Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SPECTRA OF CYCLOPENTADIENYLALKALI AND CYCLOPENTADIENYLMAGNESIUM COMPOUNDS IN TETRAHYDROFURAN

WARREN T. FORD
Department of Chemistry, University of Illinois, Urbana, Illinois 61801 (U.S.A.)

(Received April 14th, 1971)

SUMMARY

Dicyclopentadienylmagnesium, cyclopentadienylmagnesium chloride, cyclopentadienylmagnesium bromide, cyclopentadienyllithium and cyclopentadienylsodium were examined by UV, IR, and PMR spectroscopy in tetrahydrofuran. None of them exhibited UV maxima at >210 nm. All of their infrared spectra indicated D_{5h}, D_{5d} or C_{5v} symmetry. All of their PMR spectra consisted of sharp single peaks at room temperature. The results are interpreted in terms of metal cyclopentadienide ion pairs in which the metal atom lies on or near the C_5 axis of the cyclopentadienide ion.

INTRODUCTION

The crystallographic unit cell parameters of magnesiumcyclopentadienide, $(C_5H_5)_2Mg$, suggest that it is isostructural with ferrocene[1], a result corroborated by infrared studies in solid and gas phases and in benzene solution[2-4]. Its vibrational spectra have been interpreted in terms of ionic[3] and covalent[4] bonding between magnesium and the two cyclopentadienide rings. Similarly, solid phase infrared spectra of alkali cyclopentadienides indicated that the alkali metal was located over the cyclopentadienide ring[5]. Recently Cotton and Marks[6] summarized the characterization by infrared spectroscopy of *pentahapto-* (C_{5v} or D_{5d} symmetry) and *monohapto-* (C_s) cyclopentadienylmetal compounds, in which the cyclopentadienyl ligands may be described as delocalized and diene types respectively.

Several calculations of the electronic spectrum of the cyclopentadienide ion[7,8] have predicted that it should show maxima at 210 nm (oscillator strength $f=0$) and 175 nm ($f=0.880$)[8], in contrast to observed spectra of cyclopentadiene (λ_{max} 241 nm) and 5-(trimethylsilyl)cyclopentadiene (λ_{max} 241 nm)[9]. However, previous reports of alkali cyclopentadienide electronic spectra have agreed[8,10] and disagreed[11] with the calculations. The results of Wagner and Ebel[8] and results in this paper indicate that some of the earlier spectra[11] have been due to substantial impurities.

This investigation was undertaken to determine whether cyclopentadienylmagnesium bromide and cyclopentadienylmagnesium chloride had the ionic delocalized or covalent diene-type structure in tetrahydrofuran (THF). A solution to this problem was needed to help decipher the mechanism of their cycloadditions to benzyne in THF[12]. None of the earlier spectral studies of $(C_5H_5)_2Mg$ were performed in an ether. An infrared spectrum of cyclopentadienylpotassium in diethyl ether[5b], which indicated a free cyclopentadienide ion of D_{5h} symmetry, and the conflicting reports of alkali cyclopentadienide electronic absorption spectra[8,10,11] were the only structural information about alkali cyclopentadienides in solution. Conductivity studies in diethyl ether and in THF indicated that $(C_5H_5)_2Mg$ was as little dissociated as diethylmagnesium[13]. In view of ebullioscopic evidence for monomeric diethylmagnesium in THF[14] the conductivities supported either a covalent structure or a tightly bound ion triplet for $(C_5H_5)_2Mg$ In THF. None of this information was considered sufficient to assign C_5H_5MgCl and C_5H_5MgBr in THF either delocalized or diene-type structures.

EXPERIMENTAL

Materials

Cyclopentadiene was obtained from its dimer by distillation, stored at −78°, and transferred to a drybox just before use. Tetrahydrofuran was freshly distilled from sodium–potassium alloy. Lithium and sodium were used in dispersion form[15]. Methylmagnesium bromide, 2.95 *M* in diethyl ether, and ethylmagnesium chloride, 3.0 *M* in THF, were obtained from Alfa Inorganics. Dicyclopentadienylmagnesium was prepared from magnesium turnings and cyclopentadiene at 570° [16].

