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Reactions of Diphenylmagnesium with Lithium Aluminum Hydride in Diethyl Ether and Tetrahydrofuran. Preparation of PhMgH and PhMg$_2$H$_3$

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The reactions of diphenylmagnesium with lithium aluminum hydride in diethyl ether and THF have been studied in detail. Although MgH$_2$ as an insoluble solid and LiAlPh$_n$H$_{4-n}$ in solution are formed when the Ph$_2$Mg:LiAlH$_4$ ratio is 3:2, 1:1, and 1:2 in ether, no MgH$_2$ is formed when Ph$_2$Mg is allowed to react with LiAlH$_4$ in THF in ratios varying from 4:1 to 1:2. Instead, compounds of the type PhMgH and PhMg$_2$H$_3$ are formed and are soluble in THF. These types of compounds are reported for the first time and their existence is supported by IR and NMR analysis.

Introduction

Our interest in the reactions of diphenylmagnesium with lithium aluminum hydride is twofold. First, we have been engaged in the synthesis of complex metal hydrides of magnesium, such as LiMgH$_3$, Li$_2$MgH$_4$, etc. by the reaction of LiMgR$_3$ with LiAlH$_4$. According to earlier reports,[1] lithium triphenylmagnesate, LiMgPh$_3$, dissociates in ether to PhLi and Ph$_2$Mg. If LiAlH$_4$ is then added to LiMgPh$_3$ in ether, one would expect to form LiH and MgH$_2$ as well as LiMgH$_3$. Since the reaction of LiAlH$_4$ and Ph$_2$Mg has not been studied, we thought it worthwhile to study this reaction to determine if indeed MgH$_2$ is formed. Second, the existence of compounds like RMgH has been the subject of interest and controversy for some time.[2,3] Indeed our own earlier attempts to prepare RMgH compounds by the reaction of LiAlH$_4$ with (C$_2$H$_5$)$_2$Mg failed. However, all previous studies were carried out in diethyl ether, a solvent in which MgH$_2$ precipitation took place immediately on mixing the reagents. On the other hand, our attempts to form MgH$_2$ by the same reaction in THF produced a clear solution indicating the possible formation of RMgH compounds.

In this paper, we wish to report the reactions of diphenylmagnesium with lithium aluminum hydride in ether as well as in THF in order to show the significant difference in the reaction course depending on the solvent.

Experimental Section

Apparatus. Reactions were performed under dry nitrogen at the bench or in a glovebox equipped with a recirculating system using manganese(II) oxide to remove oxygen.[5] Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer using KBr and CsI liquid or mull cells. NMR spectra were recorded on a Varian A-60. The x-ray powder diffraction pattern data were obtained on a Philips-Norelco x-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in a 0.5-mm capillary and exposed to x rays for 6 h. The d spacings were read on a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually.

Analyses. Gas analysis was accomplished by hydrolysis of samples with HCl on a standard vacuum line equipped with a Toepler pump. Aluminum was determined by adding excess EDTA and back-titrating with standard zinc acetate at pH 4 in 50% ethanol with dithizone as an indicator. When aluminum was present, it was masked by complexation with triethanolamine. Phenyl groups present in the complexes were determined as benzene by hydrolysis of the samples with water and analyzing the filtrate by GLC using an SE 30 column at 70 °C. Mesitylene was used as the solvent and 1-hexanol was used as the internal standard.

Materials. Solvents were distilled immediately prior to use over lithium aluminum hydride (ether) or sodium aluminum hydride (THF, benzene, and mesitylene).

Diphenylmagnesium (Ph$_2$Mg) was prepared by heating a mixture of triply sublimed magnesium (Dow Chemical Co.) and diphenylmercury at 155 °C for 40 h. The crude reaction mixture was extracted with freshly distilled ether or THF and the resulting solution standardized by magnesium analysis. Dimethyl- and diethyl-

magnesium were prepared by stirring a mixture of dimethyl- or diethylmercury with magnesium metal at room temperature for 24 h followed by extraction of the crude reaction mixture with ether or THF.

Lithium aluminum hydride (LiAlH$_4$) was obtained from Ventron, Metal Hydrides Division. A solution was prepared by refluxing LiAlH$_4$ in ether or THF overnight followed by filtration through a glass-fritted funnel (medium) using predried Celite Analytical filter Aid (Johns-Mansville). The clear solution was standardized by aluminum analysis.

Lithium tetraphenylaluminate (LiAlPh$_4$) was prepared by the addition of phenyllithium solution in ether to triphenylaluminum in ether with continuous stirring. A viscous insoluble layer separated from the ether and crystallized from solution overnight. The white solid is soluble in tetrahydrofuran but insoluble in diethyl ether. Anal. Calcd for LiAl(C$_6$H$_5$)$_4$: Li:Al:Ph = 1.0:1.0:4.0. Found: Li:Al:Ph = 1.00:1.06:4.10.

