Syntheses and Electronic Structures of Decamethylmanganocenes

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Abstract: The syntheses of $[(C_5(CH_3)_5)_2Mn]PF_6$, $(C_5(CH_3)_5)_2Mn$, and $Na[(C_5(CH_3)_5)_2Mn]$ are described. Magnetic susceptibility, infrared, electrochemical, NMR, and reactivity studies suggest the formulation of these complexes as low-spin 16-, 17-, and 18-electron planar metallocenes. EPR spectra of the neutral complex are consistent with the $^2E_{2g}$ configuration determined for other low-spin 17-electron metallocenes.

Introduction

The unusual magnetic properties, structural parameters, and reactivity of manganocene [$(\eta$-$C_5H_5)_2Mn$ or Cp_2Mn] and 1,1′-dimethylmanganocene [$(\eta$-$CH_3C_5H_4)_2Mn$ or $(MeCp)_2Mn$] have been extensively studied for over 20 years. While all other transition-metal metallocenes are low-spin complexes, Cp_2Mn exhibits both high-spin $^6A_{1g}[e_{2g}{}^2a_{1g}{}^1e_{1g}{}^2]$ and low-spin $^2E_{2g}[e_{2g}{}^3a_{1g}{}^2]$ ground states depending on the environment.[2,3] In the gas phase and in toluene solution $(MeCp)_2Mn$ exists in thermal equilibrium between high-spin $^6A_{1g}$ and low-spin $^2E_{2g}$ electronic configurations with the latter predominating at lower temperatures.[2b,c,3] Rettig and coworkers have suggested that Cp_2Mn is close to the high-spin to low-spin crossover point and the addition of electron-donating alkyl groups to the rings stabilizes the low-spin configuration.[2b,c] This view is supported by our recent observation that the fully methylated derivative, decamethylmanganocene ($(\eta$-$(CH_3)_5C_5)_2Mn$ or $(Me_5Cp)_2Mn$), possesses a rigorously low-spin, doublet electronic configuration up to at least 313 K.[4]

Structural studies of manganocenes have demonstrated the dependence of the metal to ring carbon distances (R(M–C)) on the spin state of the molecules. Gas-phase electron-diffraction studies by Haaland and co-workers revealed R(M–C)s of 2.383 (3) and 2.433 (8) Å for Cp_2Mn and high-spin $(MeCp)_2Mn$, respectively.[5,6] These R(M–C)s are the longest of all transition-metal metallocenes and are comparable to the distance found in the ionic Cp_2Mg (2.339 (4) Å).[7] The R(M–C) found for the low-spin form of $(MeCp)_2Mn$, 2.144 (12) Å,[6] is nearly 0.3 Å shorter than the distances found in the high-spin manganocenes. The shorter ring to metal distance observed for the low-spin species is consistent with ligand field arguments which predict a higher ring to metal bond order in the low-spin manganocenes.[6,8]

The structures of $(Me_5Cp)_2Fe$ and $(Me_5Cp)_2Mn$ were recently determined by X-ray crystallography.[8] Both molecules are normal, planar metallocenes with the rings in the staggered configuration and the R(M–C) of the Mn derivative, 2.112 (3) Å, is very close to Haaland's gas-phase values for low-spin $(MeCp)_2Mn$. In addition, the crystal structure of $(Me_5Cp)_2Mn$ revealed distortions from the ideal D_{5d} symmetry exhibited by the Fe derivative. These distortions, involving a variation in both the metal to ring carbon (2.105 (2) to 2.118 (2) Å) and ring carbon to ring carbon (1.409 (2) to 1.434 (2) Å) distances, suggested a static Jahn–Teller distortion resulting from an orbitally degenerate electronic configuration. In the present work, EPR studies of $(Me_5Cp)_2Mn$ are described which support the formulation of the orbitally degenerate $^2E_{2g}$ ground state.

Cp_2Mn and $(MeCp)_2Mn$ are among the most reactive of all metallocenes; they are pyrophoric, instantly hydrolyzed by water, and undergo ring-exchange reactions characteristic of ionic cyclopentadienides.[2a,9,10] We noted earlier that, while $(Me_5Cp)_2Mn$ is relatively inert with respect to ring loss, cyclic voltammetric results suggested the accessibility of both oxidized and reduced forms of the neutral complex.[4] Previously we reported the chemical preparation and isolation of the novel decamethylmanganocene anion; we now describe the isolation of the decamethylmanganocene cation and the results of magnetic, electrochemical, and reactivity studies of the cation, anion, and parent neutral complex.

