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# Reactions of Alkali Metal Hydrides with Magnesium Alkyls. Preparation of $MMgR_2H$ and $MMg_2R_4H$ Compounds[1,2]

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Lithium hydride was shown not to react with dimethylmagnesium in ether; however, in THF intermediate complexes formed which cleaved the THF solvent. Ether cleavage also resulted when LiH and NaH were allowed to react with $(C_6H_5)_2Mg$ in THF. On the other hand, a stable insoluble complex $[KMg_2(C_6H_5)_4H]$ was formed when KH and $(C_6H_5)_2Mg$ were allowed to react in ether solvent. In benzene solvent alkali metal hydrides reacted with $R_2Mg$ compounds to form stable soluble complexes, e.g., $NaMg_2(s\text{-}C_4H_9)_4H$, $KMg(s\text{-}C_4H_9)_2H$, and $KMg(n\text{-}C_4H_9)_2H$. The 1:1 complex of KH and $(s\text{-}C_4H_9)_2Mg$ prepared in benzene is soluble in THF and reacts with LiBr to form $LiMg(s\text{-}C_4H_9)_2H$ and KBr. The corresponding reaction in ether forms the soluble complex $LiMg_2(s\text{-}C_4H_9)_4H$ and precipitates a mixture of KBr and LiH. The reaction of $KMg(s\text{-}C_4H_9)_2H$ with tri-*n*-octyl-*n*-propylammonium bromide in THF produced $NR_4Mg(s\text{-}C_4H_9)_2H$ and the reaction of $KMg(s\text{-}C_4H_9)_2H$ with NaI in THF resulted in the precipitation of KI and the formation of $NaMg(s\text{-}C_4H_9)_2H$. A total of eight new complex metal hydrides of magnesium were prepared.

## Introduction

The reaction of diethylmagnesium with lithium, sodium, and potassium hydrides is reported to result in complex formation; however, extensive ether cleavage resulted and the complexes could not be isolated.[3] Although stable complexs of beryllium and zinc such as $NaH\cdot Et_2Be$,[4] $NaH\cdot 2Et_2Zn$,[5,6] $LiH\cdot Ph_2Zn$, and $LiH\cdot Ph_2Be$,[7] are known, still no stable complexes of alkali metal hydrides and $R_2Mg$ compounds have been reported.

Our interest in alkali metal complexes of magnesium alkyls resides in the potential of these compounds as intermediates in the preparation of alkali metal complex hydrides of magnesium, e.g., $KMgH_3$, $LiMg_2H_5$, etc. Since previous attempts to prepare $LiMgH_3$ by the reaction of LiH and $MgH_2$ failed,[8] it was felt that either hydrogenolysis or reduction of compounds such as $MMgR_2H$ might result in the formation of $MMgH_3$.

$$MMgR_2H \begin{cases} \xrightarrow{H_2} MMgH_3 + 2RH \\ \xrightarrow{LiAlH_4} MMgH_3 + LiAlR_2H_2 \end{cases} \qquad (1)$$

Since Coates and coworkers[3] had already attempted to prepare $MMgR_2H$ compounds in ether solvents and had observed extensive ether cleavage, it was clear that such complexes would have to be prepared in nonether solvents. Although most $R_2Mg$ compounds are not soluble in hydrocarbon solvents, it has been recently found that $(s\text{-}C_4H_9)_2Mg$ is soluble in benzene.[9] Therefore, it was decided to attempt to carry out these reactions in benzene solvent and hence have at least one reactant in solution and also avoid ether cleavage. Reactions between NaH and KH with $(s\text{-}C_4H_9)_2Mg$ in benzene did proceed nicely to form benzene soluble complexes.[2] The reactions were easily monitored by observing the solubilization of the alkali metal hydride as the reaction proceeded.