X-ray powder diffraction data for LiAlPh$_4$ showed the following lines: 8.5 (s), 6.8 (w), 6.0 (w–m), 5.4 (vw), 4.8 (vw), 4.4 (vs), 4.15 (s), 3.8 (w), 3.25 (m–s), 2.95 (m), 2.82 (w), 2.76 (w), 2.63 (w), 2.55 (w), 2.43 (w), 2.30 (vw), 2.25 (vs), 2.13 (vs), 2.05 (vs), 2.00 (vw), 1.90 (w), 1.78 (w), 1.58 (w) Å.

Infrared Study of the Reaction of LiAlH$_4$ with Ph$_2$Mg. (a) In Diethyl ether. A 100-mL portion of a 0.10 M solution of diphenylmagnesium in diethyl ether was placed in a three-neck round-bottom flask equipped with a condenser, magnetic stirrer, and an addition funnel. To this was added dropwise a 0.73 M solution of lithium aluminum hydride in diethyl ether in regular increments with continuous stirring. After each addition, the mixture was stirred for 0.5 h and the precipitate formed was allowed to settle. A small sample of the clear supernatant solution was withdrawn for infrared analysis. The addition of lithium aluminum hydride was continued until it was in large excess. The entire experiment was repeated by reversing the mode of addition using 0.79 M diphenylmagnesium and 0.415 M lithium aluminum hydride solutions. Figure 1 shows the infrared spectra of starting materials and the solutions produced on reaction of Ph$_2$Mg and LiAlH$_4$ at several stoichiometric ratios.

(b) In THF. The above experiment was repeated in a similar manner using diphenylmagnesium and lithium aluminum hydride in THF. The infrared spectra of the supernatant solutions were recorded (Figure 2).

Reaction of Ph$_2$Mg with LiAlH$_4$ in 1:2, 1:1, and 3:2 Stoichiometric Ratios in Diethyl Ether. Lithium aluminum hydride (0.415 M) solution in diethyl ether was added in various stoichiometric proportions to magnetically stirred diphenylmagnesium solution in diethyl ether (0.79 M) at a very slow rate (due to the slightly exothermic nature of the reaction) so that the reaction temperature could be kept at 25 °C. Reaction mixtures were stirred for an additional 0.5 h, and the precipitate formed was filtered, washed with ether, and dried under vacuum. Elemental analyses of the precipitates as well as of the filtrates are summarized in Table I.

Reaction of Ph$_2$Mg with LiAlH$_4$ in a 2:1 Molar Ratio. To 10 mL of 0.79 M solution of Ph$_2$Mg in diethyl ether (7.9 mmol) was added dropwise 9.5 mL of 0.415 M ether solution of LiAlH$_4$ (3.95 mmol) with continuous stirring at room temperature. The reaction was exothermic and a white precipitate in addition to a colorless insoluble viscous product was observed. The reaction mixture was then stirred for 48 h. The amount of the white precipitate decreased with time and a grayish black sticky precipitate was observed at the bottom of
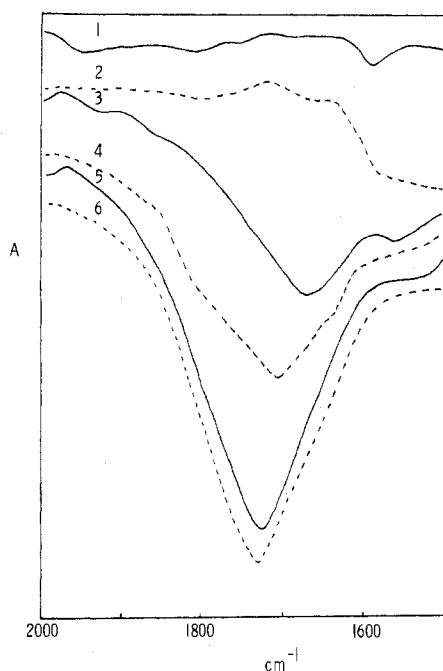
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Figure 1. Infrared spectra of the supernatant solution on addition of $LiAlH_4$ to Ph_2Mg in diethyl ether. $Ph_2Mg:LiAlH_4$ ratio: (1) pure Ph_2Mg, (2) 2:1, (3) 3:2, (4) 1:1, (5) 1:2, (6) pure $LiAlH_4$.

Table I. Elemental Analyses of the Reaction Products of Ph_2Mg and $LiAlH_4$ (in 1:2, 1:1, and 3:2 Molar Ratios)

Reactants			Precipitate	Filtrate
Amt, mmol				
Ph_2Mg	$LiAlH_4$	Ratio	Mg:Al:H	Li:Mg:Al:H:Ph
3.50	7.02	1:2	1.00:0:2.02	1.02:0:1.00:2.90:1.0
4.24	4.24	1:1	1.00:0:2.07	1.0:0:1.06:1.98:2.0
10.52	7.02	3:2	1.00:0:2.10	1.0:0:1.03:1.01:3.0

the flask below the viscous insoluble layer. The supernatant liquid was separated and analyzed. Anal. Calcd for $LiAlHPh_3$: Li:Al:H:Ph = 1:1:1:3. Found: Li:Mg:Al:H:Ph = 1.00:0:1.06:0.98:3.04. To the viscous liquid and the grayish black precipitate was added about 15 mL of THF and the viscous product dissolved. The mixture was filtered and washed with THF, and both the filtrate and solid were dried under vacuum. The analysis of the THF-soluble solid is as follows. Anal. Calcd for $LiAlPh_4$ + $3MgH_2$: Li:Mg:Al:H:Ph = 1:3:1:6:4. Found: Li:Mg:Al:H:Ph = 1.00:2.96:1.00:5.10:4.95. Analysis of the THF-insoluble solid is as follows. Anal. Calcd for Mg metal: Mg:H:Ph = 1:0:0. Found: 1.00:0.20:0.16.