Experimental Section

General. Reagent grade tetrahydrofuran (THF) was predried over CaH_2. Hexane and THF were purified by distillation from sodium benzophenone ketyl and stored under nitrogen. Acetone was purified by distillation from anhydrous K_2CO_3 and stored under nitrogen. Spectroscopic grade acetonitrile was distilled from P_2O_5 and freeze–thaw degassed for optical and electrochemical studies. For EPR studies, spectroscopic grade toluene and methylcyclohexane were distilled from sodium and stored under nitrogen. 1,2,3,4,5-Pentamethylcyclopentadiene[11] and decamethylferrocene[12] were prepared by literature procedures. All other chemicals were reagent grade and used without further purification.

Air-sensitive solids were stored and manipulated in a Vacuum Atmospheres glovebox equipped with a modified dry train. Air-sensitive solutions and dry, deoxygenated solvents were transferred with 18-gage stainless steel cannulae connected by polyethylene tubing (Clay-Adams, Intramedic, Fischer Scientific Co.). Unless otherwise noted, all reactions were carried out in dry, deoxygenated solvents under an inert atmosphere using standard Schlenk tube techniques. Solutions for NMR, EPR, and optical studies were prepared and transferred to appropriate cells inside a glovebox.

Infrared spectra were recorded with a Perkin-Elmer 597 spectrophotometer which was calibrated with polystyrene. Samples were prepared as KBr pellets or mulls (Nujol or Kel-F) between CsI plates. ^1H NMR spectra and magnetic susceptibility measurements by the Evans NMR method were recorded on a Varian T-60 spectrometer. Proton decoupled ^{13}C NMR spectra were obtained at 25 MHz in the pulsed Fourier transform mode with a Nicolet TT-23 spectrometer. All chemical shifts are reported in parts per million (δ) with reference to tetramethylsilane. Optical spectra were recorded on a Varian Associates Cary 14 with a nitrogen-purged sample compartment.

Bulk magnetic susceptibility measurements were made on a PAR Model 155 vibrating sample magnetometer calibrated with $HgCo(SCN)_4$ and equipped with a Janus Research Model 153 liquid helium Dewar. Field strength was monitored with a George Associates rotating coil gaussmeter. Temperature was measured with a calibrated GaAs diode.

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X-band EPR spectra of $(Me_5Cp)_2Mn$ in frozen toluene or methylcyclohexane solution (~0.1 M) or diluted in $(Me_5Cp)_2Fe$ at 10-15 K were obtained using a Varian E-12 spectrometer employing an Air Products Helitran cooling system mounted in the Varian room temperature cavity. The cavity frequency was measured with a Hewlett-Packard transfer oscillator and frequency counter, and the magnetic field with a ^1H NMR gaussmeter. The spectra obtained have very broad lines for $g_\perp$ with line widths on the order of 700 and 1200 G for the toluene and methylcyclohexane glasses, respectively. The $g_\parallel$ line widths were approximately 250 G for the two samples. No spectra were observed at room temperature.

Cyclic voltammograms were recorded in the three-electrode configuration with a platinum disk working electrode, a platinum wire auxiliary electrode, and a $Ag/AgNO_3$ (CH_3CN) reference electrode inside an inert atmosphere box. All potentials were referenced to the saturated calomel electrode (SCE) by measuring the ferrocene/ferricenium couple under identical conditions. Triangular waves were generated by the Princeton Applied Research (PAR) 175 programmer in conjunction with the PAR 173 potentiostat, and current-voltage curves were recorded on a Houston Omnigraphics 2000 x-y recorder. For controlled-potential coulometry, a platinum basket working electrode was employed, and the current integrated with the PAR 179 digital coulometer.

Mass spectra were recorded on an AEI-MS 12 mass spectrometer equipped with a direct inlet system. Elemental analyses were performed by the Microanalytical Laboratory of the University of California, Berkeley. Melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected.