Preparation of cyclopentadienide solutions

All preparations and transfers of cyclopentadienide solutions were carried out in a Vacuum Atmospheres Corporation drybox equipped with a drytrain[17]. Alkali cyclopentadienides were obtained by refluxing 4 h a solution of 10.0 mmol cyclopentadiene in about 7 ml THF with excess lithium or sodium dispersion. The resulting mixtures were filtered through sintered glass, and the filtrates were diluted to 10.0 ml to obtain 1.00 *M* solutions of C_5H_5Li and C_5H_5Na. Potassium cyclopentadienide was too insoluble in THF for IR or NMR studies. Solutions of CH_3MgBr and C_2H_5MgCl were prepared by dilution of the commercial samples with THF. Cyclopentadienyl Grignard solutions were prepared by refluxing 10.0 mmol C_5H_6 and 5 ml THF 24 h with 10.5 mmol CH_3MgBr or 4 h with 10.5 mmol C_2H_5MgCl and diluting the solutions to 10.0 ml (1.00 *M*). The 1 *M* solution of C_5H_5MgBr therefore contained 33% diethyl ether and 67% THF as solvent. A 0.51 *M* THF solution of $(C_5H_5)_2Mg$ was prepared from the solid. Dilutions of each of the solutions gave samples for UV spectra which were 4.7×10^{-4} to 1.00×10^{-2} *M*. All of the organomagnesium solutions were slightly colored because of impurities in the commercial Grignard solutions and in $(C_5H_5)_2Mg$, but no impurities could be detected in the PMR spectra of the most concentrated solutions prepared.

Spectra

All cells were filled in the drybox and kept under argon until immediately before use. All spectra were run at ambient temperature.

UV spectra were recorded on a Cary 14 instrument in 0.5, 1.0 and 5.0 mm cells. The spectra were reproducible after leaving the serum-capped cells 60 min in air. To confirm that the UV spectra observed were actually of cyclopentadienides, PMR spectra of the same solutions were taken. Also when 2–4 drops of water were added to each sample, regenerated C_5H_6, λ_{max} 241 nm (log ε=3.48), was detected in every case. The absorbance at 241 nm of the hydrolyzed sample was used to establish its concentration. Samples $\leqslant 1.00 \times 10^{-3}$ M sometimes appeared to be partially hydrolyzed when the first spectra were obtained. Consequently, only results from more concentrated solutions are reported in Fig. 1–2.

IR spectra were run with concentrated solutions in 0.1 mm sealed NaCl cells on a Perkin–Elmer 521 instrument under normal qualitative conditions. Frequencies were calibrated with the 3027.1, 1601.4, 1028.0, and 698.9 cm^{-1} bands of polystyrene.

PMR spectra were obtained on Varian A-60-A and HA-100 instruments. Chemical shifts were measured relative to the β-CH_2 of THF (1.767 ppm of 2% TMS in THF) with a Varian V-4315 frequency counter on the HA-100. All cyclopentadienides appeared as sharp single peaks $\leqslant$ 1.2 Hz wide at half height. PMR spectra of 0.5–1.0×10^{-2} M solutions identical to those used for UV study showed only the C_5H_5 peak, but peaks due to impurities could have been hidden by the low signal/noise.

RESULTS

Ultraviolet spectra of alkali and magnesium cyclopentadienides and the Grignard reagents and C_5H_6 from which they were prepared appear in Fig. 1–2. All of the cyclopentadienides apparently have strong maxima ($\varepsilon > 10^4$) at < 210 nm. The present data agree nicely with spectra of lithium and potassium cyclopentadienide in diethyl ether reported by Wagner and Ebel[8] and agree roughly with molecular orbital calculations for the cyclopentadienide ion[7,8]. The C_5H_5MgCl and C_5H_5MgBr had identical spectra. In contrast, CH_3MgBr and C_2H_5MgCl had substantially different spectra with the former exhibiting a maximum at 228 nm (log ε=3.31). Although the commerical Grignard reagents employed contained visible impurities, it is unlikely that the impurities were major contributions to their absorption at 210–280 nm because of the dramatic differences between the spectra of C_5H_5MgBr and CH_3MgBr and between the spectra of C_5H_5MgCl and C_2H_5MgCl. The ca. 233 nm shoulder in $(C_5H_5)_2Mg$ (Fig. 2) could be due to C_5H_6 produced by partial hydrolysis.

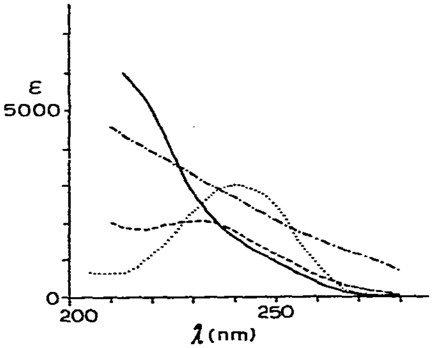

Fig. 1. Absorption of C_5H_6 (......), CH_3MgBr (------), C_2H_5MgCl (-·-·), C_5H_5MgCl (——) and C_5H_5MgBr (——) in THF at ambient temperature.