Reaction of Ph_2Mg with $LiAlH_4$ in a 4:1 Ratio. To 20 mL of 0.79 M diphenylmagnesium solution in ether (15.8 mmol) was added 9.6 mL of a 0.615 M ether solution of lithium aluminum hydride (3.96 mmol) dropwise with stirring. A colorless viscous liquid, insoluble in ether, was formed. The reaction mixture was stirred for an additional 1 h and then the viscous insoluble product was isolated by removing the supernatant solution with a syringe. The viscous layer was then washed with ether and, the next day, on standing overnight, gave a crystalline solid. The solid was dried and analyzed. Anal. Calcd for $LiAlPh_4$ + $^4/_3PhMg_2H_3$: Li:Al:Mg:H:Ph = 1.0:1.0:2.7:4.0:5.3. Found: Li:Al:Mg:H:Ph = 1.00:1.05:2.85:4.32:5.29. X-ray powder diffraction pattern: 2.5 (s), 6.8 (w), 6.0 (w–m), 5.0 (vvw), 4.8 (vw), 4.4 (vs), 4.1 (s), 3.8 (w), 3.29 (m–s), 2.95 (m), 2.82 (w), 2.74 (w), 2.63 (w), 2.55 (w), 2.53 (w), 2.3 (vw), 2.25 (vw), 2.13 (vw), 2.05 (vw), 2.00 (vw), 1.90 (w), 1.78 (w), 1.58 (w) Å. When 20 mL of THF was added to the above white solid, complete solution took place indicating the absence of MgH_2.

Attemped Preparation of PhMgH by the Reaction of Ph_2Mg with Active MgH_2 in Diethyl Ether in a 1:1 Ratio. (a) Active MgH_2 (3.75 mmol) was prepared by adding 5 mL of Ph_2Mg (0.795 M) in ether (3.95 mmol) dropwise to 9.01 mL of 0.415 M solution of $LiAlH_4$ (3.95 mmol) with continuous stirring. A white crystalline precipitate appeared at once and was seperated from the supernatant liquid. The
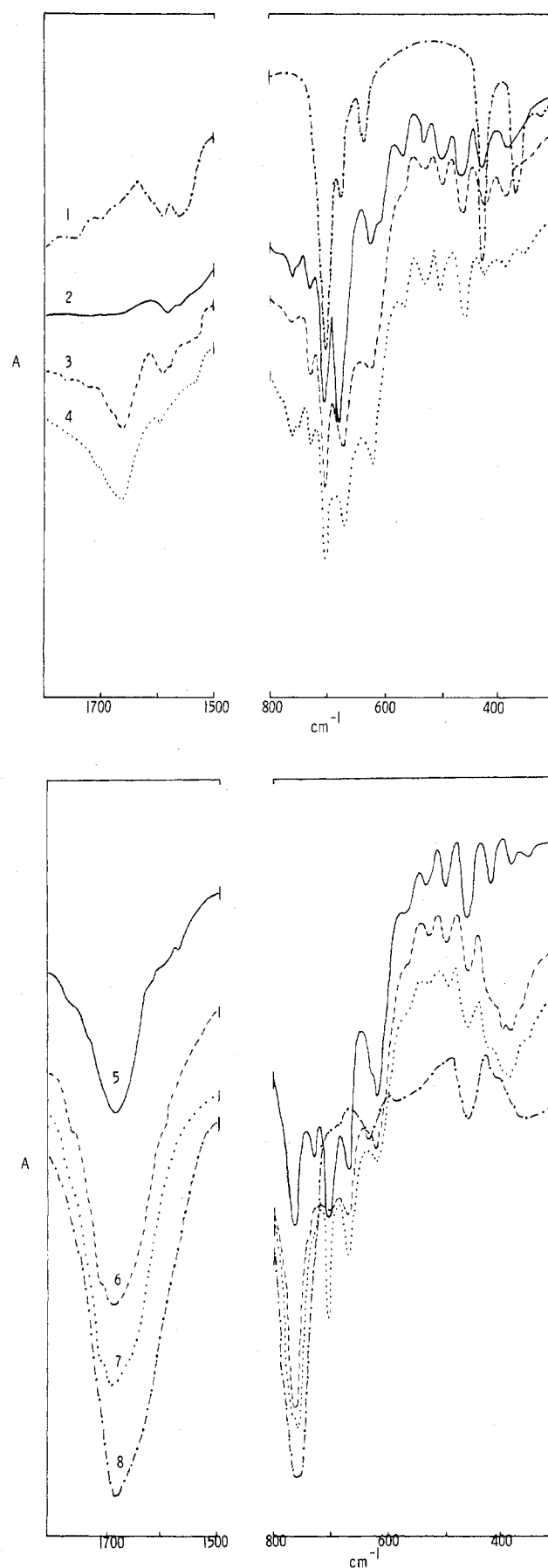

