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Preparation and Characterization of $LiMgH_3$, $LiMg_2H_5$, $LiMgRH_2$, $LiMgR_2H$, and $LiMg_2H_3R_2$ Compounds

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Received August 8, 1977

When $LiAlH_4$ in diethyl ether solution was added to $LiMgPh_3$ in diethyl ether, a mixture of Li_3AlH_6 and MgH_2 in a 1:2 ratio was formed. However when the mode of addition was reversed ($LiMgPh_3$ added to $LiAlH_6$), $LiMgH_3$ was formed instead. It was also possible to prepare $LiMgH_3$ by the reaction of $LiAlH_4$ with ate complexes of the type $LiMgH_2R$ and $LiMgHR_2$ (where R = Me, Et, or Bu). The ate complexes, $LiMgH_nR_{3-n}$ (where $n = 1$ and 2), were prepared as THF-soluble products by the reactions of alkyllithium compounds with alkylmagnesium hydrides or magnesium hydride. When *n*-butyllithium was allowed to react with MgH_2 in a 1:2 molar ratio, $LiMg_2H_5$ formed (as an insoluble solid) and was characterized by elemental analyses, infrared and NMR spectroscopy, DTA–TGA, and x-ray powder diffraction analysis. The ebullioscopic molecular weight studies of $LiMgR_2H$ compounds (where R = Me and Et) showed them to be dimeric in refluxing THF.

Introduction

The preparation of stable complexes of magnesium alkyls and aryls has been the subject of considerable interest during the past few years.[1,2] Although stable complexes of beryllium and zinc, e.g., $NaH{\cdot}Et_2Be$,[3] $NaH{\cdot}2Et_2Zn$,[4,5] $LiH{\cdot}Ph_2Zn$, and $LiH{\cdot}Ph_2Be$,[6] are known, little is known about the complexes of alkali metal hydrides of magnesium. Coates and coworkers[7] reported attempts to prepare $MMgR_2H$ compounds in ether solvents and showed that extensive ether cleavage resulted. Recently, we prepared several hydrido ate complexes of magnesium, e.g., $KMgR_2H$ and KMg_2Ph_4,[8] and showed that the reaction of these complexes with $LiAlH_4$ resulted in the formation of the corresponding complex metal hydrides $KMgH_3$ and KMg_2H_5.[9] However, our earlier attempts to prepare similar complexes of lithium and magnesium by either (1) the reaction of LiH and MgH_2 or (2) the reaction of $LiMgMe_3$ with $LiAlH_4$ failed, and only a mixture of LiH and MgH_2 was obtained. In this paper we wish to report the synthesis of some new stable ate complexes of magnesium and lithium and their subsequent reduction with $LiAlH_4$ as a possible route to the preparation of complex metal hydrides of magnesium.

Experimental Section

Apparatus. All operations were performed either under a nitrogen atmosphere using a nitrogen-filled glovebox equipped with a special recirculating system to remove oxygen and moisture[10] or on the bench using Schlenk-tube techniques.[11] All glassware was flash flamed and flushed with dry nitrogen prior to use.

Infrared spectra were obtained using a Perkin-Elmer 621 grating spectrophotometer equipped with cesium iodide windows. Solid-state spectra were recorded as Nujol mulls. NMR spectra were recorded on a Varian A-60 spectrophotometer using diethyl ether and THF as solvents.

X-ray powder diffraction 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 0.5-mm capillaries and exposed to x rays for 6 h. *d* spacings were read on a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually.

Simultaneous DTA–TGA measurements were carried out on a Mettler Thermoanalyzer II. Samples were loaded in alumina or aluminum crucibles using 60-mesh alumina in the reference crucible. Heating rates between 2 and 8°/min were employed. Samples were loaded onto the thermoanalyzer under an atmosphere of argon, and during the run a continuous flow of argon was maintained. Sample weight was monitored at two sensitivities (10 and 1 mg/in.) so that gross weight losses, e.g., solvent, as well as fine losses, e.g., hydrogen, could be observed.

Analytical Procedures. Gas analyses were performed by hydrolyzing a measured or weighted sample inside a high-vacuum line with ~6 M hydrochloric acid and passing the evolved gas through dry ice–acetone and liquid nitrogen traps. Hydrogen was transferred to a calibrated measuring bulb with a Toepler pump. Butane was collected in a separate measured portion of the vacuum line. Methane and ethane in the presence of hydrogen were determined using a tensimeter. Magnesium was determined by EDTA titration at pH 10 using Eriochrome Black T as an indicator. Aluminum determinations were carried out by adding an excess of standard EDTA and then back-titrating at pH 4 with standard zinc acetate in water–ethanol dithizone as indicator. Lithium was determined by flame photometry. The phenyl group in ate complexes was analyzed in benzene by hydrolyzing the samples and carrying out GLC analysis at 80 °C using an S.E. 30 column. Mesitylene was used as the solvent and hexanol as the internal standard.

