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Project No: G-33-687 (Follow-on to G-33-605)

Principal Investigator: Dr. E. C. Ashby

Sponsor: Office of Naval Research, Arlington, Va. 22217

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Defense Priority Rating: DO-C9 under DMS Reg. 1

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Date: August 24, 1978

Project Title: Complex Metal Hydrides, High Energy Fuel Components for Solid Propellant Rocket Motors

Project No: G-33-687

Project Director: Dr. E. C. Ashby

Sponsor: Office of Naval Research; Arlington, VA 22217

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- ☒ Final Report of Inventions
- ☒ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other \_\_\_\_\_

Assigned to: Chemistry (School/Laboratory)

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Annual Report  
to the  
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"Complex Metal Hydrides. High Energy Fuel Components  
for Solid Propellant Rocket Motors."

E. C. Ashby, Principal Investigator  
Georgia Institute of Technology, Atlanta, Georgia 30332

January 1, 1975 - December 31, 1975

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Papers Published Since the Last Report

- (1) E. C. Ashby, John J. Watkins and H. S. Prasad, "Existence of Complexes of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in Ether Solvents and in the Solid State", Inorg. Chem., 14, 583 (1975).
- (2) E. C. Ashby and H. S. Prasad, "Reactions of Aluminum Hydride with Group 1b, 2a, and 2b Metal Halides", Inorg. Chem., 14, 1608 (1975).
- (3) E. C. Ashby, Robert Arnott and Suresh Srivastava, "Reactions of Alkali Metal Hydrides with Magnesium Alkyls. Preparation of  $\text{MMgR}_2\text{H}$  and  $\text{MMg}_2\text{R}_4\text{H}$  Compounds<sup>1,2</sup>", Inorg. Chem., 14, 2422 (1975).
- (4) E. C. Ashby and H. S. Prasad, "Alkali Metal "ate" Complexes and Complex Metal Hydrides of Beryllium," Inorg. Chem., 14, 2869 (1975).

## CONCERNING THE DIRECT SYNTHESIS OF POLYIMINOALANES

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### Abstract

Our study of the direct reaction of aluminum, hydrogen and primary amines to demonstrate the feasibility of preparing polyiminoalanes has been completed. With aniline the reaction proceeds beyond the polyiminoalane stage producing a material containing a N:Al ratio greater than one aluminum-nitrogen whereas tert-butylamine and isopropyl amine in THF yield polyiminoalanes. Two different schemes have been proposed for the formation of polyiminoalanes.

### Introduction

Polyiminoalanes are reported to be excellent co-catalysts for polymerizing ethylene and isoprene,<sup>1</sup> however, these compounds are either inconvenient or expensive to prepare by known procedures.<sup>2-5</sup> Recently, we have demonstrated that aminoalanes can be prepared by a convenient and economical synthesis involving direct reaction of aluminum, hydrogen and secondary amines.<sup>6</sup> These results suggested to us that polyiminoalanes could be prepared by a similar route and preliminary results of our initial investigation were reported earlier.<sup>7,8</sup> Since then we have studied the reaction of aluminum, hydrogen and primary amines in detail as a route to iminoalanes. More recently, S. Cucinella, et. al.<sup>9,10</sup> have studied the synthesis and structure of poly(N-alkyliminoalanes) in detail while this work was in progress. They reported the direct synthesis of poly(N-alkylaminoalanes) in-

volving reaction of aluminum metal with primary amines in hydrocarbon solvents under hydrogen pressure.

In this report, we have summarized our findings and feel that although the presence of a catalytic amount of  $\text{MAlH}_4$  facilitates the formation of polyiminoalanes considerably, polyiminoalanes can be prepared by the direct reaction of aluminum and hydrogen with primary amines without a catalyst.

### Experimental

Manipulation of air-sensitive materials was accomplished by employing a dry box equipped with a recirculating atmosphere for removal of oxygen and moisture.<sup>12</sup>

Benzene and tetrahydrofuran were purchased from Fisher Chemical Co. (Certified ACS grade) and distilled from  $\text{NaAlH}_4$  prior to use. Aniline, isopropyl-, *n*-butyl-, and *t*-butylamine were purchased from Eastman Chemical Co. and distilled under nitrogen from anhydrous KOH on to active molecular sieve, Type 4-A, prior to use. Atomized aluminum powder (MD202) was obtained from the Alcan Aluminum Corp. Aluminum was "activated" prior to use by a method described earlier.<sup>13</sup> Ultra pure hydrogen was obtained from the Matheson Corp. and used without further purification.

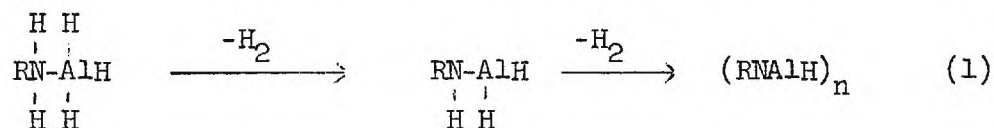
Analyses. Iminoalanes are readily hydrolyzed by dilute acids. Analyses were performed by hydrolyzing an aliquot sample of the reaction solution with 5N HCl and determination of the hydrogen content by gas evolution analysis. Aluminum in the same sample was determined by EDTA titration. Amines were determined by potentiometric titration of the solution obtained on hydrolysis of an aliquot sample

with glacial acetic acid in the same solvent. In order to distinguish between the amine in the form of the iminoalane and unreacted amine, solvent and free amine were removed from the reaction mixture prior to hydrolysis on the vacuum line and condensed into a trap at  $-196^{\circ}$ , containing glacial acetic acid. Molecular weight measurements were conducted cryoscopically in benzene or ebullioscopically in THF.<sup>14</sup>

General Procedure for Direct Synthesis of Polyiminoalanes. Hydrogenation reactions were performed using a 300 ml magne drive autoclave (Autoclave Engineers, Inc.). The chamber was charged in the dry box with a weighed amount of activated aluminum<sup>13</sup>, 150 ml solvent and 5.0 ml of primary amine. The reactants were then heated under a hydrogen pressure of 3000 to 4000 psi for a predetermined period at  $140^{\circ}$ . After sufficient cooling, the chamber was vented and soluble products were filtered from excess unreacted aluminum in the dry box. The volume of the filtrate was measured and aliquot samples were analyzed. Reaction conditions and the results from several experiments are reported in Table I.

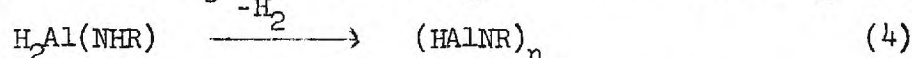
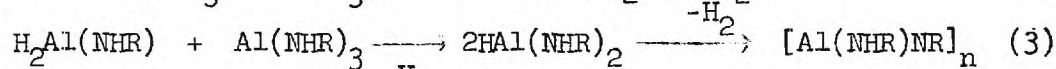
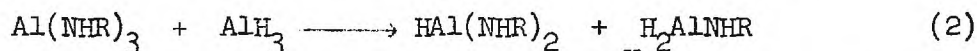
### Results and Discussion

The reaction between a primary amine, aluminum and hydrogen presumably occurs by initial formation of an unstable amine-alane followed by loss of hydrogen to form the iminoalane.<sup>5</sup> A similar scheme was suggested earlier for the direct synthesis of bis-dialkylaminoalanes.<sup>6</sup>

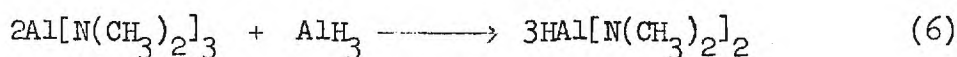
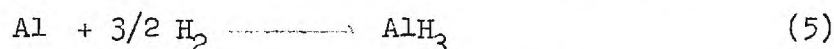


An alternative mechanism proposes first the formation of a tris-

aminoalane, which then redistributes with alane, for example:



This proposal is reasonable on the basis that the initial product  $\text{RHN}_2 \cdot \text{AlH}_3$  is formed in the presence of excess  $\text{RNH}_2$  and is further supported by a comparison of a similar reaction between aluminum, hydrogen and tris-dimethylaminoalane, which led to bis-dimethylaminoalane.<sup>6</sup> We cannot distinguish between these two mechanisms and in-



deed it is possible that both are operating simultaneously.

Reaction Between Aluminum, Hydrogen and a Primary Amine with Two  $\alpha$ -Hydrogen Atoms. In the first experiments with n-butylamine, aluminum and hydrogen in benzene, the reaction products were monitored by determining hydrolyzable hydrogen and aluminum in solution, in an attempt to find the most favorable conditions for formation of the iminoalane product. We also checked for the possibility of promoting the reaction with the aid of triethylamine as a catalyst. In all instances the aluminum:hydrogen ratio was low, indicating appreciable amounts of aminoiminoalane formation  $[\text{Al}(\text{NHR})\text{NR}]$  or tris-aminoalane formation  $[\text{Al}(\text{NR})_3]$ . On the other hand, when the reaction was conducted in THF, the product was insoluble in THF, benzene, hexane and ether and therefore could not be separated from the unreacted aluminum by filtration. Attempted sublimation ( $p < 10\mu$ ,  $T$  to  $210^\circ$ ) produced only the unreacted n-butylamine. However, hydrolysis of the mixture of

reaction products with glacial acetic acid revealed a ratio  $H:Al:C_4H_9NH_2$  of 0.66:1.00:1.60. It is thus clear that the best results in forming the iminoalanes are obtained in THF, however, the product is in admixture with aminoiminoalanes or tris-aminoalane.

Reaction Between Aluminum, Hydrogen and Primary Amines Without  $\alpha$ -Hydrogen Atoms. (a) Aniline. A similar reaction in benzene employing aniline as the 1° amine produced a benzene soluble product (yield, 58% based on aniline). When the benzene solvent was removed under vacuum a yellow solid was isolated. Analysis showed the product contained aluminum, nitrogen and hydrolyzable hydrogen in 1.00:1.32:0.25 ratio. Apparently the reaction involving aniline can proceed beyond the polyiminoalanes stage to produce a material containing a greater number of aluminum-nitrogen bonds.

(b) tert-Butylamine. When the reaction of t-butylamine with aluminum and hydrogen was carried out in benzene, the resulting product in solution had the approximate formula  $H_{0.44}Al_{1.0}NBu^t_{1.69}$ . The infrared spectrum of this compound showed bands in the Al-H stretching region at  $1850\text{ cm}^{-1}$ , with a shoulder at  $1825\text{ cm}^{-1}$ . Molecular weight measurements in benzene gave a molecular weight of 1370.

When the reaction was carried out in THF, the results were much better in terms of forming the pure iminoalanes ( $HALNBu^t$ ). The hydrogen content of the product increased as the ratio of aluminum:amine increased. The best product exhibited an aluminum:hydrogen ratio of 1.0:0.8, obtained from an aluminum:amine reactant ratio of 10:1.

The product isolated by THF removal could be sublimed at  $120^\circ$  at  $10\mu$ . The infrared spectrum of the sublimate in nujol showed bands at  $1860\text{ cm}^{-1}$  with a shoulder at 1825. The white crystalline product

exhibited an aluminum:hydrogen:amine ratio of 1.0:0.8:1.3. When the sublimed solid was redissolved in THF it showed a band at  $1855\text{ cm}^{-1}$ . The molecular weight of this sublimed material in benzene showed a value of 370. NMR of the sublimed material showed no THF present.

Reaction Between Aluminum, Hydrogen and Primary Amine with one  $\alpha$ -Hydrogen. When the reduction of isopropylamine, aluminum and hydrogen was carried out in benzene, a soluble product of low Al:H ratio (1.0:0.25) was obtained even using a 9 fold excess of aluminum in the reaction. When the benzene was removed an oil was isolated. The infrared spectrum of the neat oil showed an Al-H band at  $1860\text{ cm}^{-1}$  and a band at  $3400\text{ cm}^{-1}$  indicating the presence of N-H groups. On the other hand, when the reaction was performed in THF, isopropyliminoalane was the only product formed and in quantitative yield. A molecular association study in THF gave an  $i$  value of 2.6. After removal of excess solvent, the solid was sublimed producing a white crystalline solid ( $\sim 10\mu$ ,  $130-170^\circ$ ).

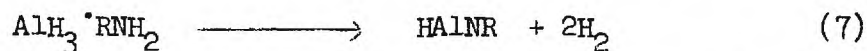
Anal. Calcd. for  $\text{HAlNC}_3\text{H}_7 \cdot \text{C}_4\text{H}_8\text{O}$ : active H, 0.64; N, 8.91; Al, 17.16. Found: active H, 0.61; N, 7.92; Al, 17.46. An X-ray powder pattern exhibited the following lines: 8.6 br. vs.; 7.8 br. vs.; 6.2 w; 5.9 w; 5.2 vw; 5.1 vw; 4.85 vw; 4.65 w; 4.4 w; 3.22 vw; 2.83 vw. Mass spectral data show clearly the presence of an isopropyl group.

In a separate experiment, isopropyl amine, aluminum and hydrogen were allowed to react in THF. The aluminum to amine ratio was 10:1 in this experiment whereas it was 7:1 in the above case. The product was sublimed at  $130-170^\circ$  at  $10\mu$ . The molecular weight of this compound in benzene gave a value of 561. The sublimate was a waxy solid which showed infrared bands at 1855, 1825 sh, 1380, 1335, 1285, 1160,

1120, 1005, 970, 955, 835, 745, and 685 (broad)  $\text{cm}^{-1}$ . The crystalline compound above (Al:N - 7:1) gave bands at 1848, 1150, 1110, 965, 955, 830, 750, 675  $\text{cm}^{-1}$ . The NMR of the waxy sublimate in benzene shows no  $\alpha$  methylene protons due to THF whereas the product from the Al:N - 7:1 ratio experiment sublimed as the THF etherate.

All of the polyiminoalanes exhibited strong aluminum-hydrogen stretching absorptions between 1835 and 1860  $\text{cm}^{-1}$ , which compare favorably with Al-H values reported for similar polyiminoalanes.<sup>4,5</sup>

It is interesting to note the effects on the products formed by varying the aluminum:amine ratio of the reactants and by changing solvent from benzene to THF. In general, increasing the aluminum:amine ratio causes the hydrogen:aluminum ratio of the product to decrease. In THF, products of higher hydrogen:aluminum ratio are isolated in similar reactions in benzene. For example, isopropyl amine in THF gave products with hydrogen:aluminum ratios of 1.0, whereas in benzene the ratio of hydrogen:aluminum was approximately 0.25. We would offer the following explanation. Aluminum hydride cannot be formed from the high pressure reaction of  $\text{H}_2$  and Al except in the presence of a strongly coordinating ligand [e.g.,  $(\text{CH}_3)_2\text{NH}$ ]. Therefore, in benzene the  $\text{AlH}_3$  is formed using  $\text{RNH}_2$  as the coordinating ligand. This would then react according to eq. 7. The  $\text{HALNR}$



would then react with more 1° amine in the system to form a product of low H:Al ratio. When all the 1° amine is consumed the production of  $\text{AlH}_3$  then stops resulting in the formation of a product of low H:Al ratio.

In THF, however, even when all the 1° amine has reacted,  $\text{AlH}_3$  can

still be produced using THF as the coordinating ligand. The  $\text{AlH}_3$  produced would then redistribute with the aminoalane in solution to yield compounds of higher hydrogen:aluminum ratio, such as the iminoalane ( $\text{HAlNR}$ ).

Another point which needs to be made is the effect of solvent on the degree of association of the compounds formed. In benzene, compounds of high molecular weight are formed compared to THF. This is in keeping with the greater solvating power of THF which would prevent the formation of higher molecular weight polymers by solvating the aluminum.

In conclusion, we have succeeded in preparing polyiminoalanes, by a methods heretofore unknown. This method represents such a convenient and economic route to iminoalanes that further investigation of new uses of iminoalanes should be encouraged.

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Table 1. Results of Reactions of Primary Amines with Aluminum and Hydrogen.

Amine	Ratio (Al:Amine)	Solvent	Analysis			Amine	Comments
			H	:	Al		
$C_6H_5NH_2$	1.0	$C_6H_6$	0.25	:	1.0	1.31	
$n-C_4H_9NH_2$	1.0	$C_6H_6$	0.11	:	1.0	1.2	
"	1.0	"	0	:	1.0	1.33	1ml $Et_3n$ used as catalyst
"	4.0	THF	0.66	:	1.00	1.60	product not solu- ble in THF
$i-C_3H_7NH_2$	2.0	$C_6H_6$	0.2	:	1.0	1.44	
"	8.6	"	0.16	:	1.0	1.73	
"	10.0	THF	0.25	:	1.0	-	
"	7.0	"	0.96	:	1.0	0.95	product sublimed
$t-C_4H_9NH_2$	2.0	THF	0.5	:	1.0	1.93	
"	5.0	"	0.76	:	1.0	1.14	
"	10.0	"	0.78	:	1.0	1.30	product sublimed
"	10.0	$C_6H_6$	0.44	:	1.0	1.69	

REDISTRIBUTION REACTIONS BETWEEN  
LITHIUM ALUMINUM HYDRIDE AND LITHIUM TETRAPHENYL ALUMINATE

E. C. Ashby, H. S. Prasad and A. B. Goel

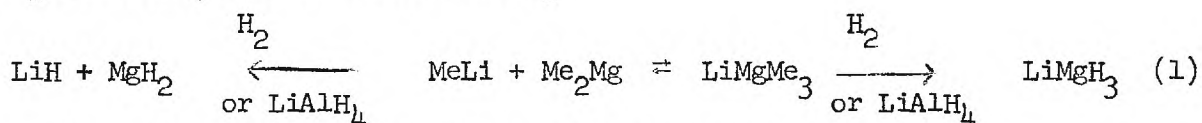
School of Chemistry, Georgia Institute of Technology, Atlanta, Ga. 30332

Abstract

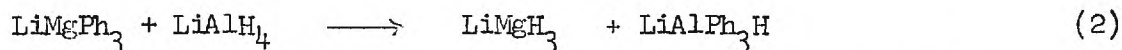
Redistribution reactions between  $\text{LiAlH}_4$  and  $\text{LiAlPh}_4$  were performed by mixing the reagents in appropriate ratios. The products  $\text{LiAlH}_3\text{Ph}$ ,  $\text{LiAlH}_2\text{Ph}_2$  and  $\text{LiAlHPh}_3$  have been characterized by their elemental analysis, infrared and nmr spectra in ether.

Introduction

Previous attempts to prepare  $\text{LiMgH}_3$  by (1) the reaction of  $\text{LiH}$  and  $\text{MgH}_2$ , (2) the hydrogenolysis of  $\text{LiMgMe}_3$  and  $\text{LiMgR}_2\text{H}$  or (3) the reduction of  $\text{LiMgR}_3$  and  $\text{LiMgR}_2\text{H}$  with  $\text{LiAlH}_4$  gave instead only a mixture of  $\text{LiH}$  and  $\text{MgH}_2$ . It was suggested that  $\text{LiMgMe}_3$  was not stable in ether and dissociated into  $\text{MeLi}$  and  $\text{Me}_2\text{Mg}$  which on reaction with  $\text{H}_2$  or  $\text{LiAlH}_4$  produced  $\text{LiH}$  and  $\text{MgH}_2$ .



In view of this result, we decided to prepare a stable "ate" complex such as  $\text{LiMgPh}_3$  which on reaction with  $\text{H}_2$  or  $\text{LiAlH}_4$  would produce  $\text{LiMgH}_3$ . Reaction of  $\text{LiMgPh}_3$  with  $\text{LiAlH}_4$  would probably form  $\text{LiMgH}_3$  as an ether insoluble solid and  $\text{LiAlPh}_3\text{H}$  as soluble product in ether. In order to help characterize  $\text{LiAlPh}_3\text{H}$  and  $\text{LiAlPh}_2\text{H}_2$ ,



it was decided to study the reaction of  $\text{LiAlPh}_4$  and  $\text{LiAlH}_4$  in ether by ir, and nmr analysis.

### Experimental

Apparatus. Reactions were performed under dry nitrogen at the bench or in a glove box equipped with a recirculating system using manganese oxide to remove oxygen. Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer using KBr and CsI liquid or mull cells. NMR spectra were recorded on Varian-A-60 in ether. The X-ray powder diffraction pattern of  $\text{LiAlPh}_4$  was obtained on a Philips-Norelco X-ray unit using a 114.6 mm camera with nickel filtered  $\text{Cu-K}_\alpha$  radiation. The sample was sealed in 0.5 mm capillary and exposed to X-rays for 6 hr. '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. Lithium was determined by flame photometry. Phenyl groups present in the complexes were determined as benzene by hydrolyzing the samples with water and analyzing the filtrate by glc using an S.E. 30 column at 70°. Mesitylene was used as the solvent and hexanol was used as an internal standard.

### Materials

Solvents were distilled immediately prior to use over lithium aluminum hydride (ether) or sodium aluminum hydride (THF, benzene and mesitylene). Phenyl lithium was prepared by the reaction of iodobenzene with n-butyllithium in hexane. Benzene was used as

solvent. The solid product was dissolved in ether, recrystallized at  $-78^{\circ}$ , redissolved in freshly distilled ether and standardized by the Watson and Eastham analysis.

It has been observed that phenyllithium cleaves ether at room temperature to give the product  $\text{Li}_2(\text{OET})\text{Ph}$  after 24 hr. Ether cleavage could be slowed down by keeping the solution at  $-15^{\circ}$ .

Diphenylmagnesium ( $\text{Ph}_2\text{Mg}$ ) was prepared by heating a mixture of triply sublimed magnesium (Dow Chemical Co.) and diphenylmercury at  $155^{\circ}$  for 40 hr. dissolving in freshly distilled ether and standardized by magnesium analysis. Triphenylaluminum was prepared by refluxing a mixture of diphenylmercury and aluminum chips in toluene for 40 hr. and filtering the resulting mixture hot through glass wool using nitrogen pressure. The product was recrystallized in hot toluene and dried under reduced pressure (0.05 mm) for 1 hr at  $60^{\circ}$ .

Lithium aluminum hydride ( $\text{LiAlH}_4$ ) was obtained from Ventron, Metal Hydride Division. A solution was prepared by refluxing  $\text{LiAlH}_4$  in ether overnight. The solution was filtered through a glass-fritted funnel using dried Celite Analytical Filter-Aid (Johns-Manville). The clear solution was standardized by aluminum analysis.

Lithium tetraphenylaluminate ( $\text{LiAlPh}_4$ ) 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. Analysis of the white solid gave the following results: Calcd. for  $\text{LiAl}(\text{C}_6\text{H}_5)_4$ :  $\text{Li}:\text{Al}:\text{Ph} = 1.0:1.0:4.0$ . Found:  $1.00:1.06:4.10$ .

X-ray powder diffraction data for  $\text{LiAlPh}_4$  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, 2.3 vw, 2.25 vw, 2.13 vw, 2.05 vw, 2.00 vw, 1.90 w, 1.78 w, 1.58 w.

Redistribution of  $\text{LiAlH}_4$  and  $\text{LiAlPh}_4$  as determined by infrared analysis. A 0.615 M solution of  $\text{LiAlH}_4$  in ether was added in increments to a magnetically stirred slurry of  $\text{LiAlPh}_4$  in ether. When the ratio of  $\text{LiAlH}_4$  to  $\text{LiAlPh}_4$  was 1:3, a clear solution resulted. After each addition the solution was stirred for 1 hr. at room temperature. Infrared spectra were obtained by withdrawing samples of the solutions by syringe under nitrogen. The additions were then continued until  $\text{LiAlH}_4$  was in excess. Figure 1 shows the infrared spectra obtained in this study.

Preparation of  $\text{LiAlHPh}_3$ . To a slurry of  $\text{LiAlPh}_4$  (6.258 g, 12.45 mmoles) in ether was added 10 ml of 0.615 M solution of  $\text{LiAlH}_4$  in ether (4.15 mmoles) with continuous stirring. A clear solution resulted and the reaction mixture was stirred for an additional hour. The excess ether was removed under reduced pressure to give a viscous product which on standing at room temperature for 5 days gave crystals. Elemental analysis gave the following ratios: Li:Al:H:Ph:ether = 1.00:1.00:1.03:2.97:2.10. Required for  $\text{LiAlPh}_3\text{H} \cdot 2\text{Et}_2\text{O}$ ; 1.0:1.0:1.0:3.0:2.0. Coordinated ether could be removed by drying the product in vacuum for 1 hour. The infrared spectrum in ether was similar to the spectrum obtained above.

Preparation of  $\text{LiAlH}_2\text{Ph}_2$ . To a slurry of  $\text{LiAlPh}_4$  (2.839 g; 8.30 mmoles) in ether was added dropwise 20 ml of 0.615 M solution of  $\text{LiAlH}_4$  in ether (2.30 mmole) with constant stirring. This reaction mixture was stirred for 1 hour after a clear solution was obtained.

The ether was removed under vacuum producing a pasty mass which crystallized after keeping for 3 days at room temperature. Elemental analysis gave the following ratios:  $\text{Li:Al:H:Ph:Et}_2\text{O} = 1.02:1.00:2.06:1.98:1.94$ . Required for  $\text{LiAlH}_2\text{Ph}_2 \cdot 2\text{Et}_2\text{O} = 1.0:1.0:2.0:2.0:2.0$ .

Preparation of  $\text{LiAlH}_3\text{Ph}$ . To a slurry of  $\text{LiAlPh}_4$  (1.780 g; 5.2 mmole) in ether was added dropwise 37.6 ml of 0.615 M solution (15.6 mmole) of  $\text{LiAlH}_4$  in ether. The resulting solution was stirred for 1 hour and excess solvent was removed under vacuum. When about 10 ml of ether was left a white crystalline product appeared which was separated by decantation, washed with ether and dried at room temperature under reduced pressure (0.05 mm) for 15 min. The crystalline product then changed to a viscous product. When a freshly distilled ether was added to this viscous product, it again changed to a crystalline solid. The solid was separated and dried at  $0^\circ$  for 1 hour under vacuum (0.005 mm) and then analyzed. Elemental analysis gave the following ratio:  $\text{Li:Al:H:Ph:Ether} = 1.0:1.0:0.95:3.0:4.0$ . Required for  $\text{LiAlHPh}_3 \cdot 4\text{Et}_2\text{O}; 1.0:1.0:1.0:3:4$ .

#### Results and Discussion

In order to establish the redistribution of  $\text{LiAlPh}_4$  and  $\text{LiAlH}_4$ , ether solutions of  $\text{LiAlPh}_4$  and  $\text{LiAlH}_4$  were mixed in 1:1, 1:3, and 3:1 ratios followed by infrared analysis of the resulting solutions. In this connection  $\text{LiAlPh}_4$  was synthesized by the reaction of  $\text{PhLi}$  with  $\text{AlPh}_3$ . The NMR spectrum of  $\text{LiAlPh}_4$  in THF was different from that of the reactants. The chemical shift separation between the highest peaks of the multiplets due to ortho and meta-para protons of the phenyl groups have been shown to be different for  $\text{PhLi}$ ,  $\text{Ph}_3\text{Al}$

and  $\text{LiAlPh}_4$  recorded at room temperature.

$\text{PhLi} = 0.99 \text{ ppm (in diethyl ether)}$

$\text{Ph}_3\text{Al} = 0.51 \text{ ppm (in THF)}$

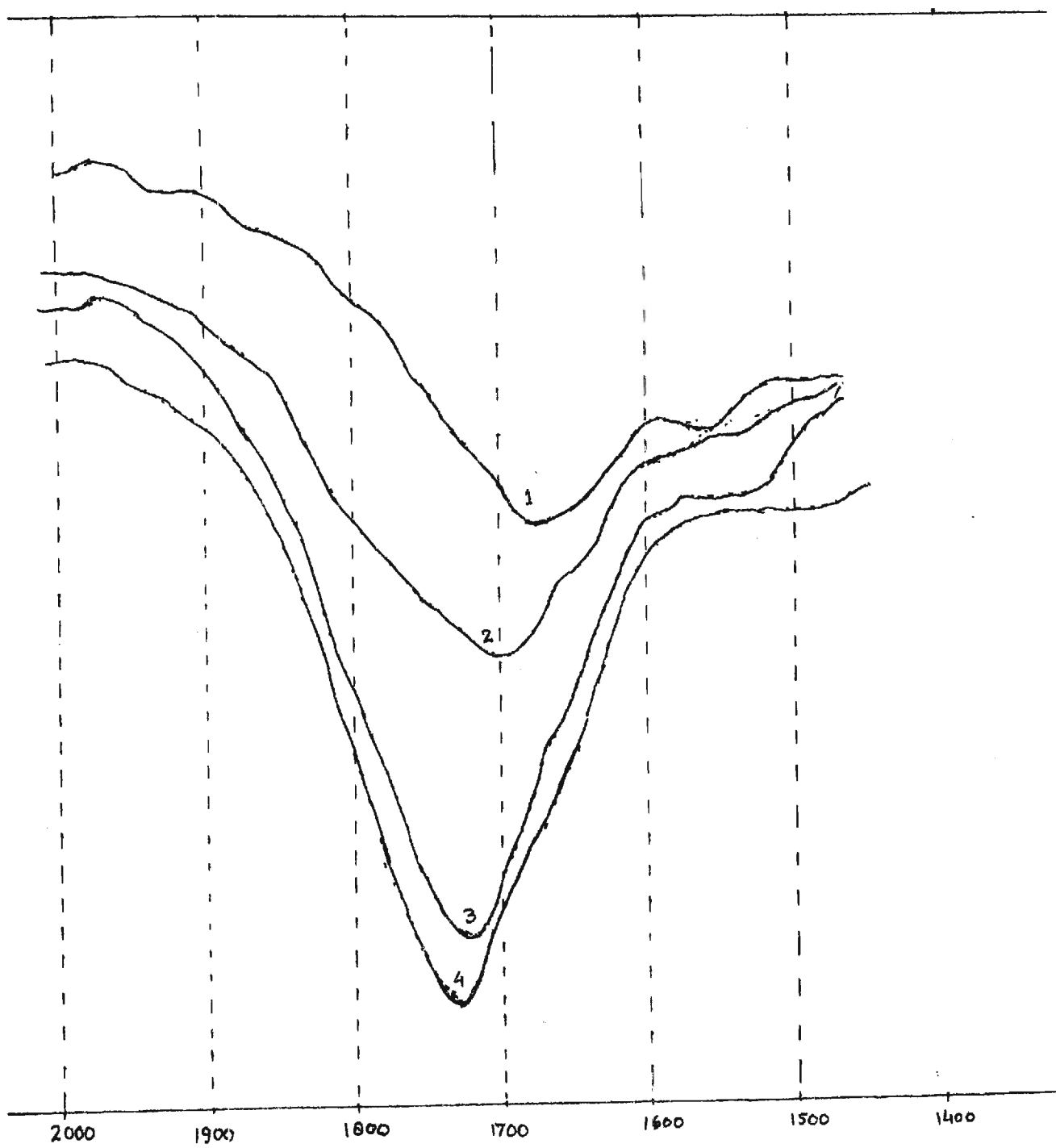
$\text{LiAlPh}_4 = 0.60 \text{ ppm (in THF)}$

When lithium aluminum hydride solution in ether was added to a slurry of  $\text{LiAlPh}_4$  in ether a clear solution was obtained when the ratio of  $\text{LiAlH}_4$  to  $\text{LiAlPh}_4$  was 3:1. An infrared spectrum of the resulting solution showed the presence of a band at  $1730 \text{ cm}^{-1}$  ( $\text{LiAlH}_4$  shows Al-H stretching at  $1740 \text{ cm}^{-1}$  in ether) due to Al-H stretching suggesting the presence of  $\text{LiAlH}_3\text{Ph}$ . When the ratio of  $\text{LiAlH}_4$  to  $\text{LiAlPh}_4$  was 1:1 this band shifted to  $1710 \text{ cm}^{-1}$  indicating the presence of  $\text{LiAlH}_2\text{Ph}_2$ . When the ratio of  $\text{LiAlH}_4$  to  $\text{LiAlPh}_4$  was 1:3 a broad band at  $1680 \text{ cm}^{-1}$  was observed indicating the presence of  $\text{LiAlPh}_3\text{H}$ .

All these products,  $\text{LiAlH}_n\text{Ph}_{4-n}$  ( $n = 1-3$ ) have been isolated and characterized by elemental analysis. FMR spectra showed the chemical shift separation between the highest peaks of the multiplets due to ortho and meta-para protons of the phenyl groups ranging from 0.60 ppm to 0.62 ppm. These products are soluble in THF and ether and the solubility increases with the number of hydride groups.

Molecular weight and X-ray-crystallographic studies are in progress.

FIGURE 1. Infrared spectra of the solution on addition of  $\text{LiAlH}_4$  to  $\text{LiAlPh}_4$  in diethyl ether.  $\text{LiAlH}_4$ : $\text{LiAlPh}_4$  ratio:  
(1) 1:3; (2) 1:1; (3) 3:1; (4) pure  $\text{LiAlH}_4$



REACTIONS OF DIPHENYLMAGNESIUM  
WITH LITHIUM ALUMINUM HYDRIDE IN DIETHYL ETHER

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Abstract

The reactions of diphenylmagnesium with lithium aluminum hydride in diethyl ether have been studied in detail.  $\text{MgH}_2$  as an insoluble solid and  $\text{LiAlPh}_n\text{H}_{4-n}$  in solution are formed when the  $\text{Ph}_2\text{Mg}$  to  $\text{LiAlH}_4$  ratio is 3:2, 1:1 and 1:2. Synthesis of  $\text{PhMgH}$  and  $\text{PhMg}_2\text{H}_3$  is also reported. The integrity of the products have been established by ir, nmr and X-ray powder diffraction data.

Introduction

As mentioned earlier in the previous report, our preliminary aim is to synthesize complex metal hydrides of magnesium, such as,  $\text{LiMgH}_3$ ,  $\text{Li}_2\text{MgH}_4$ , etc. by the reaction of  $\text{LiMgR}_3$  with  $\text{LiAlH}_4$ . According to earlier reports<sup>1</sup>, lithium triphenylmagnesiates dissociates in ether to  $\text{PhLi}$  and  $\text{Ph}_2\text{Mg}$ . If  $\text{LiAlH}_4$  is then added to  $\text{LiMgPh}_3$  in ether, one would expect to form  $\text{LiH}$  and  $\text{MgH}_2$  as well as  $\text{LiMgH}_3$ . Since the reaction of  $\text{LiAlH}_4$  with  $\text{Ph}_2\text{Mg}$  has not been studied, we thought it worthwhile to study this reaction to determine if indeed  $\text{MgH}_2$  is formed. Reactions of diethylmagnesium with lithium aluminum hydride have been studied in our laboratories<sup>2</sup>; however, the literature gives no mention regarding the reactions of  $\text{LiAlH}_4$  with  $\text{Ph}_2\text{Mg}$ .

Experimental

All manipulations of air sensitive compounds were carried out

under nitrogen.

Apparatus. See previous section.

Analyses. See previous section for lithium aluminum, phenyl group and gas analysis. Magnesium was determined by titration with EDTA at pH 10 using Erischorome Black T as an indicator. When aluminum was present, it was masked by complexation with triethanolamine.

Materials. Solvents were dried by standard procedures. Diphenylmagnesium was prepared by heating a mixture of diphenylmercury and triply sublimed magnesium metal at 155° for ~48 hours followed by the dissolution of the product in freshly distilled ether.

Preparation of ether solutions of  $\text{LiAlH}_4$  has been reported in the earlier section.

Infrared Study of the Reaction of  $\text{LiAlH}_4$  with  $\text{Ph}_2\text{Mg}$  in Diethyl-ether. A 100 ml portion of a 0.40 M solution of diphenylmagnesium in diethyl ether was placed in a three-necked round bottomed flask equipped with a condenser, an addition funnel. To this was added dropwise a 0.73 M solution of lithium aluminum hydride in regular increments with continuous magnetic stirring. After each addition, the mixture was stirred for another 1/2 hour 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  $\text{Ph}_2\text{Mg}$  and  $\text{LiAlH}_4$  at several stoichiometric ratios.

Reaction of  $\text{Ph}_2\text{Mg}$  with  $\text{LiAlH}_4$  in 1:2, 1:1 and 3:2 Stoichiometric Ratios. 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 slightly exothermic nature of the reaction so that the reaction temperature could be kept at 25°. Reaction mixtures were stirred for an additional 1/2 hour, 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 1.

Reaction of  $\text{Ph}_2\text{Mg}$  with  $\text{LiAlH}_4$  in 2:1 Molar Ratio. To 10 ml of 0.79 M solution of  $\text{Ph}_2\text{Mg}$  in diethyl ether (7.9 mmoles) was added dropwise 9.5 ml of 0.415 M ether solution of  $\text{LiAlH}_4$  (3.95 mmoles) with continuous stirring at room temperature. The reaction was exothermic and a white precipitate along with a colorless insoluble viscous product was observed. The reaction mixture was then stirred for 48 hr. The amount of the white precipitate decreased and a grayish black sticky precipitate was observed at the bottom of the flask below the viscous insoluble layer. The supernatant liquid was separated and analyzed. Found: Li:Mg:Al:H:Ph - 1.00:0.1.06:0.98:3.04. Required for  $\text{LiAlHPh}_3$  = Li:Al:H:Ph = 1:1:1:3. To the viscous liquid and the grayish black precipitate was added about 15 ml THF and the viscous product dissolved. The mixture was filtered, washed with THF and both filtrate and the solid were dried under vacuum.

THF Soluble Solid. Found, Li:Mg:Al:H:Ph = 1.0:2.96:1.0:5.1:4.95. Required for  $\text{LiAlPh}_4 + 3\text{MgH}_2$ , 1:3:1:6:4. The X-ray powder diffraction

pattern of the solid showed weak lines for  $\text{LiAlPh}_4$ .

Insoluble Solid. Found,  $\text{Mg:H:Ph} = 1.00:0.2:0.16$ . Required for Mg metal,  $\text{Mg:H:Ph} = 1.00:0:0$ .

Reaction Between  $\text{Ph}_2\text{Mg}$  and  $\text{LiAlH}_4$  in 4:1 Ratio. To 20 ml of 0.79M diphenylmagnesium solution in ether (15.8 mmoles) was added 9.6 ml of 0.615 M ether solution of lithium aluminum hydride (3.96 mmoles) dropwise with magnetic stirring. A colorless viscous liquid, insoluble in ether, was formed. The reaction mixture was stirred for 1 hr. and the viscous insoluble product separated by removing the supernatant solution by syringe. The viscous layer was then washed with ether and left overnight to give a crystalline solid. It was dried and analyzed. Found,  $\text{Li:Al:Mg:H:Ph} = 1.0:1.05:3.25:4.0:7.89$ . Required for  $\text{LiAlPh}_4 + 4\text{PhMgH}$ ,  $\text{Li:Al:H:Ph} = 1:1:4:4$ . X-Ray powder diffraction pattern: 2.55, 6.8 w, 6.0 w-m, 5.0 vw, 4.8 vw, 4.4 vs, 4.1 s, 3.8 w, 3.25 m-s, 2.95 m, 2.82 w, 2.74 w, 2.63 w, 2.55 w, 2.43 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. To this white solid, 20 ml of THF was added. Complete solution of the solid took place indicating the absence of  $\text{MgH}_2$ .

Preparation of  $\text{PhMgH}$  by the Reaction of  $\text{Ph}_2\text{Mg}$  with Active  $\text{MgH}_2$  in 1:1 Ratio. (a) Active  $\text{MgH}_2$  (3.95 mmoles) was prepared by adding 5 ml of  $\text{Ph}_2\text{Mg}$  (0.795 M) in ether (3.95 mmoles) dropwise to 9.01 ml of 0.415 M solution of  $\text{LiAlH}_4$  (3.95 mmoles) with continuous stirring. A white crystalline precipitate appeared at once which was separated from the supernatant liquid. The white solid was washed with ether and was added to 5 ml of 0.795 M ether solution of  $\text{Ph}_2\text{Mg}$  dropwise with constant stirring. The precipitate changed into a bulky

precipitate. This reaction mixture was stirred for about 6 hours more than half of this bulky precipitate dissolved while the remainder of the solid turned into a sticky mass, grayish black in color. The solid was filtered, washed with ether, dried under vacuum and analyzed. Found: Mg:H:Ph = 2.0:3.02:1.0. Required for  $\text{Mg}_2\text{H}_3\text{Ph}$ , Mg:H:Ph = 2:3:1.

(b) The above experiment was repeated and instead of stirring the mixture of  $\text{MgH}_2$  and  $\text{Ph}_2\text{Mg}$  for 6 hours, it was stirred for only 10 minutes. The bulky precipitate changed to a sticky mass. The sticky mass was filtered, washed with ether, dried in vacuum and analyzed. Found, Mg:H:Ph = 2.0:3.03:1.0. Required for  $\text{Mg}_2\text{H}_3\text{Ph}$  = 2:3:1.

(c) The above experiment has been repeated again and this time the precipitate was filtered just after addition of  $\text{Ph}_2\text{Mg}$  to  $\text{MgH}_2$ . It was washed with ether and dried. Found, Mg:H:Ph = 1.10:1.30:1.0. Required for  $\text{PhMgH}$  = 1:1:1.

(d) To the supernatant solution of the previous experiments (a), which was characterized earlier to be  $\text{LiAlH}_2\text{Ph}$ , (3.9 mmoles) was added 6.5 ml of 0.79 M ether solution of  $\text{Ph}_2\text{Mg}$  (3.60 mmoles) with continued stirring at room temperature. A white precipitate along with some insoluble colorless viscous liquid appeared. This reaction mixture was stirred for 1 hr. and kept overnight, while the viscous liquid crystallized to a white solid. These solids were 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. Found, Li:Mg:Al:H:Ph = 1.06:1.00:1.01:2.02:4.04. Required for  $\text{LiAlPh}_4 + \text{MgH}_2$  = 1:1:1:2:4.

(e) To the supernatant solution obtained from the reaction of  $\text{Ph}_2\text{Mg}$  and  $\text{LiAlH}_4$  [ $\text{LiAlH}_2\text{Ph}_2$  (3.90 mmoles)], was added 6.5 ml of 0.79 M solution of  $\text{Ph}_2\text{Mg}$  in ether (3.60 mmoles) with continued stirring. A white bulky solid appeared immediately after the addition of  $\text{Ph}_2\text{Mg}$ . The reaction mixture was stirred for 5 min. during which time no viscous insoluble liquid appeared. The white solid was filtered and washed with ether, dried in vacuo and analyzed:  $\text{Mg:H:Ph} = 1.10:1.39:1.0$ . Required for  $\text{PhMgH}$ ; 1:1:1. For the filtrate was found;  $\text{Li:Al:H:Ph} = 1.07:1.00:0.96:3.06$ . Required for  $\text{LiAlHPh}_3 = 1:1:1:3$ .

Reaction Between  $\text{MgH}_2$  and  $\text{LiAlPh}_4$ . Active  $\text{MgH}_2$  (3.95 mmoles) was prepared by the reaction of  $\text{Ph}_2\text{Mg}$  (3.95 mmoles) and  $\text{LiAlH}_4$  (3.95 mmoles) in ether. To the resulting solid was added  $\text{LiAlPh}_4$  (1.336 g, 3.90 mmoles) in 10 ml of ether. The reaction mixture was stirred for 25 min. No reaction was observed. Ether was removed under vacuum, 15 ml of THF added and the resulting mixture stirred for 5 min. The solid material dissolved. Infrared and nmr spectra of this solution were recorded. The solvent was removed under vacuum and benzene added. The solid was stirred for 1/2 hr. and then filtered, dried under vacuum and analyzed. Solid analysis found;  $\text{Li:Mg:Al:H:Ph} = 1.03:1.01:1.02:1.96:3.99$ . Required for  $\text{MgH}_2 + \text{LiAlPh}_4$ ; 1.0:1:1:2:4.

The above solid was dissolved in 10 ml THF and 5 ml of benzene was added after which some insoluble solid appeared. This reaction mixture was stirred overnight and then filtered. The precipitate was washed with ether and dried. Found;  $\text{Li:Al:Mg:H:Ph} = 0.11:0.12:1.0:1.01:1.0$ . Required for  $\text{PhMgH} + (\text{LiAlPh}_4 \text{ as impurity}) = \text{Mg:H:Ph} = 1:1:1$ .

The above  $\text{LiAlPh}_4$  impurity contaminated the  $\text{PhMgH}$  and could not be removed by repeating the above mentioned separation technique.

The filtrate of the above reaction mixture was treated with 15 ml of ether which produced an insoluble white solid which was filtered, washed with ether and dried. Found;  $\text{Li:Al:H:Ph} = 1.00:1.10:0.64:3.42$ . Infrared spectra showed a very weak broad band at  $1680\text{ cm}^{-1}$  due to Al-H stretching.

Reaction Between  $\text{MgH}_2$  and  $\text{Ph}_2\text{Mg}$  (1:1 molar ratio) in THF. To  $\text{MgH}_2$  (3.95 mmoles) prepared by the reaction of  $\text{Ph}_2\text{Mg}$  (5 ml; 0.795 M, 3.95 mmoles) with  $\text{LiAlH}_4$  (9.8 ml or 0.615 M, 3.95 mmoles) in ether was added 12 ml of THF and 5 ml of 0.795 M solution of  $\text{Ph}_2\text{Mg}$  (3.95 mmoles) and this reaction mixture was stirred at room temperature for 15 min. to give a clear colorless solution. This was dried under reduced pressure and washed with ether and dried. Found;  $\text{Mg:H:Ph} = 1.00:1.18:0.91$ . Required for  $\text{PhMgH} = 1.0:1.0:1.0$ .

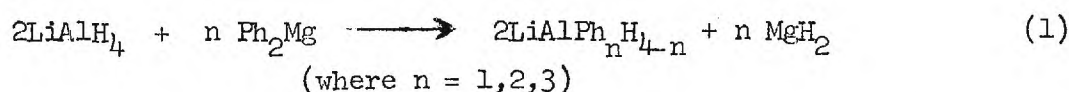
Reaction Between  $\text{MgH}_2$  and  $\text{Ph}_2\text{Mg}$  in 3:1 molar ratio in THF. To  $\text{MgH}_2$  (11.25 mmoles) prepared by the reaction of  $\text{Ph}_2\text{Mg}$  (15 ml of 0.795 M; 11.85 mmol) with  $\text{LiAlH}_4$  (29.6 ml of 0.415 M; 11.25 mmoles) in ether was added 10 ml of THF and 5 ml of 0.795 M solution of  $\text{Ph}_2\text{Mg}$  (0.395 mmoles). 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. Found;  $\text{Mg:H:Ph} = 2.00:2.97:1.00$ . Required for  $\text{PhMg}_2\text{H}_3 = 2.0:3.0:1.0$ . The ether solution contained no magnesium.