## Experimental Section

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

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

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

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

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

**Analytical Procedures.** Gas analyses were performed by hydrolyzing a measured or weighed sample inside a high vacuum line with ~6 *M* hydrochloric acid and passing the evolved gases through Dry Ice-acetone and liquid nitrogen traps. Hydrogen was transferred to a calibrated measuring bulb with a Toepler pump. Butane was collected in a separate measured portion of the vacuum line. Magnesium was determined by EDTA titration at pH 10 using Eriochrome Black T as an indicator. Aluminum, when present, was masked with triethanolamine. Aluminum determinations were carried out by adding an excess of standard EDTA and then back titrating at pH 4 with standard zinc acetate in water-ethanol with dithizone as indicator. Halide determinations were performed by the Volhard titration. Alkali metals were determined by flame photometry using appropriate filters.

**Materials.** All solvents were distilled immediately prior to use. Tetrahydrofuran and benzene (Fisher Certified reagent grade) were distilled under nitrogen over $NaAlH_4$ and diethyl ether (Fisher reagent) over $LiAlH_4$. Benzyl chloride (Fisher reagent grade) was distilled over $P_2O_5$ under reduced pressure and 2-chloropropane and 1-chloropentane (Eastman Organic Chemicals) were dried and distilled over $MgSO_4$ prior to use. Grignard grade magnesium turnings were used except in the preparation of dimethylmagnesium when triply sublimed magnesium (Dow Chemical Co.) was employed. *sec*-Butyllithium was obtained as a 11.9% solution in hexane from the Foote Mineral Co. and stored at -20° until ready to use. Methyllithium used was a 5.0% solution in diethyl ether obtained from the Lithium Corporation of America. Lithium bromide and lithium iodide (Foote Mineral Co.) were dried at 130° under vacuum for 24 hr and used without further purification. Tri-*n*-octyl-*n*-propylammonium bromide (Eastman Organic Chemicals) was dried at 55° under vacuum for 2 days and used without any subsequent purification. Ultrapure hydrogen (99.9995%) obtained from Matheson Corporation was employed in hydrogenation experiments. Dimethylmercury was obtained from Orgmet, Inc., and used without further purification. Potassium and sodium hydride (as a suspension in mineral oil), $LiAlH_4$, and $NaAlH_4$ were obtained from Ventron Metal Hydrides

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

| d | | | |
|---|---|---|---|
| KH + $2Mg(C_6H_5)_2$ | KH + $Mg(C_6H_5)_2$ | 2KH + $Mg(C_6H_5)_2$ | 5KH + $Mg(C_6H_5)_2$ |
| | 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 |

Division. Solutions of $LiAlH_4$ and $NaAlH_4$ in diethyl ether or tetrahydrofuran were prepared by making a slurry of the compounds in the respective solvents and stirring for 48 hr, followed by centrifugation and filtration. All solutions were freshly analyzed immediately before use. Other materials such as $(CH_3)_2Mg$[12] and $(s\text{-}C_4H_9)_2Mg$[9] were prepared according to methods described previously. Active NaH was prepared by hydrogenation of 0.5 mol of sodium in 150 ml of benzene at 400°F and 3000 psi $H_2$ in a 300 ml Magne-stirrer autoclave. The Na:H ratio was 1.0:1.0. Active potassium hydride was prepared similarly except that the reaction temperature was 300°F. Active LiH was prepared by reaction of *tert*-butyllithium (150 ml of 1.25 *M* solution) in pentane with hydrogen at 3000 psi at room temperature for 16 hr. The Li:H ratio of the resulting slurry was 1.0:1.0.

**Reactions of Alkali Metal Hydrides with Magnesium Alkyls and Aryls. Preparation of $KMg_2(C_6H_5)_4H$ in Ether.** Potassium hydride and $(C_6H_5)_2Mg$ were mixed in diethyl ether in several stoichiometries to give K:Mg ratios from 0.33:1 to 5:1. In all cases an insoluble complex formed.

In a typical reaction $(C_6H_5)_2Mg$ (50 ml of a 0.8 *M* solution in diethyl ether, 40 mmol) was added to KH (3.20 g, 80 mmol) in 50 ml of ether. The mixture was stirred for 3 days and filtered. Analysis of the filtrate revealed that all of the magnesium containing species had precipitated.