Materials. All solvents were distilled immediately prior to use. Tetrahydrofuran (Fisher Certified reagent grade) was distilled under nitrogen over $NaAlH_4$ and diethyl ether over $LiAlH_4$. Triply sublimed magnesium (Dow Chemical Co.) was used for the preparation of the dialkylmagnesium compounds. Dimethyl-, diethyl-, and diphenylmercury were obtained from Orgmet, Inc., and used without further purification. $LiAlH_4$ and $NaAlH_4$ were obtained from Ventron Metal Hydrides Division. Solutions of $LiAlH_4$ in diethyl ether and tetrahydrofuran were prepared by making a slurry of the hydrides in the respective solvents and stirring for 48 h followed by centrifugation and filtration. Both solutions were freshly analyzed for aluminum before use.

Methyllithium in THF was prepared by the reaction of a lithium dispersion with dimethylmercury. Solutions of Me_2Mg, Et_2Mg, and Ph_2Mg in diethyl ether and THF were prepared by reacting the appropriate dialkylmercury compounds with magnesium metal (neat) at room temperature for Me_2Mg, 60–80 °C for Et_2Mg, and 150 °C for Ph_2Mg followed by addition of the appropriate solvents, followed by filtration.

Preparation of Active Magnesium Hydride in THF. When 15.0 mmol of $LiAlH_4$ solution in diethyl ether (30 mL) was added dropwise to a magnetically well-stirred solution of Et_2Mg (15.0 mmol) in diethyl ether (35 mL), an exothermic reaction occurred and an immediate precipitate appeared. This reaction mixture was allowed to stir for ~1 h at room temperature followed by centrifugation of the soluble white solid. The supernatant solution was separated by syringe, and the insoluble white solid was washed with diethyl ether 3–4 times and finally made into a slurry in THF. The analysis of this slurry showed that it contained Mg and H in a ratio of 1.00:2.02. The x-ray powder diffraction pattern of the solid is given in Table I.

Preparation of Alkyl- and Arylmagnesium Hydrides in THF. To a well-stirred slurry of magnesium hydride in THF was added slowly the dialkyl- or diarylmagnesium solution in THF in equimolar proportions. This reaction mixture was stirred at room temperature to give a clear solution within a few minutes. The reactions were monitored by observing the solubilization of the magnesium hydride as the reaction proceeded. These clear, colorless solutions were analyzed (results are given in Table II).

Reactions of Alkylmagnesium Hydrides with Alkyllithium Compounds (Preparation of $LiMgHR_2$). To a well stirred solution of alkylmagnesium hydride in THF was added dropwise an equimolar

0020-1669/78/1317-0322$01.00/0

Table I. X-Ray Powder Diffraction Patterns (*d* Spacings, A)

MgH_2	LiH	Li_3AlH_6 + $2MgH_2$[a]	$LiMgH_3$[b]	$LiMgH_3$[c]	$LiMgH_3$[d]	$LiMgH_3$[e]
7.00 w	2.76 vw	6.70 w	9.2 w	4.30 w	4.32 w	6.35 w
3.90 w	2.66 vvw	4.00 vs	6.80 w	3.11 w	3.10 m	3.10 m
3.19 s	2.50 vvw	3.30 w	5.40 w	2.51 m	2.50 m	2.51 m
2.52 s	2.36 s	2.80 s	5.13 w	2.33 w	2.34 w	2.34 w
2.25 m	2.25 vw	2.55 w	4.35 s	2.05 m	2.05 m	2.05 m
1.68 s	2.04 s	2.32 s	3.90 m	1.66 w	1.65 w	1.66 w
1.51 vw	1.63 vw	2.25 w	3.30 w	1.45 w	1.46 w	1.46 w
1.43 w	1.44 ms	2.00 w	2.80 w			
1.36 w	1.23 m	1.96 w	2.00 w			
1.35 w	1.18 mw	1.80 m				
1.25 vw	1.02 w	1.76 m				
1.15 vw	0.94 w	1.52 m				
	0.91 w	1.50 w				
	0.834 vw	1.47 w				
	0.832 vw	1.41 vw				
	0.786 vw	1.33 vw				
	0.784 vw	1.31 vw				
		1.27 vw				
		1.25 vw				
		1.21 vw				
		1.15 vw				
		1.10 vw				
		1.08 vvw				
		1.03 vvw				

[a] Prepared by the reaction of $LiMgPh_3$ + $LiAlH_4$ in Et_2O. [b] $LiAlH_4$ + $LiMgPh_3$ in Et_2O. [c] $LiMgHMe_2$ + $LiAlH_4$ in THF. [d] $LiMgHBu_2$ + $LiAlH_4$ in THF. [e] $LiMgH_2Me$ + $LiAlH_4$ in THF.

amount of an appropriate alkyllithium compound. The reactions were slightly exothermic producing a clear solution. The reaction mixtures were stirred at room temperature for ~1 h and the resulting solutions analyzed (gas evolution) in order to determine if THF cleavage had occurred. The infrared and NMR spectra of the solutions were recorded (Tables III and IV).

