In presenting the dissertation as a partial fulfillment of
the requirements for an advanced degree from the Georgia
Institute of Technology, I agree that the Library of the
Institute shall make it available for inspection and
circulation in accordance with its regulations governing
materials of this type. I agree that permission to copy
from, or to publish from, this dissertation may be granted
by the professor under whose direction it was written, or,
in his absence, by the Dean of the Graduate Division when
such copying or publication is solely for scholarly purposes
and does not involve potential financial gain. It is under-
stood that any copying from, or publication of, this dis-
sertation which involves potential financial gain will not
be allowed without written permission.

7/25/68

PREPARATION AND REACTIONS OF COMPLEXES

OF MAGNESIUM ALKYLS AND ARYLS WITH

ALKALI METAL ALKYLS AND HYDRIDES

A THESIS

Presented to

The Faculty of the Graduate Division

by

Robert C. Arnott

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in the

School of Chemistry
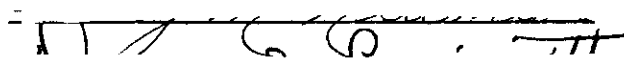
Georgia Institute of Technology

May, 1970

PREPARATION AND REACTIONS OF COMPLEXES

OF MAGNESIUM ALKYLS AND ARYLS WITH

ALKALI METAL ALKYLS AND HYDRIDES

Approved:

Chairman

Date approved by Chairman: January 15, 1971

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

Instrumentation and Apparatus

Reagents

Analysis

General Preparative Methods

Preparation of Dialkylmagnesium Compounds

Preparation of Hydrides

Preparation of Alkali Metal Alkyl Complexes of
     Magnesium Alkyls

Preparation of Alkali Metal Hydride Complexes
     of Magnesium Alkyls

Preparation of Complex Metal Hydrides

LIST OF TABLES

LIST OF ILLUSTRATIONS

SUMMARY

The reaction of dimethyl, diethyl and diphenyl mercury with magnesium (100% excess) was found to take place under much milder conditions than those indicated in previous reports. Ultra pure solutions of dialkyl magnesium reagents were obtained by extracting the reaction mixtures with the solvent of choice, leaving behind the insoluble mercury and excess magnesium. Di-s-butylmagnesium was prepared in highest purity via the exchange reaction of anhydrous magnesium chloride with s-butyllithium in benzene at 40°C. Marked differences in the reactivity of various samples of magnesium chloride was shown to be dependent on the initial source of magnesium and not on the method of preparation of the magnesium chloride itself.

When methyllithium and dimethylmagnesium were mixed in diethyl ether at 25°C, complexes were formed whose stoichiometry depended on the Li:Mg ratio in solution. At Li:Mg ratios of 2:1 or less, the composition in solution was best represented by the following equation in which a 2:1 complex existed in equilibrium with both reactants.

$$0.5(CH_3Li)_4 + (CH_3)_2Mg \rightleftharpoons Li_2Mg(CH_3)_4$$
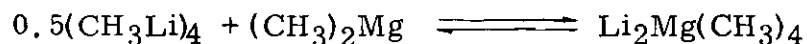
When the Li:Mg ratio was greater than 2:1, the composition in solution was best represented by the following equation.

$$0.25(CH_3Li)_4 + Li_2Mg(CH_3)_4 \rightleftharpoons Li_3Mg(CH_3)_5$$
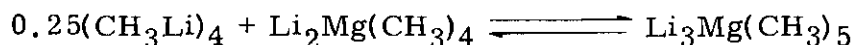
The addition of s-butyllithium to di-s-butylmagnesium in cyclohexane resulted in the formation of complexes whose stoichiometry was dependent on the Li:Mg ratio in solution. At a Li:Mg ratio of exactly 1:1 lithium tri-s-butylmagnesium was produced. A monomer-dimer equilibrium was shown to exist over a concentration range 0.11 - 0.25 molal. When the Li:Mg ratio was increased, the system was best described in terms of a 1:1 complex existing in equilibrium with a 2:1 complex. At Li:Mg ratios greater than 2:1, the infrared spectra of the solutions showed only the effect of excess s-butyllithium.

The addition of phenyllithium to an equivalent amount of diphenylmagnesium in diethyl ether resulted in the formation of an authentic 1:1 complex, lithium triphenylmagnesium.

Lithium hydride was shown not to react with dimethylmagnesium in diethyl ether. In tetrahydrofuran, intermediate complexes were formed in which the nucleophilic character of the methyl group was greater than that of the methyl in dimethylmagnesium alone. Ether cleavage then occurred to a significant degree. Ether cleavage

also resulted when lithium and sodium hydride were mixed with di-

phenylmagnesium in tetrahydrofuran. Stable insoluble complexes

were formed when potassium hydride and diphenylmagnesium were

mixed in diethyl ether. Evidently precipitation of the complex was

faster than ether cleavage.

Mixtures of alkali metal hydrides with the appropriate di-

alkylmagnesium compound in benzene resulted in the formation of

stable soluble complexes, as shown by the following equations.

$$NaH + 2(s\text{-}C_4H_9)_2Mg \longrightarrow NaH \cdot 2(s\text{-}C_4H_9)_2Mg$$

$$KH + (s\text{-}C_4H_9)_2Mg \longrightarrow KH \cdot (s\text{-}C_4H_9)_2Mg$$

$$KH + (n\text{-}C_4H_9)_2Mg \longrightarrow KH \cdot (n\text{-}C_4H_9)_2Mg$$
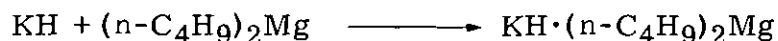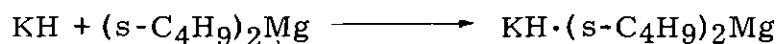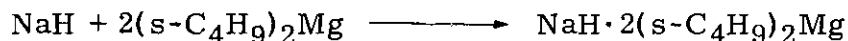
Attempts to prepare a 2:1 complex from potassium hydride and di-s-

butylmagnesium resulted in extensive metallation of the solvent.

Reduction of the sodium hydride complex shown above re-

sulted in the formation of $NaMg_2H_5$, which was shown to dissociate to

$NaMgH_3$ and MgH_2 at 115°C. Both hydrogenolysis and pyrolysis of

the complex $KH \cdot (s\text{-}C_4H_9)_2Mg$ resulted in the formation of $KMgH_3$.

Comparison of the X-ray powder diffraction patterns of $NaMgH_3$ and

$KMgH_3$ with those of $NaMgF_3$ and $KMgF_3$ revealed marked similar-

ities. The Perovskite structure has been demonstrated for the

fluoride compounds and is therefore implied for the hydride com-

pounds. Hydrogenolysis of lithium tri-s-butylmagnesium at 25°C

produced a mixture of LiH, MgH_2 and $LiMgH_3$. Simultaneous DTA-

TGA analysis revealed $LiMgH_3$, $NaMgH_3$ and $KMgH_3$ are stable to

$\sim$ 300°C.

CHAPTER I

INTRODUCTION

In recent years there has been increasing awareness of the need for high purity magnesium alkyls and aryls for kinetic and ebullioscopic measurements (1,2). A number of methods of preparation, both in ether and hydrocarbon solvents, are well documented in the literature (3, 4, 5, 6), but all suffer from some disadvantages.

The dioxane precipitation method (eq. 1) is perhaps the most widely used of these, but some dioxane is invariably complexed to the soluble dialkyl magnesium species, and can be removed only if the solvent is removed at reduced pressure and the resulting solid ($R_2Mg \cdot$ ether·dioxane) is placed under vacuum at elevated temperatures (ca. $110^{\circ}C$) (7).

$$2\ RMgX + 2\ \text{dioxane} \xrightarrow{\ Et_2O\ } R_2Mg + MgX_2 \cdot 2\ \text{dioxane} \qquad (1)$$
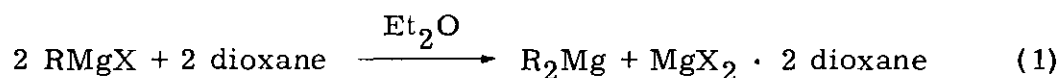
Similarly, when limited amounts of dimethyl ether are used (eq. 2), codistillation with hydrocarbon is necessary to obtain a completely desolvated species.

$$RMgCl + RLi \xrightarrow[\text{hydrocarbon}]{5\%Me_2O} R_2Mg + LiCl \qquad (2)$$
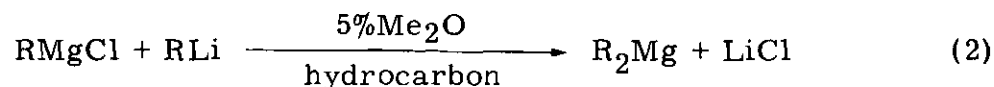
If the dialkylmagnesium compound is required to be ether free or if solvent exchange is desired (e.g., Et_2O to THF) for molecular weight measurements, the disadvantages associated with these preparations are obvious.

The exchange reaction (eq. 3) is somewhat tenuous as reported in the literature, and limited to those alkyls which cannot undergo olefin elimination at temperatures on the order of $150^\circ C$.

$$R_2Hg + Mg \xrightarrow[\text{high temperature}]{\text{sealed tube}} R_2Mg + Hg \qquad (3)$$
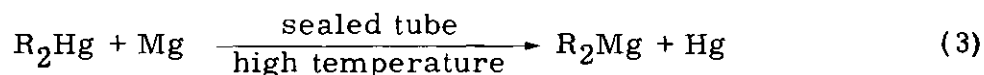
The exchange reaction (eq. 4) using anhydrous magnesium chloride slurried in benzene has been demonstrated with excellent results when R = s-butyl.

$$MgCl_2 + 2 \text{ s-BuLi} \xrightarrow[\text{or hexane}]{\text{benzene}} \text{s-Bu}_2Mg + 2 \text{ LiCl} \qquad (4)$$
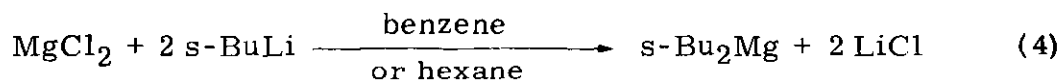
The main requirement is that the product must be soluble in hydrocarbon.

Thus, since extensive use of dialkylmagnesium compounds was planned, the initial goal of this research was to evaluate and modify (where necessary) available synthetic routes as well as to attempt to devise new and useful preparative methods leading to this class of compounds. Once high purity reagents were in hand the

reactions of magnesium alkyls could be investigated under a variety of conditions.

Whereas Grignard reagents have been extensively investigated for many years (8), much less effort has been devoted to elucidating the nature of related magnesium alkyls. It is already known that this latter class of compounds behave toward typical organic substrates such as ketones and nitriles in a fashion similar to that of the Grignard reagents. The advantage of studying other reactions of dialkylmagnesium compounds as related to Grignard reagents lies in the simple composition of this species in solution compared to the Grignard reagents themselves. Dialkylmagnesium compounds are but one of many species present in the Grignard equilibria (eq. 5) and while they are polymeric in the solid state (9), they are not associated at all in THF and only slightly in diethyl ether (Figure 1) (2).

$$\text{trimer} \rightleftharpoons \text{dimer} \rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons 2RMgX \rightleftharpoons \text{dimer} \rightleftharpoons \text{trimer} \quad (5)$$
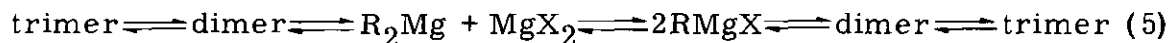
Magnesium alkyls in ethereal solvents consist mainly if not entirely of monomeric solvated molecules.

$$
\begin{array}{c}
R \diagdown \quad \diagup OR_2 \\
\quad\quad Mg \\
R \diagup \quad \diagdown OR_2
\end{array}
\rightleftharpoons
\begin{array}{c}
R \diagdown \\
\quad\quad Mg \leftarrow OR_2 + R_2O \\
R \diagup
\end{array}
\quad (6)
$$
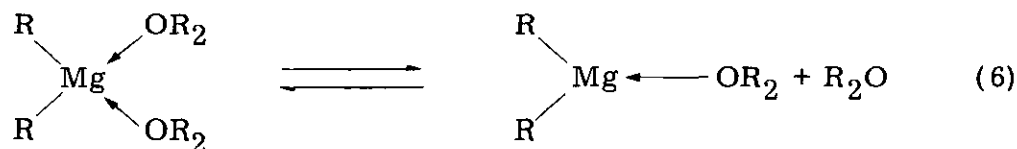
Solid State $(CH_3)_2Mg$
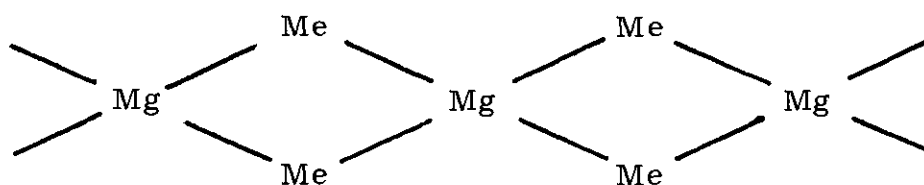
Solution
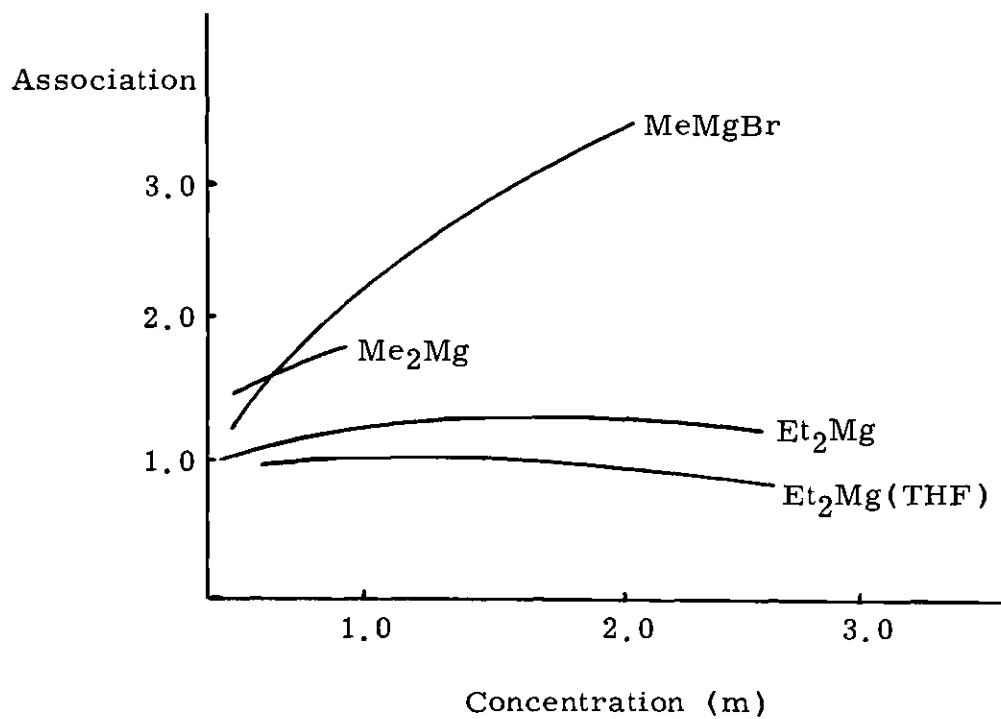
Figure 1. Nature of Association of Grignard Reagents and Magnesium Alkyls.

The magnesium alkyls, by virtue of available vacant orbitals, or by virtue of the fact that weakly basic ether can be displaced, should react with stronger bases to form acid-base complexes. Thus, (a) diethyl ether is displaced by a more basic ether such as THF and (b) it should be possible to displace the ether by a more basic metal alkyl or hydride.

$$R_2Mg \cdot 2Et_2O \xrightarrow{\text{THF}} R_2Mg \cdot 2THF + 2Et_2O \qquad (7)$$

$$R_2Mg \cdot 2Et_2O \xrightarrow{\text{LiR}} LiMgR_3 \cdot Et_2O \longrightarrow Li_2MgR_4 \qquad (8)$$
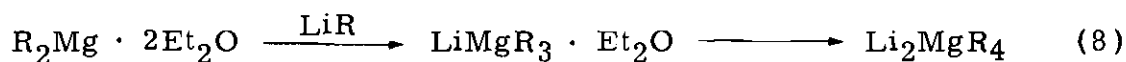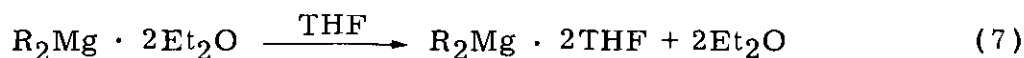
When hydrocarbon soluble species are employed such as di-s-butyl-magnesium, which is known to be dimeric (6), the same type of reaction should take place. In this case an alkyl bridge bond would be broken and complex formation would follow.

Other metal alkyls which also have orbitals available for bond formation such as Me_2Zn, Me_3Al and Me_3B readily form complexes with MeLi (10, 11). Similar complexes have been observed for Et_2Zn, Et_2Hg, and Et_2Cd with EtLi in solution (12). The structures of $Li_2Be(CH_3)_4$ and $Li_2Zn(CH_3)_4$ have been determined recently by X-ray powder analysis (13, 14).

Until recently, however, the only complex of this type known containing a magnesium atom was $LiMg\emptyset_3$, which had been isolated from diethyl ether (15).

$$\emptyset Li + \emptyset_2 Mg \longrightarrow LiMg\emptyset_3 \qquad (9)$$
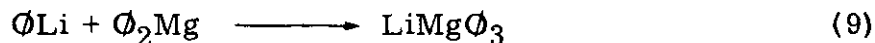
More recently Brown and co-workers studied the reaction of lithium

alkyls and aryls with magnesium alkyls and aryls using low temper-

ature nmr techniques (16). When R = Me, complexes of the type

$Li_n MgR_{2+n}$ were indicated where n = 2 or 3. Where R = $\emptyset$ both 1:1

and 2:1 complexes were observed. Very recently Seitz (17) has

shown, again using low temperature nmr, that a species $LiMg(CH_3)_3$

exists in THF, but has no evidence for the 3:1 complex in the more

basic solvent. None of these complexes were isolated, however, and

the complexes were thought to dissociate as the temperature was in-

creased. An investigation of the nature of these and related systems

at room temperature appeared warranted.

A report concerning the reaction of diethylmagnesium with

lithium, sodium and potassium hydrides later appeared (18). While

the authors concluded that complex formation may have occurred in

solution, extensive ether cleavage resulted and the complexes could

not be isolated. Although stable complexes of beryllium and zinc such

as $NaH \cdot Et_2 Be$ (19), $NaH \cdot 2Et_2 Zn$ (20, 21), $LiH \cdot \emptyset_2 Zn$ and $LiH \cdot \emptyset_2 Be$

(22) are known, no stable complexes have been reported for mag-

nesium.

Similarly, although complex metal hydrides such as $LiAlH_4$

and $NaBH_4$ are known, few attempts have been made to prepare mixed

metal hydrides of the type $M'MgH_3$ or M'_2MgH_4 where M' is an alkali

metal. Coates has reported a similar complex, Na_2BeH_4 , which

was prepared according to equation 10 (23).

$$Na(i\text{-}Bu_2Be)H \xrightarrow{\quad 70^o \quad} Na(i\text{-}BuBeH)H \longrightarrow \qquad (10)$$

$$1/2 \ i\text{-}Bu_2Be + 1/2 \ Na_2BeH_4$$
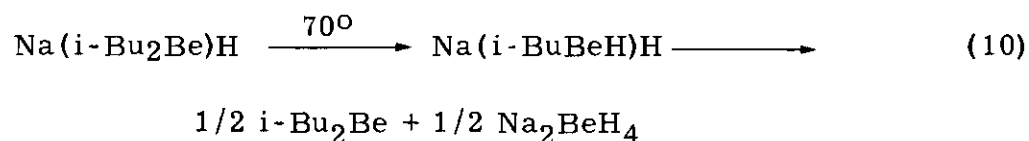
Messer, et al.(24) reported complexes of the type $LiCaH_3$, $LiBaH_3$

and $LiSrH_3$ prepared via hydrogenation of the metals at $700\text{-}750^oC$,

and indicated a Perovskite type lattice from X-ray powder analysis.

When the Ba:Li or Sr:Li ratios in the original metal mixture were >1:1

excess BaH_2 and SrH_2 were observed.

Only two attempts have been made to prepare analogous mag-

nesium species. Tanaka reported the attempted hydrogenation of a

mixture of MeLi and Me_2Mg and identified the only products as LiH

and MgH_2 (25). Coates reported the pyrolysis of a mixture of n-BuLi

and Me_2Mg produced only LiH and Me_2Mg (18).

The purpose of the research described in this thesis was

(a) to evaluate available synthetic routes leading to pure dialkylmag-

nesium compounds and to investigate new routes, and (b) to study the

reactions of this class of compounds with various alkali metal alkyls

and hydrides under a variety of conditions.

CHAPTER II

EXPERIMENTAL

Instrumentation and Apparatus

The inert atmosphere glove box was manufactured by Kewaunee (Model 2C1020) and equipped with a recirculating system to continuously remove oxygen and water contaminants from the system (26). A Little Giant vacuum-pressure pump (capacity 1.25 cfm) was used to recirculate the atmosphere.

X-ray powder diffraction patterns were obtained on a Debye-Scherrer camera of 114.6-mm diameter using $CuK\alpha(1.540\,\overset{o}{A})$ radiation with a nickel filter and Ilford Industrial G X-ray film. Single-walled capillary tubes of 0.5 mm diameter (Siemens of America) were used.

All chromatographic analyses were carried out using a dual column gas chromatograph (F & M Scientific Model 720) using columns filled with Polypak 2 or Carbowax 20M suspended on Diatoport S (F & M Scientific).

Infrared spectra were obtained using a Perkin Elmer Model 621 high resolution infrared spectrophotometer. Both potassium bromide and cesium iodide windows were employed. A Perkin Elmer variable path-length cell was used in the reference beam where

applicable. Spectra of solids were obtained in Nujol which had been dried over sodium wire, degassed and stored under nitrogen.

The nmr spectra were obtained on a Varian A-60 spectrometer.

A Coleman Model 21 flame photometer was used for alkali metal determinations.

A high pressure lab manufactured by Autoclave Engineers, capable of producing and maintaining pressures up to 4500 psi in the reaction vessel was used in all hydrogenolysis experiments.

