

On the Electronic Ground States of Manganocene and 1,1'-Dimethylmanganocene

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Abstract: Alkyl substitution on metallocene rings generally has little effect on the chemical and magnetic properties of the metallocene. However, unlike the other first transition series metallocenes, manganocene ($(\eta\text{-C}_5\text{H}_5)_2\text{Mn}$, or MnCp_2) and 1,1'-dimethylmanganocene ($\text{Mn}(\text{Cp-CH}_3)_2$) have quite different properties. In dilute solution in hydrocarbon solvents the magnetic susceptibility of $\text{Mn}(\text{Cp-CH}_3)_2$ maximizes near 310°K, while the susceptibility of magnetically dilute MnCp_2 follows the Curie law. The electron spin resonance spectrum of $\text{Mn}(\text{Cp-CH}_3)_2$ in hydrocarbon glasses indicates that the ground state of this d^5 system at 4.2°K is ${}^2E_{2g}$, the same ground state as observed for isoelectronic ferricenium-like ions. In contrast, the electron spin resonance spectrum of MnCp_2 doped into MgCp_2 at 4.2°K is consistent with the high-spin ${}^6A_{1g}$ ground state. An equilibrium involving doublet and sextet states is proposed to account for the anomalous magnetic susceptibility of $\text{Mn}(\text{Cp-CH}_3)_2$. This is the first example of high spin-low spin equilibrium in d^5 Mn(II). Nuclear magnetic resonance results (${}^1\text{H}$) for MnCp_2 and $\text{Mn}(\text{Cp-CH}_3)_2$ are also presented and discussed.

Manganocene ($(\eta\text{-C}_5\text{H}_5)_2\text{Mn}$ or MnCp_2) is unique among the metallocene class of organometallic compounds in two respects: (1) the ground electronic configuration is high spin (${}^6A_{1g}$),² while all other known MCp_2 compounds are low spin; and (2) crystalline MnCp_2 and its 1,1'-dimethyl derivative, $\text{Mn}(\text{Cp-CH}_3)_2$, behave antiferromagnetically.^{2,3} Our interest in MnCp_2 and $\text{Mn}(\text{Cp-CH}_3)_2$ was heightened when we made the unexpected observation that $\text{Mn}(\text{Cp-CH}_3)_2$ has some properties which are quite different from MnCp_2 . The most significant difference in the two compounds is in magnetic behavior; we have found that $\text{Mn}(\text{Cp-CH}_3)_2$ has a subnormal (for $S = 5/2$) and temperature dependent magnetic moment even in dilute hydrocarbon solution, in contrast to the normal magnetic behavior of MnCp_2 under similar conditions. We report here spectral and magnetic observations on these compounds which lead to the conclusion that $\text{Mn}(\text{Cp-CH}_3)_2$ is a π -sandwich molecule existing as an equilibrium mixture of doublet and sextet electronic states. After completion of this work Orchard and coworkers obtained independent evidence for high spin-low spin equilibration in gaseous $\text{Mn}(\text{Cp-CH}_3)_2$ by means of photoelectron spectroscopy.⁴ This is the only known example of a high spin-low spin equilibrium for Mn(II).

Results

The magnetic susceptibility of $\text{Mn}(\text{Cp-CH}_3)_2$ was determined in toluene solution as a function of temperature by the Evans⁵ nmr method. The $\text{Mn}(\text{Cp-CH}_3)_2$ results for solutions 5.22×10^{-2} , 2.42×10^{-2} , and 1.62×10^{-2} *M* in toluene are presented in Table I. A plot of these data is presented in Figure 1. Magnetic moments of 4.8 to 5.0 BM were also observed at 30–50° for $\text{Mn}(\text{Cp-CH}_3)_2$ solutions in benzene, cyclohexane, and mixtures of benzene and cyclohexane.

Q-band (~ 35 GHz) epr spectra of $\text{Mn}(\text{Cp-CH}_3)_2$ were obtained at 4.2°K. The samples were studied as toluene or methylcyclohexane glasses at concentrations near 10^{-1} *M*. In either medium, the observed spectrum is characteristic of randomly oriented $S = 1/2$ molecules having an axially symmetric *g* tensor. A typical spectrum is shown in Figure 2. The observed *g* values are as follows: in methylcyclohexane $g_{\parallel} = 2.909$ and $g_{\perp} = 1.893$; in toluene $g_{\parallel} = 2.887$ and $g_{\perp} = 1.900$.

Q-band epr spectra were also obtained for MnCp_2 in var-

ious media. In either toluene or methylcyclohexane (10^{-1} – 10^{-2} *M*), or as the neat solid, MnCp_2 exhibits only a single resonance near $g = 2$, whose line width varies with temperature. Line widths between 80 and 1500 G were observed, the broader lines occurring at lower temperatures. The epr spectra of MnCp_2 in glassy media were weak and featureless, consisting only of a single broad signal near $g = 2$. We believe that MnCp_2 crystallizes from these solvents and, because of its known antiferromagnetic character, it exhibits a weak epr absorption at 1.5–4.2°K. MnCp_2 doped (2%) into MgCp_2 gave very complex spectra at Q band. At 4.2°K there were four principal areas of absorption extending from 550 G ($g \sim 43$) to 14 kG ($g \sim 1.7$). The 77°K $\text{MgCp}_2/\text{MnCp}_2$ spectrum was similar to that at 4.2°K.