#### Results and Discussion

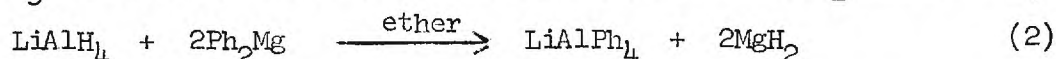
Addition of  $\text{LiAlH}_4$  to  $\text{Ph}_2\text{Mg}$  in 2:3, 1:1 and 2:1 ratio or addition

of  $\text{Ph}_2\text{Mg}$  to  $\text{LiAlH}_4$  in 1:2, 1:1, 3:2 ratio resulted in the precipitation of  $\text{MgH}_2$ . This result is consistent with the earlier report concerning the reaction of diethylmagnesium with  $\text{LiAlH}_4$ . Variation of the concentration of reagents was found to have no effect on the reaction.

An infrared study of this reaction showed that the reaction proceeds stepwise exchanging phenyl groups of the magnesium for hydride of the aluminum as shown in eq. 1.



At a  $\text{LiAlH}_4$ : $\text{Ph}_2\text{Mg}$  ratio of 1:2 (eq. 2) infrared spectrum (figure 1) of the supernatant solution showed no Al-H bands in the  $1600\text{--}1800 \text{ cm}^{-1}$  region when the reaction mixture was stirred for 1 hr. However, when the reaction mixture was stirred for 48 hr., a very weak and broad Al-H band at  $\sim 1680 \text{ cm}^{-1}$  (characteristic of  $\text{LiAlPh}_3\text{H}$ <sup>3</sup>) appeared indicating some reaction between  $\text{MgH}_2$  and  $\text{LiAlPh}_4$ .



The precipitate of reaction 1 was shown to be  $\text{MgH}_2$  by infrared, elemental and X-ray powder diffraction analysis. Filtrates of the reaction (eq. 1) have been characterized as  $\text{LiAlPh}_n\text{H}_{4-n}$  by infrared spectra<sup>3</sup> (when  $n = 3, 2, 1$ ). The Al-H stretching bands were observed at  $1670\text{--}80$ ,  $1710$  and  $1730 \text{ cm}^{-1}$  respectively. The NMR spectrum of  $\text{Ph}_2\text{Mg}$  in ether gave two multiplets due to ortho (downfield) and meta-para (upfield) protons of the phenyl groups in 2:3 ratio. The upfield multiplet centered at 5.93 ppm relative to the triplet of ether and the chemical shift separation between the two highest peaks of the multiplets has been observed to 0.68 ppm. A quartet centered at 0.57 ppm upfield to the meta-para proton

suggested the presence of two moles of solvated ether.

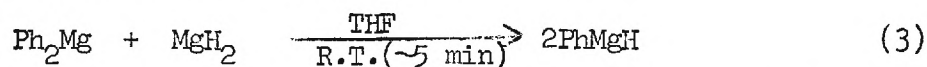
In the reaction of  $\text{Ph}_2\text{Mg}$  with  $\text{LiAlH}_4$  in ether in 2:1 molar ratio, an insoluble colorless viscous liquid and a white crystalline solid were observed. When the mixture was stirred for 48 hr. the white solid changed to a grayish black solid and the supernatant liquid was shown to be  $\text{LiAlHPh}_3$ . The insoluble colorless viscous liquid was soluble in THF and was characterized to be either a complex or a mixture of  $\text{LiAlPh}_4$  and  $3\text{MgH}_2$  and the insoluble grayish black solid insoluble in THF was shown to be magnesium metal. The nmr spectrum of the supernatant solution gave a peak due to benzene along with two multiplets due to the phenyl protons. According to the above observation, it can be supposed that the  $\text{MgH}_2$  and  $\text{LiAlPh}_4$  initially formed, probably reacted to give some of  $\text{LiAlPh}_3\text{H}$  and  $\text{PhMgH}$  which produced benzene and magnesium metal on decomposition. In order to support the above conclusion, reaction between active  $\text{MgH}_2$  (prepared by the reaction of  $\text{Ph}_2\text{Mg}$  and  $\text{LiAlH}_4$  in 1:1 ratio) and  $\text{LiAlPh}_4$  has been attempted in ether which showed no reaction after 1 hr. probably due to insolubility of the  $\text{MgH}_2$ . The same reaction in THF gave soluble species, which may be a complex of  $\text{LiAlPh}_4$  and  $\text{MgH}_2$ . An infrared spectrum of the above solution showed a very weak Al-H band at  $\sim 1680\text{ cm}^{-1}$  and the nmr spectrum in THF in an attempt to observe the Mg-H proton proved useless as the side band of THF is in the same region. Interestingly, the downfield broad multiplets due to the ortho-protons of the phenyl groups of  $\text{LiAlPh}_4$  split into two broad multiplets, the chemical shift separation 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 ob-

served to be 0.60 ppm and 0.68 ppm suggesting both Mg-Ph and Al-Ph compounds present. The above product was insoluble in benzene. In the reaction of  $4\text{Ph}_2\text{Mg}$  and  $\text{LiAlH}_4$  in ether stirred for 1/2 hours, an ether insoluble viscous liquid was observed which was soluble in THF. The viscous liquid has been characterized to be a mixture of  $\text{PhMgH}$  and  $\text{LiAlPh}_4$ . The latter compound was detected by X-ray powder diffraction analysis. Attempts to separate  $\text{PhMgH}$  from  $\text{LiAlPh}_4$  failed. If the above reaction mixture was stirred for a longer time (4 hr.) in ether, some  $\text{Ph}_2\text{Mg}$  in the supernatant solution was observed indicating the disproportionation of  $\text{PhMgH}$  into  $\text{Ph}_2\text{Mg}$  (ether soluble) and  $\text{MgH}_2$  (insoluble). Attempts to prepare pure  $\text{PhMgH}$  by the reaction of active  $\text{MgH}_2$  and  $\text{Ph}_2\text{Mg}$  at room temperature for 10 min. or 6 hr. failed and a product analyzing of  $\text{Mg}_2\text{H}_3\text{Ph}$  was obtained as an ether insoluble solid, in both cases. This white solid turned grayish after five minutes. Interestingly, if the bulky precipitate obtained just after the addition of  $\text{Ph}_2\text{Mg}$  to  $\text{MgH}_2$  in ether was separated immediately, a product was formed whose analysis was close to that of  $\text{PhMgH}$ .

Coates<sup>4</sup> has reported evidence for the intermediate  $\text{C}_2\text{H}_5\text{MgH}$  in a study of the reaction of  $(\text{C}_2\text{H}_5)_2\text{Mg}$  and  $\text{NaB}(\text{C}_2\text{H}_5)_3\text{H}$ . In another reaction of  $\text{Ph}_2\text{Mg}$  with  $\text{LiAlH}_2\text{Ph}_2$  in ether at room temperature, the bulky precipitate obtained just after the addition of  $\text{Ph}_2\text{Mg}$  to  $\text{LiAlH}_2\text{Ph}_2$  corresponded to  $\text{PhMgH}$  and  $\text{LiAlHPh}_3$  in ether. When the above reaction was run for 1/2 hr., the white precipitate and an insoluble viscous liquid were found which could not be separated but both dissolved in THF probably forming some soluble complex.

In the reaction of  $\text{MgH}_2$  and  $\text{LiAlPh}_4$  in THF, about 90% pure

PhMgH could be synthesized. Separation took place by adding benzene to the THF soluble species. Interestingly, almost pure PhMgH has been prepared by the reaction of  $\text{Ph}_2\text{Mg}$  and  $\text{MgH}_2$  in THF. The reaction was very rapid and gave a soluble specie which on washing with ether and drying under vacuum gave PhMgH.



Reaction between  $\text{Ph}_2\text{Mg}$  and  $\text{MgH}_2$  in 1:3 molar ratio in THF gave the soluble product  $\text{PhMg}_2\text{H}_3$  which was insoluble in ether. Solubility in THF ruled out the possibility of a mixture of  $\text{Ph}_2\text{Mg}$  and  $\text{MgH}_2$  and also insolubility in ether showed the absence of any  $\text{Ph}_2\text{Mg}$ .

Infrared spectra of the products PhMgH and  $\text{PhMg}_2\text{H}_3$  are shown in Figure 2. NMR spectra in THF showed the chemical shift separation between the highest peaks of the two multiplets to be 0.68 in both cases. X-Ray powder diffraction patterns have been carried out, however, good data could not be obtained in two attempts.

~ Molecular wt. and DTA-TGA studies are in progress.

### References

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2. E. C. Ashby and R. G. Beach, Inorg. Chem., 9, 2300 (1970).
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Table I

Elemental Analyses of the Reaction Products of  $\text{Ph}_2\text{Mg}$  and  $\text{LiAlH}_4$  (in 1:2, 1:1 and 3:2 Molar Ratio)

Reactants (mmoles)		Ratio	Precipitate			Filtrate				
$\text{Ph}_2\text{Mg}$	$\text{LiAlH}_4$		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

Figure 1. Infrared spectra of the supernatant solution on addition of  $\text{LiAlH}_4$  to  $\text{Ph}_2\text{Mg}$  in diethylether.  $\text{LiAlH}_4:\text{Ph}_2\text{Mg}$  ratio: (1) pure  $\text{Ph}_2\text{Mg}$ , (2) 1:2, (3) 2:3, (4) 1:1 (5) 2:1 (6) pure  $\text{LiAlH}_4$ .

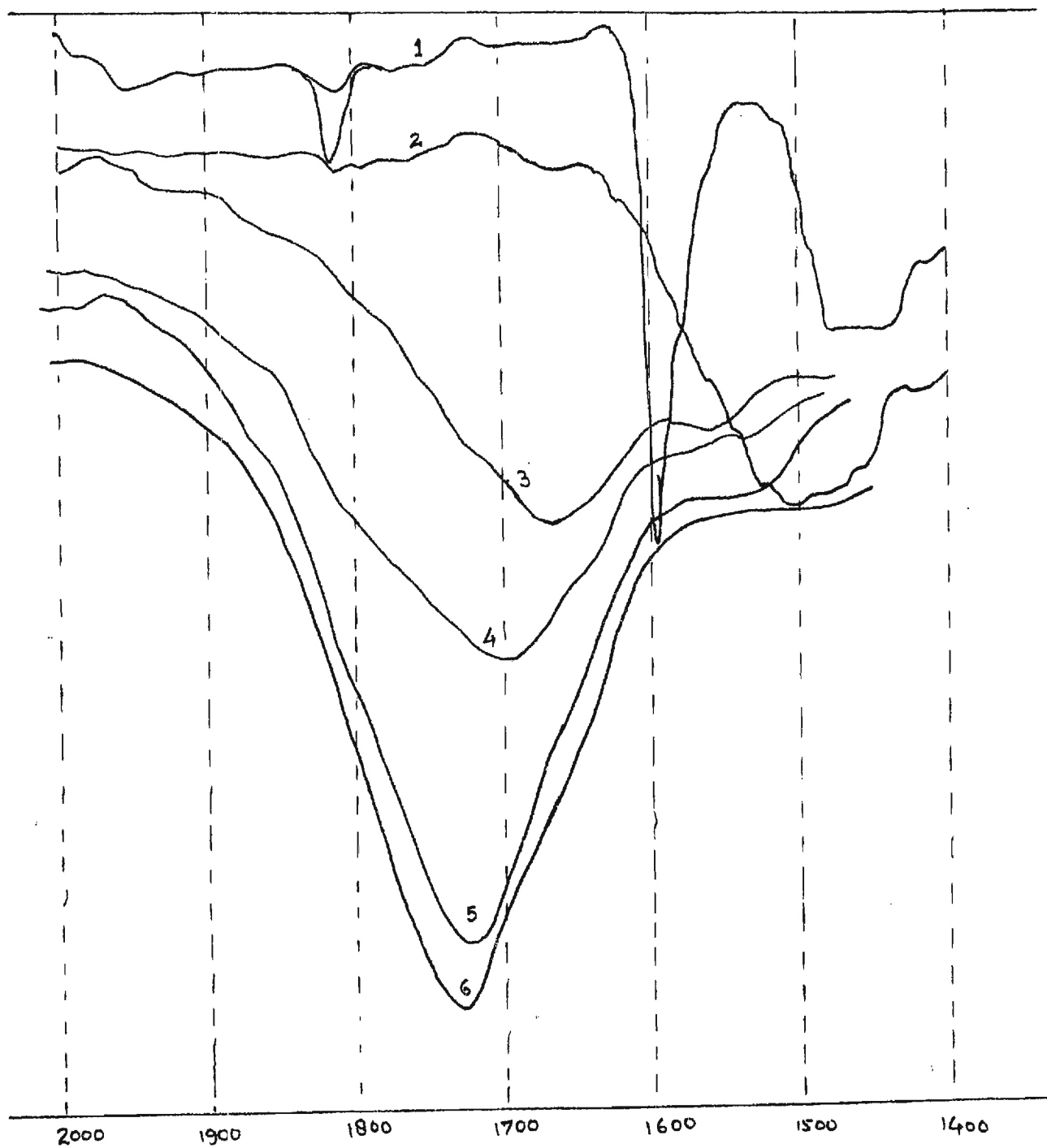
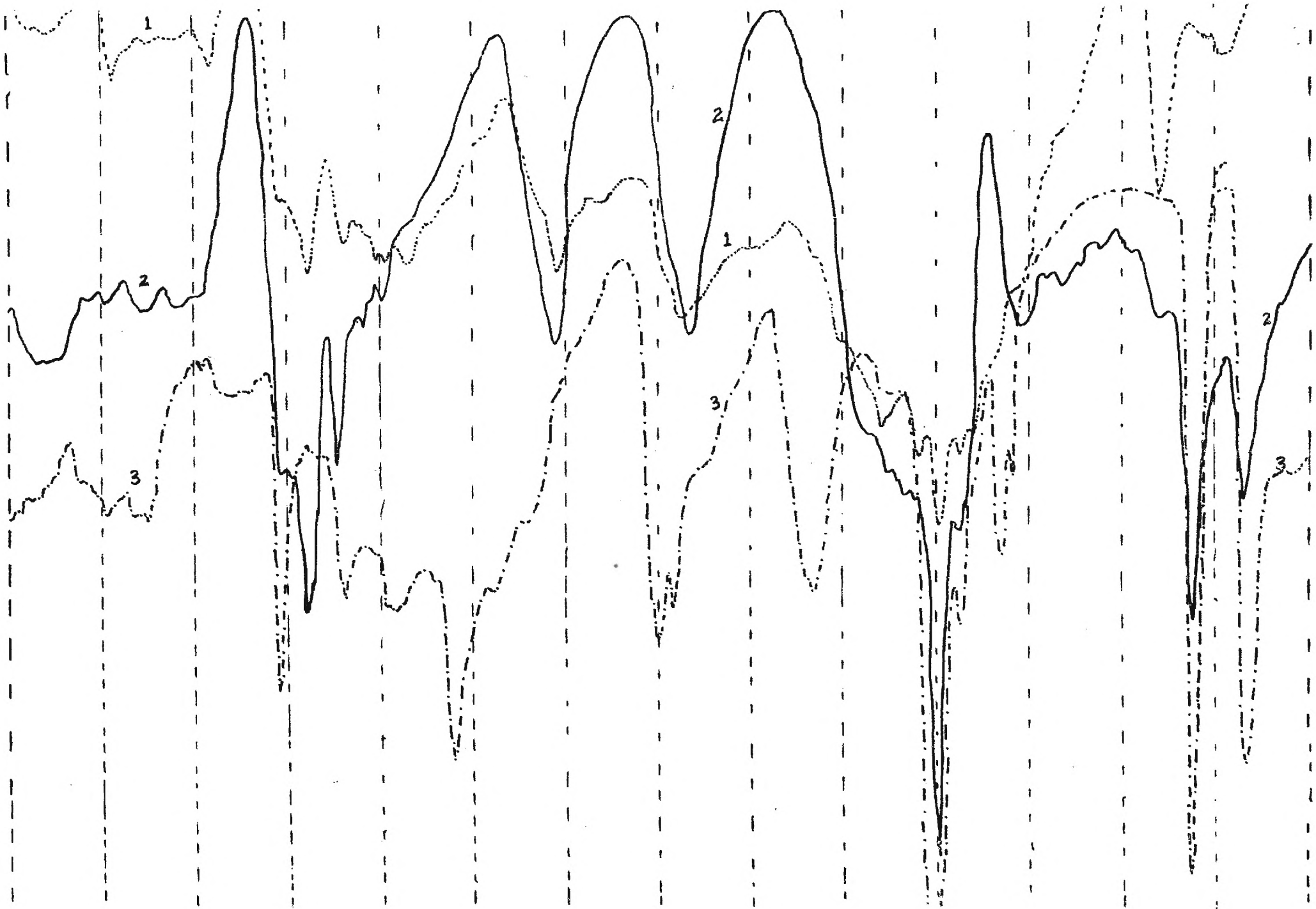


Figure 2. Infrared Spectra of (1)  $\text{PhMg}_2\text{H}_3$  in THF (...), (2)  $\text{PhMgH}$  in THF (\_\_\_), (3)  $\text{Ph}_2\text{Mg}$  in THF (- . - .)



## PREPARATION OF NEW COMPLEX METAL HYDRIDES; $\text{MgZnH}_4$ and $\text{Mg}(\text{ZnH}_3)_2$

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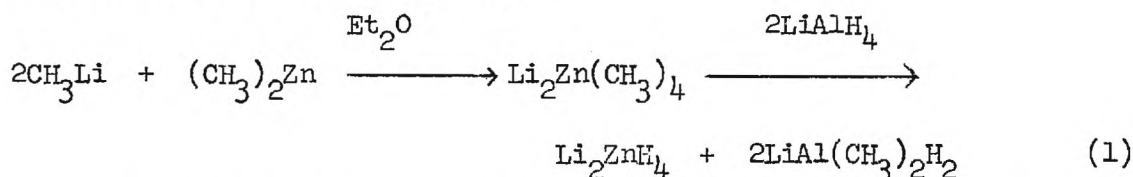
### Abstract

Magnesium bis(trihydrido-zincate)  $[\text{Mg}(\text{ZnH}_3)_2]$  and magnesium tetrahydrido-zincate ( $\text{MgZnH}_4$ ) have been synthesized by two different preparative routes. One method involves the reaction of dimethyl-magnesium with dimethylzinc in 1:2 and 1:1 molar ratio in ether followed by addition of  $\text{LiAlH}_4$  to the soluble "ate complexes" resulting in the precipitation of the insoluble hydrides  $\text{Mg}(\text{ZnH}_3)_2$  and  $\text{MgZnH}_4$ . The other method involves the metathetical reaction of  $\text{MgBr}_2$  with  $\text{LiZn}(\text{CH}_3)_3$  in 1:2 molar ratio and with  $\text{Li}_2\text{Zn}(\text{CH}_3)_4$  in 1:1 molar ratio to form so-called soluble "ate complexes". Addition of  $\text{LiAlH}_4$  to ether solutions of these "ate" complexes produced  $\text{Mg}(\text{ZnH}_3)_2$  and  $\text{MgZnH}_4$  respectively. The new hydrides were characterized by DTA-TGA, X-ray powder diffraction and elemental analysis. Detailed infrared investigation of the products presumed to be the "ate" complex referred to above revealed that the reaction products are better described by more complex equilibrium. However, the hydrides  $\text{Mg}(\text{ZnH}_3)_2$  and  $\text{MgZnH}_4$  were indeed formed by the reaction of  $\text{LiAlH}_4$  with the "ate" complex equilibrium as evidenced by X-ray diffraction studies. Proton NMR spectra of the "ate complexes" were obtained over a wide temperature range giving some information as to their composition in solution.

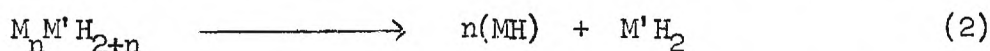
### Introduction

During the last few years we have been engaged in a general

study of the preparation and characterization of complex metal hydrides of zinc<sup>1</sup>, magnesium<sup>2</sup>, copper<sup>3</sup>, and beryllium<sup>4</sup>. The preparation of these compounds involves the reduction of an ether soluble "ate" complex ( $M_n M' R_{2m+n}$ ) with either  $LiAlH_4$  or  $AlH_3$  resulting in the precipitation of the insoluble hydride, leaving in solution the ether soluble  $LiAlR_n H_{4-n}$ . The preparation of  $Li_2 ZnH_4$  demonstrates the method (eq. 1).



From our studies of complex metal hydrides of the type,  $M_n M' H_{n+2}$  (where  $n = 1, 2$  or  $3$ ), we have found that the stability of the hydrides to disproportionation (eq. 2) is related to the electro-



positivity of  $M$  and  $M'$ . Evidence thus far indicates that if  $M$  is more electropositive than  $M'$  in the  $MM'H$  compound, the resulting complex metal hydride is stable. Since magnesium has an electronegativity of 1.2 and zinc 1.6<sup>5</sup> we thought that it should be possible to prepare  $Mg(ZnH_3)_2$  and  $MgZnH_4$  as stable complex metal hydrides. In this paper, we report the preparation and characterization of these two new complex metal hydrides as well as an attempt to characterize the nature of the "ate" complex precursors by variable temperature NMR and infrared studies.

#### Experimental Section

All operations were performed under nitrogen on the bench top using typical Schlenk tube techniques<sup>6</sup> or in a dry box equipped

with a recirculating system using manganous oxide columns to remove oxygen and moisture.<sup>7</sup> All compounds were dried to a constant weight on a high vacuum line.

Instrumentation. Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Spectra of solids were obtained as Nujol (dried over sodium and stored in the drybox) mulls between CsI plates and solutions were run in matched 0.10-mm path length KBr cells. X-Ray powder diffraction data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered  $\text{CuK}_{\alpha}$  radiation. Samples were sealed (in the drybox) in 0.5-mm capillaries and exposed to X-rays for 10 hr. d Spacings were read on a precalibrated scale equipped with viewing apparatus and the intensities of the lines were visually estimated. DTA-TGA were obtained under vacuum using a Mettler Thermoanalyzer II with a high vacuum attachment.<sup>8</sup>

Proton spectra were obtained using an A-60 spectrometer and the low temperature spectra were obtained using the standard low-temperature accessories supplied by Varian Associates.

Materials. Dimethylzinc was prepared from methyl iodide and Zn(Cu) couple by a modification of the procedure of Noller.<sup>9</sup> Dimethylmagnesium was prepared from dimethyl mercury and magnesium metal.<sup>10</sup> Ether solutions of magnesium bromide were prepared from  $\text{HgBr}_2$  and magnesium metal in ether solvent<sup>11</sup> and ether solutions of  $\text{LiAlH}_4$  (Ventron) were prepared by a previously described procedure.<sup>12</sup> Methylolithium in ether solution was obtained from Foote Mineral Co. and stored at  $-20^\circ$  until ready to use. The reactants were standardized prior to use and transferred volumetrically. Diethyl

ether was distilled fresh from  $\text{LiAlH}_4$ .

Analytical. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump. Metals were determined by compleximetric titration with EDTA. Zinc and magnesium in the presence of aluminum were determined by masking the aluminum with triethanolamine and titrating the remaining metal with EDTA. Zinc in the presence of magnesium and aluminum was determined by masking magnesium with ammonium fluoride. Aluminum and zinc in the presence of magnesium was determined by standard EDTA titration ( $\text{pH} = 4.0$ ) using dithizone indicator. Analysis for halides was carried out using the Volhard procedure.

Proton NMR Study of the "Ate" Complexes in Diethyl Ether. Ether solutions of  $\text{CH}_3\text{Li}$ ,  $(\text{CH}_3)_2\text{Mg}$  and  $(\text{CH}_3)_2\text{Zn}$  were mixed in the appropriate molar ratios to form the "ate" complexes,  $\text{LiZn}(\text{CH}_3)_3$ ,  $\text{Li}_2\text{Zn}(\text{CH}_3)_4$ , and presumably  $\text{Mg}[\text{Zn}(\text{CH}_3)_3]_2$  and  $\text{MgZn}(\text{CH}_3)_4$ . A small amount of each solution was transferred to a 5 mm thin wall, NMR tube under nitrogen, sealed and stored in dry ice or in a freezer at  $-20^\circ$ . Low temperature spectra were recorded after the system was allowed to come to equilibrium at each temperature.

Preparation of Magnesium Bis(Trihydrido-zincate),  $[\text{Mg}(\text{ZnH}_3)_2]$ .

(a) Reaction of  $\text{LiAlH}_4$  with the Product of the Reaction of  $\text{MgBr}_2$  and  $\text{LiZn}(\text{CH}_3)_3$  in 1:2 Ratio. In a 200 ml 3-neck round bottom flask containing 10 ml of 0.892 molar (8.92 mmol) dimethylzinc in diethyl ether was added under nitrogen with stirring 5.30 ml of 1.682 molar (8.92 mmol) methyllithium in ether. After stirring the solution at room temperature for one hour, 36 ml of 0.124 molar (4.46 mmol)

was added slowly to the stirred reaction mixture, a white precipitate rapidly formed which was stirred for an additional hour at room temperature. The white solid was filtered under vacuum using a medium frit filter funnel and washed with about 300 ml of freshly distilled diethyl ether in small portions. The resulting solid was vacuum dried (0.05 mm) overnight at room temperature and weighed 0.880 g (92% yield). Anal. Calcd. for  $\text{Mg}(\text{ZnH}_3)_2 \cdot 0.76(\text{C}_2\text{H}_5)_2^{13}$ : Mg, 11.16; Zn, 60.01; H, 2.77;  $(\text{C}_2\text{H}_5)_2\text{O}$ , 25.90. Found: Mg, 11.13; Zn, 60.00; H, 2.86;  $(\text{C}_2\text{H}_5)_2\text{O}$ , 26.06. The molar ratio of Mg:Zn:H is 1.00:2.00:6.20.

(b) Reaction of  $\text{LiAlH}_4$  with the Product Obtained by Reaction of  $\text{Mg}(\text{CH}_3)_2$  and  $\text{Zn}(\text{CH}_3)_2$  in 1:2 Ratio. The procedure was similar to the one above. An ether solution of dimethylmagnesium (3.44 mmol) was added dropwise to dimethylzinc (7.01 mmol) in ether. After 4 hours stirring at room temperature, the reaction mixture was diluted with 60 ml of ether, treated with 5.32 mmol of  $\text{LiAlH}_4$  solution, stirred for an additional hour, filtered and washed with about 300 ml of ether. The white solid product was vacuum dried for 17 hr. and weighed 0.535 g. The product exhibited a Mg:Zn:H ratio of 1.00:1.97:5.79. Anal. Calcd. for  $\text{Mg}(\text{ZnH}_3)_2 \cdot 0.47 \text{Et}_2\text{O}^{13}$ : Mg, 12.40; Zn, 66.72; H, 3.08;  $(\text{C}_2\text{H}_5)_2\text{O}$ , 17.78. Found: Mg, 12.95; Zn, 68.53; H, 3.10;  $(\text{C}_2\text{H}_5)_2\text{O}$ , 17.37.

Preparation of Magnesium Tetrahydrido-zincate ( $\text{MgZnH}_4$ ). (a) Reaction of  $\text{LiAlH}_4$  with the Product of the Reaction of  $\text{MgBr}_2$  and  $\text{Li}_2\text{Zn}(\text{CH}_3)_4$  in 1:1 Ratio. The procedure for this experiment is similar to the previous one. Dimethyl zinc (7.93 mmol) in diethyl ether was added to 15.86 mmol of methyllithium in ether and stirred

for about an hour at room temperature, followed by addition of 7.93 mmol of magnesium bromide ether solution. The resulting solution was stirred for 3 hr. and then 7.93 mmol of lithium aluminum hydride in ether was added. A white solid was immediately formed which was stirred for an additional hour, and then washed with 300 ml of dry ether and filtered. The compound after vacuum drying ( $10^{-5}$  mm) for 17 hr. weighed 0.670 g. (85% yield). Anal. Calcd. for  $\text{MgZnH}_4 \cdot 0.34(\text{C}_2\text{H}_5)_2\text{O}^{13}$ : Mg, 20.46; Zn, 55.04; H, 3.39;  $(\text{C}_2\text{H}_5)_2\text{O}$ , 21.09. Found: Mg, 20.34; Zn, 55.18; H, 3.34;  $(\text{C}_2\text{H}_5)_2\text{O}$ , 21.10. The molar ratio of Mg:Zn:H was 1.00:1.00:3.98.

(b) Reaction of  $\text{LiAlH}_4$  with the Product of the Reaction of  $\text{Mg}(\text{CH}_3)_2$  and  $\text{Zn}(\text{CH}_3)_2$  in 1:1 Ratio. Dimethylzinc (7.10 mmol) in diethyl ether was added dropwise to a stirred ether solution of dimethylmagnesium (7.10 mmol). After 4 hours stirring at room temperature, about 55 ml of ether was added to dilute the reaction mixture before the dropwise addition (14.20 mmol) of  $\text{LiAlH}_4$  in ether. The white precipitate which rapidly formed during the  $\text{LiAlH}_4$  addition, was stirred for an additional hour, filtered, washed with about 300 ml of ether and vacuum dried ( $10^{-5}$  mm for 17 hours) to constant weight at room temperature. The resulting solid was analyzed and the molar ratio of Mg:Zn:H was found to be 1.00:1.07:4.09. Anal. Calcd. for  $\text{MgZnH}_4 \cdot 0.28(\text{C}_2\text{H}_5)_2\text{O}^{13}$ : Mg, 21.23; Zn, 57.10; H, 3.52;  $(\text{C}_2\text{H}_5)_2\text{O}$ , 18.13. Found: Mg, 20.10; Zn, 58.12; H, 3.41;  $(\text{C}_2\text{H}_5)_2\text{O}$ , 18.30.

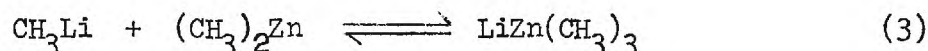
Synthesis of  $\text{MgH}_2$  and  $\text{ZnH}_2$ . Magnesium hydride was prepared by the reaction of  $\text{LiAlH}_4$  with  $\text{Mg}(\text{C}_2\text{H}_5)_2$  in 1:2 mole ratio in diethyl ether according to a previously reported procedure<sup>14</sup> and zinc

hydride was prepared by the reaction of  $\text{LiAlH}_4$  and  $\text{Zn}(\text{CH}_3)_2$  in 1:1 mole ratio in ether solution also following a previously reported procedure.<sup>15</sup> Both compounds were dried under vacuum for several hours prior to analysis. Elemental analysis of the dried products showed a Mg:H ratio of 1.00:2.08 in  $\text{MgH}_2 \cdot 0.09 (\text{C}_2\text{H}_5)_2\text{O}$  and Zn:H ratio of 1.00:2.10 in  $\text{ZnH}_2 \cdot 0.19 (\text{C}_2\text{H}_5)_2\text{O}$ . Zinc hydride slowly began to turn gray after 4 hr. of drying at room temperature but was stable indefinitely at dry ice temperature. For this reason the  $\text{ZnH}_2$  was dried at room temperature for 4 hr. followed by storage at dry ice temperature. Magnesium hydride was stable indefinitely at room temperature.

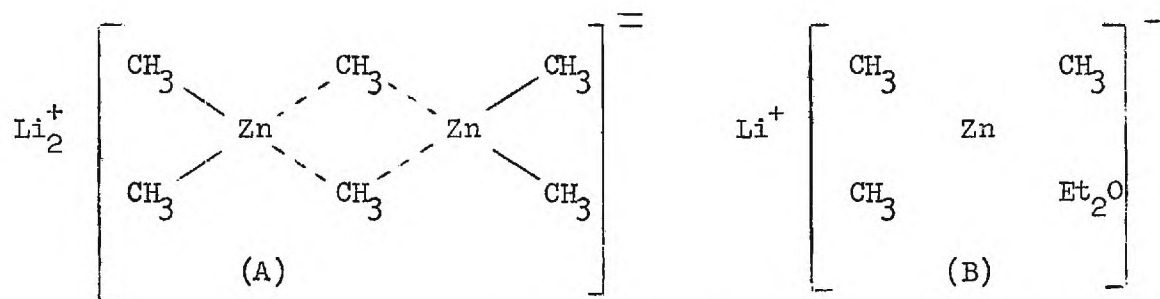
### Results and Discussion

#### Preparation of Magnesium Bis-Trihydrido-zincate $[\text{Mg}(\text{ZnH}_3)_2]$ .

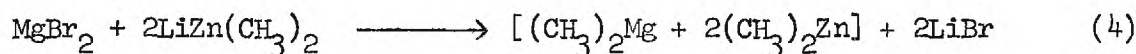
(a) Reaction of  $\text{LiAlH}_4$  with the Product of the Reaction of  $\text{MgBr}_2$  and  $\text{LiZn}(\text{CH}_3)_3$  in 1:2 Mole Ratio. The reaction of  $(\text{CH}_3)_2\text{Zn}$  and  $\text{CH}_3\text{Li}$  in 1:1 mole ratio in diethyl ether yields a clear solution. The infrared spectrum of the resultant solution showed absorption bands at 685 (s), 620 (s), 583 (s), 482 (ms) and  $425 \text{ cm}^{-1}$  (ms). Since the bands at 620 and 425 are not present in either  $\text{CH}_3\text{Li}$  or  $(\text{CH}_3)_2\text{Zn}$ , complex formation is indicated. The band at  $482 \text{ cm}^{-1}$  can be assigned to  $\nu(\text{Li}-\text{CH}_3)$  vibration in  $\text{CH}_3\text{Li}$  and the band at  $583 \text{ cm}^{-1}$  can be assigned to  $\nu_{\text{as}}(\text{Zn}-\text{CH}_3)$  vibration in  $(\text{CH}_3)_2\text{Zn}$  on the basis of assignments already reported in the literature.<sup>16,17</sup> It is therefore, probable that an equilibrium of the following type exists in solution:



The proton chemical shifts of methyllithium and dimethylzinc are 3.08 and 1.78 ppm, respectively upfield from the center of the ether triplet (Table I). The proton spectrum of a mixture of methyllithium and dimethylzinc consists of a single sharp resonance at room temperature as well as at low temperature ( $-86^{\circ}$ ). These results imply either formation of a complex with only one kind of methyl group or a very rapid methyl group exchange involving different species in solution. Although the NMR data obtained at the lowest temperature possible in ether ( $\sim 90^{\circ}$ ) are not definitive; they are consistent with the infrared results indicating an equilibrium (eq. 3). Possible structures for  $\text{LiZn}(\text{CH}_3)_3$  are represented by (A) and (B). Structure (A) is similar to the structure suggested earlier for  $\text{NaZn}(\text{C}_2\text{H}_5)_3$ <sup>18</sup> and structure (B) is similar to the structure reported earlier for similar compounds.<sup>19</sup>

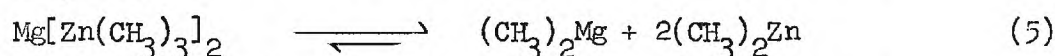


When an ether solution of  $\text{MgBr}_2$  is added in 1:2 ratio to the solution containing  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Zn}$  in 1:2 mole ratio, a metathetical reaction takes place according to eq. 4. The infrared spectrum of the resultant solution (Figure 1) showed bands at

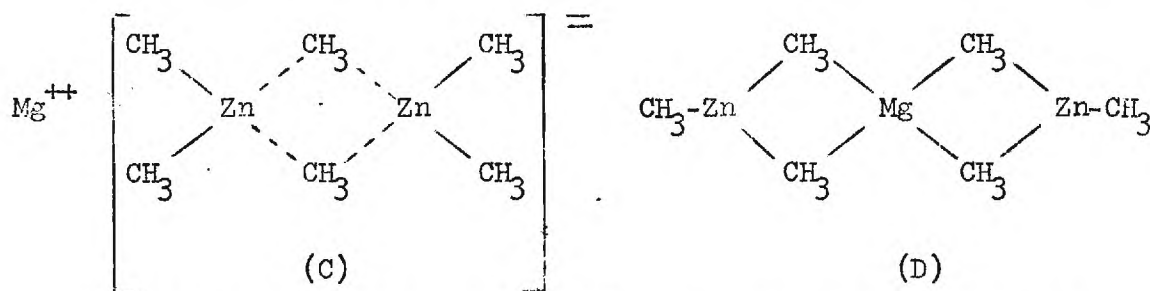


405 (w), 520 (s), 595 (s) and  $685 \text{ cm}^{-1}$  (s). The bands at 520 and  $595 \text{ cm}^{-1}$  can be assigned to  $\nu(\text{Mg}-\text{CH}_3)$  absorption in  $(\text{CH}_3)_2\text{Mg}$  and

$\nu_{as}(\text{Zn-CH}_3)$  absorption in  $(\text{CH}_3)_2\text{Zn}$ , respectively. The proton NMR spectrum of the above solution showed only one singlet at all temperatures indicating either formation of a compound with only one type of methyl group or a rapid exchange involving different species in solution. However, since the infrared spectrum does show two bands corresponding to  $\nu(\text{Mg-CH}_3)$  and  $\nu_{as}(\text{Zn-CH}_3)$  vibrations as found in  $(\text{CH}_3)_2\text{Mg}$  and  $(\text{CH}_3)_2\text{Zn}$ , it is possible that an equilibrium of the type shown in equation 5 exists in solution although no conclusive evidence was noticed for the existence of  $\text{Mg}[\text{Zn}(\text{CH}_3)_2]_2$  in solution. One could obtain a much clearer

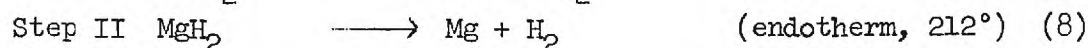
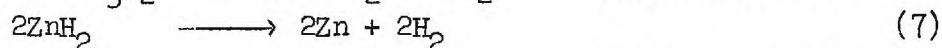
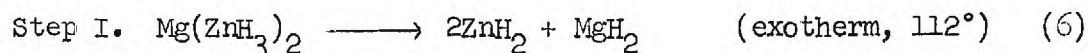


picture of the equilibrium and the structure of  $\text{Mg}[\text{Zn}(\text{CH}_3)_2]_2$  (e.g. C, D) in solution if methyl exchange on the NMR time scale at  $-86^\circ$  was sufficiently slow to observe all of the different types of methyl groups present. Unfortunately this was not the case.

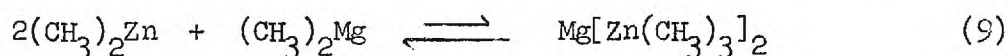


The reaction of  $\text{LiAlH}_4$  with the product of the reaction of  $\text{MgBr}_2$  and  $\text{LiZn}(\text{CH}_3)_3$  in 1:2 mole ratio gave a white solid which exhibited the empirical formula  $\text{Mg}(\text{ZnH}_3)_2$ . The infrared spectrum of the solid showed two broad bands, one at  $400\text{--}650\text{ cm}^{-1}$  and the other at  $1200\text{--}1900\text{ cm}^{-1}$ . The X-ray powder diffraction pattern showed it to be a new compound and not a physical mixture of  $\text{MgH}_2$  and  $\text{ZnH}_2$  (Table II). Non-condensable gas evolution ( $\text{H}_2$ ) during vacuum

DTA-TGA was observed at 112° and 212°. On the other hand, DTA exhibited an endotherm at 88° (loss of ether) followed by an exotherm at 112° (15.26% loss in weight) and an endotherm at 212° (1.19% loss in weight). The first weight loss at 112° is due to loss of ether and evolution of hydrogen gas whereas the second weight loss is due to evolution of hydrogen gas only and corresponds to one mole of hydrogen present in  $\text{Mg}(\text{ZnH}_3)_2$ . Thus the decomposition takes place according to eqs. 6-8 with  $\text{Mg}(\text{ZnH}_3)_2$  dissociating to  $\text{ZnH}_2$  and  $\text{MgH}_2$  at 112° which immediately decomposes to zinc and hydrogen. The decomposition of  $\text{MgH}_2$  then takes place at 212° to magnesium and hydrogen.



(b) Reaction of  $\text{LiAlH}_4$  with the Product of the Reaction of  $(\text{CH}_3)_2\text{Mg}$  and  $(\text{CH}_3)_2\text{Zn}$  in 1:2 Mole Ratio. The reaction of dimethylmagnesium with dimethylzinc in 1:2 mole ratio produces a clear solution. The infrared spectrum of the resultant solution was identical with the spectrum of the solution prepared by the reaction of  $\text{MgBr}_2$  with  $\text{LiZn}(\text{CH}_3)_3$  described previously. Similarly, the proton NMR spectrum of the above solution showed only one sharp single resonance at all temperatures (Table I). Therefore, the identity of the resultant solution can be best described by the equilibrium. Reaction of  $\text{LiAlH}_4$  with the resultant mixture produced

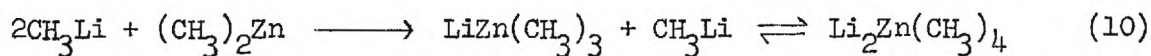


a white solid. The infrared spectrum and X-ray powder diffraction showed it to be  $\text{Mg}(\text{ZnH}_3)_2$ . The vacuum DTA-TGA of this compound was

identical with that obtained for the product of the reaction described earlier where the  $\text{Mg}[\text{Zn}(\text{CH}_3)_3]_2$  was obtained from  $\text{LiZn}(\text{CH}_3)_3$  and  $\text{MgBr}_2$  in 2:1 ratio.

Preparation of Magnesium Tetrahydridoziolate ( $\text{MgZnH}_4$ ). (a)

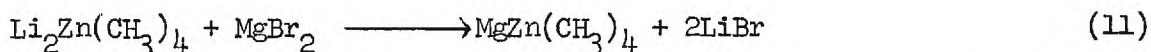
Reaction of  $\text{LiAlH}_4$  and the Product of the Reaction of  $\text{MgBr}_2$  and  $\text{Li}_2\text{Zn}(\text{CH}_3)_4$  in 1:1 Mole Ratio. The infrared spectrum of the solution obtained by stirring a solution of  $\text{CH}_3\text{Li}$  with  $(\text{CH}_3)_2\text{Zn}$  in diethyl ether in 2:1 mole ratio is recorded in Figure 2. The spectrum shows three strong bands at 430, 480 and  $620\text{ cm}^{-1}$ . Although no definite assignment of these bands has been made, the band at  $480\text{ cm}^{-1}$  can be assigned to the Li-C stretching vibration in  $\text{CH}_3\text{Li}$ . The additional bands at 430 and  $620\text{ cm}^{-1}$  are at the same frequency as the two bands attributed to  $\text{LiZn}(\text{CH}_3)_3$ . Therefore, it is probable that the solution consists predominantly of  $\text{CH}_3\text{Li}$  and  $\text{LiZn}(\text{CH}_3)_3$  with possibly a small amount of  $\text{Li}_2\text{Zn}(\text{CH}_3)_4$ . The proton NMR



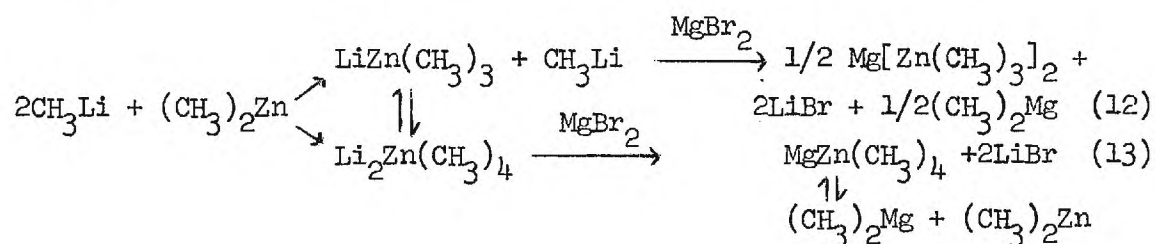
spectrum of the resultant solution showed only one sharp single resonance peak at all temperatures consistent with previously reported observations. This again implies either formation of a complex with only one kind of methyl group or rapid exchange of methyl groups.

The reaction of  $\text{MgBr}_2$  with the reaction product of  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Zn}$  in 2:1 ratio in ether (eq. 10) was carried out in an attempt to effect reaction 11. In spite of the fact that the reaction of  $\text{CH}_3\text{Li}$  with  $(\text{CH}_3)_2\text{Zn}$  in 2:1 ratio does not produce exclusively  $\text{Li}_2\text{Zn}(\text{CH}_3)_4$  (according to infrared spectra) it is still

possible that  $\text{MgZn}(\text{CH}_3)_4$  can be produced in this reaction via a more involved series of steps. The infrared spectrum of the



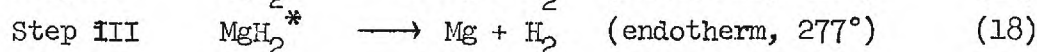
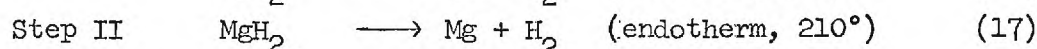
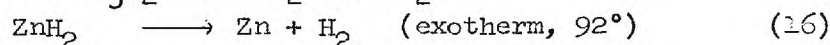
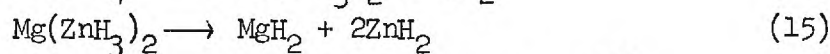
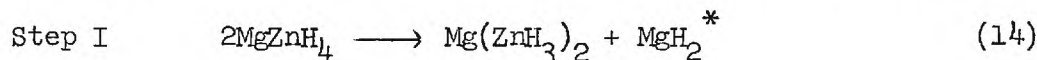
resultant solution showed bands at 400 (m), 516 (s), 585 (ms), and 680  $\text{cm}^{-1}$  (m). The bands at 516 and 585  $\text{cm}^{-1}$  can both be assigned to  $\nu(\text{Mg}-\text{CH}_3)$  absorption in  $(\text{CH}_3)_2\text{Mg}$  or the 516  $\text{cm}^{-1}$  could be assigned to  $\nu(\text{Mg}-\text{CH}_3)$  absorption in  $(\text{CH}_3)_2\text{Mg}$  and the 585  $\text{cm}^{-1}$  band to  $\nu_{\text{as}}(\text{Zn}-\text{CH}_3)$  absorption in  $(\text{CH}_3)_2\text{Zn}$ . The choice in assignment is due to the fact that the 585  $\text{cm}^{-1}$  band is exhibited by both  $(\text{CH}_3)_2\text{Mg}$  and  $(\text{CH}_3)_2\text{Zn}$  and secondly the 585  $\text{cm}^{-1}$  band is weak in  $(\text{CH}_3)_2\text{Mg}$  compared to the 515  $\text{cm}^{-1}$  band whereas it is nearly as strong in the solution formed from the reaction of  $\text{MgBr}_2$  with the reaction product of  $\text{CH}_3\text{Li}$  with  $(\text{CH}_3)_2\text{Zn}$  in 2:1 ratio. Therefore there are two reasonable interpretations of the reaction product in question and they are represented by equations 12 and 13.