Preparation of Complexes. Bis(pentamethylcyclopentadienyl)manganese(II) (Decamethylmanganocene). 1,2,3,4,5-Pentamethylcyclopentadiene (2.05 g, 15.1 mmol) in THF (150 mL) was cooled to −78 °C (dry ice-ethanol), then treated with *n*-butyllithium (6.3 mL, 2.4 M in hexane, 15.1 mmol) added with a syringe. Upon warming to room temperature, white lithium pentamethylcyclopentadienide precipitated from a bright yellow solution. The stirred suspension was cooled to −78 °C and anhydrous $MnCl_2$ (1.34 g, 10.6 mmol) added against an N_2 counterstream. The mixture was slowly warmed to 40 °C (ca. 1 h), then stirred for an additional 1 h to produce a clear orange solution. Solvent was removed in vacuo and the crude orange-brown solid sublimed (100 °C, 10^{-5} Torr) to yield the product as an air-sensitive, red-orange solid (1.87 g, 76%). Crystallization from hexane gave orange prisms, mp 292 °C. Anal. Calcd for $C_{20}H_{30}Mn$: C, 73.82; H, 9.29. Found: C, 73.96; H, 9.18. ^1H NMR (60 MHz, C_6D_6): δ −4.7 (s), line width 200 Hz at half height (320 K). Infrared (Nujol, halocarbon mulls): 2980 m, 2940 m, 2895 s, 2850 m, 2710 w, 1470 m, 1448 m, 1422 m, 1373 ms, 1355 w, 1065 m, 1023 s, 722 w, 588 w, 445 m, 361 m cm^{-1}. Mass spectrum (70 eV): *m/e* (rel abundance) $(P + 1)^+$, 326 (8), P^+, 325 (38), 189 (7), 137 (12), 136 (67), 135 (27), 133 (8), 122 (11), 121 (100), 120 (11), 119 (53), 117 (7), 115 (6), 108 (10), 107 (11), 106 (11), 105 (51), 103 (8), 94 (6), 93 (28), 91 (41), 83 (5), 81 (6), 79 (6), 78 (7), 77 (22), 71 (6), 69 (7), 65 (12), 57 (11), 55 (16), 53 (13), 51 (9).

Sodium Bis(pentamethylcyclopentadienyl)manganate(I). Naphthalene (0.53 g, 4.12 mmol) in THF (30 mL) was stirred over freshly cut sodium (0.12 g, 5.22 mmol) for 1 h. The resulting solution of sodium naphthalide was added rapidly through a cannula to solid $(Me_5Cp)_2Mn$ (1.34 g, 4.12 mmol) producing a deep red solution. After stirring at room temperature for 15 min, solvent was removed under reduced pressure and the resulting orange powder suspended in hexane (40 mL), filtered, washed with hexane (2 × 20 mL), and dried in vacuo to yield $Na[(Me_5Cp)_2Mn]$ as an orange, pyrophoric powder (1.36 g, 95%). Recrystallization from THF/hexane afforded bright orange needles which disintegrated to an orange powder upon drying. Anal. Calcd for $C_{20}H_{30}MnNa$: C, 68.95; H, 8.68. Found: C, 68.19; H, 8.72. ^1H NMR (60 MHz, THF-d_8): δ 1.87 (s). ^1H ^{13}C NMR (25 MHz, THF-d_8): δ 8.54 (s), 72.4 (s). Infrared (Nujol mull, KBr pellet): 2950 s, 2860 s, 2730 m, 2710 w, 1450 s, 1400 m, 1380 s, 1165 w, 1067 w, 1030 s, 722 m, 580 w, 498 s, 389 m, 285 s, 250 m cm^{-1}.

Bis(pentamethylcyclopentadienyl)manganese(III) Hexafluorophosphate. A mixture of $(Me_5Cp)_2Mn$ (1.41 g, 4.3 mmol) and $[Cp_2Fe]PF_6$ (1.35 g, 4.0 mmol) in acetone (50 mL) was stirred for 1 h at room temperature to give a cherry red solution. After removal of solvent under reduced pressure, the product was suspended in hexane (20 mL), filtered, and washed with additional hexane until washings were colorless (3 × 20 mL). Drying in vacuo yielded $[(Me_5Cp)_2Mn]PF_6$ as dark red microcrystals (1.6 g, 85%). Dark red prisms were obtained by recrystallization from acetone/hexane. $[(Me_5Cp)_2Mn]PF_6$ in acetone or acetonitrile solution is slowly hydrolyzed by water but the solid may be handled in air for short periods of time. Anal. Calcd for $C_{20}H_{30}MnPF_6$: C, 51.07; H, 6.43; P, 6.58. Found: C, 51.21; H, 6.40; P, 6.39. ^1H NMR (60 MHz, $(CD_3)_2CO$): δ 3.13 (s), line width = 18 Hz at 310 K. Infrared (Nujol, halocarbon mull): 2991 m, 2963 m, 2921 m, 1474 s, 1423 m, 1393 vs, 1069 m, 1022 s, 874 s, 840 vs, 722 w, 589 w, 540 vs, 505 m, 439 m, 230 w cm^{-1}.

