

## THE COMPOSITION OF GRIGNARD COMPOUNDS

### IX. THE STRUCTURE AND SOLUTION COMPOSITION OF CYCLOPENTADIENYLMETHYLMAGNESIUM IN BENZENE AND ETHER SOLVENTS

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#### Summary

A monoetherate of cyclopentadienylmethylmagnesium has been isolated. Comparison of its infrared spectrum in the  $4000-300\text{ cm}^{-1}$  region with dimethylmagnesium and dicyclopentadienylmagnesium indicates that in the solid state the magnesium atoms are associated via methyl bridge bonds and that the cyclopentadienyl ring has approximately  $D_{5h}$  symmetry. When dissolved in benzene, the methyl bridge bonds are retained, but partial dissociation of the ether occurs. There is partial cleavage of the methyl bridge bonds when the etherate is dissolved in diethyl ether. Tetrahydrofuran cleaves the methyl bridge bonds completely. Proton magnetic resonance and molecular association studies are presented to support the above interpretation. Desolvation of the solid monoetherate is achieved readily. Unsolvated cyclopentadienylmethylmagnesium retains the methyl bridge bonds but the symmetry of the cyclopentadienyl ring is modified.

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#### Introduction

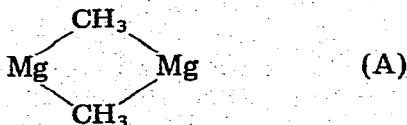
The cyclopentadienyl group is widely recognized to form a variety of bonds with metals [1-4]. The factors governing the nature of the ring-metal interaction are the number, symmetry and energy of the metal orbitals. In the case of magnesium it seems clear that the interaction with a cyclopentadienyl ring should be essentially electrostatic [5, 6] since the metal orbitals are of such high energy that any bond to carbon is highly polar [7, 8]. On the basis of electrostatic interaction, the approach of a magnesium ion is expected to be along the fivefold axis of the  $D_{5h}$  cyclopentadienyl anion. In the case of dicyclopentadienylmagnesium, it has been found experimentally that the cation polarizes the anion, reducing its symmetry to  $C_{5v}$  and lowering the charge separation between the ions as though a covalent bond had been formed [9].

In addition to spectroscopic studies, an X-ray powder diffraction study revealed that dicyclopentadienylmagnesium is isostructural with ferrocene [10]. More recently examination of the tetraethylethylenediamine adduct of cyclopentadienylmagnesium bromide indicated that the cyclopentadienide anion in this compound is undistorted; the magnesium atom lies near the fivefold axis of the ring and the bond lengths suggest that the bonding should be described in terms of hexacoordination of the magnesium ion [11]. House and co-workers [12] described a bis(tetrahydrofuran) adduct of cyclopentadienylphenylmagnesium which seems to fall into this same general pattern. They also reported the preparation of cyclopentadienylmethylmagnesium as a non-solvated compound.

## Results and discussion

### Solid phase studies

The prominent features of the solid state structure of " $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ " can be deduced by comparison of its infrared spectrum with those of similar organometallic compounds: dimethylmagnesium [13–15], dicyclopentadienylmagnesium [9], potassium cyclopentadienide [16, 17], methyl-lithium [18] and dimethylberyllium [19, 20]. As shown in Table 1, the infrared-active cyclopentadienyl fundamentals of " $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ " are most consistent with  $D_{5h}$  ring symmetry. However, slight distortion towards either  $C_{5v}$  or  $C_s$  ring symmetry cannot be ruled out since the additional bands expected for distortion towards these lower symmetries would be weak and would fall into regions of the spectrum where methyl or ether bands occur [16, 17, 21].  $D_{5h}$  symmetry of the  $C_5H_5$  anion is the limiting symmetry for weak ring-metal interactions regardless of whether the metal is on the fivefold axis (slight distortion towards  $C_{5v}$  symmetry) or on the perimeter of the ring (slight distortion towards  $C_s$  ring symmetry). The methyl fundamentals are similar to those of methyl compounds of other electropositive metals [18–20]. In particular the  $\nu(C-H)$  bands occur at relatively low frequency and the  $\delta_a(CH_3)$  band is not observed. On the other hand the  $\delta_s(CH_3)$  band is not split into two bands as noted in the other spectra listed in Table 1. The skeletal vibration region ( $600-300\text{ cm}^{-1}$ ) is dominated by several intense bands due to vibrations of a system of methyl bridge bonds. When the bridge bond system (A) is treated as a group with  $D_{2h}$  local symmetry, vibrations belonging to the



$B_{1u}$ ,  $B_{2u}$ , and  $B_{3u}$  irreducible representations are expected to be infrared-active [13–15].