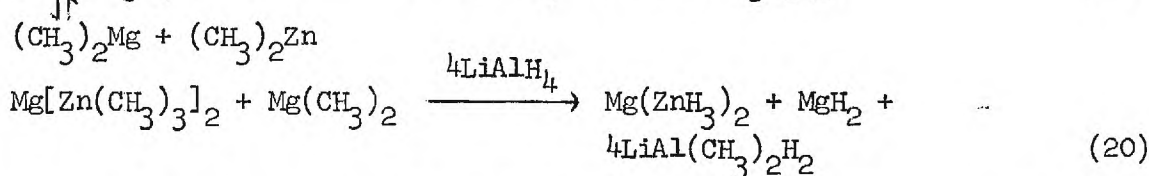
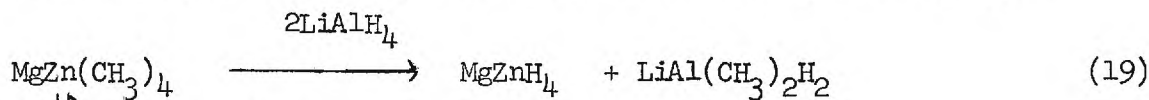
The proton NMR spectrum of the above solution showed only one single sharp resonance peak at all temperatures (Table I) indicating either formation of a complex with only one type of methyl group or a rapid exchange involving different species in solution.

Reaction of  $\text{LiAlH}_4$  with the reaction products produced in reactions 12 and 13 yields an insoluble white compound which exhibited the empirical formula  $\text{MgZnH}_4$ . The infrared spectrum of the solid

showed two broad bands at  $400\text{--}650\text{ cm}^{-1}$  and  $1200\text{--}1900\text{ cm}^{-1}$ . The X-ray powder diffraction pattern showed it to be different from a mixture of  $\text{MgH}_2$  and  $\text{ZnH}_2$  (Table II). The vacuum DTA-TGA of this compound is shown in Figure 3. The first weight loss corresponding to an endothermic change at  $80^\circ$  is due to loss of ether. The second exothermic change at  $92^\circ$  is due to loss of hydrogen gas which is also accompanied by the loss of ether. The third and fourth weight losses at  $210^\circ$  and  $277^\circ$  correspond to the decomposition of  $\text{MgH}_2$  to magnesium and hydrogen according to eqs. 14-18.



The question of course is whether the product is  $\text{MgZnH}_4$  as one would expect from eq. 19 or physical mixture of  $\text{Mg}(\text{ZnH}_3)_2$  and  $\text{MgH}_2$  as would be expected from eq. 20. Since one cannot predict the pre-

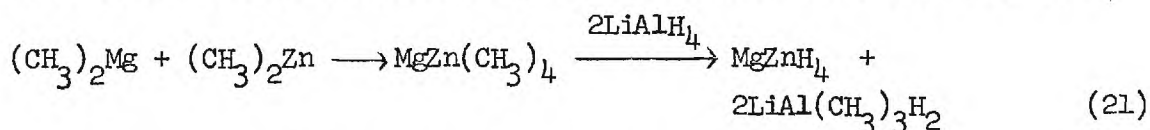


dominant reaction product from a mixture of reactants in equilibrium, it is difficult on the basis of infrared analysis of the reactant mixture to specify either pathway 19 or 20 as the reaction course. The DTA-TGA is consistent with either the formation of  $\text{MgZnH}_4$  followed by disproportionation at  $92^\circ$  to  $\text{Mg}(\text{ZnH}_3)_2$  and  $\text{MgH}_2$  or simply the direct formation of the latter. This distinction

by DTA-TGA is impossible due to the fact that such a proposed disproportionation would be masked by the other proposed transformations taking place at 92°, namely disproportionation of  $\text{Mg}(\text{ZnH}_3)_2$  to  $\text{MgH}_2$  and  $\text{ZnH}_2$  and also decomposition of the  $\text{ZnH}_2$ . Thus it is clear that the first part of Step I is  $\text{MgZnH}_4$  disproportionating to  $\text{Mg}(\text{ZnH}_3)_2$  and  $\text{MgH}_2$  may or may not take place.

On the basis then, by infrared studies of the reactant equilibrium and DTA-TGA studies, it is impossible to say whether the reaction product of  $\text{LiAlH}_4$  with the solution formed from  $\text{MgBr}_2$  and the solution of  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Zn}$  in 2:1 ratio is  $\text{MgZnH}_4$  or a physical mixture of  $\text{Mg}(\text{ZnH}_3)_2$  and  $\text{MgH}_2$ . However, the X-ray powder diffraction comparison appears to be definitive in allowing a selection between the two possibilities. The powder diffraction of the product in question is different than that of a mixture of  $\text{MgH}_2$  and  $\text{ZnH}_2$  and is also quite different from a mixture of  $\text{Mg}(\text{ZnH}_3)_2$  and  $\text{MgH}_2$  (Table II). Since this product has the empirical formula  $\text{MgZnH}_4$  and contains none of the strong X-ray lines due to  $\text{MgH}_2$ ,  $\text{ZnH}_2$  or  $\text{Mg}(\text{ZnH}_3)_2$ , then it must be a single compound of molecular formula  $\text{MgZnH}_4$ .

(b) Reaction of  $\text{LiAlH}_4$  with the Solution Products on Mixing  $(\text{CH}_3)_2\text{Mg}$  with  $(\text{CH}_3)_2\text{Zn}$  in 1:1 Mole Ratio. When an ether solution of dimethylmagnesium is added to an ether solution of dimethylzinc in 1:1 mole ratio, a clear solution results. The desired series of reaction is represented by eq. 21. The infrared spectrum of the



solution produced on mixing  $(\text{CH}_3)_2\text{Mg}$  and  $(\text{CH}_3)_2\text{Zn}$  in 1:1 mole

ratio was identical to the spectrum described earlier obtained for the solution produced on mixing  $\text{MgBr}_2$  with the solution produced on mixing  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Zn}$  in 2:1 ratio. As described earlier for the latter reaction, definitive interpretation of the infrared spectrum is not possible and hence the composition can be represented by either eqs. 12 or 13. The proton NMR spectrum of the clear solution formed in mixing  $(\text{CH}_3)_2\text{Mg}$  with  $(\text{CH}_3)_2\text{Zn}$  in ether in 1:1 ratio showed only one sharp single resonance peak at all temperatures.

Reaction of  $\text{LiAlH}_4$  with the above solutions produced a white solid. The infrared spectrum of the solid was identical with  $\text{MgZnH}_4$  formed in (a) above. The X-ray powder diffraction pattern is listed in Table II. It is surprising to note that the lines do not correspond exactly with the lines observed for  $\text{MgZnH}_4$  prepared in (a). However the lines are quite different from the patterns obtained for either a physical mixture of  $\text{MgH}_2$  and  $\text{ZnH}_2$  or  $\text{Mg}(\text{ZnH}_3)_2$ . It is of course possible that  $\text{MgZnH}_4$  prepared by this method may have a different crystal structure than the product formed in (a). The vacuum DTA-TGA of this compound was identical with  $\text{MgZnH}_4$  formed in (a) and is listed in Table III.

In conclusion,  $\text{MgZnH}_4$  and  $\text{Mg}(\text{ZnH}_3)_2$  were prepared by the reaction of  $\text{LiAlH}_4$  and the magnesium "ate" complexes of zinc in the proper mole ratios. The integrity of these complexes as a single compound rather than a physical mixture of  $\text{MgH}_2$  and  $\text{ZnH}_2$  has been established by their characteristic X-ray powder diffraction patterns.

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Table I. Proton NMR of 'Ate' Complexes.<sup>a</sup>

Reactants	Starting Materials or Expected 'Ate' Complexes	Chemical Shifts (ppm)	
		RT	-86°
	Zn(CH <sub>3</sub> ) <sub>2</sub>	1.78	1.85
	LiCH <sub>3</sub>	3.08	3.27
	Mg(CH <sub>3</sub> ) <sub>2</sub>	2.60	2.82
LiCH <sub>3</sub> + Zn(CH <sub>3</sub> ) <sub>2</sub>	LiZn(CH <sub>3</sub> ) <sub>2</sub>	2.07	2.08
MgBr <sub>2</sub> + 2LiZn(CH <sub>3</sub> ) <sub>2</sub>	2LiBr + Mg[Zn(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	2.00	2.08
2LiCH <sub>3</sub> + Zn(CH <sub>3</sub> ) <sub>2</sub>	Li <sub>2</sub> Zn(CH <sub>3</sub> ) <sub>4</sub>	2.33	2.56
MgBr <sub>2</sub> + Li <sub>2</sub> Zn(CH <sub>3</sub> ) <sub>4</sub>	2LiBr + MgZn(CH <sub>3</sub> ) <sub>4</sub>	2.22	2.28
Zn(CH <sub>3</sub> ) <sub>2</sub> + Mg(CH <sub>3</sub> ) <sub>2</sub>	MgZn(CH <sub>3</sub> ) <sub>4</sub>	2.23	2.33
2Zn(CH <sub>3</sub> ) <sub>2</sub> + Mg(CH <sub>3</sub> ) <sub>2</sub>	Mg[Zn(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>	2.08	2.19

<sup>a</sup> Chemical shifts of methyl protons of the starting materials and the expected 'ate' complexes were measured upfield from the center of the ether triplets. All the methyl resonances were observed as singlets.

Table II. X-Ray Powder Pattern d-Spacing Data

$\text{MgH}_2 \cdot 0.09 \text{Et}_2\text{O}$		$\text{ZnH}_2 \cdot 0.19 \text{Et}_2\text{O}$		$\text{MgH}_2 + \text{ZnH}_2$		$\text{MgZnH}_4 \cdot 0.34 \text{Et}_2\text{O}^a$		$\text{MgZnH}_4 \cdot 0.28 \text{Et}_2\text{O}^b$	
d, A°	I/Io	d, A°	I/Io	d, A°	I/Io	d, A°	I/Io	d, A°	I/Io
3.75	W	4.45	S	4.45	S	4.32	M	1.92	S.br
3.20	S	3.26	M	3.75	W	3.80	M	1.68	S.br
2.50	S	3.12	M	3.26	M	2.95	S		
2.02	VW	2.90	W	3.10	M	2.74	M		
1.67	M	2.78	M	2.82	W	2.67	S		
		2.50	M	2.50	MS	2.42	W		
		2.23	VW	2.18	W	1.74	VW		
		2.17	VW	2.0	W				

$\text{Mg}(\text{ZnH}_3)_2 \cdot 0.76 \text{Et}_2\text{O}^c$		$\text{Mg}(\text{ZnH}_3)_2 \cdot 0.47 \text{Et}_2\text{O}^d$	
d, A°	I/Io	d, A°	I/Io
3.80	S	3.80	S
1.98	S	1.99	S

a.  $\text{Li}_2\text{Zn}(\text{CH}_3)_4 + \text{MgBr}_2 + \text{LiAlH}_4$  in diethyl ether. b.  $(\text{CH}_3)_2\text{Zn} + (\text{CH}_3)_2\text{Mg} + \text{LiAlH}_4$  in diethyl ether. c.  $\text{LiZn}(\text{CH}_3)_3 + \text{MgBr}_2 + \text{LiAlH}_4$  in diethyl ether. d.  $2(\text{CH}_3)\text{Zn} + (\text{CH}_3)_2\text{Mg} + \text{LiAlH}_4$  in diethyl ether.

Table III. Thermal Decomposition of Complex Metal Hydrides of Zinc and Magnesium.

Compound (sample wt. mg)	Thermicity	Range of Transition (peak max.), °C	% Wt. loss
$\text{MgH}_2$ (49.5)	endo	60-180 (120)	5.8 (loss of ether)
	endo	300-390 (345)	6.0
$\text{ZnH}_2$ (40.2)	exo	105	18.4 (loss of ether and hydrogen gas)
<sup>a</sup> $\text{MgZnH}_4$ (52.5)	endo	80	(loss of ether)
	exo	80-112 (92)	10.85 (loss of ether and hydrogen gas)
	endo	170-235 (210)	1.14
	endo	240-305 (277)	0.57
<sup>b</sup> $\text{MgZnH}_4$ (54.7)	endo	90	(loss of ether)
	exo	90-120 (105)	13.71 (loss of ether and hydrogen gas)
	endo	180-230 (210)	1.09
	endo	250-300 (280)	0.73
	endo	88	(loss of ether)
<sup>c</sup> $\text{Mg}(\text{ZnH}_3)_2$ (58.3)	exo	80-130 (112)	15.26
	endo	(170-240) 212	1.19
	endo	90	(loss of ether)
<sup>d</sup> $\text{Mg}(\text{ZnH}_3)_2$ (56.4)	exo	80-130 (112)	20.4 (loss of ether and hydrogen gas)
	endo	165-210 (196)	1.06
$\text{MgH}_2 + \text{ZnH}_2$ (46.8) (1:1 molar ratio)	endo	80	(loss of ether)

Table III. Continued.

Compound (sample wt. mg)	Thermicity	Range of Transition (peak max.), °C	% Wt. loss
	exo	75-120 (95)	18.8 (loss of ether and hydrogen gas)
	endo	260-365 (315)	1.92

a.  $\text{Li}_2\text{Zn}(\text{CH}_3)_4 + \text{MgBr}_2$  b.  $(\text{CH}_3)_2\text{Zn} + (\text{CH}_3)_2\text{Mg} + 2\text{LiAlH}_4$  c.  $2\text{LiZn}(\text{CH}_3)_2 + \text{MgBr}_2 + 3/2 \text{LiAlH}_4$  d.  $2(\text{CH}_3)_2\text{Zn} + (\text{CH}_3)_2\text{Mg} + 3/2 \text{LiAlH}_4$ .

Figure 1. Infrared spectra of ether solutions of (a) ...  $\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{Zn}$  in 1:1 mole ratio, (b) \_\_\_\_\_  $(\text{CH}_3)_2\text{Zn}$ , (c) \_ \_ \_  $\text{CH}_3\text{Li}$ , (d) \_ \_ \_  $(\text{CH}_3)_2\text{Mg} + (\text{CH}_3)_2\text{Zn}$  in 1:2 mole ratio, (e)... $(\text{CH}_3)_2\text{Mg}$  (f) \_\_\_\_\_  $\text{MgBr}_2 + 2$  (solution produced on mixing  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Zn}$  in 1:1 mole ratio).

A

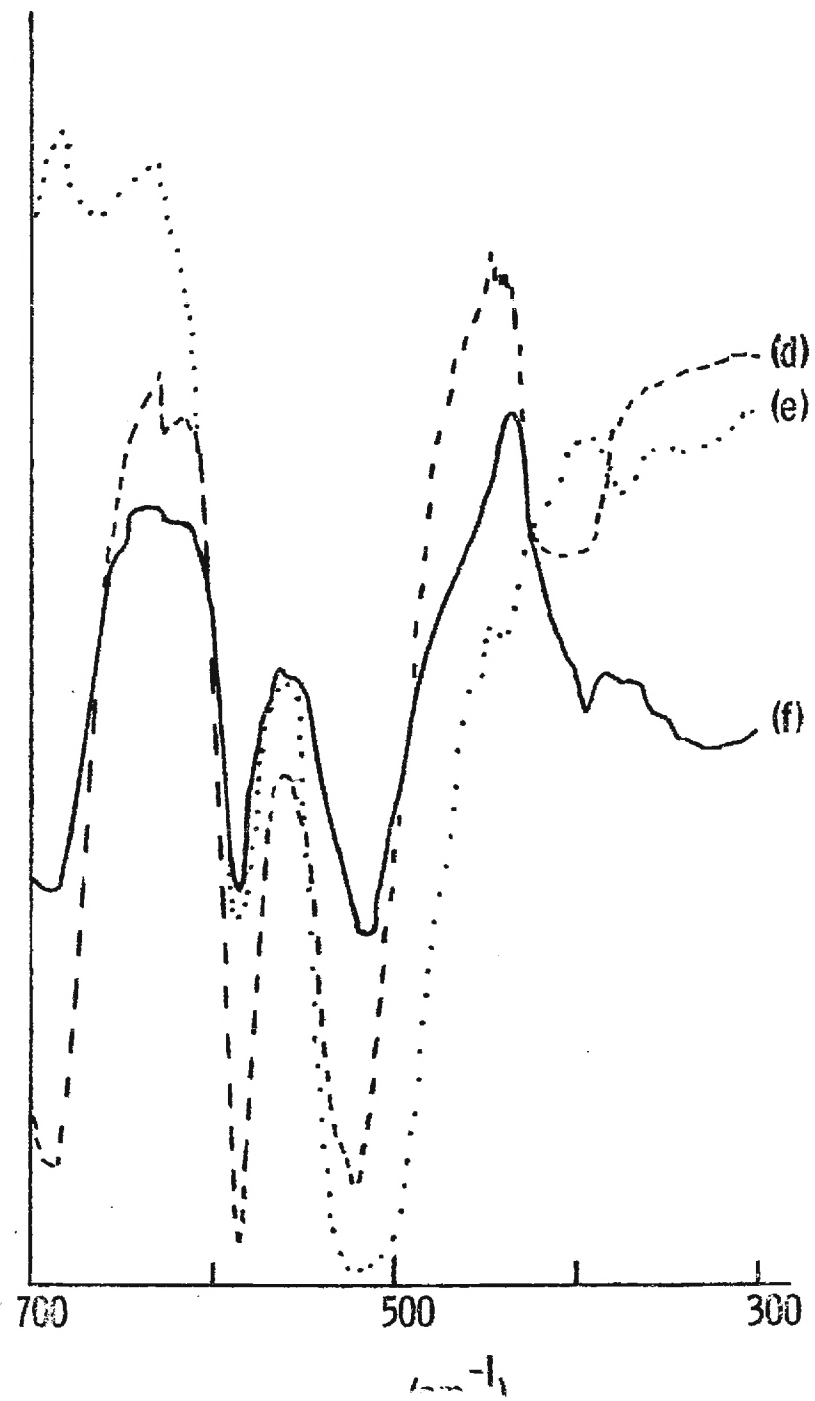
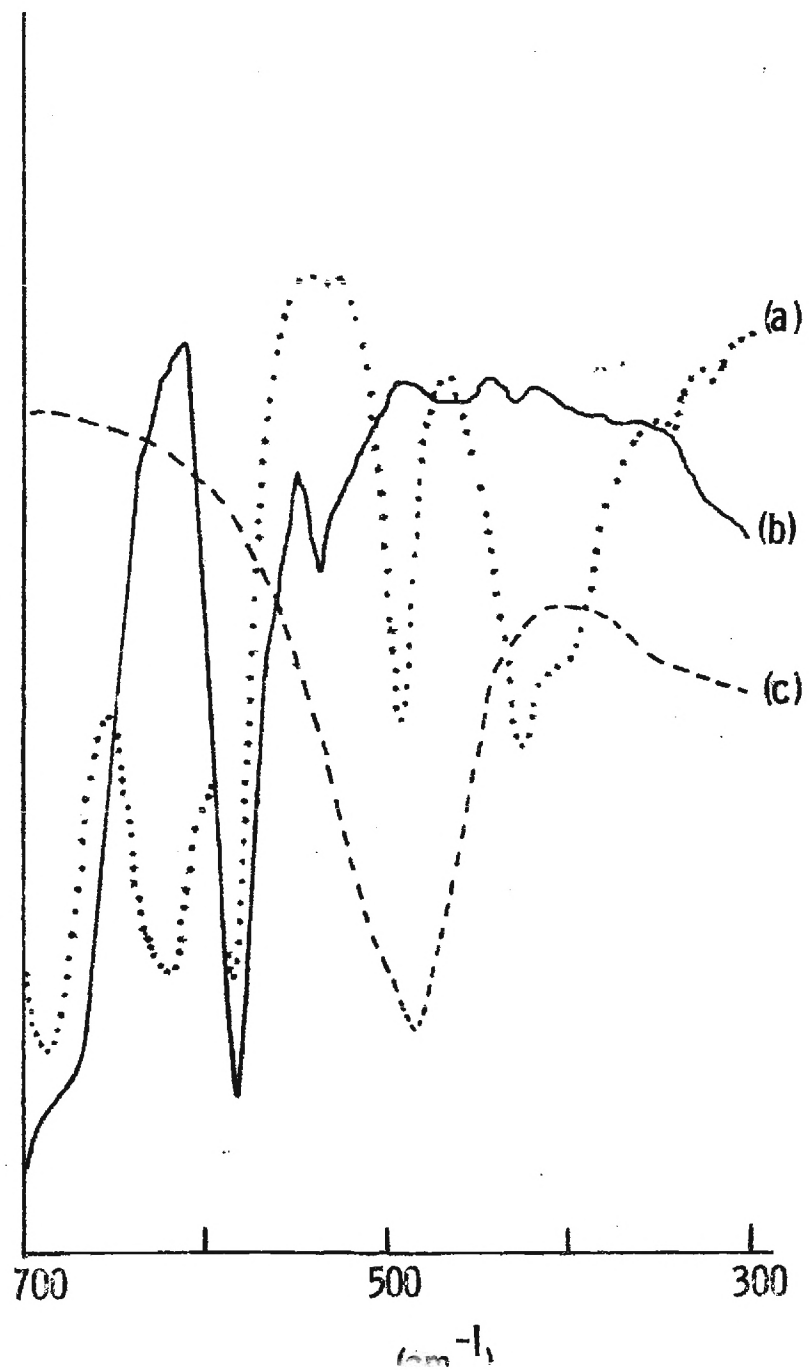


Figure 2. Infrared spectra of ether solutions of: (a) ...  $(\text{CH}_3)_2\text{Mg}$  +  $(\text{CH}_3)_2\text{Zn}$  in 1:1 mole ratio, (b) —  $\text{CH}_3\text{Li}$  +  $(\text{CH}_3)_2\text{Zn}$  in 2:1 mole ratio and (c) — — —  $\text{MgBr}_2$  + solution produced on mixing  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Zn}$  in 2:1 mole ratio.

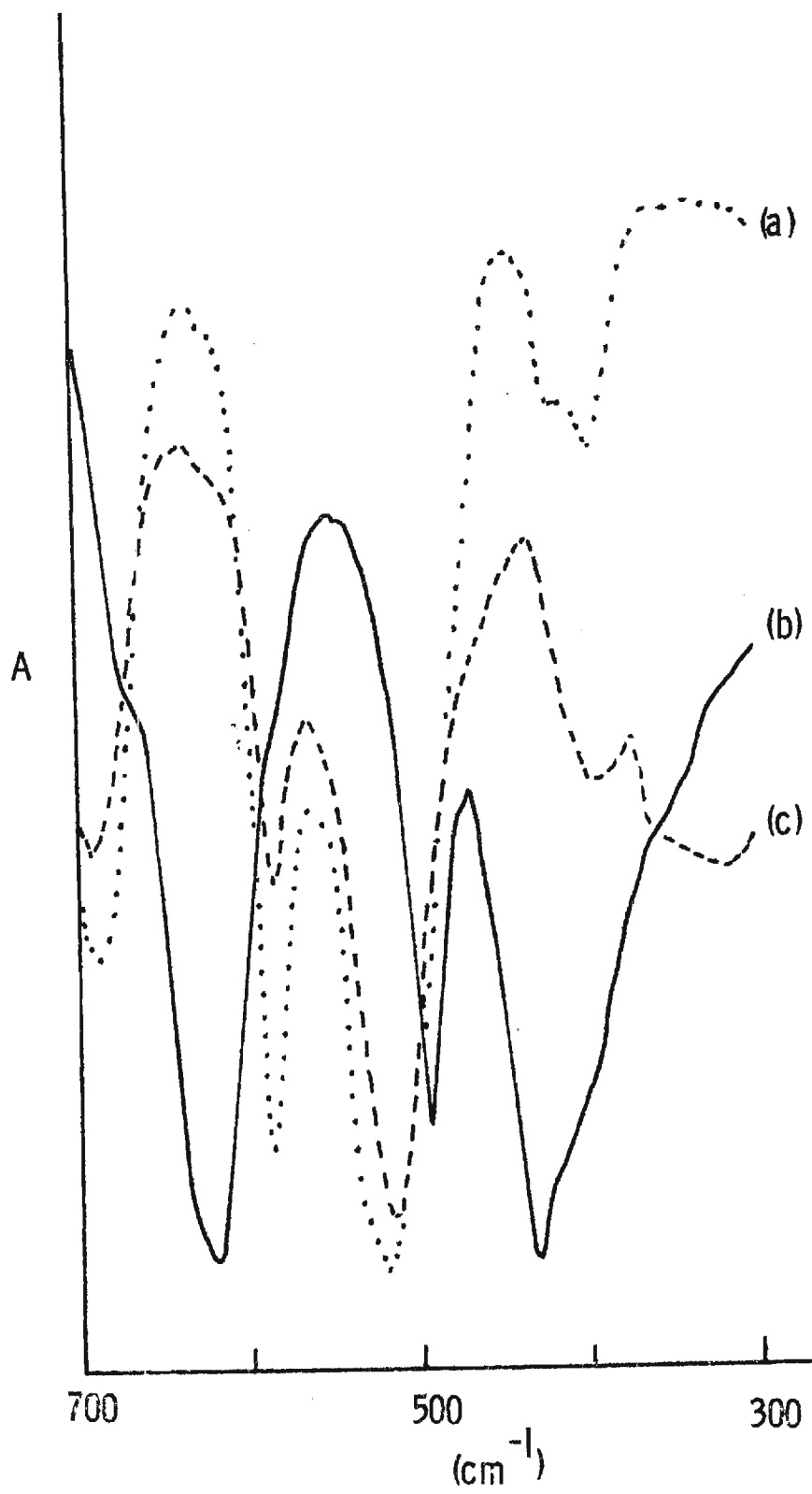
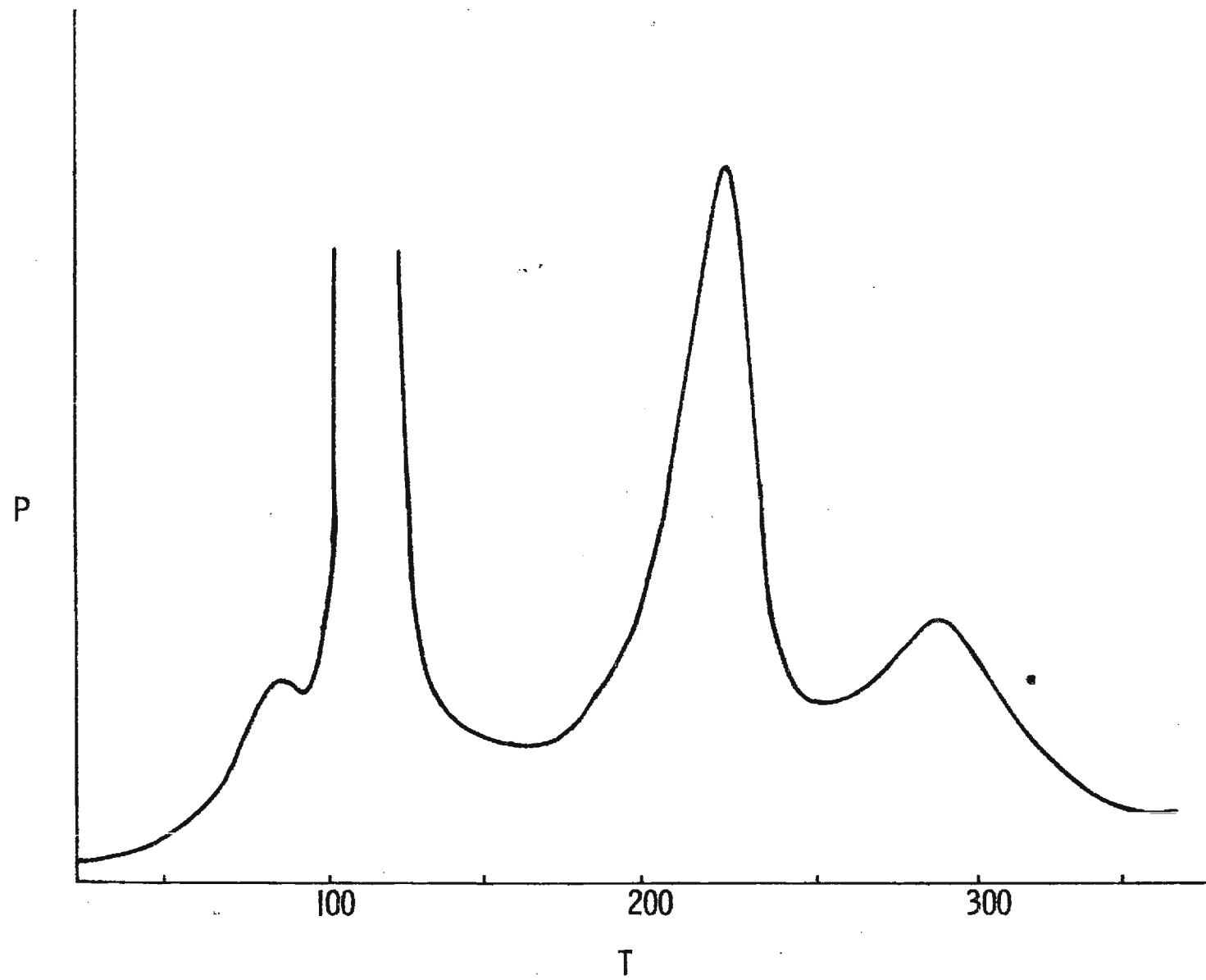


Figure 3. Vacuum DTA-TGA of  $\text{MgZnH}_4$ .



# THE REACTION OF ORGANOMAGNESIUM COMPOUNDS WITH $\text{FeCl}_3$

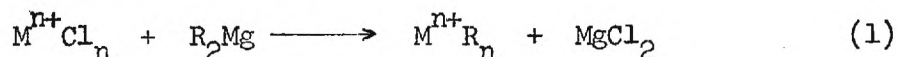
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## Abstract

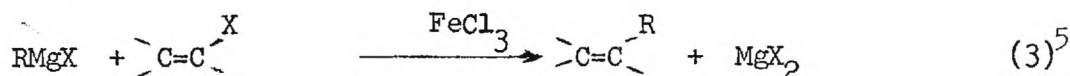
This study deals with obtaining spectroscopic evidence for the existence of certain organotransition metal compounds of the type  $\text{M}^{n+}\text{R}_n$  (where M is Fe, Co, Ni, etc. and R is  $\text{CH}_3$ , Ph,  $\text{Me}_3\text{SiCH}_2$ , neopentyl, etc.). These compounds have been postulated as intermediates in the catalysis of various Grignard reactions.<sup>1-3</sup> First row transition metal compounds with attached alkyl ligands are of particular interest.

Since many transition metal compounds are unstable at ambient temperatures and are paramagnetic, the spectroscopic methods will include low temperature, wide line sweep nmr and low temperature infrared spectroscopy. The compounds of interest will be synthesized in situ by the following general reaction:



## Introduction

It has been postulated that certain alkyl-transition metal derivatives are intermediates in the catalysis of Grignard reactions<sup>1-3</sup>. For example, iron compounds are known to be effective in coupling reactions involving Grignard reagents and organo halides.

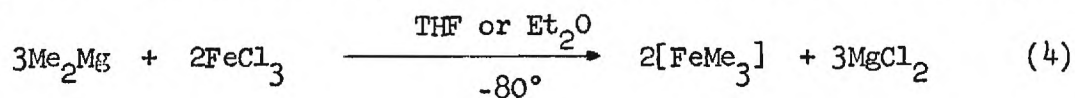


However, relatively few attempts have been made to determine spectroscopically the existence and structure of the transition metal intermediates formed in these reactions.

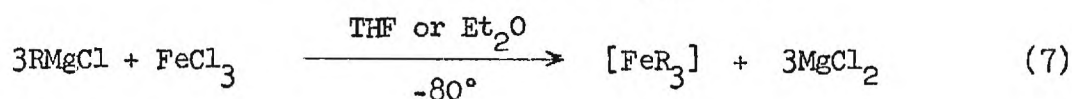
Recently, Lappert and Wilkinson, et. al.<sup>6-8</sup> have demonstrated that the supposed thermodynamic instability of  $\sigma$ -bonded, alkyltransition metal compounds is kinetic in nature. These authors have succeeded in synthesizing a number of organotransition metal compounds whose ligands do not contain a  $\beta$ -hydrogen atom. The compounds are of the type  $M^{n+}R_n$  (where M represents certain transition metals and R is  $Me_3SiCH_2$ ,  $Me_3GeCH_2$ ,  $Me_3SnCH_2$ , etc.) The R group employed by these authors imparts kinetic stability to the molecule by elevating the activation energy for convenient decomposition pathways (e.g.  $\beta$ -hydrogen elimination). For the most part, the compounds completely characterized by these authors are diamagnetic.

The objective of this research project is to develop spectroscopic systems capable of studying both stable and unstable (both paramagnetic and diamagnetic) alkyltransition metal compounds. These systems should be capable of establishing both the molecular structure of the products and stoichiometry of the reactions.

It is felt that low temperature, wide-line sweep, nmr spectroscopy combined with low temperature infrared spectroscopy offer the most promising spectroscopic tools to study these systems. Examples of specific systems investigated during this study are the following:



Where R represents  $(\text{CH}_3)_3\text{SiCH}_2$



An attempt was made to obtain evidence for each of the intermediate iron-alkyl species. The Grignard reagents were prepared by the appropriate standard methods.

Low Temperature, Wide-Line Sweep NMR Spectroscopy of Paramagnetic Compounds. Under most circumstances, the effect of a paramagnetic central metal on a hydrogen containing ligand is to broaden the proton resonance through relaxation effects. In certain cases, the broadening precludes the observation of a resonance signal. In any case, large chemical shifting of the signal occurs. This is shown by the proton resonance spectrum of the paramagnetic complex formed between Ni(II) and ethylene diamine as given in Figure 1.

It is felt that the magnitude of the chemical shift for the ligand should give some comparative indication of the number of unpaired electrons surrounding the paramagnetic central metal atom (for identical ligands on a central metal atom of different oxidation states). Thus, a speculation as to the comparative oxidation state of the central metal can be made.

More specifically, in the case of  $\text{Fe}^{+3}$  and certain other transition metals, electronic relaxation times are characteristically long and thus the nuclear resonances may be broadened to an extent that detection and particularly resolution become extremely difficult.<sup>9</sup> It should be pointed out however, that electronic relaxation times are somewhat poorly understood, at least in detail and that the strengths and symmetries of ligand fields and covalent bonding can profoundly

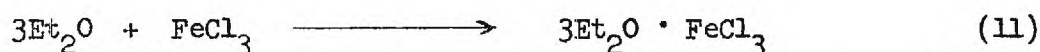
influence electronic relaxation times in rather unpredictable fashions. Each particular chelate or coordination compound of a transition metal may thus become a special case that must be examined separately.<sup>10</sup>

Low Temperature Infrared Spectroscopy. The region  $650\text{ cm}^{-1}$  to  $180\text{ cm}^{-1}$  will be examined for the presence of M-C asymmetric stretching (where M is a first row transition metal), indicative of the presence of alkyl transition metal compounds. This region will be examined using low temperature, polyethylene solution cells. Any absorbance in this region can be related to the concentration of the alkyl-transition metal compound present and thus some idea as to the stoichiometry of the reaction and the oxidation state of the metal can be established.

#### Experimental

Diethyl ether ( $\text{Et}_2\text{O}$ ) and tetrahydrofuran (THF) were investigated as solvents for  $\text{FeCl}_3$  and  $\text{FeCl}_2$  (solutions of which were to be used in low temperature nmr and infrared studies).

Preliminary results indicated that  $\text{Et}_2\text{O}$  is a better solvent for  $\text{FeCl}_3$  at room temperature. Neither solvent dissolved  $\text{FeCl}_2$  to a satisfactory extent. Evidence was obtained for adduct formation between  $\text{FeCl}_3$  and both THF and  $\text{Et}_2\text{O}$  at room temperature. The following exothermic reactions are believed to occur.



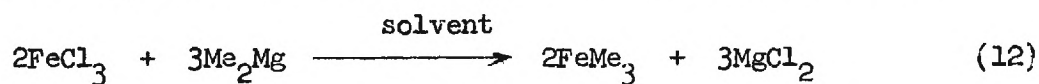
This behavior is analogous to that of  $3\text{THF} \cdot \text{CrCl}_3$ <sup>11</sup> and  $2\text{THF} \cdot \text{TiCl}_4$ <sup>12</sup> as reported in the literature.

The ambient temperature proton nmr spectra for  $\text{Et}_2\text{O}$ , THF and solutions of  $\text{Et}_2\text{O} \cdot \text{FeCl}_3$  and  $\text{THF} \cdot \text{FeCl}_3$  are given in Figures 2 -5,

respectively, using a 100 MHz spectrophotometer. The respective chemical shifts, peak areas and base line widths are given in each figure for comparison. The interpretation of paramagnetic broadening in these spectra gives evidence for adduct formation between  $\text{FeCl}_3 \cdot 3\text{THF}$  and  $\text{FeCl}_3 \cdot 3\text{Et}_2\text{O}$ .

### Results

The spectroscopic systems are now functioning. Preliminary results indicated that the proton nmr resonance of the intermediate iron-alkyl species in the following systems are not observable with low temperature, wide line nmr techniques. The considered reasons

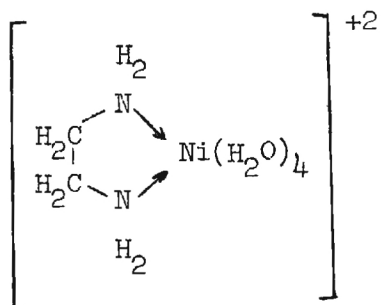


are that the alkyl compounds present in solutions of  $\text{Et}_2\text{O}$  and THF are either insoluble or that their resonances are obscured due to paramagnetic broadening. Low temperature infrared analysis should answer these questions as paramagnetic effects are not operable in the infrared.

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Figure 1.  $^1\text{H}$  Resonance Spectrum of an Aqueous Solution of a 1:1 Complex of  $\text{Ni(II)}$  and Ethylene Diamine at 56.4 MHz.<sup>13</sup>



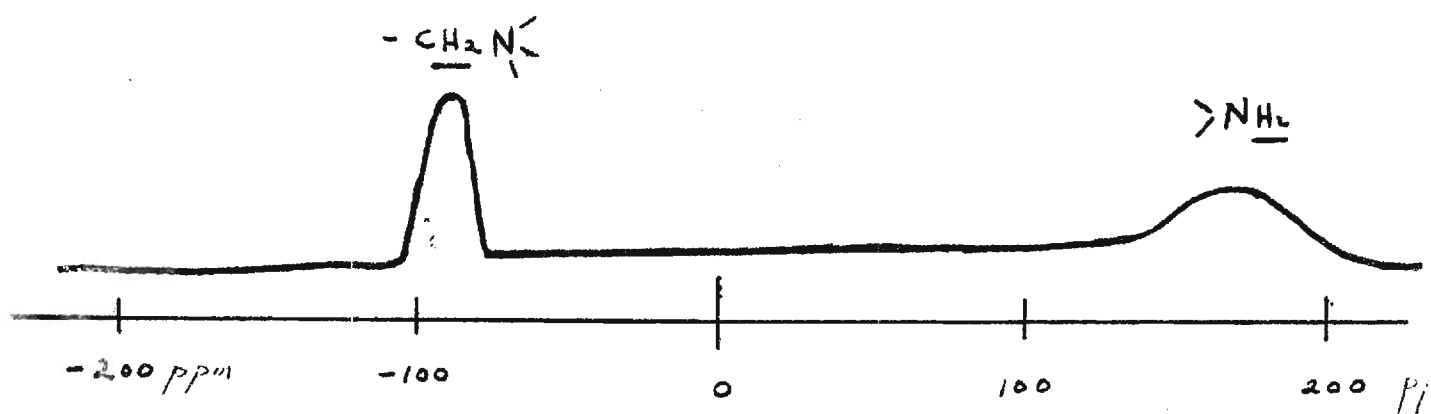


Figure 2.  $^1\text{H}$  NMR Spectra for Diethyl Ether ( $\text{Et}_2\text{O}$ )

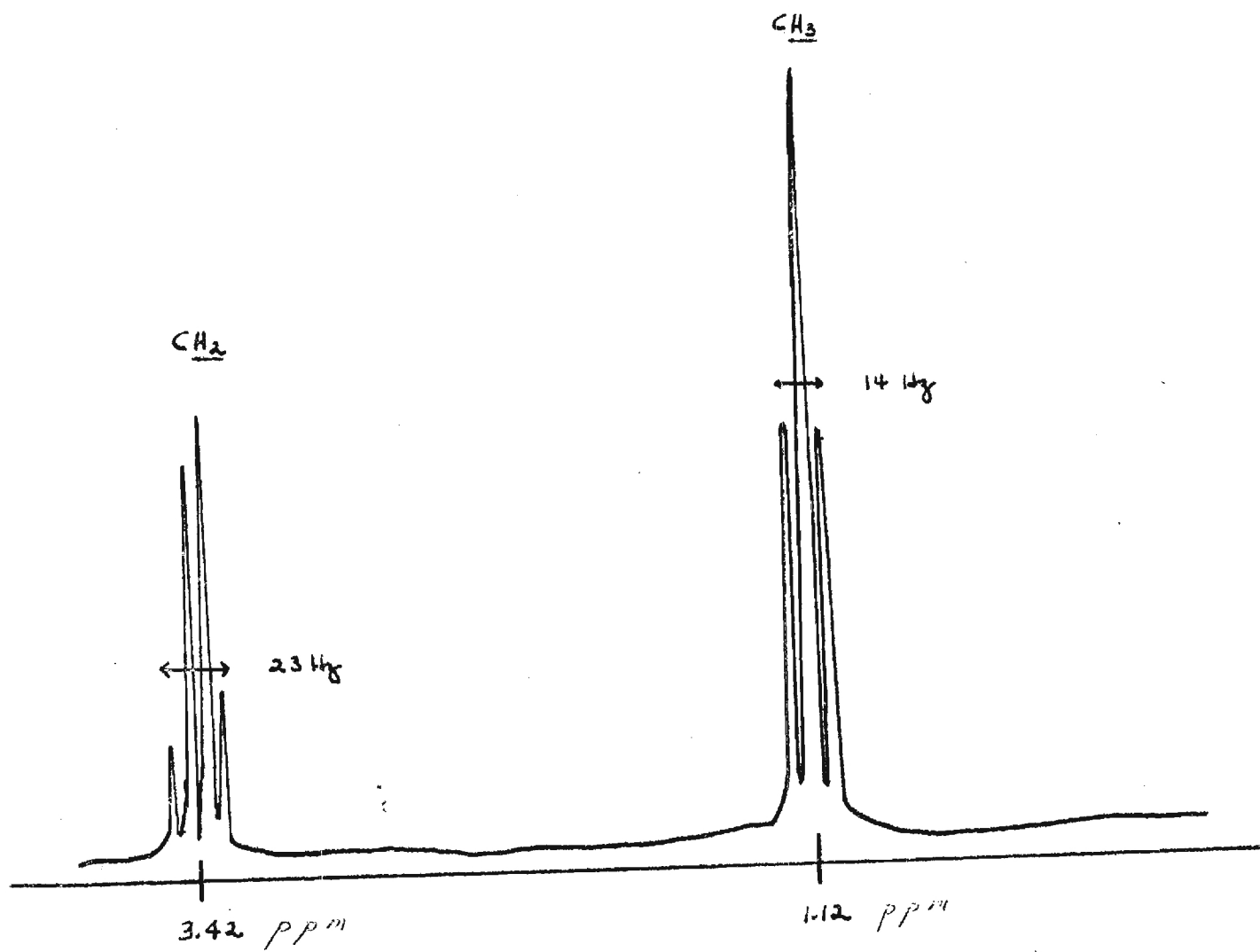


Figure 3.  $^1\text{H}$  NMR Spectrum for Tetrahydrofuran (THF).

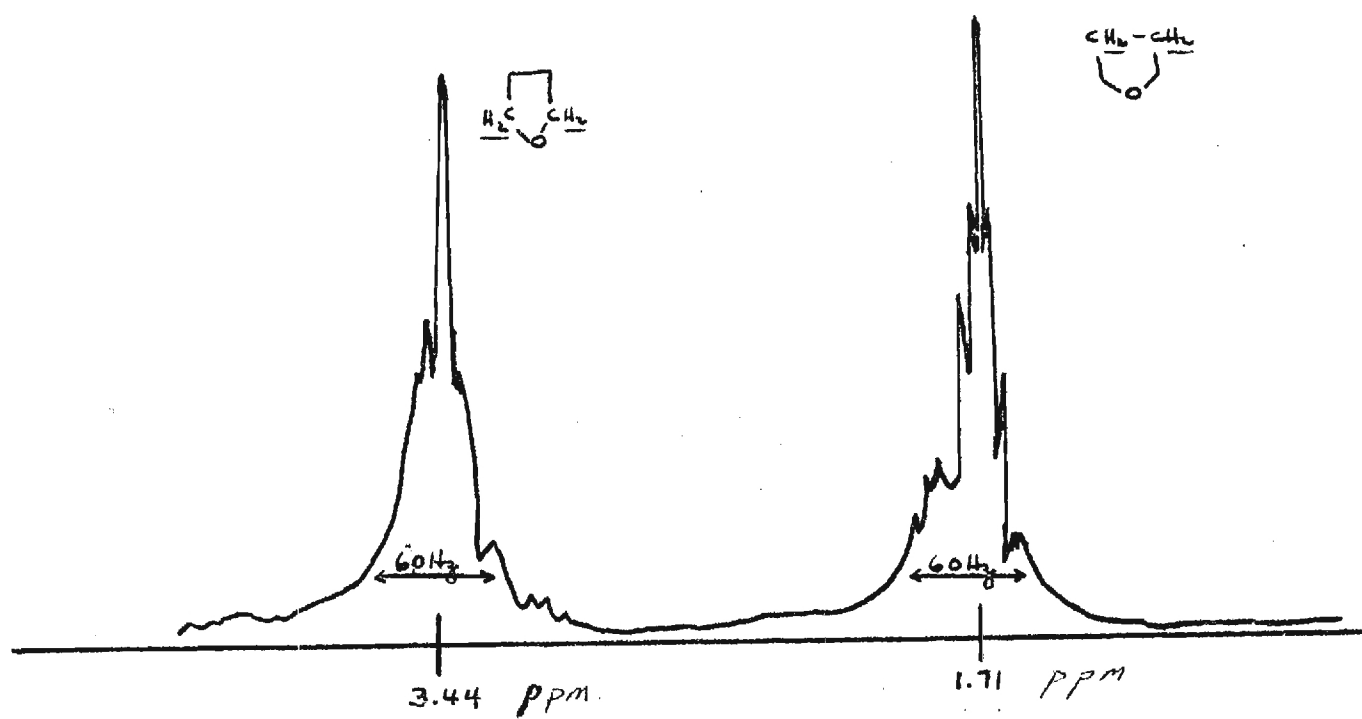


Figure 4.  $^1\text{H}$  NMR Spectrum for a Solution of  $\text{Et}_2\text{O}$  and  $\text{FeCl}_3$ .

