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Preliminary communication

CYCLOPENTADIENYLMAGNESIUM HYDRIDE. A CONVENIENT SYNTHESIS AND STUDY OF REACTIONS WITH ORGANIC SUBSTRATES VIA SINGLE ELECTRON TRANSFER

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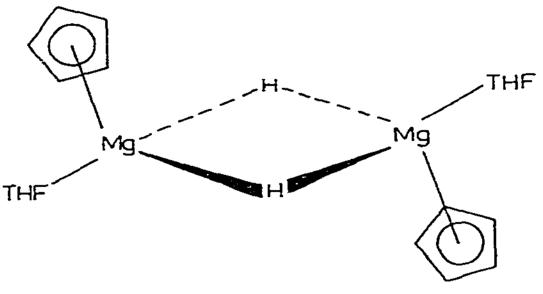
Summary

Cyclopentadienylmagnesium hydride (CpMgH) has been prepared conveniently by the reaction of magnesium hydride with cyclopentadiene in THF. The compound is soluble in THF and is a dimer in this solvent. Evidence is presented that supports the single electron transfer nature of the reactions of CpMgH with selected aromatic ketones, trityl halides and polynuclear hydrocarbons. Visible and EPR spectral studies of the colored, paramagnetic intermediates are described.

Although simple and complex metal hydrides of aluminum and boron have been known for over two decades for their reducing properties towards organic functional groups [1], very little attention has been paid to MgH_2 because of its insolubility in common organic solvents. We have recently reported a series of soluble derivatives of magnesium hydride [2] of the type HMgX (where X = Cl, Br, R, OR and NR_2) and have shown that these compounds are reasonably strong reducing agents [3]. In the course of our investigations on the reactivity of MgH_2, we have recently found that metalation [4] takes place with organic reactants such as phenylacetylene, indene and cyclopentadiene. Here we wish to report the preparation of cyclopentadienylmagnesium hydride (CpMgH) by the reaction of cyclopentadiene with MgH_2 and describe its reactions with organic substrates such as ketones, alkyl halides and polynuclear hydrocarbons.

Results and discussion

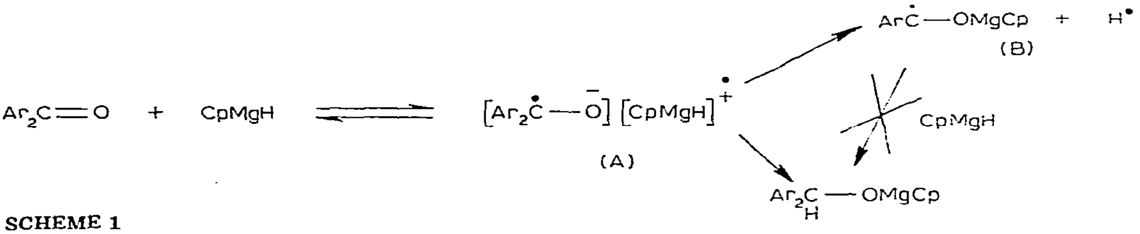
When an equimolar amount of cyclopentadiene was allowed to react with a magnetically stirred slurry of MgH_2 in THF, a clear solution was formed within a few minutes. Upon concentrating (>0.5 *M*) this solution, needle-shaped crystals were formed which corresponded by elemental analysis to CpMgH·THF (Calcd.: Mg/H/Cp/THF = 1.00/1.00/1.00/1.00. Found: Mg/H/Cp/THF = 1.00/0.98/1.01/1.08) (Mg determined by EDTA, H by gas evolution and CpH and THF by GLC). Ebullioscopic molecular association studies in THF at 32°C (under reduced pressure) showed the compound to be a dimer and the X-ray powder diffraction pattern (9.80w, 8.65w, 4.85 vs. 4.25w and 3.60m) was different from those observed for Cp_2Mg and MgH_2 [2b]. The infrared spectrum in THF exhibited bands at 750 and 720 cm^{-1} due to the cyclopentadienyl group and a broad band in the region of 1300 cm^{-1} (which shifted to ≃ 940 cm^{-1} in the deuterium analog) was assigned to Mg—H—Mg bridging. The proton NMR spectrum in THF showed a singlet at δ 2.27 ppm downfield from the THF multiplet, due to the Cp protons. The spectrum at low temperature (−95°C) showed two peaks, one at δ 2.23 and one at 1.67 ppm downfield fromthe THF multiplet, in approximately 5/1 ratio. The peak at δ 2.23 ppm was assigned to the Cp hydrogens and the peak at δ 1.67 ppm was assigned to the hydrogens attached to magnesium [5,6]. Although the peak at δ 1.67 ppm (with respect to the THF multiplet) was at a remarkably low position for a hydridic hydrogen, similar low position signals have been observed by Shriver [5] (for the complex $NaH \cdot 2ZnEt_2$), and by us [6] (for the complex $KMg\text{-}s\text{-}Bu_2H$). The shift of the NMR signals at −95°C is probably due to increased solvation at the lower temperature. On the basis of molecular association, IR and NMR studies, a dimeric structure with bridging hydrogens is assigned [7].



