A Mass Spectroscopic Study of Benzene(cyclopentadienyl)manganese(I)

R. G. Denning and R. A. D. Wentworth

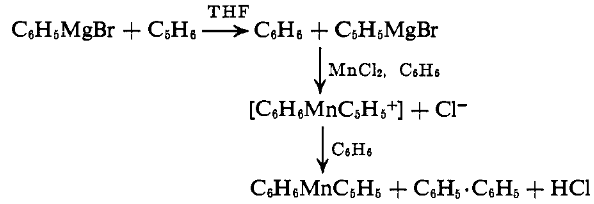
Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received May 2, 1966*

Abstract: Benzene(cyclopentadienyl)manganese(I) has been prepared and its spectral properties reported. It has a typical sandwich structure. The mass spectrum is compared with that of ferrocene and (dibenzene)chromium. A novel rearrangement is suggested to account for the fragmentation pattern, and an empirical criterion for the most abundant ions in the spectra is noted.

As part of a systematic investigation of the electronic absorption spectra of cyclopentadienyl- and arene-metal complexes, we have prepared benzene(cyclopentadienyl)manganese(I). The preparation of this compound has been reported in a thesis[1] and its infrared spectrum has been obtained.[2] We now wish to report a preparative method, some properties of the compound, and the results of a mass spectral investigation.

Results and Discussion

Benzene(cyclopentadienyl)manganese(I) (BCM) was prepared in poor yield by the route



$$\begin{aligned} &C_6H_5MgBr + C_5H_6 \xrightarrow{THF} C_6H_6 + C_5H_5MgBr \\ &\qquad\qquad\downarrow{\scriptstyle MnCl_2,\ C_6H_6} \\ &\qquad [C_6H_6MnC_5H_5{}^+] + Cl^- \\ &\qquad\qquad\downarrow{\scriptstyle C_6H_6} \\ &\qquad C_6H_6MnC_5H_5 + C_6H_5\cdot C_6H_5 + HCl \end{aligned}$$

After chromatography on alumina the product was still contaminated with biphenyl from which it was separated by sublimation and hand separation of the red crystals. It was stable in air for about 2 days. The infrared spectrum is in good agreement with that previously reported[2] and is virtually a superposition of the spectra of ferrocene and dibenzenechromium. This implies little vibrational interaction between the two halves of the sandwich.

The proton nmr spectrum shows single peaks in benzene solution at τ 6.17 and 5.49, having relative areas 5 and 6, corresponding to the cyclopentadienyl and benzene resonances, respectively. The solution nmr of (dibenzene)chromium does not seem to have been reported hitherto, possibly because of its low solubility and relative ease of oxidation to paramagnetic species. Standard vacuum-line techniques, however, allowed the preparation of stable, dilute solutions of the compound in benzene. A weak resonance was found at τ 4.85. Ferrocene has its resonance at τ 5.95 in the same solvent. The nmr and infrared spectra of BCM confirm the sandwich structure.

The principal peaks in the mass spectra of BCM and (dibenzene)chromium are presented in Table I. In addition, the mass spectrum of ferrocene, which was orginally reported by Friedman, Irsa, and Wilkinson,[3] has been reinvestigated and the results are included in the table. The numbers in parentheses are the theoretical values of the subsidiary peaks in each group calculated with reference to the major peak from the metal and carbon isotopic abundances.

The most obvious feature of the spectra is the different stability patterns of the three isoelectronic species. Ferrocene shows a very stable molecular ion, which it has been suggested is characteristic of di-π-cyclopentadienyls.[3] The manganese compound has the primary fragmentation product $MnC_5H_5{}^+$ as the base peak, while in (dibenzene)chromium the base peak appears to be benzene, with the metal ion as the next most abundant species. The abundance of the benzene ion is, however, artificially large because some decomposition of the (dibenzene)chromium occurs during its introduction into the spectrometer. The metal ion is probably the true base peak. These patterns then reflect the well-known decrease in stability from ferrocene to (dibenzene)chromium, the manganese compound being apparently an intermediate case.