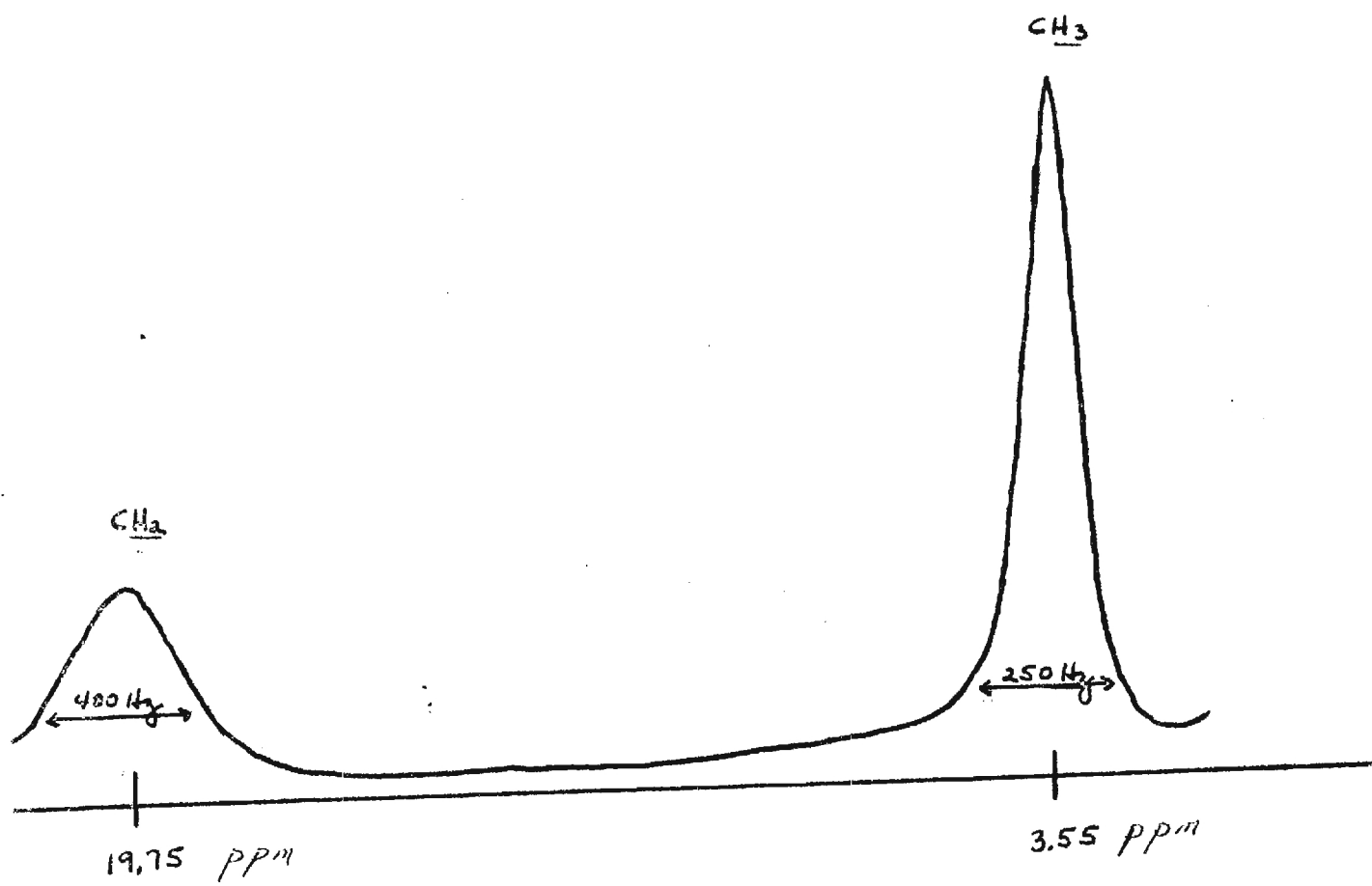
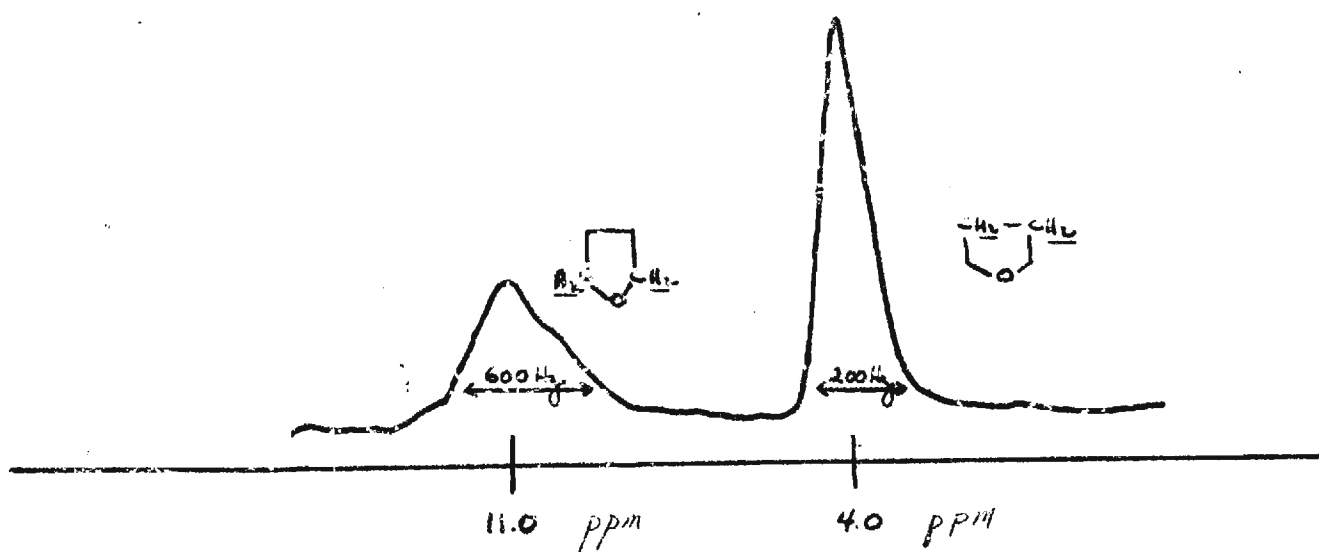


Figure 5.  $^1\text{H}$  NMR Spectrum for a Solution of THF and  $\text{FeCl}_3$ .



# REACTIONS OF $\text{LiCu}(\text{CH}_3)_2$ WITH MAGNESIUM BROMIDE AND DIMETHYLMAGNESIUM

## ATTEMPTED PREPARATION OF $\text{Mg}(\text{CuH}_2)_2$ .

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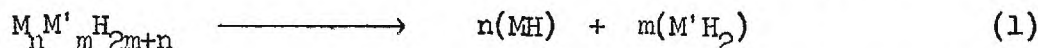
### Abstract

The reaction of  $\text{LiCu}(\text{CH}_3)_2$  with magnesium bromide in diethyl ether yielded a yellow solid of empirical formula  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$ . In dilute solution this complex was found to dissociate into methylcopper and a soluble complex with a composition corresponding to the formula  $\text{MgCu}(\text{CH}_3)_3$ . The proton nmr spectra of diethyl ether solutions of  $\text{LiCu}(\text{CH}_3)_2$  and  $\text{MgBr}_2$  in 2:1, 3:1, and 4:1 molar ratio have been obtained at low temperature ( $-91^\circ$ ). The spectra show that there is either a rapid exchange of methyl groups between  $\text{LiCu}(\text{CH}_3)_2$  and  $(\text{CH}_3)_2\text{Mg}$  or complex formation,  $\text{LiMg}[\text{Cu}(\text{CH}_3)_2]_3$ . The reaction of methylcopper with  $\text{MgBr}_2$  and  $(\text{CH}_3)_2\text{Mg}$  was investigated as a possible route to the formation of soluble "ate" complexes of copper and magnesium. Methylcopper is found to form an adduct with magnesium bromide whereas there is no reaction of methylcopper with dimethylmagnesium. Attempts have been made to prepare  $\text{Mg}(\text{CuH}_2)_2$  by the reaction of  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$  and  $\text{LiAlH}_4$  and by the reaction of  $\text{LiCuH}_2$  with  $\text{MgBr}_2$ . The reaction product was found to be unstable at room temperature and possibly, contained more than one product.

### Introduction

Recently we have reported the synthesis of complex metal hydrides of zinc<sup>1</sup>, magnesium<sup>2,3</sup> and beryllium.<sup>4</sup> The preparation of these compounds involved the reduction of an "ate" complex  $(\text{M}_n\text{M}'_m\text{R}_{2m+n})$

with either  $\text{LiAlH}_4$  or  $\text{AlH}_3$ . From the studies of these complex metal hydrides, we have found that the stability of the hydrides to disproportionation (eq. 1) is related to the electronegativity of M



and M'. Thus far it has been observed that if M is more electropositive than M', the resulting complex metal hydride is stable. Since magnesium has an electronegativity of 1.2 and copper 1.9, we decided to study the "ate" complexes of the type  $\text{M}_n \text{M}'_m (\text{CH}_3)_{2m+n}$  and prepare complex metal hydrides of the type  $\text{M}_n \text{M}'_m \text{H}_{2m+n}$ . Since we succeeded in preparing the first stable complex metal hydrides of copper,  $\text{LiCuH}_2^5$  by the reduction of  $\text{LiCu}(\text{CH}_3)_2$  with  $\text{LiAlH}_4$  in diethyl ether, this route has become the method of choice in preparing the "ate" complexes involving magnesium and copper metals and hence the corresponding complex metal hydrides.

In this report, we describe the preparation of  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]$  and the attempts made to synthesize  $\text{Mg}(\text{CuH}_2)_2$ . The reaction of methylcopper with  $\text{MgBr}_2$  and  $(\text{CH}_3)_2\text{Mg}$  has been also investigated as a possible route to soluble "ate" complexes of magnesium and copper. The system  $\text{LiCu}(\text{CH}_3)_2/\text{MgBr}_2$  in diethyl ether was studied by proton nmr spectroscopy in order to define the composition of the "ate" complex in solution.

### Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and moisture<sup>6</sup> or on the bench top using typical Schlenk tube techniques.<sup>7</sup>

Instrumentation. Proton nmr spectra were obtained at 60 MHz using

a Varian A60 spectrometer. The low temperatures were obtained using the standard low temperature accessories supplied by Varian Associates.

Analytical Procedures. Gas analyses were carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Copper was analyzed by electro-deposition of copper onto a platinum electrode. Magnesium and aluminum analyses were carried out by compleximetric titration with EDTA. Analysis for bromine was carried out using a modified Volhard procedure. Analysis for carbon-bonded and oxygen-bonded metals was carried out by the Watson-Eastham<sup>8</sup> method using 2,2'-biquinoline and phenolphthalein indicators.

Materials. Diethyl ether (Fisher anhydrous ether) was distilled over  $\text{LiAlH}_4$  immediately prior to use. Benzene (Fisher certified reagent) and hexane (olefin free) were distilled over sodium aluminum hydride. Lithium aluminum hydride was obtained as a gray powder from Ventron, Metal Hydrides Division. Solutions of  $\text{LiAlH}_4$  in diethyl ether was prepared by the method reported earlier.<sup>9</sup> Cuprous iodide was purified according to a previously described procedure.<sup>10</sup> Similarly, cuprous bromide was prepared by the method described in literature.<sup>11</sup>

Lithium dispersion (30%) in petrolatum was purchased from Ventron, Alfa Products. Methyl sulfide and iodobenzene were obtained from Eastman Organic Chemicals. Iodobenzene was further purified by distillation at reduced pressure. Methyl chloride (99.5% pure) was purchased from Matheson Gas Products. *n*-Butyllithium was obtained from Foote Mineral Company and stored at  $-20^\circ$  until ready to use. An ether solution of  $\text{MgBr}_2$  was prepared by the method described previously.<sup>12</sup>

Preparation of Halide-Free Methyllithium from Methyl Chloride and Lithium Dispersion. About 9.2 g (2.76 g of Li, 0.397 mole) sample of 30% lithium dispersion in petrolatum (Na 2% of Li, Alfa) was weighed into a 500 ml flask, and approximately 200 ml of hexane was added. The petrolatum was stirred for 30 minutes until it was dispersed evenly into hexane. It was then filtered through a glass fritted funnel inside the glove box, always keeping the lithium suspension under the solvent. It was washed with additional hexane (200 ml), rinsed with dry ether and finally transferred into a one liter 3-necked flask as shown in Figure 1. 500 ml of dry ether was then transferred into the flask and the flask was taken outside the glove box with its mouth closed with stoppers. The flask was then attached to a high speed stirrer (Dumore) and a flame-dried dry ice-acetone condenser. The third neck was fitted with a rubber serum stopper. About 10 ml (0.182mole) of pre-condensed methyl chloride was then transferred via a cannula into the stirred lithium suspension over a period of 30 minutes. The  $\text{CH}_3\text{Cl}$  addition was begun at 25°, but shortly thereafter the reaction flask was immersed in an ice bath. As the amount of  $\text{CH}_3\text{Cl}$  to be added became just a few ml, the ice bath was removed. After the addition was complete, the reaction mixture (brown colored suspension with a small amount of lithium floating on top) was stirred for 4 hours at room temperature and then allowed to stand and settle overnight inside the refrigerator. The supernatant solution was then filtered inside the glove box through a glass fritted funnel. The clear filtrate was analyzed for chloride, total base and residual base. The solution was found to be 0.647 M in  $\text{CH}_3\text{Li}$  (0.690 M total base, 0.043 residual base) and

halide ion concentration was found to be 0.0216 M (5% of the  $\text{CH}_3\text{Li}$  concentration).

Preparation of Halide Free Phenyllithium. 40 ml of dry benzene was added to a flame dried 500 ml round bottomed flask containing a magnetic bar and its mouth closed with a serum stopper. The iodobenzene (23.7 g, 0.116 mole) was weighed out in a syringe on the Mettler balance requiring ca. 12.9 ml. The  $\text{n-BuLi}$  72 ml (1.61 M, 0.116 mole), was then added slowly to the reaction flask via syringe. A flocculant white precipitate of phenyllithium formed shortly after the initial addition of  $\text{n-butyllithium}$ . The resulting thick white slurry was stirred for 30 minutes after the complete addition of  $\text{n-BuLi}$ . The flask was then transferred to the glove box and the solid was filtered through a glass fritted funnel. The white solid was washed with hexane several times and then transferred into a 500 ml flask fitted with a serum stopper. It was taken out of the glove box, dissolved in cold (dry ice) ether and purified by crystallizing the white solid from ether at  $-78^\circ$ . The crystallization was done twice by syringing out the mother liquor and redissolving the solid in fresh cold ether. The solution was clear and colorless. Analysis of the solution gave total base 0.893 M and 0.028 residual base. The halide ion concentration was found to be 0.7%.

Preparation of  $\text{Br-Cu}[(\text{CH}_3)_2\text{S}]_2$ . About 40 g of freshly prepared cuprous bromide was dissolved in excess methyl sulfide with stirring and the solution filtered. Hexane was added dropwise to the clear filtrate until crystals started to separate. After crystallization was complete, the crystals were filtered, washed with hexane and dried

under high vacuum for 24 hours.

Reactions of  $\text{LiCu}(\text{CH}_3)_2$  and  $\text{MgBr}_2$ . A. Attempted preparation of  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$ . To a slurry of  $\text{CuI}$  (14.75 mmol) in diethyl ether (150 ml), 29.5 mmol of methyllithium was added slowly at  $-78^\circ$ . The color of the slurry changed to yellow separating some yellow solid of methylcopper which redissolved on further addition of methyllithium. After complete addition of methyllithium the resultant solution was stirred for one hour followed by addition of magnesium bromide (7.37 mmol) in ether. The resultant mixture remained clear until near the end of magnesium bromide addition when a yellow solid started to precipitate. The reaction mixture was stirred for another hour, allowed to settle at  $-78^\circ$  and then washed with cold ether several times withdrawing the supernatant liquid with a syringe. The elemental analysis of the slurry showed methane:Cu in the ratio of 1.00:1.06 and negligible amounts of magnesium and lithium. The yellow solid decomposed turning black when it was allowed to warm up to room temperature. The elemental analysis of the wash liquid showed approximately 50% of the total copper (7 mmole) and 100% (7.0 mmol) of magnesium.

B. Preparation of  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$ . To a slurry of  $\text{CuI}$  (2.42 mmol) in diethyl ether (10 ml), 4.84 mmol of methyllithium was added slowly at  $-78^\circ$ . The mixture was stirred for one hour till the solution became clear and colorless. 1.21 mmol of magnesium bromide was then added dropwise with stirring when a yellow solid precipitated. The resultant mixture was stirred for another hour and the solvent was partially removed under vacuum at  $-50^\circ$  to  $-60^\circ$ . The low temperature proton nmr spectrum of the supernatant liquid showed the absence

of signals due to methyl protons. When the yellow solid was allowed to warm to room temperature, it did not show any appreciable change of color (from yellow to black) during 3 hours warming. Elemental analysis of the reaction product showed methane:Cu:Mg in the ratio of 3.05:2.25:1.26. The elemental analysis indicates 100% recovery of magnesium and copper.

Reaction of  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$  and  $\text{LiAlH}_4$ . Attempted Preparation of  $\text{Mg}(\text{CuH}_2)_2$ . A. To a clear solution of  $\text{LiCu}(\text{CH}_3)_2$  (11.56 mmol) in diethyl ether at  $-78^\circ$  prepared by the method described earlier, an ether solution of magnesium bromide (5.78 mmol) was added rapidly followed by immediate addition of  $\text{LiAlH}_4$  (11.56 mmol) in diethyl ether. The color of the resultant mixture changed to yellowish brown. The mixture was first stirred at  $-78^\circ$  for one hour and then at  $20^\circ$  for another hour. The mixture was then allowed to settle, the supernatant liquid removed by syringe and the solid washed several times with dry ether. Elemental analysis of the solid slurry showed Mg:Cu:H in the ratio of 0.917:0.604:1.155. Analysis of wash liquid showed only 6.8% of the total copper. The yellow solid slowly turned black when it was allowed to stand at room temperature overnight.

B. To a slurry of CuI (9.8 mmol) in diethyl ether (10ml) at  $-78^\circ$  was added slowly 19.6 mmol of methyllithium. The mixture was stirred for one hour during which time the solution became clear and colorless. 4.9 mmol of magnesium bromide solution in ether was then added to the resultant solution when a yellow solid precipitated. The mixture was stirred for one hour at  $-78^\circ$  and ether was partially removed under vacuum at  $-60^\circ$ . The low temperature

proton nmr spectrum of the supernatant liquid showed the absence of a resonance peak due to methyl protons. The thick slurry of yellow solid was cooled to  $-78^{\circ}$  and 4.9 mmol of  $\text{LiAlH}_4$  in ether added slowly. The color of the reaction mixture rapidly changed from yellow to dark brown to black. The mixture was stirred for 3 hours and allowed to settle at  $-78^{\circ}$ . The low temperature proton nmr spectrum of the supernatant liquid showed one single resonance peak at 2.33 ppm upfield from the ether triplet. The elemental analysis of the liquid showed Mg:Cu:methane in the ratio of 0.771:0.08:2.28 with a large amount of lithium. The solid was washed with ether several times and analyzed for lithium, magnesium, copper and hydrogen. Analysis of the solid slurry showed Li:Mg:Cu:H in the ratio of 0.27:0.151:0.229:0.476.

Reaction of  $\text{LiCuH}_2$  and  $\text{MgBr}_2$ . Attempted Preparation of  $\text{Mg}(\text{CuH}_2)_2$ .

To a solution of  $\text{LiCu}(\text{CH}_3)_2$  (3.94 mmol) in diethyl ether at  $-78^{\circ}$  (prepared by the reaction of  $\text{CuI}$  and methyllithium described earlier) was added slowly 3.94 mmol of  $\text{LiAlH}_4$  in diethyl ether. The resultant clear yellow solution was stirred for one hour at  $-78^{\circ}$  and then allowed to warm to room temperature.  $\text{LiCuH}_2$  precipitated as yellow solid which settled to the bottom of the flask. It was washed several times with ether by decantation using a syringe. To the slurry of  $\text{LiCuH}_2$  in ether at  $-78^{\circ}$  was added slowly 1.97 mmol of magnesium bromide in ether and the mixture stirred for eight hours at room temperature. The resulting solid was washed with ether several times and analyzed. The elemental analysis showed Li:Mg:Cu:H in the ratio of 0.176:0.484:0.505:1.354.

In a separate experiment,  $\text{LiCuH}_2$  was prepared as described earlier

and the reaction was performed exactly the same way except that the reaction mixture ( $2\text{LiCuH}_2 + \text{MgBr}_2$ ) was stirred for 3 days at  $-78^\circ$ . The resultant yellow solid was washed with ether and the slurry was analyzed for Li, Mg, Cu and hydrogen. Elemental analysis showed Li:Mg:Cu:H in the ratio of 0.583:0.82:1.463:3.179.

Attempted Preparation of  $\text{LiCu}(\text{C}_6\text{H}_5)_2$ . A. To a slurry of CuI (4.56 mmol) in diethyl ether (50 ml) at  $-78^\circ$ , 9.12 mmol of freshly prepared phenyllithium in diethyl ether was added slowly. After complete addition of phenyllithium the temperature of the bath was raised to  $0^\circ$  and the mixture was stirred for one hour. The color of the solution gradually turned to green and it turned completely black indicating the decomposition of phenylcopper.

B. To a clear solution of  $\text{Br-Cu}[(\text{CH}_3)_2\text{S}]_2$  (5.67 mmol) in excess methyl sulfide and diethyl ether at  $0^\circ$ , 11.34 mmol of phenyllithium was added dropwise with constant stirring. First there was a precipitation of white solid which appeared to dissolve slowly but on further addition of phenyllithium the color of the resultant mixture turned to dark green and the white solid did not dissolve even after complete addition of phenyllithium. In order to obtain a clear solution, 20-30% of excess phenyllithium was required.

C. An attempt was made to obtain a clear colorless solution of  $\text{LiCu}(\text{C}_6\text{H}_5)_2$  in diethyl ether by the reaction of CuBr and phenyllithium in methyl sulfide but the color of the resultant solution was green to dark brown and an excess amount of phenyllithium was required to obtain a clear solution.

Reaction of  $\text{CH}_3\text{Cu}$  and  $\text{MgBr}_2$ . Methylcopper was obtained by the reaction of CuI (2.73 mmol) and methyllithium (2.73 mmol) in diethyl

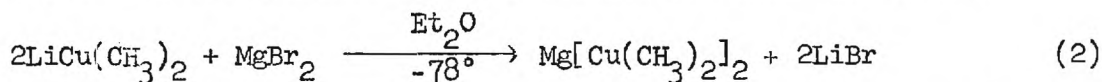
ether at  $-78^{\circ}$ . A solution of magnesium bromide (1.36 mmol) was then added to the slurry of  $\text{CH}_3\text{Cu}$  in ether and the mixture stirred for 3 hours. The yellow solid remained undissolved and the low temperature proton nmr spectrum of the supernatant liquid on concentration did not show any signal due to methyl protons. When the solid was allowed to warm to room temperature, it remained yellow for a few hours but then turned black when kept at room temperature overnight. Elemental analysis of the decomposed product showed total Cu:Mg in the ratio of 2.55:1.27 which indicated 100% recovery of copper and magnesium.

Reaction of  $\text{CH}_3\text{Cu}$  and  $(\text{CH}_3)_2\text{Mg}$  in Diethyl Ether. To a slurry of  $\text{CH}_3\text{Cu}$  (3.84 mmol) in diethyl ether at  $-78^{\circ}$  was added 3.84 mmol of  $(\text{CH}_3)_2\text{Mg}$ . The reaction was stirred for 5 hours at  $-78^{\circ}$ , ether was partially removed under vacuum at  $-50^{\circ}$  and the proton nmr spectrum of the supernatant liquid recorded at  $-81^{\circ}$ . The nmr spectrum showed only one resonance peak at 2.800 ppm. The reaction product was then warmed to room temperature and stirred for one hour. The proton nmr spectrum of the clear liquid showed only one resonance peak at 2.400 ppm (RT) and 2.792 ppm ( $-81^{\circ}$ ). The yellow solid turned black when kept at room temperature overnight.

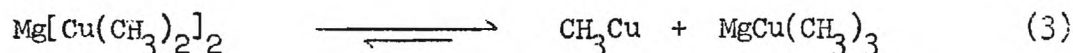
Proton NMR Study of the Reaction of  $\text{LiCu}(\text{CH}_3)_2$  with  $\text{MgBr}_2$  and  $(\text{CH}_3)_2\text{Mg}$  in Diethyl Ether. Ether solutions of freshly prepared  $\text{LiCu}(\text{CH}_3)_2$  and  $\text{MgBr}_2$  were mixed in the appropriate molar ratios to form  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]$ ,  $\text{LiMg}[\text{Cu}(\text{CH}_3)_2]_3$ , and  $\text{Li}_2\text{Mg}[\text{Cu}(\text{CH}_3)_2]_4$ . Similarly,  $\text{LiCu}(\text{CH}_3)_2$  and  $(\text{CH}_3)_2\text{Mg}$  were mixed in 1:1 molar ratio to form  $\text{LiMgCu}(\text{CH}_3)_4$ . The solutions were transferred into 5 mm nmr tubes under nitrogen and stored in dry ice.

## Results and Discussion

Reaction of  $\text{LiCu}(\text{CH}_3)_2$  and  $\text{MgBr}_2$ . The reaction of  $\text{LiCu}(\text{CH}_3)_2$  and  $\text{MgBr}_2$  in 2:1 molar ratio in diethyl ether takes place according to eq. 2. In the presence of large amounts of ether the complex



$\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$  slowly dissociates into methylcopper which separates out as a yellow solid and a soluble complex of the composition  $\text{MgCu}(\text{CH}_3)_3$  results. Elemental analysis of the yellow solid confirms

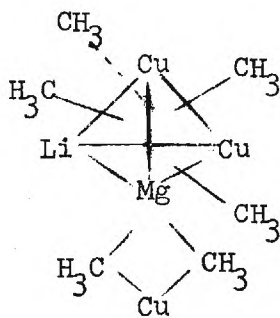


it to be methylcopper. The yellow solid was quite unstable at room temperature.

In the presence of a minimum amount of diethyl ether,  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$  remains undissociated as a yellow solid. The low temperature nmr spectrum of the clear liquid shows the absence of resonance peaks due to methyl protons, thus an indication of the formation of an insoluble complex of the formula  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$ . Elemental analysis of the solid showed 100% of the total copper and magnesium changed in the reaction.

The proton nmr spectrum of  $\text{LiCu}(\text{CH}_3)_2/\text{MgBr}_2$  in different mole ratios are recorded in Table 1. In 2:1 mole ratio, the low temperature nmr spectrum of the supernatant liquid does not show the presence of any methyl protons indicating the formation of an insoluble complex. In 3:1 molar ratio, the proton nmr spectrum shows a single sharp resonance peak at 2.08 ppm upfield from the ether triplet whereas in 4:1 molar ratio a single sharp resonance peak was obtained at 2.166 ppm upfield from the ether triplet. The nmr spectrum of  $\text{LiCu}(\text{CH}_3)_2$

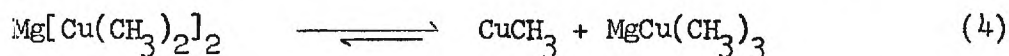
in diethyl ether shows a resonance peak at 2.216 ppm. These results suggest that in 3:1 molar ratio probably there is a formation of the complex of the type  $\text{LiMg}[\text{Cu}(\text{CH}_3)_2]_2$  having the following structure (I).



(I)

In 4:1 molar ratio, the chemical shift (2.166 ppm upfield with respect to the ether triplet) of methyl protons suggests a rapid exchange of methyl groups between  $\text{LiCu}(\text{CH}_3)_2$  and probably  $\text{LiMg}[\text{Cu}(\text{CH}_3)_2]_3$ .

Reaction of  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]$  and  $\text{LiAlH}_4$ . Attempted Preparation of  $\text{Mg}(\text{CuH}_2)_2$ . A. When  $\text{LiAlH}_4$  was allowed to react with  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]$  in 1:1 molar ratio in the presence of large amounts of diethyl ether, a yellowish brown solid was obtained. Elemental analysis of the solid shows that probably the yellow solid is a mixture of several metal hydrides. If we assume that in dilute solution there is an equilibrium of the type shown in eq. 4, then addition of  $\text{LiAlH}_4$  to the above



reaction mixture should produce a mixture of  $\text{CuH}$ ,  $\text{MgCuH}_3$  and  $\text{Mg}(\text{CuH}_2)_2$ . The possibility of  $\text{CuH}$  formation can be easily ruled out on the basis that the reaction product was stable at room temperature for a reasonably longer period of time than would be expected for  $\text{CuH}$ . At the present time this reaction is under further investigation.

B. The reaction of  $\text{LiAlH}_4$  and  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$  in 1:1 molar ratio produces a dark brown solid in the presence of a small amount of diethyl ether. The low temperature ( $-81^\circ$ ) proton nmr of the supernatant liquid showed only one resonance peak at 2.333 ppm upfield from the ether triplet. This indicates a rapid exchange between  $\text{LiAl}(\text{CH}_3)_4$  and some other species having methyl protons, the chemical shift of that species being at higher field from the ether triplet than the chemical shift of  $\text{LiAl}(\text{CH}_3)_4$  (2.29 ppm). The elemental analysis of the supernatant liquid showed Li:Mg:Cu:H in the ratio of Xs:0.771:0.08:2.28 whereas the analysis of the solid slurry after washing with ether showed Li:Mg:Cu:H in the ratio of 0.27:0.151:0.229:0.476. It appears that the reaction of  $\text{LiAlH}_4$  and  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$  in 1:1 molar ratio yields a complex metal hydride which is quite unstable at  $-78^\circ$  and partially decomposes to copper metal and hydrogen..

Reaction of  $\text{LiCuH}_2$  and  $\text{MgBr}_2$  in 2:1 molar ratio in ether. The reaction of  $\text{LiCuH}_2$  and  $\text{MgBr}_2$  in 2:1 molar ratio in diethyl ether produces a yellow brown solid which is quite stable at room temperature as long as it is kept under the solvent. It does turn brown giving off hydrogen when left exposed to nitrogen atmosphere. The elemental analysis of the solid (slurry) after 8 hours stirring and washing with ether showed: Li:Mg:Cu:H in the ratio of 0.583:0.82:1.463:3.179. This indicates that either the reaction did not go to completion during this length of time thus containing unreacted  $\text{LiCuH}_2$ , or it contained a mixture of several complex metal hydrides. The first possibility can be easily ruled out since the analysis of the reaction product obtained after ten days of stirring was consistent with the previous data. Therefore it seems that the solid product might be

either a mixture of  $\text{LiMgH}_3 + 2\text{CuH}$  or  $\text{LiMgCu}_2\text{H}_5$  or a mixture of  $\text{LiH} + \text{Mg}(\text{CuH}_2)_2$ . The presence of  $\text{CuH}$  can be again ruled out since the compound was quite stable at room temperature. Since it is quite difficult to isolate the solid in pure form an attempt will be made to isolate a pure compound by the reaction of  $\text{LiCuH}_2$  and  $\text{MgBr}_2$  in 1:1 molar ratio.

Reaction of  $\text{CH}_3\text{Cu}$  and  $\text{MgBr}_2$ . When a solution of  $\text{MgBr}_2$  in diethyl ether was added to a slurry of  $\text{CH}_3\text{Cu}$  in ether in 1:2 molar ratio at  $-60^\circ$  and the reaction product was stirred for 3 hours at  $-60^\circ$ , a yellow solid was obtained. The proton nmr of the supernatant liquid did not show the presence of any methyl protons, indicating the absence of  $\text{Mg}(\text{CH}_3)_2$  or any soluble "ate" complex of magnesium and copper. The elemental analysis of the yellow solid slurry showed Cu:Mg in the ratio of 2.55:1.27. It means that  $\text{CH}_3\text{Cu}$  forms an adduct with  $\text{MgBr}_2$  which being insoluble in diethyl ether precipitates out as a yellow solid. The yellow solid was more stable than methyl copper at room temperature. No appreciable decomposition was noticed during 3 hours warming of the sample at room temperature.

Reaction of  $\text{CH}_3\text{Cu}$  and  $(\text{CH}_3)_2\text{Mg}$  in Diethyl Ether. When a solution of  $(\text{CH}_3)_2\text{Mg}$  in diethyl ether is added to a slurry of  $\text{CH}_3\text{Cu}$  in ether in 1:1 molar ratio at  $-60^\circ$  and the reaction product is stirred for 3 hours, the yellow solid ( $\text{CH}_3\text{Cu}$ ) remains unreacted. The proton nmr of the clear liquid shows the presence of unreacted  $(\text{CH}_3)_2\text{Mg}$ . Therefore, there is no exchange reaction between methylcopper and dimethylmagnesium.

Proton NMR Study of the Reaction of  $\text{LiCu}(\text{CH}_3)_2$  with  $\text{MgBr}_2$

and  $(\text{CH}_3)_2\text{Mg}$  in Diethyl Ether. When a solution of  $\text{MgBr}_2$  in diethyl ether is added to a solution of  $\text{LiCu}(\text{CH}_3)_2$  in diethyl ether in 1:2 mole ratio at  $-78^\circ$  a yellow solid precipitates. The proton nmr spectrum of the clear liquid on concentration under vacuum shows the absence of methyl protons. This indicates the formation of insoluble  $\text{Mg}[\text{Cu}(\text{CH}_3)_2]_2$  according to equation 2. The reaction of  $\text{LiCu}(\text{CH}_3)_2$  and  $\text{MgBr}_2$  in 3:1 and 4:1 mole ratios yields a clear solution. The chemical shift of the methyl protons are listed in Table 1. An examination of these chemical shifts reveals the fact that either there is a formation of soluble "ate" complexes of magnesium and copper or there is a fast exchange of methyl protons between  $\text{LiCu}(\text{CH}_3)_2$  and  $\text{Mg}(\text{CH}_3)_2$ .

In conclusion, several attempts have been made to prepare complex metal hydrides of copper and magnesium. The hydrides appear to be associated with some impurities which prevents the exact description of the complexes. At the present time work is in progress to obtain pure complex metal hydrides of copper and magnesium and to characterize them by physical methods.

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Table I.

Sample	Temperature	Chemical Shifts <sup>*</sup>
$\text{LiCu}(\text{CH}_3)_2$	-91	2.216
$3\text{LiCu}(\text{CH}_3)_2 + \text{MgBr}_2$	"	2.08
$4\text{LiCu}(\text{CH}_3)_2 + \text{MgBr}_2$	"	2.166
$\text{LiCu}(\text{CH}_3)_2 + \text{MgBr}_2$	"	-

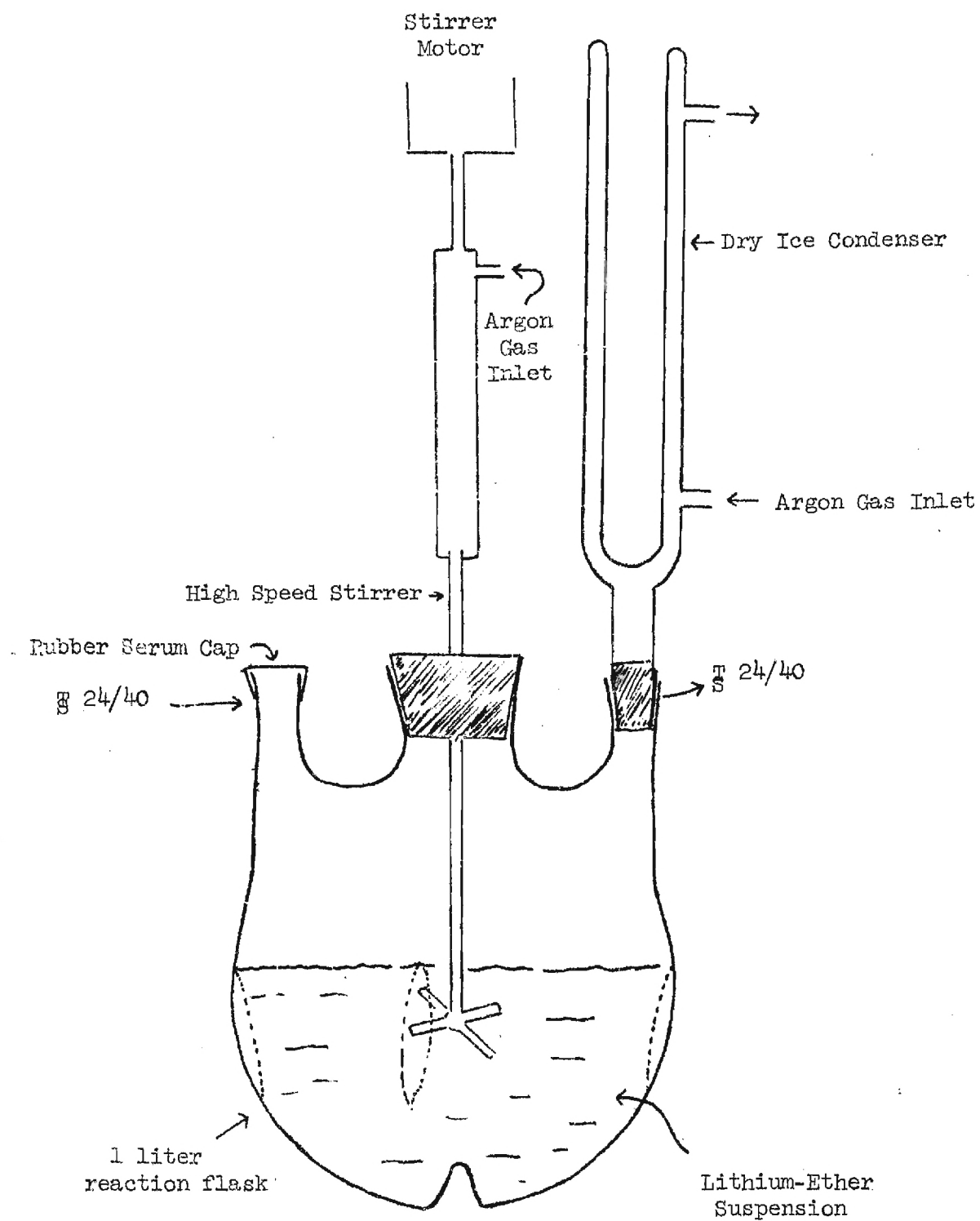


Figure 1

Contribution from the Department of Chemistry,  
Georgia Institute of Technology, Atlanta, Georgia 30332

## Existence of Complexes of $\text{LiAlH}_4$ and $\text{AlH}_3$ in Ether Solvents and in the Solid State

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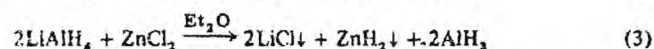
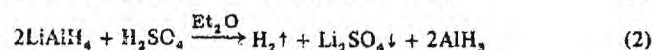
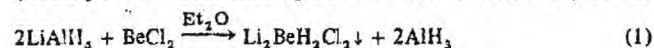
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The reaction between  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in 1:1, 1:2, 1:3, and 1:4 molar ratios in both diethyl ether and THF has been investigated by infrared spectroscopy. Also solutions of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in diethyl ether were evaporated to dryness and the resulting solids were examined by dta-tga and X-ray powder diffraction methods. Previous reports claiming the preparation of  $\text{LiAl}_2\text{H}_7$  and  $\text{LiAl}_3\text{H}_{10}$  by the reaction of  $\text{LiAlH}_4$  with  $\text{BeCl}_2$  in ether and also the reaction of  $\text{LiH}$  with  $\text{AlH}_3$  were studied in detail and attempts were made to prepare the complexes by exactly the same procedure reported. Contrary to previous reports, in no case was any evidence found to indicate the existence of  $\text{LiAl}_2\text{H}_7$ ,  $\text{LiAl}_3\text{H}_{10}$ , or any complex between  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in ether or THF solution or in the solid state as products in the reactions studied.

### Introduction

Recently we found that diethyl ether soluble aluminum hydride can be prepared by a number of different methods.<sup>1,2</sup> (See eq 1-3.) This finding allows a convenient study of the



interaction between  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in diethyl ether which has been reported by a number of laboratories to be strong enough so as to produce stable complexes ( $\text{LiAlH}_4 \cdot n\text{AlH}_3$ , where  $n = 1-4$ ). Although aluminum hydride can be prepared in tetrahydrofuran,<sup>3</sup> complexes between  $\text{LiAlH}_4$  and  $\text{AlH}_3$  would not be expected to be stable due to the strong aluminum-oxygen bond in  $\text{H}_3\text{Al-OC}_4\text{H}_8$ .

Recent Russian work<sup>4</sup> claims the preparation of  $\text{LiAl}_2\text{H}_7$  ( $\text{LiAlH}_4 \cdot \text{AlH}_3$ ) and  $\text{LiAl}_3\text{H}_{10}$  ( $\text{LiAlH}_4 \cdot 2\text{AlH}_3$ ) in diethyl ether; however, the compounds were reported to be more stable in the solid state than in ether solution. Also a recent study concerning the structure and properties of  $\text{LiAl}_2\text{H}_7$  has appeared in the French literature.<sup>5</sup> These workers reported  $\text{LiAl}_2\text{H}_7$  to be stable in the solid state but unstable in diethyl ether solution. In addition, other French workers<sup>6</sup> have reported the preparation of the compound  $\text{LiAl}_4\text{H}_{13}$  ( $\text{LiAlH}_4 \cdot 3\text{AlH}_3$ ) by the reaction of  $\text{LiH}$  with  $\text{AlH}_3$  in ether solvent. In each case the reports claim solid-state stability of the complexes but report diethyl ether solutions as being unstable.

On the other hand, several reports have appeared that claim the formation of complexes of the type  $\text{LiAlH}_4 \cdot n\text{AlH}_3$  in ether solvent. It has been reported that the electrical conductivity of solutions of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in diethyl ether indicates the formation of ions alternate to those arising from  $\text{LiAlH}_4$  and  $\text{AlH}_3$  separately.<sup>7,8</sup> Because of these reports and because of the analogy to the  $\text{MAIH}_4 \cdot n\text{AlR}_3$  systems,<sup>9</sup> further claims for the existence of  $\text{MAIH}_4 \cdot n\text{AlH}_3$  complexes have been made, in particular,  $\text{LiAl}_2\text{H}_7$ .<sup>10</sup>

We have been evaluating new hydrides as stereoselective reducing agents and felt that  $\text{LiAlH}_4 \cdot \text{AlH}_3$  compounds would

behave differently from either  $\text{LiAlH}_4$  or  $\text{AlH}_3$ . Reduction studies in this laboratory have shown that a mixture of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in ether solvent gives the same stereochemistry of reduction of 4-*tert*-butylcyclohexanone and 3,3,5-trimethylcyclohexanone as would be expected for a simple physical mixture of  $\text{LiAlH}_4$  and  $\text{AlH}_3$ . At this point we decided to take a closer look at the so-called complexes " $\text{LiAlH}_4 \cdot n\text{AlH}_3$ " both in ether solution by infrared spectroscopy and in the solid state by dta-tga and powder diffraction.

### Experimental Section

**Apparatus.** Reactions were performed under nitrogen at the bench using Schlenk tube techniques.<sup>11</sup> Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system using manganese oxide columns to remove oxygen and Dry Ice-acetone traps to remove solvent vapors.<sup>12</sup>

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solids were run as Nujol mulls between CsI plates. Solutions were run in matched 0.10-mm path length NaCl cells. X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered  $\text{Cu K}\alpha$  radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr.  $d$  spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually. Dta-tga data were obtained under vacuum with a modified Mettler thermoanalyzer, Model II. A more detailed description of this apparatus has been given elsewhere.<sup>13,14</sup>

**Analytical Work.** Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.<sup>11</sup> Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration.

**Materials.**  $\text{LiAlH}_4$  was obtained as gray, lumpy solids from Ventron, Metal Hydrides Division. Solutions of  $\text{LiAlH}_4$  in diethyl ether and THF were prepared by stirring the solid hydride for 24 hr with freshly distilled solvent, followed by filtration, to yield a clear, colorless solution. Lithium hydride was prepared by the hydrogenation of *tert*-butyllithium at room temperature at 3000 psi for 24 hr. A slurry of  $\text{LiH}$  in diethyl ether was used. Aluminum hydride in diethyl ether was prepared by the reaction of  $\text{LiAlH}_4$  with  $\text{BeCl}_2$  in a 2:1 molar ratio.<sup>12</sup> The white solid was removed by filtration leaving a nearly lithium-free clear solution of aluminum hydride. The molar ratios of Al to H to Li in this solution were 1.00:3.13:0.043. Aluminum hydride in THF was prepared by the reaction of 100%  $\text{H}_2\text{SO}_4$  with  $\text{LiAlH}_4$  in THF according to the procedure of Brown.<sup>3</sup>  $\text{Li}_2\text{SO}_4$  was

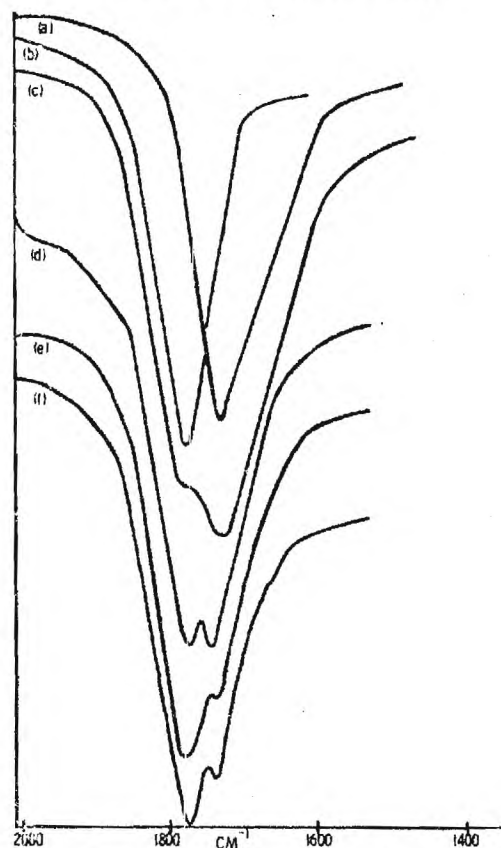


Figure 1. Infrared spectra of mixtures of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in diethyl ether: (a)  $\text{LiAlH}_4$ ; (b)  $\text{AlH}_3$ ; (c) 1:1  $\text{LiAlH}_4$  +  $\text{AlH}_3$ ; (d) 1:2  $\text{LiAlH}_4$  +  $\text{AlH}_3$ ; (e) 1:3  $\text{LiAlH}_4$  +  $\text{AlH}_3$ ; (f) 1:4  $\text{LiAlH}_4$  +  $\text{AlH}_3$ .