In a similar reaction where the initial K:Mg ratio was 1:3, only 66% of the magnesium containing species precipitated, leaving the remainder of the $(C_6H_5)_2Mg$ in solution. In this case a 1:2 complex $KH{\cdot}2Mg(C_6H_5)_2$ was formed. The solid residues were analyzed and gave the following results. (Benzene was determined by difference.) Anal. Calcd for $KH{\cdot}2Mg(C_6H_5)_2$: K, 9.85; Mg, 12.25; $C_6H_6$, 77.65; H, 0.25. Found: K, 10.52; Mg, 11.0; $C_6H_6$,78.3; H, 0.25. When 2 equiv of $(C_6H_5)_2Mg$ was allowed to react with 1 equiv of KH, analysis indicated a K:Mg:H ratio of 1.18:2.00:1.26. The X-ray diffraction pattern indicated occluded KH. If this is subtracted from the analysis, the ratio is 1.00:2.00:1.08. (Found: K, 9.90; Mg, 11.3; $C_6H_6$,78.54; H, 0.25.) Calcd for $KH{\cdot}Mg(C_6H_5)_2$: K, 17.94; Mg, 11.10; $C_6H_6$, 70.50; H, 0.46. Found: K, 16.35; Mg, 10.20; $C_6H_6$, 73.09; H, 0.36. Calcd for $2KH{\cdot}Mg(C_6H_5)_2$: K, 30.40; Mg, 9.40; $C_6H_6$, 59.40; H, 0.80. Found: K, 29.20; Mg, 9.40; $C_6H_6$, 60.60; H, 0.72. Calcd for $5KH{\cdot}Mg(C_6H_5)_2$: K, 51.60; Mg, 6.42; $C_6H_6$, 40.76; H, 1.32. Found: K, 54.70; Mg, 6.56; $C_6H_6$, 38.49; H, 1.25. The X-ray powder pattern for each of these solids is reported in Table I.

**Preparation of $NaMg_2(s\text{-}C_4H_9)_4H$ in Benzene.** Di-*sec*-butylmagnesium (101 ml of a 0.496 *M* solution, in benzene, 50 mmol) was added to NaH (0.6559 g, 27.4 mmol) and stirred for 2 days. Analysis of the resulting solution showed a $Na:Mg:C_4H_9:H$ ratio of 0.90:2.0:3.96:0.85. The NMR spectrum and the ir spectrum of the solution were significantly different from that of $Mg(s\text{-}C_4H_9)_2$.

In a similar experiment, 1 equiv of NaH and $Mg(s\text{-}C_4H_9)_2$ were combined under the above conditions. Once the ratio of Na:Mg in solution reached 0.45:1.0, no further uptake of sodium was observed even after several days.

**Preparation of $KMg(s\text{-}C_4H_9)_2H$ in Benzene.** Potassium hydride (1.138 g, 28.4 mmol) was slurried with 50 ml of freshly distilled benzene and added to $(s\text{-}C_4H_9)_2Mg$ (95 ml of a 0.30 *M* solution, 28.4 mmol) with rapid stirring. After 20 hr the mixture was filtered producing a straw colored filtrate and a darker residue (~100 mg). Analysis of an aliquot of the solution showed a $K:Mg:C_4H_9:H$ ratio of 1.0:1.0:1.9:0.95. The yield was >90%. Cryoscopic molecular weight measurements (Figure 2) indicated a monomer–dimer equilibrium over the concentration range 0.06–0.16 *m*.

Successful synthesis was also carried out in benzene–cyclohexane mixtures. The complex $KMg(s\text{-}C_4H_9)_2H$ was insoluble in pure alkanes, however, and attempted synthesis in cyclohexane alone proved unsatisfactory.

**Preparation of $KMg(n\text{-}C_4H_9)_2H$ in Benzene.** Potassium hydride (28.8 mmol) in 190 ml of freshly distilled benzene was added to $(n\text{-}C_4H_9)_2Mg$ (31.0 mmol) and stirred at 40° for 48 hr. Analysis of an aliquot of the filtrate revealed a K:Mg ratio of 0.97:1.0. The filtrate was 0.11 *M* in complex (70% yield). Cryoscopic molecular weight measurements (Figure 2) indicated a dimeric species in benzene over the concentration range 0.08–0.32 *m*.