Figure 2. Infrared study of the reactions of Ph_2Mg with $LiAlH_4$ in tetrahydrofuran in the following ratios: (1) pure Ph_2Mg, (2) 4:1, (3), 2:1 (4) 3:2, (5) 1:1, (6) 1:2, (7) 1.2.5, (8) pure $LiAlH_4$.

white solid was washed with ether and was added to 4.5 mL of 0.795 M ether solution of Ph₂Mg dropwise with constant stirring. The precipitate changed into a bulky precipitate. This reaction mixture was stirred for about 6 h more during which time half of this bulky precipitate dissolved while the remainder of the solid turned into a sticky, grayish black mass. The solid was filtered, washed with ether, dried under vacuum, and analyzed. Anal. Calcd for PhMg₂H₃: Ph:Mg:H = 1:2:3. Found: Ph:Mg:H = 1.00:2.00:3.02.

(b) The above experiment was repeated and instead of stirring the mixture of MgH₂ and Ph₂Mg for 6 h we stirred it for only 10 min. The bulky precipitate changed to a sticky mass. The sticky mass was filtered, washed with ether, dried under vacuum, and analyzed. Anal. Calcd for PhMg₂H₃: Ph:Mg:H = 1:2:3. Found: Ph:Mg:H = 1.00:2.00:3.03.

(c) To 3.9 mmol of the supernatant solution from experiment (a) (which was characterized earlier to be LiAlH₂Ph₂) was added 6.5 mL of a 0.79 M solution of Ph₂Mg (3.60 mmol) in ether at room temperature with stirring. A white precipitate along with some insoluble colorless viscous liquid appeared. This reaction mixture was stirred for 1 h and allowed to stand overnight during which time the viscous liquid crystallized to a white solid. The solid was filtered, washed with ether, and treated with 20 mL of THF; the precipitate dissolved. The THF was then removed under vacuum and the resulting solid was dried and analyzed. Anal. Calcd for LiAlPh₄ + MgH₂ or LiAlPh₃H + PhMgH: Li:Mg:Al:H:Ph = 1:1:1:2:4. Found: Li:Mg:Al:H:Ph = 1.06:1.00:1.01:2.02:4.04.

Reaction of MgH₂ with LiAlPh₄. Active MgH₂ (3.75 mmol) was prepared by the reaction of Ph₂Mg (3.95 mmol) and LiAlH₄ (3.95 mmol) in ether. To the resulting solid was added LiAlPh₄ (1.30 g, 3.70 mmol) in 10 mL of ether and the reaction mixture stirred for 25 min. No reaction was observed. The ether solvent was then removed under vacuum and 15 mL of THF was added. The solid material dissolved after stirring for 5 min. Infrared and NMR spectra of this solution were recorded. The solvent was removed under vacuum and benzene added. The solid was stirred for 0.5 h and then filtered, dried under vacuum, and analyzed. Anal. Calcd for MgH₂ + LiAlPh₄ or PhMgH + LiAlH₂Ph₂: Li:Mg:Al:H:Ph = 1.0:1:1:2:4. Found: Li:Mg:Al:H:Ph = 1.03:1.01:1.02:1.96:3.99.

The above solid was dissolved in 10 mL THF and 5 mL of benzene was added after which time some insoluble solid appeared. The mixture was stirred overnight and then filtered. The precipitate was dried at 25 °C (0.1 mm) for 0.5 h. Anal. Calcd for PhMgH: Ph:Mg:H = 1:1:1. Found: Li:Al:Mg:H:Ph = 0.11:0.12:1.00:1.01:1.22. PhMgH contaminated by LiAlPh₄ could not be purified further by repeating the above purification technique.

The filtrate of the above reaction mixture was treated with 15 mL of ether which produced an insoluble white solid. The solid was filtered, washed with ether, and dried. Anal. Found: Li:Al:H:Ph = 1.00:1.10:0.64:3.42. Infrared spectra showed a very weak broad band at 1680 cm⁻¹ due to Al–H stretching.

Reaction of MgH₂ with Ph₂Mg (1:1 Molar Ratio) in THF. To MgH₂ (3.75 mmol) prepared by the reaction of Ph₂Mg (5 mL, 0.795 M, 3.95 mmol) with LiAlH₄ (9.8 mL or 0.615 M, 3.95 mmol) in ether were added 12 mL of THF and 4.6 mL of 0.795 M solution of Ph₂Mg (3.95 mmol) in THF. The reaction mixture was stirred at room temperature for 15 min and gave a clear colorless solution. The solvent was removed under reduced pressure and the resulting solid dried and analyzed. Anal. Calcd for PhMgH: Ph:Mg:H = 1:1:1. Found: Ph:Mg:H = 0.94:1.00:1.02.