Cryoscopic molecular weight measurements were obtained in benzene and cyclohexane in an apparatus specially designed for handling air sensitive compounds (27). A cross-sectional view of this apparatus is provided in Figure 2. An outlet (n) is used to provide an inert gas purge, or evacuate the system. Both solvent and test solutions were added from a tared syringe through a rubber septum at (s). A Beckman differential thermometer (b) was used to monitor temperature changes. The stirring helix (h), was driven up and down by an external mechanically driven magnet, acting on an iron core attached to the helix.

DTA-TGA analyses were obtained using a Mettler Thermoanalyzer II, which had been adapted to handle air and moisture sensitive compounds.
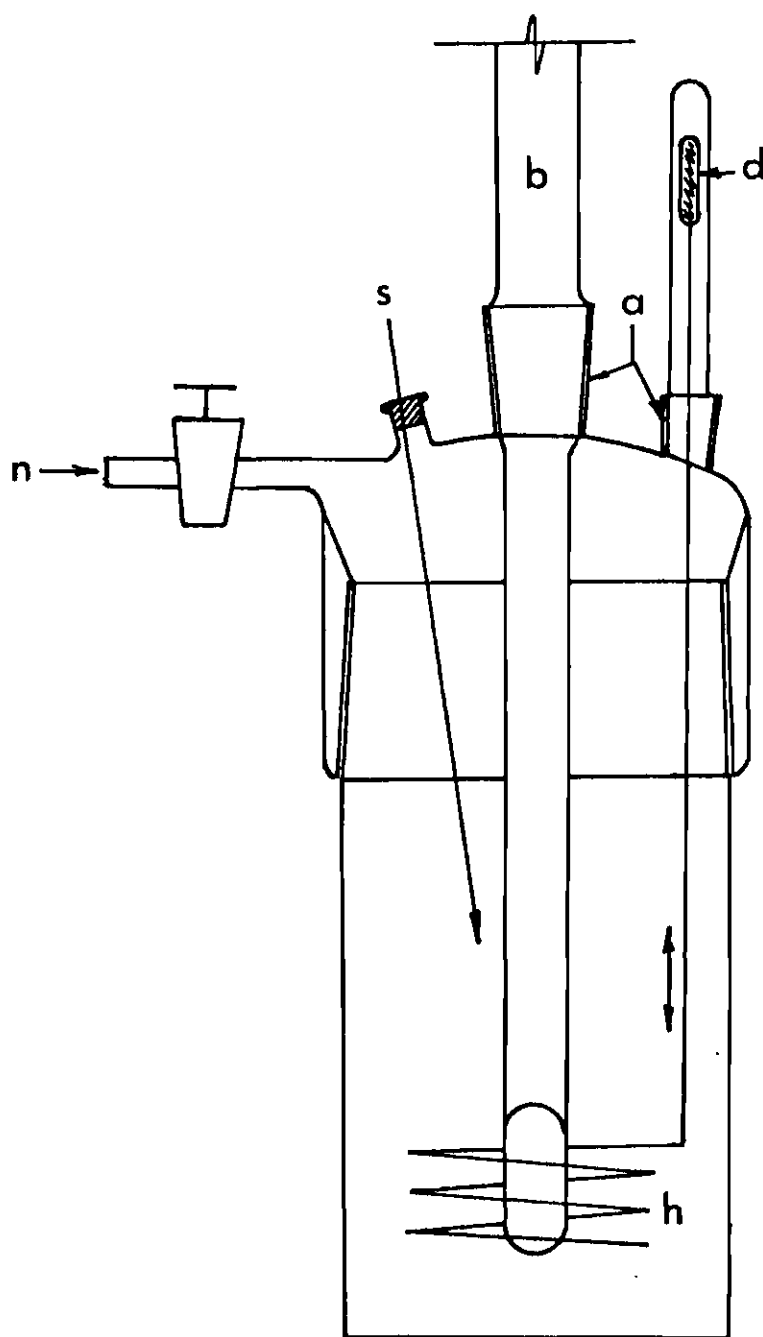
Figure 2. Cryoscopic Molecular Weight Apparatus.

Reagents

Dialkylmercury compounds (Metallomer) and alkyllithium compounds (Foote Mineral Co., Lithium Corporation of America) were used as received. Lithium and sodium aluminum hydride (Ventron Metal Hydrides Division) were used as drying agents without further purification. Lead alkyls were obtained from the Ethyl Corporation.

Potassium and sodium (Baker Analyzed) were cut under mineral oil and washed with toluene or benzene prior to use. Lithium, sodium and potassium hydride (Ventron Metal Hydrides Division) were obtained in mineral oil and washed with hexane prior to use.

Tetrahydrofuran (Fisher Certified), benzene (Baker Thiophene-free), toluene (Fisher Certified), xylene (Fisher Certified) and p-dioxane (Fisher Certified) were distilled from $NaAlH_4$ through a two-foot vigreaux column under dry nitrogen just prior to use. Hexane was washed with concentrated H_2SO_4, water, dried over anhydrous $MgSO_4$ and distilled from $NaAlH_4$. Diethyl ether (Fisher Certified) was distilled from $LiAlH_4$.

The alkyl and aryl halides (Reagent Grade from Eastman) were dried over anhydrous $MgSO_4$, and distilled under an atmosphere of dry nitrogen through a twenty-inch column filled with glass helices. Methylbromide was distilled directly from the bottle through a one-foot column packed with NaOH and molecular sieve type 4-A into the reaction system.

Inorganic salts used as catalysts in the tetraethyllead experiments, e.g., $HgCl_2$, $AlCl_3$, and BCl_3, were dried under vacuum at 100°C prior to use. In some cases water was trapped by P_2O_5.

Grignard grade magnesium turnings (Fisher Reagent) and triply sublimed magnesium (Dow) were used where specified. Both grades of magnesium were washed with ether, dried in vacuo, and stored. The metal was dried a second time in the apparatus used to prepare all of the compounds.

High purity hydrogen (Airco) was used in all hydrogenation experiments.

All manipulations of the chemicals were carried out in the glove box (dry nitrogen atmosphere) or on the bench using Schlenk techniques (28). All equipment that came in contact with the reagents was dried by flash flaming under vacuum or under a rapid nitrogen purge.

Analysis

Samples were prepared for analysis as follows. Liquid samples (e.g., 2ml of a Grignard compound in diethyl ether) were cooled to -78°C and hydrolyzed with distilled water. Using this technique, the water first froze, then as the sample was allowed to warm, melting and slow hydrolysis took place. In this fashion very reactive samples could be effectively hydrolyzed with no charring. Solid

samples were dried on a vacuum manifold, weighed into a tared vessel under nitrogen, covered with ether and treated in a like manner. After hydrolysis, the samples were acidified with dilute sulfuric acid, (the ether was removed under vacuum), and diluted to volume with distilled water.

For magnesium analysis, aliquots were withdrawn, buffered to pH 10, and a small quantity of eriochrome black T and methyl red indicators added. The samples were warmed to $60^{\circ}C$ and titrated with EDTA to the end point. For halogen analysis, aliquots were treated with 5 ml of benzyl alcohol, 2 ml of ferric alum indicator and titrated with excess $AgNO_3$. The sample was then back titrated to the end point with KCNS.

For alkali metal analysis standard curves were prepared as follows. Salts (Li_2CO_3, NaCl, KCl) were dried at $110^{\circ}C$ overnight, weighed into a tared weighing bottle, dissolved in distilled water, and then transferred to a volumetric flask and diluted to volume. Standard solutions (Li, 0-10 meq/L; Na, 0-5 meq/L; K, 0-0.6 meq/L) were prepared by subsequent dilutions and used to prepare standard curves on the flame photometer. Accurate determination of alkali metal content was obtained by comparing the unknown to these standard curves.

Hydridic hydrogen and butane analyses were performed on a vacuum line (28). The residues remaining after hydrolysis were

acidified and treated as previously described for magnesium and alkali metal analysis.

For vpc analysis, samples (aliquots of liquids or weighed amounts of solid, covered with diethyl ether or benzene) were hydrolyzed in the manner previously described, using a saturated NH_4Cl solution instead of distilled water. The organic layer separated readily and test samples were withdrawn with a Hamilton Syringe for analysis.

<u>General Preparative Methods</u>

<u>Preparation of Grignard Reagents</u>

Grignard reagents were used repeatedly in this study as precursors in the preparation of dialkylmagnesium compounds and magnesium chloride. The preparation of iso-propylmagnesium chloride will illustrate the method employed. Two addition funnels, one with 2-chloropropane (31.4 g, 0.4 moles) and one with diethyl ether (200.0 ml) were connected to one side of a 0.5 liter 3-necked round bottom flask with a Claissen adapter. A mechanical stirrer (motor assembly with an oil-sealed bearing) was inserted at the center neck and a dry ice-acetone condenser connected to the remaining neck. Reaction was initiated by the addition of 3 to 5 ml of the halide along with 50 ml of ether (sometimes gentle warming was required) to the magnesium turnings (12.15 g, 0.5 moles). The remaining halide was added drop-

wise along with ether at a rate sufficient to maintain mild reflux, usually over a two-hour period. The resulting clear, colorless solutions, over excess magnesium, consistently gave a magnesium: halogen ratio of 1:1 (within 3%) on analysis. The next operation was dictated by the specific preparation in progress.

Preparation of Anhydrous Magnesium Chloride

Method A: From the Reaction of iso-Propylmagnesium Chloride with Anhydrous Ethereal Hydrogen Chloride. In a typical reaction iso-propylmagnesium chloride (200 ml of a 1.6 molar solution in diethyl ether, 0.32 moles) was placed in a 500 ml three-necked round bottom flask equipped with a mechanical stirrer, dropping funnel and water cooled condenser. Hydrogen chloride (210 ml of a 1.5 molar solution in ether, 0.32 moles) was added slowly over a period of two hours. The reaction began immediately and was slightly exothermic, with a continuous precipitation of magnesium chloride observed throughout. When the evolution of propane ceased, the mixture was filtered, the magnesium chloride etherate washed with two 100 ml portions of benzene and slurried in an additional 300 ml of benzene.

The sample was then placed on a distillation apparatus consisting of a 20-inch column filled with glass helicies and a fractional distillation head. The temperature was raised and codistillation of the solvents continued until the head temperature reached 80°C. At

this point vpc analysis of a portion of the slurry consistently indicated

that only 0.3 to 0.5 mole percent ether remained, relative to mag-

nesium. This final slurry was then used in the exchange reactions

with s-butyllithium.

Method B: From the Reaction of iso-Propylmagnesium

Chloride and Benzyl Chloride. In a typical reaction iso-propylmag-

nesium chloride (100 ml of a 1.5 molar solution in diethyl ether, 0.15

moles) was placed in an apparatus similar to that described above.

Benzyl chloride (19 g, 0.15 moles) was diluted to 60 ml with ether

and added at reflux. Normally 30% of the benzyl chloride was added

and the mixture kept stirring at reflux until the reaction began, then

the rest of the halide was added. Reaction was immediate only when

the Grignard concentration was at least 2.0 molar. Once the reaction

was complete, the sample was treated as described in Method A above.

Preparation of Dialkylmagnesium Compounds

Preparation of Me$_2$Mg

Method A. A Grignard reagent was prepared in the usual way

from methyl bromide (250 g, 2.6 moles) and triply sublimed magne-

sium (75.0 g, 3.0 moles). Methyl bromide was passed through a one-

foot column packed with NaOH and molecular seive type 4-A (1/16 inch

pellets) and condensed directly into the halide dropping funnel by a dry

ice-acetone condenser. The final solution was 1.7 molar in magnesium.

p-Dioxane (252 g, 2.86 moles) was added directly to the reaction mix-

ture over a three-hour period, and produced a voluminous white pre-

cipitate of $MgBr_2 \cdot 2dioxane$. The mixture was stirred overnight, then

taken into the dry box and allowed to settle. The clear supernatent

was decanted from the mixture and later combined with excess ether

used to wash the precipitate in order to extract the remaining dimethyl-

magnesium. Analysis indicated that the final solution was 0.725 molar

in magnesium and contained no halogen.

Method B. Dimethylmercury (30.69 g, 0.134 moles) was

added to triply sublimed magnesium (7.3 g, 0.3 moles) in a 250 ml

round bottom flask and placed under a water cooled reflux condenser.

The reaction was spontaneous, and heat release ended after 1.5 hours.

The flask was allowed to sit for 12 hours and then placed under vacuum

for two hours at 60°C to remove any unreacted dimethylmercury. The

fluffy white dimethylmagnesium was extracted with diethyl ether and

separated from the residual magnesium amalgam by filtration. Anal-

ysis of the filtrate indicated the solution to be 0.435 molar in magne-

sium, and the standard test for mercury using 2,2'-dipyridyl was

negative. The yield of dimethylmagnesium was nearly quantitative.

Preparation of n-Bu$_2$Mg

Method A. A Grignard reagent was prepared in the usual

way from 1-chlorobutane (84.5 g, 0.91 moles) and triply sublimed

magnesium (31.0 g, 1.3 moles) to give a solution 1.3 molar in mag-

nesium. p-Dioxane (88 g, 1.0 moles) was added and after filtration
the final solution was placed under vacuum for solvent removal. The
resulting white solid (n-Bu$_2$Mg·Et$_2$O) was heated to 120°C under a
vacuum of 0.5 mm for 18 hours (7). <u>Anal</u>:[*] Calcd for n-Bu$_2$Mg: Mg,
17.50%; Found: Mg, 17.34%. The yield was approximately 80%.

<u>Method B</u>. A Grignard compound was prepared as described
above, and the reaction mixture filtered in the dry box to produce a
clear solution of n-butylmagnesium chloride, in 98% yield. n-Butyl-
magnesium chloride (0.5 moles in 500 ml of ether) was placed in a
one liter three-necked round bottom flask equipped with a magnetic
stirrer, dry ice-acetone condenser and a dropping funnel containing
n-butyllithium (0.50 moles in 225 ml of benzene). The lithium reagent
was added dropwise over a period of two hours. The reaction was
instantaneous; a precipitate of LiCl was produced continuously. After
filtration the clear solution was subjected to codistillation until the
head temperature reached 80°C. During this time, n-Bu$_2$Mg was pre-
cipitated continuously from solution. The product was isolated by
filtration, and dried <u>in vacuo</u>. <u>Anal</u>.[**] Calcd for n-Bu$_2$Mg: Mg,
17.50%; Found: Mg, 17.30%; Cl, 0.00%.

---

[*]vpc analysis indicated ∼1% residual dioxane remained in this
product.

[**]vpc analysis indicated ∼0.5% residual ether.

Preparation of s-Bu$_2$Mg

Method A: Disproportionation of s-Butylmagnesium Chloride

(29). s-Butylmagnesium chloride (0.4 moles) was prepared in the usual manner in diethyl ether from 2-chlorobutane and triply sublimed magnesium. The sample was filtered to remove excess magnesium and the solvent was then removed in vacuo to produce a viscous liquid which was heated to 80°C under vacuum of 1 mm for 12 hours to remove solvated ether. Benzene (100 ml) was added and during a 48-hour period the solution thinned out producing a straw colored supernatent and a white solid. The mixture was then filtered. Analysis showed the filtrate to be 0.525 molar in magnesium and 0.14 molar in chloride ion. The solid residue was found to contain hydridic hydrogen and gave a magnesium:chloride:hydrogen ratio of 2:3:1. The X-ray powder diffraction patterns showed this solid to be a mixture of magnesium hydride and unsolvated magnesium chloride. This solid mixture was later used in an exchange reaction with s-butyllithium to produce di-s-butylmagnesium. The filtrate contained di-s-butylmagnesium and ether solvated s-butylmagnesium chloride. Thus, under the above conditions desolvation of the initial Grignard reagent was incomplete and a pure sample of di-s-butylmagnesium was not obtained.

Method B: From Magnesium Chloride and s-Butyllithium.

Anhydrous magnesium chloride was prepared from (a) disproportion-

ation of s-butylmagnesium chloride in benzene, (b) reaction of iso-propylmagnesium chloride with anhydrous ethereal hydrogen chloride, and (c) reaction of iso-propylmagnesium chloride with benzyl chloride. The latter means of preparation was most often used.

In a typical exchange reaction, a slurry of magnesium chloride in benzene (0.150 moles in 200 ml of benzene) was transferred into a 500 ml round bottom flask fitted with a three-way stopcock suited for additions via syringe under a counterflow of nitrogen. s-Butyllithium (70 ml of a 1.46 molar solution in cyclohexane, 0.10 moles) was added with stirring, while the temperature was maintained at 40°C with an oil bath. After stirring overnight two additional portions of the lithium reagent were added (50 mmoles each) at ~ 6 hour intervals. After again stirring overnight, a sample of the slurry was withdrawn and centrifuged, and an aliquot of the supernatent was taken for lithium analysis. The exchange was considered complete when the lithium analysis was negative. After filtration to remove LiCl, the mixed hydrocarbon was removed at reduced pressure and replaced with freshly distilled benzene prior to use in subsequent reactions.

Preparation of $(C_7H_{15})_2Mg$

Triply sublimed magnesium (10.0 g,~0.4 moles) was placed in a creased three-necked round bottom flask equipped with a high speed stirrer (20,000-30,000 rpm), reflux condenser and two dropping

funnels. n-Heptylbromide (53.7 g, 0.3 moles) which had been freshly

distilled at 62°C and 14 mm was placed in one dropping funnel and 200

ml of hexane in the other. The reaction was initiated by adding 10% of

the halide directly to the magnesium and heating gently. The mixture

began to smoke almost immediately. Enough hexane was added to

allow efficient stirring to take place and the remaining halide and sol-

vent were added slowly. The reaction temperature was maintained at

40°C. After complete addition, the mixture was stirred for several

hours and then filtered to produce a clear solution of di-n-heptylmag-

nesium, free of halogen. The final solution was 0.096 molar in mag-

nesium.

Preparation of $(C_6H_5)_2Mg$

Method A. Phenylmagnesium bromide (1 mole in 500 ml of

diethyl ether) was prepared in the usual manner using triply sublimed

magnesium. p-Dioxane (92 g, 1.05 moles) was diluted with 200 ml of

ether and added dropwise as previously described. The resulting mix-

ture was filtered in the dry box. Analysis indicated that the filtrate

was 0.79 molar in magnesium and halide free. The yield was approx-

imately 85%.

Method B. Diphenylmagnesium was prepared from diphenyl-

mercury (17.70 g, 0.05 moles) in a manner previously described for

the preparation of dimethylmagnesium from dimethylmercury, except

that the reaction temperature was maintained at 155°C for 40 hours.

Initially, some $HgØ_2$ sublimed to the top of the flask and in the lower

inch of the condenser, but this was easily melted back into the flask

with a stream of hot air against the outside of the apparatus. The

reaction mixture was extracted with freshly distilled diethyl ether.

The yield was approximately 95%.

Attempted Preparation of Et_2Mg from $PbEt_4$

Tetraethyllead was purified prior to use according to the

following scheme. An aliquot of the oily liquid was placed over acti-

vated charcoal for several hours and then isolated by filtration.[*] The

sample was then dried over a molecular seive, degassed under vacuum

and stored under a nitrogen atmosphere shielded from light.

In a typical reaction, triply sublimed magnesium (2.0 g, 80

mmoles) was placed in a 100 ml two-necked Morton flask equipped

with a high speed stirrer (20,000 rpm max) and water cooled con-

denser. Tetraethyllead (3.3 g, 10 mmoles) was introduced along with

anhydrous aluminum chloride (25 mg) and covered with toluene. The

mixture was heated to 80°C with an oil bath and stirred rapidly at this

temperature for 48 hours. Metallic lead was deposited during this

---

[*] Naphthalene is added to commercial samples of TEL as a stabilizer. The scheme for its removal was suggested by the Ethyl Corporation.

period and the magnesium had been sheared repeatedly to a small particle size. No diethylmagnesium was observed visually. The supernatent was not hydrolytically active. The mixture was filtered and the residue extracted with diethyl ether. The ether washings were not hydrolytically active and a test for magnesium was negative. The magnesium metal was quite reactive and on addition of water, hydrogen was evolved.

Several experiments were carried out under a variety of conditions. The results are given in Table 1. In no case was diethylmagnesium produced, even in poor yield.

Attempted Preparation of Me_2Mg from $PbMe_4$

Tetramethyllead (9.8 g, 25.0 mmoles) and triply sublimed magnesium (2.4 g, 100 mmoles) were combined in a 100 ml round bottom flask with a catalytic amount of dimethylmercury. The mixture was covered with toluene, heated to 65°C under a water cooled condenser for six hours and then handled in the same manner as described in the previous experiment. No reaction took place under the above conditions.

Table 1

Experimental Conditions for the Attempted Synthesis of Diethylmagnesium

Experiment	TEL (mmoles)	Mg (mmoles)	Catalyst	Solvent	Temperature and Time
1	10	40	--	--	55^O - 3 days 80^O - 1 day
2^a	10	40	Hg	--	55^O - 1.5 days 80^O - 1 day
3^b	10	40	$Hg-Me_2Mg-Me_2Hg$	--	55^O - 3 days
4	10	40	$BiCl_3$	--	80^O - 2 days
5	25	100	--	$15ml Et_2O$	50^O - 2 days
6^c	5	20	--	$20\ \emptyset CH_3$	reflux - 2 days
7	10	80	$BF_3 \cdot Et_2O$	$20\ \emptyset CH_3$	30^O - 2 days 80^O - 1 day
8	10	80	$AlCl_3$	$20\ \emptyset CH_3$	80° - 2 days

a. In a similar experiment refluxing ether was used as a solvent.

b. Catalyst obtained from $HgMe_2$ + Mg reaction.

c. Mercuric chloride added after 20 hours.

Preparation of Hydrides

Preparation of Lithium Hydride[*]

t-Butyllithium (150 ml of a 1.25 molar solution in pentane, 0.187 moles) was transferred via syringe to an autoclave under a nitrogen atmosphere. The vessel was installed in the system and the sample subjected to a hydrogen pressure of 3000 psi at 25°C for 16 hours. After decreasing the pressure to one atmosphere, the resulting slurry of lithium hydride in pentane was transferred via syringe to a round bottom flask. A 1 ml sample of the slurry was withdrawn for analysis on the vacuum line and after hydrolysis the residue was analyzed by flame photometry for lithium. The lithium:hydrogen ratio was found to be exactly 1.00:1.00. The lithium hydride obtained in this reaction was snow-white.