The principal path of decomposition is shown by metastable peaks at *m/e* 78.8 and 25.8 for ferrocene and *m/e* 72.7 and 25.2 for BCM.[4] These correspond to the reactions (Cp = cyclopentadienyl, Bz = benzene)

$$FeCp_2{}^+ \longrightarrow FeCp^+ + Cp$$

$$FeCp^+ \longrightarrow Fe^+ + Cp$$

$$BzMnCp^+ \longrightarrow MnCp^+ + Bz$$

$$MnCp^+ \longrightarrow Mn^+ + Cp$$

Examination of the metal-containing fragments in the BCM spectrum shows same remarkable features: (a) the species MnC_2H^+ is the fourth most abundant in the spectrum, (b) there is an appreciable MnH^+ peak, and (c) the peak corresponding to $BzMn^+$ is small but that of $BzMnH^+$ is four times larger. As the ionizing potential is decreased the ratio of $BzMnH^+$ to $BzMn^+$ increases. At 20 ev no $BzMn^+$ is detectable and the abundance of $BzMnH^+$ is comparable with that of Mn^+. If we look for the structural analogs in the other spectra we find evidence for FeC_2H^+ and FeH^+ but in relatively small abundance. There is no evidence for the species $FeCpH^+$. Similarly there is no indication of the formation of CrH^+ and only relatively small yields of CrC_2H^+ and $CrBzH^+$ can be present.

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[1] S. Breitschaft, Diploma Thesis, University of Munich, 1962.

[2] H. P. Fritz and J. Manchot, *J. Organometal. Chem.*, **2**, 8 (1964).

[3] H. L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955).

[4] A small metastable peak at *m/e* 78.2 in the BCM spectrum appears only at low ionizing potentials. It does not interrelate any of the observed mass peaks.

Table I. Mass Spectra

	Cp$_2$Fe		BzCpMn		Bz$_2$Cr	
m/e	Ion	$I^{a,b}$	Ion	$I^{a,b}$	Ion	$I^{a,c}$
39	$C_3H_3^+$	2.53	$C_3H_3^+$	5.20	$C_3H_3^+$	3.10
40					$C_3H_4^+$	4.00
50					Cr^{50+} $C_4H_2^+$	4.15 (2.39)
51			$C_4H_3^+$	1.66	$C_4H_3^+$	7.62
52			$C_4H_4^+$	1.55	Cr^{52+}	45.3
53					Cr^{53+}	4.91 (5.18)
54	Fe^{54}	1.0 (0.92)			Cr^{54+}	1.43 (1.42)
55			Mn^+	70.5		
56	Fe^{56+}	14.4	MnH^+	3.44		
57	Fe^{56+} $Fe^{56}H^+$	0.72 (0.36)				
65	$C_5H_5^+$	0.72	$C_5H_5^+$	1.89		
77			$C_6H_5^+$	1.26	$C_6H_5^+$	6.26
78			$C_6H_6^+$	2.82	$C_6H_6^+$	100.00
79					$C_5C^{13}H_6^+$	3.62 (6.6)
80			MnC_2H^+	7.76		
81	$Fe^{56}C_2H^+$	2.53				
91					$Cr^{52}C_3H_3^+$	1.74
94	$Fe^{56}C_3H_2^+$	2.41				
95	$Fe^{56}C_3H_3^+$	3.50				
104					$CrC_4H_4^+$	2.40
119	$Fe^{54}Cp^+$	1.69 (1.71)	$MnC_5H_4^+$	2.56		
120			$MnCp^+$	100.00		
121	$Fe^{56}Cp^+$	26.5	$MnC_4C^{13}H_5^+$	5.92 (5.5)		
122	$Fe^{56}Cp^+$	1.81 (2.10)				
130	$C_{10}H_{10}^+$	0.48			$Cr^{52}Bz^+$	16.5
131					$Cr^{53}Bz^+$	4.4 (3.0)
133			$MnBz^+$	0.37		
134			$MnBzH^+$	1.48		
184	$Fe^{54}Cp_2^+$	7.1 (6.5)				
186	$Fe^{56}Cp^{2+}$	100.0				
187	$Fe^{56}Cp_2^+$ $Fe^{56}C_9C^{13}H_{10}^+$	12.8 (13.4)				
198			$MnCpBz^+$	42.6		
199			$MnC_{10}C^{13}H_{11}^+$	5.55(4.75)		
208					Bz_2Cr^{52+}	10.8
209					Bz_2Cr^{53+}	2.4 (2.6)

[a] Relative ion current. [b] At 70 ev. [c] At 50 ev.

The criterion for stability of the manganese-containing fragments appears to be association of a formally dipositive, d^5, manganese ion with a species which can form a relatively stable anion. Thus $MnCp^+$ and MnC_2H^+ can be considered to contain the cyclopentadienide and acetylide ions, respectively, while MnH^+ and $MnBzH^+$ contain the hydride ion. On the other hand, $MnBz^+$ does not satisfy the requirement and is present in low abundance. This pattern also applies to the other metals. $FeCp_2^+$, a formally d^5 ion, is more stable than $FeCp^+$, a formally d^6 ion. In the case of chromium the species Cr^+, $CrBz^+$, and $CrBz_2^+$ are all formally d^5 ions but there is no evidence of species such as CrH^+. This pattern could be related to the especially great stability of the ^6S state for a field-free d^5 ion.