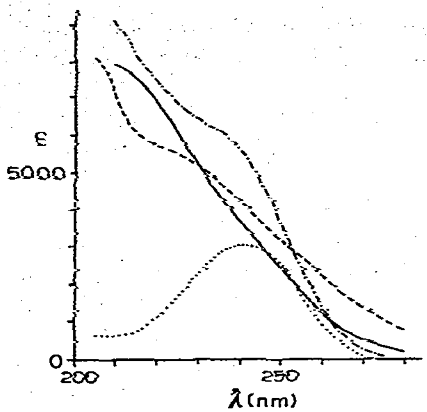

Fig. 2. Absorption spectra of C_5H_6 (.....), C_5H_5Li (——), C_5H_5Na (------), and $(C_5H_5)_2Mg$ (–·–·) in THF at ambient temperature.

Infrared spectra of cyclopentadienides in THF are compared to earlier solid phase IR spectra in Table 1. Unfortunately, parts of the solution spectra were hidden by solvent absorption. The spectra of C_5H_5Li, C_5H_5Na, C_5H_5MgCl, and $(C_5H_5)_2Mg$ were alike except for minor changes in absorption frequencies and intensities.

TABLE 1

INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF CYCLOPENTADIENIDES IN TETRAHYDROFURAN AND IN SOLID PHASE

C_5H_5Li		C_5H_5Na		C_5H_5MgCl 1 *M* THF	$(C_5H_5)_2Mg$			C_5H_6 1 *M* THF
1 *M* THF	Solid nujol^a	1 *M* THF	Solid nujol^a		0.5 *M* THF	1 *M* benzene^b	Solid KBr^c	
3065 s	3048 m	3055 s	3048 m	3075 s	3065 s	3080 s	3063 m	3100 m
^{d}	2906 w	^{d}	2907 w	^{d}	^{d}			3070 m
	1742 m		1700 sw	1715 w	1715 w	1736 vvw	1751	3040 w
	1629 m	1645 w				1625 vw	1629 m	1630 w
1545 w	1548 w	1530 m	1569 w	1594 w	1595 m	16[illegible] m		1592 w
	1513 w					1516 vvw	1516	
^{d}		^{d}	1464 w	^{d}	^{d}	1425 vw		^{d}
	1426 m		1422 w			1420 w	1428 m	
1340 w	1364 sw	1380 m	1362 w	1380 m	1340 w	1344 vvw	1364	1366 s
	1304 w		1298 sw					
	1258 w						1257	
^{d}	1166 w	^{d}	1144 w	^{d}	^{d}			^{d}
^{d}	1110 w	^{d}		^{d}	^{d}	1108 m	1108	^{d}
1004 s	1003 s	1003 s	998 s	1004 s	1001 s	1008 s	1004 s	
^{d}	935 sw	^{d}	956 w	^{d}	^{d}		959	957 s
^{d}		^{d}	912 m	^{d}	^{d}	915 vvw	913	^{d}
^{d}	887 sw	^{d}	890 m	^{d}	^{d}	890 vw	891	^{d}
725 vs	746 ss		750 m	750 vs	750 s	783	779 ss	800 m
		700 s	712 ss	720 s	715 vs		758 ss	664 m
675 m	662 sw	660 m	663 m		675 m		663 m	658 m

^{a} Ref. 5b. ^{b} Ref. 4. Some bands labeled vvw have been omitted. ^{c} Ref. 18. Some of the weak bands have been omitted. ^{d} No detection possible because of solvent absorption.

Some PMR chemical shifts of cyclopentadienides appear in Table 2. All of them except $(C_5H_5)_2Mg$ were markedly concentration dependent. Grutzner[19] reported that chemical shifts of C_5H_5Li and C_5H_5Na in THF were slightly temperature dependent, a variable which could account for ±0.01 ppm differences in results obtained in four different laboratories.

The single peak ambient temperature PMR spectra of cyclopentadienylmagnesium compounds could be assigned either to delocalized rings or to diene-type cyclopentadiene rings in which migration of the C–Mg σ-bond to all ring carbon atoms is fast on the NMR time scale. To test the latter possibility a 0.25 *M* solution of C_5H_5MgCl in 75/25 by volume dimethyl ether/THF was cooled to $-115°$. Two sharp peaks at δ 6.05 and δ 5.96 with relative areas about 6/1 replaced the single peak seen at ambient temperature, but there was no sign of the complex splitting expected of a diene-type spectrum.