Desolvation of " $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ " under mild conditions to yield " $C_5H_5MgCH_3$ " has little effect upon the methyl fundamentals or skeletal vibrations. However, there are noticeable changes involving the cyclopentadienyl fundamentals, including reduction of the intensity of the  $\nu(CH)$  band, which lead to the suggestion that the unexpectedly easy desolvation is facilitated by electronic reorganization in the cyclopentadienyl group.

TABLE 1

COMPARISON OF INFRARED SPECTRA OF METHYL AND CYCLOPENTADIENYL ORGANOMETALLIC COMPOUNDS <sup>a,b</sup>

| Vibrations   | $(\text{CH}_3\text{Li})_4$ <sup>c</sup>        | $[(\text{CH}_3)_2\text{Be}]_n$ <sup>d</sup>     | $[(\text{CH}_3)_2\text{Mg}]_n$                            | " $\text{CpMgCH}_3 \cdot \text{Et}_2\text{O}$ " | " $\text{CpMgCH}_3$ " |
|--|--|---|---|---|-----------------------|
| <i>Methyl fundamentals</i>   |  |   |   |   |                       |
| $\nu(\text{CH})$   | 2840<br>2780                                   | 2912<br>2885                                    | 2850<br>2780  | 2865<br>2790                                    | 2860<br>2790          |
| $\delta_d(\text{CH}_3)$  | 1480<br>1427                                   |   |   |   |                       |
| $\delta_s(\text{CH}_3)$  | 1096<br>1061                                   | 1255<br>1243                                    | 1200<br>1186  | 1188  | 1185                  |
| $\rho_r(\text{CH}_3)$  |  | 835 <sup>e</sup>                                | 712   | 860   | 860                   |
| Vibrations   | CpK <sup>f</sup><br>( $D_{5h}$ ring)           | CpLi <sup>f</sup><br>( $C_{5v}$ ring)           | $\text{Cp}_2\text{Mg}$ <sup>f,g</sup><br>( $C_{5v}$ ring) | " $\text{CpMgCH}_3 \cdot \text{Et}_2\text{O}$ " | " $\text{CpMgCH}_3$ " |
| <i>Cyclopentadienyl fundamentals</i>                               |  |   |   |   |                       |
| $\nu(\text{CH})$   | 3048   | 3048<br>2906                                    | 3067<br>2913  | 3070<br><i>h</i>                                | 3070<br><i>h</i>      |
| $\nu(\text{CC})$<br>(ring deformation)                             | 1145   | 1426<br>1120                                    | 1428<br>1108  | <i>h</i>  | 1418                  |
| $\delta(\text{CH})$  | 1009   | 1003  | 1004  | 1006  | 1001                  |
| $\pi(\text{CH})$   | 702  |   | 779   | 775   | 770                   |
|  |  | 746   | 758   |   | 720                   |
| $[(\text{CH}_3)_2\text{Be}]_n$ <sup>d</sup><br>( $D_{2h}$ )        | $[(\text{CH}_3)_2\text{Mg}]_n$<br>( $D_{2h}$ ) | " $\text{CpMgCH}_3 \cdot \text{Et}_2\text{O}$ " | " $\text{CpMgCH}_3$ "                                     | $\text{Cp}_2\text{Mg}$ <sup>g</sup>             |                       |
| <i>Skeletal vibrations (above 250 <math>\text{cm}^{-1}</math>)</i> |  |   |   |   |                       |
| 567  | 575  | 570   | 575   | 520   |                       |
| 535  | 440  | 517   | 510   | 435   |                       |
| 427  | 400  | 409   | 410   |   |                       |
| 403  | 310  | 310   | 308   |   |                       |
| 292  |  |   |   |   |                       |