Proton nmr spectra of the manganese metallocenes were obtained in benzene-*d*₆ and in cyclohexane-*d*₁₂, at 100 MHz and 310°K. In benzene-*d*₆, MnCp_2 exhibits a single resonance, with an isotropic shift of -21.8 ± 0.5 ppm (to low field, referenced to FeCp_2) and a line width of *ca.* 1500 Hz. Also in benzene-*d*₆ the spectrum of $\text{Mn}(\text{Cp-CH}_3)_2$ consists of two broad overlapping peaks with isotropic shifts of -137 ± 14 and -77 ± 4 ppm (referenced to $\text{Fe}(\text{Cp-CH}_3)_2$); in cyclohexane-*d*₁₂ these isotropic shifts are -113 ± 8 and -66 ± 3 ppm. The uncertainties in the peak positions are due to the extreme widths of about 7 and 6 kHz, respectively. In benzene-*d*₆, the lower field absorption for $\text{Mn}(\text{Cp-CH}_3)_2$ appeared partially resolved into two broad peaks, and the combined area of the partially resolved lower field absorptions was slightly greater than that at -77 ± 4 ppm. These observations are consistent with the assignment of the lowest field absorption(s) to the Cp ring hydrogens, with the attached methyl occurring as the narrow resonance at *ca.* -70 ppm.

Discussion

It has been known for many years that the magnetic properties of both MnCp_2 and $\text{Mn}(\text{Cp-CH}_3)_2$ are distinctly anomalous.^{2,3} MnCp_2 is antiferromagnetic as a crystalline solid but behaves as a normal $S = 5/2$ d^5 complex when magnetically dilute (doped into MgCp_2 or dissolved in benzene).² $\text{Mn}(\text{Cp-CH}_3)_2$ also behaves antiferromagnetically both in the crystalline solid and in the melt, while its solutions in tetrahydrofuran have normal, temperature-independent moments appropriate for the $S = 5/2$ state.³ Wilkinson

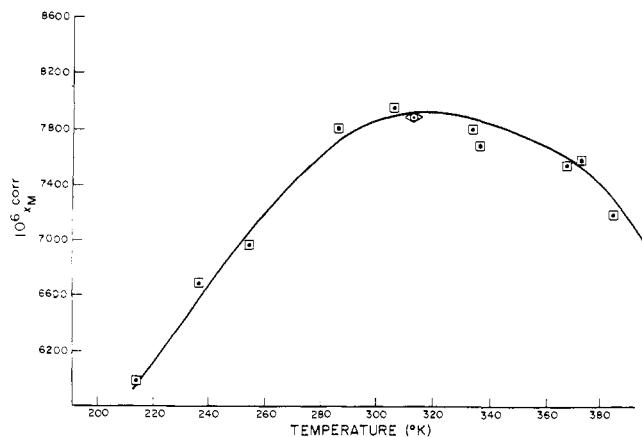


Figure 1. Temperature dependence of χ_M^{corr} for $\text{Mn}(\text{Cp-CH}_3)_2$: \square $5.22 \times 10^{-2} M$; \circ $2.42 \times 10^{-2} M$; \diamond $1.62 \times 10^{-2} M$.

Table I. Temperature Dependence of the Magnetic Susceptibility of $\text{Mn}(\text{Cp-CH}_3)_2$ in Toluene

$[\text{Mn}(\text{Cp-CH}_3)_2]$, M	T , $^\circ\text{K}$	$10^6 \chi_M^{\text{corr}}$ a,b	μ_{eff} , BM ^c
5.22×10^{-2}	214	5990	3.23
	235	6680	3.55
	253	6980	3.77
	285	7810	4.23
	303	7980	4.41
2.42×10^{-2}	310	7920	4.44
	310	7920	4.44
1.62×10^{-2}	310	7920	4.44
	331	7830	4.58
5.22×10^{-2}	334	7690	4.55
	366	7580	4.73
	371	7620	4.77
	371	7620	4.77

^a χ_M^{corr} is χ_M corrected for ligand diamagnetism (for this correction we used the diamagnetic susceptibility of FeCp_2 as an approximation: $\chi_M(\text{FeCp}_2) = -125 \times 10^{-6}$ cgs). ^b Estimated precision $\pm 2\%$. ^c $\mu_{\text{eff}} = 2.83(\chi_M^{\text{corr}} T)^{1/2}$; estimated, ± 0.05 – 0.1 BM.

and coworkers suggested that the antiferromagnetism for both MnCp_2 and $\text{Mn}(\text{Cp-CH}_3)_2$ arises intermolecularly,^{2,3} and in the case of molten $\text{Mn}(\text{Cp-CH}_3)_2$ retention of some crystalline ordering even in the liquid was believed responsible for the liquid antiferromagnetism.³

Our observation of "antiferromagnetic" behavior for $\text{Mn}(\text{Cp-CH}_3)_2$ in dilute hydrocarbon solutions could possibly be accounted for by oligomerization equilibria. Oligomerization is ruled out, however, by the absence of concentration dependence of the observed subnormal (for $S = 5/2$) moments, and the corresponding anomalous behavior of the susceptibility must therefore arise from intramolecular equilibration of electronic doublet and sextet states of $\text{Mn}(\text{Cp-CH}_3)_2$.⁷⁻⁹ The high spin state is ${}^6A_{1g}$ derived¹⁰ from the configuration $(e_{2g})^2(a_{1g})^1(e_g^*)^2$, and the potential low spin doublet states are ${}^2E_{2g}((e_{2g})^3(a_{1g})^2)$ or ${}^2A_{1g}((e_{2g})^4(a_{1g})^1)$.