TABLE 2

PROTON CHEMICAL SHIFTS OF CYCLOPENTADIENIDES IN TETRAHYDROFURAN AT AMBIENT TEMPERATURE[a]

Compound	Concn. (*M*)	δ (ppm)	Ref.[b]
C_5H_5Li	1.0	5.59	
	0.25	5.695	19
	0.010	5.70	
C_5H_5Na	1.0	5.57	
		5.58[c]	20
	0.25	5.699	19
		5.66[c]	20
	0.010	5.72	
	0[d]	5.71[c]	20
C_5H_5MgCl	1.0	6.05	
	0.010	6.12	
C_5H_5MgBr	0.10	6.07	
$(C_5H_5)_2Mg$	0.51	5.82	
	0.25	5.80[c]	21
	0.0051	5.82	

[a] Temperature in this investigation and in ref. 19 was 27°. Temperatures in refs. 20 and 21 were not reported. [b] Results are from this investigation unless indicated otherwise. [c] Values in the original reports were measured in ppm upfield from benzene. Values in the table were calculated from $\delta(C_6H_6)=7.289$ for a 1% solution of benzene in THF/ 1% TMS measured in this investigation. [d] Extrapolated.

DISCUSSION

If magnesium formed σ-bonded *monohapto*-cyclopentadienyl compounds, C_5H_5MgCl, C_5H_5MgBr, and $(C_5H_5)_2Mg$ would be expected to have absorption spectra not greatly different from that of C_5H_6 or $C_5H_5Si(CH_3)_3$. On the other hand, if magnesium formed *π-pentahapto*-cyclopentadienyl complexes, their absorption spectra would be expected to resemble the spectra of C_5H_5Li (209 nm(sh)[8], λ_{max} < 205 nm) or C_5H_5Na (218 nm(sh), λ_{max} < 205 nm) and the calculated spectra of the cyclopentadienide ion[7,8]. Clearly the C_5H_5MgCl and C_5H_5MgBr spectra fit cyclopentadienide ion better than diene (λ_{max} 241 nm), and although $(C_5H_5)_2Mg$ had a shoulder at 233 nm, it also appeared to be headed toward an intense maximum at shorter wavelength than the 210 nm cutoff.

Similarly, for σ-bonded cyclopentadienylmetal compounds (C_s symmetry) more than one C–H stretching vibration at 3100–3000 cm^{-1} and eight normal vibrations at 1610–610 cm^{-1} have been found[5,6]. In Table 1 C_5H_6 provides a typical example of a C_s spectrum. For free cyclopentadienide ions (D_{5h}) only four and for π-complexed cyclopentadienylmetal compounds (C_{5v} or D_{5h}) only seven normal vibrations have been found[5,6]. More specifically, the presence of single sharp bands in the 3100–3000 cm^{-1} and 1012–993 cm^{-1} regions is indicative of D_{5h}, C_{5v}, or D_{5d} symmetry[6]. All of the alkali and magnesium cyclopentadienides by these criterea have delocalized, not diene-type structures.

The PMR studies were carried out primarily to confirm that the solutions used for UV and IR spectra were metal cyclopentadienides. The marked concentration dependences of chemical shifts of C_5H_5Li and C_5H_5Na most likely were due to changes in their aggregation states, perhaps contact/solvent-separated ion pair equilibria[19,22]. Essentially no free ions should have been present in the 0.01–1.0 M concentration range of this investigation[22d].

The appearance of two peaks in the PMR spectrum of C_5H_5MgCl at $-115°$ indicates that, at least at low temperature, the cyclopentadienyl Grignard reagent is composed of at least two discrete compounds. Similar observations were reported recently for a wide variety of Grignard reagents and attributed to the Schlenk equilibrium between RMgX and R_2Mg[23]. More extensive study of the low temperature PMR spectra of cyclopentadienyl Grignard reagents is in progress.

In summary, the similarity of UV and IR spectra of C_5H_5MgCl, C_5H_5MgBr, and $(C_5H_5)_2Mg$ in THF to those of C_5H_5Li and C_5H_5Na supports structures of cyclopentadienylmagnesium compounds which consist of delocalized cyclopentadienide ions with magnesium ions located on or near their C_5 axes. Like C_5H_5Li and C_5H_5Na[19], C_5H_5MgCl and C_5H_5MgBr are probably ion pairs, and $(C_5H_5)_2Mg$ is probably an ion triplet in THF since other Grignard reagents and dialkylmagnesium compounds were found to be monomeric in THF even at concentrations $>1\ M$[14]. These results concur with some earlier work on ionic organometallic compounds: The UV spectra of difluorenylmagnesium, fluorenyllithium, and fluorenylsodium in hexamethylphosphoramide were nearly identical[24]. NMR spectra of fluorenyllithium and difluorenylbarium in THF indicated that the metal atoms were located over the aromatic rings[25]. In contrast, X-ray analyses of benzyllithium and fluorenyllithium as tertiary amine complexes have shown the lithium ion to be located above the plane but outside the perimeter of the ring[26].

ACKNOWLEDGEMENT

I thank Merck and Company and E. I. du Pont de Nemours and Company for support of this research.

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