Table I. Elemental Analysis of Mixtures of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in 1:1, 1:2, 1:3, and 1:4 Ratios in Diethyl Ether

LiAl- H <sub>3</sub> :Al- H <sub>3</sub>	Analysis, %				Mole ratio Li:Al:H:Et <sub>2</sub> O
	Li	Al	H	Et <sub>2</sub> O	
1:1	7.45	56.79	7.45	28.31	1.02:2.00:7.08:0.35
1:2	4.91	55.58	6.97	32.54	1.03:3.00:10.13:0.64
1:3	3.58	53.20	6.52	36.70	1.05:4.00:13.22:1.01
1:4	2.65	51.08	6.17	40.10	1.01:5.00:16.31:1.43

removed by filtration and a nearly lithium-free solution of  $\text{AlH}_3$  in THF was obtained. The molar ratios of Al to H to Li in this solution were 1.00:3.06:0.016. These reactant solutions were standardized by aluminum analysis and transferred volumetrically. All solvents were distilled at atmospheric pressure from  $\text{LiAlH}_4$  (diethyl ether) or  $\text{NaAlH}_4$  (THF) immediately before use.

**Reactions Involving  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in Diethyl Ether.** Reaction of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in 1:1, 1:2, 1:3, and 1:4 Molar Ratios. In four separate experiments, 2.5 mmol of  $\text{LiAlH}_4$  in diethyl ether was added to 2.5, 5.0, 7.5, and 10 mmol of  $\text{AlH}_3$  in diethyl ether. The resulting clear solutions were stirred for 1 hr and the infrared spectra were recorded (Figure 1). The solvent was then removed from the solution under vacuum until a dry white solid resulted. Elemental analyses of the solid products are given in Table I, the X-ray powder diffraction patterns are recorded in Table II, and the vacuum dta-tga curves of the resulting solids are recorded in Figures 2-5. In all cases the infrared spectrum of the solids (Nujol mulls) yielded broad, nondistinct bands.

**Reaction of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in 1:1, 1:2, 1:3, and 1:4 Molar Ratios in THF.** Five-millimole amounts of  $\text{LiAlH}_4$  in THF were added to each of the following quantities of  $\text{AlH}_3$  in THF: (1) 5 mmol, (2) 10 mmol, (3) 15 mmol, and (4) 20 mmol. In each case the resulting solution was stirred for 1 hr and then the infrared spectrum was recorded. The infrared spectra for these solutions are shown in Figure 6.

**Reaction of  $\text{LiH}$  and  $\text{AlH}_3$  in 1:4 Molar Ratio in Diethyl Ether.** A slurry of 5 mmol of  $\text{LiH}$  in ether was added to 20 mmol of  $\text{AlH}_3$  in ether. The resulting clear solution was stirred for 1 hr and the infrared spectrum was recorded (Figure 7). The solvent was then

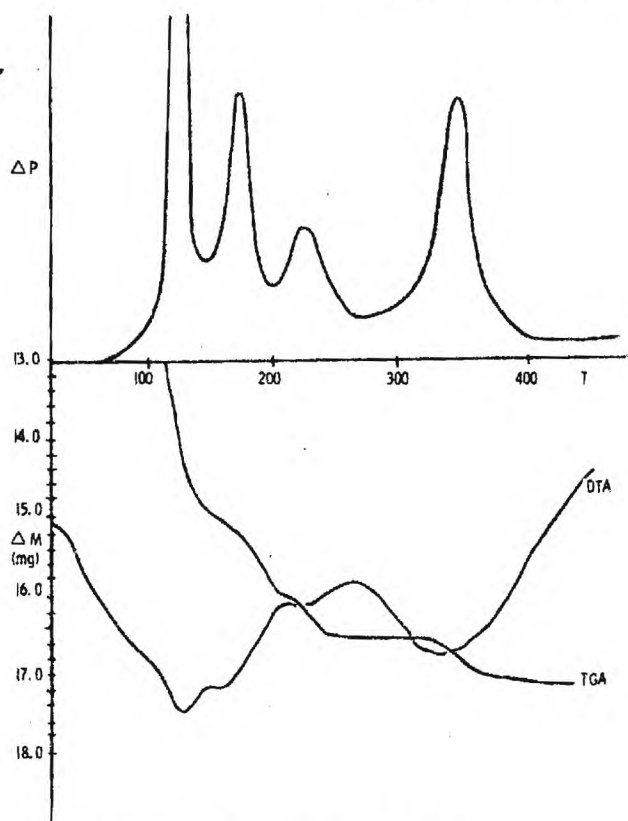


Figure 2. Vacuum dta-tga of proposed " $\text{LiAl}_2\text{H}_7$ ."

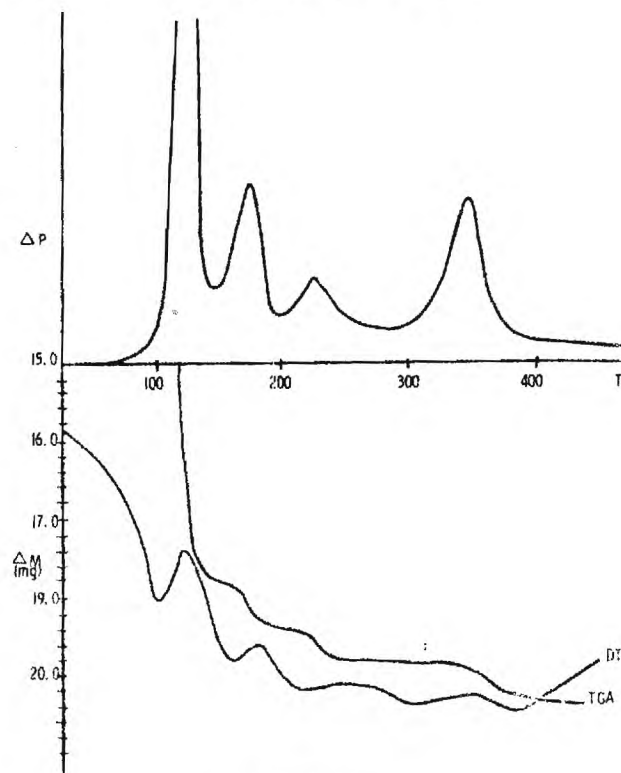
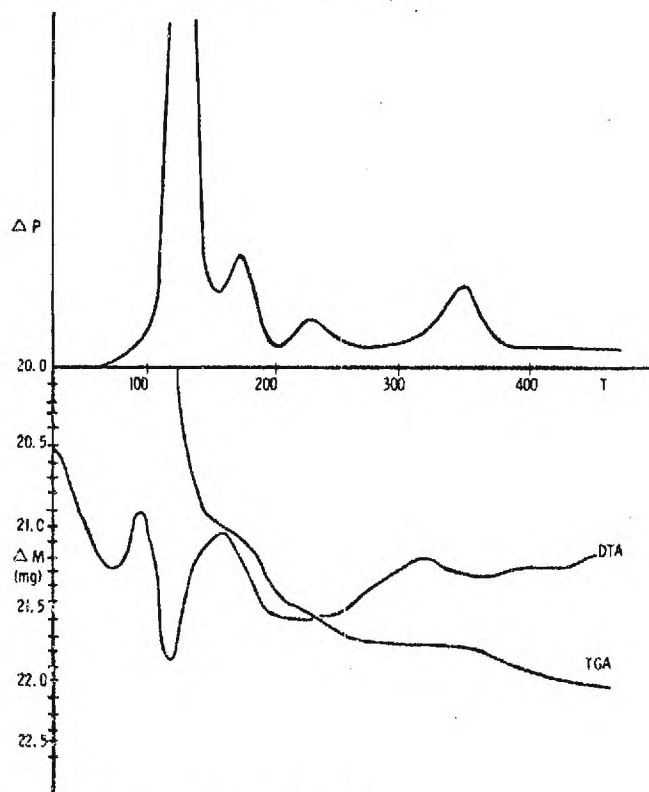
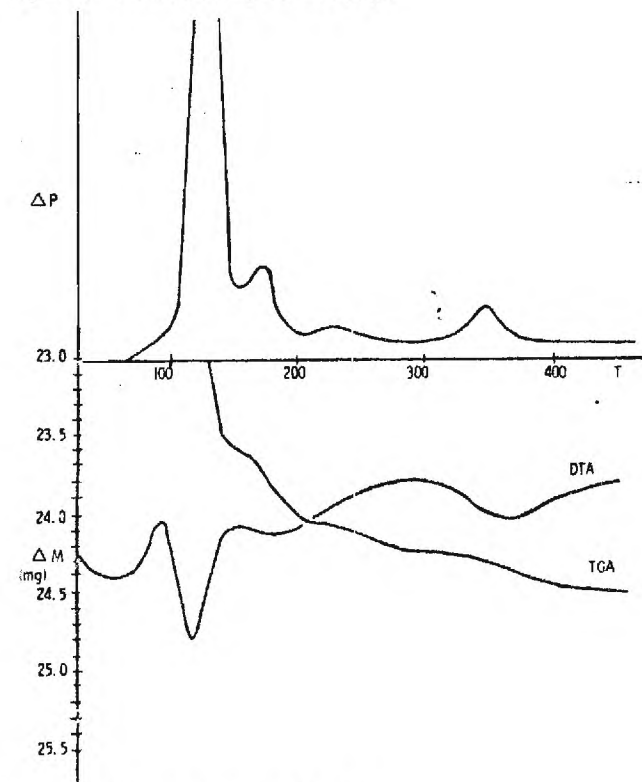


Figure 3. Vacuum dta-tga of  $\text{LiAl}_3\text{H}_{10}$ .

removed from the solution under vacuum producing a dry white solid. Elemental analysis of the solid showed Li, Al, H, and ether in molar ratio of 1.00:4.02:13.22:1.16. The X-ray powder diffraction patterns are recorded in Table II and the dta-tga diagram of resulting solid under argon atmosphere is recorded in Figure 8.

**Reaction of  $\text{LiAlH}_4$  with  $\text{BeCl}_2$  in 4:1 Molar Ratio in Diethyl Ether.** A 20-mmol amount of  $\text{LiAlH}_4$  in diethyl ether was added to 5 mmol of  $\text{BeCl}_2$  in diethyl ether. A white precipitate appeared immediately. After 30 min of stirring the precipitate was allowed to settle.

Figure 4. Vacuum dta-tga of  $\text{LiAlH}_4$ .Figure 5. Vacuum dta-tga of  $\text{LiAlH}_{16}$ .

infrared spectrum was then run on the clear solution. The spectrum is shown in Figure 9.

**Reaction of  $\text{LiAlH}_4$  with  $\text{BeCl}_2$  in 2:1 Molar Ratio in Diethyl Ether. Formation of " $\text{LiAl}_2\text{H}_7$ ."** A 10-mmol amount of  $\text{BeCl}_2$  in diethyl ether was added slowly with stirring to 20 mmol of  $\text{LiAlH}_4$  in diethyl ether cooled at  $-5^\circ$ . A white precipitate appeared immediately. The mixture was stirred for 1 hr and the precipitate was allowed to settle. The infrared spectrum of the clear solution was identical with the infrared spectrum of  $\text{AlH}_3$ .

**Reaction of  $\text{LiAlH}_4$  with  $\text{BeCl}_2$  in 3:1 Molar Ratio. Formation of " $\text{LiAl}_3\text{H}_{10}$ ."** A 15-mmol amount of  $\text{LiAlH}_4$  in diethyl ether was added

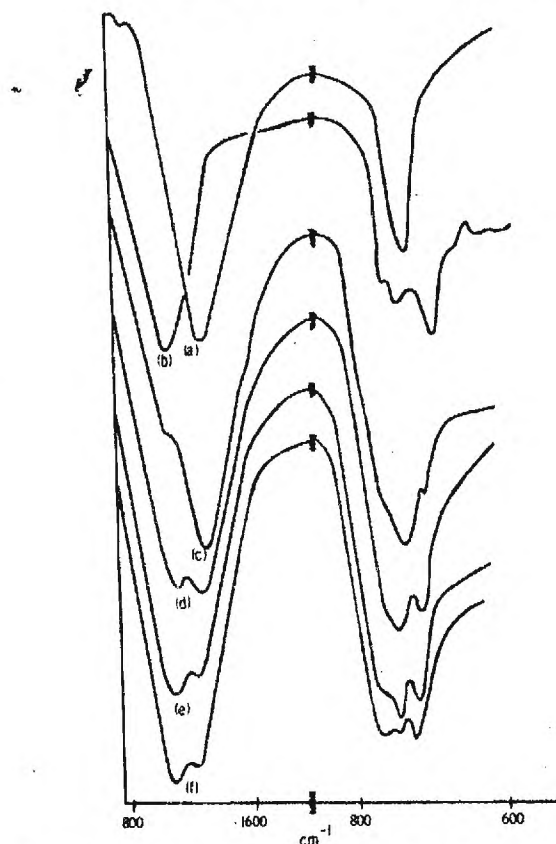


Figure 6. Infrared spectra of mixtures of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in THF: (a)  $\text{LiAlH}_4$ ; (b)  $\text{AlH}_3$ ; (c) 1:1  $\text{LiAlH}_4 + \text{AlH}_3$ ; (d) 1:2  $\text{LiAlH}_4 + \text{AlH}_3$ ; (e) 1:3  $\text{LiAlH}_4 + \text{AlH}_3$ ; (f) 1:4  $\text{LiAlH}_4 + \text{AlH}_3$ .

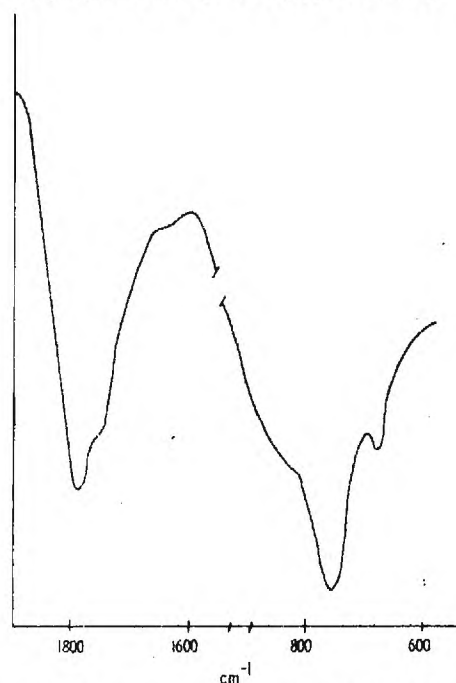


Figure 7. Infrared spectrum of the solution resulting on admixture of  $\text{LiH}$  and  $\text{AlH}_3$  in 1:4 molar ratio in diethyl ether.

to 5 mmol of  $\text{BeCl}_2$  in diethyl ether. A white precipitate appeared immediately. After 30 min of stirring, the precipitate was allowed to settle. An infrared spectrum was then run on the clear solution. The spectrum is shown in Figure 9.

### Results and Discussion

The infrared spectra of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in diethyl ether and tetrahydrofuran as well as mixtures of these compounds in 1:1, 1:2, 1:3, and 1:4 ratios are shown in Figures 1 and 6. In each case the infrared spectrum of a mixture of  $\text{LiAlH}_4$

Table II. X-Ray Powder Diffraction Patterns of the Solid Products Obtained in the Reactions of  $\text{LiAlH}_4$  with  $\text{AlH}_3$  in Diethyl Ether

$^a\text{LiAl}_2\text{H}_7$		$^b\text{LiAl}_3\text{H}_{10}$		$^c\text{LiAl}_4\text{H}_{13}$		$^d\text{LiAl}_5\text{H}_{16}$		$\text{LiAlH}_4$		$\text{AlH}_3$		$\text{LiAl}_2\text{H}_7$		$\text{LiAl}_3\text{H}_{10}$		$\text{LiAl}_4\text{H}_{13}$	
d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>
11.4	m	11.6	m	11.6	s	11.6	s	5.36	w	11.6	vs	4.43	ms	9.450	ms	11.6	s
5.31	w	5.30	w	5.33	w	4.61	ms	4.48	m	4.59	s	4.20	w	5.586	w	6.7	w
4.51	mw	4.65	m	4.62	m	4.47	vw	4.00	vw	3.24	ms	3.89	s	5.265	vw	4.55	s
4.43	m	4.41	m	4.44	w	3.87	ms	3.89	s	2.89	ms	3.68	vw	4.548	s	4.30	s
3.85	s	3.85	s	3.85	s	3.65	vw	3.68	m			3.55	mw	4.439	vs	3.85	s
3.67	m	3.63	m	3.66	w	3.31	w	3.53	vw			3.30	mw	3.045	ms	3.66	m
3.41	m	3.47	m	3.45	w	3.25	s	3.43	w			2.90	vw	3.888	s	3.45	m
3.31	m	3.30	m	3.33	m	3.00	vw	3.32	m			2.65	mw	3.666	vs	3.33	w
3.22	mw	3.24	m	3.24	s	2.87	ms	3.24	m			2.588	w	3.527	w	3.02	w
3.00	w	3.01	w	3.01	w	2.66	vw	3.03	m			2.504	m	3.456	m	2.95	m
2.92	w	2.96	w	2.95	w	2.40	vw	3.00	w			2.376	w	3.324	w	2.85	s
2.85	mw	2.85	m	2.85	m			2.95	m			2.337	vw	3.229	vs	2.65	vw
2.67	w	2.65	w	2.65	w			2.68	m			2.295	vw	3.035	ms	2.54	m
2.45	w	2.45	vw	2.45	vw			2.54	vw			2.093	mw	2.952	vw	2.39	w
2.16	w	2.40	w	2.39	vw			2.45	w			1.992	mw	2.882	vs	2.29	m
2.01	w	2.02	vw	2.12	vw			2.42	m			1.949	mw	2.799	vw	2.25	w
1.78	w							2.24	w			1.929	vw	2.680	w	2.075	w
								2.15	w			1.883	vw	2.566	vw	1.98	vw
								2.05	w			1.782	vw	2.506	vw	1.80	w
								2.01	vw			1.765	w	2.424	w	1.69	vw
								1.98	w			1.655	w	2.405	w	1.65	vw
								1.92	vw			1.604	vw	2.342	s	1.54	vw
								1.89	vw			1.572	vw	2.316	s	1.52	vw
								1.80	vw			1.558	vw	2.271	ms	1.34	vw
								1.78	w			1.517	w	2.220	ms		
								1.76	w			1.480	w	2.038	ms		
								1.74	w			1.375	vw	1.530	ms		
												1.352	vw	1.473	w		
												1.301	vw	1.442	w		
												1.281	vw	1.415	w		
												1.194	vw	1.344	w		

<sup>a</sup> Solid from  $\text{LiAlH}_4 + \text{AlH}_3$  in 1:1 molar ratio. <sup>b</sup> Solid from  $\text{LiAlH}_4 + \text{AlH}_3$  in 1:2 molar ratio. <sup>c</sup> Solid from  $\text{LiAlH}_4 + \text{AlH}_3$  in 1:3 molar ratio. <sup>d</sup> Solid from  $\text{LiAlH}_4 + \text{AlH}_3$  in 1:4 molar ratio. <sup>e</sup> Solid from evaporating ethereal  $\text{LiAlH}_4$ . <sup>f</sup> Solid from evaporating ethereal  $\text{AlH}_3$ . <sup>g</sup>  $\text{AlH}_3$  prepared from 2:1  $\text{BeCl}_2 + \text{LiAlH}_4$ . <sup>h</sup> Key: s, strong; m, moderate; w, weak; v, very. <sup>i</sup> See ref 5. <sup>j</sup> See ref 6.

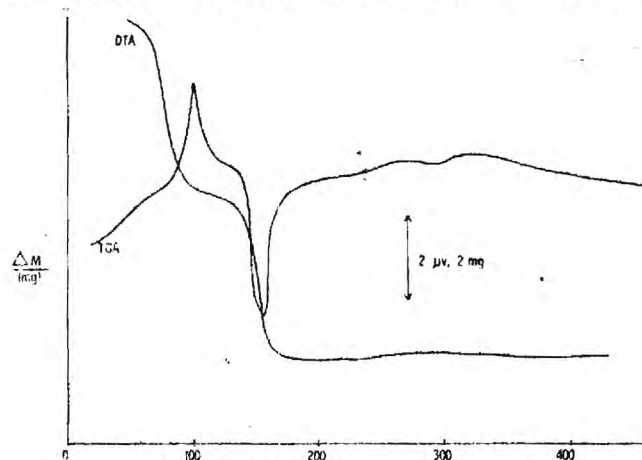


Figure 8. Dta-tga of  $\text{LiAl}_4\text{H}_{13}$  ( $\text{LiAlH}_4 + 3\text{AlH}_3$ ) under static argon atmosphere.

and  $\text{AlH}_3$  corresponds to a superposition of the same bands for  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in the same solvent. If an actual complex between  $\text{LiAlH}_4$  and  $\text{AlH}_3$  were formed in any of the four cases studied, the infrared spectrum of the resulting solution would be expected to be different from the individual components. For example, a complex between  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in solution would be expected to exhibit an Al-H-Al bridge bond. The asymmetric Al-H stretching vibration for such a bond in diethyl ether or tetrahydrofuran would be expected to occur between 1600 and 1400  $\text{cm}^{-1}$ .<sup>9</sup> No such band was observed for any of the mixtures mentioned above; therefore, in diethyl ether or THF solution there is no evidence that  $\text{LiAlH}_4$  and  $\text{AlH}_3$  form complexes of the type  $\text{LiAlH}_4 \cdot n(\text{AlH}_3)$  where  $n = 1, 2, 3$  or 4.

Other workers<sup>4-6</sup> have reported that complexes of the type  $\text{LiAlH}_4 \cdot n(\text{AlH}_3)$  are not stable in diethyl ether or tetra-

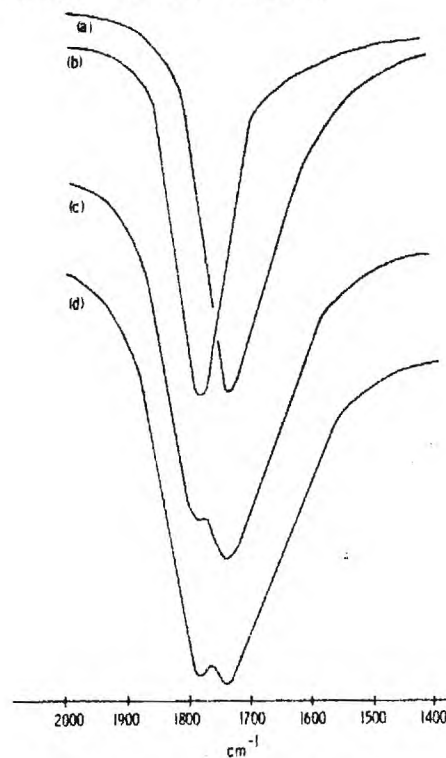
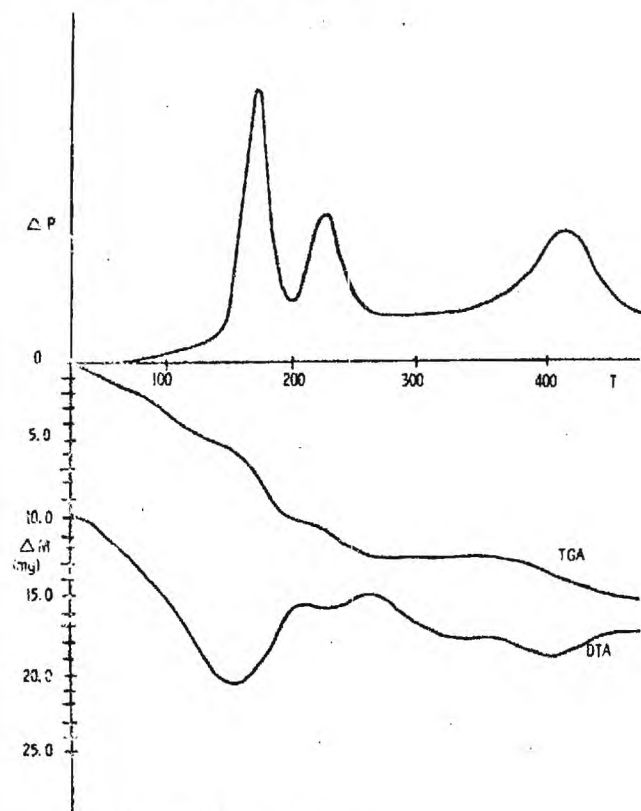


Figure 9. Infrared spectra in the 2000-1400- $\text{cm}^{-1}$  region for diethyl ether solutions of (a)  $\text{LiAlH}_4$ , (b)  $\text{AlH}_3$ , (c) the supernatant remaining after the reaction of  $\text{LiAlH}_4$  with  $\text{BeCl}_2$  in 4:1 molar ratio, " $\text{LiAl}_2\text{H}_7$ ," and (d) the supernatant remaining after the reaction of  $\text{LiAlH}_4$  with  $\text{BeCl}_2$  in 3:1 molar ratio, " $\text{LiAl}_3\text{H}_{10}$ ."

hydrofuran but are stable in the solid state. In order to investigate this possibility, the same 1:1, 1:2, 1:3, and 1:4 mixture of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in diethyl ether, on which the infrared

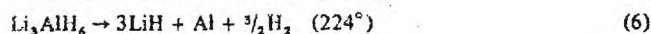
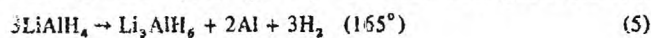
Figure 10. Vacuum dta-tga of  $\text{LiAlH}_4$ .

spectra were taken, were evaporated to dryness. Analysis of the resulting white solids indicated the appropriate empirical formula (Table I) ( $\text{LiAl}_2\text{H}_7$ ,  $\text{LiAl}_3\text{H}_{10}$ ,  $\text{LiAl}_4\text{H}_{13}$ , and  $\text{LiAl}_5\text{H}_{16}$ ) which indicated the proper stoichiometric ratios and the absence of hydrolysis or ether cleavage. In each case these white solids were subjected to dta-tga and X-ray powder diffraction analysis.

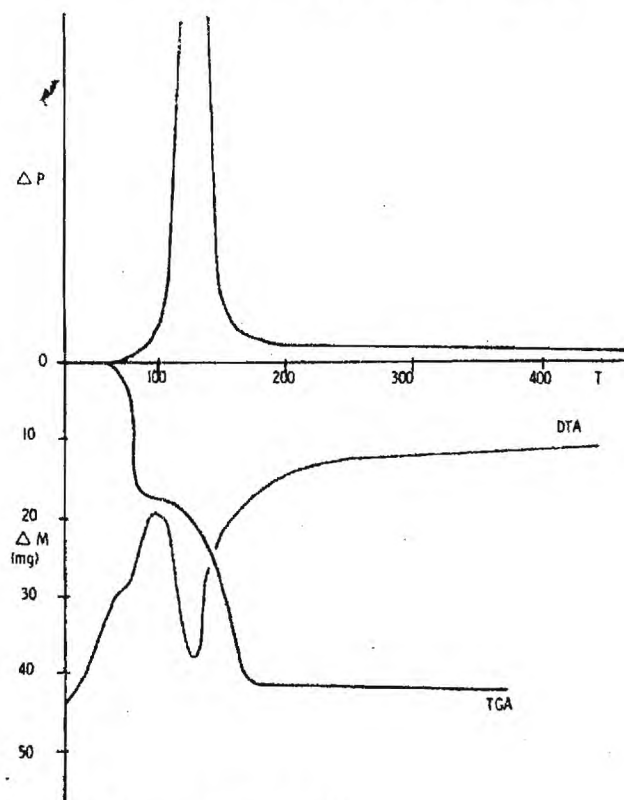
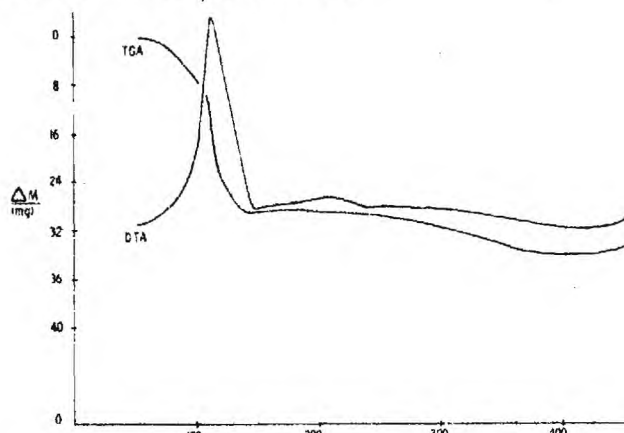
The X-ray powder diffraction pattern for " $\text{LiAl}_2\text{H}_7$ " is shown in Table II. It is readily seen that the so-called complex corresponds to a mixture of  $\text{LiAlH}_4$  and  $\text{AlH}_3$ . The vacuum dta-tga of " $\text{LiAl}_2\text{H}_7$ " is shown in Figure 2. The thermogram shows gas evolution at 110, 163, 221, and 355° with simultaneous weight losses of 14.75, 1.00, 0.50, and 0.50 mg. The vacuum dta-tga diagrams of separate samples of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  are shown in Figures 10 and 11. (The dta-tga diagram of  $\text{AlH}_3$  under static argon pressure is shown in Figure 12.) Aluminum hydride (Figure 11) is seen to decompose at 110° with almost simultaneous loss of both solvent and hydrogen. (See eq 4.) The first gas evolution in Figure 2 for " $\text{LiAl}_2\text{H}_7$ "



also occurs at 110° and its corresponding large weight loss is undoubtedly due to loss of both solvent and hydrogen. Due to large amounts of solvent loss, only the lower portions of the tga curves are shown in Figures 2-5 so that the weight losses for the last three gas evolutions could be seen more easily.  $\text{LiAlH}_4$  (Figure 10) is seen to decompose with gas evolution at 165, 224, and 410° with simultaneous weight loss in the ratio of 2:1:1. (See eq 5-7.) The last three gas evolutions

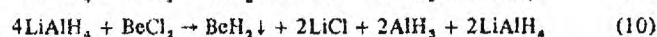
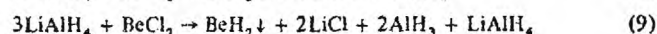
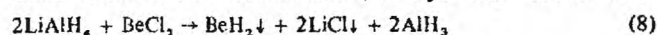


in Figure 2 correspond exactly with the gas evolutions in Figure 10, except for the last one; however, the ratio of the weight loss for the last three gas evolutions in Figure 2 is 2:1:1, the same as for  $\text{LiAlH}_4$ . When " $\text{LiAl}_2\text{H}_7$ " was heated to 130° under vacuum and stopped, the X-ray powder pattern of the

Figure 11. Vacuum dta-tga of  $\text{AlH}_3$ .Figure 12. Dta-tga of  $\text{AlH}_3$  under static argon atmosphere.

resulting solid showed only lines for  $\text{LiAlH}_4$  and  $\text{Al}$ . The dta-tga diagram for " $\text{LiAl}_2\text{H}_7$ ," shown in Figure 2, is readily interpreted to be due to a 1:1 mixture of  $\text{LiAlH}_4$  and  $\text{AlH}_3$ . Thus, the product of solution of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  is not a complex but a physical mixture.

The data indicating the composition of " $\text{LiAl}_2\text{H}_7$ " as a physical mixture of  $\text{AlH}_3$  and  $\text{LiAlH}_4$  could be explained by assuming the existence of the complex  $\text{LiAl}_2\text{H}_7$  which then dissociates at 110° to  $\text{LiAlH}_4$  and  $\text{AlH}_3$ . However, the powder diffraction data were obtained at room temperature which shows the product " $\text{LiAl}_2\text{H}_7$ " to be actually a physical mixture of  $\text{LiAlH}_4$  and  $\text{AlH}_3$ . Although the preparations of  $\text{LiAl}_2\text{H}_7$  and  $\text{LiAl}_3\text{H}_{10}$  have been reported<sup>4</sup> by the reaction of  $\text{LiAlH}_4$  and  $\text{BeCl}_2$ , the infrared spectra (Figure 9) of the solutions obtained by allowing  $\text{LiAlH}_4$  and  $\text{BeCl}_2$  to react in diethyl ether in 4:1 and 3:1 mole ratios clearly show the presence of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in the solution. (See eq 8-10.) The infrared



spectrum of the solution obtained by the reaction of  $\text{LiAlH}_4$  and  $\text{BeCl}_2$  in diethyl ether at  $-5^\circ$  in 2:1 mole ratio indicates the presence of only  $\text{AlH}_3$  in solution.

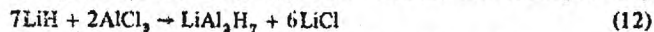
The X-ray powder diffraction patterns for the proposed compounds " $\text{LiAl}_3\text{H}_{10}$ ," " $\text{LiAl}_4\text{H}_{13}$ ," and " $\text{LiAl}_5\text{H}_{16}$ " are shown in Table II. The dta-tga thermograms for these compounds are shown in Figures 3-5. Analogous to the reasoning used for " $\text{LiAl}_2\text{H}_7$ ," these compounds are also shown to be mixtures of  $\text{LiAlH}_4$  and  $\text{AlH}_3$ .

We have repeated the work of Bousquet and coworkers<sup>6</sup> in an attempt to prepare  $\text{LiAl}_4\text{H}_{13}$  by the method used in their laboratory. The infrared spectrum of the solution obtained by reaction of an ether solution of  $\text{LiAlH}_4$  with an ether solution of  $\text{AlH}_3$  (eq 11) is shown in Figure 7. The infrared



spectrum of the solution clearly shows the presence of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in the solution. The X-ray powder pattern of the solid obtained on complete removal of solvent is shown in Table II. It is readily seen that the proposed complex closely corresponds to a mixture of  $\text{LiAlH}_4$  and  $\text{AlH}_3$ . The dta-tga thermograms for the solids obtained by ether evaporation of the solutions formed on mixing  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in diethyl ether in 1:3 mole ratio and by reaction 11 are shown in Figures 8 and 13. The dta-tga diagrams of both solids are identical. Also there is a striking similarity between these thermograms and the dta-tga of a physical mixture of 1 mol of  $\text{LiAlH}_4$  and 3 mol of  $\text{LiAlH}_4$ .

The X-ray powder pattern for " $\text{LiAl}_2\text{H}_7$ " reported by Mayet and coworkers<sup>5</sup> is shown in Table I. This powder pattern resembles that of  $\text{LiAlH}_4$ , although no lines for  $\text{AlH}_3$  can be detected. The " $\text{LiAl}_2\text{H}_7$ " was prepared by the reaction shown in eq 12. Unfortunately, these workers did not report any



dta-tga data or infrared spectra in their studies.

In this study, evidence has been presented to show that  $\text{LiAlH}_4$  and  $\text{AlH}_3$  do not react, under the conditions studied, to form complexes of the type  $\text{LiAlH}_4 \cdot n(\text{AlH}_3)$  in either diethyl ether or THF solution. Also, evidence has been presented showing that the solids left after evaporation of the solvent from 1:1, 1:2, 1:3, and 1:4 mixtures of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in diethyl ether failed to produce complexes of the type  $\text{LiAlH}_4 \cdot n(\text{AlH}_3)$ . The equivalence of solutions formed by (1) addition of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  in diethyl ether, (2) reaction

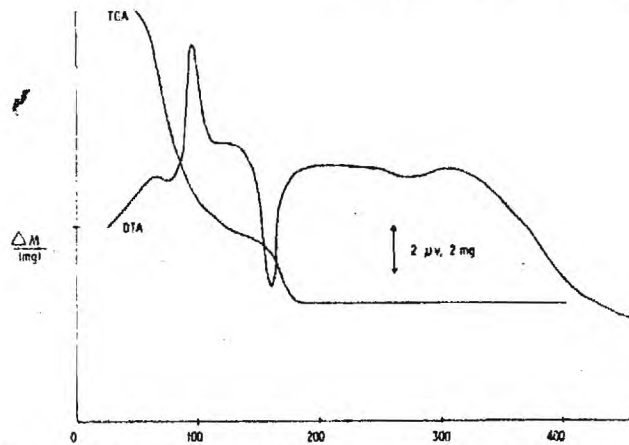


Figure 13. Dta-tga of  $\text{LiAl}_4\text{H}_{13}$  ( $\text{LiH} + 4\text{AlH}_3$ ) under static argon atmosphere.

of  $\text{LiAlH}_4$  and  $\text{BeCl}_2$  in diethyl ether, and (3) reaction of  $\text{LiH}$  and  $\text{AlH}_3$  has been demonstrated and the solids resulting from these solutions have been shown by X-ray powder diffraction and dta-tga to be physical mixtures of  $\text{LiAlH}_4$  and  $\text{AlH}_3$ .<sup>12</sup>

Registry No.  $\text{LiAlH}_4$ , 16853-85-3;  $\text{AlH}_3$ , 7784-21-6;  $\text{LiH}$ , 7580-67-8;  $\text{BeCl}_2$ , 7787-47-5.

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- (15) Note Added in Proof. We have recently repeated the work of Dymova<sup>4</sup> ( $\text{LiAlH}_4 + \text{AlCl}_3$ ) and Mayet<sup>5</sup> ( $\text{LiH} + \text{AlCl}_3$ ) and have found evidence for  $\text{LiAl}_2\text{H}_7$  as reported. We shall report in detail on our findings in a separate paper.

# Reactions of Aluminum Hydride with Group 1b, 2a, and 2b Metal Halides

E. C. ASHBY\* and H. S. PRASAD

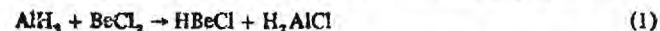
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The reaction of aluminum hydride with several group 2a and 2b metal halides in diethyl ether has been studied in detail. Hydrogen-halogen exchange in the system  $\text{AlH}_3\text{-MX}_2$  ( $\text{M} = \text{Ca, Mg, Zn, Cd, Cu; X} = \text{Cl, Br, I}$ ) has been found to depend on the electronegativities of the metals concerned. Thus, calcium bromide and magnesium bromide did not undergo exchange with aluminum hydride whereas zinc chloride and zinc bromide did react with aluminum hydride to produce a new complex metal hydride of the type  $\text{H}_3\text{Zn}_2\text{X}$  (where  $\text{X} = \text{Cl or Br}$ ). The reaction of zinc iodide with aluminum hydride yielded a complex of the composition  $\text{ZnI}_2\text{-AlH}_3$ . Cadmium bromide reacted very slowly with aluminum hydride at  $-40^\circ$  to yield a compound of empirical formula  $\text{HCdX}$ . Cuprous chloride was shown to react with  $\text{AlH}_3$  in ether at  $-78^\circ$  to form  $\text{CuH}$  and  $\text{CuAlH}_4$  both of which decompose when allowed to warm to room temperature. All compounds were characterized by X-ray powder diffraction, infrared spectroscopy, and elemental analyses.

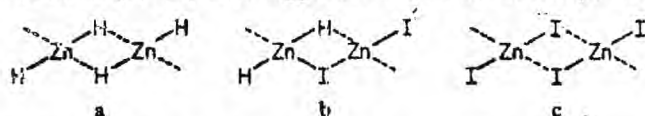
## Introduction

In view of our recent study of the redistribution reaction of aluminum hydride with beryllium chloride (eq 1) in diethyl



ether and the possibility of the existence of  $\text{HMX}$  compounds (where  $\text{M} =$  group 2a and 2b metals and  $\text{X} = \text{Cl, Br, or I}$ ), we have extended our investigation of redistribution reactions involving  $\text{AlH}_3$  to include other group 2a and 2b metal halides in addition to  $\text{BeCl}_2$  and  $\text{BeBr}_2$ .<sup>1</sup>

Although there have been several reports of the preparation and characterization of group 2a and 2b metal hydrides in the literature,<sup>2</sup> very little is known about the corresponding hydridometal halides ( $\text{HMX}$ ). In 1951 Wiberg and Henle<sup>3</sup> reported that the addition of an ether solution of zinc chloride to a solution of aluminum hydride and aluminum chloride (1:1 mole ratio) in ether produced impure zinc hydride. These workers also reported<sup>4</sup> the preparation of a white solid corresponding to the formula  $\text{HZnI}$  by the reaction of zinc iodide with lithium hydride in diethyl ether. Since  $\text{HZnI}$  could not be isolated in pure form and contained different amounts of iodine, depending on the conditions of isolation, resonance structures (a, b, c) were suggested to describe the compound.



Wiberg and Henle<sup>5</sup> also studied the reaction between cadmium iodide in THF and lithium aluminum hydride in diethyl ether at  $-70$  to  $-40^\circ$ . In this case only cadmium hydride was obtained as a white solid which decomposed at a slow rate at  $-20^\circ$  and decomposed spontaneously to the elements at room temperature. No evidence was obtained for either  $\text{Cd(AlH}_4)_2$  or  $\text{HCdI}$ .

The preparation of hydridomagnesium halides has been reported by several workers;<sup>6-8</sup> however, it has been found recently<sup>9</sup> that these compounds actually exist as physical mixtures of magnesium hydride and the corresponding magnesium halide.

In this paper we report the reactions of aluminum hydride in ether solvent with calcium bromide, magnesium bromide, zinc halides, and cadmium bromide in several stoichiometric ratios. In this study we have isolated new complexes of zinc halides of the types  $\text{H}_3\text{Zn}_2\text{X}$  ( $\text{X} = \text{Cl or Br}$ ) and  $\text{ZnI}_2\text{-AlH}_3$ . No conclusive evidence has been found for the existence of " $\text{HMX}$ " species.

## Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and moisture<sup>10</sup> or on the bench using typical Schlenk-tube techniques.<sup>11</sup>

**Instrumentation.** Infrared spectra were obtained with a Perkin-Elmer Model 621 Grating infrared spectrophotometer using  $\text{NaCl}$  and  $\text{CsI}$  liquid cells. Solid samples were prepared as mulls in Nujol and the spectra were measured using polyethylene and  $\text{CsI}$  plates. X-Ray powder diffraction data were obtained using a Philips Norelco X-ray unit, using an 11.46-cm diameter camera with  $\text{Ni}$ -filtered  $\text{Cu K}\alpha$  radiations. The samples were exposed for 6.0 hr.  $d$  spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. DTA-TGA analyses were carried out using a Mettler Thermoanalyzer II with high-vacuum attachment.<sup>12</sup>

**Reagents.** Diethyl ether (Fisher anhydrous ether) was distilled over  $\text{LiAlH}_4$  immediately prior to use. All metal halides were Fisher Certified reagent grade. Aluminum halides were purified by vacuum sublimation and ether solutions were prepared at  $-20^\circ$  by slow addition of the aluminum halide to precooled ether. An ether solution of  $\text{MgBr}_2$  was obtained by the method described previously.<sup>13</sup> Zinc halides were dried by heating the compounds slowly with a Bunsen flame under vacuum until they sublimed completely. Ether solutions of  $\text{ZnBr}_2$  were obtained by dissolving the sublimed material in ether at room temperature. Anhydrous  $\text{CdBr}_2$  was dried further by heating at  $115^\circ$  overnight under vacuum. Ether-soluble aluminum hydride was prepared by the reaction of  $\text{LiAlH}_4$  and  $\text{BeCl}_2$  in diethyl ether.<sup>14</sup> **Caution!** Special care must be taken while handling beryllium compounds due to their toxic character.

**Analytical Procedures.** Hydrogen analysis was carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Metals were determined by complexometric titration with EDTA. Zinc, magnesium, and cadmium in the presence of aluminum were determined by masking the aluminum with triethanolamine and titrating the remaining metal with EDTA. Analysis for chloride, bromide, or iodide was carried out using a modified Volhard procedure.

**Infrared Study of the Reaction of  $\text{AlH}_3$  with  $\text{AlCl}_3$  and  $\text{AlBr}_3$  in Diethyl Ether.** The hydridoaluminum halides  $\text{H}_y\text{AlX}_{3-y}$  (where  $\text{X} = \text{Cl or Br}$ ) were prepared by mixing solutions of  $\text{AlH}_3$  and aluminum halides in ether at  $0^\circ$  in the appropriate ratios. Redistribution reactions between  $\text{AlH}_3$  and aluminum halides have been discussed by a number of authors.<sup>15</sup> The infrared spectra are reported in Figure 1.

**Reaction of  $\text{AlH}_3$  with  $\text{MgBr}_2$ . (a) In 1:1 Mole Ratio.** A solution of  $\text{AlH}_3$  (10 ml, 2.732 mmol) in ether was added slowly with stirring to a solution of  $\text{MgBr}_2$  (21.45 ml, 2.732 mmol) in ether. There was no immediate precipitate and the mixture remained clear even after 24 hr of stirring. The infrared spectrum of the clear solution showed strong bands at 1785 and 760  $\text{cm}^{-1}$  and a band of medium intensity at 380  $\text{cm}^{-1}$ . The infrared spectrum of the solid obtained by complete removal of ether from the reaction mixture showed bands at 1800 (w) and 1600  $\text{cm}^{-1}$  (br, s). Elemental analysis of the solid gave the ratio  $\text{Mg:Al:H:Br} = 1.0:1.04:2.90:2.11$ . X-Ray powder diffraction patterns of the solid showed it to be essentially a physical mixture of  $\text{MgBr}_2$  and  $\text{AlH}_3$ . When the reaction mixture was allowed to stand for a few weeks, some gray solid compound precipitated. The solid was filtered, dried under vacuum, and analyzed:  $\text{Mg:Al:H:Br} = 1.24:1.0:1.02:1.95$ . The infrared spectrum showed a very weak broad band at  $\sim 1600 \text{ cm}^{-1}$ .