The general course of the fragmentation can be rationalized in terms of the stability of the products. The resonance energy of benzene as a neutral fragment favors its dissociation from the manganese, but the loss of a cyclopentadienyl radical does not produce a resonance-stabilized species and requires the homolytic fission of a more polar bond. Even so the absence of any $MnBz^+$ at 20 ev is remarkable. It implies either that this species has an appearance potential higher than 20 ev or that it has such a short lifetime that it is not observed in the mass spectrometer. The appearance potential of the $FeCp^+$ fragment from ferrocene in which essentially the same bond is broken is 14.4 ev.[3] Furthermore even at very high ionizing potentials (70 ev) the $MnBz^+$ peak is still very small compared to other fragments. We can then conclude that the absence of $MnBz^+$ in the spectrum is due to its very rapid decomposition to Mn^+ and benzene. The appearance potential of $MnBz^+$ must therefore approach the appearance potential of the Mn^+ ion which it generates, *i.e.*, 17.9 ev. Figure 1 shows the relative ion abundance curves. The molecular ion curve (*m/e* 198) shows two apparent breaks, one at the energy at which $MnCp^+$ (*m/e* 120) is produced, and one at the energy at which the metal ion (*m/e* 55) appears. We suggest that these correspond to processes in which the Mn–Bz and Mn–Cp bonds, respectively, are broken. These are the two principal ways the molecular ion can dissociate. The energy of the latter process, 17–18 ev, supports the previous explanation for the short lifetime of the $MnBz^+$ ion.

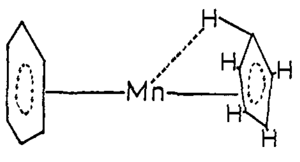
These results show that the dissociation energy of the Mn–Cp bond in $BzMnCp^+$ (10–11 ev) is much higher than that in $MnCp^+$, evaluated from the appearance potentials of $MnCp^+$ and Mn^+ (5.6 ev, see Table II). Clearly the concept of transferable bond dissociation energies is meaningless in a molecule with extensive delocalization. This is demonstrated by the data of Friedman, *et al.*[3] From their measurements the values (ev) of *D*(Mn–Cp) for MCp_2^+ and MCp^+, respectively, are: Mg, 3.2, 3.4; V, 5.1, 5.6; Mn, 4.0,

Table II. Appearance Potentials with Argon as a Reference

m/e	Ion	Method	Ap, ev
198	$BzCpMn^+$	Extrapolation	7.1
		Disappearance	7.1
		Honig	6.8
134	$MnBzH^+$	Extrapolation	12.1
120	$MnCp^+$	Extrapolation	12.3
55	Mn^+	Extrapolation	17.9

2.8; Cr, 6.5, 2.2; Fe, 7.3, 2.7; Co, 8.0, 1.9; Ni, 5.6. 1.7. The values for Mg and Mn, which are often regarded as ionic, are similar for both steps of the decomposition, but the Cr, Fe, Co, and Ni compounds, in which extensive delocalization is expected, require approximately three times as much energy for the first step as for the second. The vanadium compound appears anomalous. The results for BCM therefore follow the same stepwise stability as ferrocene, with which it is isoelectronic. Similarly, the dissociation of Bz from $BzMnCp^+$ (5.3 ev, see Table II) is expected to require several times more energy than the dissociation of $BzMn^+$. From our previous arguments we estimate the latter process to require only 0–1.0 ev. We conclude that, if the $MnBz^+$ ion has any lifetime at all, it rapidly dissociates into Mn^+ and Bz and is therefore effectively absent from the mass spectrum.

The species shown in Figure 1 are the only peaks (apart from metastable peaks) which occur below 20 ev. The appearance of m/e 134, $MnBzH^+$ at 12 ev, comparable to the energy at which $MnCp^+$ appears, is then remarkable. Two mechanisms are possible: (a) the very reactive intermediate $MnBz^+$ abstracts a hydrogen from a neutral molecule; (b) the bond to hydrogen is formed by a concerted mechanism during the loss of the cyclopentadienyl skeleton. Alternative (a) may be excluded. Firstly, operating pressures in the ion source (1.5×10^{-7} mm) are below those at which hydrogen abstraction generally occurs.[5] Secondly, if the $MnBz^+$ species had sufficient lifetime to abstract a hydrogen from another molecule one would expect to observe it in the mass spectrum. Thirdly, the energy required to break the Mn–Cp bond is 17–18 ev, much higher than the observed appearance potential. It is, therefore, necessary to postulate a concerted mechanism to explain the formation of this ion. This