At room temperature, our results indicate the presence of nearly equal amounts of the doublet and sextet forms of $\text{Mn}(\text{Cp-CH}_3)_2$. The room-temperature solution infrared spectrum of $\text{Mn}(\text{Cp-CH}_3)_2$ is very similar to that of $\text{Fe}(\text{Cp-CH}_3)_2$; therefore major structural changes accompanying spin state changes are not indicated. Both high and low spin states of $\text{Mn}(\text{Cp-CH}_3)_2$ are thus believed to be "sandwich" species with pentahapto rings. This conclusion is reinforced by the observation of an epr spectrum of $\text{Mn}(\text{Cp-CH}_3)_2$ at 4.2°K which is very similar to that observed for isoelectronic π sandwich¹¹ ferricenium-like ions.^{12,13} Further indication of the intervention of a nonsextet state for $\text{Mn}(\text{Cp-}$

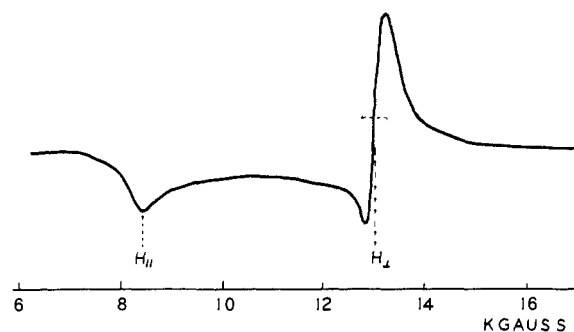


Figure 2. Q-band epr spectrum of $\text{Mn}(\text{Cp-CH}_3)_2$ in glassy methylcyclohexane at 4.2°K .

$\text{CH}_3)_2$ is found in the electronic spectrum, where the visible absorptions, which are presumed to be d-d bands, are six- to tenfold stronger than those observed for MnCp_2 . All d-d transitions for MnCp_2 are spin forbidden, a restriction which would not apply to a doublet state.

The bulk susceptibility of dilute MnCp_2 in MgCp_2 has been determined down to 77°K ,² and it is apparent from the bulk susceptibility of $\text{MnCp}_2/\text{MgCp}_2$ that at 77°K there is no antiferromagnetism and the only populated state is ${}^6A_{1g}$. Our 77°K epr spectrum for MnCp_2 in MgCp_2 therefore must be the spectrum characteristic of the ${}^6A_{1g}$ state of MnCp_2 . Since there are transitions near zero field in the Q-band spectrum (~ 35 GHz), the value of D , the zero-field splitting parameter, must be substantially larger than those usually observed for manganous salts, perhaps as large as 0.5 cm^{-1} . The various peaks observed in the spectrum are allowed transitions among the M_s sublevels of ${}^6A_{1g}$, but a complete assignment appears impossible without single-crystal data. The spectrum is essentially of the same form down to 1.5°K , with some band shifts believed to arise from a temperature dependence of D .

Voitländer and coworkers^{14a,b} have previously investigated the epr of MnCp_2 at X band. The published experimental work^{14a} was limited to a temperature study of undiluted single crystals with the briefest mention that the g values (2.01 and 1.99) are unchanged above 156° when MnCp_2 is doped into MgCp_2 . A later theoretical interpretation^{14b} dealt only with the single-crystal results. It was concluded that the observation of only one resonance near $g = 2$ was the result of either (a) exchange averaging of the expected fine and hyperfine structure or (b) observation of only the $-1/2 \rightarrow +1/2$ transition due to a large zero-field splitting combined with the limitations of X-band operation. Our magnetically dilute Q-band results for $\text{MnCp}_2/\text{MgCp}_2$ are in accord with expectations^{14b} of a large zero-field splitting. Thus Krieger and Voitländer^{14b} obtained a theoretical value of $D = 0.24 \text{ cm}^{-1}$. The transition observed in the present work near zero field (actually ~ 550 G) could either be assigned to the allowed $-3/2 \rightarrow -1/2$ ($\sim 2D$) or to the allowed $-5/2 \rightarrow -3/2$ ($\sim 4D$) transition. This would place $|D|$ in the range 0.25 – 0.50 cm^{-1} .

Direct observation of doublet $\text{Mn}(\text{Cp-CH}_3)_2$ was accomplished with Q-band epr measurements at 4.2°K . The spectra obtained in methylcyclohexane and toluene glasses (Figure 2) are very similar to the spectra of ${}^2E_{1g}$ ferricenium-like cations;^{12,13} further, the observed spectra are not at all consistent with expectations for a sextet state, as are the $\text{MnCp}_2/\text{MgCp}_2$ results. The g anisotropy observed for $\text{Mn}(\text{Cp-CH}_3)_2$ is consistent only with the ground configuration $\dots(e_{2g})^3(a_{1g})^2\dots$, or ${}^2E_{2g}$, and we may use the theory developed by Maki and Berry¹² to obtain bonding information from the g values. It was shown¹² that if the crystal-line field affecting the metal in sandwich cations departs

from axial symmetry (measured by a parameter δ), then the g values for the ${}^2E_{2g}$ state are given by

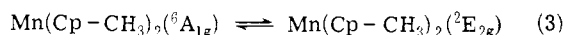
$$g_{\parallel} = 2 + 4k'(1 - \xi^2)/(1 + \xi^2) \quad (1)$$