Reaction of MgH₂ with Ph₂Mg in 3:1 Molar Ratio in THF. To MgH₂ (11.25 mmol) prepared by the reaction of Ph₂Mg (15 mL of 0.795 M, 11.85 mmol) with LiAlH₄ (29.6 mL of 0.415 M, 11.85 mmol) in ether was added 10 mL of THF and 4.6 mL of 0.795 M solution of Ph₂Mg (3.75 mmol). The reaction mixture was stirred at room temperature for 10 min to give a clear colorless solution. The solvent was removed under vacuum and the resulting solid was dried, washed with ether, and dried. Anal. Calcd for PhMg₂H₃: Ph:Mg:H = 1:2:3. Found: Ph:Mg:H = 1.00:2.00:2.97. The ether solution contained no magnesium.

Reaction of Ph₂Mg with LiAlH₄ in a 1:1 Ratio in THF. To 8 mL of 0.7 M Ph₂Mg solution in THF (5.6 mmol) was added 8.4 mL of 0.67 M LiAlH₄ in THF (5.6 mmol) with stirring at room temperature. The reaction was exothermic and resulted in a clear colorless solution. The infrared spectrum of this solution exhibited an absorption band at 1680 cm⁻¹ characteristic of Al–H stretching in LiAlH₃Ph in THF. The solvent was removed under reduced pressure and the resulting

product washed several times with ether to give a white insoluble solid which was dried and analyzed. Anal. Calcd for PhMg₂H₃: Ph:Mg:H = 1:2:3. Found: Ph:Mg:H = 0.98:2.00:3.05. This solid contained 5% Li–Al impurity.

Reaction of Ph₂Mg with LiAlH₄ in a 2:1 Ratio in THF. To 10 mL of 0.70 M Ph₂Mg solution in THF (7.0 mmol) was added dropwise 5.20 mL of 0.67 M solution of LiAlH₄ in THF (3.50 mmol) with stirring at room temperature, producing a clear solution. The solvent was removed under vacuum and the resulting residue washed with ether and dried to give a white solid. Anal. Calcd for PhMg₂H₃ + LiAlHPh₃ (as impurity): Li:Al:Ph:Mg:H = 1.00:1.00:5.26:4.51:7.75. Found: Li:Al:Ph:Mg:H = 1.00:1.05:5.20:4.51:7.59. LiAlHPh₃ present as an impurity could not be removed completely by ether washing.

Results and Discussion

Addition of Ph₂Mg to LiAlH₄ in 3:2, 1:1, and 1:2 ratios in ether, or the corresponding inverse addition, resulted in the precipitation of MgH₂. This result is consistent with the earlier report[4] concerning the reaction of diethylmagnesium with LiAlH₄ in ether which states that MgH₂ precipitates immediately on addition of either reagent to the other. The immediate precipitation of MgH₂ when LiAlH₄ was slowly added to Et₂Mg was considered evidence that EtMgH was not formed in the reaction. Variation of the concentration of LiAlH₄ and Ph₂Mg was found to have no effect on the reaction.

An infrared study of the reaction of LiAlH₄ with Ph₂Mg showed that the reaction proceeds stepwise exchanging phenyl groups of the magnesium for hydride of the aluminum as shown in eq 1. The precipitate formed in the reactions (eq 1) initially was shown to be MgH₂ by infrared, elemental, and

$$n\text{Ph}_2\text{Mg} + 2\text{LiAlH}_4 \xrightarrow[\substack{(n=1-3)}]{\text{Et}_2\text{O}} 2\text{LiAlPh}_n\text{H}_{4-n} + n\text{MgH}_2 \quad (1)$$

x-ray powder diffraction analysis and the filtrate of the reaction (eq 1) was characterized as LiAlPh$_n$H$_{4-n}$ by infrared spectra[5] (when $n = 3, 2, 1$). The Al–H stretching bands were observed at 1670–1680, 1710, and 1730 cm⁻¹, respectively. The NMR spectrum of Ph₂Mg in ether gave two multiplets due to ortho (downfield) and meta–para (upfield) protons of the phenyl groups in a 2:3 ratio. The upfield multiplet was centered at 5.93 ppm relative to the triplet of ether and the chemical shift separation between the two highest peaks of the multiplets was 0.68 ppm.

In spite of these results, an initial indication of the formation of PhMgH was found by studying the reaction of LiAlH₄ and Ph₂Mg in ether in a 1:2 ratio (eq 2). The infrared spectrum

$$2\text{Ph}_2\text{Mg} + \text{LiAlH}_4 \xrightarrow{\text{ether}} \text{LiAlPh}_4 + 2\text{MgH}_2 \quad (2)$$
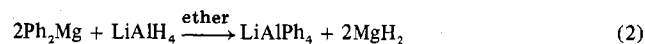
(Figure 1) of the supernatant solution showed no Al–H stretching bands in the 1600–1800-cm⁻¹ region after the reaction mixture had been stirred for 1 h. However, when the reaction mixture had been stirred for 48 h, a very weak and broad Al–H stretching band at 1680 cm⁻¹ (characteristic of LiAlPh₃H[6]) appeared indicating some reaction between MgH₂ and LiAlPh₄ (eq 3). Furthermore, in this reaction, an in-