mechanism satisfactorily accounts for the low appearance potential since one bond is made as the other is broken. Furthermore it explains the low abundance of the ion. The ionization efficiency curve of m/e 134 suggests that it is stable up to 17 ev so that the low abundance (~40-fold less than $MnCp^+$) cannot be explained by instability of the product. Since the formation occurs at an equal activation energy to $MnCp^+$ the low yield must be due to a low transmission coefficient. This would be expected for such a specific mechanism having a high entropy of activation.

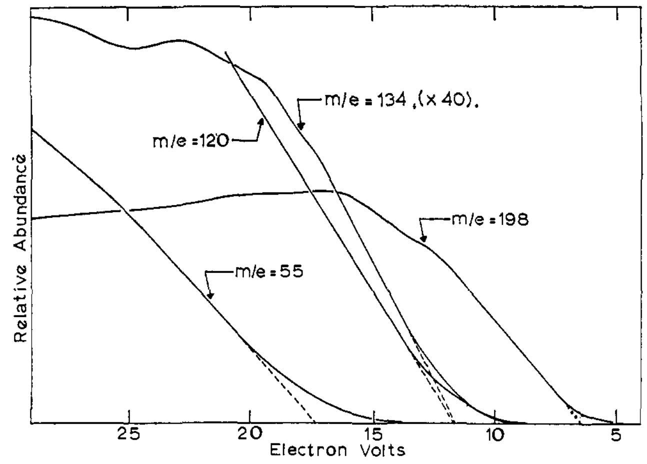
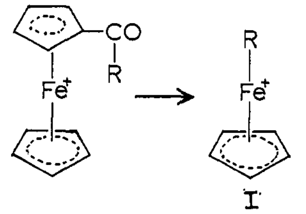


Figure 1. Ionization efficiency curves for benzene(cyclopentadienyl)manganese(I) fragments.

Unfortunately no metastable peak corresponding to this process could be observed. If we assume this peak to have an intensity 40-fold less than that corresponding to loss of the benzene residue (the ratio found for the product ions), its amplitude would lie below the noise level of the instrument at reasonable ionizing potentials.

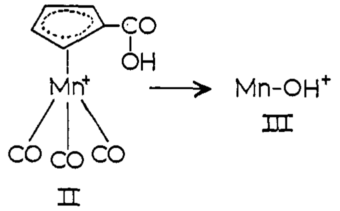
Hydrogen atom transfers are frequently encountered in organic systems, generally in those in which six-membered ring transition states may be formed, while there is some evidence for four-membered ring transition states.[6] The present case can be considered as a pseudo-four-membered ring transition state, but in a rather novel system. Paradoxically, ferrocene shows no evidence of this mechanism although the initial fragmentation requires the breaking of a similar bond.

A related, but different, rearrangement, shown below, has recently been observed for substituted ferrocenes.[7]



I

The relative abundances of I were (R, relative yield); Me, 0.0; p-$CH_3OC_6H_4$, 1.0; C_6H_5, 2.8; OCH_3, 44; OH, 100. The yield of I rises with increasing stability of the anion R^- and provides support for the use of this criterion for stability in the isoelectronic BCM fragments. The same workers[8] showed that the manganese tricarbonyl derivative II gives III with relative abundance 17.7, presumably by a similar mechanism.



II

III

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(5) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N, Y., 1962, p 55, and references therein.

(6) F. W. McLafferty in "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p 309.

(7) A. Mandelbaum and M. Cais, *Tetrahedron Letters*, 3847 (1964).

(8) N. Maoz, A. Mandelbaum, and M. Cais, *ibid.*, 2087 (1965).

Several methods are available for the determination of appearance potentials. The vanishing current[9] and extrapolation[10] methods and Honig's[11] procedure were all applied to the molecular ion. The results, shown in Table II, are similar, with respect to argon as a reference, for all these methods. The extrapolation method, which is relatively straightforward to apply, was therefore used for the other ions.

With the usual qualification that the appearance potential may well include excess energy over the true ionization potential, we can deduce an upper limit for the energy of formation of BCM. This is given by the difference in the spectroscopic first ionization potential of manganese (7.43 ev) and the appearance potential of this ion in the mass spectrometer (Table II). We obtain

$$C_6H_6(g) + C_5H_5(g) + Mn(g) \longrightarrow BCM(g) \quad \Delta H = -10.5 \text{ ev}$$

The mean metal–ring bond energy is then 5.25 ev, somewhat higher than the value of 4.60 ev found for the iron–cyclopentadienyl bond in ferrocene.[3] Since the product ions in the mass spectrometer may be in any of a number of electronic excited states this increase is probably not significant.