$$g_{\perp} = 4\xi/(1 + \xi^2) \quad (2)$$

In eq 1 and 2, $\xi = (\delta/\xi_0)/[1 + \{1 + (\delta/\xi_0)^2\}^{1/2}]$ with $\xi = k'\xi_0$, where k' is the orbital reduction factor for the metal e_{2g}^{\pm} orbitals and ξ_0 is the spin-orbit coupling constant for the gaseous bare metal ion. Using the experimental g values for $Mn(Cp-CH_3)_2$ in methylcyclohexane ($g_{\parallel} = 2.909$; $g_{\perp} = 1.893$) and setting $\xi_0 = 305 \text{ cm}^{-1}$ (appropriate¹⁵ for Mn^+ , $3d^5 4s^1$), we find that $k' = 0.71$ and $|\delta| = 630 \text{ cm}^{-1}$. For comparison, Prins^{13a} finds $k' = 0.83$ and $|\delta| = 500 \text{ cm}^{-1}$ for $Fe(Cp-CH_3)_2^+I_3^-$ in glassy *N,N*-dimethylformamide; however, Prins' results^{13a} may have suffered from decomposition of the cations and have been questioned^{13d-f} (however, see ref 13g). Rowe and McCaffery^{13f} found that $|\delta| = 1043 \text{ cm}^{-1}$ and $k' = 0.75$ for $[FeCp_2]BF_4$ in methacrylic acid. Maki and Berry¹² found ranges of $364\text{--}750 \text{ cm}^{-1}$ (δ) and $0.76\text{--}0.90$ (k') for carborane analogs of $FeCp_2^+$. The relatively large observed $|\delta|$ for $Mn(Cp-CH_3)_2$ in the nonpolar medium suggests that the ring substituents can make a substantial contribution to the lowering of the symmetry of the ligand field. It is interesting that the orbital reduction factor for $Mn(Cp-CH_3)_2$ is smaller than any observed for iron sandwich species,^{12,13} which could indicate that the e_{2g}^{\pm} metal orbitals of Mn are more involved in "back donation" to the Cp rings than is the case in the iron compounds. Since Mn is in the zero (formal) oxidation state compared to the +1 state for the iron compounds, greater back donation for Mn is understandable.

According to the theory, the ${}^2E_{2g}$ state is actually split into two Kramers' doublets in the iron compounds¹² and therefore also in $Mn(Cp-CH_3)_2$. For $Mn(Cp-CH_3)_2$, the energy difference between these doublets is $2(\xi^2 + \delta^2)^{1/2}$ or 1340 cm^{-1} . This may be compared to a splitting of 1200 cm^{-1} observed for $Fe(Cp-CH_3)_2^+$,^{13a} and 1043 cm^{-1} for $FeCp_2^+$.^{13f} The 1340-cm^{-1} splitting of the two Kramers' doublets in $Mn(Cp-CH_3)_2$ is too large to permit significant population of the higher energy doublet, even at our highest temperature for measurement of bulk susceptibility (371 K). At that temperature the population of the upper state would be only *ca.* 0.5% of the lower state.

If we assume that at all temperatures we are dealing with thermal equilibration of only two electronic states, namely ${}^6A_{1g}$ and ${}^2E_{2g}$, then the data in Table I may be used for calculation of ΔH° and ΔS° for the reaction



The experimental magnetic moments (μ_{exp}) are related¹⁶ to the high and low spin moments by eq 4 where

$$\mu_{\text{exp}}^2 = \mu_{1s}^2 X_{1s} + (1 - X_{1s}) \mu_{hs}^2 \quad (4)$$

μ_{1s} and μ_{hs} are the effective moments for the ${}^2E_{2g}$ and ${}^6A_{1g}$ states, respectively, while X_{1s} and $(1 - X_{1s})$ are the mole fractions of low and high spin states, respectively. Equation 5 relates the experimental g values for the ${}^2E_{2g}$ state to μ_{1s} ,

$$\mu_{1s} = \left\{ \frac{1}{3} (g_{\parallel}^2 + 2g_{\perp}^2) (S)(S + 1) \right\}^{1/2} \quad (5)$$

and using methylcyclohexane g values, we find $\mu_{1s} = 1.98 \text{ BM}$. Finally, we assume that $\mu_{hs} = 5.92 \text{ BM}$, which is appropriate for the ${}^6A_{1g}$ state and close to the value obtained for $MnCp_2$ when magnetically dilute.² Equation 4 was solved for X_{1s} and therefore $K_{\text{eq}} = X_{1s}/(1 - X_{1s})$ at each temperature from $214\text{--}371 \text{ K}$, using the data in Table I for the $5.22 \times 10^{-2} M$ solution. The results are presented in

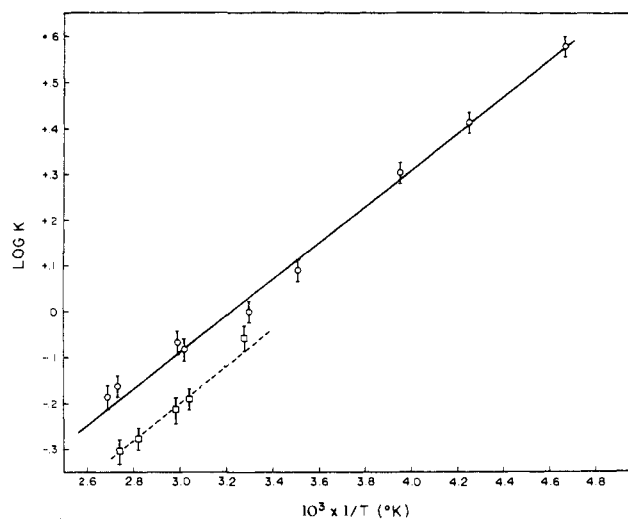


Figure 3. Plots of $\log K$ vs. $1/T$ for $Mn(Cp-CH_3)_2$ in toluene (O) and for neat liquid $Mn(Cp-CH_3)_2$ (□).

Table II. Temperature Dependence of the Spin Equilibrium of $Mn(Cp-CH_3)_2$

$T, ^\circ K$	X_{1s}	X_{hs}	$K = X_{1s}/X_{hs}$
214	0.791	0.209	3.78
235	0.721	0.279	2.58
253	0.669	0.331	2.02
285	0.551	0.449	1.23
303	0.501	0.499	1.00
331	0.452	0.548	0.825
334	0.461	0.537	0.855
366	0.407	0.593	0.686
371	0.395	0.605	0.653

Table II, and a plot of $\log K$ vs. $1/T$ is shown in Figure 3. The linearity of the $\log K$ vs. $1/T$ plot supports our assumption of a two-state equilibration, as in eq 3. From the plot we find $\Delta H^\circ = -1800 \pm 100 \text{ cal/mol}$ and $\Delta S^\circ = -5.8 \pm 0.6 \text{ eu}$.