Reaction of Methyllithium with MgH_2 in 1:1 and 2:1 Molar Ratios in THF. (a) MeLi:MgH_2 = 1:1. When CH_3Li (5.5 mmol) in THF (15 mL) was added dropwise to a well stirred slurry of MgH_2 (5.5 mmol) in THF (15 mL) and the reaction mixture stirred at room temperature for ~1 h, a clear solution resulted. The course of the reaction was monitored by observing the disappearance of insoluble MgH_2. The clear solution was analyzed. Anal. Calcd for $LiMgH_2Me$: Li:Mg:H:Me = 1.00:1.00:2.00:1.00. Found: 1.07:1.00:0.94:1.06.

(b) MeLi:MgH_2 = 2:1. Methyllithium (7.0 mmol) was allowed to react with MgH_2 (3.5 mmol) in THF (20 mL) by stirring at room temperature for ~1 h. The clear solution was analyzed. Anal. Calcd for $Li_2MgH_2Me_2$: Li:Mg:H:Me = 2.00:1.00:2.00:2.00. Found: 2.05:1.00:1.91:2.05.

Reaction of $LiMgHR_2$ Compounds and $LiMgH_2Me$ with $LiAlH_4$ in THF. To a clear solution of $LiMgHR_2$ or $LiMgH_2Me$ prepared as above was added $LiAlH_4$ in THF slowly with continued stirring. Immediate precipitation took place. The reaction mixture was stirred at room temperature for ~1 h and the insoluble solid filtered, washed with THF, and analyzed. The results of these reactions are summarized in Table V.

Reaction of $Li_2MgH_2Me_2$ with $LiAlH_4$ in THF. To 4.0 mmol of a MgH_2 slurry in THF (15 mL) was added dropwise 8.0 mmol of CH_3Li in THF (20 mL). The reaction mixture was stirred for ~1 h during which time the MgH_2 dissolved. Four millimoles of $LiAlH_4$ in THF was added to this solution and precipitation occurred immediately. The nature of the precipitate was gelatinous which produced some difficulty in filtration. The filtrate of the reaction showed Al–H stretching at 1675 cm^{-1} (characteristic of $LiAlH_2Me_2$) in the infrared spectrum. The filtrate contained about 15% of the initial magnesium indicating only slight solubility of the magnesium complex. The insoluble solid when dried under reduced pressure resulted in an amorphous solid which did not produce an x-ray diffraction pattern. Anal. Calcd for Li_2MgH_4: Li:Mg:H = 2.00:1.00:4.00. Found: 2.05:1.00:3.85.

Reaction of *n*-Butyllithium with MgH_2 in 1:2 Molar Ratio. To 7.0 mmol of *n*-BuLi in hexane was added 14.0 mmol of a MgH_2 slurry in THF (50 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The insoluble solid was filtered, washed, and dried under vacuum. Filtrate anal. Calcd for $LiMg_2H_3Bu_2$: Li:Mg:H:Bu = 1.00:2.00:3.00:2.00. Found: 1.07:2.00:2.85:2.05. Insoluble solid anal. Calcd for $LiMg_2H_5$: Li:Mg:H = 1.00:2.00:5.00. Found: 1.02:2.00:4.82. The solid did not produce an x-ray diffraction pattern.

Proton NMR Studies of Phenyllithium, Diphenylmagnesium, Lithium Triphenylmagnesiate, and Lithium Hydridophenylaluminate Complexes. Solutions of PhLi (0.65 and 1.38 M), Ph_2Mg (0.8 and 0.73 M) and $LiAlH_nPh_{4-n}$ (n = 1–3) (0.6 M) were prepared in diethyl ether and their proton NMR spectra recorded. In every case two multiplets due to phenyl ring protons (downfield—ortho protons; upfield–meta–para protons) were observed. The chemical shift separation between the highest peaks of the multiplets decreases with increasing electronegativity of the attached metal. The chemical shift separation between the triplet of the ether and the highest peak of the upfield multiplets due to the phenyl protons at the meta–para position were found to be almost the same (5.93 ppm). The chemical shift separations between the highest peaks of the phenyl proton multiplets are listed in Table VI.

Table II. Preparation and Analyses of Alkylmagnesium Hydrides in THF

Soln no.	Amt of reactants, mmol		Reacn time, min	Anal. ratio, Mg:H:alkyl	IR data, ν_{Mg-C}, cm^{-1}	NMR (in THF), ppm[a]
	MgH_2	R_2Mg				
1	10.5	10.5 (Me_2Mg)	15	1.00:0.97:1.02	525, 400	3.53 s
2	8.7	8.7 (Et_2Mg)	25	1.00:0.99:1.04	505, 405	0.58 t 2.52 q
3	5.0	5.0 (Bu_2Mg)	30	1.00:1.02:0.95	460, 400	
4	6.0	6.0 (Ph_2Mg)	15	1.00:0.95:1.02	460, 420	5.17 m[b] 5.88 m[b]

[a] Upfield from THF. Key: s, singlet; t, triplet; q, quartet; m, multiplet. [b] Downfield to upper THF multiplet.