Experimental Section

Preparation of Benzene(cyclopentadienyl)manganese(I). With continuous stirring, bromobenzene (1.15 moles) was added slowly to 30 g of magnesium turnings (1.25 g-atoms) under a nitrogen atmosphere. After formation of the Grignard reagent, 41 ml of cyclopentadiene (0.6 mole) was added during 15 min, whereupon 70 g of anhydrous manganese chloride (1.8 moles) and 100 ml of benzene were added rapidly and the reaction was allowed to proceed at 65° for 20 min followed by boiling under reflux for 30 min. The reaction was cooled in ice, hydrolyzed with 300 ml of methyl alcohol and 500 ml of water, and allowed to stand overnight. The organic layer was then separated and evaporated to dryness. The residue was extracted with cyclohexane and purified by chromatography on alumina. The pink solution from the column was evaporated to dryness and the residue sublimed under vacuum. The product forms large deep red crystals which are easily separated by hand from the white crystals of biphenyl, mp 205° (with decomposition *in vacuo*), yield 0.45 g, *d* 1.45 (flotation in aqueous KI solution).

Anal. Calcd for $MnC_{11}H_{11}$: Mn, 27.72; C, 66.68; H, 5.60. Found: Mn, 27.26; C, 67.02; H, 5.67.

Infrared spectra were obtained in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer 521 infrared spectrophotometer. Nmr spectra were obtained on a Varian A-60 spectrometer from benzene solutions prepared *in vacuo*. TMS was present as an internal standard. The mass spectra of ferrocene and benzene(cyclopentadienyl)manganese were obtained on an Atlas CH-4 mass spectrometer at an ionizing potential of 70 ev. The mass spectrum of dibenzene(chromium) was obtained on a Bendix time-of-flight mass spectrometer at an ionizing potential of 50 ev, the sample reservoir containing the solid being maintained at approximately 60°. The appearance potentials were obtained on the latter instrument by a comparison of the ion current of argon and the molecular ion at suitable voltage intervals between 30 and 0 ev, and subsequently by a comparison of the ion current of the other species with that of the molecular ion. The relative abundances of the manganese-containing fragments are therefore correct. The data were corrected for trap current and pressure variations.

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(9) T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 807 (1947).

(10) R. H. Vought, *ibid.*, **71**, 93 (1947).

(11) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

The Nuclear Magnetic Resonance and Microwave Spectra of Some Deuterio Derivatives of 2,4-Dicarbaclovoheptaborane(7)

Thomas Onak, Gary B. Dunks,[1a] Robert A. Beaudet,[1b] and Robert L. Poynter[1c]

Contribution from the Departments of Chemistry, California State College at Los Angeles, Los Angeles, California, and University of Southern California, University Park, Los Angeles, California 90007, and the Jet Propulsion Laboratory, Pasadena, California 91103. *Received January 20, 1966*

Abstract: In spite of the known structure of 2,4-dicarbaclovoheptaborane(7), ambiguous nmr assignments were obtained for both the ^{11}B and ^{1}H nmr spectra of this molecule. Deuterium exchange was expected to aid in the nmr analysis of this molecule. Although deuterium exchanges completely at high temperatures (400°), at lower temperatures (100°) deuterium exchanges in only three definite positions. A determination of these deuterium atom locations by microwave spectroscopy for the partially deuterated isotopic species allows an unequivocal assignment to be made for both the ^{11}B and ^{1}H nmr spectra. For the partially deuterated molecule, the three deuterium atoms are preferentially substituted on the boron atoms in the base plane. These results are compatible with the nmr spectra for related boron compounds.

The structure of the dicarbaclovoheptaborane(7) prepared from pyrolysis of 2,3-dicarbahexaborane(8)[2] has been determined to be that of a pentagonal bipyramid with the two carbon atoms in the 2,4 positions[3] (Figure 1). Although the structure is known, an unambiguous assignment of certain ^{11}B and ^{1}H nmr resonance lines has not, heretofore, been possible.

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(1) (a) California State College; (b) University of Southern California; (c) Jet Propulsion Laboratory.

(2) (a) T. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **85**, 3378 (1963); (b) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

(3) R. A. Beaudet and R. L. Poynter, *J. Am. Chem. Soc.*, **86**, 1258 (1964).