Preparation of Sodium Hydride

Sodium hydride was prepared in toluene at 400°F under a hydrogen pressure of 1900 psi, in a manner similar to that described for KH. The autoclave reaction vessel was cooled after 20 hours and

---

[*]While several methods of preparation for lithium hydride were attempted, such as (a) pyrolysis of n-butyllithium in hexane, (b) vacuum pyrolysis of n-butyllithium in mineral oil, and (c) hydrogenolysis of t-butyllithium in pentane, only the latter gave good results.

the gray white product transferred to a round bottom blask in the dry box. The product contained traces of unreacted sodium.

Preparation of Potassium Hydride

Potassium metal (approximately 13 g, approximately 0.3 moles) was cut under mineral oil, washed with toluene and added to freshly distilled toluene (150 ml) in the autoclave reaction vessel.[*] The vessel was pressurized to 1400 psi at a temperature of 300°F. The reaction proceeded readily as was indicated by a decrease in the hydrogen pressure. Once during the reaction the system had to be repressurized. After 1.5 hours the temperature was lowered to 25°C and the product was then transferred from the autoclave reaction vessel to a round bottom flask in the dry box. When a small sample of the solid was squeezed between two glass plates, traces of unreacted metal were observed.

---

[*]The quality of potassium hydride prepared in the autoclave is somewhat dependent on the reaction conditions. If mineral oil was used, incomplete hydrogenation was observed. When toluene was used, with a reaction time of 1.5 hours, a slight green coloration was observed in the product. This could be removed by washing with dyglyme. If the temperature was maintained at 300°F for 24 hours, the amount of green material increased drastically, suggesting some interaction of the potassium metal or potassium hydride with the solvent. The highest purity potassium hydride, a gray white solid, was prepared when benzene was used as the diluent under the reaction conditions described above. Evidently an aromatic hydrocarbon is a much better diluent than mineral oil, probably because it may help solubilize the metal via interaction with the π electron cloud.

Preparation of Alkali Metal Alkyl Complexes of Magnesium Alkyls

$CH_3Li + (CH_3)_2Mg$ in Diethyl Ether

Dimethylmagnesium (23.4 ml of a 0.66 molar solution, 15.3 mmoles) and methyllithium (20.0 ml of a 1.53 molar solution, 30.6 mmoles) were combined in a 200 ml round bottom flask. The mixture was stirred for one hour at 25°C, and an aliquot was removed for spectral analysis. The IR spectrum indicated that complex formation had occurred.

In an attempt to obtain solids by fractional crystallization, an aliquot was placed in a flask and solvent removed at reduced pressure. No precipitate was observed until approximately 95% of the ether had been removed; however, the solution had become increasingly viscous. At this stage the mixture could not be filtered, and the resulting solid was dried in vacuo for several hours. An IR spectrum of the solid, obtained as a Nujol mull, indicated that no complexed ether remained in the sample. The X-ray powder diffraction pattern was recorded.

An attempt to obtain solids by fractional crystallization of the 1:1 mixture of dimethylmagnesium and methyllithium was also unrewarding. This mixture was treated as above and the solid isolated and dried in vacuo.

Two other solutions were prepared in a similar manner, in which the Li:Mg ratio was 1.3:1.0 and 3.0:1.0 respectively. The

solvent was removed from each solution at 25°C under reduced pressure, and the resulting white solids were dried in vacuo for several hours. The X-ray powder patterns were recorded and are presented in Table 7.

CH$_3$Li + (CH$_3$)$_2$Mg in Diethyl Ether - Infrared Study

A systematic study was undertaken in an attempt to define the nature of the species present in solution when methyllithium and dimethylmagnesium are mixed at various stoichiometries.

An apparatus was assembled consisting of a 250 ml round bottom flask equipped with a teflon coated magnetic stirring bar and a three-way stopcock for the addition or withdrawal of samples via syringe. Initially methyllithium (5 ml of a 1.49 molar solution, 7.48 mmoles) was added to dimethylmagnesium (75.0 ml of a 0.435 molar solution, 32.6 mmoles) and after stirring for 20 minutes, a 1 ml aliquot was withdrawn and used to obtain an IR spectrum of the solution. Successive additions of methyllithium gradually increased the Li:Mg ratio in solution, and the IR spectra were obtained at each stage of the addition. Continuous corrections were made to allow for the nonequivalent loss of both reagents during the sampling. The analysis of the solution at each stage is given in Table 2. A discussion of the spectra is given in Chapter III.

Table 2

Preparation of CH_3Li-$(CH_3)_2Mg$ Mixtures for Infrared Analysis

Addition	Mg Conc.	Li Conc.	Li/Mg	IR#
1	0.435 meq/l			A
2	0.409	0.094 meq/l	0.23	B
3	0.384	0.177	0.46	C
4	0.361	0.253	0.70	D
5	0.325	0.378	1.17	E
6	0.294	0.483	1.64	F
7	0.268	0.573	2.12	G
8	0.247	0.648	2.62	H
9	0.228	0.710	3.10	I
10	0.212	0.765	3.62	J
11	0.198	0.818	4.14	K
12	0.137	1.097	7.87	L

n-C_4H_9Li + $(n$-$C_4H_9)_2Mg$ in Hexane

n-Butyllithium (22.25 ml of a 1.5 molar solution, 33.5 mmoles) was added to di-n-butylmagnesium (4.629 g, 33.5 mmoles) in a 250 ml round bottom flask along with 70 ml of freshly distilled hexane. After stirring for 12 hours, the solid di-n-butylmagnesium had completely

dissolved. Simultaneously, in a second reaction vessel a 2:1 mixture was prepared by adding n-butyllithium (68 mmoles) to di-n-butylmagnesium (34 mmoles). Again, the solid di-n-butylmagnesium dissolved rapidly when stirred. The IR spectra of both clear, straw-colored liquids were recorded; both were quite similar to the spectra of n-butyllithium itself, exhibiting only one broad band at 550 cm^{-1}. Therefore, little information regarding the nature of these complexes could be obtained.

Attempts were made to obtain solids by fractional crystallization of both reaction mixtures but in each case the solution became increasingly viscous as the solvent was removed under reduced pressure. An amorphous solid was finally produced after extended drying periods in vacuo. No further work was performed on this system.

$s-C_4H_9Li + (s-C_4H_9)_2Mg$ in Cyclohexane-Benzene

Di-s-butylmagnesium (100 ml of a 0.67 molar solution in benzene, 67 mmoles) and s-butyllithium (45 ml of a 1.49 molar solution in cyclohexane, 67 mmoles) were combined in a 250 ml round bottom flask and stirred at 25°C. The nmr spectrum of the mixture confirmed complex formation.

The solvent was removed from a portion of this solution, at reduced pressure. The resulting straw-colored liquid was stirred gently under vacuum for several hours at room temperature. Nitrogen

was bled back into the system and freshly distilled benzene was added.
The molecular weight of the organometallic species in solution was
determined cryoscopically. The results are given in Table 8.

The remainder of the solution was used in the preparation of
$LiMgH_3$.

s-C_4H_9Li + (s-$C_4H_9)_2Mg$ in Cyclohexane - Infrared Study

An experiment, similar to the one described above for the
methyllithium-dimethylmagnesium system, was undertaken in an
attempt to define the nature of the species in solution when s-butyl-
lithium (1.46 molar) and di-s-butylmagnesium are combined in cyclo-
hexane. The analysis of the solution at each stage is given in Table 3.

Table 3

Preparation of s-C_4H_9Li-(s-$C_4H_9)_2Mg$ Mixtures for Infrared Analysis

Addition	Mg Conc.	Li Conc.	Li/Mg	IR#
1	0.559 meq/l	--	--	A
2	0.469	0.234 meq/l	0.5	B
3	0.406	0.400	0.99	C
4	0.359	0.527	1.47	D
5	0.320	0.630	1.97	E
6	0.287	0.715	2.48	F
7	0.262	0.785	3.00	G
8	0.239	0.843	3.52	H

Preparation of LiMgØ₃ in Diethyl Ether

Phenyllithium was prepared according to a modification of the procedure of Schlosser and Ladenburger (30). Iodobenzene (25.0 g, 0.15 moles) was diluted with 80 ml of benzene in a 300 ml Schlenk tube equipped with a teflon coated magnetic stirring bar and a dropping funnel containing n-butyllithium (65 ml of a 1.6 molar solution in hexane, 0.10 moles). The butyllithium was added dropwise over a one hour period, during which time a precipitate of phenyllithium was formed continuously. The solid product was isolated on a fritted glass filter, washed with benzene, dissolved in a minimum amount of diethyl ether and collected into a round bottom flask. The phenyllithium was recrystallized once by cooling to -78°C, withdrawing the supernatent liquid via syringe, and redissolving the residue in fresh ether. The final solution was shown by analysis to be 1.02 molar in lithium. The double titration method (31) indicated that the sample contained 96% carbon bound lithium and 4% lithium alkoxide.

Diphenylmagnesium (30 ml of a 0.332 molar solution, 10 mmoles) was added to phenyllithium (9.80 ml of a 1.02 molar solution, 10 mmoles) in a 200 ml Schlenk tube. The mixture was stirred for 0.5 hours at room temperature. The solvent was removed under reduced pressure and the resulting solid dried under vacuum of 1.0 mm at 25°C for 2 hours. The temperature was then raised to 80°C for an

additional 2 hours. p-Xylene (50 ml) was added and after stirring for 2 hours at 90°C the hot sample was filtered. The residue was collected in a round bottom flask and dried in vacuo. The filtrate was allowed to cool and remained at room temperature for several hours. No crystallization was observed, so the filtrate was placed in the refrigerator at -20°C for 48 hours. A crystalline solid was then isolated from the mother liquor. A sample which had been withdrawn for analysis revealed that the filtrate was 0.10 molar in both lithium and magnesium immediately after filtration. The recrystallized $LiMg\emptyset_3$ gave the following analysis. <u>Anal</u>: Calcd for $LiMg\emptyset_3$: Li, 2.67%; Mg, 9.26%; $\emptyset$, 88.07%. Found: Li, 2.20%; Mg, 7.81%; $\emptyset$ (by difference), 89.99%. The X-ray diffraction pattern of the insoluble portion of the solid was identical to that of the recrystallized solid materials later obtained from the refrigerated sample, and noticeably different from a powder pattern obtained for phenyllithium. In addition, the $LiMg\emptyset_3$ was much less sensitive to photo decomposition than phenyllithium itself.

<u>Preparation of Alkali Metal Hydride Complexes of Magnesium Alkyls</u>

Attempted Preparation of $LiH\cdot(CH_3)_2Mg$ in Diethyl Ether

Dimethylmagnesium (51.12 ml of a 0.66 molar solution, 33.6 mmoles) was added to lithium hydride (0.267 g, 33.6 mmoles) in a 200 ml round bottom flask and the mixture was stirred for 24 hours. Analysis of an aliquot of the supernatent indicated that no reaction had

taken place during this period. The mixture was then refluxed for an
additional 40 hours and after cooling taken into the dry box and filtered.
Analysis of the filtrate revealed that all of the magnesium was still in
solution, and that no lithium was present. The IR spectrum of the fil-
trate was identical to that of the dimethylmagnesium in ether. The
residue was shown by analysis to be lithium hydride. Anal. Calcd for
LiH: Li, 87.4%; H, 12.6%. Found: Li, 87.0%; H, 12.6%. No re-
action occurred under the above conditions.

Attempted Preparation of LiH·$(CH_3)_2$Mg in Tetrahydrofuran

Dimethylmagnesium (20.0 ml of a 0.93 molar solution, 18.6
mmoles) was added to lithium hydride (0.6629 g, 83.5 mmoles) in a
100 ml round bottom flask. The mixture was stirred at reflux for 36
hours, allowed to cool to room temperature and filtered in the dry box.
The filtrate was found to contain 18 mmoles of magnesium and 1.2
mmoles of lithium (Li:Mg ratio, 1:15). Analysis revealed that the
residue was mainly lithium hydride. Anal. Calcd for LiH: Li, 87.4%;
H, 12.6%. Found: Li, 81.2%. A trace of magnesium was found in
the residue.

In a similar experiment a mixture of dimethylmagnesium and
lithium hydride was stirred at 25°C for 7 days and then filtered. The
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

the sample had decreased by 20%. Apparently, ether cleavage had

resulted, a possibility suggested earlier by Coates (18).

Attempted Preparation of LiH·$\emptyset_2$Mg in Tetrahydrofuran

Diphenylmagnesium (35.0 ml of a 0.915 molar solution, 32

mmoles) was added to lithium hydride (0.646 g, 81 mmoles) in a 200

ml round bottom flask along with an additional 35 ml of THF. The

sample was refluxed for several days, allowed to cool, and filtered

in the dry box. Analysis of the filtrate revealed a Li:Mg ratio of 0.61:

1.00, with 80% of the magnesium recovered in the filtrate. No hydro-

gen was evolved on hydrolysis of the filtrate, again indicating that

ether cleavage had occurred.

Attempted Preparation of NaH·$\emptyset_2$Mg in Diethyl Ether

Diphenylmagnesium (71 ml of a 0.52 molar solution, 36.8

mmoles) was stirred with sodium hydride (0.883 g, 36.8 mmoles) for

5 days at 25°C. The reaction mixture was then filtered in the dry box.

Analysis of the filtrate revealed a Li:Mg ratio of 0.38:1.00 with 83%

of the magnesium recovered in the filtrate. No hydrogen was evolved

on hydrolysis of the filtrate, again indicative of ether cleavage by the

complexed hydride species.

Preparation of KH·$\emptyset_2$Mg Complexes in Diethyl Ether

Potassium hydride and diphenylmagnesium 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 diphenylmagnesium (50 ml of a 0.8 molar

solution in diethyl ether, 40 mmoles) was added to potassium hydride

(3.20 g, 80 mmoles) in a 200 ml round bottom flask, along with an

additional 50 ml of diethyl ether. The mixture was stirred for 3 days

and filtered in the dry box. Analysis of the filtrate revealed that all

of the magnesium containing species had precipitated.*

In one similar reaction where the initial K:Mg ratio was ·1:3,

only 66% of the magnesium containing species precipitated, leaving

the remainder of the diphenyl magnesium in solution. In this case a

1:2 complex $KH \cdot 2\emptyset_2 Mg$ was formed. The solid residues were ana-

lyzed and gave the following results. (Benzene was determined by

difference). <u>Anal.</u> Calcd for $KH \cdot 2\emptyset_2 Mg$: K, 9.85%; Mg, 12.25%;

$\emptyset$, 77.65%; H, 0.25. Found:** K, 10.52%; Mg, 11.0%; $\emptyset$, 78.3%;

H, 0.25%. Found:*** K, 9.90%; Mg, 11.3%; $\emptyset$, 78.54%; H, 0.25%.

---

*The observation applies to all experiments for which K:Mg
ratio is 0.5:1 or greater.

**This sample was prepared by stirring 3 equivalents of di-
phenylmagnesium with one equivalent of potassium hydride.

***This sample was prepared by stirring 2 equivalents of di-
phenylmagnesium with one equivalent of potassium hydride. 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.

Calcd for KH·ϕ_2Mg: K, 17.94%; Mg, 11.10%; ϕ, 70.50%; H, 0.46%.

Found: K, 16.35%; Mg, 10.20%; ϕ, 73.09%; H, 0.36%. Calcd for

2KH·ϕ_2Mg: K, 30.40%; Mg, 9.40%; ϕ, 59.40%; H, 0.80%. Found:

K, 29.20%; Mg, 9.40%; ϕ, 60.60%; H, 0.72%. Calcd for 5KH·ϕ_2Mg:

K, 51.60%; Mg, 6.42%; ϕ, 40.76%; H, 1.32%. Found: K, 54.70%;

Mg, 6.56%; ϕ, 38.49%; H, 1.25%.

The X-ray powder pattern for each of these solids is reported

in Table 10.

Attempted Preparation of NaH·$(n-C_7H_{15})_2$Mg in Hexane

Di-n-heptylmagnesium (77.8 ml of a 0.093 molar solution,

7.2 mmoles) and sodium hydride (0.173 g, 7.2 mmoles) were mixed

in a 100 ml round bottom flask and placed under a water cooled con-

denser. The mixture was stirred for 18 hours at the temperature of

refluxing solvent, cooled and taken into the dry box. Filtration pro-

duced a clear colorless solution and a gray solid. Analysis revealed

that the filtrate contained 7.0 mmoles (95%) of the magnesium species

and no sodium. The residue was shown by analysis to be sodium hy-

dride. Anal. Calcd for NaH: Na, 95.8%; H, 4.2%. Found: Na,

94.5%; H, 3.9%. No reaction took place under the above conditions.[*]

---

[*]Under similar conditions potassium hydride also failed to
react with $(n-C_7H_5)_2$Mg after 72 hours at reflux in hexane solvent.

Attempted Preparation of LiH·s-Bu$_2$Mg in Benzene

A mixture of di-s-butylmagnesium (30.0 ml of a 0.58 molar solution, 17.4 mmoles) and lithium hydride (5 ml of a pentane slurry, 9.5 mmoles) was stirred at room temperature in a 100 ml round bottom flask equipped with a teflon coated stirring bar and a three-way stopcock for additions via syringe.[*] After 3 days, stirring was ceased and since the solid did not settle very rapidly, an aliquot of the mixture was centrifuged. Analysis of a portion of the supernatent liquid indicated that no reaction had occurred. All of the magnesium was still in solution and no lithium hydride had dissolved. The reaction mixture was then heated to 40°C for an additional 2 days, cooled and treated as before. Analysis again revealed that no reaction had taken place. In addition, the nmr spectrum did not show any perturbation of the signal at 9.8τ attributed to the αH of the butyl group. This signal is invariably shifted upfield when complexation occurs.

Preparation of Sodium bis-Di-s-butylmagnesium Hydride in Benzene

Di-s-butylmagnesium (101 ml of a 0.496 molar solution, in benzene, 50 mmoles) was added to sodium hydride (0.6559 g, 27.4 mmoles) in a 200 ml round bottom flask, equipped with a three-way

---

[*]The lithium hydride used in this reaction was extremely reactive and ignited readily when exposed to the atmosphere. Two commercial samples of lithium hydride also did not react with di-s-butylmagnesium in benzene.

stopcock for addition via syringe and a teflon coated stirring bar.
The mixture was stirred for two days under nitrogen, filtered, and
an aliquot taken for analysis. <u>Anal</u>: Calcd for $NaH \cdot 2s\text{-}Bu_2Mg$:
Na:Mg:Bu:H = 1.0:2.0:4.0:1.0. Found: 0.90:2.0:3.96:0.65. The
nmr spectrum and the IR spectrum of the solution were significantly
different from those of di-s-butylmagnesium and were indicative of
complex formation.

In a similar experiment, an equivalent amount of sodium
hydride and di-s-butylmagnesium were combined under the above con-
ditions. Once the ratio of Na:Mg in solution reached 0.45:1.0 no
further uptake of sodium was observed even after several days. Thus,
this complex represents the limiting stoichiometry for this system.

<u>Preparation of Potassium Di-s-Butylhydridomagnesium in Benzene</u>

Potassium hydride (1.138 g, 28.4 mmoles) was placed in a
200 ml round bottom flask equipped with a three-way stopcock for
additions via syringe against a counterflow of nitrogen and a teflon
coated magnetic stirring bar. The hydride was slurried with 50 ml
of freshly distilled benzene. Di-s-butylmagnesium (95 ml of a 0.30
molar solution, 28.4 mmoles) was added via syringe with rapid
stirring. After twenty hours the mixture was filtered to give a straw-
colored filtrate and a darker residue (∼100 mg). An aliquot of the
solution was taken for analysis and gave the following results. <u>Anal</u>:

Calcd for KH·s-Bu$_2$Mg: K:Mg:Bu:H = 1.00:1.00:2.00:1.00. Found: K:Mg:Bu:H = 1.0:1.0:1.9:0.95. The yield was>90%.

The nmr spectrum was markedly different from that of di-s-butylmagnesium in benzene. Also, the IR spectrum of the filtrate was indicative of complex formation. Cryoscopic molecular weight measurements indicated a monomer-dimer equilibrium over a concentration range 0.06 - 0.16 molal.

Successful synthesis was carried out also in benzene-cyclohexane mixtures. The KH·s-Bu$_2$Mg complex was insoluble in pure alkanes, however, and attempted synthesis in cyclohexane itself proved unsatisfactory.

Preparation of Potassium Di-n-butylhydridomagnesium

Potassium hydride (2.51 g, 62.6 mmoles) and di-n-butylmagnesium (8.64 g, 62.5 mmoles) were combined in a 500 ml round bottom flask and covered with 300 ml of freshly distilled cyclohexane. After stirring for 44 hours at room temperature, the resulting gray-white slurry was allowed to settle. An aliquot of the supernatent liquid was taken for analysis. The solution was found to be 0.027 molar in magnesium and 0.0134 molar in potassium, K:Mg = 0.5:1.0. The slurry was filtered in the dry box to remove the solvent, and the residue was put into another 500 ml flask and covered with 300 ml of benzene.

The benzene slurry was stirred at 80°C for 3 days, allowed
to cool, and filtered in the dry box. The filtrate was shown by anal-
ysis to be 0.11 molar in both potassium and magnesium. Enough of
the solvent was removed from a portion of the filtrate at reduced pres-
sure to give a solution 0.68 molar in complex. Analysis of an aliquot
of this solution revealed a K:Mg:H ratio of 0.98:1.0:0.85. When com-
plete solvent removal was effected a white solid resulted. This solid
(which was not analyzed),when heated in a melting point capillary,
began to decompose at 115°C. Di-n-butylmagnesium itself is stable
at 115°C (7).

An X-ray powder diffraction pattern showed only very faint
lines attributable to potassium hydride. This indicated that the com-
plex itself is amorphous.

The remainder of the filtrate was concentrated by solvent re-
moval at reduced pressure until the solution was 0.378 molar in com-
plex. Both the nmr spectrum and the IR spectrum of this solution were
consistent with complex formation.

The X-ray diffraction pattern of the residue obtained from
filtration of the benzene solution was also quite interesting. The
strong lines attributable to KH at 3.24 Å, 2.00 Å and 1.71 Å were
clearly absent, while broad lines at 2.83 Å, 2.07 Å and 1.65 Å which
can be attributed to $KMgH_3$ were present. Thus, some pyrolysis of

the n-butyl groups in the complex had occurred while the mixture was stirring at 80°C in benzene.