Bis(pentamethylcyclopentadienyl)iron(III) Hexafluorophosphate. In air, $FeCl_3$ (0.2 g, 1.23 mmol) was added to a solution of $(Me_5Cp)_2Fe$ (0.52 g, 1.61 mmol) in THF (20 mL) to give a blue-green solution of $[(Me_5Cp)_2Fe]^+$. After the solution was stirred for 30 min at room temperature, solid NH_4PF_6 (0.5 g, 3 mmol) was added and stirring continued for an additional 30 min. The resulting solid was filtered, washed with THF (2 × 10 mL) and H_2O (2 × 10 mL), then dried in vacuo to yield $[(Me_5Cp)_2Fe]PF_6$ as air-stable, blue-green microcrystals (0.52 g, 90% based on $FeCl_3$). Recrystallization from acetone gave blue-green prisms. Anal. Calcd for $C_{20}H_{30}FePF_6$: C, 50.97; H, 6.42. Found: C, 51.12; H, 6.43. Infrared (Nujol, halocarbon mulls): 2990 m, 2960 s, 2922 s, 2860 s, 1470 s, 1458 sh, 1420 m, 1390 s, 1380 s, 1072 m, 1023 s, 878 s, 843 vs, 778 w, 722 vw, 590 w, 558 vs, 532 m, 450 m, 348 m cm^{-1}. These values are in agreement with previously reported IR spectra of $[(Me_5Cp)_2Fe]PF_6$.[13]

Results and Discussion

Synthesis and Characterization. $(Me_5Cp)_2Mn$ was prepared in high yield via the reaction of anhydrous $MnCl_2$ with $(Me_5Cp)Li$ in THF. The crystalline solid decomposes slowly in air and solutions of the complex are extremely oxygen sensitive. $(Me_5Cp)_2Mn$ in THF solution does not react with $FeCl_2$ and is hydrolyzed only slowly (over a period of hours) by water. This behavior is in marked contrast to that of Cp_2Mn and $(MeCp)_2Mn$, both of which are pyrophoric solids, are instantly hydrolyzed by water, and react rapidly with $FeCl_2$ in THF to yield the corresponding ferrocenes.[2a,9]

As both the thermodynamic and kinetic stability of metal complexes is dependent on spin state, it is worth noting that Cp_2Mn and $(MeCp)_2Mn$ possess thermally accessible high-spin ($^6A_{1g}$) electronic configurations, while $(Me_5Cp)_2Mn$ exists solely in a low-spin ($^2E_{2g}$) state (vide infra). In contrast to the high-spin d^5 case, the low-spin d^5 configuration possesses substantial crystal field stabilization[14] with attendant increase in ring metal bond strength. The observation of shorter (by nearly 0.3 Å) metal to ring carbon distances in the low-spin manganocenes[8] is consistent with these predictions.

The contrasting reactivity of high- and low-spin manganocenes parallels the situation observed in Mn(II) coordination chemistry. No crystal field activation energy for ligand displacement is expected for high-spin octahedral d^5 systems and, accordingly, high-spin Mn(II) complexes, such as $Mn(phen)_3{}^{2+}$, are notoriously labile.[15] In the low-spin d^5 case, a significant activation energy prevails and low-spin species such as $Mn(CN)_6{}^{4-}$ are relatively inert.[15,16] While $(Me_5Cp)_2Mn$ is inert toward ring loss and hydrolysis, it does undergo reversible one-electron oxidation as well as reduction to yield isolable low-spin 16- and 18-electron species in a fashion similar to $Mn(CN)_6{}^{4-}$.[17,18]