It is of interest to compare our dilute solution results to those obtained by Reynolds and Wilkinson³ for neat molten $Mn(Cp-CH_3)_2$. Applying the same assumptions to that set of data as to our own, we find for the melt that $\Delta H^\circ = -1900 \pm 100 \text{ cal/mol}$ and $\Delta S^\circ = -6.5 \pm 0.6 \text{ eu}$ (see Figure 3). Since the results for the melt are practically the same as for the dilute solution, we conclude that in both cases equilibration of doublet and sextet states is responsible for the anomalous magnetic behavior. It was found in the earlier work³ that $Mn(Cp-CH_3)_2$ behaves as a normal $S = 5/2$ complex on dissolving in tetrahydrofuran. This in no way conflicts with our solution results, since it is known that $MnCp_2$ (and presumably also $Mn(Cp-CH_3)_2$) is strongly solvated by tetrahydrofuran;² this solvation probably disrupts the π -sandwich structure.¹⁷

The observed nmr spectra of $MnCp_2$ and $Mn(Cp-CH_3)_2$ at 310 K are quite different from one another, which behavior is unprecedented, since methyl substitution has not previously been observed to significantly alter the net spin density at Cp hydrogens.^{18,19} However, as we have shown, at 310° there is a nearly equal population of doublet and sextet $Mn(Cp-CH_3)_2$ in solution; thus the unusually large isotropic shifts of $Mn(Cp-CH_3)_2$ compared to $MnCp_2$ are initially not surprising.

The relatively small isotropic shift of $MnCp_2$ converts to a hyperfine coupling constant, A_H , of $+0.073 \text{ MHz}$.²⁰ Since there is no reason to expect a significant dipolar (pseudocontact) shift for the ${}^6A_{1g}$ state of $MnCp_2$, the

0.073-MHz coupling constant must be mainly Fermi contact in origin. The other paramagnetic first-row metallocenes have been found^{18,19} to have electron-ring hydrogen A_H values as follows: VCp₂ (2.33 MHz), CrCp₂ (3.92 MHz), CoCp₂ (-2.39 MHz), and NiCp₂ (-3.53 MHz). It is apparent that the MnCp₂ result is anomalously small, only 3% of the smallest A_H for the other metallocenes. Perhaps such a finding is not surprising, in view of the long held notion that the bonding in MnCp₂ is essentially "ionic" in nature.^{2,3} However, an alternative and more likely explanation for the very small MnCp₂ coupling constant would involve cancellation of spin density at the Cp hydrogens, due to the combined effects of unpaired σ and π electron delocalization. The ground configuration of MnCp₂ is $\dots(e_{2g})^2(a_{1g})^1(e_{1g}^*)^2\dots$, with five unpaired spins, based on earlier magnetic susceptibility data² and our own epr results. On the basis of previous work with VCp₂ and CrCp₂^{18,19} as well as with FeCp₂^{+,13a,21,22} the unpaired e_{2g} ($d_{xy}, d_{x^2-y^2}$) electrons are expected to have only a small effect on observed proton contact shifts. However, the a_{1g} (d_{z^2}) and e_{1g}^* (d_{xz}, d_{yz}) electrons may well have comparable contributions to A_H , but of opposite sign.^{10,18,19} In principle, these contributions may be sorted out by means of methyl substitution, but in so doing, as has been shown above, the problem intensifies with the appearance of doublet as well as sextet Mn(Cp-CH₃)₂.

The nmr spectrum of Mn(Cp-CH₃)₂ is particularly curious in view of the large observed isotropic shift of the Cp and CH₃ hydrogens. The observed spectrum at 310°K is presumably time averaged over nearly equal populations of doublet and sextet states, and methyl substitution is not expected to significantly alter the spin-density distribution in the sextet state. Further, other things being equal, the doublet shifts should be only *ca.* 8.5% of the sextet shifts because of the much weaker magnetization of doublet Mn(Cp-CH₃)₂.²³ Clearly, the mode of electron delocalization cannot be the same in doublet and sextet Mn(Cp-CH₃)₂; the point is that whatever the mode of delocalization in doublet Mn(Cp-CH₃)₂, it must be highly efficient to produce such large isotropic shifts in an $S = 1/2$ system. If we assume (a) that our interpretation of the bulk susceptibility correctly implies that at 310°K the relative populations of sextet and doublet Mn(Cp-CH₃)₂ are nearly equal and (b) that methyl substitution does not significantly alter the spin density at Cp hydrogens in the sextet state, then we find that the Cp hydrogen coupling constant in doublet Mn(Cp-CH₃)₂ is *ca.* 9 MHz. This coupling constant is two to four times larger than those observed for any other neutral metallocene,^{18,19} and it is about ten times larger than the largest possible Fermi contact coupling to Cp hydrogen in ²E_{2g} ferricenium ions.^{13a,21,22} Both molecular orbital^{10,19} (MO) and experimental^{13a,18,21,22} results suggest that a ²E_{2g} configuration is unlikely to produce a Cp hydrogen coupling constant of anything like +9 MHz. In fact, the MO results predict negative coupling *via* e_{2g} d_{π} - p_{π} back donation.^{10,19} The possibility of a large pseudocontact contribution to the 9-MHz coupling constant is unlikely. The Mn ring centroid distance in MnCp₂ has been determined to be 2.05 Å by electron diffraction.²⁴ If we assume a slight shortening to 2.0 Å in doublet Mn(Cp-CH₃)₂ and use our experimental g values along with Prins' geometric factors,^{13a} we find that the expected dipolar coupling would be approximately 0.30 and -0.16 MHz for the Cp ring hydrogen and the methyl hydrogen, respectively.