In a similar experiment, 28.8 mmoles of potassium hydride and 31.0 mmoles of di-n-butylmagnesium were combined in a 250 ml round bottom flask and covered with 190 ml of freshly distilled benzene. The mixture was stirred for 48 hours at 40°C, cooled and filtered in the dry box. Analysis of an aliquot of the filtrate revealed a K:Mg ratio of 0.97:1.0. The filtrate was 0.11 molar in complex, and a 70% yield was obtained. Thus, this complex forms under relatively mild conditions, making unnecessary the use of refluxing benzene in order to obtain reaction.

Cryoscopic molecular weight measurements indicated a dimeric species in benzene over a concentration range 0.08 - 0.32 molal. The data are shown in Figure 11.

Attempted Preparation of Potassium Di-s-butyldihydridomagnesium

Potassium hydride (1.193 g, 29.8 mmoles) was placed in a 250 ml round bottom flask and slurried with 50 ml of benzene in the manner described for the preparation of $KMg(s-Bu)_2H$. To this was added potassium di-s-butylhydridomagnesium (99.5 ml of a 0.306 molar solution, 30.4 mmoles). The mixture was stirred for 18 hours and then filtered in the dry box. 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 $K_2Mg(s-Bu)_2H_2$: K, 36.75%; Mg, 11.10%; Bu, 52.20%;

H, 0.95%. K:Mg:Bu:H = 2.0:1.0:2.0:2.0. 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 was consistent with the analyt-

ical data. The strong C-Mg stretching band at 521 cm^{-1}, attributable

to butyl-magnesium stretching, was severely diminished in the sup-

posed 2:1 complex. In addition, when the solid was dumped onto a dry

ice-ether slurry under nitrogen, and the resulting mixture acidified,

appreciable quantities of benzoic acid were produced along with 2-

methyl-butyric acid. Thus, metallation of the benzene solvent had

occurred to a significant extent, ~56% butyl-phenyl exchange. Similar

results were obtained when two equivalents of KH were stirred with

one equivalent of $(s-C_4H_9)_2Mg$, under similar reaction conditions.

Preparation of Complex Metal Hydrides

Preparation of $LiMgH_3$

Lithium tri-s-butylmagnesium was prepared in a benzene-

cyclohexane mixture in a manner described elsewhere in this thesis.

The solution was 0.46 molar in complex and analysis indicated a Li:

Mg ratio of 1.0:0.96. An aliquot of the solution was hydrogenated at

a pressure of 4000 psig at 25°C for 4 hours. A gray solid was isolated

from the reaction mixture as well as a clear colorless filtrate. Analysis revealed that quantitative precipitation had occurred. The solid had a Li:Mg:H ratio of 0.95:1.0:2.80.

The X-ray diffraction pattern of this solid showed lines attributable to LiH and MgH_2 as well as one unknown line, all of which were broad and diffuse indicating small particle size. Thermal analysis of the hydrogenation product revealed a strong endotherm at 310°C accompanied by the loss of hydrogen (90% of calculated). A weak endotherm occurred at 480°C accompanied by loss of hydrogen (10% of calculated). The 480°C endotherm is assigned to the decomposition of LiH by comparison to the thermogram of an authentic sample of LiH. The endotherm at 310°C may then be attributed to simultaneous decomposition of MgH_2 and some $LiMgH_3$. This interpretation would indicate a mixture of 33% LiH and MgH_2 and 67% $LiMgH_3$.

Preparation of $NaMg_2H_5$ and $NaMgH_3$

Sodium bis di-s-butylmagnesium hydride was prepared in benzene to give a solution 0.3 molar in complex. Analysis indicated a Na:Mg:Bu:H ratio of 0.92:2.0:3.92:0.65. Hydrogenolysis of a portion of this solution (90 ml) under 1500 psig hydrogen pressure at 25°C for 4 hours resulted in a light yellow solid which reacted violently when exposed to the atmosphere. Analysis revealed a Na:Mg:H ratio of 0.90:2.00:4.00. No butane was produced on hydrolysis, and the

low hydrogen analysis is unexplained. The X-ray diffraction pattern revealed only two very broad lines centered at d spacings of 2.7 $\overset{O}{A}$ and 4.9 $\overset{O}{A}$. The IR spectrum gave continuous broad absorption throughout the Mg-H stretching and deformation region. DTA-TGA analysis revealed an exotherm at 115°C and three endotherms at ~300°C, 320°C and 340°C. The exotherm at 115°C is attributed to the dissociation of $NaMg_2H_5$ to $NaMgH_3$ and MgH_2. The endotherms are harder to assign, but must in part be due to the dissociation of $NaMgH_3$ to NaH and MgH_2 and the decomposition of these species. When a sample was heated to 150°C and allowed to cool, the powder pattern clearly showed lines attributable to MgH_2 and $NaMgH_3$, the latter being quite similar to $NaMgF_3$ (31).

A mixture of $NaMgH_3$ and MgH_2 was also prepared by pyrolysis of the complex $NaH \cdot 2s\text{-}Bu_2Mg$ in mineral oil at 105°C under vacuum for 2 hours. The powder pattern was identical to that of the hydrogenolysis sample which had been heated to 150°C. Analysis indicated a Na:Mg:H ratio of 0.88:1.0:4.52. Again, no butane was evolved on hydrolysis.

Preparation of $KMgH_3$
_____

Potassium di-s-butylhydridomagnesium was prepared in benzene to give a solution 0.5 molar in complex, (K:Mg:Butyl:H = 1.0: 1.0:1.9:0.95). Hydrogenolysis of a portion of this solution (100 ml)

under 3000 psig hydrogen pressure at 25°C for 4 hours resulted in quantitative precipitation of a yellow solid which reacted violently when exposed to the atmosphere. Analysis gave a K:Mg:H ratio of 1.0:1.0: 3.0. Anal: Calcd for $KMgH_3$: K, 58.7%; Mg, 36.8%; H, 4.52%. Found: K, 58.9%; Mg, 36.2%; H, 4.56%. No butane was produced on hydrolysis indicating complete reduction and formation of a $KH:MgH_2$ species. X-ray powder analysis revealed a unique diffraction pattern in which the strongest line for KH (at 3.30 Å) and strongest lines for MgH_2 (at 3.19, 2.495, 1.67 and 1.59 Å) are clearly absent. The IR spectrum of $KMgH_3$ in Nujol exhibited two broad absorptions centered at 1150 and 680 cm^{-1}, a slight shift from the absorptions of MgH_2 at 1160 and 650 cm^{-1}. In addition, DTA-TGA analysis revealed a weak broad exotherm at ∿300°C which may indicate disproportionation to KH and MgH_2 followed by endothermic effects at 320°C and 420°C due to decomposition of KH and MgH_2 respectively.

$KMgH_3$ was also prepared by the pyrolysis of $KMg(s-Bu)_2H$ in mineral oil at 80°C under vacuum. The powder diffraction pattern was identical to that of the sample prepared via hydrogenation. The individual lines were sharper, however, indicative of larger particle size in the product.

Attempted Preparation of Di-potassium Tetrahydridomagnesium

The solid residue from the reaction of two molar equivalents of potassium hydride with one equivalent of di-s-butylmagnesium was

ground to a powder and transferred to an autoclave along with 150 ml of dry benzene. The autoclave was placed under a hydrogen pressure of 4000 psig at 25°C and after 10 minutes the pressure had dropped to 600 psig. The pressure was again set at 4000 psig. After a period of 4 hours the resulting yellow green solid was isolated via filtration of the reaction mixture.

The infrared spectrum of this solid, obtained in Nujol, indicated that complete reduction had occurred. A powder diffraction pattern revealed only lines due to KH and $KMgH_3$.

CHAPTER III

RESULTS AND DISCUSSION

Before beginning any discussion regarding the synthesis of organometallic compounds some mention should be made as to the nature of these reagents. In the course of this investigation extensive use was made of dialkyl and diaryl magnesium compounds as well as alkali metal alkyls. All of these types of compounds are extremely sensitive to oxygen and moisture, producing either metal alkoxides as is the case with oxygen or metal hydroxides with water.

$$MgR_2 \xrightarrow{\quad O_2 \quad} ROMgR \xrightarrow{\quad H_2O \quad} ROH + RH + Mg(OH)_2 \qquad (11)$$

$$MgR_2 + H_2O \longrightarrow 2RH + Mg(OH)_2 \qquad (12)$$
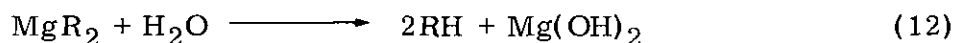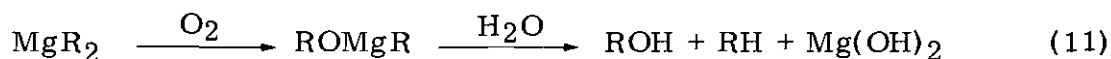
Alkylmagnesium alkoxides are often soluble in solutions of the dialkyl-magnesium reagent and once formed are difficult if not impossible to remove. Organo alkali metal compounds are subject to the same types of reactions shown by magnesium alkyls. Organomercury and organolead compounds, however, are not nearly as sensitive to oxygen and water but are quite toxic. They have appreciable vapor pressure at room temperature and therefore must also be handled with care and in a closed system.

Preparation of Magnesium Alkyls

The dioxane precipitation method (eq. 1) in which dioxane is added to a Grignard reagent in diethyl ether is well documented in the literature and is straightforward (3). Precipitation of the magnesium halide is essentially quantitative when a 5 - 10% excess of dioxane is used. The principle limitation of this method is that some dioxane becomes complexed to the resulting dialkylmagnesium compound and is difficult to remove, even when the solid etherate (dioxanate) is placed under vacuum and heated in order to effect desolvation (7). Furthermore, in the case of branched chain alkyls, elimination to give magnesium hydride will readily occur at temperatures close to those required for desolvation. When the final product, the unsolvated magnesium alkyl, must be put into another solvent for ebullioscopic molecular weight determination, the residual traces of previous solvents then constitute an intolerable impurity which, due to its volatility, would invalidate ebullioscopic association studies. This factor also becomes quite critical if dialkylmagnesium compounds of unusual purity are needed for kinetic studies.

The preparation of dialkylmagnesium compounds recently reported by Eastham and Kamienski (4) involving the use of organo-lithium reagents in an ether/hydrocarbon solution (eq. 2) would be satisfactory for most cases where the alkyl chain is of sufficient

length to insure solubility. The authors reported that the addition of hydrocarbon and removal of ether, both in a continuous manner, to the lithium halide-free dialkylmagnesium resulted in the removal of all but 0.01% of the dimethyl ether. In addition the yields were essentially quantitative.

Thus the removal of solvated ethers from R_2Mg compounds has always been a little tedious. The solution to this problem would be to prepare these reagents in such a manner that no ether was ever present. Existing reports in the literature discuss the preparation of R_2Mg compounds from R_2Hg compounds (eq. 3), usually in ether solvent. Initial reports involved a sealed tube reaction at a temperature of 130°C for the reaction of diethylmercury with magnesium using no solvent (5). Gilman reported that no reaction took place at 130°C unless a trace of mercuric chloride was added. In an attempt to promote reaction at 150°C using no catalyst the sealed tube exploded. Not only are sealed tube reactions inconvenient in most cases, but the product obtained from this procedure usually contains ether insoluble material which probably is RMgH or MgH_2 produced by olefin elimination at such high temperatures.

In this investigation it was found that sealed tubes are not necessary and that successful reaction can be obtained by mixing the reagents in a flask using no catalyst. A mixture of dimethylmercury

and excess magnesium was found to react spontaneously at room temperature after a short induction period (15 minutes). The temperature of the reaction rose to about 60°C in two hours and produced dimethylmagnesium in essentially 100% yield. The product was isolated by extracting the reaction mixture with the solvent of choice, leaving behind the insoluble mercury and excess magnesium metal. Diethylmercury behaved similarly at reaction temperatures of 60 - 90°C. Diphenylmercury and magnesium had to be heated to 150°C; however, diphenylmagnesium was produced in high yield. Traces of unreacted dialkylmercury can be removed under vacuum prior to effecting solution (diphenylmercury can be sublimed from the reaction mixture). This modification produced ultra-pure solutions of magnesium alkyls in high yield under much milder conditions than had been previously reported. Analysis of the solutions for mercury were negative for all of the above preparations.

Since mercury alkyls were found to react so readily with magnesium metal, it was felt that lead alkyls might react just as well. Considering that tetramethyl- and tetraethyllead are available for about $.60/lb compared to $350/lb for the corresponding mercury alkyls, such a preparation would be of obvious merit. The bulk of this experimentation was carried out using tetraethyllead. In some cases neat tetraethyllead was used and in others solvents such as

ether, hexane and toluene were employed. Aluminum chloride, bismuth chloride, triethylbismuth, dimethylmagnesium, diethylmercury and mercury were used as catalysts in a number of reactions. Temperatures ranging from 25 - 100°C were investigated. Purified tetraethyllead decomposed readily in light to give lead deposits and reactions were carried out both in sunlight and in the dark. In some attempts high speed stirring was used to insure fresh surface on the magnesium for reaction sites. In no case did reaction take place to produce the desired dialkylmagnesium product.

The preparation reported by Eastham and Kamienski (6) involving the use of magnesium chloride (eq. 4) was found to be the best method of preparation of unsolvated branched chain dialkylmagnesium compounds, (e.g., di-s-butylmagnesium), that are soluble in hydrocarbon solvents. Since less than 0.5 mole percent ether was present during the exchange, there was no need to later subject the product to higher temperatures at which cracking can occur. The reaction was carried out at 40°C, a temperature at which di-s-butylmagnesium is quite stable. An added advantage of this route over the R_2Hg exchange route is that toxicity problems are avoided.

In the course of this investigation di-s-butylmagnesium was used extensively, and some interesting observations were made concerning the nature of the magnesium chloride used in the exchange.

Kamienski (29) was well aware that the source of $MgCl_2$ was critical and influenced the yield to a great extent. He found that commercially available "anhydrous" magnesium chloride gave poor results and it was necessary to activate the halide prior to use. One method of activation consisted of stirring the $MgCl_2$ with diethyl ether overnight and then removing the ether by codistillation with benzene. When the s-butyllithium was added to the benzene slurry di-s-butylmagnesium was produced in 61% yield. Another method consisted of ball-milling the $MgCl_2$ prior to use, but the yield in the subsequent exchange reaction was only 21%. When the $MgCl_2$ was treated with alcohol, and the alcohol later removed as a toluene azeotrope (97.5% effective) the yield was 76%. When $MgCl_2 \cdot 6H_2O$ was stirred with isoamyl alcohol, first a water-alcohol mixture was removed and then the remaining alcohol was removed as an azeotrope with tetralin. Di-s-butylmagnesium was produced in 77% yield using this source of magnesium chloride.

In contrast, when the magnesium chloride was prepared under inert atmosphere conditions, either as a by-product from the disproportionation of a Grignard reagent or via the reaction of a Grignard reagent with either chlorine or benzyl chloride, the corresponding yields were quite high on the order of 80 - 95%. The explanation given for the widely differing results was that a salt with a particular crystal

structure is the most important factor in reactivity toward the exchange.

In the present study marked differences in the reactivity of various samples of magnesium chloride toward exchange were also noted. It appeared, however, that the observed differences were dependent on the quality of the magnesium used to prepare magnesium chloride rather than attributable to differences in crystal structure of the magnesium chloride itself.

A Grignard reagent was prepared from three different sources of magnesium, Dow triply sublimed and two different lots of Fisher Grignard grade turnings, lots #734625 and 750404. Once the Grignard reagents were in hand, each was used in subsequent reactions with hydrogen chloride and benzyl chloride.

$$i-C_3H_7Cl + Mg \longrightarrow i-C_3H_7MgCl \begin{array}{c} \xrightarrow{\phi CH_2Cl} MgCl_2 \quad (13) \\ \xrightarrow{HCl} MgCl_2 \quad (14) \end{array}$$
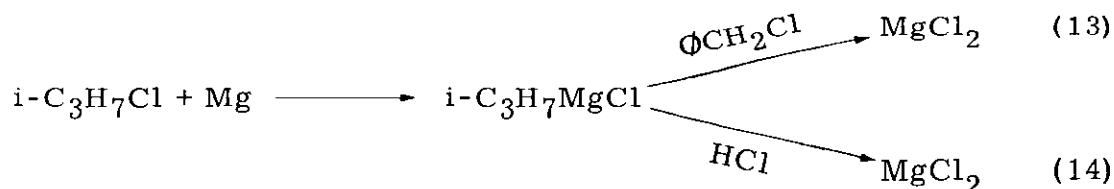
All of the resulting samples of magnesium chloride were handled in the same manner, and desolvated by codistillation with benzene. In the subsequent exchange reaction with s-butyllithium, exchange of 75% of the available halide was attempted by adding aliquots of the lithium reagent to the magnesium chloride-benzene slurry at 40°C.

When Dow triply sublimed magnesium was employed, the exchange reaction was quite slow and did not proceed to completion even when only 33% exchange was attempted. Appreciable quantities of s-butyllithium were found in solution even after the mixture had stirred for 48 hours at 40°C. Complete exchange could be effected only by swamping the reaction mixture with fresh magnesium chloride. When the magnesium chloride was prepared using Grignard grade turnings, lot #750404, the results were quite similar. In contrast, when the initial source of magnesium was lot #734625, the required 75% exchange occurred readily. No lithium was found in solution 6 hours after the last aliquot of s-butyllithium had been added. Identical results were obtained regardless of whether the magnesium chloride was prepared via the hydrogen chloride or benzyl chloride route.

These results suggest that perhaps some transition metal impurity in the magnesium may inhibit or enhance the exchange rate when these two reagents are mixed. In a recent paper, Ashby et al (32) have pointed out significant differences in the amount of benzopinicol formed as a by-product in the reaction of methylmagnesium bromide with benzophenone under pseudo-first-order conditions, when different sources of magnesium were used to make up the Grignard solution. They also attributed these variations to transition metal impurities in the magnesium.

In an attempt to learn the reason for the difference in reactivity of the various types of magnesium chloride, samples of each source of magnesium were examined by emission spectroscopy. The results which are given in Table 4 are more qualitative than quantitative. While relative amounts of each impurity are accurately described in a given column, absolute concentrations are accurate only to 50%. Surprisingly little difference in transition metal impurity between triply sublimed magnesium and Grignard grade turnings was found. However, the conclusion of this study was that some transition metal, not necessarily one reported in the table, must act as a catalyst in the final exchange reaction.

Table 4

Transition Metal Impurities Present in Different Magnesium
Samples as Determined by Emission Spectroscopy[a]

Metal Impurity	Source of Magnesium		
	Dow	Lot #734625	Lot #750404
Cu	20	25	30
Ag	10	6	12
Fe	700	500	1200
Al	60	65	120
Va	180	125	240
Mn	--	65	240
Si	350	310	480

[a]Concentrations are given in ppm.

As a result of this study it is now possible to choose the best method in order to prepare dialkyl and diarylmagnesium compounds in high yield and high purity for use in subsequent investigations.

Preparation of Alkali Metal Alkyl Complexes of Magnesium Alkyls

It is well established that dimethyl and diethylmagnesium are polymeric in the solid state (9, 33) and the structures of both of these compounds have been elucidated by X-ray analysis. In dimethylmagnesium the metal atoms are connected by pairs of methyl bridge bonds with almost tetrahedral arrangement of the methyl groups around each magnesium atom. In general as the length of the carbon chain increases, or as branching occurs these bridge bonds are weakened and the electron deficient polymeric chains are more easily broken. This effect is reflected in the solubilities of several magnesium alkyls in hydrocarbon as shown in Table 5 (7). A major break in the series occurs when R = s-butyl. In this case not only are the alkyl bridge bonds weak, but because of steric interaction there is little tendency to form polymeric chains. This compound does not associate beyond a dimer and is actually a liquid.

A more basic solvent can also attack and disrupt the polymeric chains. Dimethylmagnesium, although insoluble in hydrocarbon is soluble in ether solvents. The composition in solution consists mainly of solvated monomeric species. In like manner, other basic

molecules can attack the polymeric dialkylmagnesium reagent and form stable soluble complexes. Examples of this are noted when alkyllithium reagents are mixed with dialkylmagnesium compounds in hydrocarbon solvent. The principal requirement for solubility is that the carbon chain must be long enough to insure solubility of the resulting complex.

Table 5

Solubility of Magnesium Alkyls in Benzene and Heptane in g/l

	Solvent	
MgR_2	Benzene	Heptane
$Mg(C_2H_5)_2$	1.3	0.1
$Mg(n\text{-}C_3H_7)_2$	1.3	0.35
$Mg(i\text{-}C_3H_7)_2$	2.7	0.37
$Mg(n\text{-}C_4H_9)_2$	3.3	0.42
$Mg(s\text{-}C_4H_9)_2$	Miscible in all proportions (6)	

Until recently, the only complex of this type known containing a magnesium atom was $LiMg\emptyset_3$, which had been prepared in diethyl ether (15). It was observed early in this study that when a hexane solution of n-butyllithium was stirred with di-n-butylmagnesium the insoluble magnesium compound dissolved. Since so little was known about the nature of the complexes formed, a systematic study was

undertaken to learn more about the composition of these solutions.

One of the principal diagnostic tools used in this study was infrared spectroscopy. The region of the spectrum utilized extended from 1500 cm^{-1} to 200 cm^{-1}. Absorption in this region occurs for C-C stretch, C-Metal (M) stretch, C-M-C deformations, and in addition, discrete bands are observed for ether molecules complexed to an organometallic compound. The region of the spectrum found to be most interesting was that portion from 600 cm^{-1} to 300 cm^{-1}. Absorptions due to C-M stretching are found in this region for the di - alkylmagnesium and alkyllithium compounds as well as for complexes.

$CH_3Li + (CH_3)_2Mg$ in Diethyl Ether

Brown and coworkers (16) have studied the reaction of methyllithium with dimethylmagnesium in diethyl ether using low temperature nmr techniques. When the Li:Mg ratio was 2:1, a single resonance was observed at all temperatures for the ^1H and ^7Li spectra. When the ratio was less than 2:1, a signal for free dimethylmagnesium was observed at -60°C and when the ratio was greater than 2:1, a signal for free methyllithium was observed in both the ^1H and ^7Li spectra. When the Li:Mg ratio was greater than 2:1, a 3:1 complex was also observed which was apparently in equilibrium with the 2:1 complex and excess methyllithium at -60°C. The proposed structures

for these complexes are shown in Figure 3 (16b). The coordinated solvent has been omitted for simplicity.