Cp_2Mn is unique among planar transition metal metallocenes in that no cationic derivative has been isolated. $(Me_5Cp)_2Mn$, however, is readily oxidized by $[Cp_2Fe]^+$ in acetone to yield the dark red complex $[(Me_5Cp)_2Mn]^+$. The cyclic voltammogram of $[(Me_5Cp)_2Mn]PF_6$ (Figure 1) shows that this compound is reduced in two reversible one-electron steps at −0.56 and −2.17 V vs. SCE,[19] with peak separations of 60 and 80 mV, respectively. The latter separation exceeds the theoretical value of 60 mV[20] because of its proximity to the cathodic wave of CH_3CN. Controlled-potential coulometry on the first reduction established that $n = 0.98 \pm 0.02$, verifying the one-electron nature of the reduction. In acetone so-

Table I. ^1H and ^{13}C NMR Data for Diamagnetic Decamethylmetallocenes[a]

	^1H	^{13}C[b] ring C	^{13}C[b] methyl C	solvent
$Na[(Me_5Cp)_2Mn]$	1.83	72.4	8.5	THF-d_8
$(Me_5Cp)_2Fe$	1.70	78.4	9.6	C_6D_6
$(Me_5Cp)Na$	2.01	105.1	11.8	THF-d_8

[a] All values in parts per million (δ) vs. tetramethylsilane. [b] Proton decoupled.

lution $[(Me_5Cp)_2Mn]^+$ is hydrolyzed slowly by H_2O but rapidly in the presence of strong acid.

As the cyclic voltammogram in Figure 1 suggests, $(Me_5Cp)_2Mn$ may also be reduced by one electron to an anionic derivative. Treatment of $(Me_5Cp)_2Mn$ with sodium naphthalide in THF gives a solution of $Na[(Me_5Cp)_2Mn]$,[21] which is isolated as an orange, pyrophoric powder soluble in THF, 1,2-dimethoxyethane, and *N,N,N′,N′*-tetramethylethylenediamine, but insoluble in aromatic and hydrocarbon solvents. The electrochemical reductions of Cp_2V, Cp_2Cr, Cp_2Co, and Cp_2Ni have been reported but the reduced species were neither isolated nor characterized in solution.[22] Therefore, $Na[(Me_5Cp)_2Mn]$ represents the first example of a stable, isolable metallocene anion. $Na[(Me_5Cp)_2Mn]$ reacts with CH_3CN, $(CH_3)_2CO$, MeI, and H_2O to give $(Me_5Cp)_2Mn$ with no evidence for products derived from addition of the electrophile. The complex also reacts with $FeCl_2$ in THF again to give $(Me_5Cp)_2Mn$ with no detectable amount of $(Me_5Cp)_2Fe$.

$Na[(Me_5Cp)_2Mn]$ is a diamagnetic 18-electron metallocene isoelectronic with $(Me_5Cp)_2Fe$. In Table I ^1H and proton decoupled ^{13}C NMR data for these compounds and $(Me_5Cp)Na$ are compared. The similarity of ^1H and ^{13}C chemical shifts in the Mn(I) and Fe(II) complexes provides evidence for the π-sandwich structure in $Na[(Me_5Cp)_2Mn]$. From the data in Table I it is clear that the chemical shift of the ring carbon is the most sensitive to electronic effects induced by variation of metal ion. The order of decreasing chemical shift, $\delta(Na) \gg \delta(Fe) > \delta(Mn)$, follows the expected order of increasing metal-to-ring electron donation.

An X-ray crystallographic study has verified the planar metallocene structure for $(Me_5Cp)_2Mn$ in the solid state.[8] Infrared spectra provide evidence for retention of this structure for $(Me_5Cp)_2Mn$ in all three oxidation states. Mull spectra of the neutral complexes $(Me_5Cp)_2Mn$ and $(Me_5Cp)_2Fe$ are superimposable in the region 900-4000 cm^{-1} with characteristic absorptions between 2800 and 3000 (four bands), 1500 and 1350 (five bands), and 1000 and 1100 cm^{-1} (two bands). Spectra of $[(Me_5Cp)_2Mn]PF_6$, $[(Me_5Cp)_2Fe]PF_6$, and $Na[(Me_5Cp)_2Mn]$ are similar, but more poorly resolved. Because these absorptions do not vary significantly in this series of compounds, they probably represent primarily ligand vibrational modes in the planar decamethylmetallocenes. Similarly, the reversibility observed in the cyclic voltammogram of $Mn(Me_5Cp)_2$ is consistent with simple oxidation-reduction reactions in a series of complexes retaining the planar metallocene structure.