$$\text{MgH}_2 + \text{LiAlPh}_4 \rightarrow \text{PhMgH} + \text{LiAlPh}_3\text{H} \quad (3)$$
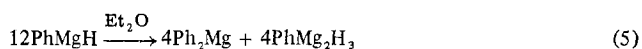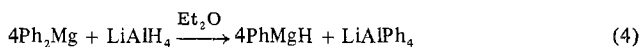
soluble colorless viscous liquid and a white crystalline solid were observed. When the mixture was stirred for 48 h, the white solid changed to a grayish black solid and the supernatant liquid was shown by infrared analysis to be LiAlPh₃H. The insoluble colorless viscous liquid was soluble in THF and was characterized to be either a complex or a mixture of LiAlPh₄ and 3 MgH₂ and the insoluble grayish black solid insoluble in THF was shown to be magnesium metal. The NMR spectrum of the supernatant solution (LiAlPh₃H) contained an absorption due to benzene in addition to two multiplets due to phenyl protons. According to the above

observation, it can be supposed that the MgH_2 and $LiAlPh_4$ initially formed probably reacted to give some of $LiAlPh_3H$ and $PhMgH$ which produced benzene and magnesium metal on decomposition.

In order to support the above conclusions, reaction between active MgH_2 (prepared by the reaction of Ph_2Mg and $LiAlH_4$ in a 1:1 ratio) and $LiAlPh_4$ in a 1:1 ratio was attempted in ether. No reaction was obvious after 1 h. However, when the reaction mixture was stirred for 2 days, a weak Al–H stretching band was observed at 1680 cm^{-1}. When the same reaction was carried out in THF, a clear solution resulted. An infrared spectrum of the clear THF solution showed a very weak Al–H band at 1655 cm^{-1} characteristic of $LiAlPh_3H$ in THF. An NMR spectrum in THF did not show the MgH proton as the side bands of THF were in the expected region; however, the downfield broad multiplets due to the ortho protons of the phenyl groups of the $LiAlPh_4$ starting material split into two broad multiplets. The chemical shift separation in the NMR spectrum of the clear reaction mixture between the highest peak of the upfield multiplet (due to meta–para protons) and the two downfield multiplets (due to ortho protons of phenyl ring) were observed to be 0.68 and 0.60 ppm suggesting both Mg–Ph and Al–Ph compounds present. The presence of $LiAlPh_3H$ as demonstrated by IR analysis (Al–H, 1655 cm^{-1}) and the presence of a Mg–Ph compound (by NMR analysis) indicate the presence of PhMgH according to eq 3. When benzene was added slowly to the clear reaction mixture and the latter allowed to stand for some time, an insoluble white solid was observed which, when analyzed, was shown to be PhMgH contaminated with a small amount of $LiAlPh_3H$.

In the reaction of Ph_2Mg with $LiAlH_4$ in ether in a 4:1 ratio, an insoluble viscous liquid was observed. However, the supernatant solution contained about 30% of the initial amount of diphenylmagnesium as determined by elemental and IR analyses. The viscous liquid, when analyzed, corresponded to a mixture of $PhMg_2H_3$ and $LiAlPh_4$. When this viscous liquid was kept overnight, it crystallized producing a white solid. An x-ray powder diffraction pattern of the solid gave strong lines due to $LiAlPh_4$. The above information leads to the probable pathway

$$4Ph_2Mg + LiAlH_4 \xrightarrow{Et_2O} 4PhMgH + LiAlPh_4 \qquad (4)$$

$$12PhMgH \xrightarrow{Et_2O} 4Ph_2Mg + 4PhMg_2H_3 \qquad (5)$$

In order to support our assumption about the dissociation of PhMgH to Ph_2Mg and $PhMg_2H_3$ (eq 5), pure PhMgH (prepared by reaction of Ph_2Mg and MgH_2 to be described later) was stirred in diethyl ether. The resulting supernatant solution was shown to be Ph_2Mg in ether and the insoluble solid corresponded to $PhMg_2H_3$ according to complete elemental analysis.

In another reaction of Ph_2Mg with $LiAlH_2Ph_2$ in ether at room temperature, a white precipitate and an insoluble viscous liquid were formed which could not be separated; however, both the solid and viscous liquid dissolved in THF. Infrared and NMR analysis of the resulting solution indicated that the MgH_2 and $LiAlPh_4$ initially formed reacted rapidly in THF to form PhMgH and $LiAlPh_3H$ (eq 6).