2:1   3:1
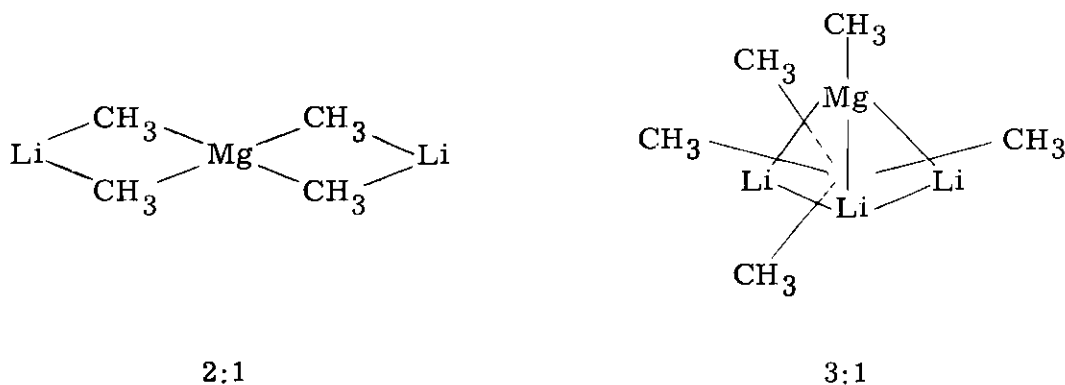
Figure 3. Proposed Structures for 2:1 and 3:1 Complexes Containing Methyllithium and Dimethylmagnesium

Brown dismissed the possibility of a 1:1 complex in ether on the grounds that since dimethylmagnesium compounds showed little tendency to associate in ether solution, replacement of a second lithium atom in the tetrahedral arrangement shown in Figure 3 was unlikely. More recently, Seitz (17) has obtained evidence for a 1:1 complex in tetrahydrofuran at low temperature and attributed its stability to increased solvation by the more basic solvent. It is interesting to note, however, that dialkylmagnesium compounds show less tendency to associate in tetrahydrofuran than in ether (2).

It is more uncertain which species are present in solution at 25°C. Brown (16b) indicated that extrapolation of low temperature data favored the formation of a 3:1 complex as well as dissociation of

the 2:1 complex, at higher temperature. Since an exact description

of the species in solution at room temperature was critical to a later

portion of this work, a study was undertaken in an attempt to describe

this system more fully. Since nmr techniques could not be applied to

this system at higher temperature due to coalescence of the various

signals, the reactions were followed using infrared spectroscopy.

The infrared spectrum of dimethylmagnesium in diethyl ether

contained bands at 520, 590, 780, 830, 897, 999 and 1040 cm^{-1} when

a compensating cell was used to remove solvent bands due to uncom-

plexed diethyl ether. The two bands at 520 and 590 cm^{-1} have both

been attributed to asymmetric C-Mg stretching vibrations (34). The

intensity of the band at 590 cm^{-1} increased as the concentration was

increased, relative to the band at 520 cm^{-1} and was attributed to

associated forms of dimethylmagnesium, while the band at 520 cm^{-1}

was attributed to monomeric solvated species. The bands at 780, 830,

897, 999 and 1040 cm^{-1} have been assigned to ether molecules which

are coordinated to magnesium atoms (35). When no compensating

cell was used in the reference beam, the spectrum of free diethyl

ether was superimposed on the spectrum described above. Since the

ether band at 500 cm^{-1} interfered with the band attributed to the C-Mg

stretching vibration a compensating cell was used in all of this work.

The spectrum of methyllithium showed bands at 485, 787,

832, 910, 1003 and 1050 cm^{-1}. West and Glaze (36) studied the

infrared spectra of alkyllithium compounds in the solid and vapor

phase and observed a band at 514 cm^{-1} which was assigned to the C-Li

stretching vibration in the solid. A band at 565 cm^{-1} in the spectrum

of ethyllithium was assigned also to a C-Li stretching vibration. Due

to its proximity to bands known to represent C-Li stretching vibra-

tions, the band observed at 485 cm^{-1} was tentatively assigned to the

C-Li stretching vibration for methyllithium in ether. The other bands,

due to similarity with the dimethylmagnesium spectrum were attrib-

uted to ether molecules coordinated to a metal atom.

In an attempt to identify the species in solution when methyl-

lithium and dimethylmagnesium were mixed in diethyl ether, a series

of spectra was obtained in a manner described on page 28 of this thesis.

The region of the spectrum examined included that portion between 600

and 400 cm^{-1} since that is the region in which bands due to C-M

stretching vibrations are observed. The spectra obtained are shown

in Figures 4, 5 and 6. The concentrations of reagents are given in

Table 2.

When the Li:Mg ratio was 0.5:1.0 bands due to dimethylmag-

nesium and methyllithium at 590, 520 and 485 cm^{-1} were clearly seen.

When the ratio was 0.7:1.0, associated dimethylmagnesium was still

observed and in addition a new band was seen at 551 cm^{-1}, indicative

of complex formation. When the molar ratio reached 1.2:1.0, a

shoulder at 590 cm^{-1} was still observed as well as the complex band
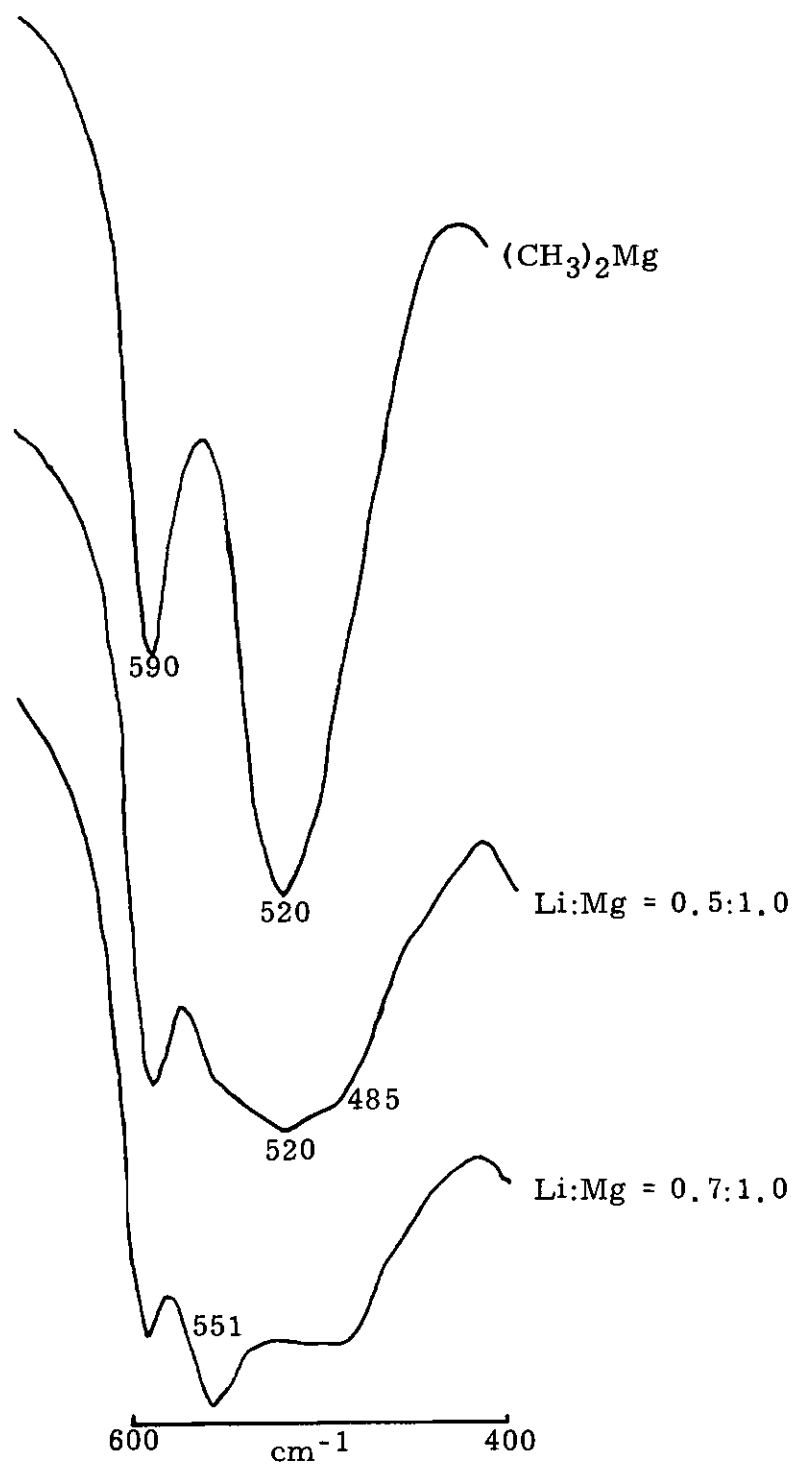
Figure 4. Infrared Spectra of Methyllithium-dimethylmagnesium in
Diethyl Ether.
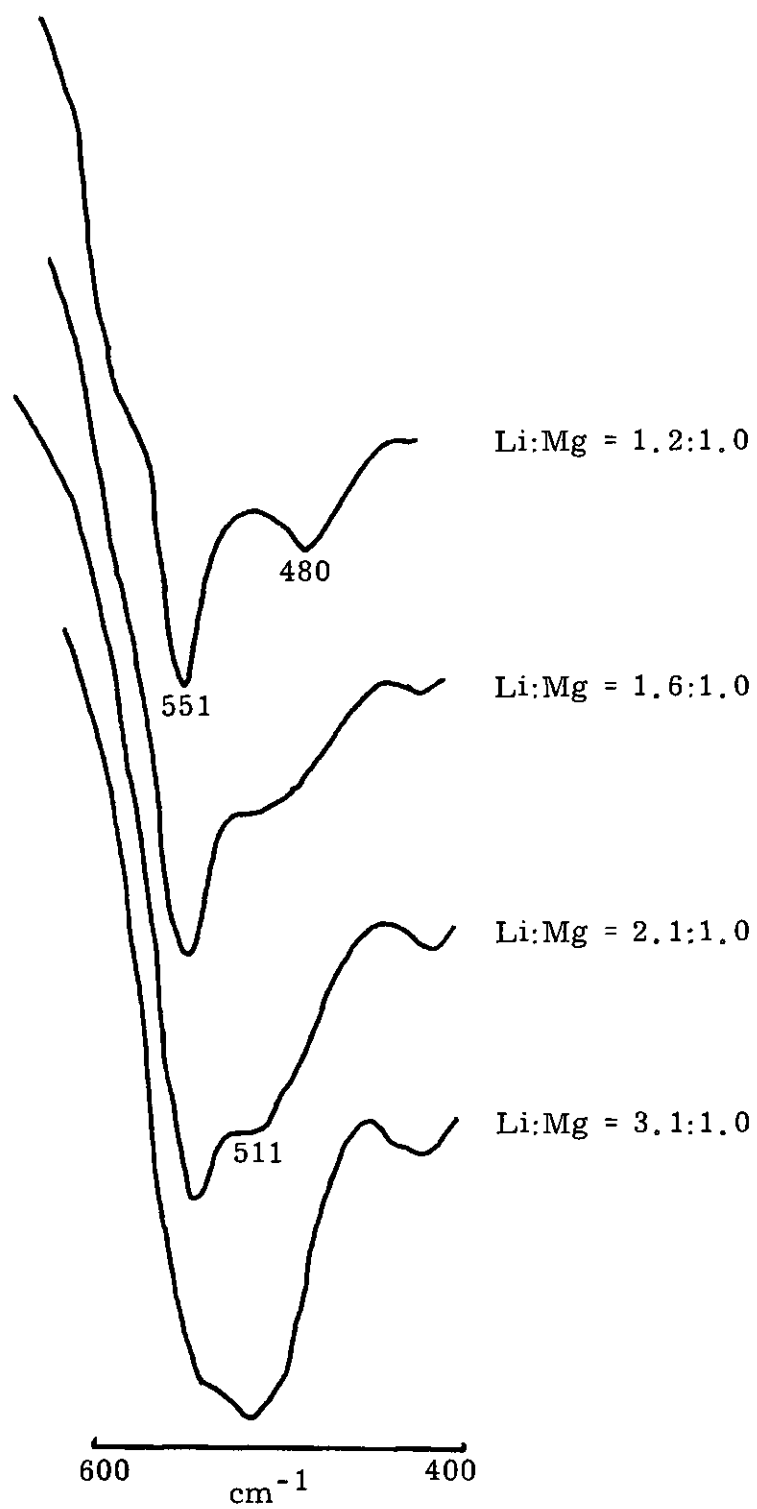
Figure 5. Infrared Spectra of Methyllithium-dimethylmagnesium in Diethyl Ether.
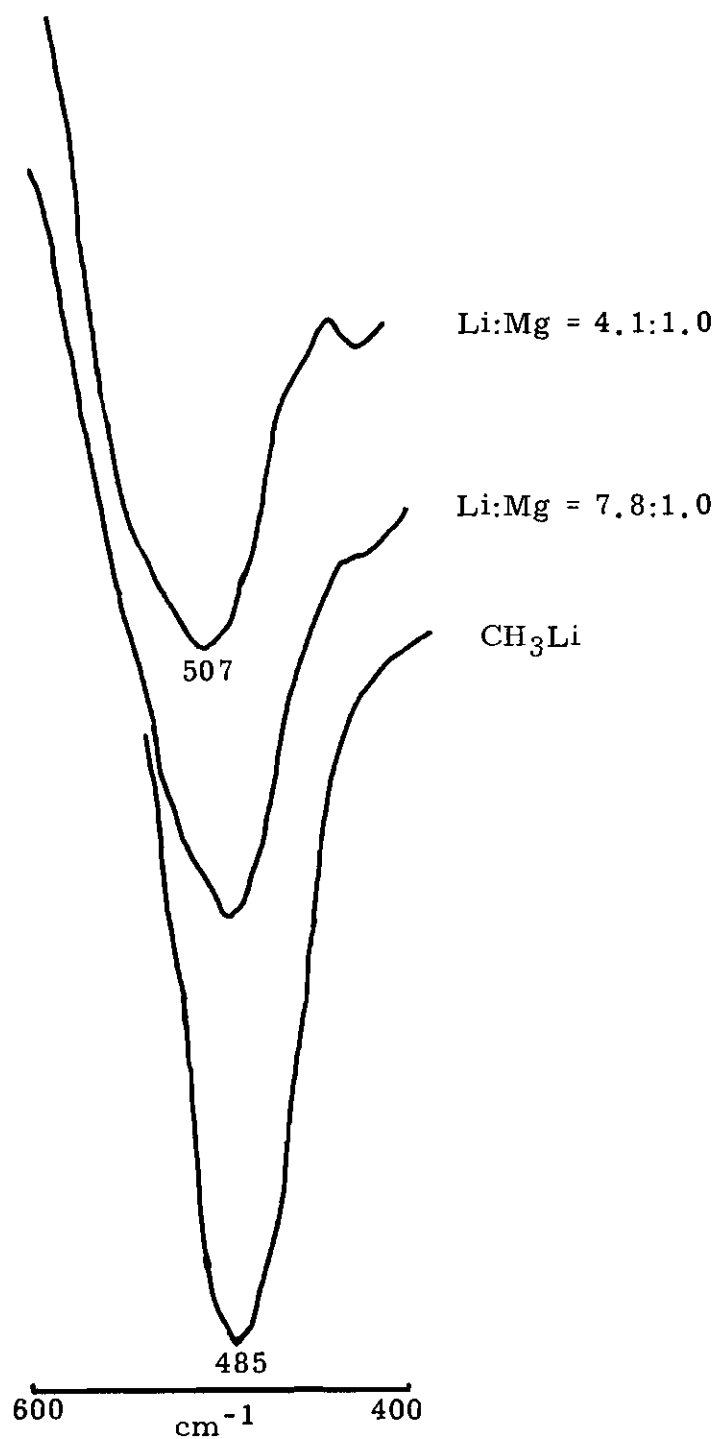
Figure 6. Infrared Spectra of Methyllithium-dimethylmagnesium in
Diethyl Ether.

at 551 cm^{-1}. In addition a band at 480 cm^{-1} appeared. It would appear that little if any monomeric dimethylmagnesium remained in solution at this ratio. The band at 480 cm^{-1} was harder to assign. It was unlikely that the absorption due to free methyllithium would shift 5 cm^{-1}; it was more likely that this band was also due to the complex. If Brown's low temperature nmr data can be extrapolated to room temperature, at a ratio of 1.2:1.0 one would expect to see only excess dimethylmagnesium in addition to a 2:1 complex which may be slightly dissociated. Also since solvation would decrease, not increase, at higher temperature it is unlikely that a 1:1 complex stabilized by basic ether molecules as suggested by Seitz for the reaction in THF would be formed. Therefore the following equilibrium is suggested which probably lies to the left when equivalent amounts of both reagents are present in solution.

$$0.5(CH_3Li)_4 + (CH_3)_2Mg \rightleftharpoons Li_2Mg(CH_3)_4 \qquad (15)$$
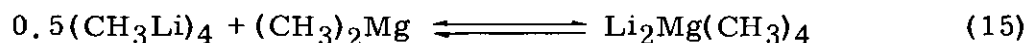
More methyllithium would be "tied up" in the complex than dimethylmagnesium.

The appearance of a second complex band at 511 cm^{-1} when the Li:Mg ratio reached 2.1:1.0 suggests that this may be a C-M stretching band due to a 3:1 complex, since the band continued to grow as the ratio reached and surpassed 3:1. At this stoichiometry no

bands attributed to free dimethylmagnesium were observed in the spectrum. The width of this band and its gradual shift at higher Li: Mg ratios suggested that some free methyllithium was present in solution. The following equilibrium is suggested for those cases in which the Li:Mg ratio is 2.1:1.0 or greater.

$$1/4(LiCH_3)_4 + Li_2Mg(CH_3)_4 \rightleftharpoons Li_3Mg(CH_3)_5 \qquad (16)$$
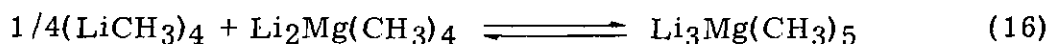
It is likely that the equilibrium shifts toward the 3:1 complex as the amount of methyllithium is increased.

The results of this experiment indicated that at any given concentration there are several species in equilibrium and at no time does a single complex exist in solution. The results of this study are best interpreted in terms of the same equilibria as the low temperature nmr study of Brown.

At attempt was made to fractionally crystallize solutions prepared by mixing methyllithium and dimethylmagnesium at Li:Mg ratios of 1:1, 2:1, and 3:1, by partial removal of solvent under reduced pressure. In all cases no precipitate was observed until approximately 95% of the ether had been removed. The samples were then too viscous to filter and were taken to dryness and placed on the vacuum manifold for several hours. The infrared spectra of the solid mixtures were obtained in Nujol (Figure 7) and compared to the mull spectra of
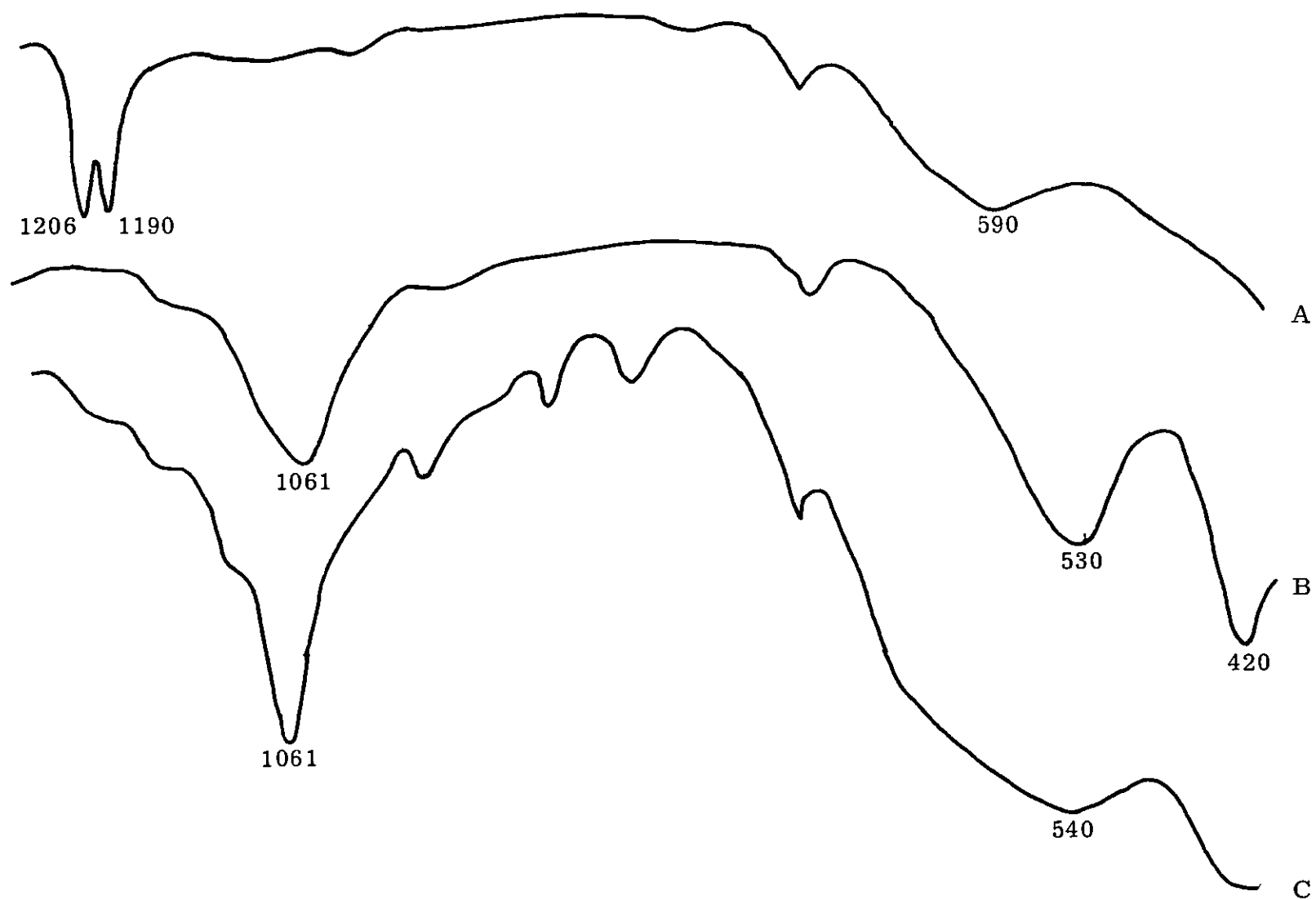
Figure 7. Infrared Spectra of A, $(CH_3)_2Mg$; B, CH_3Li; and C, $Li_3Mg(CH_3)_5$ in Nujol.

methyllithium and dimethylmagnesium. The spectrum of the 2:1 solid was virtually identical to that of the 3:1 solid; only the latter spectrum is shown for simplicity.