(A)

Cyclopentadienylmagnesium hydride dissolved in THF reacted readily with cyclopentadiene, HCl, ROH, and R_2NH to give soluble compounds of the type Cp_2Mg, CpMgCl, CpMgOR, and $CpMgNR_2$, respectively [9]. Cyclic ketones such as 2-methylcyclohexanone, 3,3,5-trimethylcyclohexanone, 4-t-butylcyclohexanone were found to react with CpMgH rapidly in THF to produce both addition and reduction products [4].

Aromatic ketones such as benzophenone, 2,2′-dimethylbenzophenone and dimesityl ketone (DMK) were reduced by CpMgH in THF and the rates of reduction were found to be much faster than those observed when the same ketones were reduced by HMgX compounds [8]. When CpMgH was allowed to react with DMK (≃ 0.07 *M*) in THF, at room temperature, a deep blue colored solution (λ_{max} 638 nm) was formed within a few minutes. This solution was found to be EPR active and showed a complex EPR spectrum (Fig. 1; *g* value = 2.0041), thus suggesting the existence of a paramagnetic species. Both the intensity of the visible absorption and the EPR signal increased with time and reached a maximum in about 4 days. Reduction product was obtained during this time period. Preliminary results (visible and EPR maximum absorption) indicate that after 4 days the decay of the intermediate is related directly to the formation of reduction product. After 7 days, about 70% reduction product was obtained. On the basis of these results, a probable mechanistic scheme (Scheme 1) involving an intermediate radical anion-radical cation pair is proposed. The unusually high stability of the intermediate A might lead one to conclude that it is the free ketyl B. However, this possibility can be excluded since we have observed that the free ketyl B prepared independently does not abstract hydrogen either from THF or from the free metal hydride to give the reduction product. Furthermore, the EPR spectrum of the reaction intermediate (Fig. 1) was observed to be different from that