**Attempted Preparation of $K_2Mg(s\text{-}C_4H_9)_2H_2$ in Benzene.** Potassium hydride (1.193 g, 29.8 mmol) slurried with 50 ml of benzene was added to $KMg(s\text{-}C_4H_9)_2H$ (99.5 ml of a 0.306 *M* solution, 30.4 mmol). The mixture was stirred for 18 hr and then filtered. A light straw colored solution and a tan solid were separated. Analysis of the filtrate revealed that nearly quantitative precipitation of the magnesium containing species had occurred. Analysis of the solid gave the following results. Anal. Calcd for $K_2Mg(s\text{-}C_4H_9)_2H_2$: Mg, 11.10; Bu, 52.20; H, 0.95; Mg:Bu:H = 1.0:2.0:2.0. Found: Mg, 10.2; Bu, 16.20; H, 0.89; Mg:Bu:H = 1.0:0.67:2.1.

The ir spectrum of this solid showed the strong C–Mg stretching band at 521 $cm^{-1}$, attributable to butyl–magnesium stretching, was severely diminished in the supposed 2:1 complex. In addition, when the solid was added to a Dry Ice–ether slurry under nitrogen and the resulting mixture acidified, appreciable quantities of benzoic acid and methylbutyric acid were produced. Similar results were obtained when 2 equiv of KH was allowed to react with 1 equiv of $(s\text{-}C_4H_9)_2Mg$ under similar reaction conditions.

**Metal Exchange Reactions. Preparation of $LiMg_2(s\text{-}C_4H_9)_4H$. Reaction of $KMg(s\text{-}C_4H_9)_2H$ with Lithium Bromide in Ether.** $KMg(s\text{-}C_4H_9)_2H$ was prepared by the reaction of potassium hydride with $(s\text{-}C_4H_9)_2Mg$ in benzene. The benzene was removed under vacuum resulting in an orange-red viscous residue. This was dissolved in diethyl ether to give a clear solution and used immediately. Lithium bromide (2.763 g, 31.8 mmol) was dissolved in 100 ml of ether and added to 141.3 ml of the $KMg(s\text{-}C_4H_9)_2H$ solution in ether (0.225 *M* in $K^+$; 31.8 mmol) with vigorous stirring. The mixture was stirred for 6 hr and then filtered. The white precipitate was washed several times with ether and dried under vacuum at room temperature for 4 hr. The light orange filtrate on analysis gave the following ratios: $Li:Mg:C_4H_9:H$ = 0.56:1.00:2.0:0.50. Potassium and bromine were absent. The precipitate gave the following ratios: Li:K:H:Br = 1.0:2.0:1.0:1.9.

**Preparation of $LiMg(s\text{-}C_4H_9)H$. Reaction of $KMg(s\text{-}C_4H_9)_2H$ with LiBr in THF.** To lithium bromide (8.52 g, 98.1 mmol) dissolved in 100 ml of THF was added 255.7 ml of a 0.384 *M* solution of $KMg(s\text{-}C_4H_9)_2$ in THF. A precipitate formed immediately and was shown to be KBr. The filtrate, on solvent removal under vacuum, produced a viscous, orange material. Analysis produced the following ratios: $Li:Mg:C_4H_9:H$ = 1.00:1.12:2.04:0.93. Potassium and bromide analyses were negative.

**Preparation of $NaMg(s\text{-}C_4H_9)_2H$. Reaction of Sodium Iodide with $KMg(s\text{-}C_4H_9)_2H$ in THF.** Sodium iodide solution (105 ml) in THF (0.252 *M*; 26.5 mmol) was added, with stirring, to 125 ml of a freshly prepared solution of $KMg(s\text{-}C_4H_9)_2H$ in THF (25.2 mmol in Mg). An immediate creamy yellow precipitate formed. After stirring for 4 hr, the mixture was filtered and the precipitate washed with several small portions of THF. The precipitate was found to be potassium iodide upon analysis. The filtrate exhibited a composition corresponding to $NaMg(s\text{-}C_4H_9)_2H$.