Magnetic Susceptibility. The metallocene molecular orbital energy level diagram[23] allows the possibility of a low-spin ($^2A_{1g}[e_{2g}{}^4a_{1g}{}^2]$, $^2E_{2g}[e_{2g}{}^3a_{1g}{}^2]$) or high-spin ($^6A_{1g}[e_{2g}{}^2a_{1g}{}^1e_{1g}{}^2]$) ground configuration in a d^5 system such as Cp_2Mn. Magnetic susceptibility studies have shown that the spin state of manganocene is sensitive to temperature, environment, and methyl substituents.

Solid Cp_2Mn undergoes a phase transition at 432 K from its low-temperature brown form to a pink form. The pink form displays normal Curie behavior for an $S = 5/2$ molecule, as does Cp_2Mn in benzene and ether solutions or diluted in Cp_2Mg. Below the phase transition temperature, however, the susceptibility of Cp_2Mn shows a temperature dependence suggestive of antiferromagnetism.[2a] Bunder and Weiss's recent crystallographic study of the brown form showed that it does not consist of discrete Cp_2Mn molecules, but rather exhibits a polymeric zigzag chain structure.[24] Crystalline $(MeCp)_2Mn$ was also found to be antiferromagnetic, but THF solutions obey the Curie-Weiss law for an $S = 5/2$ system.[9] Rettig and co-workers demonstrated that the anomalous magnetic behavior of $(MeCp)_2Mn$ in toluene solution is due to a spin-state equilibrium with $\Delta H° = -1.8 \pm 0.1$ kcal mol^{-1} and $\Delta S° = -5.8 \pm 0.6$ eu for the high- to low-spin conversion in toluene.[2b]

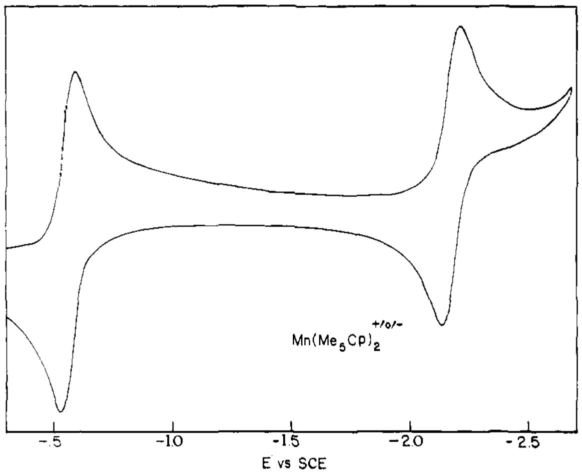

Figure 1. Cyclic voltammogram of $[(Me_5Cp)_2Mn]PF_6$ in CH_3CN on Pt disk electrode with 0.1 M $[(n\text{-}Bu)_4N]BF_4$ electrolyte. Scan rate = 100 mV s^{-1}

The magnetic susceptibility measurements on solid $(Me_5Cp)_2Mn$, $[(Me_5Cp)_2Fe]PF_6$, and $[(Me_5Cp)_2Mn]PF_6$ indicate Curie-Weiss behavior ($\chi^m = C/(T - \theta)$) in each case. The results of these experiments, and the solution magnetic moments as determined by the Evans NMR method,[26] are summarized in Table II. For solid $(Me_5Cp)_2Mn$ our data reveal a temperature-independent moment of 2.18 μ_B up to 117 K, in agreement with the solution moment measurement at 313 K. These data are consistent with the formulation of a low-spin doublet ground state for $(Me_5Cp)_2Mn$; the temperature independence of the moment indicates that thermal population of the $^6A_{1g}$ state is negligible up to 313 K. By comparison, a magnetic moment of 2.26 μ_B is obtained for the isoelectronic molecule $[(Me_5Cp)_2Fe]PF_6$. Both these values are close to the magnetic moment of low-spin $(MeCp)_2Mn$ ($\mu_{eff} = 1.98$ μ_B at 15 K) calculated from EPR spectral data.[2b,c]

All of these moments are significantly larger than the spin-only value expected for an $S = 1/2$ molecule, 1.73 μ_B. Deviations from this value probably represent the spin-orbit contributions to the moment expected in orbitally degenerate d^4, d^5, and d^7 metallocenes.[27] Both the solid and solution moments of $[(Me_5Cp)_2Fe]PF_6$ are somewhat larger than the values for $(Me_5Cp)_2Mn$, which may reflect a greater degree of spin-orbit contribution in the Fe(III) system.