<sup>a</sup> Throughout the table and the text we have adopted the nomenclature used by Nakamoto [17] to describe the fundamental vibrations of various groups:  $\nu$ , stretching;  $\delta$ , in-plane bending or deformation;  $\pi$ , out-of-plane bending;  $\rho_w$ , wagging;  $\rho_r$ , rocking;  $\rho_t$ , twisting. Subscripts "s" or "sym" mean symmetric; "a" or "asym" means antisymmetric (or asymmetric); "d" means degenerate. The antisymmetric methyl deformation  $\delta_a(\text{CH}_3)$ , is also referred to as the degenerate methyl deformation,  $\delta_d(\text{CH}_3)$ . All frequencies are cited in wave numbers,  $\text{cm}^{-1}$ . <sup>b</sup> The formulae " $\text{CpMgCH}_3 \cdot \text{Et}_2\text{O}$ " and " $\text{CpMgCH}_3$ " where Cp =  $\text{C}_5\text{H}_5$  denote the empirical formula of the materials and are not intended to convey other than the most general structural information. <sup>c</sup> Ref. 18. <sup>d</sup> Ref. 15, 19 and 20. <sup>e</sup> In the gas phase methyl rocking modes have been assigned at 1086, 1032 and 816  $\text{cm}^{-1}$ . <sup>f</sup> Ref. 16 and 17. <sup>g</sup> Ref. 9. <sup>h</sup> Detection impossible due to other absorptions in this region.

The stability of solid " $\text{C}_5\text{H}_5\text{MgCH}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ " was investigated by thermogravimetric analysis. The finely ground sample was placed on the balance in an argon atmosphere. As the furnace was evacuated at 25°, a rapid loss of weight was observed and a condensable gas,  $(\text{C}_2\text{H}_5)_2\text{O}$ , was evolved as indicated by the shaded area on the extreme left of the pressure plot in Fig. 1. After four hours the pressure before and after the liquid nitrogen trap had equilibrated. Heating was begun at a rate of one degree per minute. Between approximately 60° and 140° the sample sublimed out of the crucible. Sublimation of " $\text{C}_5\text{H}_5\text{MgCH}_3$ " is accompanied by substantial disproportionation to  $(\text{C}_5\text{H}_5)_2\text{Mg}$  and  $(\text{CH}_3)_2\text{Mg}$ . House and co-workers [12] sublimed " $\text{C}_5\text{H}_5\text{MgCH}_3$ " into a mass spectrometer and observed that the peak for  $[(\text{C}_5\text{H}_5)_2\text{Mg}]^+$

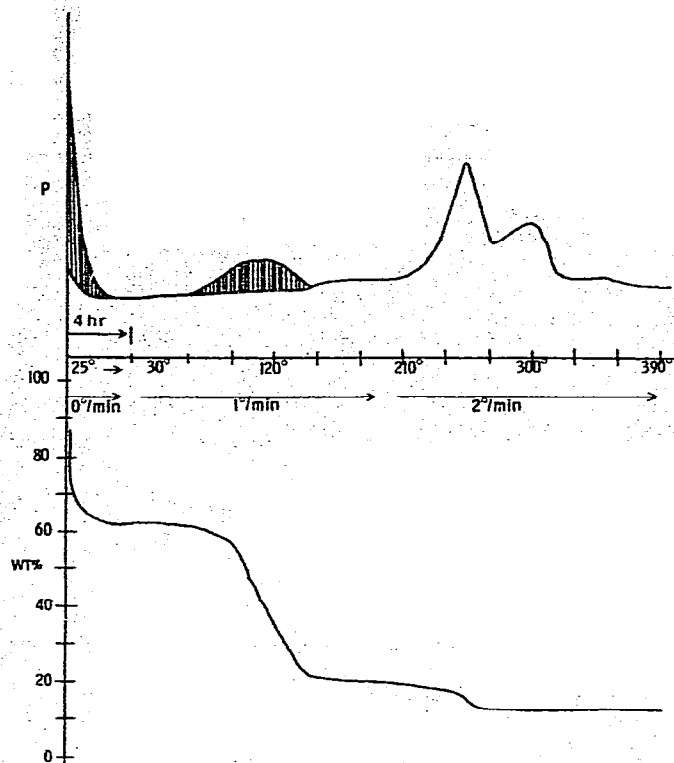
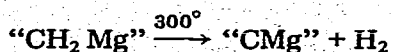
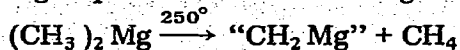


Fig. 1. Thermogravimetric analysis and differential pressure curves for the desolvation and sublimation of cyclopentadienylmethylmagnesium monoetherate.