SCHEME 1

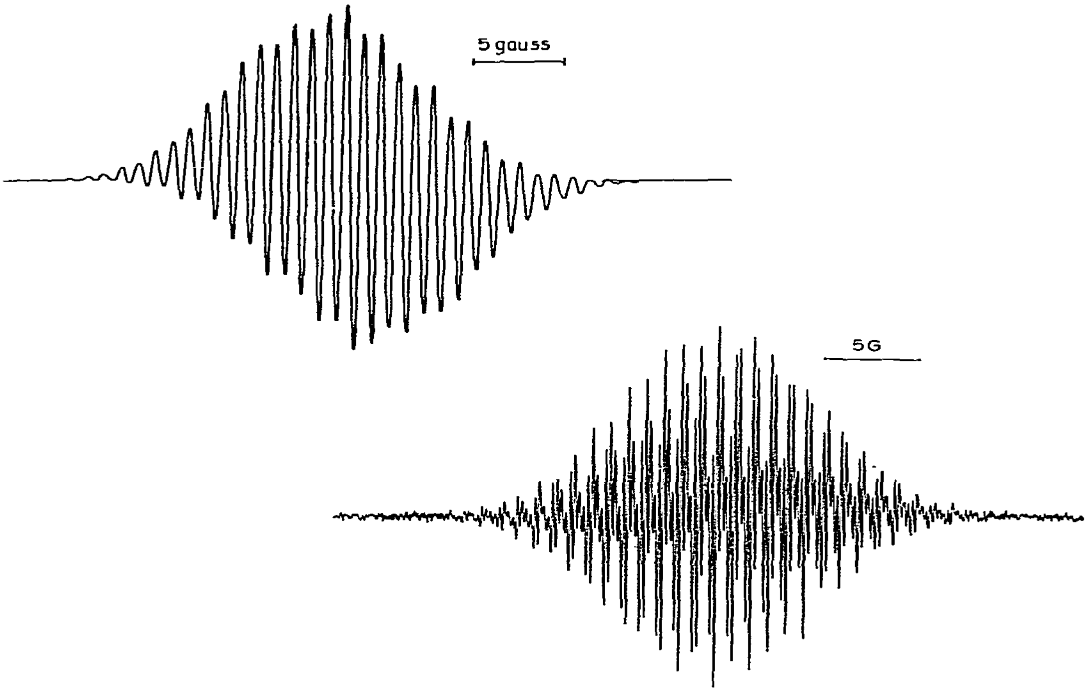
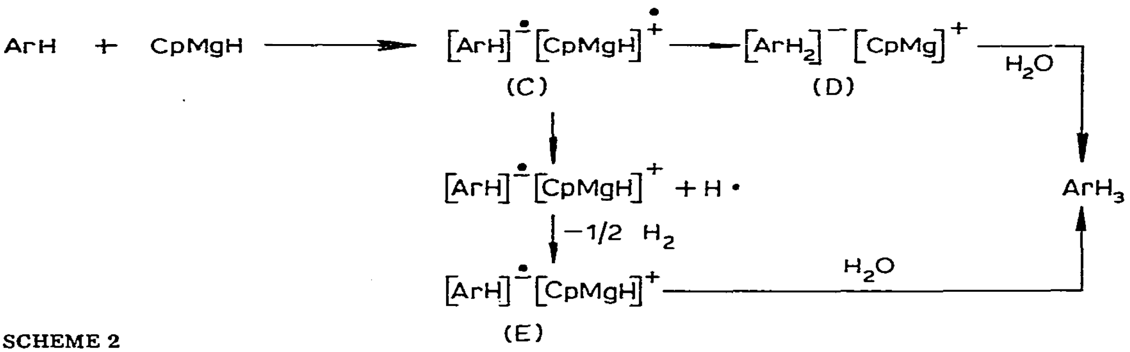


Fig. 1. EPR spectrum of the radical intermediate formed in the reaction of dimesitylketone with CpMgH in THF at room temperature. (A) Partially refined, (B) Refined spectrum; *g* value = 2.0041.

of the free ketyl and also from that of the intermediate formed on reacion of HMgBr with dimesityl ketone.

Similarly, CpMgH reacts with polynuclear hydrocarbons such as perylene, 2,3-benzathracene, benzo[*a*]pyrene and anthracene to give colored intermediates which were found to be paramagnetic. The EPR and visible absorption spectra of these colored species were similar to those of the corresponding radical anions reported previously [11—13], which suggests that they are solvent-separated radical pairs [$(\mathrm{ArH})^{\dot{-}}$ + $(\mathrm{CpMgH})^{\dot{+}}$].