**Preparation of $R_4NMg(s\text{-}C_4H_9)_2H$. Reaction of $KMg(s\text{-}C_4H_9)_2H$**

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

## Results and Discussion

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

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

In contrast, the reaction of KH with $(C_6H_5)_2Mg$ in ether, at K:Mg ratios ranging from 0.3:1 to 5:1, resulted in complex formation. Precipitation of the complex must have occurred faster than ether cleavage could take place. When KH and $(C_6H_5)_2Mg$ were mixed in 1:3 molar ratio, 66% of the magnesium containing compound precipitated from solution. Since only $^2/_3$ of the magnesium species precipitated, the limiting ratio of K:Mg in the complex must therefore be 1:2.

$$KH + 2(C_6H_5)_2Mg \rightarrow KMg_2(C_6H_5)_4H \qquad (2)$$

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

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

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

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

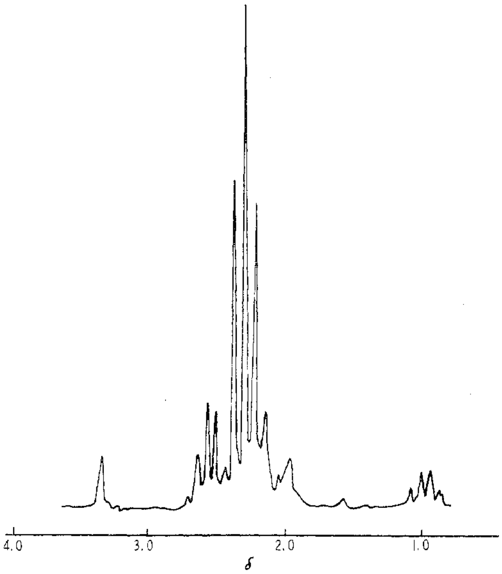


Figure 1. NMR spectrum of potassium di-*sec*-butylhydridomagnesium in benzene.

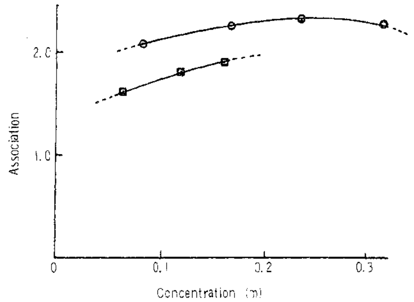


Figure 2. Association of potassium di-*sec*-butylhydridomagnesium (□) and potassium di-*n*-butylhydridomagnesium (○) in benzene.

$$KH + (s\text{-}C_4H_9)_2Mg \rightarrow KMg(s\text{-}C_4H_9)_2H \qquad (3)$$

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

**Reaction of KH with $(n\text{-}C_4H_9)_2Mg$ in Benzene.** A second complex was prepared analogous to that described above in which the R group was *n*-butyl instead of *sec*-butyl. Initially, potassium hydride was stirred with an equivalent amount of $(n\text{-}C_4H_9)_2Mg$ in benzene at 40°. After 48 hr analysis of an aliquot of the supernatant revealed a K:Mg ratio of 0.97:1.0 and the concentration of magnesium was shown to be 0.11 mmol/ml. As was observed in the previous example, a soluble complex was not formed in cyclohexane.

$$KH + (n\text{-}C_4H_9)_2Mg \rightarrow KMg(n\text{-}C_4H_9)_2H \qquad (4)$$

The NMR spectrum of a 0.378 *M* solution of $KMg(n\text{-}C_4H_9)_2H$ in benzene at 25° was consistent with complex formation. The triplet attributed to the $\alpha$ methylene protons was observed at $\delta$ -0.59 and a low intensity signal was observed at $\delta$ 3.47 which was attributed to the hydridic hydrogen. Cryoscopic molecular weight measurements (Figure 2) indicate that $KMg(n\text{-}C_4H_9)_2H$ is dimeric over the concentration range 0.08–0.32 *m* in benzene.

**Reaction of NaH with $(s\text{-}C_4H_9)_2Mg$ in Benzene.** When sodium hydride and $(s\text{-}C_4H_9)_2Mg$ were stirred in benzene, a complex was formed in which the Na:Mg ratio was 1:2.

$$NaH + 2(s\text{-}C_4H_9)_2Mg \rightarrow NaMg_2(s\text{-}C_4H_9)_4H \qquad (5)$$

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

The NMR spectrum of a 0.23 *M* solution of the complex in benzene was recorded at room temperature using benzene as the internal standard. The spectrum was similar to that observed for $KMg(s\text{-}C_4H_9)_2H$ with the hydridic hydrogen observed at $\delta$ 3.40.