( $m/e$  154) was six or seven times as large as the peak for  $[\text{C}_5\text{H}_5\text{MgCH}_3]^+$  ( $m/e$  104). Above  $150^\circ$  only dimethylmagnesium remains in the crucible and, as we have observed for pure, authentic samples of dimethylmagnesium, it decomposes in two steps at  $250^\circ$  and  $300^\circ$  with loss of non-condensable gases. The weight loss ratios are roughly 7 to 1 and may be represented by the following sequence of reactions originally proposed some years ago [22]:



The outstanding features of cyclopentadienylmethylmagnesium monoetherate as deduced from the experiments described above are incorporated in the structure proposed in Fig. 2.

#### Solution studies

In Fig. 3, the infrared spectra of the skeletal  $\text{CH}_3\text{—Mg}$  region of solutions of cyclopentadienylmethylmagnesium monoetherate is compared with the solid state spectrum. Salinger and Mosher [23] have shown that monomeric dimethylmagnesium in diethyl ether or tetrahydrofuran has a single  $\nu(\text{C—Mg})$  band at approximately  $530\text{ cm}^{-1}$ . In concentrated diethyl ether solutions or the solid

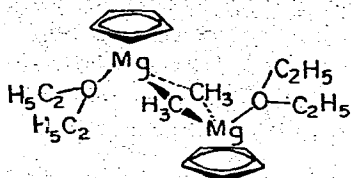


Fig. 2. Proposed solid state structure of cyclopentadienylmethylmagnesium monoetherate deduced from infrared spectroscopy.

state, where dimethylmagnesium exists as methyl bridged polymers, an additional band at  $593\text{ cm}^{-1}$  was observed due to the methyl bridge system. A single band is observed in the spectrum of the tetrahydrofuran solution of " $\text{C}_5\text{H}_5\text{-MgCH}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ ", (A) at  $490\text{ cm}^{-1}$ . In concentrated diethyl ether solution (B) additional bands at  $570$ ,  $520$  and  $400\text{ cm}^{-1}$  appear though the band at  $490\text{ cm}^{-1}$  is still predominant. In benzene (C) the bands at  $575$ ,  $520$  and  $400\text{ cm}^{-1}$  are more intense and the spectrum is very similar to the solid phase spectrum

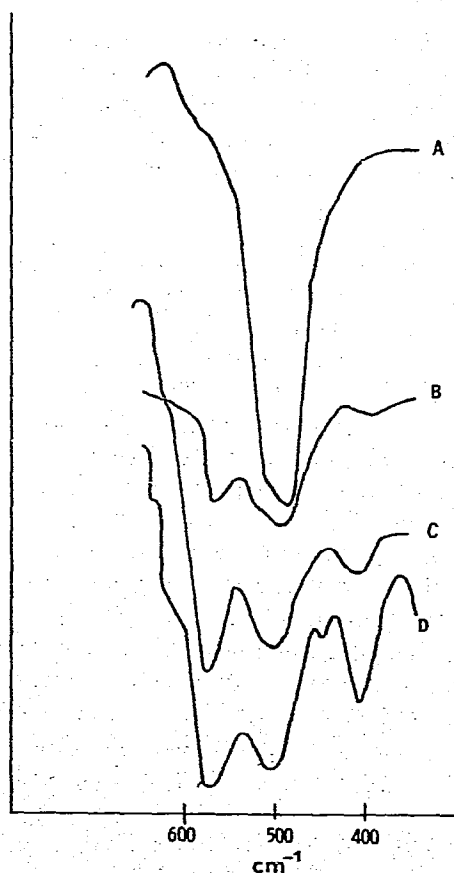
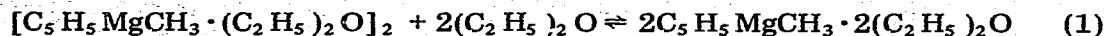


Fig. 3. The infrared spectra of cyclopentadienylmethylmagnesium monoetherate between  $650$  and  $350\text{ cm}^{-1}$ . A. Tetrahydrofuran solution. B. Diethylether solution. C. Benzene solution. D. Solid (nujol mull).