$$Ph_2Mg + LiAlH_2Ph_2 \xrightarrow{Et_2O} MgH_2 + LiAlPh_4 \xrightarrow{THF} PhMgH$$
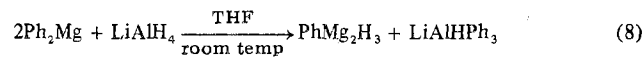$$+ LiAlHPh_3 \qquad (6)$$
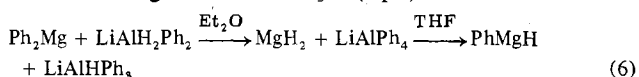
When Ph_2Mg in THF was allowed to react with $LiAlH_4$ in THF in molar ratios varying from 4:1 to 1:2, no precipitate of MgH_2 was observed and a clear solution resulted in every case. An infrared spectrum of the 4:1 reaction mixture showed no bands due to Al–H stretching in the region 1600–1800 cm^{-1} but did show the presence of Ph–Mg stretching at 420 cm^{-1}

suggesting a reaction according to eq 7. When the ratio of

$$4Ph_2Mg + LiAlH_4 \xrightarrow[\text{room temp}]{THF} 4PhMgH + LiAlPh_4 \qquad (7)$$
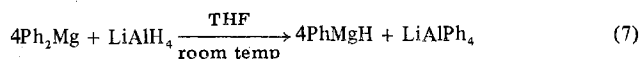
Ph_2Mg to $LiAlH_4$ was 2:1, a weak band at 1655 cm^{-1} due to $LiAlHPh_3$ in THF[5] was observed suggesting a reaction according to eq 8. When the solvent of the above reaction 8

$$2Ph_2Mg + LiAlH_4 \xrightarrow[\text{room temp}]{THF} PhMg_2H_3 + LiAlHPh_3 \qquad (8)$$

was removed under vacuum and the product washed with ether to remove $LiAlHPh_3$, a white solid resulted which was shown by elemental analysis to be $PhMg_2H_3$. The compound contained a small amount of $LiAlHPh_3$ impurity which could not be removed by further washing with ether.

When Ph_2Mg and $LiAlH_4$ were allowed to react in a 1:1 ratio in THF, $LiAlPhH_3$ was formed as indicated by the Al–H stretching band at 1680 cm^{-1} characteristic of $LiAlPhH_3$ in THF.[5] When the solvent was removed under vacuum and the product washed with ether, a white solid was isolated that was shown by elemental analysis to be $PhMg_2H_3$. These observations suggest the reaction

$$2Ph_2Mg + 2LiAlH_4 \xrightarrow{THF} PhMg_2H_3 + LiAlH_2Ph_2$$
$$+ LiAlH_3Ph \qquad (9)$$
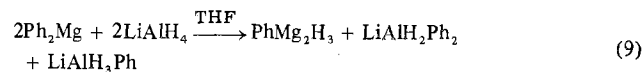
The reactions in THF suggest that if at any stage MgH_2 is formed, it redissolves by reacting with some other species in solution to form a THF-soluble product. In the reaction of Ph_2Mg with $LiAlH_4$ in a 2:1 ratio in THF, one might expect MgH_2 and $LiAlPh_4$ as products as was the case in ether solvent (eq 3). Thus, the absence of any insoluble MgH_2 indicates a possible reaction between MgH_2 and $LiAlPh_4$ in THF. In order to test this hypothesis, MgH_2 was allowed to react with $LiAlPh_4$ in THF with the result that the MgH_2 dissolved. The infrared spectrum of the reaction mixture showed a weak Al–H stretching band at 1655 cm^{-1} (due to $LiAlPh_3H$) and the presence of bands at 460, 420, and 380 cm^{-1} characteristic of Ph–Mg and Ph–Al compounds. Separation of the prepared PhMgH and $LiAlPh_3H$ took place by adding benzene to the THF solution followed by fractional crystallization of the less soluble PhMgH. PhMgH was isolated 90% pure.

We have succeeded in preparing PhMgH in a pure state by the reaction of MgH_2 with Ph_2Mg in THF. The reaction was very rapid as indicated by the rapid dissolution of MgH_2 and the production of a clear solution. When the THF was removed under vacuum, a white solid was formed which analyzed well for PhMgH.

$$Ph_2Mg + MgH_2 \xrightarrow{THF} 2PhMgH \qquad (10)$$

In a similar manner when Ph_2Mg and MgH_2 in a 1:3 molar ratio in THF were allowed to react, a clear solution formed. When the THF was removed under vacuum, a white solid was formed which analyzed well for $PhMg_2H_3$. The product redissolved in THF but was insoluble in ether. Solubility in THF rules out the possibility of the product being a mixture of Ph_2Mg and MgH_2 and the insolubility in ether indicates the absence of Ph_2Mg.

Infrared spectra of the products PhMgH and $PhMg_2H_3$ in THF consisted of the following bands: PhMgH, 3040 (w), 1410 (sh), 1380 (m), 1342 (m), 1280 (m, b), 1110 (m), 970 (m), 790 (s, b), 700 (s), 686 (sh), 425 (m), 370 (m) cm^{-1}; $PhMg_2H_3$, 3040 (w), 1410 (sh), 1380 (m), 1340 (m), 1300 (m), 1270 (m, b), 1108 (m), 970 (m), 760 (s), 700 (s), 684 (sh), 460 (m), 386 (m) cm^{-1}. Bands at 425 and 370 cm^{-1} in PhMgH and at 460 and 386 cm^{-1} in $PhMg_2H_3$ are due to Mg–C in the Ph–Mg compound. Probably the broad band at 1270–1280 cm^{-1} is due to Mg–H stretching in bridging systems[7] by analogy with beryllium analogues.[8] NMR spectra

in THF showed the chemical shift separation between the highest peaks of the two multiplets to be 0.68 ppm in both cases.