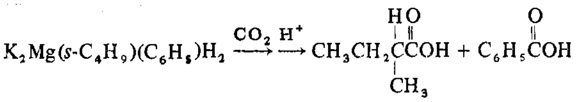
**Reaction of LiH with $(s\text{-}C_4H_9)_2Mg$ in Benzene.** Several attempts to prepare a complex by mixing lithium hydride and $(s\text{-}C_4H_9)_2Mg$ in benzene were unsuccessful. Even when extremely reactive lithium hydride, prepared by low temperature hydrogenation of *tert*-butyllithium in pentane, was used, no reaction was observed after several days. The NMR spectrum of the filtrate obtained from this reaction mixture was identical with that of $(s\text{-}C_4H_9)_2Mg$ in benzene. Analysis revealed that none of the lithium hydride had dissolved and all of the magnesium remained in solution.

**Reaction of Excess KH with $(s\text{-}C_4H_9)_2Mg$ in Benzene.** Repeated attempts were made to prepare an authentic 2:1 complex by mixing potassium hydride with $(s\text{-}C_4H_9)_2Mg$ in benzene in a 2:1 molar ratio. Invariably, all of the magnesium containing species precipitated and could be isolated by filtration of the reaction mixture. Analysis of this residue indicated that extensive metallation of the solvent had occurred. When a portion of the solid was carboxylated both 2-methylbutyric acid and benzoic acid were produced. The X-ray powder diffraction pattern revealed that some potassium hydride had been occluded in the solid. Similar results were obtained when a previously prepared solution of potassium di-*sec*-butylhydridomagnesium was added to a benzene slurry of potassium hydride. All of the magnesium containing species again precipitated and the residue was found to be identical with the solid described above.

The results of these experiments were quite interesting. It had been observed earlier that when a benzene solution of $KMg(s\text{-}C_4H_9)_2H$ was allowed to stand at room temperature, a precipitate containing phenyl groups bonded to magnesium was formed slowly, whereas $KMg(n\text{-}C_4H_9)_2H$ was stable under these conditions. Furthermore, if a slight excess of KH was used in the preparation of the *sec*-butyl complex, the yield of 1:1 complex was significantly decreased. Apparently complexation with a second equivalent of potassium hydride greatly enhanced the ionic character of the C–Mg bond and metallation of the solvent occurred farily 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.

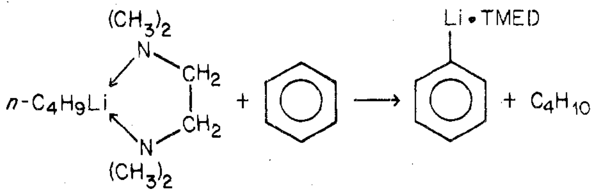
$$\left.\begin{array}{l} 2KH + (s\text{-}C_4H_9)_2Mg \\ KH + KMg(s\text{-}C_4H_9)_2H \end{array}\right] \rightarrow K_2Mg(s\text{-}C_4H_9)_2H_2$$

$$K_2Mg(s\text{-}C_4H_9)_2H_2 \xrightarrow{C_6H_6} K_2Mg(s\text{-}C_4H_9)(C_6H_5)H_2 \qquad (6)$$



$$K_2Mg(s\text{-}C_4H_9)(C_6H_5)H_2 \xrightarrow{CO_2} \xrightarrow{H^+} CH_3CH_2\overset{HO}{\underset{CH_3}{C}}COH \text{(=O)} + C_6H_5\overset{O}{\overset{\|}{C}}OH \qquad (7)$$

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[13] reported that *n*-butyllithium-*N*,*N*,*N'*,*N'*,-tetramethylethylenediamine metallated benzene and ferrocene. Similarly, Langer[14] 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.