Previous nmr and epr studies of sandwich molecules and ions have shown that those systems having (at least) an unpaired electron in the a_{1g} orbital exhibit large positive hyperfine coupling to the ring hydrogens (the a_{1g} orbital is derived from d_{z^2} , which is directed along the principal sym-

metry axis). For some such systems, the observed coupling constants are as follows: VCp₂, 2.33 MHz;¹⁸ CrCp₂, 3.92 MHz;¹⁸ bis(η -benzene)chromium(I), 9.69 MHz;^{25a} bis(η -benzene)vanadium(0), 11.2 MHz;^{25b} bis(η -benzene)vanadium(I), 3.16 MHz;^{25b} (η -cycloheptatrienyl)(η -cyclopentadienyl)vanadium(0), 5.0 MHz (C₅H₅) and 12.0 MHz (C₇H₇);^{26a} (η -benzene)(η -cyclopentadienyl)chromium(0), 6.58 MHz (C₅H₅) and 13.0 MHz (C₆H₆);^{26b} (η -cyclopentadienyl)(η -cyclohexatrienyl)chromium(I), 6.05 MHz (C₅H₅) and 10.1 MHz (C₇H₇).^{26b} In all these systems, the positive hyperfine coupling indicates substantial direct delocalization of unpaired d_{z^2} electron density to ring hydrogens.^{10,19,25,26} Our observation of a large positive hyperfine coupling in Mn(Cp-CH₃)₂ therefore suggests that at higher temperatures there is actually thermal equilibration among *three* states: ⁶A_{1g} (from $(e_{2g})^2(a_{1g})^1(e_{1g}^*)^2$); ²E_{2g} (from $(e_{2g})^3(a_{1g})^2$), and ²A_{1g} (from $(e_{2g})^4(a_{1g})^1$). It is the last configuration which is expected to lead to a large positive A_H , by analogy with the other sandwich systems above. None of the three configurations is expected to have large dipolar shifts, either because of favorable geometric factors (²E_{2g}) or because of lack of g anisotropy (⁶A_{1g},¹⁴ ²A_{1g}¹²).

Thermal population of the ²A_{1g} state in ferricenium type ions has been suggested as one factor to consider in interpreting the temperature dependence of μ_{eff} for ferricenium cations.^{13c,27,28} However, Cowan and coworkers discount thermal population of ²A_{1g} in their biferrocene cations, since no epr absorption attributable to the ²A_{1g} state was observed at high temperature, nor was there any significant deviation of the observed μ_{eff} from expectations based on the low temperature (²E_{2g}) g values.^{13c} Both Cowan and coworkers^{13c} and Prins^{13a} used photoelectron results²⁹ for FeCp₂ to estimate that the ²A_{1g} state in FeCp₂⁺ probably lies \sim 2800 cm⁻¹ above the ²E_{2g} ground state, too high to affect strongly the magnetic results. These earlier estimates of $\Delta(^2E_{2g} - ^2A_{1g})$ for FeCp₂⁺ are in agreement with more recent photoelectron spectroscopy results for FeCp₂.^{30,31} Hendrickson and coworkers²⁸ computed similar separations between the ²A_{1g} and ²E_{2g} levels from the magnetic susceptibility data for [FeCp₂]₃ (2317 cm⁻¹) and [FeCp₂]⁺DDQH⁻ (3380 cm⁻¹) (DDQH = 2,3-dichloro-5,6-dicyanobenzohydroquinone). Perhaps more closely related to the present findings is the proposal³⁰ that the electronic ground state of *gaseous* MnCp₂ is ²A_{1g}.³² All these observations suggest the possibility that the ²A_{1g} state in Mn(Cp-CH₃)₂ may well lie quite near the ground ²E_{2g} state, and our high-temperature pmr data may therefore be reasonably explained.

The intervention of a second doublet state (²A_{2g}) at higher temperatures should not seriously affect our earlier conclusions from the χ_M vs. T data, since the expected magnetic moment of the ²A_{2g} state should be close to the spin only value of 1.73 BM, which is coincidentally similar to the value of 1.98 BM derived for the ²E_{2g} state.³³

Conclusion

The magnetic susceptibility and epr results reported here are fully consistent with equilibration of high spin ($S = 3/2$) and low spin ($S = 1/2$) forms of the π -sandwich molecule Mn(Cp-CH₃)₂. There is no indication of any such equilibration of MnCp₂ either dissolved in organic solvents² or doped into MgCp₂, even down to 1.5°K. However, it seems likely that in the condensed phase MnCp₂ (the only "high-spin" metallocene) is itself close to a high spin-low spin crossover, since small perturbations such as volatilization^{30,32} or addition of two methyl groups lead to doublet ground states. Methyl groups are ordinarily considered to be electron releasing compared to hydrogen, and this evidently is important enough in Mn(Cp-CH₃)₂ to significant-

ly increase the donor character of the ligands and cause spin pairing. Evidence of increased ring electron density in $\text{Fe}(\text{Cp-CH}_3)_2$ compared to FeCp_2 is found in their respective behavior toward oxidation. $\text{Fe}(\text{Cp-CH}_3)_2$ is more readily oxidized, presumably because of the electron-releasing character of the substituent methyl groups.^{2,34}

The pairing energies for d^4 , d^5 , and d^6 are similar,⁹ and both the d^4 (CrCp_2) and d^6 (FeCp_2) metallocenes are low spin. Since MnCp_2 seems very near a magnetic crossover point, we conclude that the overall d-orbital splittings in MnCp_2 are similar to its neighbors. Thus, although MnCp_2 behaves ionically in that it reacts rapidly with ferrous salts,² dissociates to give conducting solutions,² and exchanges rings instantaneously with LiC_5D_5 ,³⁵ our results suggest that the overall degree of M-Cp orbital mixing is similar for Mn and for Fe, a conclusion which is not surprising since the electronegativities of Mn and Fe are practically the same, regardless of the scale used. In this connection we note that Orchard and coworkers,⁴ who have provided independent evidence supporting the high spin-low spin equilibrium in $\text{Mn}(\text{Cp-CH}_3)_2$ (from the photoelectron spectrum), have observed that the ligand field splitting parameters deduced for FeCp_2 should lead to a low-spin ground state for MnCp_2 , if such parameters were to be directly transferred.