**(b) In 2:1 Mole Ratio.** Ether solutions of  $\text{AlH}_3$  (8.578 mmol) and  $\text{MgBr}_2$  (4.289 mmol) were mixed as described above. In this case

Table I. X-Ray Powder Pattern  $d$ -Spacing Data

$\text{MgBr}_2 \cdot 0.89\text{Et}_2\text{O}$		$\text{MgBr}_2 + \text{AlH}_3 \cdot 1.24\text{Et}_2\text{O}$		$\text{MgBr}_2 + 2\text{AlH}_3 \cdot 1.62\text{Et}_2\text{O}$		$\text{ZnH}_2$		$\text{ZnCl}_2$		$\text{ZnCl}_2 \cdot 0.11\text{Et}_2\text{O}$		$\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.20\text{Et}_2\text{O}$	
$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$
9.25	vw	9.50	w	9.50	s, br	4.51	vw	4.85	s	6.85	m	7.8	s
8.0	s	8.0	s	8.25	w	4.23	s	4.70	s	5.50	m	5.80	w
7.25	s	7.25	s	7.25	w	3.80	vw	3.80	w	4.80	s	5.40	w
5.8	m	5.7	vw	6.6	w	3.40	m	3.26	m	4.50	m	4.0	m
5.4	m	5.4	m	5.90	w	2.97	vw	3.19	m	3.80	vw	3.55	w
4.8	s	4.8	vw	5.4	vw	2.82	vw	3.02	s	3.55	m	3.15	w
3.95	vw	3.95	vw	4.6	vw	2.608	w	2.87	s	3.42	w	2.75	s
3.72	vw	3.55	ms	3.62	w	2.468	vw	2.85	w	3.30	w	2.65	s
3.55	s	3.25	ms	3.50	w	2.387	m	2.35	w	3.05	s	2.37	m
3.25	s	2.97	w	3.25	m	2.290	m	2.22	w	2.87	m	2.00	w
3.01	ms	2.75	w	3.15	s	2.225	m	2.12	vw	2.57	w	1.79	vw
2.77	s	2.63	w	2.72	ms	2.135	w	1.960	vw	2.35	m	1.69	w
2.75	w	2.52	w	2.63	vw	2.085	w	1.920	m	2.20	m	1.58	m
2.64	w	2.36	w	1.92	s	2.017	vw	1.860	s	2.06	w	1.55	w
2.52	m	2.25	vw	1.65	ms	1.905	w	1.730	s	1.97	w	1.51	w
2.42	w	2.125	vw	1.58	vw	1.764	w	1.620	w	1.95	m		
2.36	w	1.91	ms	1.255	w	1.688	vw	1.592	s	1.865	s		
2.25	vw	1.71	w	1.223	w	1.630	vw	1.490	w	1.730	m		
2.19	m					1.562	vw	1.455	w	1.620	m		
1.91	w					1.486	vw	1.280	vw	1.590	w		
1.75	w					1.464	vw	1.265	vw	1.570	m		
1.61	w					1.416	vw	1.145	vw	1.485	vw		
1.53	w							1.350	vw	1.350	vw		
1.440	w							1.265	vw	1.265	vw		
								1.215	vw	1.215	vw		
								1.095	vw	1.095	vw		

$\text{AlH}_3 \cdot 0.35\text{Et}_2\text{O}$		$\text{ZnI}_2$		$\text{ZnI}_2 \cdot 0.35\text{Et}_2\text{O}$		$\text{ZnI}_2 \cdot \text{AlH}_3 \cdot 0.192\text{Et}_2\text{O}$		$\text{ZnBr}_2 \cdot 0.285\text{Et}_2\text{O}$		$\text{H}_3\text{Zn}_2\text{Br} \cdot 0.29\text{Et}_2\text{O}$	
$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}$	$I/I_0$	$d, \text{\AA}^a$	$I/I_0$
11.5	s	3.45	s	3.45	s	8.80	m	6.5	vw	1.95	s
4.55	m	3.05	w	3.05	vw	7.00	m	4.2	w	1.70	m
3.85	m	2.17	w	2.17	vw	5.40	vw	3.4	s	1.64	w
2.85	m	2.12	m	2.12	m	4.90	w	2.80	vw	1.27	w
2.32	m	1.84	m	1.84	m	4.35	w	2.55	vw	1.150	vw
		1.78	w	1.78	w	3.95	w	1.99	m		
		1.37	vw	1.375	vw	3.4	s				
		1.235	vw	1.245	vw						

<sup>a</sup> Powder diffraction lines were obtained as two broad halos and these are only approximate distances.

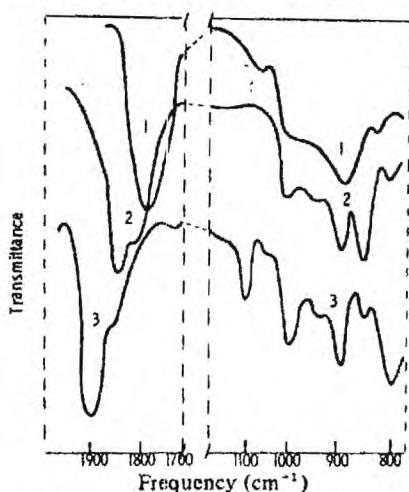


Figure 1. Infrared study of the reaction of  $\text{AlH}_3$  with  $\text{AlCl}_3$  in diethyl ether: 1,  $\text{AlH}_3$ ; 2,  $\text{AlH}_2\text{Cl}$ ; 3,  $\text{AlHCl}_2$ .

also there was no immediate precipitate and the mixture stayed clear for more than 24 hr. The infrared spectra of the clear mixture and the solid obtained after complete removal of ether were identical with the spectra obtained in part (a). Similarly X-ray powder patterns from (a) and (b) were identical. In this case, however, it was noticed that the formation of gray solid compound was faster than in (a) and in 1 week 33% of the solid (calculated on the basis of solid  $\text{MgBr}_2 \cdot 2\text{AlH}_3$ ) precipitated from solution. Analysis of the gray powder showed:  $\text{Mg}:\text{Al}:\text{H}:\text{Br} = 1.0:1.70:2.22:1.41$ .

**Reaction of  $\text{AlH}_3$  with  $\text{ZnCl}_2$ . Preparation of  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.35(\text{C}_2\text{H}_5)_2\text{O}$ .** In a typical reaction, a solution of aluminum hydride in

ether was added slowly to a solution of zinc chloride in ether in an appropriate ratio (see below). An immediate precipitation of a white solid took place. The mixture was stirred for 10 min and then filtered. The white residue was washed with ether, dried under vacuum, and stored at  $-20^\circ$ . Anal. Calcd for  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.35(\text{C}_2\text{H}_5)_2\text{O}$ : Zn, 66.99; H (hydrolyzable), 1.57; Cl, 18.16. Found: Zn, 66.52; H (hydrolyzable), 1.59; Cl, 17.82. The yield of product based on this analysis was 95%. The infrared spectrum of the white solid showed a very broad band with a maximum at  $\sim 1550 \text{ cm}^{-1}$  and a weak band at  $\sim 460 \text{ cm}^{-1}$ . The X-ray powder diffraction data given in Table I showed lines different from those of  $\text{ZnCl}_2$  and  $\text{AlH}_3$ .

The reaction was repeated in the following ratios of  $\text{AlH}_3:\text{ZnCl}_2$ : 1:1, 1:2, 1:3, and 4:1. The white precipitate obtained in each case was subjected to complete elemental analysis and characterized by infrared spectra and X-ray powder diffraction. Similarly, the filtrate, after isolation of the white solid, was characterized by infrared spectroscopy and elemental analysis. The results are described separately.

**(a) In 1:1 Mole Ratio.** Aluminum hydride, 6.75 mmol in ether solvent, was mixed with zinc chloride, 6.75 mmol, in ether solvent. Analysis of the resulting white solid gave  $\text{Al}:\text{Zn}:\text{H}:\text{Cl} = 0.07:1.00:1.74:0.41$ . Infrared analysis of the solid (Nujol mull) showed two broad bands at  $\sim 1550$  and  $600\text{--}350 \text{ cm}^{-1}$  centered at  $460 \text{ cm}^{-1}$ . The X-ray powder pattern of the solid was different from the patterns obtained for  $\text{ZnCl}_2$  and  $\text{AlH}_3$  (Table I). Elemental analysis of the filtrate showed  $\text{H}:\text{Al}:\text{Cl}:\text{Zn} = 1.60:1.00:1.57:0.00$  and infrared analysis showed the bands 1898 (s), 1850 (ms), 775 (s), and  $720 \text{ (s) cm}^{-1}$ .

**(b) In 1:2 Mole Ratio.**  $\text{AlH}_3$ , 6.846 mmol, in ether solvent, was mixed with  $\text{ZnCl}_2$ , 13.692 mmol, in ether solvent. Elemental analysis of the solid residue showed  $\text{Al}:\text{Zn}:\text{H}:\text{Cl} = 0.05:1.00:1.56:0.486$ . The infrared spectrum and X-ray powder diffraction pattern were similar to the solid described earlier in part (a). The infrared spectrum of the filtrate did not show any bands at  $2000\text{--}1600$  and  $800\text{--}700 \text{ cm}^{-1}$ .

(c) **In 1:3 Mole Ratio.**  $\text{AlH}_3$ , 2.259 mmol, in ether solvent was mixed with 6.779 mmol of  $\text{ZnCl}_2$  in ether solvent. Analysis of the resulting precipitate gave  $\text{Al}:\text{Zn}:\text{H}:\text{Cl} = 0.00:1.00:1.49:0.57$ . An infrared spectrum and X-ray powder pattern were obtained as in the previous cases. The analysis of the filtrate showed  $\text{Al}:\text{Zn}:\text{Cl}:\text{H} = 1.00:0.64:3.98:0.00$ . Infrared analysis did not show any absorption bands due to a hydridoaluminum halide.

(d) **In 4:1 Mole Ratio.**  $\text{AlH}_3$ , 5.957 mmol, in ether solvent was mixed with 1.489 mmol of  $\text{ZnCl}_2$  in ether solvent. Analysis of the resulting white precipitate gave  $\text{Al}:\text{Zn}:\text{H}:\text{Cl} = 0.07:1.00:1.91:0.43$ . The infrared spectrum of the filtrate showed strong bands at 1900, 1850 (sh), 1785, and  $760\text{ cm}^{-1}$ .

**Reaction of  $\text{AlCl}_3$  with  $\text{ZnCl}_2$ .**  $\text{AlCl}_3$ , 40 ml (7.404 mmol), in ether was added slowly to a solution of zinc chloride, 21.8 ml (7.404 mmol) in ether. There was an immediate precipitation of a white solid. The mixture was stirred for about 10 min and then filtered. The residue was washed, dried under vacuum, and analyzed:  $\text{Al}:\text{Zn}:\text{H}:\text{Cl} = 0.12:1.00:1.40:0.76$ . The infrared spectrum of the filtrate showed a broad band near  $1500\text{--}1400\text{ cm}^{-1}$ .

**Reaction of  $\text{AlH}_3$  with  $\text{ZnBr}_2$ .** Preparation of  $\text{H}_3\text{Zn}_2\text{Br}\cdot 0.29(\text{C}_2\text{H}_5)_2\text{O}$ . A solution of aluminum hydride was added slowly with stirring to a solution of zinc bromide in ether and the mixture stirred about 10 min. The white solid was filtered, washed with ether, and dried under vacuum. The compound was stored at  $-20^\circ$ . Anal. Calcd for  $\text{H}_3\text{Zn}_2\text{Br}\cdot 0.29(\text{C}_2\text{H}_5)_2\text{O}$ : H (hydrolyzable), 1.28; Zn, 55.51; Br, 33.93. Found: H (hydrolyzable), 1.17; Zn, 61.42; Br, 26.58. The infrared spectrum of the solid showed a broad band near  $1600\text{ cm}^{-1}$ . X-Ray powder diffraction data are given in Table I. The above reaction was carried out in several mole ratios of  $\text{AlH}_3:\text{ZnBr}_2$  and the results are described below.

(a) **In 1:1 Mole Ratio.**  $\text{AlH}_3$ , 6.357 mmol, in ether solvent was added to  $\text{ZnBr}_2$ , 6.357 mmol, in ether solvent. A white solid precipitated and was analyzed:  $\text{Al}:\text{Zn}:\text{H}:\text{Br} = 0.03:1.00:1.91:0.37$ . Infrared analysis of the solid (Nujol mull) showed a broad band near  $1600\text{ cm}^{-1}$ . The infrared spectrum of the filtrate showed the bands 1900 (s), 1850 (sh), 765 (s), and  $700\text{ cm}^{-1}$  (ms). The filtrate on standing overnight at room temperature deposited some gray powder which was mostly metallic zinc.

(b) **In 1:2 Mole Ratio.**  $\text{AlH}_3$ , 5.495 mmol, in ether solvent was added to  $\text{ZnBr}_2$ , 10.99 mmol, in ether solvent. Elemental analysis of the resulting solid gave  $\text{Al}:\text{Zn}:\text{H}:\text{Br} = 0.04:1.01:1.66:0.36$ . The infrared spectrum of the solid showed a broad band near  $1600\text{ cm}^{-1}$  whereas the infrared spectrum of the filtrate did not show any band between  $2000$  and  $1600\text{ cm}^{-1}$  and between  $800$  and  $700\text{ cm}^{-1}$ .

(c) **In 1:3 Mole Ratio.**  $\text{AlH}_3$ , 7.334 mmol, in ether solvent was mixed with  $\text{ZnBr}_2$ , 22.00 mmol, in ether solvent. Analysis of the white precipitate gave the molar ratio  $\text{Al}:\text{Zn}:\text{H}:\text{Br} = 0.04:1.00:2.06:0.41$ . The infrared spectrum of the filtrate did not show any absorption band due to hydridoaluminum compounds.

**Reaction of  $\text{AlH}_3$  with  $\text{ZnI}_2$ .** Preparation of  $\text{ZnI}_2\cdot\text{AlH}_3\cdot 1.79(\text{C}_2\text{H}_5)_2\text{O}$ . Solutions of aluminum hydride and zinc iodide in ether solvent were allowed to react. The white solid which precipitated immediately after mixing was filtered, washed with ether, dried under vacuum, and stored at  $-20^\circ$ . Anal. Calcd for  $\text{ZnI}_2\cdot\text{AlH}_3\cdot 1.79(\text{C}_2\text{H}_5)_2\text{O}$ : Zn, 13.55; I, 52.64; Al, 5.59; H (hydrolyzable), 0.627. Found: Zn, 13.86; I, 53.07; Al, 5.99; H (hydrolyzable), 0.693. The infrared spectrum of the white solid showed the following bands in addition to bands due to diethyl ether: 1630 (vs, br), 670 (s), 520 (m), and  $325\text{ cm}^{-1}$  (w). The X-ray powder diffraction pattern of the solid is listed in Table I. The reaction was carried out in several mole ratios of  $\text{AlH}_3:\text{ZnI}_2$  and the results are described below.

(a) **In 1:2 Mole Ratio.**  $\text{AlH}_3$ , 1.473 mmol, in ether solvent was mixed with  $\text{ZnI}_2$ , 2.947 mmol, in ether solvent. Analysis of the white solid precipitate gave a molar ratio of  $\text{Zn}:\text{Al}:\text{H}:\text{I} = 1.0:1.07:2.99:1.97$ . An infrared spectrum and X-ray powder diffraction pattern were identical with those described for the reaction carried out in 1:1 ratio. Analysis of the filtrate showed  $\text{Al}:\text{Zn}:\text{H}:\text{I} = 0.09:1.00:0.04:2.12$ . An infrared spectrum of the filtrate did not show any absorption bands near  $2000\text{--}1600$  and  $800\text{--}700\text{ cm}^{-1}$ . In a separate experiment, ether solutions of  $\text{AlH}_3$  and  $\text{ZnI}_2$  were mixed together in 1:2 mole ratio, and the mixture was stirred at  $0^\circ$  for 2 days. The white solid was then filtered, washed with ether, and dried under vacuum. The elemental analysis and the infrared spectrum of the white solid were identical with those described above.

(b) **In 4:1 Mole Ratio.**  $\text{AlH}_3$ , 5.825 mmol, in ether solvent was mixed with  $\text{ZnI}_2$ , 1.453 mmol, in ether solvent. A white solid which

precipitated immediately after mixing showed a molar ratio of  $\text{Al}:\text{Zn}:\text{H}:\text{I} = 1.04:1.00:3.26:1.91$ . The infrared spectrum and X-ray powder diffraction data were identical with those described above. However, the infrared spectrum of the filtrate showed absorption bands at  $1785$  (s) and  $760\text{ cm}^{-1}$  (s).

**Reaction of  $\text{AlH}_3$  with  $\text{CaBr}_2$ .** A solution of aluminum hydride (20.1 ml, 4.794 mmol) in diethyl ether was added to a slurry of  $\text{CaBr}_2$  (0.9583 g, 4.794 mmol) in 100 ml of ether. The mixture was stirred for 3 days at room temperature. It was then filtered and washed with ether, and the residue was dried under vacuum. Elemental analysis of the residue gave  $\text{Ca}:\text{H}:\text{Br} = 1.00:0.02:1.97$ . An infrared spectrum of the filtrate showed bands due to aluminum hydride only at  $1785$  (s) and  $760\text{ cm}^{-1}$  (s).

**Reaction of  $\text{AlH}_3$  with  $\text{CdBr}_2$ .**  $\text{CdBr}_2$  (1.9495 g, 7.161 mmoles) was transferred to a 250-ml Schlenk tube followed by the addition of 50 ml of diethyl ether. The mixture was stirred at  $-40$  to  $-30^\circ$  for about 15 min and then a solution of aluminum hydride (26.0 ml, 7.161 mmol) in diethyl ether was added to the  $\text{CdBr}_2$  slurry dropwise keeping the temperature of the reaction mixture always below  $-30^\circ$ . The mixture was stirred for 4 days at  $-40$  to  $-30^\circ$  during which time infrared spectra of the clear solution were recorded in order to follow the progress of the reaction. When the reaction was complete, a small portion of the solution was analyzed:  $\text{Al}:\text{Cd}:\text{H}:\text{Br} = 1.00:0.00:2.12:0.79$ . The infrared spectrum of the filtrate showed bands at  $1860$  (s, br),  $760$  (s), and  $700\text{ cm}^{-1}$  (s). The solid residue (slightly gray) was washed twice with cold ( $-70^\circ$ ) ether allowing the precipitate to settle to the bottom of the Schlenk tube while removing the clear liquid by syringe under nitrogen. The solid was analyzed:  $\text{Cd}:\text{H}:\text{Br} = 1.00:1.00:1.14$ . Hydrogen analysis was carried out by attaching the Schlenk tube with the solid directly to the vacuum line and allowing the solid to decompose at room temperature.

This reaction was studied in detail under the following conditions.

(a) **Reaction Product Allowed to Warm to Room Temperature.**  $\text{CdBr}_2$  and  $\text{AlH}_3$  were mixed in 1:1 mole ratio in diethyl ether in the same way as described above. The mixture was stirred for 6 hr at  $-78^\circ$  and then allowed to warm slowly to room temperature. When the temperature of the reaction mixture reached  $-20^\circ$ , it started turning dark and at room temperature became completely black giving off hydrogen gas. The black solid was separated by filtration, washed with ether, and dried under vacuum. The infrared spectrum of the solid did not show any absorption bands due to metal hydrides. The infrared spectrum of the filtrate on concentration showed bands at  $1906$  (s),  $762$  (s), and  $700\text{ cm}^{-1}$  (s). Analysis of the filtrate showed  $\text{Al}:\text{H}:\text{Br} = 1.00:0.576:2.00$  and it contained 73% of the total aluminum. Elemental analysis of the black residue gave  $\text{Al}:\text{Cd}:\text{H}:\text{Br} = 0.08:1.00:0.00:1.73$ .

(b) **Reaction in THF.** Since  $\text{CdBr}_2$  is more soluble in THF than diethyl ether, a solution of  $\text{AlH}_3$  (3.3 ml, 1.320 mmol) in THF was added to a solution of  $\text{CdBr}_2$  (200 ml, 1.320 mmol) in THF at  $-78^\circ$ . The mixture was stirred at  $-35^\circ$  for 4 hr and then allowed to settle overnight inside a dewar flask. It was noticed that even after 16 hr the mixture remained turbid. The supernatant liquid was then removed carefully, with a syringe, and the remaining solid was washed with cold THF. The resulting solid was analyzed:  $\text{Al}:\text{Cd}:\text{H}:\text{Br} = 0.93:1.00:1.00:2.09$ .

(c) **Reaction in 3:1 Mole Ratio in Ether.**  $\text{CdBr}_2$  and  $\text{AlH}_3$  were mixed in 3:1 mole ratio in ether and the mixture stirred for 6 hr at  $-40$  to  $-35^\circ$ . The mixture was allowed to settle and the infrared spectrum of the clear solution showed the absence of any hydridoaluminum compound. The reaction mixture was then cooled to  $-76^\circ$  and transferred inside the glove box as fast as possible, flushing the entryport with nitrogen for 10 min. It was then filtered and washed with cold ( $-40^\circ$ ) ether. The white solid residue turned black within a few seconds. The infrared spectrum of the filtrate on concentration did not show any absorption bands due to aluminum-hydrogen compounds. Analysis of the filtrate showed  $\text{H}:\text{Al}:\text{Cd}:\text{Br} = 0.00:1.00:0.00:0.76$ , corresponding to 36.2% of the total aluminum.

**Reaction of  $\text{H}_2\text{AlBr}$  with  $\text{CdBr}_2$  in Ether.**  $\text{H}_2\text{AlBr}$  (61 ml, 7.585 mmol) in ether was added to a slurry of  $\text{CdBr}_2$  (2.0649 g, 7.585 mmol) in ether stirred at  $-40^\circ$ . The mixture was stirred for 5 days at  $-40$  to  $-30^\circ$  until the reaction was complete. The infrared spectrum of the clear solution showed a strong and broad band at  $1900\text{--}1800\text{ cm}^{-1}$  with a maximum at  $1850\text{ cm}^{-1}$ . The position of the band did not change on further stirring. Analysis of the solution showed  $\text{Al}:\text{Cd}:\text{H}:\text{Br} = 1.00:0.04:1.90:1.15$ , whereas the analysis of the residue on decomposition at room temperature and subsequent hydrolysis gave

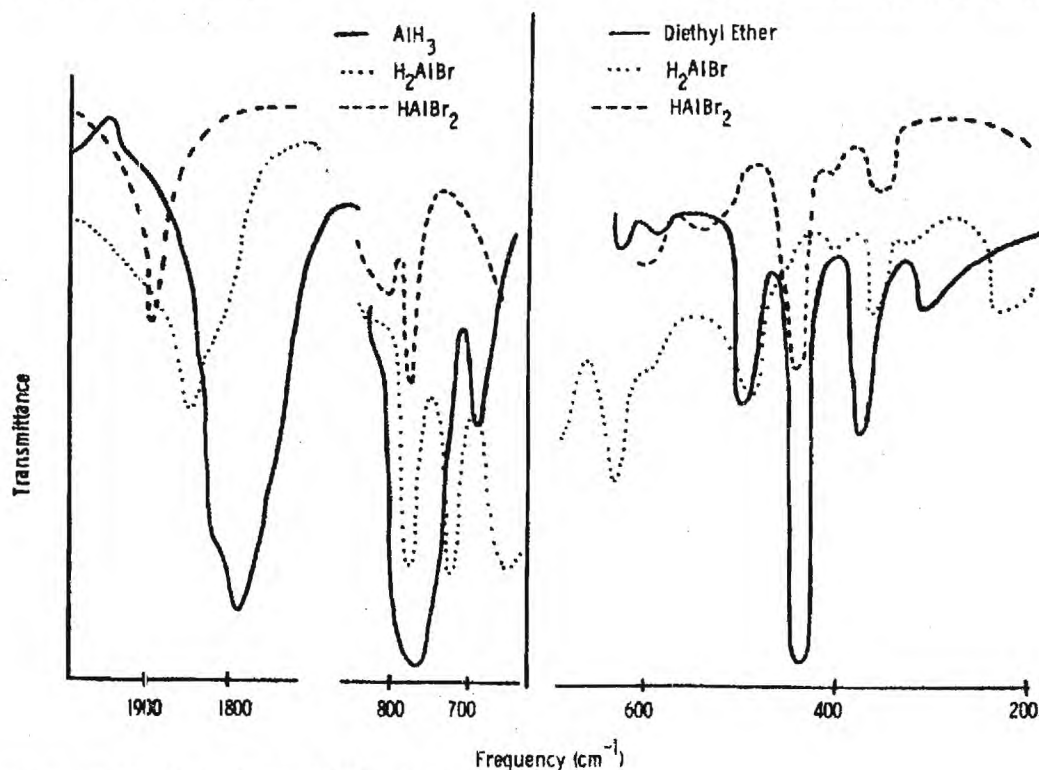


Figure 2. Infrared spectra of  $\text{AlH}_3$ ,  $\text{H}_2\text{AlBr}$ , and  $\text{HAIBr}_2$  in diethyl ether.

$\text{Al}:\text{Cd}:\text{H}:\text{Br} = 0.09:1.00:0.19:1.94$ .

**Reaction of  $\text{AlH}_3$  with  $\text{CuCl}$  in Ether.** Aluminum hydride solution (42.7 ml, 12.89 mmoles) in ether was added to a slurry of  $\text{CuCl}$  (1.276 g, 12.89 mmol) in ether. The mixture was stirred for 6 hr at  $-76^\circ$  and then allowed to warm to room temperature. At  $-40^\circ$ , the color of the reaction mixture started to turn black, and by the time the temperature rose of  $0^\circ$ , it was almost completely black giving off some gas and depositing a black precipitate at the bottom of the flask. It was then filtered and washed with ether, and the residue was dried at room temperature. The infrared spectrum of the filtrate showed a strong band at  $1900\text{ cm}^{-1}$  with a shoulder at  $1850\text{ cm}^{-1}$  and a strong band at  $775\text{ cm}^{-1}$ . Analysis of the filtrate gave a molar ratio of  $\text{Al}:\text{H}:\text{Cl} = 1.04:1.00:1.80$  corresponding to 44.2% of the total aluminum.

### Results and Discussion

The reaction of aluminum hydride with group 1b, 2a, and 2b metal halides can be considered as a metathetical exchange reaction in which one or more hydrogen atoms of alane are exchanged with the halogen atom of the metal halide. The electronegativity differences for metal halides are calculated from the eq 2, where  $Q$  is the standard heat of formation and

$$Q = 23\Sigma(X_A - X_B)^2 \quad (2)$$

$X_A - X_B$  is the electronegativity difference for the elements A and B.<sup>16</sup> The electronegativity differences for metal halides are listed in Table II. A comparison of the electronegativity differences with the experimental observations shows that if the electronegativity of the group 1 or 2 metal is higher than aluminum, the exchange reaction does not take place. However, in the case of comparable or lower electronegativity differences the exchange does take place. This simply means that in the exchange reaction between  $\text{AlH}_3$  and metal halide the reaction will proceed to form the most thermodynamically stable products which are those resulting from the most electronegative group (halogen) residing on the most electropositive metal. Therefore,  $\text{AlH}_3$  would not be expected to react with  $\text{LiCl}$  to form  $\text{AlCl}_3$  and  $\text{LiH}$  but would be expected to react with  $\text{ZnBr}_2$  to form  $\text{AlBr}_3$  and  $\text{ZnH}_2$ .

As reported previously,<sup>14</sup> redistribution reactions are studied by mixing ether solutions of metal hydrides with metal halides in various mole ratios followed by complete elemental analysis

Table II. Electronegativities of Elements and Electronegativity Difference between the Metal and Halogen

Elements	Electro-negativity	Metal halide	Electronegativity difference
Ca	1.04	$\text{CaBr}_2$	1.87
Mg	1.23	$\text{MgBr}_2$	1.64
Be	1.47	$\text{BeCl}_2$	1.56
Al	1.47	$\text{AlCl}_3$	1.55
Zn	1.66	$\text{ZnCl}_2$	1.47
Cd	1.70	$\text{AlBr}_3$	1.35
Cu	1.90	$\text{ZnBr}_2$	1.30
H	2.20	$\text{CdBr}_2$	1.27
I	2.5	$\text{CuCl}$	1.18
Br	2.8	$\text{AlI}_3$	1.04
Cl	3.0	$\text{ZnI}_2$	1.04

of the resulting solution and precipitate that forms. The precipitate is further analyzed by X-ray powder diffraction, DTA-TGA, and infrared analysis whereas the solutions are analyzed further only by infrared spectroscopy.

**Reactions of  $\text{AlH}_3$  with  $\text{AlX}_3$  ( $X = \text{Cl}, \text{Br}$ ).** Since hydrogen exchange in the  $\text{AlH}_3\text{-MX}_2$  system would be expected to form hydridoaluminum halides, it was necessary first to prepare  $\text{HAIX}_2$  and  $\text{H}_2\text{AlX}$  (where  $X = \text{Cl}$  and  $\text{Br}$ ) in order to obtain the necessary infrared spectroscopic information for identification purposes. Ether-soluble  $\text{AlH}_3$  was found to exhibit bands in its infrared spectrum at  $1785$  and  $770\text{ cm}^{-1}$ . These bands are assigned to the  $\text{Al-H}$  stretching and  $\text{Al-H}$  deformation vibrations, respectively. The hydridoaluminum halides (where  $X = \text{Cl}$  and  $\text{Br}$ ) were prepared in ether solvent by simply mixing ether solutions of  $\text{AlH}_3$  and the appropriate aluminum halide at low temperature in order to avoid ether cleavage. The infrared spectra are recorded in Figures 1 and 2.



**Reactions of  $\text{AlH}_3$  with  $\text{CaBr}_2$ .** Calcium bromide does not undergo an exchange reaction with  $\text{AlH}_3$  due to the fact that calcium is more electropositive than aluminum. Elemental analysis as well as the infrared analysis of the products obtained

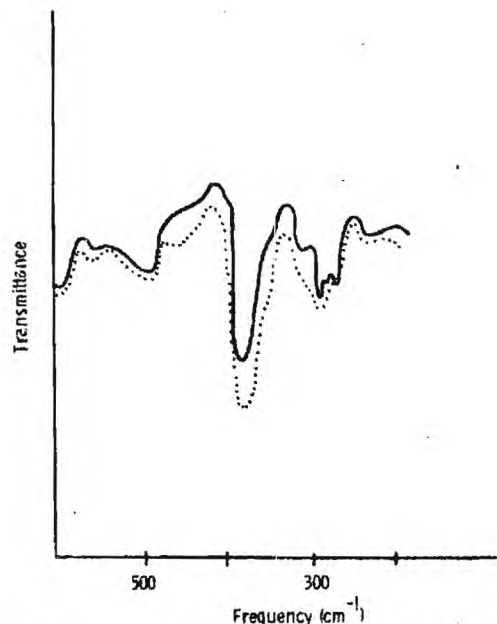
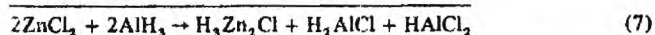
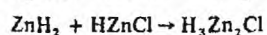
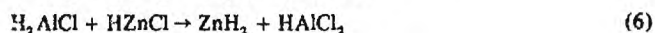
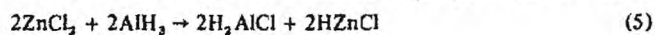


Figure 3. Infrared spectra of (a) the reaction product of  $\text{MgBr}_2 + \text{AlH}_3$  (—) and (b)  $\text{MgBr}_2 \cdot n(\text{C}_2\text{H}_5)_2\text{O}$  (···).

after mixing an ether solution of  $\text{AlH}_3$  with  $\text{CaBr}_2$  results in a quantitative recovery of unreacted calcium bromide and  $\text{AlH}_3$ .

**Reactions of  $\text{AlH}_3$  with  $\text{MgBr}_2$ .** Similarly,  $\text{MgBr}_2$  does not react with  $\text{AlH}_3$  in diethyl ether. Although there is no immediate precipitate after mixing an ether solution of  $\text{MgBr}_2$  with  $\text{AlH}_3$ , the possibility of some soluble complex metal hydride could not be ruled out completely. Therefore, in order to isolate and characterize any possible complex, the infrared spectra of magnesium bromide and  $\text{AlH}_3$  were determined in the near- and far-infrared regions in order to establish metal-hydrogen (deformation) and metal-halogen stretching frequencies. The infrared spectra of both  $\text{MgBr}_2$  and the reaction mixture showed only one medium intense band at  $380 \text{ cm}^{-1}$  other than weak bands for diethyl ether (Figure 3). This band may be assigned to the Mg-Br stretching vibration. Powder diffraction patterns were obtained for  $\text{MgBr}_2$  and  $\text{AlH}_3$  containing nearly the same number of solvent molecules (Table I) as that of the product after solvent removal. The X-ray powder pattern of the product was consistent with a physical mixture of  $\text{MgBr}_2$  and  $\text{AlH}_3$ . Similarly, the TGA analysis of the solid showed it to be either a very weak complex of  $\text{AlH}_3$  or  $\text{AlH}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  mixed with  $\text{MgBr}_2$ . On standing for several days at room temperature the reaction mixture decomposed to hydrogen and aluminum which precipitated as a gray powder. The absence of infrared absorption bands characteristic of the Mg-H stretching vibration ruled out the possibility of the existence of either  $\text{MgH}_2$  or  $\text{HMgBr}$  in the gray solid.

**Reactions of  $\text{ZnCl}_2$  with  $\text{AlH}_3$ .** In 1:1 mole ratio  $\text{ZnCl}_2$  and  $\text{AlH}_3$  react to produce a stable white solid of empirical formula  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.35(\text{C}_2\text{H}_5)_2\text{O}$ .<sup>17</sup> The infrared spectrum of the filtrate showed absorption bands at  $1900 \text{ (s)}$ ,  $1850 \text{ (s)}$ ,  $780 \text{ (s)}$ , and  $720 \text{ cm}^{-1} \text{ (s)}$ , indicating the presence of  $\text{HAlCl}_2$  and  $\text{H}_2\text{AlCl}$  in solution. These results suggest that the reaction takes place as in eq 5-7. The infrared spectrum as well as



the X-ray powder diffraction pattern of the solid product shows it to be a unique compound and not a physical mixture of

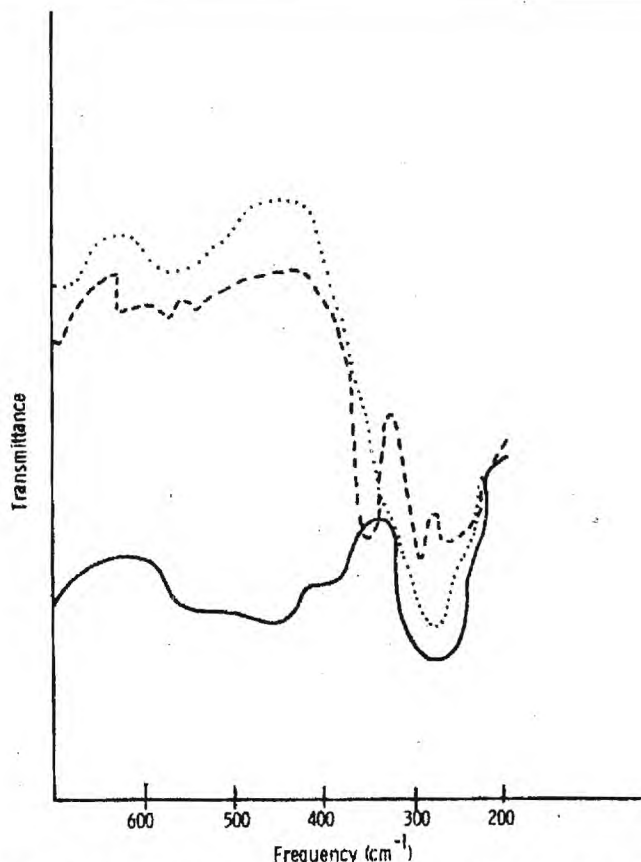
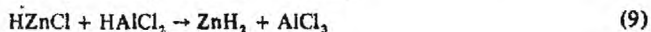
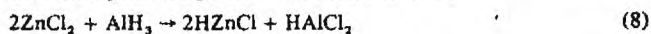


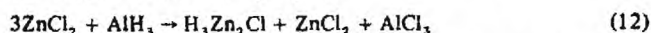
Figure 4. Infrared spectra of (a)  $\text{ZnCl}_2$  (···), (b)  $\text{ZnCl}_2 \cdot 0.11\text{Et}_2\text{O}$  (---), and (c)  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.35\text{Et}_2\text{O}$  (—).

$\text{ZnCl}_2$  and  $\text{ZnH}_2$ . The infrared spectra of  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.35(\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{ZnCl}_2 \cdot 0.11\text{Et}_2\text{O}$ , and  $\text{ZnCl}_2$  in the solid state are reported in Figure 4 and the X-ray powder diffraction patterns are listed in Table I. An X-ray powder diffraction pattern of  $\text{ZnCl}_2 \cdot 0.35(\text{C}_2\text{H}_5)_2\text{O}$  could not be obtained because the solid was quite sticky. Possibly the most convincing piece of information suggesting that  $\text{H}_3\text{Zn}_2\text{Cl}$  is a single compound and not a mixture of  $\text{ZnH}_2$  and  $\text{ZnCl}_2$  in 3:1 ratio is the fact that  $\text{ZnCl}_2$  is soluble in ether, yet the  $\text{H}_3\text{Zn}_2\text{Cl}$  ratio is maintained under a variety of conditions.

In 2:1 mole ratio,  $\text{ZnCl}_2$  and  $\text{AlH}_3$  reacted to yield the same solid compound,  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.35(\text{C}_2\text{H}_5)_2\text{O}$ , which was characterized by elemental analysis, X-ray powder diffraction, and infrared analysis. However, the infrared spectrum and elemental analysis of the filtrate showed it to contain only  $\text{AlCl}_3$  indicating the sequence of reactions 8-11.



The infrared spectrum and elemental analysis of the solid compound obtained by allowing  $\text{ZnCl}_2$  and  $\text{AlH}_3$  to react in a 3:1 mole ratio showed the solid product to be  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.38(\text{C}_2\text{H}_5)_2\text{O}$ ; however, the filtrate contained 1 mol of  $\text{AlCl}_3$  as well as 1 mol of unreacted  $\text{ZnCl}_2$  as expected from the results described by eq 12.



When  $\text{ZnCl}_2$  and  $\text{AlH}_3$  were allowed to react in 1:4 mole ratio,  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.31\text{Et}_2\text{O}$  was again obtained; however, the elemental analysis gave a molar ratio of  $\text{Al}:\text{Zn}:\text{H}:\text{Cl} = 0.07:1.00:1.91:0.43$ . The high hydrogen ratio indicates that in the presence of excess  $\text{AlH}_3$  some  $\text{HZnCl}$  reacts further with  $\text{AlH}_3$  to form  $\text{ZnH}_2$  rather than complex with  $\text{ZnH}_2$  already

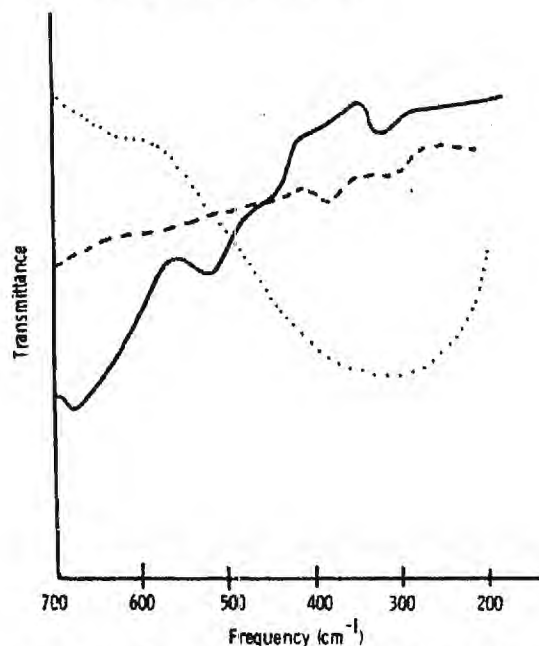
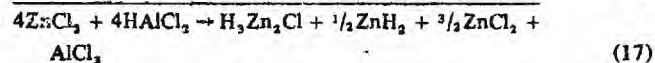
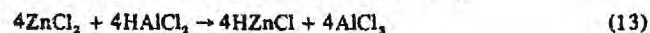


Figure 5. Infrared spectra of (a)  $\text{ZnI}_2$  (· · ·), (b)  $\text{ZnI}_2 \cdot 0.35\text{Et}_2\text{O}$  (---), and (c)  $\text{ZnI}_2 \cdot \text{AlH}_3$  (—).

present to form  $\text{H}_3\text{Zn}_2\text{Cl}$ . Thus, the  $\text{H}_3\text{Zn}_2\text{Cl}$  formed is contaminated with  $\text{ZnH}_2$ .

In an attempt to verify the existence of  $\text{HZnCl}$ , zinc chloride and  $\text{HAlCl}_2$  were allowed to react in a 1:1 mole ratio in diethyl ether. In this case a white solid was obtained corresponding to a molar ratio of  $\text{Al}:\text{Zn}:\text{H}:\text{Cl} = 0.12:1.00:1.40:0.76$  suggesting the formation of  $\text{H}_3\text{Zn}_2\text{Cl}$  (see eq 13–17).



Unfortunately  $\text{HZnCl}$  was not isolated as anticipated according to eq 13. This means either that  $\text{HZnCl}$  reacts more rapidly with  $\text{HAlCl}_2$  than  $\text{ZnCl}_2$  to form  $\text{ZnH}_2$  or that  $\text{HZnCl}$  disproportionates according to eq 14. Either way  $\text{ZnH}_2$  is formed which then complexes  $\text{HZnCl}$  to form the apparently stable  $\text{H}_3\text{Zn}_2\text{Cl}$ .

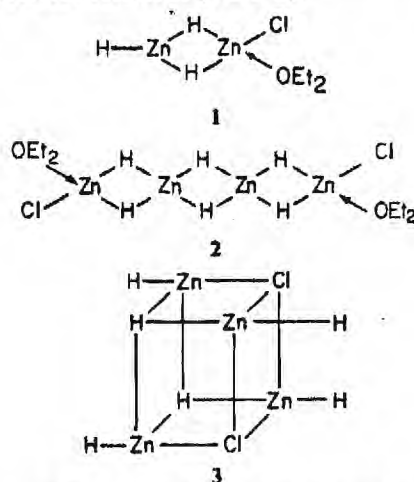
**Reactions of  $\text{ZnBr}_2$  with  $\text{AlH}_3$ .** Like  $\text{ZnCl}_2$ ,  $\text{ZnBr}_2$  was also allowed to react with  $\text{AlH}_3$  in 1:1 and 2:1 mole ratios in ether. As in the previous case a white solid was formed closely corresponding to the empirical formula  $\text{H}_3\text{Zn}_2\text{Br} \cdot 0.29\text{Et}_2\text{O}$ . However,  $\text{H}_3\text{Zn}_2\text{Br}$  appears to be less stable than  $\text{H}_3\text{Zn}_2\text{Cl}$  since the white solid decomposed (producing a light gray solid) rapidly when the reaction mixture was stirred for the same period of time at room temperature. The light gray color is presumably due to the formation of zinc metal. The reactions were in general comparable with the reactions of  $\text{ZnCl}_2$  with  $\text{AlH}_3$ . X-Ray powder diffraction patterns for  $\text{ZnBr}_2$ ,  $\text{ZnBr}_2 \cdot 0.28\text{Et}_2\text{O}$ , and  $\text{H}_3\text{Zn}_2\text{Br} \cdot 0.29\text{Et}_2\text{O}$  are shown in Table I. The fact that  $\text{ZnBr}_2$  is soluble in ether and yet  $\text{H}_3\text{Zn}_2\text{Br}$  precipitated indicates that  $\text{H}_3\text{Zn}_2\text{Br}$  cannot be a mixture of  $\text{ZnH}_2$  and  $\text{ZnBr}_2$  in a 3:1 ratio.

**Reactions of  $\text{ZnI}_2$  with  $\text{AlH}_3$ .** In a 2:1 mole ratio,  $\text{ZnI}_2$  and  $\text{AlH}_3$  in diethyl ether react to yield a white solid corresponding to the composition  $\text{ZnI}_2 \cdot \text{AlH}_3 \cdot 1.79\text{Et}_2\text{O}$ . Infrared analysis and X-ray powder diffraction of the solid compound showed it to be different from a physical mixture of  $\text{ZnI}_2$  and  $\text{AlH}_3$ . The infrared spectrum as well as elemental analysis of the filtrate did not show the presence of any hydridoaluminum halides.

Similarly, when the reaction was carried out in a 1:4 mole ratio ( $\text{ZnI}_2:\text{AlH}_3$ ), a white solid resulted having the same composition. An infrared spectrum of the filtrate showed absorption bands due to  $\text{AlH}_3$  alone. Therefore, it is safe to conclude that zinc iodide and  $\text{AlH}_3$  in all stoichiometric ratios react to form  $\text{ZnI}_2 \cdot \text{AlH}_3 \cdot n\text{Et}_2\text{O}$ .

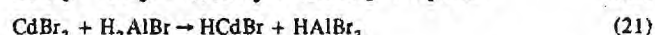
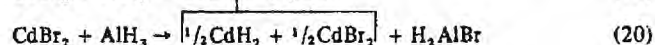
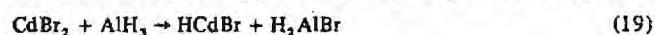


Very little can be said about the structures of the new zinc-hydrogen compounds ( $\text{H}_3\text{Zn}_2\text{Cl}$ ,  $\text{H}_3\text{Zn}_2\text{Br}$ ,  $\text{ZnI}_2 \cdot \text{AlH}_3$ ) prepared in this study. If the compounds were soluble in some solvent, molecular weight and infrared studies could reveal much structural information. However, all of the hydrides were insoluble in all solvents in which they were tested leaving only single-crystal X-ray diffraction studies as a source of further information. In any case it might be worthwhile to point out at least some of the structural possibilities that should be considered for  $\text{H}_3\text{Zn}_2\text{Cl}$  (see 1–3).