The bands at 1190 and 1206 cm^{-1} in the spectrum of dimethyl-magnesium have been assigned to methyl deformation modes. The band at 590 cm^{-1} was assigned to the C-Mg stretching vibration in the associated form, in this case polymer. The band at 1061 cm^{-1} in the spectrum of methyllithium has been attributed to methyl deformation vibrations and the bands at 530 and 420 cm^{-1} have been assigned to C-Li stretching vibrations (36). In the spectrum of the complex, the bands at 1190 and 1206 cm^{-1} are clearly absent. Either these bands have disappeared due to complexation as is the case when the metal atom is coordinated to ether or have shifted under the band found at 1061 cm^{-1} in the spectrum. In any event, no free dimethylmagnesium was present in the solid sample at Li:Mg ratios of 2:1 and 3:1.

The d spacing for the lines found in the X-ray powder diffraction pattern of methyllithium and dimethylmagnesium are shown in Table 6. These two patterns agree very well with the literature values of Weiss (37, 9). The d spacing of the lines found in the powder patterns of the complex solid mixtures are given in Table 7.

There are certain limitations in X-ray powder diffraction analysis. One is that if the d spacing values are to be extremely

Table 6

X-Ray Powder Diffraction Pattern for
Methyllithium and Dimethylmagnesium

CH_3Li		$(CH_3)_2Mg$	
5.116	m	5.706	s
3.603	m	5.227	s
2.954	m	3.276	ms
2.548	vvw	3.215	vvw
2.286	vw	2.647	vvw
1.927	vvw	2.440	vvw
1.701	vvw	2.402	vvw
		2.138	vvw
		2.072	w
		2.004	vvw
		1.963	vvw
		1.893	vvw

accurate an internal standard must be used to compensate for film

shrinkage. In this study all of the films were treated in a similar

manner with respect to time in the developing solutions and water

bath, so that any film shrinkage should have been similar in all cases.

Secondly, the reported intensities were read visually. Another more

serious limitation is that in order for the lines due to a particular

species to be identifiable that species should be present in the sample

in at least five to ten percent by weight.

The data in Table 7 can be interpreted quite well, keeping

these limitations in mind. When the Li:Mg ratio was 1.3:1.0, lines

due to both reactants were observed. When the ratio was 2:1, lines

Table 7

X-Ray Powder Diffraction Pattern of the Solid Residues
Obtained by Removing Solvent from Methyllithium-
Dimethylmagnesium Mixtures in Diethyl Ether[a]

"$Li_{1.3}Mg(CH_3)_{3.3}$"		"Li_2MgR_4"		"Li_3MgR_5"	
10.10	m	5.47	s	5.49	m
6.22	vw	5.22	w	5.13	s
5.77	vw	4.79	vw	4.41	m
5.52	vs	4.39	vs	3.61	m
5.10	w	3.63	w	3.37	vw
4.65	s	3.38	m	3.22	w
4.39	w	3.25	m	2.96	w
4.15	vw	2.98	w	2.30	w
4.08	vw	2.84	w	1.94	vw
3.87	m	2.64	w	1.82	vw
3.76	m	2.49	m	1.71	vw
3.63	w	2.38	w		
3.39	s	2.30	vw		
3.31	w	2.15	w		
3.08	vw	2.10	w		
2.96	w	2.05	w		
2.85	w	1.92	w		
2.74	vw				
2.41	vvw				
2.37	w				
2.30	w				
2.11	w				
1.97	vw				

[a]The quotation marks imply the stoichiometry of the reagents,
not the presence of a specific complex of this stiochiometry.

due to a complex and lines due to methyllithium could be seen, indi-

cating that most if not all of the dimethylmagnesium must be "tied up"

in a complex. When the ratio was 3:1, the lines due to methyllithium

are much more intense. Two factors must be considered. One is that the weight percentage of methyllithium was steadily increasing although this alone would not account for the sharp increase in line intensities. A second factor was that there was evidently much more free methyllithium in this solid mixture than in any previous case. Lines attributed to the complex become successively weaker, indicating a dilution with methyllithium.

The conclusions that can be drawn from this data are in general agreement with those that were made previously from the infrared study. At low stoichiometries, an equilibrium exists in which appreciable quantities of the reactants can be found in the solid mixture. At a Li:Mg ratio of 2:1 the equilibrium lies toward complex. At a Li:Mg ratio of 3:1 appreciable quantities of free methyllithium are found, indicating that the 3:1 complex is somewhat dissociated and in equilibrium with methyllithium and what is probably a 2:1 complex.

$n-C_4H_9Li + (n-C_4H_9)_2Mg$ in Hexane

In this study solutions were prepared by stirring n-butyllithium in hexane with di-n-butylmagnesium. Complex formation was clearly indicated since the normally insoluble magnesium reagent dissolved within a period of twelve hours. Solutions were prepared in which the Li:Mg ratios were 1:1 and 2:1.

An infrared study was initiated in an attempt to describe the composition of the solutions, but was inconclusive since n-butyl-

lithium and both complex solutions had only one broad, strong absorption at 550 cm^{-1}. Attempts to fractionally crystallize the reaction mixtures were unsuccessful. In both cases, the solutions became increasingly viscous as the solvent was removed at reduced pressure. Extended drying on a vacuum manifold finally produced amorphous solids, which did not exhibit a definite X-ray diffraction pattern.

Thus, the only conclusions that can be drawn are that complexes of unknown description are formed when these two reagents are mixed in hydrocarbon solvent.

s-C_4H_9Li + (s-$C_4H_9)_2$Mg in Cyclohexane

The infrared spectra of solutions prepared by mixing s-butyllithium and di-s-butylmagnesium in cyclohexane were recorded in a manner analogous to that described for the similar system where R = CH_3. The only region of the spectrum in which significant changes occurred was that portion between 600 cm^{-1} and 400 cm^{-1}. The spectra are shown in Figure 8.

The spectrum of s-butyllithium contained two bands at 510 and 445 cm^{-1}, attributable to C-Li stretching vibrations. The spectrum of di-s-butylmagnesium contained three bands at 550, 519 and 439 cm^{-1}. This compound is dimeric in cyclopentane (6) and is therefore assumed to be dimeric in cyclohexane. By analogy to the spectrum of dimethylmagnesium, the band in this spectrum at 550 cm^{-1} was assigned to the
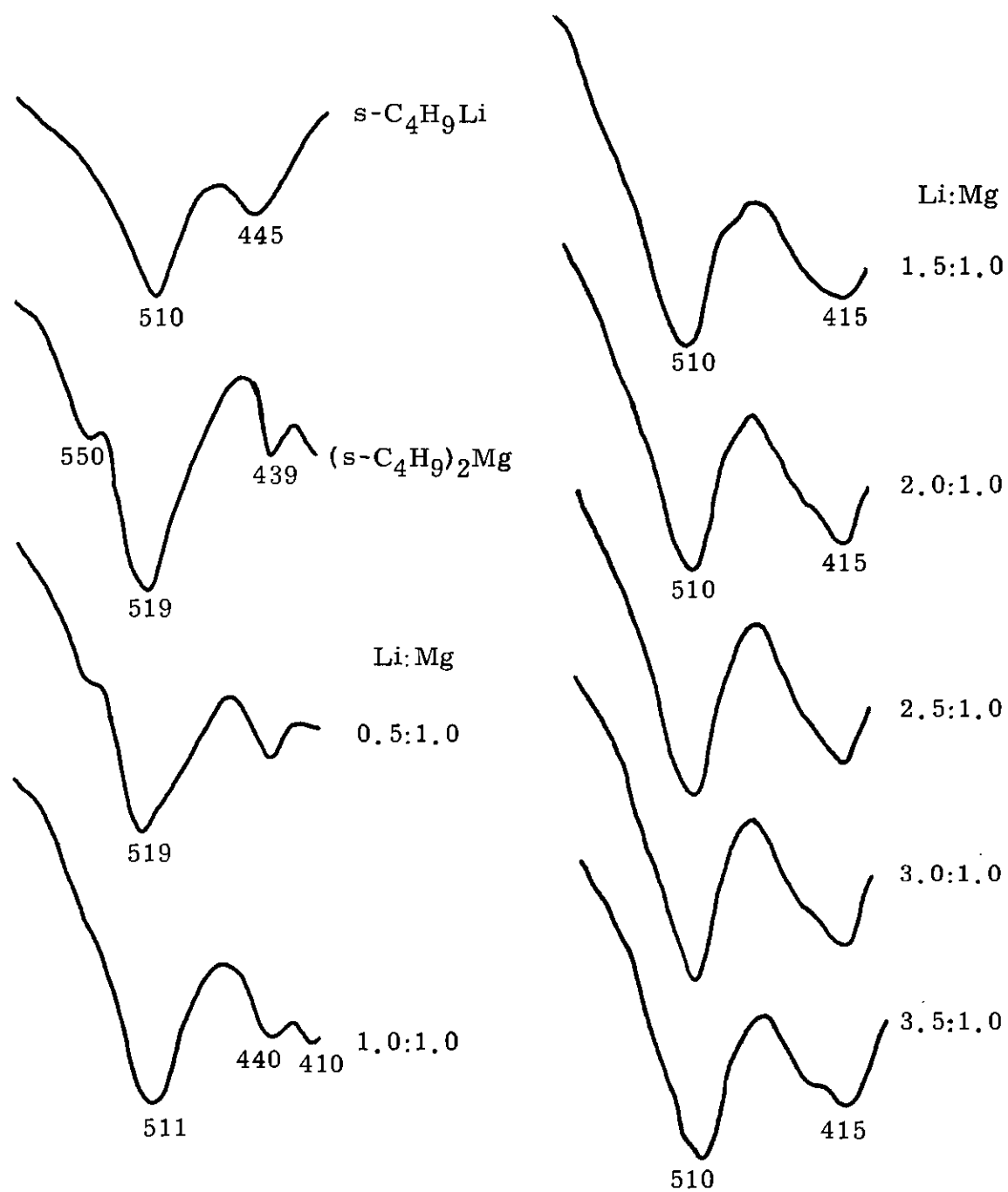
Figure 8. Infrared Spectra of s-Butyllithium-di-s-butylmagnesium in Cyclohexane.

C-Mg stretching vibration for bridging alkyl groups and the band at

519 cm^{-1} was assigned to terminal alkyl-Mg stretching vibrations.

No significant changes were observed until the Li:Mg ratio

reached 1:1. At this point, the shoulder at 550 cm^{-1} had disappeared

and a new band at 410 cm^{-1} had appeared. The maximum for the C-M

stretching vibration was found at 511 cm^{-1}, very near the position for

the C-Li stretching vibration itself. As the Li:Mg ratio was increased

the most noticeable change in the spectra was an increase in the size

of the band at 415 cm^{-1} which can be attributed to complex formation

since this band was clearly absent in the spectra of the reactants.

Once the stoichiometry surpassed 2:1, the spectra showed only the

effect of added s-butyllithium. These data imply that a complex was

formed although no definite stoichiometry could be described. It is

likely that once the molar ratio was greater than 2:1 the addition of

more s-butyllithium did not alter the nature of the complex.

The molality of solutions prepared by mixing s-butyllithium

and di-s-butylmagnesium in benzene and cyclohexane was determined

cryoscopically. The results are given in Table 8.

The cryoscopic data can be interpreted in a number of ways.

If no reaction had taken place when the reagents were mixed, the ob-

served molality would have been the sum of the contributions of each

reactant. If a reaction had taken place and monomeric lithium tri-s-

butylmagnesium had been produced, the molality of the reaction mix-
ture would have been 33% higher than the sum of the contributions from
the reactants since three particles would have produced four particles
according to the following equation.

$$2(s\text{-}C_4H_9)_2Mg + (s\text{-}C_4H_9Li)_4 \longrightarrow 4LiMg(s\text{-}C_4H_9)_3 \qquad (17)$$

Table 8

Molality of Solutions Prepared by Mixing s-Butyllithium and

Di-s-Butylmagnesium in Benzene and Cyclohexane

Li:Mg Ratio 1:1 in Benzene			
m^a	m^b	m^c	m^d
0.058	0.029	0.087	0.087
0.104	0.052	0.156	0.147
0.129	0.064	0.193	0.178

Li:Mg Ratio 1.15:1.00 in Cyclohexane			
m^a	m^b	m^c	m^d
0.044	0.025	0.069	0.068
0.081	0.046	0.127	0.115
0.119	0.068	0.187	0.170
0.146	0.084	0.230	0.207
0.171	0.098	0.269	0.237

[a]Molality of dimeric di-s-butylmagnesium.

[b]Molality of tetrameric s-butyllithium.

[c]Additive molality of the reactants.

[d]Observed molality of the solution.

Another possibility is that an equilibrium exists between the complex

and the reactants in which the complex is self associated. This latter

possibility seems likely since hydrogenolysis of the 1:1 mixture in

benzene produced a mixture of LiH, MgH_2 and $LiMgH_3$, and the infra-

red study also indicated that complex formation had occurred.

$C_6H_5Li + (C_6H_5)_2Mg$ in Diethyl Ether

Wittig (15) prepared $LiMg\emptyset_3$ in diethyl ether by mixing

phenyllithium and diphenylmagnesium in 1:1 stoichiometry. He then

removed the solvent under reduced pressure and recrystallized the

resulting solid from hot xylene. Analysis of the recrystallized solid

indicated a Li:Mg ratio of exactly 1.00:1.00.

Brown and Seitz (38) studied the phenyllithium-diphenylmag-

nesium system in diethyl ether using low temperature nmr techniques

and concluded that when the Li:Mg ratio is $<2:1$, a 1:1 complex exists

in solution. They also reported the presence of a 2:1 complex when

the Li:Mg ratio is 2:1 or greater.

In an attempt to describe this system more fully at room

temperature, the preparation of $LiMg\emptyset_3$ was repeated. When 10

mmoles of phenyllithium and 10 mmoles of diphenylmagnesium were

mixed in diethyl ether and the solvent removed under reduced pres-

sure, a white solid resulted. Whereas solid phenyllithium is quite

sensitive to photodecomposition, this solid was much more stable to

light. The product of this reaction was recrystallized from hot xylene.
Analysis of the mother liquor revealed that at 90°C the complex was
soluble to the extent of 0.1 mmoles/ml, and a Li:Mg ratio of exactly
1.0:1.0 was indicated. Analysis of the recrystallized solid also indi-
cated an exact Li:Mg ratio of 1.0:1.0.

The d spacings of the lines in the X-ray powder diffraction
patterns of phenyllithium and lithium triphenylmagnesium are given
in Table 9. Diphenylmagnesium is amorphous and does not give a
powder pattern. Clearly, there is no phenyllithium in the recrystal-
lized sample. Furthermore, a powder pattern of the unrecrystallized
reaction product was compared visually to that of both phenyllithium
and the complex and was almost identical to that of the complex. No
lines attributable to phenyllithium were observed in the unrecrystal-
lized sample. This data indicates that a true 1:1 complex was formed
and that it is not appreciably dissociated at room temperature.

$$\emptyset Li + Mg\emptyset_2 \xrightarrow{\text{Et}_2\text{O}} LiMg\emptyset_3 \qquad (18)$$
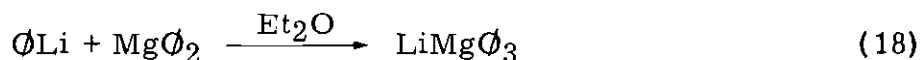
Preparation of Alkali Metal Hydride Complexes of Magnesium Alkyls

A natural extension of the work reported thus far was to study
the reactions of dialkylmagnesium compounds with alkali metal hydrides
and prepare a second series of complexes similar to those prepared
via the reactions with alkali metal alkyls. There is only one report in

Table 9

X-Ray Powder Diffraction of Phenyllithium and

Lithium Triphenylmagnesium

ØLi		LiMgØ₃[a]	
9.21	w	10.22	m
5.92	w	9.31	m
5.25	vs	8.59	s
4.74	s	7.28	w
4.57	s	6.84	w
4.15	vs	5.75	w
3.41	s	5.20	m
3.27	m	4.94	m
3.22	m	4.42	m
2.95	w	4.30	m
2.83	w	4.08	w
2.75	w	3.97	w
2.60	w	3.82	m
		3.57	w
		3.51	w
		3.37	w
		3.25	w
		2.99	w
		2.87	vw

[a]Recrystallized sample. Very weak lines were observed with d spacings less than 2.87 but are not shown in this table.

the literature (18), in which attempts to prepare complexes of this type have been made using a magnesium alkyl.

Coates and Heslop reported the reaction of lithium, sodium and potassium hydride with diethylmagnesium in boiling diethyl ether, tetrahydrofuran and 1,2-dimethoxyethane. These authors found that

no reaction took place when diethyl ether was used as a solvent and reaction times of 24 - 72 hours were employed. In contrast, with tetrahydrofuran and 1,2-dimethoxyethane, hydrolysable ethyl groups gradually disappeared from solution and were not found in the solid residues removed by filtration. Since diethylmagnesium itself was stable under the reaction conditions, it was concluded that intermediate complexes were formed in which the nucleophilic character of the ethyl group in the complex exceeded that of ethyl in diethylmagnesium itself. Ether cleavage then occurred to a significant degree, accounting for the loss of ethyl groups.

A portion of Coates' work was repeated in the present study using dimethyl and diphenylmagnesium instead of diethylmagnesium and both diethyl ether and tetrahydrofuran were employed as solvents. The conclusions were in general agreement with those of previous workers.

When lithium hydride was refluxed with dimethylmagnesium in diethyl ether no reaction was observed. When tetrahydrofuran was used as the solvent some reaction had taken place during the 36 hour 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, lithium hydride and dimethylmagnesium were

stirred for 7 days at 25°C and then filtered. Analysis of the 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 when higher temperatures and shorter reaction times were employed.

Several experiments were conducted using diphenylmagnesium. When a mixture of lithium hydride and diphenylmagnesium was refluxed for several days in tetrahydrofuran and then filtered, 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, in this case via reaction with the complexed hydride. Similar results were obtained by mixing sodium hydride with diphenylmagnesium in diethyl ether. After 5 days at 25°C the reaction mixture was filtered and analysis of the filtrate revealed a Na:Mg ratio of 0.38:1.00. Again, no hydride was evolved on hydrolysis of the solution.

In contrast, the reaction of potassium hydride with diphenylmagnesium in diethyl 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. When potassium hydride and diphenylmagnesium 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.

$$KH + 2\emptyset_2Mg \longrightarrow KMg\emptyset_2H\cdot Mg\emptyset_2 \qquad (19)$$
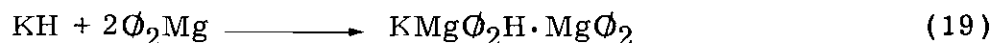
This particular stoichiometry has been observed many times in com-

plexes of this type (20, 21, 39). When the potassium to magnesium

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 these

solids and the d spacings are given in Table 10. Lines assigned to

potassium hydride at d spacings of 3.81, 3.27, 2.84, 2.61, 2.02 and

1.71 $\overset{o}{A}$ were observed in 1:1, 2:1 and 5:1 mixtures. The strongest

line for potassium hydride at 3.24 $\overset{o}{A}$ were very faint in the 0.5:1 com-

pound. Lines at d spacings of less than 2.26 $\overset{o}{A}$ were too weak to be

read accurately. Lines attributed to complex formation decreased in

intensity as this species was diluted with solid potassium hydride.

The exact stoichiometry of complexes other than a 1:2 complex cannot

be determined on the basis of this data alone. Most of the lines attrib-

utable to the complex are fairly low in intensity. There are two ex-

planations for the presence of lines due to potassium hydride in the

1:1 mixture. Either the stable complex has a molar ratio of 1:2 and

the solid contains an equivalent molar amount of potassium hydride,

or it may be that some potassium hydride is occluded in what is primarily a 1:1 complex.

Table 10

X-Ray Powder Diffraction Pattern of Potassium

Hydride-Diphenylmagnesium Complexes

KH·2Φ₂Mg		KH + Φ₂Mg		2KH + Φ₂Mg		5KH + Φ₂Mg	
d	I	d	I	d	I	d	I
		8.74	w	8.68	w-br		
8.00	w	8.00	vvw				
7.42	w	7.46	vvw	7.36	vvw		
6.50	w	6.50	vvw	6.47	vvw		
5.80	w	5.88	vvw	5.85	vvw		
5.10	m	5.15	w	5.12	w-br	5.19	vvw
4.76	w	4.71	vw	4.82	vw		
4.50	w	4.37	w-br	4.39	w-br	4.44	vvw
4.35	m	4.19	vw	4.19	vw		
4.16	w	4.05	vw	4.04	vw		
4.00	w	3.81	vvw	3.82	vvw		
3.75	w	3.75	vvw	3.63	vvw	3.64	vvw
3.45	w	3.27	m	3.28	vs	3.28	vs
3.25	vw	3.06	vw	3.05	vw	3.19	vvw
3.04	m	2.93	vvw	2.93	m	2.84	s
2.92	m	2.84	m	2.85	m		
2.81	m	2.70	vw	2.69	vvw		
2.67	vw	2.61	vvw	2.61	vvw	2.60	vvw
2.59	vw	2.29	vvw	2.50	w-br	2.23	vvw
2.48	w-br	2.02	w	2.02	m		
2.32	w	1.72	w	1.91	vvw	1.91	vvw
2.26	w			1.72	m	1.71	m

$(s-C_4H_9)_2Mg$ + KH in Benzene

Of considerably more interest is the formation of stable com-
plexes in solvents in which ether cleavage is avoided. In this connec-
tion the hydrocarbon soluble di-s-butylmagnesium recently reported
by Eastham and Kamienski is an excellent candidate for the prepara-
tion of stable complexes of dialkylmagnesium compounds with alkali
metal hydrides.