Table III. Preparation and Characterization of $LiMgHR_2$ Compounds in THF

Soln no.	Reactants, mmol		Probable product	Anal. ratio Li:Mg:H:R	NMR (in THF), ppm[a]
	RMgH	RL			
1	MeMgH, 8.0	MeLi, 8.0	$LiMgHMe_2$	1.07:1.00:0.98:1.02	3.58 s
2	EtMgH, 8.5	EtLi, 8.5	$LiMgHEt_2$	1.05:1.00:0.95:1.01	0.58 t 2.53 q
3	BuMgH, 5.0	BuLi, 5.0	$LiMgHBu_2$[b]	1.03:1.00:0.92:1.00	
4	PhMgH, 5.0	PhLi, 5.0	$LiMgHPh_2$[c]	1.05:1.00:0.90:1.03	5.18 m 5.90 m

[a] Upfield (or downfield) from THF multiplet. Key: s, singlet; t, triplet; q, quartet; m, multiplet. [b] Low hydrogen is probably due to some THF cleavage during the reaction course. [c] Product cleaved THF very rapidly to give insoluble white solid after 5 h, with an empirical formula $LiMgPh_2(OBu)$.

Table IV. Infrared Bands of $LiMgHR_2$ and $LiMgH_2Me$ Complexes (cm^{-1})

$LiMgHMe_2$ (THF)	$LiMgHEt_2$	$LiMgH_2Me_2$	$LiMgDMe_2$
2770 m	2765 m	2770 m	2772 m
1575 sh	1472 sh	1600 sh	1570 sh
1470 sh	1406 s	1470 sh	1475 sh
1400 s	1305 s	1405 s	1400 s
1340 sh	1280 s, b	1380 s	1339 sh
1250 b	1125 sh	1250 b	1135 sh
1135 sh	1105 m	1135 sh	1100 m
1100 m	960 m	1105 m	960 m
960 m	700 s, b	960 mb	930 m
900 m	650–70 s, b	745 sh	900 m
700 s, b	510 s, b	690–50 s, b	700 s, b
650 s	460 m	520 s	650 m
520 s, b	415 m	415 m	520 s, b
425 s			460 s, b
400 m			425 s
			440 m

Preparation of $LiMgPh_3$ and Its Reactions with $LiAlH_4$. To 10 mL of a 1.38 M solution of PhLi in ether (13.8 mmol) at −30 °C was added 23 mL of a 0.6 M solution of Ph_2Mg in ether (13.8 mmol) dropwise with continuous stirring. No appreciable change in appearance was observed.

(i) To a part (20 mL; 8.3 mmol) of this solution was added 11.86 mL of a 0.706 M solution of $LiAlH_4$ in ether (8.3 mmol) dropwise at −60 °C with continued stirring. No precipitate was observed initially; however, after 15 min a white crystalline solid precipitated. The solid was filtered and dried producing a viscous pasty product. Found: Li:Mg:Al:H:Ph = 1.96:1.00:1.10:3.04:3.96. Required for $LiAlH_2Ph_2$ + $LiMgHPh_2$: 2.0:1.0:1.0:3.0:4.0.

(ii) To the other part of the original solution (11.0 mL; 4.6 mmol) was added 13.0 mL of a 0.706 M solution (9.2 mmol) of $LiAlH_4$ in diethyl ether at room temperature (reaction was slightly exothermic). The reaction mixture was stirred for 4 h during which time a slight white turbidity was observed. The reaction mixture was stirred for 100 h and the white precipitate was filtered, washed with ether, and dried in vacuo. Found: Li:Mg:Al:H = 3.06:2.02:1.00:10.60. Required for Li_3AlH_6 + $2MgH_2$: 3.0:2.0:1.0:10.0. X-ray powder pattern (Å): 4.00 (vs), 3.30 (w), 2.80 (s), 2.55 (w), 2.32 (s), 2.25 (s), 2.00 (s), 1.96 (w), 1.80 (m), 1.76 (m), 1.52 (m), 1.50 (m), 1.47 (w), 1.41 (vs), 1.33 (vw), 1.27 (vw), 1.25 (vs), 1.21 (vw), 1.15 (vw), 1.10 (vw), 1.08 (vw), 1.04 (vw), 1.03 (vw).

Preparation of $LiMgH_3$. To 20 mL of a 0.65 M solution of phenyllithium (16.25 mmol) in diethyl ether was added 22.2 mL of a 0.73 M solution (16.21 mmol) of Ph_2Mg in diethyl ether at room temperature.

(i) A part of the solution (15 mL, 5.36 mmol) was added to 12.9 mL of a 0.65 M $LiAlH_4$ (5.36 mmol) in diethyl ether dropwise with continued stirring to give a white insoluble solid. This reaction mixture was stirred for 6 h and the white precipitate was filtered, washed with ether, and dried under vacuum. Found: Li:Mg:H = 1.10:1.00:3.16. Required for $LiMgH_3$: 1.0:1.0:1.0. X-ray powder pattern (Å): 0.2 (vw), 6.8 (vw), 5.13 (w), 4.35 (m) 3.9 (w), 3.30 (w), 2.80 (w), 2.0 (w).