Ebullioscopic molecular weight data for PhMgH in THF showed it to be monomer at infinite dilution with the molecular weight increasing sharply with concentration [mol wt of PhMgH (molality vs. association): 0.0284 m, 1.27; 0.0712 m, 1.95; 0.124 m, 3.02; 0.1774 m, 4.10]. However, the molecular weight of $PhMg_2H_3$ could not be determined as it cleaved THF at reflux to give an insoluble product of empirical formula $PhMg_2(O\text{-}n\text{-}Bu)_3$.

The product PhMgH·0.5THF gave x-ray powder diffraction pattern lines at 8.05 (s), 6.60 (m), 5.40 (w), 4.80 (m), 4.60 (w), 4.21 (vs), 3.85 (w), 3.60 (w), 3.40 (w), 3.30 (w), 3.05 (w), 2.80 (w), 2.43 (w), and 2.40 (w) Å. The amorphous solid $PhMg_2H_3$ which contains an indefinite amount of ether did not give any x-ray powder pattern. Vacuum DTA–TGA studies of PhMgH·0.5THF showed loss of THF at 100 °C after which a continued weight loss with an increase in temperature was observed. The maximum weight loss was observed at 300 °C due to benzene evolution. No hydrogen gas evolution was noticed. In the case of the etherate of

$PhMg_2H_3$, the first weight loss was observed at 100–120 °C (due to loss of ether) after which a continued weight loss with an increase in temperature was observed. Hydrogen evolution was observed at 300–360 °C. The trapped gases were ether, benzene, and some ethanol.

The difference between the infrared, NMR, and powder diffraction data for Ph_2Mg and MgH_2 as compared to the products PhMgH and $PhMg_2H_3$ provides additional evidence for the integrity of the latter compounds as true compounds rather than physical mixtures of Ph_2Mg and MgH_2.

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Nature of Alkyl–Hydrogen Exchange Reactions Involving Aluminum and Zinc. 1. Reactions of LiZn(CH₃)₂H and LiZn₂(CH₃)₄H with Aluminum Hydride

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When AlH_3 is allowed to react with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ in tetrahydrofuran in 1:1 molar ratio, $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ are formed as soluble complexes. These two compounds are the first reported triple metal hydride complexes involving lithium, aluminum, and zinc. Their solution composition is inferred from spectroscopic and colligative property studies. The mechanisms of formation of these compounds by the reaction of AlH_3 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ in THF are discussed in light of the spectroscopic results.

Introduction

Recently we have reported the synthesis of several complex metal hydrides of zinc:[1-3] Li_3ZnH_5, Li_2ZnH_4, $LiZnH_3$, Na_2ZnH_4, $NaZnH_3$ [4], $NaZn_2H_5$, K_2ZnH_4, $KZnH_3$, and KZn_2H_5. All but two of these complex metal hydrides were prepared by alkyl–hydrogen exchange reactions between either $LiAlH_4$, $NaAlH_4$, or AlH_3 and an ate complex of zinc. Li_3ZnH_5, Li_2ZnH_4, and $LiZnH_3$ were prepared by reacting the ate complexes $Li_3Zn(CH_3)_5$, $Li_2Zn(CH_3)_4$, and $LiZn(CH_3)_3$ with $LiAlH_4$ in diethyl ether. $NaZnH_3$ was obtained by the reaction of $NaZn(CH_3)_2H$ with $NaAlH_4$ in THF, and $KZnH_3$ was prepared by the analogous reaction of $KZn(CH_3)_2H$ with $LiAlH_4$. The reactions of AlH_3 with $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ in THF produced $NaZn_2H_5$ and KZn_2H_5.

Since our discovery of the use of aluminohydrides in the synthesis of main-group complex metal hydrides, we have been very interested in the nature of exchange reactions between Al–H species and main-group alkyl–metal species. The reaction of $LiZn(CH_3)_2H$ with AlH_3, while it would have been expected to give $LiZnH_3$ in a manner similar to the above reactions, resulted instead in the formation of the THF-soluble complex $LiZn(CH_3)_2AlH_4$. The similar complex $LiZn_2(CH_3)_4AlH_4$ was then prepared by reacting $LiZn_2(CH_3)_4H$ with AlH_3 in THF. We feel that, in addition to providing a possible route to triple metal hydrides, an in depth study of the for-

mation of these complexes could provide insight into the nature of exchange reactions between aluminohydride compounds and ate complexes of zinc.

Experimental Section

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

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solutions were studied in matched 0.10-mm path length NaCl or KBr cells. X-ray powder 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 equipped with viewing apparatus. Intensities were estimated visually. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer equipped with a standard variable-temperature unit. Ebullioscopic molecular association studies were carried out in THF under vacuum (240 mmHg absolute) using the technique developed by Walker and Ashby.[7]

Analytical Work. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[5] Methane in the presence of hydrogen was determined in a previously described tensimeter.[5] Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc in the absence of other metals was determined by EDTA titration.