observed at any stage. When the reaction mixture was stirred for 4 h, the insoluble solid product was shown to be $MgZnH_4{\cdot}2THF$, and the supernatant solution was shown to be $MgZnMe_4$ (eq 14). An

$$2Me_2Mg + 2ZnH_2 \xrightarrow{THF} MgZnH_4 + MgZnMe_4 \quad (14)$$

NMR spectrum of the supernatant solution showed a singlet at 2.80 ppm upfield from THF, and an infrared spectrum showed bands at 508 and 572 cm^{-1} indicating the presence of $Mg-CH_3$ and $Zn-CH_3$ bonds.

When the above reaction was carried out in 1:2 ratio in an attempt to prepare $Mg(ZnH_3)_2$, the resulting insoluble solid was found to be a mixture of $MgZnH_4$ and ZnH_2 as indicated by elemental analysis and X-ray powder diffraction data which showed lines due only to $MgZnH_4$. The filtrate was shown to be $MgZnMe_4$. It seems clear that ZnH_2 does not react with $MgZnMe_4$ although MgH_2 does (eq 13 and 15).

$$2Me_2Mg + 4ZnH_2 \xrightarrow{THF} MgZnH_4 + MgZnMe_4 + 2ZnH_2 \quad (15)$$

The reaction of MgH_2 with Me_2Zn in a 1:2 ratio in THF resulted in the formation of insoluble $MgZnH_4$ and a solution containing a mixture of Me_2Zn and $Mg(ZnMe_3)_2$ (eq 16).

$$2MgH_2 + 4Me_2Zn \rightarrow MgZnH_4\downarrow + Mg(ZnMe_3)_2 + Me_2Zn \quad (16)$$

Magnesium tetrahydridozincate, $MgZnH_4$, was also prepared by the reaction of the corresponding "ate" complex $MgZnMe_4$ in THF with lithium aluminum hydride. The insoluble solid formed gave an elemental analysis corresponding to $MgZnH_4{\cdot}2THF$, and the X-ray powder diffraction pattern showed lines similar to that of $MgZnH_4{\cdot}2THF$ prepared by the other methods.

$$Me_2Mg + Me_2Zn \xrightarrow{THF} MgZnMe_4 \xrightarrow{2LiAlH_4} MgZnH_4 + 2LiAlH_2Me_2 \quad (17)$$

Vacuum DTA–TGA studies of $MgZnH_4{\cdot}2THF$ prepared by the reaction of Me_2Zn with MgH_2 have been carried out (Figure 1). The following information is suggested from the DTA–TGA curves. The only trapped gas evolved during the

$$MgZnH_4{\cdot}2THF \xrightarrow{70\ °C} MgZnH_4{\cdot}THF + THF \quad (endo)$$

$$MgZnH_4{\cdot}THF \xrightarrow{95-100\ °C} Mg(ZnH_3)_2 + MgH_2{}^* + THF \quad (exo)$$

$$Mg(ZnH_3)_2 \xrightarrow{100\ °C} MgH_2 + 2ZnH_2 \quad (exo)$$

$$ZnH_2 \xrightarrow{120\ °C} Zn + H_2 \quad (exo)$$

$$MgH_2 \xrightarrow{270\ °C} Mg + H_2 \quad (endo)$$

$$MgH_2{}^* \xrightarrow{318\ °C} Mg + H_2 \quad (endo)$$

decompositions was determined to be THF which suggests that THF is not cleaved during the thermal decomposition. The DTA–TGA curves for all samples of $MgZnH_4$ prepared from other reactions were identical showing that the products are identical.

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Registry No. MgH_2, 7693-27-8; Ph_2Mg, 555-54-4; Et_2Mg, 557-18-6; $LiAlH_4$, 16853-85-3; ZnH_2, 14018-82-7; Ph_2Zn, 1078-58-6; $ZnBr_2$, 7699-45-8; Me_2Zn, 544-97-8; $MgZnH_4{\cdot}2THF$, 69745-61-5; Me_2Mg, 2999-74-8; $MgZnMe_4$, 69745-62-6; $MgBr_2$, 7789-48-2; $MgZnBr_4$, 69745-63-7.

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