(D). Thus, the infrared spectra suggest that cyclopentadienylmethylmagnesium monoetherate dissolves in benzene with retention of the methyl bridge system deduced in the solid state structure. On the other hand, polar solvents, such as diethyl ether and particularly tetrahydrofuran, cleave the bridge bonds according to Equilibrium 1. Ebullioscopic molecular association studies in ether support



this conclusion since the apparent molecular weight in diethyl ether is 1.70 times the monomeric molecular weight near saturation (0.111 *M*) and decreases with dilution approaching the monomeric molecular weight at infinite dilution. In tetrahydrofuran the ether is apparently completely replaced by tetrahydrofuran and Equilibrium 1 is driven far to the right. It has been reported that " $\text{C}_5\text{H}_5\text{MgCH}_3$ " is monomeric in tetrahydrofuran over a wide concentration range [12]. It is likely that disolvated monomers are the predominant species in tetrahydrofuran solution.

Two lines of evidence suggest that ether partially dissociates from the methyl bridged dimer of cyclopentadienylmethylmagnesium monoetherate in benzene solution according to Equilibrium 2. The apparent molecular weight



of cyclopentadienylmethylmagnesium monoetherate as determined by cryoscopy in benzene is 1.26 to 1.29 times that of the solvated monomer in the concentration range 0.100–0.238 *M*. This result by itself does not distinguish between Equilibria 2 and 3, although the infrared spectra in Fig. 3 have revealed that the methyl bridge bonds remain largely intact in benzene solution. Direct



evidence for dissociation of ether as suggested by Equilibrium 2 comes from the infrared spectra of cyclopentadienylmethylmagnesium monoetherate in benzene between 1200 and 1000  $\text{cm}^{-1}$  as shown in Fig. 4. In addition to  $\delta_s(\text{CH}_3)$  at 1190  $\text{cm}^{-1}$  and  $\delta(\text{C}_5\text{H}_5)$  at 1005  $\text{cm}^{-1}$ , there are five ether skeletal vibrations in this region near 1145, 1115, 1087, 1045 and 1025  $\text{cm}^{-1}$  [24]. The intensities of these bands depend upon the conformation of the ether molecules [13, 25]. For free diethyl ether diluted with benzene these bands are broad and overlap due to the presence of numerous slightly different conformers and the band at 1115  $\text{cm}^{-1}$  tends to be the most intense, (C). In the solid state spectrum of " $\text{C}_5\text{H}_5\text{MgCH}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ ", the ether bands are sharp with characteristic intensities since the ether molecules are constrained to a preferred conformation (A). The ether spectrum for cyclopentadienylmethylmagnesium monoetherate in benzene (B), consists of five moderately sharp bands superimposed on a broad envelope of absorption. The envelope absorption is assigned to free ether molecules, while the sharper peaks are assigned to coordinated ether. Comparing the relative intensities of the sharp peaks in Spectra A and B suggests that the preferred conformation of the coordinated ether molecules is different in the solid state and in solution.

As seen in Table 2, the proton magnetic resonance signal for the  $\text{C}_5\text{H}_5$  group of " $\text{C}_5\text{H}_5\text{MgCH}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ " is sensitive to the solvent employed

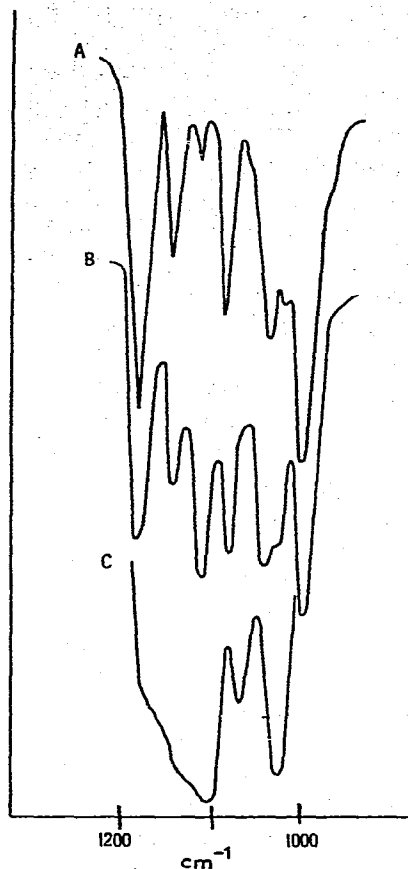


Fig. 4. Effect of coordination on the skeletal bands of diethylether. A. Solid cyclopentadienylmethylmagnesium monoetherate. B. Benzene solution of cyclopentadienylmethylmagnesium monoetherate. C. Benzene solution of diethylether.