Like Cp_2Cr, $[(Me_5Cp)_2Mn]PF_6$ is a 16-electron metallocene with three possible ground-state electronic configurations: $^3A_{2g}[e_{2g}{}^2a_{1g}{}^2]$, $^3E_{2g}[e_{2g}{}^3a_{1g}{}^1]$, and $^5E_{1g}[e_{2g}{}^2a_{1g}{}^1e_{1g}{}^1]$. Warren and Gordon recently reported moments of 3.23 and 3.17 μ_B for Cp_2Cr and $(MeCp)_2Cr$, respectively.[28] These values were consistent with an $S = 1$ spin system ($\mu_{eff} = 2.83$ μ_B) with significant spin-orbit contributions to the moment. On the basis of this evidence and the results of UV-photoelectron studies, the orbitally degenerate $^3E_{2g}$ ground state has been assigned to the chromocenes.[3] Our magnetic data for

Table II. Magnetic Susceptibility Data for Decamethylmetallocenes

			solid		solution	
molecule	C	θ^b	$\mu_{eff}{}^a$	temp range^b	$\mu_{eff}{}^a$	temp^b
$(Me_5Cp)_2Mn$	0.59	0	2.17 ± 0.1	4.2-117	1.97 ± 0.1	313^c
$[(Me_5Cp)_2Fe]PF_6$	0.63	0	2.25 ± 0.1	4.2-70	2.40 ± 0.1	310^d
$[(Me_5Cp)_2Mn]PF_6$	1.18	−4	3.07 ± 0.1	4.2-65	2.90 ± 0.1	310^d

[a] Values in Bohr magnetons. [b] Temperatures in K. [c] Measured in toluene solution. [d] Measured in acetone solution.

Table III. EPR Results for the Low-Spin Manganocene Type Compounds

compd	$g_\parallel$	$g_\perp$	k'	ξ, cm^{-1}	$\lvert\delta\rvert$, cm^{-1}	$2(\xi^2 + \delta^2)^{1/2}$, cm^{-1}	ref
$(Me_5Cp)_2Mn$ in toluene glass at 12 K	3.26 ± 0.01	1.68 ± 0.02	0.58	177	274	652	this work
$(Me_5Cp)_2Mn$ in methylcyclohexane glass at 12 K	3.36 ± 0.01	1.42 ± 0.04	0.48	147	148	417	this work
$(Me_5Cp)_2Mn$ in $(Me_5Cp)_2Fe$ at 12 K	3.508 ± 0.004^b	1.17 ± 0.01	0.47	142	102	350	this work
Cp_2Mn in Cp_2Fe at 4.2 K	3.519 ± 0.004	1.222 ± 0.010	0.48	146^a	113^a	369	2c
Cp_2Mn in Cp_2Ru at 4.2 K	3.548 ± 0.004	1.069 ± 0.020	0.46	140^a	88^a	330	25
Cp_2Mn in Cp_2Os at 4.2 K	3.534 ± 0.004	1.126 ± 0.01	0.46	142^a	96^a	342	25
$(MeCp)_2Mn$ in toluene glass at 4.2 K	2.887	1.900	0.71	217	659	1388	2b
$(MeCp)_2Mn$ in methylcyclohexane glass at 4.2 K	2.909	1.893	0.70	215	630	1331	2b
$(MeCp)_2Mn$ in $(MeCp)_2Mg$ at 4.2 K	3.00 ± 0.02	1.889 ± 0.002	0.76	232^a	667^a	1412	2c
$(MeCp)_2Mn$ in $(MeCp)_2Fe$ at 4.2 K	3.06 ± 0.02	1.850 ± 0.002	0.70	213^a	518^a	1120	2c

[a] These values have been recalculated using the Maki and Berry theory. [b] ^{55}Mn hyperfine coupling observed. $A_\parallel = (61.9 \pm 0.3) \times 10^{-4}$ cm^{-1}; $A_\perp$ not resolved.