When di-s-butylmagnesium was stirred with an equivalent
amount of potassium hydride in either benzene or a 50:50 benzene-
cyclohexane mixture, the hydride species dissolved and a stable sol-
uble 1:1 complex was formed.

$$KH + (s-C_4H_9)_2Mg \longrightarrow KMg(s-C_4H_9)_2H \qquad (20)$$

An attempt to prepare the complex in pure cyclohexane was unsuccess-
ful, largely due to the fact that potassium di-s-butylhydridomagnesium
is insoluble in this solvent. In this experiment an oily gummy residue
resulted. When commercial potassium hydride was employed, the re-
action mixture was stirred overnight in order to achieve a yield on the
order of 90%, but when "active" potassium hydride which had been pre-
pared in the autoclave was employed the reaction was complete in less
than one hour. Furthermore, the best results were obtained when the
potassium hydride was slurried with benzene prior to the addition of
di-s-butylmagnesium.

The nmr spectra of di-s-butylmagnesium and the 1:1 complex

are shown in Figures 9 and 10 respectively. Both solutions were

approximately 0.4 molar in benzene, and benzene was used as the

internal standard. The apparent sextet, attributed to the αH of the

s-butyl group is centered at 9.81r in the spectrum of di-s-butylmag-

nesium. In the 1:1 complex with potassium hydride, the αH signal

was shifted upfield 0.81 ppm and became somewhat broadened. In

addition, a new signal was observed at 6.60r which was attributed to

the hydridic hydrogen in the complex. Integration of these two signals

gave a ratio of 0.83:1.00 consistent with complex formation. The

position of the hydride signal was at a lower field than would have been

predicted. However, Shriver (21) has shown that the hydride signal

in NaH$\cdot$2Et$_2$Zn is also found at remarkably low field. Another notice-

able change in the spectra was that the triplet and doublet in the spec-

trum of di-s-butylmagnesium had merged in the spectrum of the com-

plex.

The infrared spectra of both di-s-butylmagnesium and the

1:1 complex were recorded but are not nearly so informative as were

the nmr spectra. Whereas the spectrum of di-s-butylmagnesium in

benzene contained an absorption band at 521 cm^{-1}, this band was

broadened and of much lower intensity in the complex. This effect

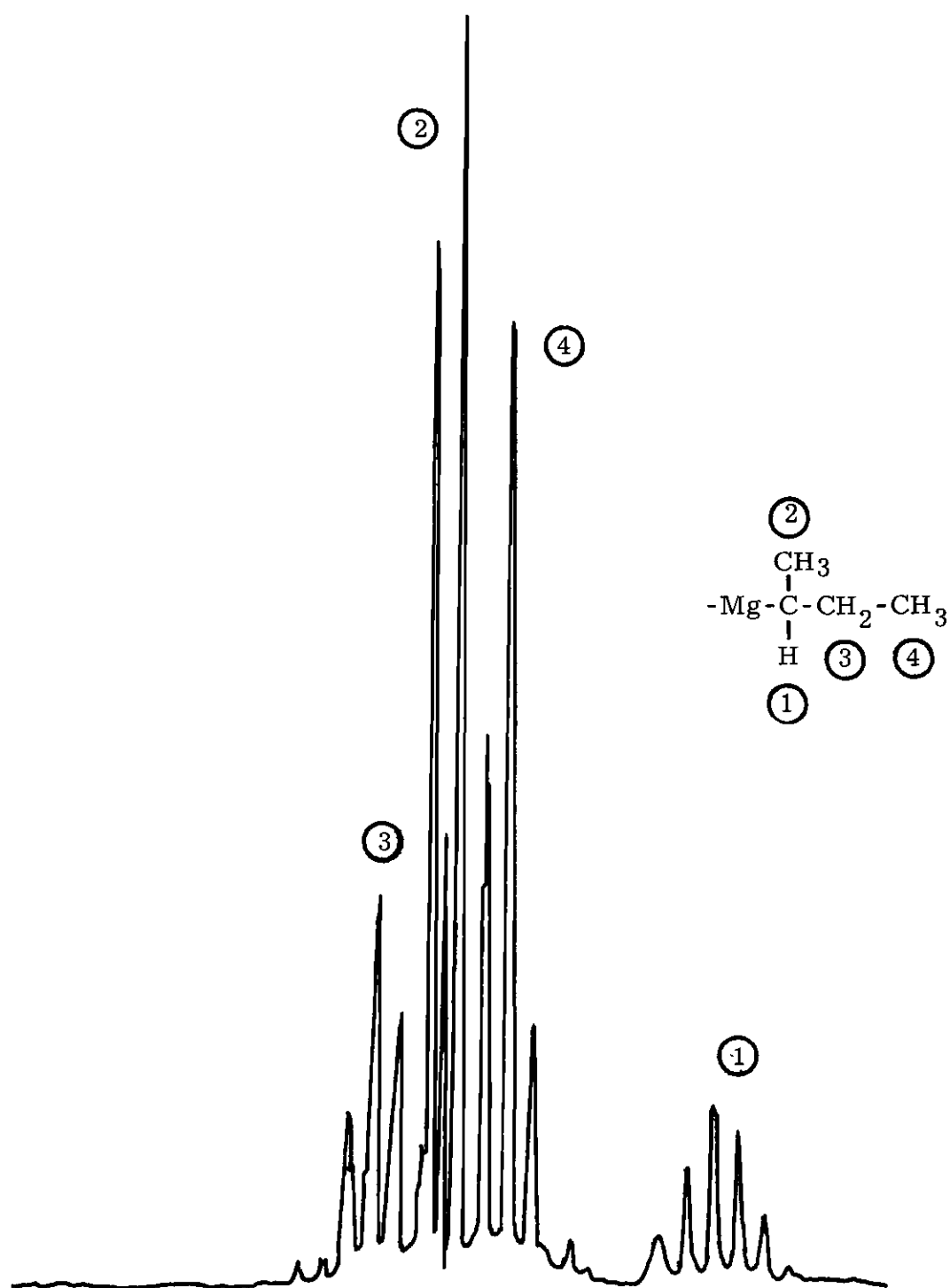was undoubtedly due to the lowering of the symmetry around the

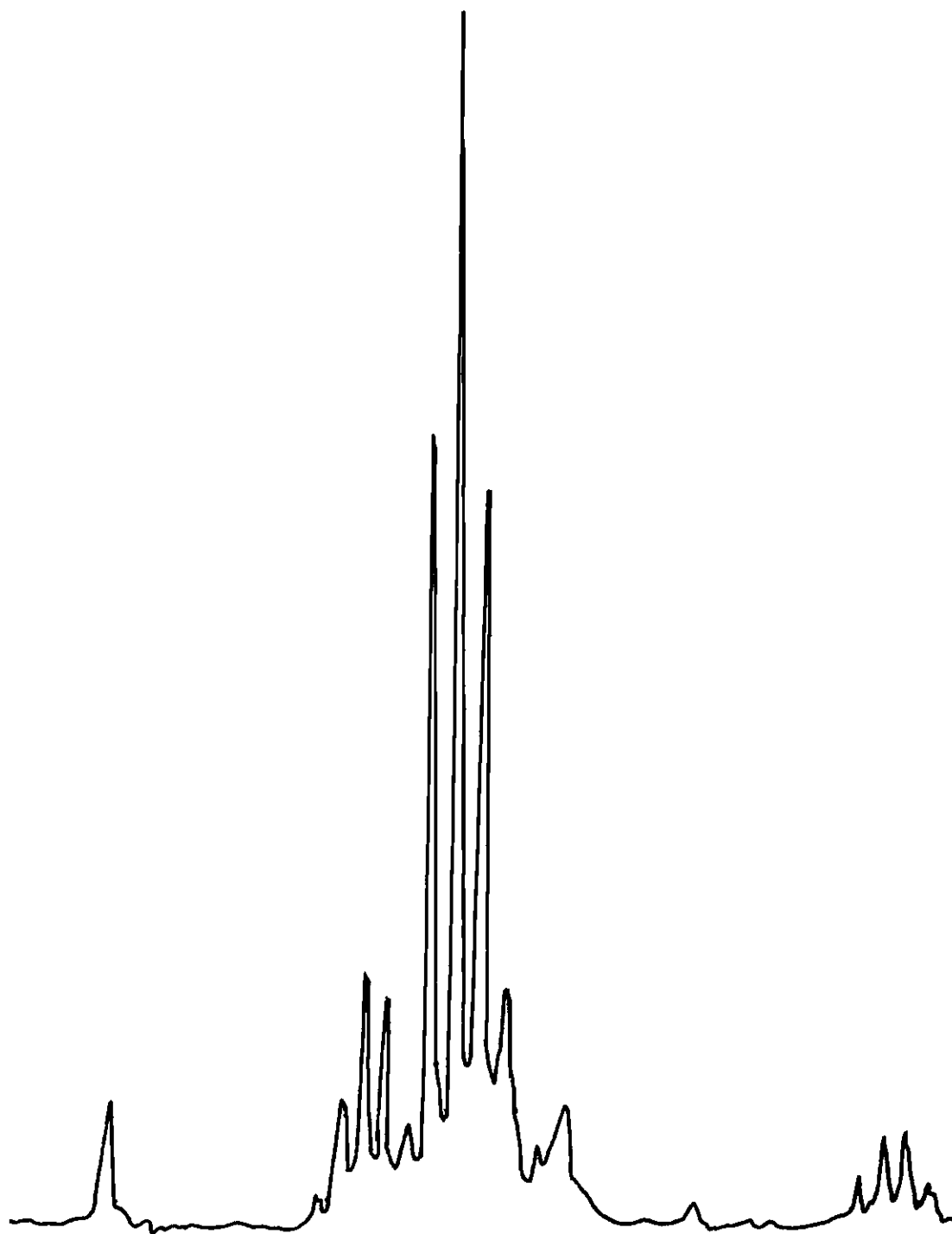Figure 9. NMR Spectrum of Di-s-butylmagnesium in Benzene.

Figure 10. NMR Spectrum of Potassium Di-s-butylhydridomagnesium
in Benzene.

magnesium atom in the complex. A broad absorption band was also observed indicative of Mg-H stretching vibrations.

Cryoscopic molecular weight measurements indicated a monomer-dimer equilibrium over a concentration range 0.06 - 0.16 molal. These data are shown in Figure 11.

Since it had been reported earlier (18) and also confirmed in this study that complexes of this type could not be prepared in ethers due to solvent cleavage, it was of interest to determine the stability of potassium di-s-butylhydridomagnesium in the presence of limited amounts of diethyl ether.

Accordingly, 0.33 mmoles of the complex in 1 ml of benzene and 1.0 mmoles of diethyl ether were mixed in an nmr sample tube, and the spectrum was recorded within 15 minutes. The hydride signal in this mixture was observed at 6.36τ corresponding to a downfield shift of 0.24 ppm, and was adjacent to the ether quartet. A similar downfield shift of 0.20 ppm was observed for the sextet attributed to the αproton of the s-butyl group. The relative areas of these signals were identical to that of the complex in pure benzene, and only a slight decrease in the intensity was observed due to the dilution effect. Spectra recorded at 30 and 45 minutes after mixing were identical to the spectrum taken 15 minutes after mixing.

These data indicate that the complex is stable in the presence of limited amounts of ether for at least one hour at room temperature.

The cleavage observed in the direct preparation in ether solvents was therefore a consequence of both higher temperatures and longer reaction times.

The reactivity of potassium di-s-butylhydridomagnesium toward olefins was also investigated. A mixture was prepared in which 0.23 mmoles of the complex in one ml of benzene was combined with an equimolar amount of cyclohexene in an nmr tube. The nmr spectrum of this mixture remained unchanged for a period of 24 hours at 25°C. At this time the spectrum was identical to that of a spectrum of 0.23 mmoles of cyclohexene in one ml of benzene superimposed on the spectrum of the complex. No change in the position of any of the signals due to complex had occurred as a result of olefin addition. Thus, it was concluded that no reaction took place under the above conditions. Tests carried out at an independent laboratory revealed that this complex did not act as a catalyst in the polymerization of ethylene, but did act as a telemerization catalyst for butadiene.

$(n-C_4H_9)_2Mg$ + KH in Benzene

A second complex was prepared analogous to that described above in which the R group was n-butyl instead of s-butyl. Initially, potassium hydride was stirred with an equivalent amount of di-n-butyl-magnesium in cyclohexane. After 44 hours analysis of an aliquot of the supernatent revealed a K:Mg ratio of 0.5:1.0 and the concentration

of magnesium was shown to be 0.027 mmoles/ml. As was observed in the previous example, a soluble complex was not formed in cyclohexane. The insoluble portion of this reaction mixture was isolated on a fritted glass filter in the dry box, transferred to another flask and covered with 300 ml of benzene.

The benzene mixture was stirred for 3 days at 80°C, cooled and filtered in the dry box. The filtrate was shown by analysis to be 0.11 molar in complex, and a K:Mg:H ratio of 0.98:1.00:0.85 was indicated. When the solvent was partially removed from a portion of this sample, a solution 0.68 molar in complex was obtained and no precipitation had occurred. Solvent removal was continued until a white solid was produced; this was then dried on a vacuum manifold at reduced pressure for several hours. A small portion of the solid was heated in a melting point capillary tube. Decomposition was observed at 115°C, a temperature at which di-n-butylmagnesium itself is stable. The X-ray powder diffraction pattern of this solid showed only very, very weak lines with d spacings of 3.90, 3.46, 3.03, 2.78, 2.68, 2.20 and 2.11 $\overset{\text{o}}{\text{A}}$ which can be attributed to potassium hydride. The complex itself is an amorphous solid, as is di-n-butylmagnesium.

The nmr spectrum of a 0.378 molar solution of potassium di-n-butylhydridomagnesium in benzene at 25°C was consistent with complex formation. The triplet attributed to the α methylene protons

was observed at 10.59τ. In the spectrum of di-n-butylmagnesium in

benzene this signal is found at 9.49τ (29). A low intensity signal was

observed at 6.53τ which was attributed to the hydridic hydrogen. In

some of the nmr spectra of this complex, the signal for the hydridic

hydrogen was not observed even though elemental analysis confirmed

the presence of hydridic hydrogen in solution.

In one preparation a sample of the supernatent was taken

prior to complete formation of the 1:1 complex. Analysis revealed a

K:Mg ratio of 0.8:1.0. The triplet attributed to the α methylene pro-

tons in the spectrum of this solution was observed at 10.49τ. Either

a 1:2 complex existed in equilibrium with a true 1:1 complex giving

rise to a slight downfield shift or the 1:1 complex was undergoing

rapid exchange with di-n-butylmagnesium. Considering the extremely

low solubility of di-n-butylmagnesium the first explanation is more

likely. The positions of the multiplets due to the other protons of the

butyl group were unchanged. Continued stirring of the reaction mix-

ture produced a 1:1 complex.

Cryoscopic molecular weight measurements indicated that

potassium di-n-butylhydridomagnesium is dimeric over a concentra-

tion range 0.08 - 0.32 molal in benzene. These data are shown in

Figure 11.

Analysis of the residue recovered after filtration of the ben-

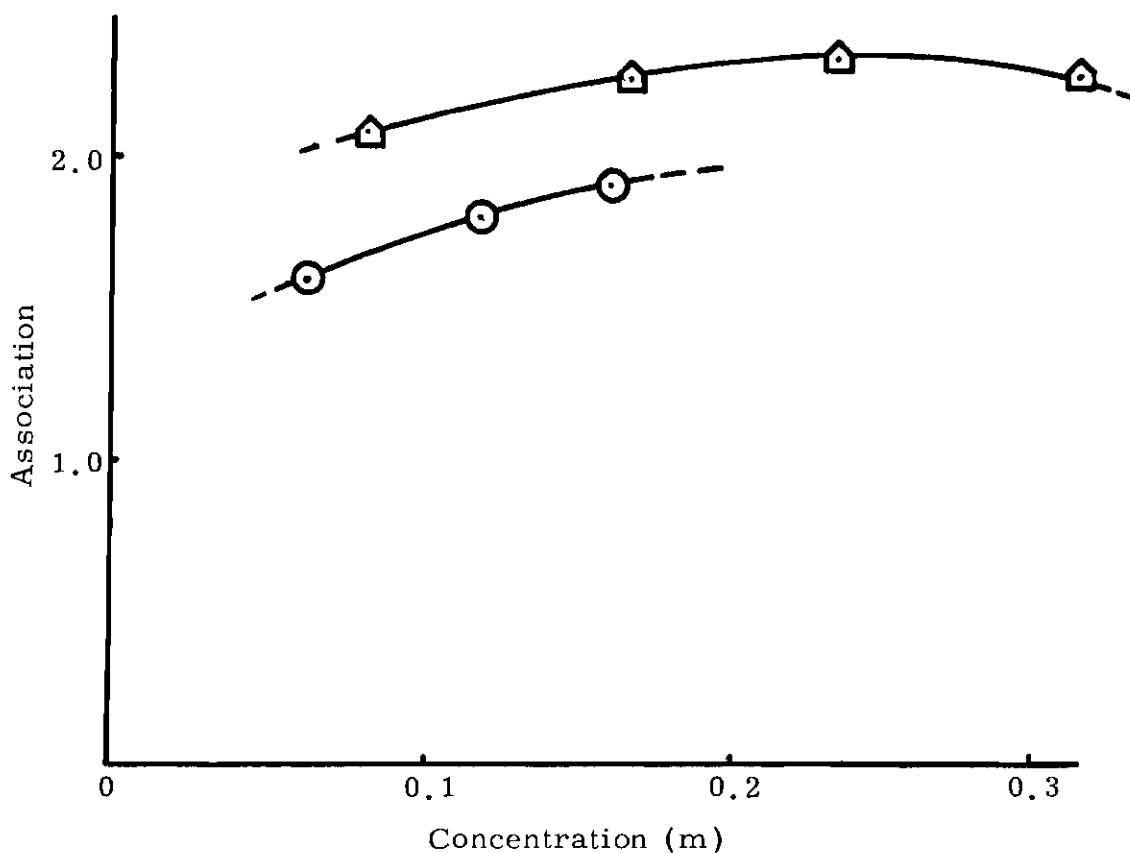zene solution containing the 1:1 complex proved quite interesting.

Figure 11. Association of Potassium Di-s-butylhydridomagnesium —o—,
and Potassium Di-n-butylhydridomagnesium ⬠ in Benzene.

The powder pattern of this solid revealed lines at d spacings of 2.83,

2.07 and 1.65 $\overset{\text{o}}{\text{A}}$ indicative of the species $KMgH_3$ described in a later

portion of this thesis. The strong line at 3.24 $\overset{\text{o}}{\text{A}}$ in the powder pattern

of potassium hydride was clearly absent from this powder pattern.

Evidently complexation had weakened the C-Mg bond and pyrolysis of

the complex occurred at 80°C in benzene.

$(s-C_4H_9)_2Mg$ + NaH in Benzene

When di-s-butylmagnesium and sodium hydride were stirred in benzene, a complex was formed in which the Na:Mg ratio was 1:2.

$$NaH + 2(s-C_4H_9)_2Mg \longrightarrow NaMg(s-C_4H_9)_2H \cdot (s-C_4H_9)_2Mg \quad (21)$$
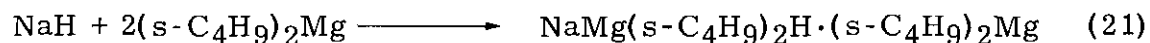
This was the case even when the reagents were mixed in a molar ratio of 1:1 and the reaction mixture was stirred for several days.

The nmr spectrum of a 0.23 molar solution of the complex in benzene was recorded at room temperature using benzene as the internal standard. In this sample, the apparent sextet attributable to the αH of the butyl group was shifted upfield, but only 0.66 ppm. Since only one hydridic hydrogen is available in this complex containing two magnesium atoms, less shielding should occur and a smaller shift than that observed for the 1:1 potassium hydride complex was expected. In addition a new signal was observed at 6.60τ for the hydridic hydrogen. As was the case with the potassium hydride - di-n-butylmagnesium complex this signal is somewhat broadened compared to that of the 1:1 potassium hydride - di-s-butylmagnesium complex. This signal was observed, however, in all of the nmr spectra recorded for the sodium hydride complex.

