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The preparation of stable hydride complexes of magnesium alkyls and aryls

E.C. ASHBY and R.C. ARNOTT
School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 (U.S.A.)

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There has been considerable interest in the past few years in the preparation of stable complexes of magnesium alkyls and aryls. In this connection Wittig[1] has reported the preparation and characterization of the compound $LiMgPh_3$ prepared by the reaction of PhLi and Ph_2Mg. Later Brown and co-workers studied the reactions of lithium alkyls and aryls with magnesium alkyls and aryls in diethyl ether by NMR techniques[2]. Complexes of the type, $Li_nMgR_2R'_n$, were indicated where $n = 1$, 2 or 3 depending on the nature of the R group, however the proposed compounds were not isolated. We have recently studied some of the same systems by high resolution infrared spectroscopy and find in general that when RLi and R_2Mg compounds are allowed to react in ether solvent, equilibrium mixtures results[3].

More recently a report concerning the reaction of diethylmagnesium with alkali metal hydrides in ether solvents has appeared[4]. While the authors concluded that complexes may exist in solution, extensive ether cleavage results and thus the complexes could not be isolated. Although stable alkali metal hydride complexes of beryllium[5] and zinc[6,7] are known ($NaH{\cdot}BeEt_2$, $NaH{\cdot}2ZnEt_2$), no such complexes of magnesium are known. We wish to report at this time the synthesis and isolation of several stable alkali hydride complexes of magnesium alkyls and aryls, some of which are also soluble in hydrocarbon solvent.

We first investigated the reaction of dimethyl and diphenylmagnesium with lithium, sodium and potassium hydride in diethyl ether and tetrahydrofuran. Our results were generally consistent with those reported by Coates and Heslop[4]; in most cases ether cleavage took place masking the formation and isolation of any discrete complexes. We did observe the formation of one stable complex in ether solvent when diphenylmagnesium was stirred with potassium hydride in diethyl ether at room temperature. An insoluble solid was isolated whose analysis was consistent with the formula $KH{\cdot}2MgPh_2$. (*Anal.:* Found: K, 9.90; Mg, 11.3; H, 0.265. K/Mg/H = 1.18/2.00/1.26. $KH{\cdot}2MgPh_2$ calcd.: K, 9.90; Mg, 12.3; H, 0.252. Some KH exists in the product probably as a result of occlusion. If this is subtracted from the analysis, K/Mg/H = 1.00/2.00/1.08.) Presumably the complex precipitated before ether cleavage had sufficient time to take place, thus the required amount of active hydrogen was found in the solid product. This is unlike the reaction of Et_2Mg and KH which results in extensive ether cleavage.

Of considerably more interest is the formation of stable complexes in solvents in which ether cleavage is avoided. In this connection the hydrocarbon soluble di-s-butylmagnesium recently reported by Eastham and Kamienski[8] is an excellent candidate for the preparation of stable complexes of dialkylmagnesium compounds with metal hydrides. When di-s-butylmagnesium was stirred with an equivalent amount of potassium hydride in benzene or cyclohexane, the potassium hydride dissolved. Analysis of the solution gave a K/Mg/H ratio of 1.01/1.00/1.02.

$$\mathrm{KH + s\text{-}Bu_2Mg \rightarrow KMg\text{-}s\text{-}Bu_2H} \qquad (1)$$

When the solvent was removed under vacuum a light yellow oil resulted whose infrared spectrum shows a broad absorption indicative of the Mg—H stretching vibration and a slight broadening of the absorption band at 521 cm^{-1} observed for the C—Mg stretching vibration of di-s-butylmagnesium. A cryoscopic molecular weight determination in benzene indicated a monomer—dimer equilibrium over a concentration range from 0.06—0.16 *M*. The NMR spectrum★ was also consistent with complex formation. An apparent sextet★★, attributed to the α H of the s-butyl group in di-s-butylmagnesium was centered at τ 9.81. In the KH complex, this sextet was shifted 0.87 ppm upfield and became somewhat broadened. In addition a new peak was observed at τ 6.60. Integration of the absorption peaks gives a ratio (0.83/2.00) consistent with the complex KMg-s-Bu_2H. Shriver has shown that the hydridic hydrogen in $NaH \cdot 2ZnEt_2$ gives rise to a peak in the NMR spectrum which also is remarkably low for a hydride[7].

We have observed that when (1) a benzene solution of KMg-s-Bu_2H is left standing for several days at room temperature slow precipitation of the magnesium containing species occurs and (2) that when the 1/1 complex is stirred with additional KH or when 2 moles of KH are stirred with 1 mole of s-Bu_2Mg in an attempt to prepare a 2/1 complex precipitation also occurs. In the latter case precipitation is essentially quantitative overnight. Analysis of these precipitates indicates that metallation of the benzene solvent is occurring (up to 80% exchange of butyl groups by phenyl) and is greatly enhanced by the presence of excess KH. Further attempts to prepare the complex, K_2Mg-s-Bu_2H_2 are in progress.

In studies with sodium hydride, a complex was also formed. In this case, however, two moles of magnesium reagent are required to effect solution of only one mole of sodium hydride.

$$\mathrm{NaH + 2\ s\text{-}Bu_2Mg \rightarrow NaMg\text{-}s\text{-}Bu_2H \cdot s\text{-}Bu_2Mg} \qquad (2)$$

The infrared spectrum again shows a broad absorption indicative of the Mg—H stretching vibration. The C—Mg absorption band is observed at 515 cm^{-1}, a small shift from the band at 521 cm^{-1} observed for the dialkylmagnesium itself. A new peak in the NMR spectrum is observed at τ 6.60 for the hydridic hydrogen, the apparent sextet due to the α H of the

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★All NMR spectra recorded at room temperature in benzene at ~0.5 *M* using benzene as an internal standard.

★★The coupling constants for the $-CH_3$ and $-CH_2$ groups adjacent to the α proton are very nearly equivalent.

butyl group is again shifted upfield, but in this case only 0.66 ppm. Since only one hydridic hydrogen is available in this adduct containing two magnesium atoms, less shielding should occur. Hence the shift in the sodium hydride complex should be smaller than in the 1/1 adduct with potassium hydride.

So far we have been unable to effect reaction between lithium hydride and di-s-butylmagnesium in hydrocarbon even after heating at 40° for several days. In contrast, the potassium hydride complex is formed in a few hours and the sodium hydride complex is formed in about two days.

This report contains evidence for the first soluble magnesium hydride containing species, similar to adducts reported for other Group II elements. We are continuing our studies in this area in an attempt to determine the scope of stable complex formation between alkali metal hydrides and magnesium alkyls and aryls in both polar and non-polar solvents.

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