The concentrations of the radical intermediates in these reactions have been determined by visible and EPR spectroscopy. The rate of formation of the radical intermediate was found to be dependent on the reduction potential of the polynuclear hydrocarbon and the concentration of the reagent. Under identical conditions of concentration, the rates of reaction of the hydrocarbons studied followed the order: perylene > 2,3-benzanthracene > benzo[*a*]-pyrene > anthracene. Thus it appears from the EPR and visible spectra studies of the intermediates produced in these reactions that a single electron is transferred from CpMgH to the hydrocarbon, forming a radical ion pair C; $[\mathrm{ArH}]^{\dot{-}}$ $[\mathrm{CpMgH}]^{\dot{+}}$, which then either gives the reduction product D; $[\mathrm{ArH_2}]^{-}[\mathrm{MgCp}]^{+}$, by hydrogen radical abstraction or generates the solvent separated ion pair; $[\mathrm{ArH}]^{\dot{-}}[\mathrm{CpMg}]^{+}$ (E) by dissociation (Scheme 2). Hydrolysis of the latter intermediate (E) can produce the reduction product either via a dianion, as reported earlier in the case of perylene radical anion protonation, or via its reaction with H_2O followed by attack of another anion as demonstrated in the case of anthracene protonation [12,13]. A preliminary study of the product-forming step in the reaction of CpMgH with anthracene indicates that in the major reaction pathway only a small amount of D is formed prior to hydrolysis. This conclusion is based on the results of the reactions of CpMgH and CpMgD with this hydrocarbon followed by hydrolysis with D_2O or H_2O in which the amount of deuterium incorporation in the reduction product was determined. For example, reaction of CpMgH with anthracene followed by hydrolysis with D_2O produced mainly $ArHD_2$ and reaction of CpMgD with anthracene followed by reaction with H_2O produced mainly ArH_3. The EPR spectrum of the reaction intermediate in the reaction of CpMgH with perylene is shown in Fig. 2.



SCHEME 2

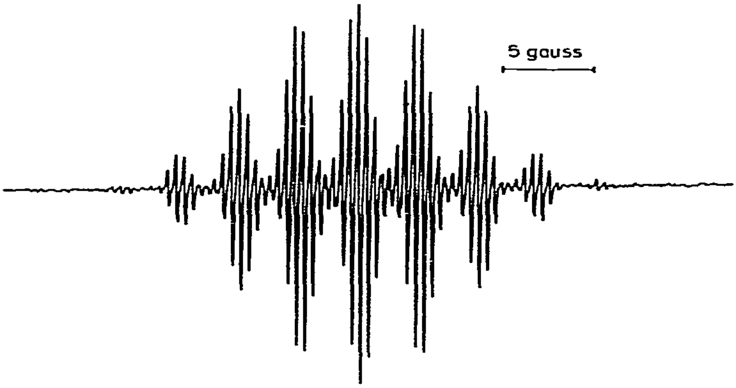


Fig. 2. EPR spectrum of the radical intermediate formed in the reaction of perylene with CpMgH at room temperature. g value = 2.0029; $a_\alpha = 2.53$, $a_\beta = 3.09$ and $a_\gamma = 0.46$.

Cyclopentadienylmagnesium hydride reacted readily with trityl halides (Ph_3CX; X = Cl or Br) in THF and gave an orange-red solution. These solutions were EPR active and showed an EPR spectrum identical with that previously reported for the trityl radical ($Ph_3C^\bullet$) [14]. The concentration of this radical increased with time, as observed by EPR spectroscopy, and reached a maximum (estimated intensity ≃ 15%), beyond which the intensity of the radical decreased. The product of the reaction after 1 day was triphenylmethane, Ph_3CH (Scheme 3). When CpMgD was used, the reduction product was found to be mainly Ph_3CD (≃ 90%) indicating that the hydrogen is transferred mainly from CpMgH.

$$\begin{tikzcd}
Ph_3CBr + CpMgH \arrow[r] & {[(Ph_3CBr)^{\dot{-}}\ (CpMgH)^{\dot{+}}]} \arrow[d] \\
Ph_3CH + CpMgBr & {[Ph_3\dot{C} + Br^- + (CpMgH)^{\dot{+}}]} \arrow[l]
\end{tikzcd}$$

SCHEME 3

Detailed mechanistic studies of the reactions of CpMgH with other organic substrates are in progress. We are also studying the reactions of CpMgH with transition metal halides in the hope of developing a direct route to cyclopentadienylmetal hydride complexes.

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