The infrared spectra of films of di-s-butylmagnesium and the 1:2 sodium hydride complex were recorded. A small shift in the posi-
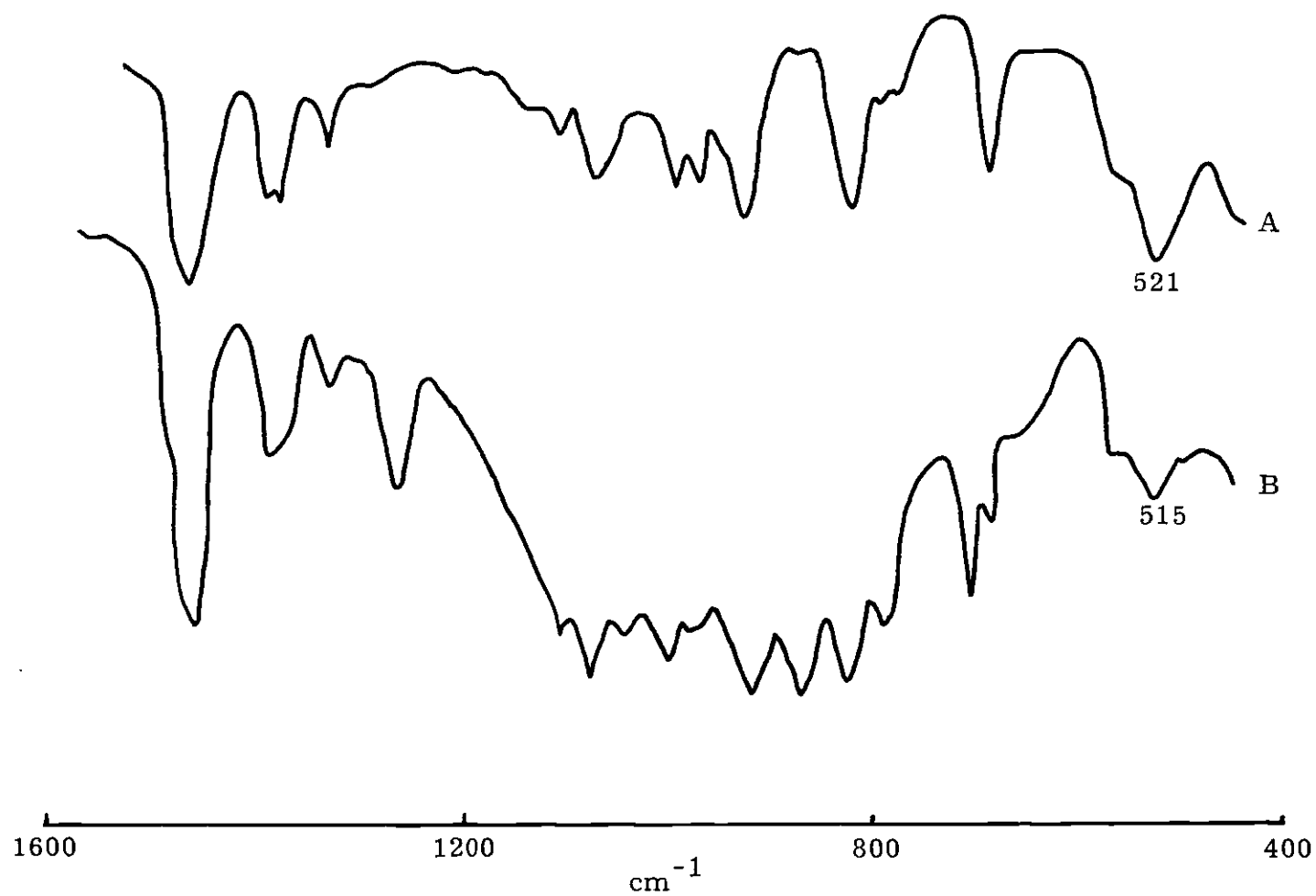
Figure 12. Infrared Spectra of (A), Di-s-butylmagnesium, and (B), Sodium Bis-di-s-butylmagnesium Hydride.

tion of the C-Mg absorption band was observed in the spectrum of the complex as well as a broad envelope indicative of magnesium-hydrogen stretching vibrations.

$(s-C_4H_9)_2Mg$ + LiH in Benzene

Although several attempts were made to prepare a complex by mixing lithium hydride and di-s-butylmagnesium in benzene, all of these were unsuccessful. Even when extremely reactive lithium hydride, prepared in an autoclave via the low temperature hydrogenation of t-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 to that of di-s-butylmagnesium in benzene. Analysis revealed that none of the lithium hydride had dissolved and all of the magnesium remained in solution.

$(s-C_4H_9)_2Mg$ + 2KH in Benzene

Repeated attempts were made to prepare an authentic 2:1 complex by mixing potassium hydride with di-s-butylmagnesium 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-s-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 to the solid described above.

The exact nature of the metallated species is uncertain. Hydrogenolysis of the solid which resulted when two equivalents of potassium hydride were stirred with one equivalent of di-s-butylmagnesium in benzene resulted in the formation of only KH and $KMgH_3$. This data would suggest that either K_2MgH_4, once formed, disproportionates readily to give KH and $KMgH_3$, or that the solid was really a mixture of different species and not an authentic 2:1 complex containing mixed alkyl-aryl groups.

The results of these experiments were quite interesting. It had been observed earlier that when a benzene solution of $KMg(s-C_4H_9)_2H$ was allowed to stand at room temperature, a precipitate containing phenyl groups bonded to magnesium was formed slowly, whereas $KMg(n-C_4H_9)_2H$ was stable under these conditions. Furthermore, if a slight excess of KH was used in the preparation of the s-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 (40) reported that n-butyllithium-N,N,N',N',-tetramethylethylenediamine metallated benzene and ferrocene. Similarly, Langer (41) reported 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.

Preparation of Complex Metal Hydrides

The importance of complex metal hydrides of aluminum and boron (e.g., $LiAlH_4$ and $NaBH_4$) in both organic and inorganic chemistry is well known (42). Complex metal hydrides of alkali metals with magnesium are as yet unknown, although analogous species containing a Group II metal have been reported (23, 24). In an attempt to prepare $LiMgH_3$, Tanaka reported that the hydrogenolysis of a mixture

of methyllithium and dimethylmagnesium in ether at elevated temper-
atures produced only lithium hydride and magnesium hydride.

The preparation of stable complexes of alkali metal hydrides
and dialkylmagnesium compounds proved to be the key step in the
preparation of species of this type. The solubility of these complexes
in benzene is unique and avoids the necessity of conducting reactions
in more basic solvents such as ethers, thus eliminating the competi-
tion between solvent and hydride ion for coordination sites in the ex-
pected product. In addition, secondary butyl groups bonded to rela-
tively electropositive metals are known to undergo hydrogenolysis
under relatively mild conditions. This factor allows reduction of
these complexes at room temperature where it is known that authentic
complexes exist. At higher temperatures, Lewis acid-base complexes
of this type may dissociate, according to the equation shown below,
leading to reduction of the independent reagents and not the complex
itself.

$$KMgR_2H \xrightarrow{\Delta} KH + MgR_2 \xrightarrow{H_2} KH + MgH_2 + 2RH \qquad (22)$$
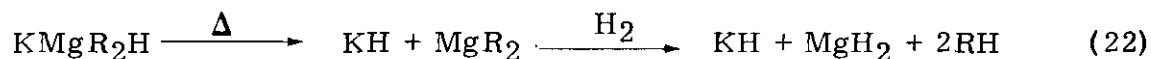
KMgH$_3$

Hydrogenolysis of a 0.5 molar solution of potassium di-s-
butylhydridomagnesium in benzene under 3000 psig hydrogen pressure
resulted in quantitative precipitation of a yellow solid, which reacted

violently when exposed to the atmosphere. Elemental analysis of this

solid revealed a K:Mg:H ratio of 1:1:3, consistent with either forma-

tion of authentic $KMgH_3$ or a physical mixture of potassium hydride

and magnesium hydride. However, X-ray analysis (Table 11) revealed

a unique diffraction pattern, different from the patterns for KH and

MgH_2 indicating that the reaction product is not a physical mixture.

The strongest line for KH (at 3.30 Å) and strongest lines for MgH_2

(at 3.19, 2.495, 1.67 and 1.59 Å) are clearly absent from the $KMgH_3$

pattern. Thus, the reaction proceeded according to equation 23.

$$KMg(s\text{-}C_4H_9)_2H + H_2 \xrightarrow{\quad 25^o \quad} KMgH_3 \qquad (23)$$
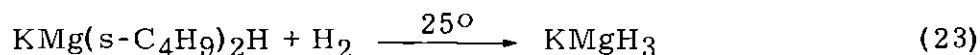
Comparison of the powder pattern data for $KMgH_3$ with that

of $KMgF_3$ suggests that these two compounds are isomorphous, a re-

sult predicted from the similar ionic radii of F^- and H^-. The Perov-

skite structure was demonstrated for $KMgF_3$ (43) and is thus implied

for $KMgH_3$. This structure is found for ABX_3 systems (A and B =

metal cations, X = anion) in which one cation is much larger than the

other. It is described as a cubic close-packed arrangement of the

anions and the larger cations, with the smaller cations occupying octa-

hedral positions in an ordered pattern (44). It is proposed that each

magnesium cation of $KMgH_3$ is surrounded by an octahedral arrange-

ment of hydride ions. The crystal structure of MgH_2 was clearly

shown (45) to be that of rutile which also involves an octahedral array

of hydride ions about each magnesium cation. The environment about

magnesium in $KMgH_3$ and MgH_2 is therefore predicted to be essentially

equivalent.

Table 11

X-Ray Powder Diffraction Data for Potassium Hydride, Magnesium

Hydride, Potassium Trihydridomagnesium and

Potassium Trifluoromagnesium

KH		MgH_2		$KMgH_3$		$KMgF_3$	
3.30	vs	3.19	vs	4.003	vw		
2.86	s	2.76	vw	3.137	vvw		
2.02	s	2.495	vs	2.835	vs	2.80	m
1.72	s	2.29	m	2.311	m	2.29	m
1.43	m	1.59	s	2.007	s	1.99	vs
1.65	m	1.67	s	1.794	vw		
1.31	m	1.50	m	1.639	s	1.625	m
1.28	m	1.42	w	1.420	m	1.408	m
1.17	m	1.36	w	1.268	m	1.259	w
1.10	m	1.335	w	1.184	m	1.201	s
1.01	w	1.246	w	1.158	w	1.150	w
		1.150	w	1.122	vw		
		1.125	w				

Independent verification of this prediction is obtained from

comparison of the infrared spectra (obtained as a Nujol mull between

KBr salt plates) for these two compounds. MgH_2 exhibits two broad

absorption envelopes centered at 1160 and 650 cm^{-1}. These are

assigned to metal-hydrogen stretching and deformation vibrations respectively. The infrared spectrum of $KMgH_3$ revealed two similarly broad absorptions centered at 1150 and 680 cm^{-1}. The absence of pronounced shifts is verification of nearly equivalent environments in these compounds.

Potassium trihydridomagnesium is insoluble in common hydrocarbon and ether solvents, stable to disproportionation and does not cleave ether solvents. A study of the thermal properties of $KMgH_3$ as determined by simultaneous DTA-TGA analysis revealed a weak, broad exothermic effect at $\sim 300^oC$ consistent with disproportionation to KH and MgH_2 followed by endothermic effects at 320 and 420^oC due to decomposition of MgH_2 and KH respectively.

$KMgH_3$ was also prepared by a pyrolytic olefin elimination reaction when $KMg(s-C_4H_9)_2H$ was heated in light mineral oil at 80^oC under vacuum.

$$KMg(s-C_4H_9)_2H \longrightarrow KMgH_3 + 2C_4H_8 \tag{24}$$
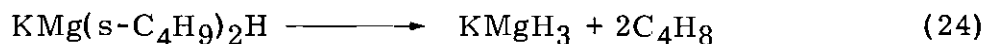
$NaMg_2H_5$ and $NaMgH_3$

Hydrogenolysis of a 0.3 molar solution of the 1:2 complex, prepared by mixing sodium hydride and di-s-butylmagnesium in benzene, under 1500 psig hydrogen pressure at 25^oC for four hours resulted in quantitative precipitation of a light yellow solid which reacted

violently when exposed to the atmosphere. Analysis revealed a

Na:Mg:H ratio of 0.90:2.00:4.00. No butane was produced on hydrol-

ysis. The elemental analysis is consistent with the formation of

either an authentic complex, $NaMg_2H_5$, a mixture of $NaMgH_3$ and

MgH_2 or a mixture of NaH and 2 molar equivalents of MgH_2. The IR

spectrum contained a continuous broad absorption throughout the

Mg-H stretching and deformation region.

A study of the properties of this compound by simultaneous

DTA-TGA analysis revealed an exotherm at 115°C and 3 endotherms

at 300, 320 and 340°C. There was no weight loss associated with the

exotherm and a continuous weight loss corresponding to 8% of the

sample weight was recorded over the three endotherms. Theoretically

the weight percent hydrogen in this sample was 6.6%. The exotherm

at 115°C must correspond to either the thermal dissociation of

$NaMg_2H_5$ or some molecular rearrangement in the crystal structure

since no weight loss was associated with it. The endotherms are

harder to assign, but must in part be due to the dissociation of the

resulting species.

The X-ray powder pattern exhibited by this solid revealed

only two very broad diffuse lines. When a portion of this solid was

heated to 150°C and then cooled, the powder pattern of the "rearranged"

species exhibited lines clearly indicative of MgH_2 as well as a second

set of lines which by analogy to the powder pattern of $NaMgF_3$ (32) was assigned to $NaMgH_3$. These results are shown in Table 12.

Table 12

X-Ray Powder Diffraction Data for Sodium Hydride,

Sodium Trihydridomagnesium and

Sodium Triflouromagnesium

NaH		NaMgF$_3$		NaMgH$_3$[a]	
5.72	vvw	3.83	m	3.85	vw
3.13	w	2.71	m	3.16	br-s
3.03	vw	2.30	w	3.00	w
2.82	vs	2.23	w	2.83	vvw
2.72	vw	2.20	vw	2.75	vs
2.44	s	1.92	vs	2.50	w
2.37	w	1.58	vw	2.26	w
1.73	m	1.55	w	1.92	m
1.63	vw	1.35	vw	1.67	w
1.47	m			1.56	m
1.41	w			1.35	w
1.22	w			1.21	w
1.12	w			1.11	w
1.09	w			1.03	w

[a]Many of the weak lines are actually due to MgH_2.

The pattern of $NaMgH_3$ is very similar to that of $KMgH_3$; the only difference is that the lines are indicative of a smaller unit cell than in the potassium case. A slightly distorted Perovskite structure has also been demonstrated for $NaMgF_3$ (31).

A second experiment was carried out in which the 1:2 complex was pyrolyzed in mineral oil at 80°C under vacuum. Analysis of the resulting solid revealed a Na:Mg:H ratio of 0.88:2.00:4.52. The exotherm observed at 115°C was clearly absent in the DTA-TGA thermogram of this solid, and only two endotherms (at 320 and 340°C) were observed. Although a small shoulder was present on the low temperature side of the 320°C endotherm, the powder pattern of this solid revealed lines for both MgH_2 and $NaMgH_3$. These data indicate that at 80°C $NaMg_2H_5$ dissociates slowly according to equation 25.

$$NaMg_2H_5 \longrightarrow NaMgH_3 + MgH_2 \qquad (25)$$
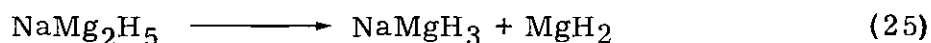
$LiMgH_3$

Hydrogenolysis of a 0.46 molar solution of the complex prepared by mixing s-butyllithium and di-s-butylmagnesium under 4000 psig hydrogen pressure at 25°C for 4 hours quantitatively precipitated a gray white solid. Elemental analysis indicated a Li:Mg:H ratio of 0.95:1.0:2.80.

The X-ray diffraction pattern of this solid showed lines attributable to LiH and MgH_2 as well as one unknown line, all of which were broad and diffuse indicating small particle size. Thermal analysis of the hydrogenation product revealed a strong endotherm at 310°C accompanied by the loss of hydrogen (90% of calculated). A weak

endotherm occurs at 480°C accompanied by loss of hydrogen (10% of calculated). The 480°C endotherm is assigned to the decomposition of LiH by comparison to the thermogram of an authentic sample of LiH. The endotherm at 310°C may then be attributed to simultaneous decomposition of MgH_2 and some $LiMgH_3$. This interpretation would indicate a mixture of 33% LiH and MgH_2 and 67% $LiMgH_3$.

CHAPTER IV

CONCLUSIONS

When dialkylmagnesium compounds and alkali metal alkyls were mixed in either ether or hydrocarbon solvents, equilibrium mixtures resulted in which complexes existed in equilibrium with the reactants although the position of the equilibrium was found to be dependent on the molar ratio of the reactants. Thus any further reactions attempted using these solutions will result in the formation of products arising from all of the species present in solution under the reaction conditions employed.

The reaction of alkali metal hydrides with dialkylmagnesium compounds in ether solvents produced intermediate complexes in which the nucleophilic character of the alkyl group was greatly enhanced by complexation with the hydride, resulting in ether cleavage. The one exception was the reaction of potassium hydride with diphenylmagnesium in ether. In this case precipitation of the complex must have occurred prior to cleavage.

Those complexes which were soluble in benzene were much more stable so long as the alkali metal:magnesium ratio was 1:1 or less. Furthermore, the fact that potassium di-s-butylhydridomagnesium was stable in the presence of limited amounts of ether at 25°C

for periods of at least one hour suggested that the cleavage reactions observed in ether were the results of higher temperatures and/or longer reaction times. Solvent interaction in benzene was observed, however, in the attempted preparation of an authentic 2:1 complex from the reaction of di-s-butylmagnesium with two equivalents of potassium. In this case, complexation with a second molecule of potassium hydride was necessary before the nucleophilic character of the butyl group had been enhanced enough to metallate benzene.

The preparation of complex metal hydrides containing a magnesium atom was achieved for the first time. The key step in this synthesis was the preparation of stable precursors. The stoichiometries of the complexes formed reflected generally on the composition of the solution which was reduced. In this connection, $KMgH_3$ was prepared from the 1:1 complex, $KMg(s-C_4H_9)_2H$; $NaMg_2H_5$ was prepared from the 1:2 complex, $NaH \cdot 2(s-C_4H_9)_2Mg$; $LiMgH_3$ was prepared from a solution in which the 1:1 complex, $LiMg(s-C_4H_9)_3$, was evidently in equilibrium with some of the reactants. Simultaneous DTA-TGA analysis revealed $LiMgH_3$, $NaMgH_3$ and $KMgH_3$ are stable to $\sim 300^{\circ}C$.

LITERATURE CITED[a]

1. E. C. Ashby and R. C. Arnott, J. Organometal. Chem., 14, (1968) 1.

2. F. W. Walker and E. C. Ashby, J. Am. Chem. Soc., 91, (1969) 3845.

3. W. Schlenk and W. Schlenk, Jr., Ber., 62B, (1929) 920.

4. C. W. Kamienski and J. F. Eastham, J. Organometal. Chem., 8, (1967) 542.

5. H. Gilman and F. Schulze, J. Am. Chem. Soc., 49, (1927) 2328.

6. C. W. Kamienski and J. F. Eastham, J. Org. Chem., 34, (1969) 1116.

7. W. Strohmeier and F. Seifert, Ber., 94, (1961) 2356.

8. M. S. Kharasch and D. Rheinmuth, Grignard Reactions of Non-metallic Substances, Prentice-Hall, Inc., New York, (1954).

9. E. Weiss, J. Organometal. Chem., 2, (1964) 314.

10. L. I. Zakharkin and V. V. Gavrilenko, Zhumal Obshchei Khemii, 32, No. 3, (1962) 689.

11. D. T. Hurd, J. Org. Chem., 13, (1948) 711.

12. S. Toppet, G. Slinckx and G. Smets, J. Organometal. Chem., 9, (1967) 205.

13. E. Weiss and R. Wolfrum, J. Organometal. Chem., 12, (1968) 257.

14. E. Weiss and R. Wolfrum, Ber., 101, (1968) 35.

---

[a]For complete titles to all journals referred to, see Chemical Abstracts, 50, (1950) 15.

15. G. Wittig, F. J. Meyer and G. Lange, _Annalen_, 571, (1951) 167.

16. L. M. Seitz and T. L. Brown, _J. Am. Chem. Soc._, 88, (1966) 2174, 4140; _Ibid._, 89, (1967) 1607.

17. L. M. Seitz and B. F. Little, _J. Organometal. Chem._, 18, (1969) 227.

18. G. E. Coates and J. A. Heslop, _J. Chem. Soc._, (A), (1968) 514.

19. G. E. Coates and G. F. Cox, _Chem and Ind._, (1962) 269.

20. P. Kobetz and W. E. Becker, _J. Inorg. Chem._, 2, (1962) 859.

21. G. Kubas and D. R. Shriver, Abstracts of Papers No. 69, 157th A.C.S. National Meeting, (1969).

22. G. Wittig and P. Hornberger, _Annalin_, 577, (1952) 11.

23. G. E. Coates and R. E. Pendlebury, _J. Chem. Soc._, (A), (1970) 156.

24. C. E. Messer, J. C. Eastman, R. G. Mers and A. J. Maeland, _J. Inorg. Chem._, 3, (1964) 776.

25. J. Tanaka and R. Westgate, Abstracts of Papers No. 155, 157th A.C.S. National Meeting, (1969).

26. T. L. Brown, D. W. Dickerhoof, D. A. Bafus and G. L. Morgan, _Rev. Sci. Instrum._, 33, (1962) 491.

27. J. R. Sanders, Doctoral Dissertation, Georgia Institute of Technology, (1970).

28. D. F. Shriver, _The Manipulation of Air Sensitive Compounds_, McGraw-Hill, New York, (1969).

29. C. W. Kamienski, Doctoral Dissertation, University of Tennessee, (1967).

30. M. Schlosser and V. Ladenburger, _J. Organometal. Chem._, 8, (1967) 193.

31. E. C. T. Chao, H. T. Evans, Jr., B. J. Skinner and C. Milton, The American Minerologist, 46, (1961) 379.

32. E. C. Ashby, F. W. Walker and H. M. Neumann, J. Chem. Soc., (D), (1970) 330.

33. E. Weiss, J. Organometal. Chem., 4, (1965) 101.

34. R. M. Salinger and H. S. Mosher, J. Am. Chem. Soc., 86, (1964) 1782.

35. T. Holm, Acta Chemica Scandinavica, 19, (1965) 1819.

36. R. West and W. Glaze, J. Am. Chem. Soc., 83, (1961) 3580.

37. E. Weiss and E. A. C. Lucken, J. Organometal. Chem., 2, (1964) 197.

38. L. M. Seitz and T. L. Brown, J. Am. Chem. Soc., 89, (1967) 1602.

39. E. C. Ashby and R. C. Arnott, J. Organometal. Chem., 21, (1970) 29.

40. M. D. Rausch and D. J. Ciappenelli, J. Organometal. Chem., 10, (1967) 127.

41. A. W. Langer, Trans. N. Y. Acad. Sci., 27, (1965) 745.

42. N. G. Gaylord, Reductions with Complex Metal Hydrides, Interscience Publishers, New York, 1956.

43. R. C. DeVries and Rustum Roy, J. Am. Chem. Soc., 75, (1953) 2479.

44. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, John Wiley and Sons, Inc., New York, (1964) 668.

45. K. M. Mackay, Hydrogen Compounds of the Metallic Elements, Wilmer Brothers Limited, Birkenhead, Cheshire, (1966) 40.

VITA

Robert C. Arnott was born in Cornwall, New York, on August 18, 1941. He attended both primary and secondary schools in Cornwall.

His undergraduate work was done at Clarkson College of Technology, Potsdam, New York, where he received a Bachelor of Science degree in chemistry in 1963.

Graduate work was begun at the Georgia Institute of Technology in 1963 and he started research under the direction of Dr. E. C. Ashby in 1964. He was awarded a Master of Science degree in 1967. He then continued his research under the direction of Dr. Ashby.

The author is married to the former Gemma M. Morrison.