Finally, our results, together with the photoelectron results for gaseous MnCp_2 ,^{30,32} raise the possibility that the crystalline antiferromagnetism of both MnCp_2 and $\text{Mn}(\text{Cp-CH}_3)_2$, long believed to be intermolecular in origin, actually may arise intramolecularly.

Experimental Section

Instrumentation. Uv-visible spectra were recorded on a Cary 14 spectrophotometer. Ir spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer. A Varian HA-100 nmr spectrometer with an external Hewlett-Packard XY recorder was used to record the nmr spectra of the metallocenes; a Varian A-60D nmr spectrometer was used for the determination of the magnetic moments. Epr spectra were recorded at Q band. The field was calibrated using an nmr gaussmeter employing a D_2O sample. The frequency was measured with a Hewlett-Packard 5245L frequency counter. The sample and cavity were immersed directly in liquid He during measurements. Air-sensitive compounds were generally handled and stored in a Vacuum-Atmospheres Company Dri-Train dry box.

Solvents. For syntheses and magnetic moment measurements, reagent-grade solvents were degassed with prepurified nitrogen and dried with Linde 3A or 5A molecular sieves. For infrared and nmr spectra, spectral grade solvents were treated similarly. Methylcyclohexane for the epr and uv-visible studies was stirred for several hours with sulfuric acid, washed with distilled water, and distilled from BaO under nitrogen; toluene for the epr study was degassed with prepurified nitrogen and dried with Linde 3A molecular sieves.

Synthesis of Compounds. MnCp_2 was prepared from MnBr_2 and NaCp by the published method.² MnCp_2 was isolated by sublimation at 200° (0.5 mm) from the reaction vessel and freshly resublimed at 80° (0.5 mm) just before use.

$\text{Mn}(\text{Cp-CH}_3)_2$ was prepared from $\text{Na}(\text{Cp-CH}_3)$ and MnBr_2 in THF essentially by the method of Reynolds and Wilkinson.³ After removal of the solvent, the $\text{Mn}(\text{Cp-CH}_3)_2$ was extracted into pentane, and the pentane was evaporated. If the product did not crystallize spontaneously, it was vacuum distilled at <200° (1 mm). Seeding reliably induced crystallization. The product was further purified by several sublimations at 40° (0.5 mm). A small amount of MnCp_2 was always present in the $\text{Mn}(\text{Cp-CH}_3)_2$ prepared by this method.

MgCp₂. CpMgBr was prepared by the method of Jolly.³⁶ After removal of benzene, conversion to MgCp_2 was effected by heating the residue to 200° and removing the product by sublimation.

$\text{Fe}(\text{Cp-CH}_3)_2$ was purchased from Alfa Inorganics and was sublimed before use.

Preparation of Samples for Spectra. Samples for the uv-visible study were prepared in volumetric flasks by mixing freshly resublimed metallocene with purified methylcyclohexane in the dry box. MnCp_2 ($1.47 \times 10^{-2} M$) and $3.87 \times 10^{-2} M$ $\text{Mn}(\text{Cp-CH}_3)_2$ were used. For the infrared studies 0.469 M $\text{Fe}(\text{Cp-CH}_3)_2$ in benzene, 0.347 M $\text{Fe}(\text{Cp-CH}_3)_2$ in cyclohexane, 0.3 M $\text{Mn}(\text{Cp-CH}_3)_2$ in benzene, and 0.349 M $\text{Mn}(\text{Cp-CH}_3)_2$ in cyclohexane were run vs. the corresponding solvent in 1.0 mm KBr solution cells; $\text{Fe}(\text{Cp-CH}_3)_2$ was also run as a neat liquid between NaCl plates.

Electronic spectra of both MnCp_2 and $\text{Mn}(\text{Cp-CH}_3)_2$ dissolved in methylcyclohexane were recorded at room temperature with the following results: for MnCp_2 (λ_{max} , nm (ϵ_{max} , $M^{-1} \text{ cm}^{-1}$)) 475 sh (3.6), 390 sh (50), 300 (1200), and very strong absorption below 300 nm; for $\text{Mn}(\text{Cp-CH}_3)_2$ 470 sh (31), 408 (316), 303 sh (610), and very strong absorption below 303 nm.

Infrared spectra of $\text{Mn}(\text{Cp-CH}_3)_2$ and $\text{Fe}(\text{Cp-CH}_3)_2$ were determined at room temperature in solution in both cyclohexane and benzene. In the regions not blocked by strong solvent absorption, and above the M-C region, it was found that the spectra are very similar. The major absorptions are as follows (composites from the two solvents): for $\text{Fe}(\text{Cp-CH}_3)_2$ (ν_{max} in cm^{-1} (w = weak, m = medium, s = strong, vs = very strong)) 3915 (w), 3090 (s), 2910 (s), 2870 (s), 2740 (w), 1750 (m), 1725 (m), 1680 (m), 1635 (m), 1445 (m), 1370 (m), 1350 (m), 1235 (s), 1115 (m), 1010 (m), 935 (s), 920 sh (m), 810 (s), 635 (m), 615 (m), 480 (s), 395 (w); and for $\text{Mn}(\text{Cp-CH}_3)_2$ 3920 (w), 3080 (m), 2910 (s), 2860 (s), 2740 (m), 1710 (w), 1660 (m), 1605 (m), 1550 (m), 1440 (m), 1370 (m), 1340 (m), 1240 (m), 1060 (m), 1010 (m), 935 (s), 915 sh (m), 815 (vs), 760 (vs), 635 (s), 600 (s), 380 (s).