TABLE 2

PMR SPECTRA OF  $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ ,  $(C_5H_5)_2Mg$  AND  $(CH_3)_2Mg$  IN TETRAHYDROFURAN, ETHER AND BENZENE(TOLUENE) <sup>a</sup>

| Compound                         | Solvent           | Chemical shifts ( $\tau$ ) <sup>b</sup> |  |
|----------------------------------|-------------------|---|--|
|                                  |                   | $C_5H_5$                                | $CH_3$   |
| $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ | Tetrahydrofuran   | 4.13 (4.13) <sup>c</sup>                | 12.13 (12.10) <sup>c</sup>                     |
|                                  | Diethyl ether     | 4.03                                    | 11.70  |
|                                  | Benzene (toluene) | 3.67                                    | 11.17  |
| $(C_5H_5)_2Mg$                   | Tetrahydrofuran   | 4.13 (4.13) <sup>c</sup>                |  |
|                                  | Diethyl ether     | 3.99 (3.99) <sup>c</sup>                |  |
|                                  | Benzene (toluene) | 3.85                                    |  |
| $(CH_3)_2Mg$ <sup>d</sup>        | Diethyl ether     |   | 11.00–11.40 <sup>d</sup><br>(bridging)         |
|                                  |                   |   | 11.60–11.75 <sup>d</sup><br>(terminal monomer) |
|                                  | Tetrahydrofuran   |   | 11.80–11.85 <sup>d</sup><br>(monomer)          |

<sup>a</sup> All spectra recorded at ambient temperature. <sup>b</sup> Benzene internal standard (2.70  $\tau$ ). <sup>c</sup> From ref. 12.

<sup>d</sup> From ref. 26.

as is the signal for  $(C_5H_5)_2Mg$ . Temperatures as low as  $-80^\circ$  have little if any effect upon the  $C_5H_5$  signal of these compounds in the stated solvents. The methyl proton resonance of " $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ " is also solvent sensitive as would be expected from Equilibria 1 and 2 [26]. The strong anisotropic field of the  $C_5H_5$  group can potentially shield or deshield the methyl group depending upon the relative positions of the two groups. In tetrahydrofuran where the principal species in solution is the solvated monomer of " $C_5H_5MgCH_3$ ", the methyl group appears to fall within the shielding cone of the  $C_5H_5$  group though it is not necessarily on the fivefold axis of the ring as previously suggested [12]. In view of Equilibria 1 and 2, the interaction of anisotropic and local diamagnetic electron shielding upon the observed methyl proton chemical shifts in diethyl ether, benzene or toluene is not easily predicted. Although assignments of chemical shifts cannot be made with certainty, the following assignments appear reasonable and are consistent with both the infrared and molecular association studies. The low field position of the  $Mg-CH_3$  protons in benzene or toluene solutions (11.17  $\tau$ ) is characteristic of a bridging methyl group and therefore is consistent with the methyl bridged dimer which has been proposed. On the other hand, the high field position of the  $Mg-CH_3$  protons in tetrahydrofuran (12.13  $\tau$ ) is characteristic of a terminal methyl group and therefore is consistent with the proposed monomeric structure in tetrahydrofuran. There is little temperature effect upon the methyl signal in tetrahydrofuran or toluene at temperatures as low as  $-80^\circ$ ; however, in diethyl ether three signals were resolved (11.66, 11.88 and 12.02  $\tau$ ) at  $-65^\circ$  in the ratio of approximately 1/1/2. The highest field signal is probably due to a solvated monomer of " $C_5H_5MgCH_3$ " whereas the two lower field signals are probably due to the methyl signals of the mono and disolvated dimer (eqn. 2). The two lower field signals disappear when the solution is allowed to stand at  $-65^\circ$  simultaneous with the appearance of a white precipitate. When the solution is allowed to warm to room temperature, the precipitate redissolves. Presumably the higher molecular weight dimeric species precipitate at low temperature leaving the lower molecular weight monomeric species in solution.