(ii) Fifteen milliliters (5.36 mmol) of the previously prepared $LiMgPh_3$ solution was added dropwise to 37 mL of a 0.415 M solution of $LiAlH_4$ (15.40 mmol) in diethyl ether with continued stirring to give a white solid. This reaction mixture was stirred for 6 h, filtered, washed with ether, and dried. Found: Li:Mg:H = 1.07:1.00:3.26. Required for $LiMgH_3$: 1.00:1.00:1.00.

Results and Discussion

$$LiH + MgH_2 \xleftarrow{LiAlH_4} MeLi + Me_2Mg \rightleftharpoons LiMgMe_3 \xrightarrow{LiAlH_4} LiMgH_3 \qquad (1)$$

Since we found that $LiMgMe_3$ exists in diethyl ether as an equilibrium mixture of MeLi and Me_2Mg (eq 1), it was not surprising that its reaction with $LiAlH_4$ produced a mixture of LiH, MgH_2, and $LiMgH_3$. During our present studies, it was decided to prepare a more stable complex than $LiMgMe_3$ to react with $LiAlH_4$ in the hope of preparing $LiMgH_3$ uncontaminated with LiH and MgH_2. In this connection, $LiMgPh_3$ was prepared in diethyl ether solution by the reaction of phenyllithium with diphenylmagnesium (eq 2).

$$PhLi + Ph_2Mg \xrightarrow{Et_2O} LiMgPh_3 \qquad (2)$$

Brown reported $LiMgPh_3$ to be a stable complex in solution[13] and that it could be isolated as a crystalline solid. The NMR spectrum of the resulting solution gave two multiplets due to ortho and meta–para protons of the phenyl group. The internal chemical separation, δ_{int}, between the two highest peaks of these multiplets was found to be 0.93 ppm (δ_{int}(for PhLi) = 0.99 ppm and δ_{int}(for Ph_2Mg) = 0.68 ppm). When $LiMgPh_3$ (prepared in this manner) in diethyl ether was allowed to react with $LiAlH_4$ at −78 °C, no precipitation occurred. Even when the reaction mixture was allowed to warm to room temperature, no precipitation took place even after stirring for 1 h. It is worthwhile to mention here that when phenyllithium[14] or diphenylmagnesium[15] is allowed to react with $LiAlH_4$ under similar conditions, an immediate precipitation of LiH and MgH_2 occurs (eq 3 and 4).

$$2PhLi + LiAlH_4 \rightarrow 2LiH + LiAlH_2Ph_2 \qquad (3)$$

$$Ph_2Mg + LiAlH_4 \rightarrow MgH_2 + LiAlH_2Ph_2 \qquad (4)$$

Furthermore, the NMR spectrum of this solution showed that δ_{int} betweeen the ortho and meta–para proton multiplets is 0.73 ppm. These observations indicated that no dissociation of the complex $LiMgPh_3$ to PhLi and Ph_2Mg takes place. When the above solution (that had been allowed to warm to room temperature) was cooled to −78 °C, a crystalline white solid appeared (PhLi, Ph_2Mg, and $LiMgPh_3$ have been shown not to crystallize from diethyl ether at −78 °C). The infrared spectrum of the solid dissolved in diethyl ether at room temperature showed an Al–H stretching band at 1710 cm^{-1} (characteristic of $LiAlH_2Ph_2$[16]) and bands at 460 and 425 cm^{-1} due to Al–Ph and Mg–Ph groups. This information in addition to elemental analysis indicates that the solid product is a mixture of $LiMgH_2Ph$ and $LiAlH_2Ph_2$ (eq 5).

$$LiMgPh_3 + LiAlH_4 \xrightarrow{Et_2O} LiMgH_2Ph + LiAlH_2Ph_2 \qquad (5)$$

When the reaction mixture of $LiMgPh_3$ with $LiAlH_4$ in 1:2 molar ratio was stirred at room temperature for 100 h, a white solid formed during the course of the reaction (eq 6).

$$2LiMgPh_3 + 4LiAlH_4 \rightarrow Li_3AlH_6 + 2MgH_2 + 3LiAlH_2Ph_2 \qquad (6)$$

Analysis of this solid corresponded to a mixture of Li_3AlH_6 and $2MgH_2$, and x-ray powder diffraction pattern gave lines due to Li_3AlH_6. The filtrate of this reaction mixture showed a band in the IR spectrum at 1710 cm^{-1} characteristic of the Al–H stretching band of $LiAlH_2Ph_2$.