(8)

**Potassium Exchange in Reactions with $KMg(s\text{-}C_4H_9)_2H$.** Although the direct reaction of KH with $(s\text{-}C_4H_9)_2Mg$ did not proceed in tetrahydrofuran, the compound $KMg(s\text{-}C_4H_9)_2H$ prepared from benzene dissolved readily in THF. The solution was not very stable at room temperature; however, at low temperature it was found to be stable up to 5 days, and no THF cleavage was observed.

When a tetrahydrofuran solution of $KMg(s\text{-}C_4H_9)_2H$ was added to tri-*n*-octyl-*n*-propylammonium bromide in THF,

$$KMg(s\text{-}C_4H_9)_2H + N(C_8H_{17})_3(C_3H_7)Br \rightarrow N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H + KBr \qquad (9)$$

quantitative precipitation of KBr took place and the filtrate upon solvent removal produced the oily orange $N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H$. Analysis of the THF solution of this compound was not quite as difficult as the product prepared in benzene solution. The Mg:Bu:H ratios were found to be 1:1.90:0.92. The infrared spectrum of the neat material was similar to that of $KMg(s\text{-}C_4H_9)_2H$ with the characteristic broad absorption envelope between 1200 and 600 $cm^{-1}$ ($\nu$(Mg–H)).

When a freshly prepared solution of $KMg(s\text{-}C_4H_9)_2H$ in tetrahydrofuran was added to an equivalent amount of lithium bromide in THF, KBr precipitated quantitatively during overnight stirring.

$$KMg(s\text{-}C_4H_9)_2H + LiBr \xrightarrow{THF,\ 25^\circ} LiMg(s\text{-}C_4H_9)_2H + KBr \qquad (10)$$

Analysis of the clear filtrate gave the following ratios: Li:Mg:Bu:H = 1.00:1.12:2.04:0.93. Upon solvent removal under vacuum, an orange viscous material resulted. It was very difficult to remove the last traces of solvent at room temperature, even under high vacuum. The viscous product readily dissolved in benzene giving a clear orange solution. NMR spectra of this benzene solution showed the presence of a small amount of tetrahydrofuran. The infrared spectrum of this product was similar to those of the analogous potassium and tetraalkylammonium compounds. Tetrahydrofuran solutions of $LiMg(s\text{-}C_4H_9)_2H$ at room temperature are apparently more stable than that of the potassium compound. When a benzene solution of $KMg(s\text{-}C_4H_9)_2H$ was added to a lithium bromide slurry in benzene, no reaction occurred even after several days of stirring. No lithium was detected in the supernatant solution which essentially retained its original composition.

There is an interesting basic difference between the reactions of $KMg(s\text{-}C_4H_9)_2H$ with lithium bromide in THF and diethyl ether. In the case of tetrahydrofuran, $LiMg(s\text{-}C_4H_9)_2H$ is formed; however, when diethyl ether is the solvent, $LiMg_2(s\text{-}C_4H_9)_4H$ is the product.

$$2KMg(s\text{-}C_4H_9)_2H + 2LiBr \xrightarrow[25°]{Et_2O} LiMg_2(s\text{-}C_4H_9)_4H + 2KBr + LiH \tag{11}$$

The solid product obtained from this reaction was analyzed and found to be a mixture of KBr and LiH formed in 2:1 ratio. It seems reasonable to suggest that $LiMg(s\text{-}C_4H_9)_2H$ is formed in the reaction and that it slowly disproportionates to $LiMg_2(s\text{-}C_4H_9)_4H$ and LiH.

On addition of sodium iodide to $KMg(s\text{-}C_4H_9)_2H$ in THF, a quantitative precipitate of KI was obtained. Analysis of

$$KMg(s\text{-}C_4H_9)_2H + NaI \xrightarrow[25°]{THF} NaMg(s\text{-}C_4H_9)_2H + KI \tag{12}$$

the resulting solution showed a Na:Mg:Bu:H ratio of 1.00:1.07:1.87:0.92 establishing the formation of $NaMg(s\text{-}C_4H_9)_2H$ in solution.