**Reactions of  $\text{CdBr}_2$  with  $\text{AlH}_3$ .** In a 1:1 mole ratio,  $\text{CdBr}_2$  and  $\text{AlH}_3$  in diethyl ether were allowed to react at  $-40$  to  $-30^\circ$  for 40 hr with stirring to yield a slightly gray solid which exhibited a molar ratio of  $\text{Cd}:\text{H}:\text{Br} = 1.00:1.00:1.143$ . The solid decomposed to  $\text{Cd}$ ,  $\text{H}_2$ , and  $\text{CdBr}_2$  slowly at  $-20^\circ$  and more rapidly at room temperature. As reported earlier by Wiberg and Henle,<sup>2</sup>  $\text{CdH}_2$  was also found to decompose at  $-20^\circ$ . Therefore, although the elemental analysis of the solid compound suggests the formation of  $\text{HCdBr}$  compound, the possibility of a physical mixture of  $\text{CdH}_2$  and  $\text{CdBr}_2$  cannot be ruled out. Elemental analysis of the filtrate showed the presence of  $\text{H}_2\text{AlBr}$  which was also supported by an infrared spectrum which exhibited bands characteristic of  $\text{H}_2\text{AlBr}$ .

In order to establish the nature of the solid product as  $\text{HCdBr}$  (eq 19) and not a mixture of  $\text{CdBr}_2$  and  $\text{CdH}_2$  (eq 20), an attempt was made to allow a mixture of  $\text{CdBr}_2$  and  $\text{H}_2\text{AlBr}$  to react in diethyl ether in a 1:1 ratio at  $-40^\circ$ . If the reaction of  $\text{CdBr}_2$  and  $\text{AlH}_3$  proceeds according to eq 20, then  $\text{CdBr}_2$  is produced in the presence of  $\text{H}_2\text{AlBr}$ . Since it is possible that  $\text{CdBr}_2$  is reduced in the presence of  $\text{H}_2\text{AlBr}$  (eq 21), the presence of  $\text{HAlBr}_2$  would indicate the presence of  $\text{CdBr}_2$  in solution. If indeed this reaction occurs (eq 21), this would indicate the absence of  $\text{CdBr}_2$  in the reaction product of  $\text{CdBr}_2$  and  $\text{AlH}_3$ , thus eliminating eq 20 as the reaction course. Unfortunately, no reaction took place; thus, it is not

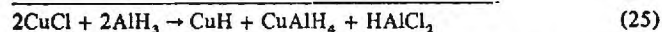


possible to tell whether the reaction product is  $\text{HCdBr}$  or a physical mixture of  $\text{CdBr}_2$  and  $\text{CdH}_2$ .

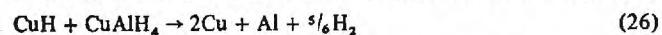
Because of the low solubility of  $\text{CdBr}_2$  in diethyl ether, an

attempt was also made to study the reaction in THF; however, the reaction was found to be too slow at  $-40$  to  $-30^\circ$  and the reaction product decomposed above  $-20^\circ$ .

**Reactions of CuCl with  $\text{AlH}_3$ .** When cuprous chloride and  $\text{AlH}_3$  were allowed to react in 1:1 mole ratio in ether at  $-78^\circ$  and then allowed to warm slowly to room temperature, the reaction mixture turned completely black giving off a gas. The elemental analysis as well as an infrared spectrum of the filtrate suggests that the reaction takes place according to the sequence of eq 22-25.



The infrared spectrum of the filtrate showed a sharp band at  $1900\text{ cm}^{-1}$  with a shoulder at  $1850\text{ cm}^{-1}$ . Elemental analysis of the filtrate indicated only 43% of the total aluminum. The infrared spectrum of the black solid product did not show any absorption bands due to either hydridoaluminum compounds or hydridocopper compounds. Thus, it appears that the black solid product is a mixture of copper and aluminum metal formed according to eq 26. Since the filtrate was shown to be an ether solution of  $\text{HAlCl}_2$  and since half of the aluminum



was in the filtrate and half in the precipitate, it appears that there are ample data to suggest the above reaction sequence.

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Registry No.  $\text{AlH}_3$ , 7784-21-6;  $\text{AlH}_2\text{Cl}$ , 14644-71-4;  $\text{AlHCl}_2$ , 13497-97-7;  $\text{AlCl}_3$ , 7446-70-0;  $\text{AlBr}_3$ , 7727-15-3;  $\text{H}_2\text{AlBr}$ , 54844-46-1;  $\text{HAlBr}_2$ , 15576-93-9;  $\text{ZnCl}_2$ , 7646-85-7;  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.35(\text{C}_2\text{H}_5)_2\text{O}$ , 54931-33-8;  $\text{ZnBr}_2$ , 7699-45-8;  $\text{H}_3\text{Zn}_2\text{Br} \cdot 0.29(\text{C}_2\text{H}_5)_2\text{O}$ , 54931-35-0;  $\text{ZnI}_2$ , 10139-47-6;  $\text{ZnI}_2 \cdot \text{AlH}_3 \cdot 1.79(\text{C}_2\text{H}_5)_2\text{O}$ , 54931-34-9;  $\text{CdBr}_2$ , 7789-42-6;  $\text{CuCl}$ , 7758-89-6.

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- (16) L. Pauling, "The Nature of The Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960, p 92.
- (17) The ether content of this compound is a result of drying the compound under vacuum for 1 hr before analysis. Further attempts to remove additional solvent by subjecting the compound to vacuum for a longer period of time resulted in decomposition of the solid.

# Reactions of Alkali Metal Hydrides with Magnesium Alkyls. Preparation of $\text{MMgR}_2\text{H}$ and $\text{MMg}_2\text{R}_4\text{H}$ Compounds<sup>1,2</sup>

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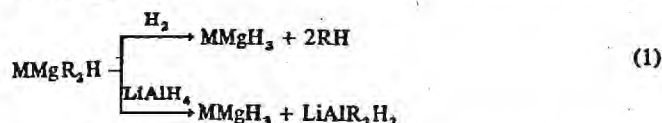
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Lithium hydride was shown not to react with dimethylmagnesium in ether; however, in THF intermediate complexes formed which cleaved the THF solvent. Ether cleavage also resulted when LiH and NaH were allowed to react with  $(\text{C}_6\text{H}_5)_2\text{Mg}$  in THF. On the other hand, a stable insoluble complex  $[\text{KMg}_2(\text{C}_6\text{H}_5)_4\text{H}]$  was formed when KH and  $(\text{C}_6\text{H}_5)_2\text{Mg}$  were allowed to react in ether solvent. In benzene solvent alkali metal hydrides reacted with  $\text{R}_2\text{Mg}$  compounds to form stable soluble complexes, e.g.,  $\text{NaMg}_2(\text{s-C}_4\text{H}_9)_4\text{H}$ ,  $\text{KMg}(\text{s-C}_4\text{H}_9)_2\text{H}$ , and  $\text{KMg}(\text{n-C}_4\text{H}_9)_2\text{H}$ . The 1:1 complex of KH and  $(\text{s-C}_4\text{H}_9)_2\text{Mg}$  prepared in benzene is soluble in THF and reacts with LiBr to form  $\text{LiMg}(\text{s-C}_4\text{H}_9)_2\text{H}$  and KBr. The corresponding reaction in ether forms the soluble complex  $\text{LiMg}_2(\text{s-C}_4\text{H}_9)_4\text{H}$  and precipitates a mixture of KBr and LiH. The reaction of  $\text{KMg}(\text{s-C}_4\text{H}_9)_2\text{H}$  with tri-*n*-octyl-*n*-propylammonium bromide in THF produced  $\text{NR}_4\text{Mg}(\text{s-C}_4\text{H}_9)_2\text{H}$  and the reaction of  $\text{KMg}(\text{s-C}_4\text{H}_9)_2\text{H}$  with NaI in THF resulted in the precipitation of KI and the formation of  $\text{NaMg}(\text{s-C}_4\text{H}_9)_2\text{H}$ . A total of eight new complex metal hydrides of magnesium were prepared.

## Introduction

The reaction of diethylmagnesium with lithium, sodium, and potassium hydrides is reported to result in complex formation; however, extensive ether cleavage resulted and the complexes could not be isolated.<sup>3</sup> Although stable complexes of beryllium and zinc such as  $\text{NaH}\cdot\text{Et}_2\text{Be}$ ,<sup>4</sup>  $\text{NaH}\cdot 2\text{Et}_2\text{Zn}$ ,<sup>5,6</sup>  $\text{LiH}\cdot\text{Ph}_2\text{Zn}$ , and  $\text{LiH}\cdot\text{Ph}_2\text{Be}$ ,<sup>7</sup> are known, still no stable complexes of alkali metal hydrides and  $\text{R}_2\text{Mg}$  compounds have been reported.

Our interest in alkali metal complexes of magnesium alkyls resides in the potential of these compounds as intermediates in the preparation of alkali metal complex hydrides of magnesium, e.g.,  $\text{KMgH}_3$ ,  $\text{LiMg}_2\text{H}_5$ , etc. Since previous attempts to prepare  $\text{LiMgH}_3$  by the reaction of LiH and  $\text{MgH}_2$  failed,<sup>8</sup> it was felt that either hydrogenolysis or reduction of compounds such as  $\text{MMgR}_2\text{H}$  might result in the formation of  $\text{MMgH}_3$ .



Since Coates and coworkers<sup>3</sup> had already attempted to prepare  $\text{MMgR}_2\text{H}$  compounds in ether solvents and had observed extensive ether cleavage, it was clear that such complexes would have to be prepared in nonether solvents. Although most  $\text{R}_2\text{Mg}$  compounds are not soluble in hydrocarbon solvents, it has been recently found that  $(\text{s-C}_4\text{H}_9)_2\text{Mg}$  is soluble in benzene.<sup>9</sup> Therefore, it was decided to attempt to carry out these reactions in benzene solvent and hence have at least one reactant in solution and also avoid ether cleavage. Reactions between NaH and KH with  $(\text{s-C}_4\text{H}_9)_2\text{Mg}$  in benzene did proceed nicely to form benzene soluble complexes.<sup>2</sup> The reactions were easily monitored by observing the solubilization of the alkali metal hydride as the reaction proceeded.

## Experimental Section

**Apparatus.** All operations were performed under a nitrogen atmosphere using either a nitrogen-filled glove box equipped with a special recirculating system to remove oxygen and moisture<sup>10</sup> or on the bench top using Schlenk tube techniques.<sup>11</sup> All glassware was flash flamed and flushed with dry nitrogen prior to use.

Infrared spectra were obtained using a Perkin-Elmer 621 grating spectrophotometer. Cesium iodide windows were used. Solid spectra were recorded as mulls in Nujol which had been dried over sodium wire and stored in a nitrogen filled glove box.

X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6 mm camera with nickel filtered  $\text{Cu K}\alpha$  radiation. Samples were sealed in 0.5 mm capillaries and exposed to X-rays for 6 hr. *d* spacings were read on a precalibrated scale equipped with

a viewing apparatus. Line intensities were estimated visually.

Hydrogenolysis experiments were performed using a 300 ml Magedrive autoclave (Autoclave Engineers, Inc.). The chamber was charged either inside the drybox or on the bench top using a hypodermic syringe under strong nitrogen flush. The contents were then heated and stirred under hydrogen for a predetermined period of time. After cooling to room temperature, the chamber was vented and the products were isolated inside the glove box.

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 weighed sample inside a high vacuum line with ~6 *M* hydrochloric acid and passing the evolved gases 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. Magnesium was determined by EDTA titration at pH 10 using Eriochrome Black T as an indicator. Aluminum, when present, was masked with triethanolamine. 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 with dithizone as indicator. Halide determinations were performed by the Volhard titration. Alkali metals were determined by flame photometry using appropriate filters.

**Materials.** All solvents were distilled immediately prior to use. Tetrahydrofuran and benzene (Fisher Certified reagent grade) were distilled under nitrogen over  $\text{NaAlH}_4$  and diethyl ether (Fisher reagent) over  $\text{LiAlH}_4$ . Benzyl chloride (Fisher reagent grade) was distilled over  $\text{P}_2\text{O}_5$  under reduced pressure and 2-chloropropane and 1-chloropentane (Eastman Organic Chemicals) were dried and distilled over  $\text{MgSO}_4$  prior to use. Grignard grade magnesium turnings were used except in the preparation of dimethylmagnesium when triply sublimed magnesium (Dow Chemical Co.) was employed. *sec*-Butyllithium was obtained as a 11.9% solution in hexane from the Foote Mineral Co. and stored at -20° until ready to use. Methyl-lithium used was a 5.0% solution in diethyl ether obtained from the Lithium Corporation of America. Lithium bromide and lithium iodide (Foote Mineral Co.) were dried at 130° under vacuum for 24 hr and used without further purification. Tri-*n*-octyl-*n*-propylammonium bromide (Eastman Organic Chemicals) was dried at 55° under vacuum for 2 days and used without any subsequent purification. Ultrapure hydrogen (99.9995%) obtained from Matheson Corporation was employed in hydrogenation experiments. Dimethylmercury was obtained from Orgmet, Inc., and used without further purification. Potassium and sodium hydride (as a suspension in mineral oil),  $\text{LiAlH}_4$ , and  $\text{NaAlH}_4$  were obtained from Ventron Metal Hydrides

Table I. X-Ray Powder Diffraction Pattern of Potassium Hydride-Diphenylmagnesium Complexes

<i>d</i>			
KH + 2Mg(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	KH + Mg(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	2KH + Mg(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	5KH + Mg(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>
8.00 w	8.74 w	8.68 w, br	
7.42 w	7.46 vw	7.36 vw	
6.50 w	6.50 vw	6.47 vw	
5.80 w	5.88 vw	5.85 vw	
5.10 m	5.15 w	5.12 w, br	5.19 vw
4.76 w	4.71 vw	4.82 vw	
4.50 w	4.37 w, br	4.39 w, br	4.44 vw
4.35 m	4.19 vw	4.19 vw	
4.16 w	4.05 vw	4.04 vw	
4.00 w	3.81 vw	3.82 vw	
3.75 w	3.75 vw	3.63 vw	3.64 vw
3.45 w	3.27 m	3.28 vs	3.28 vs
3.25 vw	3.06 vw	3.05 vw	3.19 vw
3.04 m	2.93 vw	2.93 m	2.84 s
2.92 m	2.84 m	2.85 m	
2.81 m	2.70 vw	2.69 vw	
2.67 vw	2.61 vw	2.61 vw	2.60 vw
2.59 vw	2.29 vw	2.50 w, br	2.23 vw
2.48 w, br	2.02 w	2.02 m	
2.32 w	1.72 w	1.91 vw	1.91 vw
2.26 w		1.72 m	1.71 m

Division. Solutions of LiAlH<sub>4</sub> and NaAlH<sub>4</sub> in diethyl ether or tetrahydrofuran were prepared by making a slurry of the compounds in the respective solvents and stirring for 48 hr, followed by centrifugation and filtration. All solutions were freshly analyzed immediately before use. Other materials such as (CH<sub>3</sub>)<sub>2</sub>Mg<sup>12</sup> and (s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Mg<sup>9</sup> were prepared according to methods described previously. Active NaH was prepared by hydrogenation of 0.5 mol of sodium in 150 ml of benzene at 400°F and 3000 psi H<sub>2</sub> in a 300 ml Magne-stirrer autoclave. The Na:H ratio was 1.0:1.0. Active potassium hydride was prepared similarly except that the reaction temperature was 300°F. Active LiH was prepared by reaction of *tert*-butyllithium (150 ml of 1.25 *M* solution) in pentane with hydrogen at 3000 psi at room temperature for 16 hr. The Li:H ratio of the resulting slurry was 1.0:1.0.

**Reactions of Alkali Metal Hydrides with Magnesium Alkyls and Aryls.** Preparation of KMg<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>H in Ether. Potassium hydride and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Mg were mixed in diethyl ether in several stoichiometries to give K:Mg ratios from 0.33:1 to 5:1. In all cases an insoluble complex formed.

In a typical reaction (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Mg (50 ml of a 0.8 *M* solution in diethyl ether, 40 mmol) was added to KH (3.20 g, 80 mmol) in 50 ml of ether. The mixture was stirred for 3 days and filtered. Analysis of the filtrate revealed that all of the magnesium containing species had precipitated.

In a similar reaction where the initial K:Mg ratio was 1:3, only 66% of the magnesium containing species precipitated, leaving the remainder of the (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Mg in solution. In this case a 1:2 complex KH·2Mg(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> was formed. The solid residues were analyzed and gave the following results. (Benzene was determined by difference.) Anal. Calcd for KH·2Mg(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>: K, 9.85; Mg, 12.25; C<sub>6</sub>H<sub>6</sub>, 77.65; H, 0.25. Found: K, 10.52; Mg, 11.0; C<sub>6</sub>H<sub>6</sub>, 78.3; H, 0.25. When 2 equiv of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Mg was allowed to react with 1 equiv of KH, analysis indicated a K:Mg:H ratio of 1.18:2.00:1.26. The X-ray diffraction pattern indicated occluded KH. If this is subtracted from the analysis, the ratio is 1.00:2.00:1.08. (Found: K, 9.90; Mg, 11.3; C<sub>6</sub>H<sub>6</sub>, 78.54; H, 0.25.) Calcd for KH·Mg(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>: K, 17.94; Mg, 11.10; C<sub>6</sub>H<sub>6</sub>, 70.50; H, 0.46. Found: K, 16.35; Mg, 10.20; C<sub>6</sub>H<sub>6</sub>, 73.09; H, 0.36. Calcd for 2KH·Mg(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>: K, 30.40; Mg, 9.40; C<sub>6</sub>H<sub>6</sub>, 59.40; H, 0.80. Found: K, 29.20; Mg, 9.40; C<sub>6</sub>H<sub>6</sub>, 60.60; H, 0.72. Calcd for 5KH·Mg(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>: K, 51.60; Mg, 6.42; C<sub>6</sub>H<sub>6</sub>, 40.76; H, 1.32. Found: K, 54.70; Mg, 6.56; C<sub>6</sub>H<sub>6</sub>, 38.49; H, 1.25. The X-ray powder pattern for each of these solids is reported in Table I.

**Preparation of NaMg<sub>2</sub>(s-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>H in Benzene.** Di-*sec*-butylmagnesium (101 ml of a 0.496 *M* solution, in benzene, 50 mmol) was added to NaH (0.6559 g, 27.4 mmol) and stirred for 2 days. Analysis of the resulting solution showed a Na:Mg:C<sub>4</sub>H<sub>9</sub>:H ratio of 0.90:2.0:3.96:0.85. The NMR spectrum and the ir spectrum of the

solution were significantly different from that of Mg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>.

In a similar experiment, 1 equiv of NaH and Mg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> were combined under the above conditions. Once the ratio of Na:Mg in solution reached 0.45:1.0, no further uptake of sodium was observed even after several days.

**Preparation of KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H in Benzene.** Potassium hydride (1.138 g, 28.4 mmol) was slurried with 50 ml of freshly distilled benzene and added to (s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Mg (95 ml of a 0.30 *M* solution, 28.4 mmol) with rapid stirring. After 20 hr the mixture was filtered producing a straw colored filtrate and a darker residue (~100 mg). Analysis of an aliquot of the solution showed a K:Mg:C<sub>4</sub>H<sub>9</sub>:H ratio of 1.0:1.0:1.9:0.95. The yield was >90%. Cryoscopic molecular weight measurements (Figure 2) indicated a monomer-dimer equilibrium over the concentration range 0.06–0.16 *m*.

Successful synthesis was also carried out in benzene-cyclohexane mixtures. The complex KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H was insoluble in pure alkanes, however, and attempted synthesis in cyclohexane alone proved unsatisfactory.

**Preparation of KMg(n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H in Benzene.** Potassium hydride (28.8 mmol) in 190 ml of freshly distilled benzene was added to (n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Mg (31.0 mmol) and stirred at 40° for 48 hr. Analysis of an aliquot of the filtrate revealed a K:Mg ratio of 0.97:1.0. The filtrate was 0.11 *M* in complex (70% yield). Cryoscopic molecular weight measurements (Figure 2) indicated a dimeric species in benzene over the concentration range 0.08–0.32 *m*.

**Attempted Preparation of K<sub>2</sub>Mg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H<sub>2</sub> in Benzene.** Potassium hydride (1.193 g, 29.8 mmol) slurried with 50 ml of benzene was added to KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H (99.5 ml of a 0.306 *M* solution, 30.4 mmol). The mixture was stirred for 18 hr and then filtered. A light straw colored solution and a tan solid were separated. Analysis of the filtrate revealed that nearly quantitative precipitation of the magnesium containing species had occurred. Analysis of the solid gave the following results. Anal. Calcd for K<sub>2</sub>Mg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H<sub>2</sub>: Mg, 11.10; Bu, 52.20; H, 0.95; Mg:Bu:H = 1.0:2.0:2.0. Found: Mg, 10.2; Bu, 16.20; H, 0.89; Mg:Bu:H = 1.0:0.67:2.1.

The ir spectrum of this solid showed the strong C–Mg stretching band at 521 cm<sup>−1</sup>, attributable to butyl-magnesium stretching, was severely diminished in the supposed 2:1 complex. In addition, when the solid was added to a Dry Ice-ether slurry under nitrogen and the resulting mixture acidified, appreciable quantities of benzoic acid and methylbutyric acid were produced. Similar results were obtained when 2 equiv of KH was allowed to react with 1 equiv of (s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Mg under similar reaction conditions.

**Metal Exchange Reactions.** Preparation of LiMg<sub>2</sub>(s-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>H. Reaction of KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H with Lithium Bromide in Ether. KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H was prepared by the reaction of potassium hydride with (s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Mg in benzene. The benzene was removed under vacuum resulting in an orange-red viscous residue. This was dissolved in diethyl ether to give a clear solution and used immediately. Lithium bromide (2.763 g, 31.8 mmol) was dissolved in 100 ml of ether and added to 141.3 ml of the KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H solution in ether (0.225 *M* in K<sup>+</sup>; 31.8 mmol) with vigorous stirring. The mixture was stirred for 6 hr and then filtered. The white precipitate was washed several times with ether and dried under vacuum at room temperature for 4 hr. The light orange filtrate on analysis gave the following ratios: Li:Mg:C<sub>4</sub>H<sub>9</sub>:H = 0.56:1.00:2.0:0.50. Potassium and bromine were absent. The precipitate gave the following ratios: Li:K:H:Br = 1.0:2.0:1.0:1.9.

**Preparation of LiMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H.** Reaction of KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H with LiBr in THF. To lithium bromide (8.52 g, 98.1 mmol) dissolved in 100 ml of THF was added 255.7 ml of a 0.384 *M* solution of KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> in THF. A precipitate formed immediately and was shown to be KBr. The filtrate, on solvent removal under vacuum, produced a viscous, orange material. Analysis produced the following ratios: Li:Mg:C<sub>4</sub>H<sub>9</sub>:H = 1.00:1.12:2.04:0.93. Potassium and bromide analyses were negative.

**Preparation of NaMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H.** Reaction of Sodium Iodide with KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H in THF. Sodium iodide solution (105 ml) in THF (0.252 *M*; 26.5 mmol) was added, with stirring, to 125 ml of a freshly prepared solution of KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H in THF (25.2 mmol in Mg). An immediate creamy yellow precipitate formed. After stirring for 4 hr, the mixture was filtered and the precipitate washed with several small portions of THF. The precipitate was found to be potassium iodide upon analysis. The filtrate exhibited a composition corresponding to NaMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H.

**Preparation of R<sub>4</sub>NMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H.** Reaction of KMg(s-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H

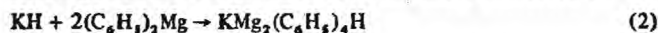
with  $R_4NBr$  in THF. To tri-*n*-octyl-*n*-propylammonium bromide (5.32 g, 11.17 mmol) in 25 ml of THF was added 50 ml of 0.222 M THF solution of  $KMg(s-C_4H_9)_2H$ . After 30 min, a precipitate began to form. After overnight stirring the mixture was filtered. Analysis of the light orange filtrate gave a  $Mg:C_4H_9:H$  ratio of 1.00:1.90:0.92. Potassium and bromide were absent. The precipitate was shown to be  $KBr$ . On complete solvent removal, a light orange oily product resulted.

## Results and Discussion

**Formation of  $MMgR_2H$  and  $MMg_2R_4H$  Compounds. Reactions of  $LiH$ ,  $NaH$ , and  $KH$  with  $(CH_3)_2Mg$ ,  $(C_2H_5)_2Mg$ , and  $(C_6H_5)_2Mg$ .** When lithium hydride in diethyl ether was allowed to reflux with dimethylmagnesium no reaction was observed; however, when THF was used as the solvent some reaction took place over a 36 hr reflux period. After filtering the reaction mixture, analysis of the resulting solution indicated a  $Li:Mg$  ratio of 1:15. The residue was shown by analysis to consist mainly of unreacted lithium hydride. In a similar experiment,  $LiH$  and  $(CH_3)_2Mg$  in THF were stirred for 7 days at  $25^\circ$ . Analysis of the reaction filtrate again revealed a  $Li:Mg$  ratio of 1:15. The amount of gas evolved on hydrolysis indicated that the number of methyl groups in solution had decreased by 20%. Similar results were noted by Coates<sup>3</sup> when higher temperatures and shorter reaction times were employed.

Several experiments were conducted using  $(C_6H_5)_2Mg$ . When a mixture of  $LiH$  and  $(C_6H_5)_2Mg$  was allowed to reflux for several days in THF, analysis of the filtrate revealed a  $Li:Mg$  ratio of 0.61:1.00. No hydrogen was evolved on hydrolysis of the solution indicating that ether cleavage had occurred. Similar results were obtained by mixing sodium hydride with  $(C_6H_5)_2Mg$  in diethyl ether. After 5 days at  $25^\circ$  the reaction mixture was filtered and analysis of the filtrate revealed a  $Na:Mg$  ratio of 0.38:1.00. Again, no hydrogen was evolved on hydrolysis of the solution.

In contrast, the reaction of  $KH$  with  $(C_6H_5)_2Mg$  in ether, at  $K:Mg$  ratios ranging from 0.3:1 to 5:1, resulted in complex formation. Precipitation of the complex must have occurred faster than ether cleavage could take place. When  $KH$  and  $(C_6H_5)_2Mg$  were mixed in 1:3 molar ratio, 66% of the magnesium containing compound precipitated from solution. Since only  $2/3$  of the magnesium species precipitated, the limiting ratio of  $K:Mg$  in the complex must therefore be 1:2.



This particular stoichiometry has been observed several other times in complexes of this type.<sup>4,13</sup> When the  $K:Mg$  molar ratio was increased stepwise to 5:1, quantitative precipitation of the magnesium containing species occurred.

The X-ray powder patterns were recorded for each of the above solids and the  $d$  spacings are given in Table I. Lines assigned to potassium hydride at  $d$  spacings of 3.81, 3.27, 2.84, 2.61, 2.02, and 1.71 Å were observed in 1:1, 2:1, and 5:1 mixtures. The strongest line for potassium hydride at 3.24 Å was very faint in the 0.5:1 compound. Lines at  $d$  spacings of less than 2.26 Å were too weak to be read accurately. Lines attributed to  $KMg_2(C_6H_5)_4H$  decreased in intensity as this species was diluted with solid potassium hydride. It appears that the 1:2 complex is the only stable complex formed between  $KH$  and  $(C_6H_5)_2Mg$ .

**Reaction of  $KH$  with  $(s-C_4H_9)_2Mg$  in Benzene.** Of considerably more interest is the formation of stable complexes in solvents in which ether cleavage is avoided. In this connection the hydrocarbon soluble  $(s-C_4H_9)_2Mg$  recently reported by Kamienski and Eastham<sup>9</sup> is an excellent candidate for the preparation of stable complexes of dialkylmagnesium compounds with alkali metal hydrides.

When di-*sec*-butylmagnesium was stirred with an equivalent amount of potassium hydride in either benzene or a 50:50 benzene-cyclohexane mixture, the hydride species dissolved

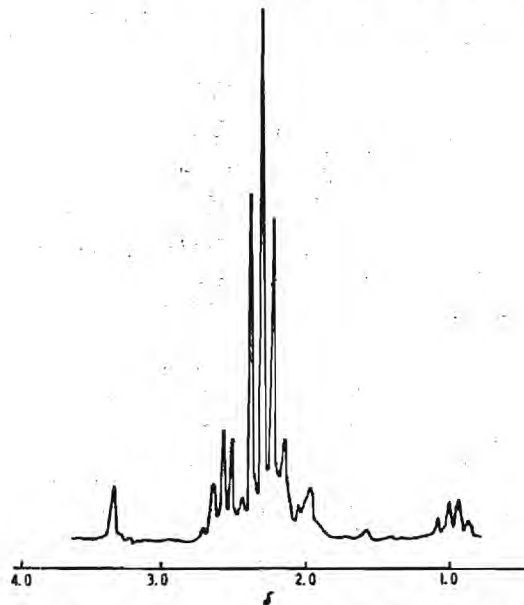


Figure 1. NMR spectrum of potassium di-*sec*-butylhydridomagnesium in benzene.

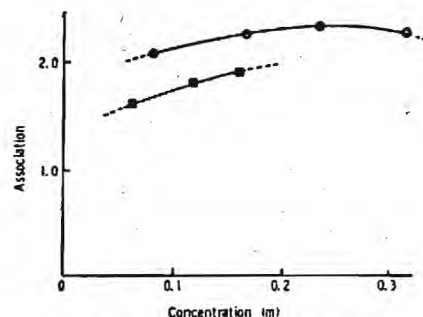
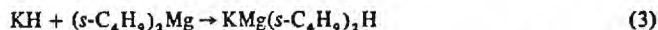


Figure 2. Association of potassium di-*sec*-butylhydridomagnesium (e) and potassium di-*n*-butylhydridomagnesium (o) in benzene.

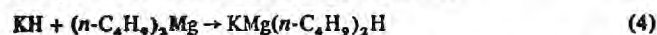
and a stable soluble 1:1 complex formed.



An attempt to prepare the complex in pure cyclohexane was unsuccessful, largely due to the fact that potassium di-*sec*-butylhydridomagnesium is insoluble in this solvent and only an oily gummy residue resulted. When commercial potassium hydride was employed, the reaction mixture was stirred overnight in order to achieve a yield on the order of 90%, but when "active" potassium hydride (freshly prepared) was employed, the reaction was complete in less than 1 hr. The NMR spectrum of the 1:1 complex is shown in Figure 1. The signal observed at  $\delta$  3.40 is attributed to the hydridic hydrogen in the complex. Integration of the  $\alpha$  hydrogen of the secondary butyl group and the hydridic hydrogen gave a ratio of 1.00:0.83 consistent with complex formation. The position of the hydride signal was similar to that observed by Shriver<sup>6</sup> for  $NaH \cdot 2Et_2Zn$ . An ether solution of the 1:1 complex was shown by NMR to be stable for at least 1 hr at room temperature. The ether cleavage then observed for the 1:1 complex in ether solvent was therefore a consequence of both higher temperature and longer reaction time. Comparison of the infrared spectra of  $(s-C_4H_9)_2Mg$  and  $KMg(s-C_4H_9)_2H$  was not nearly as informative as the NMR comparison. Cryoscopic molecular weight measurements in benzene (Figure 2) indicated a monomer-dimer equilibrium over the concentration range 0.06–0.16 *m*.

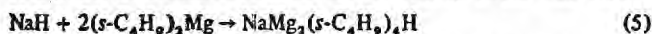
**Reaction of  $KH$  with  $(n-C_4H_9)_2Mg$  in Benzene.** A second complex was prepared analogous to that described above in which the *R* group was *n*-butyl instead of *sec*-butyl. Initially,

potassium hydride was stirred with an equivalent amount of  $(n\text{-C}_4\text{H}_9)_2\text{Mg}$  in benzene at  $40^\circ$ . After 48 hr analysis of an aliquot of the supernatant revealed a K:Mg ratio of 0.97:1.0 and the concentration of magnesium was shown to be 0.11 mmol/ml. As was observed in the previous example, a soluble complex was not formed in cyclohexane.



The NMR spectrum of a 0.378 *M* solution of  $\text{KMg}(n\text{-C}_4\text{H}_9)_2\text{H}$  in benzene at  $25^\circ$  was consistent with complex formation. The triplet attributed to the  $\alpha$  methylene protons was observed at  $\delta$  -0.59 and a low intensity signal was observed at  $\delta$  3.47 which was attributed to the hydridic hydrogen. Cryoscopic molecular weight measurements (Figure 2) indicate that  $\text{KMg}(n\text{-C}_4\text{H}_9)_2\text{H}$  is dimeric over the concentration range 0.08–0.32 *m* in benzene.

**Reaction of NaH with  $(s\text{-C}_4\text{H}_9)_2\text{Mg}$  in Benzene.** When sodium hydride and  $(s\text{-C}_4\text{H}_9)_2\text{Mg}$  were stirred in benzene, a complex was formed in which the Na:Mg ratio was 1:2.



The same results were observed even when the reagents were mixed in a molar ratio of 1:1 and the reaction mixture was stirred for several days.

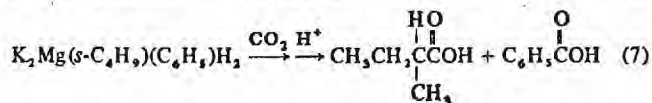
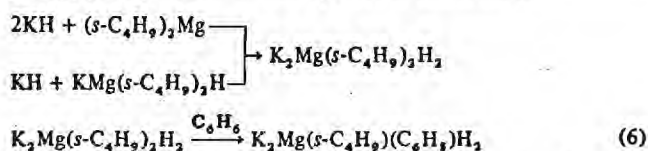
The NMR spectrum of a 0.23 *M* solution of the complex in benzene was recorded at room temperature using benzene as the internal standard. The spectrum was similar to that observed for  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  with the hydridic hydrogen observed at  $\delta$  3.40.

**Reaction of LiH with  $(s\text{-C}_4\text{H}_9)_2\text{Mg}$  in Benzene.** Several attempts to prepare a complex by mixing lithium hydride and  $(s\text{-C}_4\text{H}_9)_2\text{Mg}$  in benzene were unsuccessful. Even when extremely reactive lithium hydride, prepared by low temperature hydrogenation of *tert*-butyllithium in pentane, was used, no reaction was observed after several days. The NMR spectrum of the filtrate obtained from this reaction mixture was identical with that of  $(s\text{-C}_4\text{H}_9)_2\text{Mg}$  in benzene. Analysis revealed that none of the lithium hydride had dissolved and all of the magnesium remained in solution.

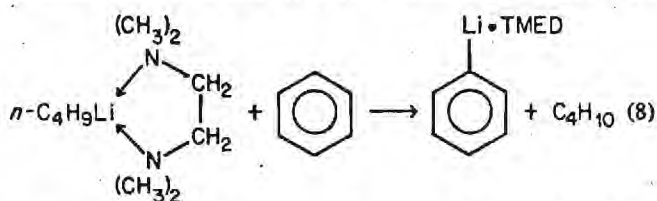
**Reaction of Excess KH with  $(s\text{-C}_4\text{H}_9)_2\text{Mg}$  in Benzene.** Repeated attempts were made to prepare an authentic 2:1 complex by mixing potassium hydride with  $(s\text{-C}_4\text{H}_9)_2\text{Mg}$  in benzene in a 2:1 molar ratio. Invariably, all of the magnesium containing species precipitated and could be isolated by filtration of the reaction mixture. Analysis of this residue indicated that extensive metallation of the solvent had occurred. When a portion of the solid was carboxylated both 2-methylbutyric acid and benzoic acid were produced. The X-ray powder diffraction pattern revealed that some potassium hydride had been occluded in the solid. Similar results were obtained when a previously prepared solution of potassium di-*sec*-butylhydridomagnesium was added to a benzene slurry of potassium hydride. All of the magnesium containing species again precipitated and the residue was found to be identical with the solid described above.

The results of these experiments were quite interesting. It had been observed earlier that when a benzene solution of  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  was allowed to stand at room temperature, a precipitate containing phenyl groups bonded to magnesium was formed slowly, whereas  $\text{KMg}(n\text{-C}_4\text{H}_9)_2\text{H}$  was stable under these conditions. Furthermore, if a slight excess of KH was used in the preparation of the *sec*-butyl complex, the yield of 1:1 complex was significantly decreased. Apparently complexation with a second equivalent of potassium hydride greatly enhanced the ionic character of the C–Mg bond and metallation of the solvent occurred fairly rapidly. Since both the NMR spectra of earlier preparations of the 1:1 complex and elemental analysis indicated a good K:Mg:Bu:H ratio in solution even when a slight excess of potassium hydride was

used, it was concluded that as metallation occurs to form a new species in which the magnesium is bonded to a phenyl group, precipitation of this species is immediate.

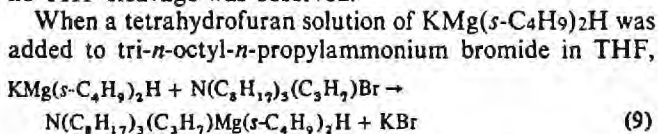


Similar examples of enhanced reactivity of an alkyl group bonded to a metal atom upon complexation have been reported in the literature. Rausch and Ciappenelli<sup>13</sup> reported that *n*-butyllithium-*N,N,N',N'*-tetramethylethylenediamine metallated benzene and ferrocene. Similarly, Langer<sup>14</sup> re-



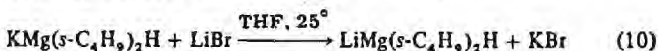
ported that this same complex metallated benzene and produced phenyllithium. Since butyllithium itself is unreactive toward benzene, the increased reactivity of the lithium reagent was attributed to complexation with an electron donating basic species.

**Potassium Exchange in Reactions with  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$ .** Although the direct reaction of KH with  $(s\text{-C}_4\text{H}_9)_2\text{Mg}$  did not proceed in tetrahydrofuran, the compound  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  prepared from benzene dissolved readily in THF. The solution was not very stable at room temperature; however, at low temperature it was found to be stable up to 5 days, and no THF cleavage was observed.



quantitative precipitation of KBr took place and the filtrate upon solvent removal produced the oily orange  $\text{N}(\text{C}_8\text{H}_{17})_3(\text{C}_3\text{H}_7)\text{Mg}(s\text{-C}_4\text{H}_9)_2\text{H}$ . Analysis of the THF solution of this compound was not quite as difficult as the product prepared in benzene solution. The Mg:Bu:H ratios were found to be 1:1.90:0.92. The infrared spectrum of the neat material was similar to that of  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  with the characteristic broad absorption envelope between 1200 and 600  $\text{cm}^{-1}$  ( $\nu(\text{Mg-H})$ ).

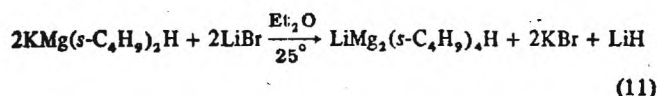
When a freshly prepared solution of  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  in tetrahydrofuran was added to an equivalent amount of lithium bromide in THF, KBr precipitated quantitatively during overnight stirring.



Analysis of the clear filtrate gave the following ratios: Li:Mg:Bu:H = 1.00:1.12:2.04:0.93. Upon solvent removal under vacuum, an orange viscous material resulted. It was very difficult to remove the last traces of solvent at room temperature, even under high vacuum. The viscous product readily dissolved in benzene giving a clear orange solution. NMR spectra of this benzene solution showed the presence of a small amount of tetrahydrofuran. The infrared spectrum of this product was similar to those of the analogous potassium and tetraalkylammonium compounds. Tetrahydrofuran so-

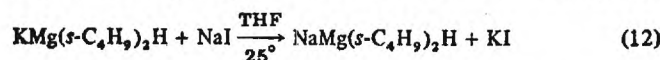
lutions of  $\text{LiMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  at room temperature are apparently more stable than that of the potassium compound. When a benzene solution of  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  was added to a lithium bromide slurry in benzene, no reaction occurred even after several days of stirring. No lithium was detected in the supernatant solution which essentially retained its original composition.

There is an interesting basic difference between the reactions of  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  with lithium bromide in THF and diethyl ether. In the case of tetrahydrofuran,  $\text{LiMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  is formed; however, when diethyl ether is the solvent,  $\text{LiMg}_2(s\text{-C}_4\text{H}_9)_4\text{H}$  is the product.



The solid product obtained from this reaction was analyzed and found to be a mixture of KBr and LiH formed in 2:1 ratio. It seems reasonable to suggest that  $\text{LiMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  is formed in the reaction and that it slowly disproportionates to  $\text{LiMg}_2(s\text{-C}_4\text{H}_9)_4\text{H}$  and LiH.

On addition of sodium iodide to  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  in THF, a quantitative precipitate of KI was obtained. Analysis of



the resulting solution showed a Na:Mg:Bu:H ratio of

1.00:1.07:1.87:0.92 establishing the formation of  $\text{NaMg}(s\text{-C}_4\text{H}_9)_2\text{H}$  in solution.

Registry No.  $\text{KMg}_2(\text{C}_6\text{H}_5)_4\text{H}$ , 55886-10-7;  $\text{NaMg}_2(s\text{-C}_4\text{H}_9)_4\text{H}$ , 55886-09-4;  $\text{KMg}(s\text{-C}_4\text{H}_9)_2\text{H}$ , 36426-31-0;  $\text{KMg}(n\text{-C}_4\text{H}_9)_2\text{H}$ , 55822-78-1;  $\text{LiMg}_2(s\text{-C}_4\text{H}_9)_4\text{H}$ , 55886-08-3;  $\text{LiMg}(s\text{-C}_4\text{H}_9)_2\text{H}$ , 55822-79-2;  $\text{NaMg}(s\text{-C}_4\text{H}_9)_2\text{H}$ , 44889-27-2;  $[(n\text{-C}_8\text{H}_{17})_3\text{N}(n\text{-C}_3\text{H}_7)]\text{Mg}(s\text{-C}_4\text{H}_9)_2\text{H}$ , 55822-81-6;  $(\text{C}_6\text{H}_5)_2\text{Mg}$ , 555-54-4; KH, 7693-26-7; NaH, 7646-69-7;  $(s\text{-C}_4\text{H}_9)_2\text{Mg}$ , 17589-14-9;  $(n\text{-C}_4\text{H}_9)_2\text{Mg}$ , 1191-47-5.

## References and Notes

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## Alkali Metal "ate" Complexes and Complex Metal Hydrides of Beryllium

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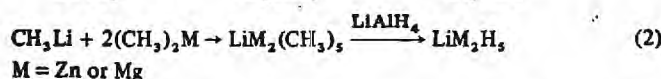
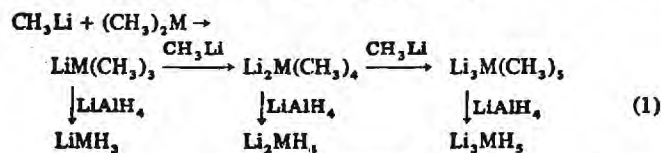
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The reactions of  $\text{LiAlH}_4$  and  $\text{AlH}_3$  with "ate" complexes of beryllium ( $\text{Li}_n\text{Be}_m\text{R}_{2m+n}$ ) in ether solvents were investigated as a possible route to complex metal hydrides of beryllium. Both the 1:1 and 2:1 complexes of methyl lithium and dimethylberyllium [ $\text{LiBe}(\text{CH}_3)_3$  and  $\text{Li}_2\text{Be}(\text{CH}_3)_4$ ] yielded  $\text{Li}_2\text{BeH}_4$  when allowed to react with  $\text{LiAlH}_4$  in diethyl ether.  $\text{Li}_3\text{BeH}_5$  was obtained by a similar reaction of methyl lithium and dimethylberyllium in 3:1 molar ratio followed by the reduction of the "ate" complex  $\text{Li}_3\text{Be}(\text{CH}_3)_5$  with  $\text{LiAlH}_4$  in diethyl ether. The 1:2 complex of methyl lithium and dimethylberyllium  $\text{LiBe}_2(\text{CH}_3)_3$  yielded a compound of indefinite composition.  $\text{LiBeH}_3$  was prepared by the reaction of  $\text{AlH}_3$  and  $[\text{LiBe}(\text{CH}_3)_3]$  in a 1:1 molar ratio in diethyl ether. The hydrides were characterized by elemental analysis, X-ray powder diffraction, and DTA-TGA analysis. Proton NMR spectra of diethyl ether solutions of methyl lithium and dimethylberyllium in 1:1, 2:1, 3:1, and 1:2 molar ratios have been obtained over a wide temperature range. The spectra show that there is rapid exchange of methyl groups between methyl lithium and the complexes formed. Evidence for the existence of more than one complex at equilibrium is discussed.

### Introduction

Recently we have reported the synthesis of complex metal hydrides of zinc,<sup>1</sup> magnesium,<sup>2</sup> and copper.<sup>3</sup> The preparation of these compounds involves the reduction of an "ate" complex ( $\text{M}_n\text{M}'_m\text{R}_{2m+n}$ ) with either  $\text{LiAlH}_4$  or  $\text{AlH}_3$ .



In 1968, Coates and Bell<sup>4</sup> reported the preparation of  $\text{Li}_2\text{BeH}_4$  by the reaction of beryllium chloride and  $\text{Li}(\text{C}_2\text{H}_5)_2\text{BeH}$ . Attempts were also made to prepare other complex metal hydrides of beryllium, e.g.,  $\text{LiBeH}_3$ ; however no evidence was found to support the existence of this compound.

Recently Seitz and coworkers<sup>5,6</sup> studied lithium-7 and proton NMR spectra of methyl lithium with  $(\text{CH}_3)_2\text{Mg}$ ,  $(\text{CH}_3)_2\text{Zn}$ , and  $(\text{CH}_3)_2\text{Cd}$  in diethyl ether. The spectra show that complexes of the type  $\text{Li}_2\text{M}(\text{CH}_3)_4$  and  $\text{Li}_3\text{M}(\text{CH}_3)_5$  (where M = Mg, Zn, or Cd) are formed in solution. No attempts were made to isolate these complexes in pure form. No evidence was available for or against the formation of a 1:1 complex. In our earlier work,<sup>2,7</sup> we studied the system methyl lithium-dimethylmagnesium in diethyl ether by high-resolution infrared spectroscopy and found in general that at any given concentration there are several "ate" complex species in equilibrium and at no time does a single complex exist in solution.

In view of our recent preparation of complex metal hydrides of zinc, magnesium, and copper by the reaction of  $\text{LiAlH}_4$  with the corresponding "ate" complexes, we decided to carry out a similar study involving the reactions of "ate" complexes of

beryllium with  $\text{LiAlH}_4$  or  $\text{AlH}_3$ . In this paper, we describe the preparation and characterization of  $\text{LiBeH}_3$ ,  $\text{Li}_2\text{BeH}_4$ , and  $\text{Li}_3\text{BeH}_5$ . Also the system  $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Be}$  in diethyl ether was studied by proton NMR and high-resolution infrared spectroscopy in order to define the composition of the "ate" complex in solution prior to reaction with  $\text{LiAlH}_4$ .

### Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and moisture<sup>8</sup> or on the bench top using typical Schlenk-tube techniques.<sup>9</sup>

**Instrumentation.** Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solid samples were obtained as mulls in Nujol between CsI plates. Solutions were run in matched 0.10-mm path length KBr cells. X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered  $\text{Cu K}\alpha$  radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 8–10 hr.  $d$  spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. DTA-TGA data were obtained under vacuum using a modified Mettler Thermoanalyzer II. Proton NMR spectra were obtained at 60 MHz using a Varian A-60 NMR spectrometer.

**Analytical Procedures.** Gas analyses were carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Aluminum analyses were carried out by complexometric titration with EDTA. Beryllium was determined by adding excess sodium fluoride to the solution at pH 7.8 and then back-titrating to pH 7.8 using standard hydrochloric acid. Lithium analysis was carried out by flame photometry. Analysis for chloride was carried out using a modified Volhard procedure. Analyses for carbon-bonded and oxygen-bonded metals were carried out by the Watson and Eastham<sup>10</sup> method using 2,2'-biquinoline and phenolphthalein indicators.

**Materials.** Diethyl ether (Fisher anhydrous ether) was distilled over  $\text{LiAlH}_4$  immediately prior to use. Benzene (Fisher Certified reagent) was distilled over sodium aluminum hydride. Lithium aluminum hydride was obtained as a gray powder from Ventron, Metal Hydrides Division. Solutions of  $\text{LiAlH}_4$  in diethyl ether were prepared by stirring the solid hydride for 24 hr with freshly distilled solvent, followed by filtration in a glove box to yield a clear, colorless solution.

Table I. X-Ray Powder Pattern *d*-Spacing Data

LiH		BeH <sub>2</sub>		Li <sub>2</sub> BeH <sub>4</sub>		Li <sub>3</sub> BeH <sub>5</sub>		LiBH <sub>2</sub>		"LiBe <sub>2</sub> H <sub>3</sub> "	
<i>d</i> , Å	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å	<i>I</i> / <i>I</i> <sub>0</sub>
3.85	w	3.85	s	3.85	w	3.65	w	6.60	vw	6.60	ww
2.65	w	3.45	w	3.69	vw	3.48	s	3.82	mw	4.85	vs
2.60	w	2.32	s	3.52	w	2.92	s	3.45	vw	3.80	m
2.35	s	2.225	vw	3.25	w	2.75	ms	3.25	vw	3.50	vw
2.25	m	2.17	vw	2.95	s	2.55	w	2.95	s	3.25	vw
2.03	s	2.02	w	2.80	vw	2.42	w	2.77	w	2.92	s
1.95	w	1.96	w	2.57	s	2.30	vw	2.55	s	2.85	w
1.59	w	1.72	ms	2.40	w	2.18	vw	1.98	w	2.55	m
1.440	s		w	2.32	vw	2.02	vw	1.80	w	2.40	w
1.225	m			2.17	vw	1.80	vw			2.30	w
1.175	w			2.04	w					1.97	mw
0.935	w			1.96	m					1.80	w
0.911	w			1.81	s						
				1.55	ms						
				1.47	w						

Anhydrous beryllium chloride was obtained from Alfa Inorganics. Solutions of beryllium chloride in diethyl ether were prepared by adding excess diethyl ether (50% excess based on the bis(etherate) of beryllium chloride) to a slurry of BeCl<sub>2</sub> in benzene cooled to 5°. Ether solutions of BeBr<sub>2</sub> were prepared as previously reported.<sup>12</sup> Ether-soluble aluminum hydride was prepared by the reaction of LiAlH<sub>4</sub> and BeCl<sub>2</sub> in diethyl ether.<sup>13</sup> Methyl lithium was obtained as a 5.4% solution in ether from Foote Mineral Co. and stored at -20° until ready to use. Sodium hydride was prepared by hydrogenation of metallic sodium in benzene at 4000 psi for 24 hr. A slurry of sodium hydride in diethyl ether was prepared in the usual manner. Lithium hydride was prepared by hydrogenolysis of *tert*-butyllithium in pentane at 4000 psi for 24 hr.

**Preparation of Dimethylberyllium in Diethyl Ether.** A solution of methyl lithium in ether was added slowly to a solution of beryllium chloride in ether in a 2:1 molar ratio. Lithium chloride precipitated immediately and was separated by filtration. The filtrate was evaporated to dryness under vacuum at room temperature and dimethylberyllium (white solid) was purified by sublimation under vacuum (0.05 mm Hg) at 110°. A solution of dimethylberyllium in ether was then prepared by dissolving the purified compound in ether. Analysis showed a Be:CH<sub>4</sub> ratio of 1.00:1.98.

**Preparation of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Be in Diethyl Ether.** *n*-C<sub>4</sub>H<sub>9</sub>Li (20 mmol) in hexane was added slowly with stirring to a cold solution (0°) of BeCl<sub>2</sub> (10 mmol) in diethyl ether. Lithium chloride precipitated and was filtered. The filtrate was concentrated and analyzed for beryllium and the *n*-butyl group in the usual manner (Be:C<sub>4</sub>H<sub>10</sub> = 1.0:1.92).

**Infrared Study of the Reaction of (CH<sub>3</sub>)<sub>2</sub>Be with CH<sub>3</sub>Li in Diethyl Ether.** To 2 ml of (CH<sub>3</sub>)<sub>2</sub>Be (0.623 M) in a 10-ml volumetric flask was added a volume of CH<sub>3</sub>Li in ether (1.586 M) calculated to give the desired (CH<sub>3</sub>)<sub>2</sub>Be to CH<sub>3</sub>Li ratio. The solution was then adjusted to the 10-ml mark and stirred. (CH<sub>3</sub>)<sub>2</sub>Be:CH<sub>3</sub>Li ratios of 1:1, 1:2, 1:3, and 2:1 were studied by infrared spectroscopy in this manner. The infrared spectra of these solutions are shown in Figure 1.

**Proton NMR Study of the Reaction of (CH<sub>3</sub>)<sub>2</sub>Be with CH<sub>3</sub>Li in Diethyl Ether.** Ether solutions of CH<sub>3</sub>Li and (CH<sub>3</sub>)<sub>2</sub>Be were mixed in the appropriate molar ratios to form Li<sub>n</sub>Be<sub>m</sub>(CH<sub>3</sub>)<sub>2m+n</sub> (*n* = 1, 2, 3 when *m* = 1; *n* = 0.5 when *m* = 2). The solutions were transferred into 5-mm NMR tubes under nitrogen and stored in Dry Ice.

**Reactions Involving (CH<sub>3</sub>)<sub>2</sub>Be with CH<sub>3</sub>Li.** (a) Reaction of LiAlH<sub>4</sub> with LiBe(CH<sub>3</sub>)<sub>3</sub> in Diethyl Ether. Attempted Preparation of LiBeH<sub>3</sub>. Methyl lithium (5 mmol) in diethyl ether was added to 5 mmol of dimethylberyllium in diethyl ether. The resulting solution was stirred at room temperature for 1 hr; then 5 mmol of LiAlH<sub>4</sub> in diethyl ether was added. A white precipitate appeared immediately. This mixture was stirred at room temperature for another hour and filtered. The white solid was dried at room temperature under vacuum and analyzed. Anal. Calcd for LiBeH<sub>3</sub>: Li, 36.56; Be, 47.49; H, 15.94. Found: Li, 46.83; Be, 28.39; H, 12.76. The molar ratio of Li:Be:H was 2.08:1.00:4.01. The filtrate contained only aluminum and a trace of beryllium and lithium. The infrared spectrum of the filtrate showed no Al-H stretching vibrations but instead was about identical with the spectrum observed for (CH<sub>3</sub>)<sub>3</sub>Al. The X-ray powder diffraction pattern of the solid product contained lines due to Li<sub>2</sub>BeH<sub>4</sub> only.

(b) Reaction of LiAlH<sub>4</sub> with Li<sub>2</sub>Be(CH<sub>3</sub>)<sub>4</sub> in Diethyl Ether. Preparation of Li<sub>2</sub>BeH<sub>4</sub>. Dimethylberyllium (20 mmol) in diethyl

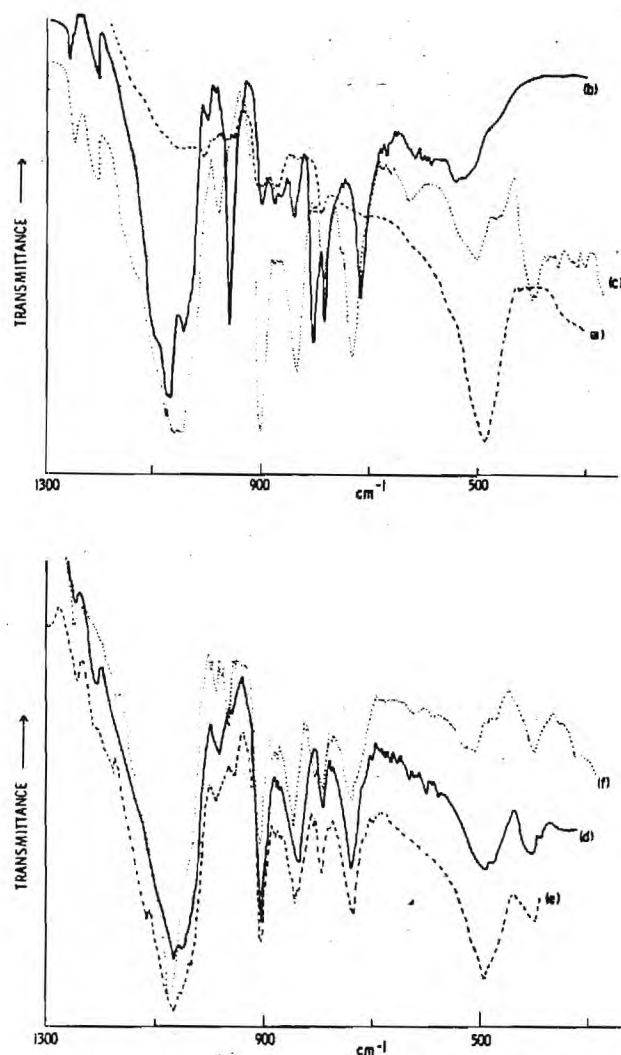


Figure 1. Infrared spectra of CH<sub>3</sub>Li, (CH<sub>3</sub>)<sub>2</sub>Be, and mixtures of CH<sub>3</sub>Li and (CH<sub>3</sub>)<sub>2</sub>Be in diethyl ether: (a) CH<sub>3</sub>Li; (b) (CH<sub>3</sub>)<sub>2</sub>Be; (c) 1:1 CH<sub>3</sub>Li + (CH<sub>3</sub>)<sub>2</sub>Be; (d) 2:1 CH<sub>3</sub>Li + (CH<sub>3</sub>)<sub>2</sub>Be; (e) 3:1 CH<sub>3</sub>Li + (CH<sub>3</sub>)<sub>2</sub>Be; (f) 1:2 CH<sub>3</sub>Li + (CH<sub>3</sub>)<sub>2</sub>Be.

ether was added to 40 mmol of methyl lithium in diethyl ether. The resulting solution was stirred for 1 hr at room temperature, followed by addition of 40 mmol of LiAlH<sub>4</sub> in diethyl ether. There was an immediate precipitation of a white solid. The mixture was stirred for an additional 1 hr at room temperature, filtered, and dried under vacuum. Anal. Calcd for Li<sub>2</sub>BeH<sub>4</sub>·0.047Et<sub>2</sub>O:<sup>14</sup> Li, 45.65; Be, 29.64; H, 13.24. Found: Li, 46.82; Be, 25.58; H, 13.04. The molar ratio of Li:Be:H in the solid is 2.13:1.00:4.09. The X-ray powder diffraction pattern, given in Table I, was almost identical with the pattern reported earlier for Li<sub>2</sub>BeH<sub>4</sub>.<sup>4</sup>

(c) **Reaction of  $\text{LiAlH}_4$  with  $\text{Li}_3\text{Be}(\text{CH}_3)_5$  in Diethyl Ether.** Preparation of  $\text{Li}_3\text{BeH}_5$ . Methylolithium (42 mmol) in diethyl ether was added to 14 mmol of dimethylberyllium in diethyl ether. The resulting solution was stirred for 1 hr at room temperature, followed by addition of 35 mmol of  $\text{LiAlH}_4$  in diethyl ether. A white precipitate appeared immediately. The mixture was stirred for 1 additional hr at room temperature and filtered. The resulting white solid was then dried at room temperature under vacuum and analyzed. Anal. Calcd for  $\text{Li}_3\text{BeH}_5 \cdot 0.23\text{Et}_2\text{O}$ :<sup>14</sup> Li, 40.09; Be, 17.35; H, 9.70. Found: Li, 38.14; Be, 18.07; H, 10.40. The molar ratio of Li:Be:H was 2.73:1.00:5.17. The amount of  $\text{Li}_3\text{BeH}_5$  recovered was 100% of the theoretical value. The X-ray powder diffraction data are given in Table I. Infrared analysis of the solid (Nujol mull) showed a broad strong band at  $1400\text{--}1800\text{ cm}^{-1}$  (centered at  $1600\text{ cm}^{-1}$ ).

(d) **Reaction of  $\text{LiAlH}_4$  with  $\text{LiBe}_2(\text{CH}_3)_5$  in Diethyl Ether.** Attempted Preparation of  $\text{LiBe}_2\text{H}_5$ . Methylolithium (10 mmol) in diethyl ether was added to 20 mmol of dimethylberyllium in diethyl ether. The resulting solution was stirred for 1 hr, followed by addition of 17.5 mmol of  $\text{LiAlH}_4$  in diethyl ether. There was an immediate precipitation of a white solid. The mixture was stirred overnight at room temperature and then filtered. The white solid was then dried at room temperature under vacuum. The X-ray powder diffraction data are given in Table I. Anal. Calcd for  $\text{LiBe}_2\text{H}_5$ : Li, 23.12; Be, 60.07; H, 16.79. Found: Li, 31.11; Be, 31.14; H, 11.61. The molar ratio of Li:Be:H was 1.28:1.00:3.31.

(e) **Reaction of NaH with  $(n\text{-C}_4\text{H}_9)_2\text{Be}$  in Diethyl Ether.** Attempted Preparation of  $\text{NaBe}(n\text{-C}_4\text{H}_9)_2\text{H}$ . A slurry of sodium hydride (10 mmol) in diethyl ether was added to 10 mmol of  $(n\text{-C}_4\text{H}_9)_2\text{Be}$  in diethyl ether. The resulting mixture was stirred for 48 hr at room temperature and then filtered. An analysis of the filtrate showed Be:H in the ratio of 0.976:0.309 and the analysis of the white residue showed it to be unreacted sodium hydride.

(f) **Reaction of  $\text{LiAlH}_4$  with  $\text{BeBr}_2$  in Diethyl Ether.** Preparation of  $\text{BeH}_2$ .  $\text{LiAlH}_4$  (14 mmol) solution in diethyl ether was added to 7 mmol of  $\text{BeBr}_2$  solution in diethyl ether and the mixture was stirred for 1 hr at room temperature. The resulting white solid was filtered, washed with ether several times, and dried at room temperature under vacuum. Anal. Calcd for  $\text{BeH}_2 \cdot 0.21\text{Et}_2\text{O}$ :<sup>14</sup> Be, 33.88; H, 7.58. Found: Be, 34.54; H, 7.25. The molar ratio of Be:H was 1.00:1.89. The X-ray powder diffraction data are given in Table I.

(g) **Reaction of  $\text{AlH}_3$  with  $\text{LiBe}(\text{CH}_3)_3$  in Diethyl Ether.** Preparation of  $\text{LiBeH}_3$ . To a solution of  $\text{LiBe}(\text{CH}_3)_3$  (10 mmol) in diethyl ether prepared by the method described above, a solution of  $\text{AlH}_3$  (10 mmol) in ether was added slowly with stirring. A white precipitate appeared immediately. The mixture was stirred for 1 hr at room temperature and then filtered and washed with ether. The white solid was dried at room temperature under vacuum and analyzed. Anal. Calcd for  $\text{LiBeH}_3 \cdot 0.27\text{Et}_2\text{O}$ :<sup>14</sup> Li, 17.89; Be, 23.24; H, 7.79. Found: Li, 17.05; Be, 21.96; H, 7.53. The amount of  $\text{LiBeH}_3$  recovered was 100% of the theoretical value. The X-ray powder diffraction data are given in Table I. Infrared analysis of the filtrate obtained after isolation of solid  $\text{LiBeH}_3$  showed the presence of only  $(\text{CH}_3)_3\text{Al}$  in the solution. The infrared spectrum of the solid showed a broad band at  $1400\text{--}1800\text{ cm}^{-1}$ .

(h) **Reaction of  $\text{AlH}_3$  with  $\text{LiBe}_2(\text{CH}_3)_5$  in Diethyl Ether.** Attempted Preparation of  $\text{LiBe}_2\text{H}_5$ . A solution of  $\text{LiBe}_2(\text{CH}_3)_5$  in diethyl ether was obtained by adding a solution of methylolithium (12.9 mmol) to a solution of dimethylberyllium (25.8 mmol) in ether. The mixture was stirred for 1 hr followed by addition of a solution of  $\text{AlH}_3$  (21.5 mmol) in ether. A white solid precipitated immediately. The mixture was stirred for 2 hr at room temperature and then filtered and washed with ether, and the solid was dried at room temperature under vacuum. The infrared spectrum of the filtrate showed a broad strong band centered at  $1650\text{ cm}^{-1}$ . The elemental analysis of the filtrate showed a Li:Be:Al:gas (hydrolyzable) ratio of 0.63:1.00:0.34:2.14. The hydrolyzed gas contained about 75% methane and 25% hydrogen. Infrared analysis of the solid showed a broad band at  $1400\text{--}1800\text{ cm}^{-1}$ . The elemental analysis of the solid showed a Li:Be:H ratio of 1.23:1.00:3.15. The X-ray powder diffraction data are given in Table I.

## Results and Discussion

**Reactions of  $\text{LiAlH}_4$  with "ate" Complexes of  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Be}$ .** (a) **Reaction of  $\text{LiAlH}_4$  with  $\text{LiBe}(\text{CH}_3)_3$  in Diethyl Ether.** Attempted Preparation of  $\text{LiBeH}_3$ . The reaction of  $(\text{CH}_3)_2\text{Be}$  with  $\text{CH}_3\text{Li}$  in diethyl ether yields a clear solution.

Table II. Chemical Shifts from the Center of the Methyl Triplet of Diethyl Ether

Sample	Chem shifts, ppm		
	Room temp	-65°	-96°
$\text{CH}_3\text{Li}$	3.08	3.08	
$(\text{CH}_3)_2\text{Be}$	2.28	2.38	2.550
$\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{Be}$	2.21	2.22	2.25 (128) 2.67 (6)
$2\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{Be}$	2.40	2.27 (46) 3.07 (14)	2.23 (82) 2.69 (134) 3.14 (22)
$3\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{Be}$	2.55	2.30 (26) 3.08 (13)	2.23 (50) 2.70 (150) 3.15 (63)
$4\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{Be}$	2.62	2.31 (31) 3.07 (28)	2.22 (48) 2.68 (138) 3.13 (122)
$\text{CH}_3\text{Li} + 2(\text{CH}_3)_2\text{Be}$			2.34
$\text{CH}_3\text{Li} + 3(\text{CH}_3)_2\text{Be}$			2.35
$6\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{Be}$			2.19 (20) 2.64 (32) 3.11 (90)

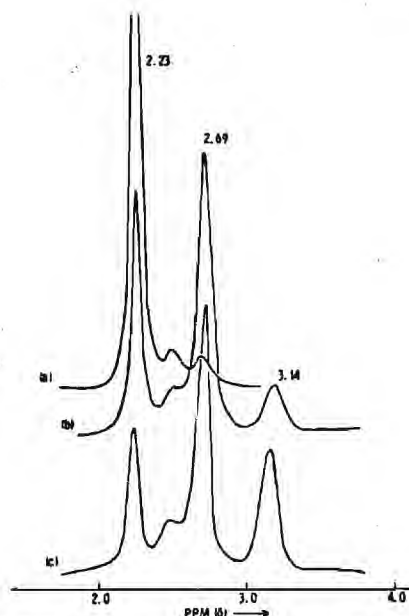


Figure 2.  $^1\text{H}$  NMR spectra in diethyl ether at  $-96^\circ$ : (a)  $\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{Be}$ ; (b)  $2\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{Be}$ ; (c)  $3\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{Be}$ . The chemical shifts are shown upfield from the center of the ether triplet.

The infrared spectrum of the resultant solution is recorded in Figure 1. Although no assignment has been made for M-C stretching vibrations, the absence of the  $483\text{-cm}^{-1}$  band characteristic of methylolithium and the absence of the medium strong band at  $960\text{ cm}^{-1}$  present in dimethylberyllium indicate the formation of a complex involving methylolithium and dimethylberyllium. The infrared spectrum of the solution shows two medium strong bands at  $500$  and  $400\text{ cm}^{-1}$  and a weak band at  $450\text{ cm}^{-1}$ .

At room temperature the proton chemical shifts of methylolithium and dimethylberyllium are 3.08 and 2.28 ppm, respectively, upfield from the center of the ether triplet (Table II). The proton spectrum of methylolithium-dimethylberyllium complex consists of a single sharp resonance at room temperature which implies either formation of a compound with only one type of methyl group or rapid exchange involving different species in solution. At low temperature ( $-96^\circ$ ) the exchange is slowed such that a multiplet structure occurs, as shown in Figure 2. The resonance peak at 2.23 ppm may be assigned to the methyl protons of the 1:1 complex, whereas

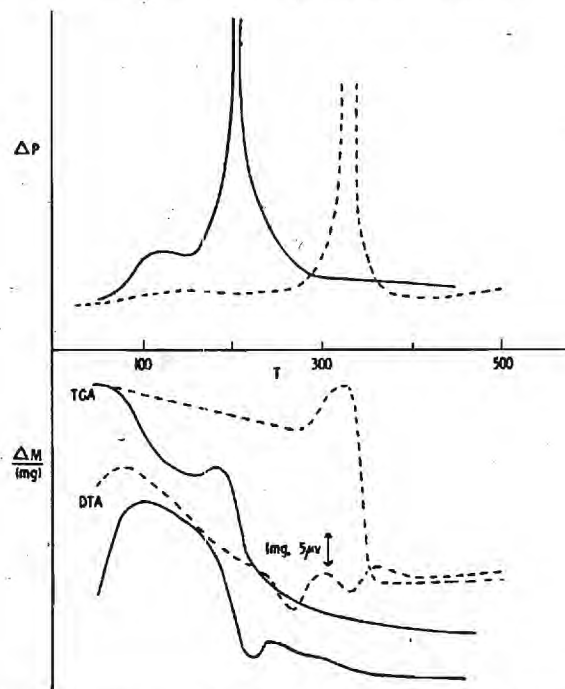
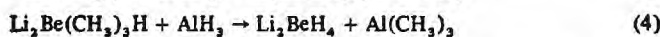
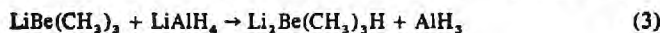


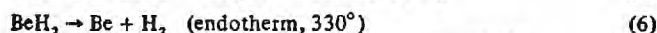
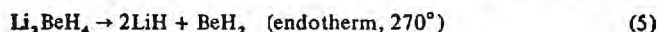
Figure 3. Vacuum DTA-TGA of  $\text{BeH}_2$  (—) and  $\text{Li}_2\text{BeH}_4$  (---).

the resonance peak at 2.65 ppm may be assigned to the methyl protons of the complex  $\text{Li}_2\text{Be}(\text{CH}_3)_4$ . The presence of the broad peak at 2.45 ppm is not well understood; however, it may be due to some kind of impurity which could not be removed from the starting materials although considerable effort was made in this direction. The occurrence of this peak at low temperature has also been noted by Seitz and Little<sup>6</sup> while studying the methyl lithium–dimethylcadmium system. It appears, therefore, that at room temperature there is a rapid exchange between 2:1 and 1:1 complexes of methyl lithium and dimethylberyllium giving a single sharp resonance and at low temperature this exchange is slowed to the extent that  $\text{LiBe}(\text{CH}_3)_3$  and  $\text{Li}_2\text{Be}(\text{CH}_3)_4$  exhibit individual methyl signals. It is clear that  $\text{LiBe}(\text{CH}_3)_3$  is by far the most predominant species in solution; however, it is in equilibrium with  $\text{Li}_2\text{Be}(\text{CH}_3)_4$  at room temperature.

The reaction of  $\text{LiAlH}_4$  and  $\text{LiBe}(\text{CH}_3)_3$  gave a solid which was shown to be  $\text{Li}_2\text{BeH}_4$  instead of  $\text{LiBeH}_3$ . The infrared spectrum of the filtrate showed no bands due to Al–H stretching vibrations between 1900 and 1700  $\text{cm}^{-1}$ ; however, it did exhibit a spectrum almost identical with that of  $(\text{CH}_3)_3\text{Al}$ . The infrared spectrum of the white solid (in Nujol mull) contained broad absorptions centered at 1600  $\text{cm}^{-1}$ . The X-ray powder diffraction pattern showed only lines for  $\text{Li}_2\text{BeH}_4$  (Table I). The route by which  $\text{Li}_2\text{BeH}_4$  is formed from  $\text{LiBe}(\text{CH}_3)_3$  and  $\text{LiAlH}_4$  is not clear but probably takes place by a series of reactions that can be represented in a simplified way by eq 3 and 4. The vacuum TGA diagram

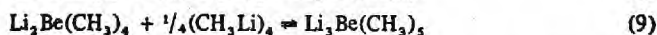
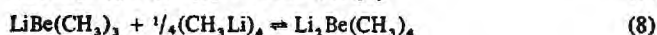
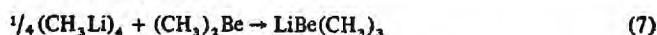


shown in Figure 3 contained one very broad peak at 330°. This observation in addition to the pressure differential curve peaking at 330° is indicative of the evolution of a noncondensable gas ( $\text{H}_2$ ) and represents the only weight loss or gas evolution up to 500°. The thermal effect (DTA) of this gas evolution is a small endotherm (330°) which is preceded by another small endotherm at 270° indicative of a structural change not involving a weight loss or gas evolution. The weight loss at 330° (8%) corresponds to the loss of 1 mol of hydrogen present in  $\text{Li}_2\text{BeH}_4$ . Thus, the decomposition takes place according to eq 5 and 6 with  $\text{Li}_2\text{BeH}_4$  dissociating to  $\text{LiH}$  and

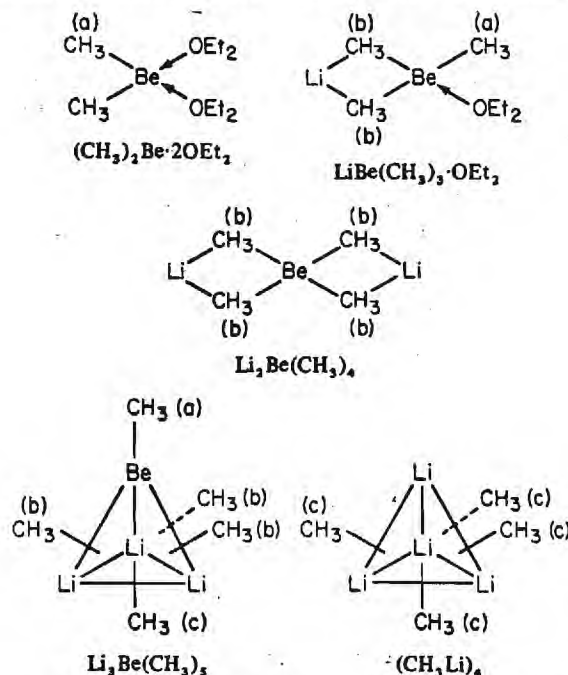


$\text{BeH}_2$  at 270° (no weight loss) followed by decomposition of the  $\text{BeH}_2$  at 330°.

(b) Reaction of  $\text{LiAlH}_4$  with  $\text{Li}_2\text{Be}(\text{CH}_3)_4$  in Diethyl Ether. Preparation of  $\text{Li}_2\text{BeH}_4$ . The reaction of  $\text{CH}_3\text{Li}$  with  $(\text{CH}_3)_2\text{Be}$  in a 2:1 molar ratio also yields a clear solution. The infrared spectrum of the resultant solution shown in Figure 1 is identical with the infrared spectrum of the 1:1 complex except that the band at 500  $\text{cm}^{-1}$  is masked by the strong band of methyl lithium at 483  $\text{cm}^{-1}$ . The proton NMR spectrum of  $\text{Li}_2\text{Be}(\text{CH}_3)_4$  in diethyl ether at room temperature is shown in Figure 2. At room temperature the proton spectrum consists of a single sharp resonance peak which again implies either a single compound or a rapid exchange among different species in solution. The low-temperature (–96°) proton spectrum (Figure 2) can be interpreted in terms of an equilibrium mixture of 1:1, 2:1, and 3:1 complexes of methyl lithium and dimethylberyllium.



The methyl group (a) bonded directly to the beryllium atom in  $(\text{CH}_3)_2\text{Be} \cdot 2\text{OEt}_2$  should be similar to one of the methyl groups in  $\text{LiBe}(\text{CH}_3)_3 \cdot \text{OEt}_2$  and  $\text{Li}_3\text{Be}(\text{CH}_3)_5$ . On the other hand the methyl group (b) bridged to Li and Be ( $\text{Li}-\text{CH}_3-\text{Be}$ ) should be similar to the methyl group (b) in  $\text{Li}_2\text{Be}(\text{CH}_3)_4$  and  $\text{Li}_3\text{Be}(\text{CH}_3)_5$ . Furthermore, the methyl group (c) bridged only to Li ( $\text{Li}-\text{CH}_3-\text{Li}$ ) should be similar to the methyl group in  $(\text{CH}_3\text{Li})_4$  and  $\text{Li}_3\text{Be}(\text{CH}_3)_5$  designated (c). The resonance



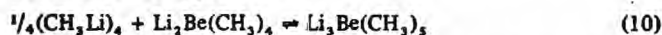
furthest downfield is assigned to the methyl group (a) attached only to beryllium since  $(\text{CH}_3)_2\text{Be} \cdot 2\text{OEt}_2$  absorbs in this region. The methyl group (c) has been assigned to the absorption furthest upfield because this methyl group is attached only to Li and therefore should resemble  $(\text{CH}_3\text{Li})_4$  which absorbs the furthest upfield. The methyl group (b) bonded to lithium and beryllium atoms should exhibit a chemical shift somewhere in between  $(\text{CH}_3)_3\text{Be} \cdot 2\text{OEt}_2$  and  $(\text{CH}_3\text{Li})_4$ . Using these ideas, the assignment of the resonance peaks can be made to substantiate the existence of equilibria 7–9.

The amount of each complex, namely,  $\text{LiBe}(\text{CH}_3)_3$ ,

$\text{Li}_2\text{Be}(\text{CH}_3)_4$ , and  $\text{Li}_3\text{Be}(\text{CH}_3)_5$  at equilibrium can be calculated by measuring the areas of each peak and taking into consideration the fact that each peak may be due either to methyl protons of only one species or to methyl protons of different species present in solution. For example, the resonance peak furthest downfield may be due to both of the methyl groups of  $(\text{CH}_3)_2\text{Be}\cdot 2\text{OEt}_2$  as well as due to the methyl group bonded to the beryllium atom in  $\text{Li}_3\text{Be}(\text{CH}_3)_5$ . Similarly, the resonance peak observed for the 2:1 complex,  $\text{Li}_2\text{Be}(\text{CH}_3)_4$ , may also be due to the three methyl groups which are bonded to both lithium and beryllium atoms in  $\text{Li}_3\text{Be}(\text{CH}_3)_5$ . The resonance peak furthest upfield may only be due to the methyl group bonded to the three lithium atoms in the complex  $\text{Li}_3\text{Be}(\text{CH}_3)_5$  or to the presence of methyl-lithium. It has been found from the measured areas (Table II) that  $\text{LiBe}(\text{CH}_3)_3$ ,  $\text{Li}_2\text{Be}(\text{CH}_3)_4$ , and  $\text{Li}_3\text{Be}(\text{CH}_3)_5$  exist in a 1:1:1 molar ratio in solution at  $-96^\circ$  when  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Be}$  are admixed in a 2:1 ratio.

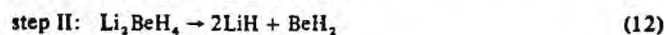
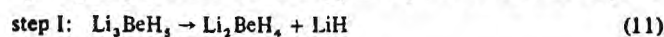
The reaction of  $\text{LiAlH}_4$  and the "ate" complex mixture produced on allowing  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Be}$  to react in a 2:1 ratio yielded a white solid of empirical formula  $\text{Li}_2\text{BeH}_4$ . The infrared spectrum of the white solid contained a broad absorption band centered on  $1600\text{ cm}^{-1}$ . The X-ray powder diffraction pattern showed it to be  $\text{Li}_2\text{BeH}_4$  (Table I). The vacuum DTA-TGA of this compound was identical with the one discussed earlier. The major weight loss (7.7%) occurred at  $330^\circ$  corresponding to 1 mol of hydrogen.

**(c) Reaction of  $\text{LiAlH}_4$  with  $\text{Li}_3\text{Be}(\text{CH}_3)_5$  in Diethyl Ether.** **Preparation of  $\text{Li}_3\text{BeH}_5$ .** The infrared spectrum of the solution obtained by stirring a solution of  $\text{CH}_3\text{Li}$  with  $(\text{CH}_3)_2\text{Be}$  in diethyl ether in a 3:1 molar ratio is recorded in Figure 1. The infrared spectrum of the solution shows two medium strong bands at  $405$  and  $335\text{ cm}^{-1}$  which are tentatively assigned to  $\text{Be}-\text{C}$  stretching vibrations. The strong band at  $480\text{ cm}^{-1}$  is assigned to the  $\text{Li}-\text{C}$  stretching vibrations. The proton spectrum of the same solution consists of a single sharp resonance at room temperature. This implies either the presence of a single compound or a rapid exchange between different species in solution. At  $-96^\circ$  three major absorptions are observed (Figure 2). The assignments of these resonance peaks are made as before describing the system as an equilibrium of the type



In order to establish the stoichiometry of these complexes at equilibrium the areas of all absorptions in the low-temperature proton spectra were measured. A calculation of the relative peak intensities shows  $\text{Li}_3\text{Be}(\text{CH}_3)_5$  to be the major species in solution with  $\sim 10\%$  dissociation to  $\text{CH}_3\text{Li}$  and  $\text{Li}_2\text{Be}(\text{CH}_3)_4$  (Table II).

Reaction of  $\text{LiAlH}_4$  with  $\text{Li}_3\text{Be}(\text{CH}_3)_5$  produced an insoluble white compound which exhibited the empirical formula  $\text{Li}_3\text{BeH}_5$ . The infrared spectrum of the solid showed a broad absorption band centered on  $1600\text{ cm}^{-1}$ . The X-ray powder diffraction pattern showed it to be a new compound and not a physical mixture of  $\text{LiH}$  and  $\text{Li}_2\text{BeH}_4$ . The vacuum DTA-TGA of this compound showed a weight loss (1.21%) at  $218^\circ$  and another weight loss (4.71%) at  $300^\circ$ , the total weight loss being 5.92% which is quite in agreement with the theoretical value (5.78%) calculated for the loss of 1 mole of hydrogen. Although this total weight loss due to evolution of hydrogen gas leads us to suggest eq 11-13 as the steps of



decomposition, the weight loss in two stages is somewhat puzzling.

Table III. Thermal Decomposition of Complex Metal Hydrides of Beryllium

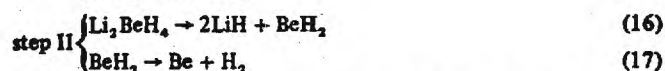
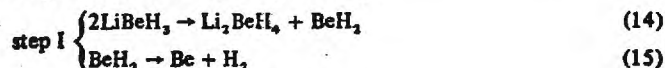
Compd (sample wt, mg)	Thermicity	Range of transition (peak max), $^\circ\text{C}$	% wt Loss
$\text{BeH}_2$ (21.5)	Exo	80-150 (125)	11.6 (loss of ether)
	Endo	170-230 (208)	13.95
$\text{Li}_2\text{BeH}_4$	Endo	250-290 (270)	Phase change
	Endo	280-360 (330)	8.0
$\text{Li}_3\text{BeH}_5$		210-226 (218)	1.21
	Endo	240-290 (262)	Phase change
	Endo	300-340 (315)	4.71
	Exo	130-190 (164)	5.27
$\text{LiBeH}_3$	Endo	250-275 (265)	Phase change
	Endo	270-325 (308)	5.1
	Exo	90-150 (130)	7.4 (loss of ether)
	Endo	170-250 (205)	6.1
$\text{BeH}_2 + \text{Li}_2\text{BeH}_4$ (52.1) (1:1 molar ratio)	Endo	250-280 (270)	Phase change
	Endo	260-330 (295)	4.8

**(d) Reaction of  $\text{LiAlH}_4$  with  $\text{LiBe}_2(\text{CH}_3)_5$  in Diethyl Ether.**  $\text{LiBe}_2\text{H}_5$ . The infrared spectrum of the resultant mixture obtained after stirring  $\text{CH}_3\text{Li}$  with  $(\text{CH}_3)_2\text{Be}$  in a 1:2 molar ratio is identical with the infrared spectrum of the so-called complex  $\text{LiBe}(\text{CH}_3)_3$ . The proton NMR spectrum of the solution consists of a single sharp resonance at room temperature as well as at low temperature ( $-96^\circ$ ) indicating a single compound or very rapid exchange of methyl groups between the complex  $\text{LiBe}(\text{CH}_3)_3$  and dimethylberyllium. The reaction of  $\text{LiAlH}_4$  with the 1:2  $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Be}$  solution resulted in a solid of indefinite analysis. The X-ray powder diffraction of the solid gave very weak lines similar to those for  $\text{Li}_2\text{BeH}_4$ , but with different intensities. It appears that the compound is a physical mixture of  $\text{Li}_2\text{BeH}_4$  and  $\text{BeH}_2$ .

**Reactions of  $\text{AlH}_3$  with "ate" Complexes of  $\text{CH}_3\text{Li}$  and  $(\text{CH}_3)_2\text{Be}$ .** **(a) Reaction of  $\text{AlH}_3$  with  $\text{LiBe}(\text{CH}_3)_3$  in Diethyl Ether.** **Preparation of  $\text{LiBeH}_3$ .** The reaction of  $\text{AlH}_3$  and  $\text{LiBe}(\text{CH}_3)_3$  in diethyl ether produced a white solid of empirical formula  $\text{LiBeH}_3$ . The infrared spectrum of this compound also contained a broad band centered on  $1600\text{ cm}^{-1}$ . The X-ray powder diffraction pattern showed it to be different from either a physical mixture of  $\text{Li}_2\text{BeH}_4$  and  $\text{BeH}_2$  or a mixture of  $\text{LiH}$  and  $\text{BeH}_2$ . Although the strong lines at  $2.95$  and  $2.55\text{ \AA}$  are common in both  $\text{LiBeH}_3$  and  $\text{Li}_2\text{BeH}_4$ , other lines are quite different. Moreover, the strong lines at  $1.81$  and  $1.55\text{ \AA}$  present in  $\text{Li}_2\text{BeH}_4$  and the lines at  $3.85$  and  $2.32\text{ \AA}$  present in  $\text{BeH}_2$  are absent in  $\text{LiBeH}_3$ . Therefore, the compound appears to have its own identity.

The vacuum DTA-TGA of  $\text{LiBeH}_3$  is reported in Table III. It contained noncondensable gas evolutions at  $164$  and  $308^\circ$ , respectively. The gas evolution at  $164^\circ$  was accompanied by a small exothermal effect and is probably due to decomposition of  $\text{BeH}_2$  into beryllium and hydrogen (step 1). The thermal effect (DTA) of the gas evolution at  $308^\circ$  is a small endotherm which is preceded by another small endotherm at  $265^\circ$  indicative of a structural change not involving a weight loss or gas evolution. The weight loss at  $164^\circ$  (5.27%) corresponds to the loss of one atom of hydrogen present in  $\text{LiBeH}_3$ .

Similarly, the weight loss at 308° (5.1%) corresponds to the weight loss of one atom of hydrogen. Therefore, the thermal decomposition of  $\text{LiBeH}_3$  is believed to occur in essentially two steps below 500° (see eq 14-17).



(b) Reaction of  $\text{AlH}_3$  with  $\text{LiBe}_2(\text{CH}_3)_5$  in Diethyl Ether. Attempted Preparation of  $\text{LiBe}_2\text{H}_5$ . The reaction of  $\text{AlH}_3$  and  $\text{LiBe}_2(\text{CH}_3)_5$  resulted in a solid of indefinite analysis. The X-ray powder diffraction of the solid gave very weak lines similar to those of  $\text{Li}_2\text{BeH}_4$ , but with different intensities. The vacuum DTA-TGA of the solid showed three noncondensable gas evolutions at 165, 243, and 308°, respectively. The thermal effect (DTA) of gas evolution at 165° is a small endotherm which probably represents the decomposition of  $\text{BeH}_2$  into beryllium and hydrogen. The gas evolution at 243° is accompanied by an exotherm whereas the gas evolution at 308° is accompanied by a small endotherm. The weight loss (1%, 2.8%, and 5.7%, respectively) indicates the presence of one or more species in the sample.

A potential route to complex metal hydrides of beryllium of the type  $\text{Na}_n\text{Be}_m\text{H}_{2n+m}$  and  $\text{K}_n\text{Be}_m\text{H}_{2n}$  involves the reaction of  $\text{NaH}$  or  $\text{KH}$  with  $(\text{CH}_3)_2\text{Be}$  followed by reaction of the resulting complex with  $\text{LiAlH}_4$ . Attempts to prepare  $\text{KBe}(\text{CH}_3)_2\text{H}$  and  $\text{NaBe}(\text{s-C}_4\text{H}_9)_2\text{H}$  in diethyl ether resulted

in incomplete reaction between potassium or sodium hydride and corresponding dialkylberyllium compounds.

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**Registry No.**  $\text{LiH}$ , 7580-67-8;  $\text{BeH}_2$ , 7787-52-2;  $\text{Li}_2\text{BeH}_4$ , 19321-21-2;  $\text{Li}_3\text{BeH}_5$ , 56792-70-2;  $\text{LiBeH}_3$ , 25282-11-5;  $\text{CH}_3\text{Li}$ , 917-54-4;  $(\text{CH}_3)_2\text{Be}$ , 506-63-8;  $\text{LiAlH}_4$ , 16853-85-3;  $\text{Li}_2\text{Be}(\text{CH}_3)_4$ , 20860-58-6;  $\text{Li}_3\text{Be}(\text{CH}_3)_5$ , 56829-59-5;  $\text{LiBe}_2(\text{CH}_3)_5$ , 56829-60-8;  $(\text{n-C}_4\text{H}_9)_2\text{Be}$ , 7367-41-1;  $\text{Et}_2\text{O}$ , 60-29-7;  $\text{BeBr}_2$ , 7787-46-4;  $\text{AlH}_3$ , 7784-21-6;  $\text{LiBe}(\text{CH}_3)_3$ , 56792-71-3.

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- (14) The ether content was determined by difference after the compound had been dried under vacuum at room temperature overnight.

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<p>During this report period work has continued on the preparation and structure elucidation of simple and complex metal hydrides of the main group elements. Four papers have appeared in "Inorganic Chemistry Journal" concerning work carried out on the ONR program. Projects completed during the past year are (1) "The Direct Synthesis of Poly-iminoalanes" and, (2) "Preparation of New Complex Metal Hydrides of Magnesium and Zinc, <math>Mg(ZnH_3)_2</math> and <math>MgZnH_4</math>". Projects in progress involve the preparation of <math>RMgH</math> and <math>RMg_2H_3</math> compounds and the attempted preparation of <math>Mg(CuH_2)_2</math>, <math>MgCuH_3</math>, <math>LiMgH_3</math>, <math>Li_2MgH_4</math> and "ate" complexes such as <math>LiMgRH_2</math>.</p>			

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	Organometallic Compounds						
	High Energy Binders						
	Burning Rate Accelerators						

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## 13. ABSTRACT

During the past 10 years, work was carried out on the preparation of new and unusual simple and complex metal hydrides of the main group elements. Several new hydrides of propellant interest were prepared and the chemistry related to the preparation and reactions of the new hydrides, elucidated.

14.

KEY WORDS

LINK A

LINK B

LINK C

ROLE

WT

ROLE

WT

ROLE

WT

Complex Metal Hydrides

High Energy Fuel

Organometallic Compounds

High Energy Binders

Burning Rate Accelerators

FINAL REPORT

To the  
Office of Naval Research

"Complex Metal Hydrides. High Energy Fuel Components for Solid  
Propellant Rocket Motors"

E. C. Ashby, Principal Investigator  
Georgia Institute of Technology, Atlanta, Georgia 30332  
March 1, 1968 - March 31, 1978

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### ABSTRACT

This is the final report of a 10 year (March 1, 1968-March 31, 1978) effort concerning the preparation of light metal hydrides of the main group elements. The purpose of this project was to prepare thermal and shock stable light metal hydrides of high calculated specific impulse ( $I_{sp} > 300$  sec.) for use as solid rocket propellants. The results of these efforts were reported each year in the annual report and in over 50 publications appearing in Inorganic Chemistry journal. A list of these publications follows.

The metals specifically covered in this work are lithium, beryllium, magnesium, zinc, aluminum, boron and copper. An effort was made to establish the fundamental chemistry leading to the preparation of new hydrides as well as the preparations themselves. Indeed, a number of serious errors in the literature were corrected and the basis for the chemistry of main group metal hydrides established. In addition, many new hydrides were prepared and characterized, some of which should have potential as solid rocket propellants, e.g.  $Li_3AlH_6$ ,  $Li_2BeH_4$ ,  $Li_5BeH_4$ ,  $Li_5CuH_6$ , etc.

The author would be happy to answer any questions pertaining to this work at any time.

PUBLICATIONS AS A RESULT OF WORK ON THIS PROJECT

1. E. C. Ashby and B. James, "Concerning the Direct Synthesis of the Alkali Metal Hexahydridoaluminates," Inorg. Chem., 8, 2468 (1969).
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