On the other hand, when the mode of addition of the above reaction was reversed, i.e., when a solution of $LiMgPh_3$ in

Table V. Reactions of $LiMgHR_2$ and $LiMgH_2Me$ with $LiAlH_4$ in THF

Soln no.	Amt of reactants, mmol		Reacn time, h	Filtrate anal. ratio, Li:Mg:Al:H:R	Filtrate IR, ν_{Al-H}, cm^{-1}	Insol solid anal. ratio, Li:Mg:H:Al
	$LiMgH_nR_{3-n}$	$LiAlH_4$				
1	5.0 ($LiMgHMe_2$)	5.0	2	1.10:0.07:1.00:2.03:2.05	1675	1.07:1.00:3.05:0.05
2	4.5 ($LiMgHEt_2$)	4.5	1	1.09:0.08:1.00:2.07:2.01	1670	1.05:1.00:3.01:0.07
3	4.5 ($LiMgHBu_2$)	4.5	$^1/_2$	1.10:0.03:1.00:1.99:2.00	1668–1670	1.08:1.00:2.90:0.08
4	6.0 ($LiMgH_2Me$)	3.0	1	1.05:0.07:1.00:2.01:1.97	1675	1.07:1.00:2.92:0.05

Table VI. Chemical Shift Separation (ppm) between Ortho and Meta-Para Proton Multiplets

Temp °C	PhLi	Ph_2-Mg	LiMg-Ph_3	LiAl-HPh_2	LiAl-H_2Ph_2	LiAl-H_3Ph	LiMg-HPh_2 + LiAl-H_2Ph_2
−15	1.06	0.70	0.94		0.60		
−65	1.17		0.95				
+34	0.99	0.68	0.93	0.61	0.60	0.59	0.68

diethyl ether was added dropwise to a diethyl ether solution of $LiAlH_4$ at room temperature, a white precipitate appeared immediately (eq 7). The solid was analyzed and found to be

$$LiMgPh_3 + LiAlH_4 \rightarrow LiMgH_3 + LiAlHPh_3 \quad (7)$$

$LiMgH_3$ which gave a unique x-ray powder pattern (Table I) different from that of a mixture of LiH and MgH_2. The filtrate of this reaction was characterized to be $LiAlHPh_3$ by elemental analysis and its IR spectrum (ν_{Al-H} 1680 cm^{-1}).

Recently we have been able to prepare a highly reactive form of MgH_2 by the reaction of diethylmagnesium with $LiAlH_4$ in diethyl ether and have been able to demonstrate that this active form of MgH_2 reacts with R_2Mg compounds in equimolar quantities to produce THF-soluble alkylmagnesium hydrides.[17]

$$Et_2Mg + LiAlH_4 \xrightarrow{Et_2O} MgH_2 + LiAlH_2Et_2 \quad (8)$$

$$MgH_2 + R_2Mg \xrightarrow{THF} 2RMgH \quad (9)$$

Reaction of these THF-soluble alkylmagnesium hydrides with alkyllithium compounds produces a clear solution of empirical formula $LiMgR_2H$ (eq 10). These products

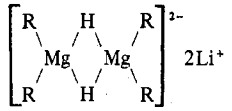
$$RMgH + RLi \xrightarrow{THF} LiMgR_2H \quad (R = Me, Et, n\text{-}Bu, Ph) \quad (10)$$

($LiMgR_2H$, where R = Me, Et, or Bu) have been found to be stable (no THF cleavage) after 1 day. Unfortunately the phenyl derivative ($LiMgHPh_2$) was found to cleave THF rapidly. The infrared spectrum of the product $LiMgHMe_2$ exhibited an absorption band at 1260 cm^{-1} due to Mg–H stretching (bridging MgH_2Mg system) which shifted to 930 cm^{-1} in the deuterio analogue $LiMgMe_2D$ prepared by the reaction of MeLi with MeMgD.[17] The ^1H NMR spectrum of $LiMgHMe_2$ in THF gave one singlet at 3.57 ppm upfield from THF (almost at the position of Me_2Mg) at room temperature and at −80 °C, 3.58 ppm upfield from THF. The ^1H NMR spectrum of $LiMgEt_2H$ showed a triplet almost at the position of Et_2Mg (centered at 0.58 ppm upfield from THF) and a quartet at 2.53 ppm. According to the ^1H NMR spectrum at room temperature, it seems that these products are mixtures of alkyllithium compounds and alkylmagnesium hydrides since the spectra exhibit signals at the position expected for alkylmagnesium hydrides or dialkylmagnesium compounds. However, at low temperature the ^1H NMR spectrum is unchanged indicating the absence of any free alkyllithium compound. The physical nature of the products also suggests that they are unique compounds rather than physical mixtures of starting materials; e.g., $LiMgHMe_2$, when dried in vacuo, appeared to be a highly viscous liquid whereas CH_3MgH and CH_3Li (starting materials) are solids. Molecular weight studies on $LiMgHMe_2$ and $LiMgHEt_2$, determined ebullioscopically in refluxing THF under reduced pressure (260 mm Hg) showed them to be strictly dimeric over a wide concentration range (Table VII). These molecular weight data further suggest ate complex formation since starting materials such as MeMgH and EtMgH show considerably higher molecular association with an increase in concentration.[18] On the basis of the infrared and NMR spectra and also molecular weight data, the following dimeric structure is suggested. The bridging-hydrogen structure is similar to that of $NaZn(CH_3)_2H$ and $NaZn(Ph_2)H$[19] reported earlier by Kubas and Shriver.