**Registry No.** $KMg_2(C_6H_5)_4H$, 55886-10-7; $NaMg_2(s\text{-}C_4H_9)_4H$, 55886-09-4; $KMg(s\text{-}C_4H_9)_2H$, 36426-31-0; $KMg(n\text{-}C_4H_9)_2H$, 55822-78-1; $LiMg_2(s\text{-}C_4H_9)_4H$, 55886-08-3; $LiMg(s\text{-}C_4H_9)_2H$, 55822-79-2; $NaMg(s\text{-}C_4H_9)_2H$, 44889-27-2; $[(n\text{-}C_8H_{17})_3N(n\text{-}C_3H_7)]Mg(s\text{-}C_4H_9)_2H$, 55822-81-6; $(C_6H_5)_2Mg$, 555-54-4; KH, 7693-26-7; NaH, 7646-69-7; $(s\text{-}C_4H_9)_2Mg$, 17589-14-9; $(n\text{-}C_4H_9)_2Mg$, 1191-47-5.

## References and Notes

(1) This work was supported by the Office of Naval Research contract No. N00014-67-A-0519-005AD and under ONR Contract Authority No. NR093-050/7-11-69(473).

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# Intra- and Intermolecular Exchange Reactions Involving Methyl and Tolyl Derivatives of Aluminum[1]

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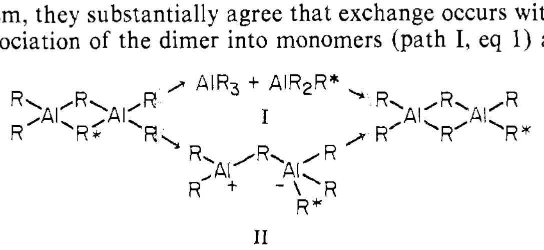
Studies of kinetic and activation parameters have been made for intramolecular bridge–terminal exchange for dimers of trimethylaluminum (TMA), tri-*p*-tolylaluminum (TPTA), and tri-*m*-tolylaluminum (TMTA). The data indicate that the first of these reactions proceeds via a dissociative mechanism as proposed earlier but the latter two most likely proceed via a mechanism involving only a partial dissociation of the electron-deficient bridge. This conclusion is supported by the unusually low activation energies of 9.7 ± 1.0 and 8.0 ± 1.0 kcal/mol, respectively, for TPTA and TMTA as well as negative entropies of activation, −9 eu for TPTA and −13 eu for TMTA. The reaction which occurs between trimethylaluminum and tetramethyldi-*p*-tolylaluminum to form pentamethyl-*p*-tolylaluminum appears to proceed via a similar mechanism with a partial dissociation of the tolyl bridges in tetramethyldi-*p*-tolylaluminum. The activation parameters for this reaction are $E_a = 11.1 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -11$ eu.

## Introduction

The exchange reaction which takes place between bridging and terminal methyl groups in the dimer of trimethylaluminum (TMA) has been studied by many workers including Brown and coworkers[2,3] and Jeffery and Mole.[4,5] While these workers differ concerning the precise details of the exchange mechanism, they substantially agree that exchange occurs with a dissociation of the dimer into monomers (path I, eq 1) and have ruled out the earlier suggested mechanism[6,7] involving the breaking of only one of the three-center bridges followed by rotation and re-formation of the second bridge (path II, eq 1). Principal support for a dissociative mechanism has been a rather large positive entropy of activation,[7] which is consistent with such a mechanism, and the fact that kinetic parameters for intermolecular exchange are quite similar to those for intramolecular exchange.[2] It has been generally assumed that intermolecular exchange would not result from an activation of the dimer by a single bridge opening (path II, eq 1), although it has been pointed out that this alternative pathway cannot be ruled out completely.[4] The major drawback to the dissociative mechanism has been the seeming discrepancy between the activation energy for the exchange process and the gas-phase dissociation energy of the TMA dimer. The activation energy for bridge–terminal exchange has been determined as 16.0 kcal/mol in cyclopentane[7] and 15.4 ± 2 kcal/mol in toluene.[2] The gas-phase dissociation energy of the TMA dimer has been determined as 20.2 ± 1 kcal/mol.[8] More recent studies have shown that the dissociation energy for the dimer in solution is less than that in the gas phase. Smith has estimated the dissociation energy of trimethyl-



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