For the nmr experiments freshly resublimed metallocenes were dissolved in dried, degassed deuterated solvents in the dry box. C_6D_6 and C_6D_{12} solutions 1 M in $\text{Mn}(\text{Cp-CH}_3)_2$ were used; since MnCp_2 is much less soluble than $\text{Mn}(\text{Cp-CH}_3)_2$, only about a 0.1 M solution in C_6D_6 could be obtained.

Measurement of Magnetic Susceptibility. Solutions 0.369 M in NiCp_2 , $5.22 \times 10^{-2} M$ in $\text{Mn}(\text{Cp-CH}_3)_2$, and $8.08 \times 10^{-2} M$ in $\text{Mn}(\text{Cp-CH}_3)_2$ were prepared in volumetric flasks in the dry box. The last solution was diluted to obtain 1.62×10^{-2} and $2.42 \times 10^{-2} M$ in $\text{Mn}(\text{Cp-CH}_3)_2$. The magnetic susceptibilities of these solutions were measured by a modification of Evans⁵ nmr method. A solution of the paramagnetic substance in a thin-walled nmr tube was thermally equilibrated with the nmr probe and its spectrum recorded; a spectrum of the pure solvent was then recorded immediately and the temperature was measured by the methanol or ethylene glycol shift method. This procedure was then repeated, and the spectrum of the pure solvent was recorded in the tube used for the solution; the results were generally reproducible and the solvent spectra in the two different tubes superimposable to within 1%. To check the accuracy of the method, the susceptibility of 0.369 M NiCp_2 was measured at 313°K. with the following result: $\chi_M^{\text{corr}} = 3250 \times 10^{-6}$ cgs; $\mu_{\text{eff}} = 2.86 \pm 0.10$ BM (lit.³⁷ 2.86 ± 0.11 BM).

Preparation of Samples for the Epr Experiments. In the dry box $10^{-1} M$ solutions of freshly resublimed metallocenes were prepared and transferred into flamed quartz sample holders; a new sample holder was used for each experiment. The samples were then sealed under vacuum and used immediately. MnCp_2 was doped into MgCp_2 by twice cosubliming the resublimed solids: the quartz sample holders for these experiments were also filled in the dry box.

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Synthesis Employing Oxidative Insertion of Palladium Atoms into Aryl, Alkyl, and Acyl Carbon-Halogen Bonds. Properties of and Phosphine Trapping of the Nonligand Stabilized RPdX and RCOPdX Intermediates^{1,2}

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Abstract: Palladium atoms oxidatively insert aryl, alkyl, and acyl carbon-halogen bonds at low temperature to yield a new series of reactive intermediates ArPdX , RPdX , and RCOPdX . Efficiency of the insertion is in the order $\text{C-I} > \text{C-Br} > \text{C-Cl}$. These species are formed in the absence of normal stabilizing ligands and their stabilities vary greatly depending on the organic group attached. For example $\text{C}_6\text{F}_5\text{PdBr}$ is stable at room temperature in the air whereas CH_3PdI decomposes at extremely low temperature under vacuum. The stability order is $\text{C}_6\text{F}_5 > \text{CF}_3 \sim \text{CF}_3\text{CF}_2 \sim \text{CF}_3\text{CF}_2\text{CF}_2 > \text{C}_6\text{H}_5 > \text{CF}_2\text{Br} > (\text{CF}_3)_2\text{CF} \sim \text{CH}_3 \sim \text{CH}_3\text{CH}_2$. The ArPdX species decompose thermally to Ar-Ar , Pd , and PdBr_2 . Some of the RPdX species decompose free radically at low temperature. The RCOPdX species decompose by decarbonylation and have stabilities in the order of $\text{R} = \text{CF}_3\text{CF}_2\text{CF}_2 > \text{CF}_3 > \text{C}_6\text{F}_5 > \text{C}_6\text{H}_5 > \text{CH}_3 \sim \text{CH}_3\text{CH}_2\text{CH}_2$. These intermediates, ArPdX , RPdX , and RCOPdX , are highly coordinatively unsaturated and thus extremely reactive with phosphines. In fact many of these materials can be readily trapped with tertiary phosphines to form the bisphosphine adducts $(\text{R}_3\text{P})_2\text{Pd}(\text{Ar})\text{X}$, $=\text{Pd}(\text{R})\text{X}$, and in some cases $=\text{Pd}(\text{RCO})\text{X}$. This serves as a rapid method of preparation of these complexes and in some cases quite high yields of these materials can be prepared by simultaneous deposition of palladium atoms, ArX , and Et_3P at -196° .

Simple organopalladium salts ArPdX and RCOPdX (no stabilizing ligands) have been proposed as intermediates in a number of important reactions. Heck,³ Henry,⁴ and Maitlis,⁵ formulate "phenylpalladium chloride ($\text{C}_6\text{H}_5\text{PdCl}$)" as the reactive intermediate formed in solutions of palladium dichloride with an arylating agent such as phenylmercuric chloride. These solutions have been used for olefin arylations, alkylations, carboalkylations, etc. Similarly, Henry⁴ and Tsuji and coworkers⁶ discuss RCOPdCl as a likely short-lived species in palladium catalyzed CO insertion

reactions, olefin carbonylation reactions, and reaction mechanisms relating to the Rosenmund reduction.⁶ Furthermore, Maitlis and coworkers⁵ have reported on interesting chemistry of "lightly stabilized" organopalladium compounds (very weak donating ligands). In light of these works, we thought it would be quite interesting to produce and study "nonligand stabilized" organopalladium compounds (no donating ligands at all).

In this paper we describe the synthesis, isolation, trapping and other studies of a series of nonligand stabilized