## Experimental

### *Preparation of cyclopentadienylmethylmagnesium monoetherate*

All manipulations involving methyl- or cyclopentadienylmagnesium were carried out under a nitrogen atmosphere. Even the briefest exposure of magnesium cyclopentadienides to oxygen results in a red color. Hydrolysis in the absence of oxygen results in a yellow color. Freshly distilled cyclopentadiene (16 ml) was added to an ether solution of dimethylmagnesium (0.1 mole/200 ml) prepared from dimethylmercury. The reaction mixture was allowed to stand undisturbed at  $20-25^\circ$ . Methane evolved slowly and was vented through a mineral oil bubbler. After five days, a deposit of large, translucent crystals had formed. The crystals were filtered, washed with ether and dried briefly in a stream of nitrogen. A weighed sample was analyzed for methane to magnesium ratio and for percent magnesium by vacuum line techniques and EDTA titration. The result was  $CH_4/Mg$ , 0.96/1.00. Found: Mg, 13.7; " $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ " calcd.: Mg, 13.6%. The yield of the monoetherate was 10.1 g or 57% based on the dimethylmagnesium.



Dicyclopentadienylmagnesium was prepared similarly using longer reaction times (8 to 10 days) and a large excess of cyclopentadiene. The soluble compound was isolated by removal of the solvent under vacuum. The product was purified by repeated sublimation in vacuo at  $\approx 100^\circ$ .

#### *Desolvation of cyclopentadienylmethylmagnesium monoetherate*

Large crystals ( $\approx 0.1$  g each) of " $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ " were desolvated on a vacuum line under a dynamic vacuum of  $\approx 10^{-4}$  mm at  $20-25^\circ$ . In three hours a 13% weight loss was observed, after one day the weight loss was 36% and after three days, 44% (theoretical weight loss is 41.5%). It was found that finely ground material could be totally desolvated in a few hours. Slow sublimation of the sample, as in the thermal analysis experiment described below, resulted in volatilization of  $(C_5H_5)_2Mg$  and a small amount of  $C_5H_5MgCH_3$ , leaving behind almost the theoretical amount of  $(CH_3)_2Mg$ .

#### *Solubility*

It was found that cyclopentadienylmethylmagnesium monoetherate is quite soluble in tetrahydrofuran and benzene ( $> 0.5 M$ ) but much less soluble in diethyl ether ( $\approx 0.12 M$ ). When the ether was removed from finely ground " $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ " at  $20-25^\circ$  and the resulting " $C_5H_5MgCH_3$ " covered with benzene and allowed to stand for six days at  $20-25^\circ$ , only traces of  $C_5H_5-$  and  $CH_3-$  were detected in the benzene by PMR. No ether was detected in the benzene. The solid rapidly dissolved when ether was added.

#### *Physical studies*

The association of these compounds in benzene was studied by cryoscopy in an apparatus modified for handling air sensitive compounds. The association of " $C_5H_5MgCH_3 \cdot (C_2H_5)_2O$ " in diethyl ether was examined by the ebullioscopic technique developed in this laboratory [27].

Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer. Solid phase spectra were taken in fluorolube ( $4000-1350\text{ cm}^{-1}$ ) or nujol ( $1375-200\text{ cm}^{-1}$ ) mulls between cesium iodide plates. Solution phase spectra were obtained using 0.1 mm path length potassium bromide cells. A matching cell containing solvent was placed in the reference beam.

Proton magnetic resonance spectra were recorded on a 60 MHz Varian NMR spectrometer at probe temperature. Low temperature spectra were recorded on a 100 MHz Jelco NMR spectrometer.

All solvents were distilled from reactive hydrides prior to use (benzene and toluene from  $NaH$ , tetrahydrofuran from  $NaAlH_4$  and diethylether from  $LiAlH_4$ ). All spectroscopic samples were prepared in a nitrogen filled dry box equipped with a recirculation purification system. Sensitive manipulations were generally carried out in the dry box or at the bench via syringe.

Thermal analysis of cyclopentadienylmethylmagnesium etherate and dimethylmagnesium was performed on a Mettler Thermoanalyzer II modified for differential pressure recording at reduced pressure. The furnace was kept under a dynamic vacuum during the thermal analysis. The evolved gases were passed over a thermal conductivity detector through a nitrogen trap, over a second detector, and then through a second liquid nitrogen trap to a mechanical pump.

The outputs from the thermal conductivity detectors were compared. If a non-condensable gas such as  $H_2$  or  $CH_4$  was evolved there was little pressure lag at the second detector caused by the intervening liquid nitrogen trap. On the other hand, the evolution of a condensable gas such as  $(C_2H_5)_2O$  was observed at the first detector but not at the second. A large weight loss with little or no pressure effect was indicative of sublimation of the sample from the crucible to cooler parts of the apparatus. A detailed description of this apparatus can be found in a recent publication from this group [28].

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