Table VII. Molecular Weight Data of $LiMgHR_2$ (R = Me, Et) Concentration vs. Molecular Complexity

	Concn (*m*) vs. molecular assocn (*i*)[a]			
Compd	*m*	*i*	*m*	*i*
$LiMgHMe_2$	0.055	1.92	0.144	2.01
	0.089	1.96	0.179	2.05
	0.107	1.94		
$LiMgHEt_2$	0.049	1.96	0.141	2.05
	0.075	0.97	0.170	2.00
	0.102	1.92		

[a] The calculations were made using the equation $i = (W_2M_1/W_1M_2)(1/e^{\Delta T_B M_1/1000k_B})^{-1}$. The additional terms include M_2, the formula weight of the solute (62.3 g for $LiMgHEt_2$ and 90.3 g for $LiMgHEt_2$); M_1, the molecular weight of the solvent, THF, and k_B, the molal boiling point elevation constant (1.98 for THF at an internal nitrogen pressure of 260 mm).



The reactions of $LiMgMe_2H$, $LiMgEt_2H$, and $LiMgBu_2H$ with $LiAlH_4$ in THF have been studied. The reactions were carried out according to eq 11, at room temperature; a gelatinous precipitate was observed in all cases. The x-ray powder diffraction patterns of the reaction products gave lines which were not very sharp; however, the elemental analyses correspond to the empirical formula $LiMgH_3$. The filtrate of these reaction mixtures showed Al–H stretching in the infrared spectra that corresponds to the compounds $LiAlH_2Me_2$ and $LiAlH_2Bu_2$.

$$LiMgHR_2 + LiAlH_4 \rightarrow LiMgH_3 + LiAlH_2R_2 \quad (R = Me, Bu) \quad (11)$$

Reaction of CH_3Li with MgH_2 in a 1:1 molar ratio in THF resulted in a clear solution after 2 h of stirring at room temperature (eq 12). Since MgH_2 is very insoluble in THF, its dissolution in THF in the presence of CH_3Li indicates reaction of the MgH_2 and formation of a soluble product. Elemental analysis of the resulting solution corresponded to the empirical formula $LiMgH_2Me$. This solution showed a broad infrared band at 1250 cm^{-1} probably due to bridging Mg–H stretching, and the ^1H NMR showed a singlet at 3.58 ppm upfield from THF.

$$MeLi + MgH_2 \rightarrow LiMgH_2Me \quad (12)$$

The compound $LiMgH_2Me$ cleaves THF at room temperature slowly. Reaction of $LiMgH_2Me$ solution in THF with $LiAlH_4$ produced a white gelatinous precipitate analyzed to be $LiMgH_3$.

Interestingly, the reaction of BuLi with MgH_2 produced an insoluble solid. The filtrate of this reaction corresponded to the empirical formula $LiMg_2H_3Bu_2$. The insoluble solid contained about 50% of the initial magnesium. On the basis of the elemental analysis the reaction route of (eq 13) can be proposed which leads to the formation of $LiMg_2H_5$ in 50% yield. The white insoluble solid $LiMg_2H_5$ did not give an x-ray powder pattern; however, vacuum DTA–TGA studies of this compound show that it first decomposed at 300 °C to give LiH and MgH_2 followed by the decomposition of MgH_2. The lithium hydride formed in the decomposition decomposes above

$$BuLi + 2MgH_2 \rightarrow [LiMg_2BuH_4] \rightarrow {}^1/{}_2LiMg_2H_5 + {}^1/{}_2LiMg_2H_3Bu_2 \quad (13)$$

450 °C. Extensive THF cleavage was observed in the temperature range 90–220 °C.

When CH_3Li was allowed to react with MgH_2 in a 2:1 ratio in THF, a clear solution resulted. Elemental analysis indicated the empirical formula $Li_2MgH_2Me_2$. The ^1H NMR spectrum of this solution at room temperature exhibited one singlet at 3.62 ppm upfield from the THF multiplet. Only one singlet due to methyl protons was found, even at −80 °C. Reaction of this solution with $LiAlH_4$ (eq 14) produced a highly gelatinous precipitate which was hard to filter. This precipitate when dried under vacuum gave a white solid whose elemental analysis corresponded to Li_2MgH_4. This compound did not exhibit an x-ray powder pattern because of its amorphous nature. The filtrate of the reaction mixture showed Al–H stretching at 1675 cm^{-1} characteristic of $LiAlH_2Me_2$ in THF.

$$Li_2MgH_2Me_2 + LiAlH_4 \rightarrow Li_2MgH_4 + LiAlH_2Me_2 \qquad (14)$$

Acknowledgment. We are indebted to the Office of Naval Research (Contract No. N00014-A-0005AD) for support of this work.

Registry No. $LiAlH_4$, 16853-85-3; MgH_2, 7693-27-8; Me_2Mg, 2999-74-8; Et_2Mg, 557-18-6; Bu_2Mg, 1191-47-5; Ph_2Mg, 555-54-4; MeMgH, 63533-51-7; EtMgH, 63533-53-9; BuMgH, 65015-67-0; PhMgH, 62086-01-5; MeLi, 917-54-4; EtLi, 811-49-4; BuLi, 109-72-8; PhLi, 591-51-5; $LiMgHMe_2$, 65015-95-4; $LiMgHEt_2$, 65015-94-3; $LiMgHBu_2$, 65015-93-2; $LiMgHPh_2$, 65015-92-1; $Li_2MgH_2Me_2$, 65015-91-0; Li_2MgH_4, 65015-90-9; $LiMg_2H_3Bu_2$, 65101-99-7; $LiMg_2H_5$, 65104-00-9; $LiMgPh_3$, 65015-89-6; Li_3AlH_6, 16941-14-3; $LiMgH_3$, 65015-88-5; $LiMgH_2Ph$, 65015-87-4; $LiAlH_2Ph_2$, 27662-04-0; $LiAlHPh_3$, 62126-58-3; $LiMgH_2Me$, 65015-86-3; $LiMgDMe_2$, 65015-85-2; LiH, 7580-67-8; $LiAlH_2Me_2$, 19528-78-0; $LiAlH_2Et_2$, 25897-84-1; $LiAlH_2Bu_2$, 65015-84-1; $LiAlH_3Ph$, 65058-51-7.

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Electron Transfer. 30. Chromium(III)-Bound Pyrazine Radicals[1]

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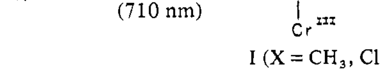
Received June 1, 1977

The pyrazine greens are strongly absorbing species (λ_{max} 645–650 nm, $\epsilon < 10^3$) formed by the action of Cr^{2+} on substituted pyrazines in aqueous acidic solution. The reactions of one of the most stable of these, derived from pyrazinecarboxamide, with a number of $(NH_3)_5Co^{III}$ complexes yield Co^{2+}, together with the same Cr(III) product as is formed in reduction by Cr^{2+} itself, but rates are several orders of magnitude lower. Such reactions are further inhibited by excess amide. Kinetic data support sequence 2, in which the green radical cation, formulated as $Cr^{III}Pz\cdot$, dissociates (k_1) to the parent pyrazine and Cr^{2+}, which, in turn, may react with Co(III) (k_2) or return to the radical cation (k_{-1}). Values of k_1/k_{-1} obtained from measurements on different Co(III) systems are in agreement, and k_2 values for the reactions of fluoro- and bromopentaamminecobalt(III) complexes with Cr^{2+} are consistent with literature rates. The calculated rate of dissociation of the green ion to Cr^{2+} is 10^{10}–10^{11} times lower than the accepted range for substitution reactions at Cr(II) centers but several orders of magnitude above the heterolysis rates of the usual Cr(III) complexes in water, suggesting that the rate of dissociation is determined by the rate of internal electron transfer within the radical cation. The equilibrium constant for the conversion of $Cr^{III}Pz\cdot$ to Cr^{2+} is found to be one-tenth of that estimated from the reduction potentials of Cr^{3+} and pyrazinecarboxamide, indicating that $Cr^{III}Pz\cdot$ is 10 times as stable toward aquation as is the pyrazinecarboxamide complex of Cr(II).

In 1965 it was reported[2] that the reaction of Cr^{2+} with pyrazine derivatives very rapidly yielded intensely absorbing green species displaying spectra quite unlike those of hydrated or partially hydrated Cr(II) or Cr(III). Because these "pyrazine greens" are not formed by the action of other reducing agents (e.g., Eu^{2+}, V^{2+}, U^{3+}, or zinc amalgam) and because they react readily with such one-electron oxidants as $(NH_3)_5CoCl^{2+}$, the proposal was made that they are chromium(III)-bound radicals (I), each featuring a reduced pyrazine ring, a suggestion which has been strengthened by the finding[3] that several of these materials exhibit ESR signals that can reasonably be attributed neither to Cr(II) nor to Cr(III). These ions, which have been prepared from a variety of substituted pyrazines and from fused-ring pyrazines (quinoxaline and phenazine), exhibit a considerable range of stabilities in aqueous solution. Some decompose in a few seconds, whereas others can be kept for almost 1 h under favorable conditions and can thus be studied using conventional mixing techniques.



I (X = CH_3, Cl, COOH, $CONH_2$)
ϵ_{max} >10^3
(648 nm)

Since these bound radicals are presumed to be structurally similar to a number of substituted-pyridine radicals which have been implicated[4] as the active intermediates in a series of reductions of bound cobalt(III) with Cr^{2+} and Eu^{2+} as catalyzed externally by certain 4-substituted pyridines, it might be anticipated that they would be much more facile reductants than these hydrated metal centers. The reverse is the case. Their oxidations by the most reactive cobalt(III) complexes

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