$[(Me_5Cp)_2Mn)PF_6$ are also consistent with a spin triplet configuration; thus this complex is a rare example of low-spin Mn(III). The solution and solid-state moments are only slightly greater than the spin-only value for an $S = 1$ system; hence it is not possible to assign unambiguously either a $^3E_{2g}$ or $^3A_{2g}$ configuration.

EPR. EPR investigations confirm the dependence of the manganocene electronic structure on methyl substituents and environment noted in magnetic susceptibility studies. Cp_2Mn in toluene or methylcyclohexane glasses and diluted in Cp_2Mg exhibits EPR spectra characteristic of the high-spin $^6A_{1g}$ configuration.[2b,c] When Cp_2Mn is diluted in Cp_2Fe, Cp_2Ru, or Cp_2Os, spectra consistent with the $^2E_{2g}$ configuration found in ferricenium systems[13] are obtained.[2c,25] As Ammeter has indicated, the ring to metal distances of Cp_2Mg and high-spin Cp_2Mn are comparable so the high-spin form is easily accommodated in such a lattice. The other metallocene hosts have much shorter ring to metal distances, thereby favoring the low-spin form of Cp_2Mn[25] (which is expected to have a distinctly shorter ring metal distance than the high-spin form). For $(MeCp)_2Mn$, spectra characteristic of the $^2E_{2g}$ state are observed at 4.2 K in methylcyclohexane or toluene glasses and in host lattices of $(MeCp)_2Fe$ and $(MeCp)_2Mg$.[2b,c]

We have measured the low-temperature EPR spectra of $(Me_5Cp)_2Mn$ both in toluene and methylcyclohexane glasses and diluted in $(Me_5Cp)_2Fe$ and found them consistent with the $^2E_{2g}$ configuration determined in other low-spin manganocenes. Our results together with earlier results on low-spin manganocenes are listed in Table III. The g values of the complex in $(Me_5Cp)_2Fe$ are very close to those found for Cp_2Mn in d^6 metallocene hosts, but differ significantly in toluene and methylcyclohexane solutions, falling between the values reported for Cp_2Mn and $(MeCp)_2Mn$. The sensitivity of g values to changes in the host observed here and for other low-spin manganocenes is typical of metallocenes with orbitally degenerate ground states, for which Jahn-Teller distortions can perturb the g values. Both the nature and magnitude of such distortions can vary with environment so that the variation of g parameters with host matrix is not unexpected.

We have used the model developed by Maki and Berry[29] to calculate values of the orbital reduction factor, k', and the parameter δ, which is a measure of the departure from axial symmetry (Table III). The g values for the $^2E_{2g}$ state are given by

$$g_\parallel = 2 + 4k'(1 - \zeta^2)/(1 + \zeta^2)$$

$$g_\perp = 4\zeta/(1 + \zeta^2)$$

$$\zeta = \left(\frac{\delta}{\xi}\right) \bigg/ \left\{1 + \left[1 + \left(\frac{\delta}{\xi}\right)^2\right]^{1/2}\right\}$$

and $\xi = k'\xi_0$, in which we have followed Switzer et al. and used 305 cm^{-1} for the value of ξ_0, the spin-orbit coupling constant for the bare metal ion Mn^+.[2b]

The k' and δ values obtained for $(Me_5Cp)_2Mn$ and Cp_2Mn in a variety of hosts are quite similar but differ significantly from those determined for $(MeCp)_2Mn$. The parameter δ is much larger for $(MeCp)_2Mn$, which may be due to the relatively low symmetry of this molecule. The k' values are also smaller in the more symmetric manganocenes, implying a greater delocalization of the unpaired electron in $(Me_5Cp)_2Mn$ and Cp_2Mn than in $(MeCp)_2Mn$. The reduction of k' can result from either increased covalency or dynamic Jahn-Teller effects. The low k' values observed for Cp_2Mn relative to $(MeCp)_2Mn$ were attributed to increased dynamic Jahn-Teller coupling in Cp_2Mn[25] and this may be the case here. The crystal structure of $(Me_5Cp)_2Mn$ revealed static distortions involving metal-ring carbon and ring carbon-ring carbon distances, but no evidence was found for dynamic Jahn-Teller distortions.[8] If this result holds for $(Me_5Cp)_2Mn$ in the matrices employed in the EPR studies, then the low k' values must result from increased covalency in the $(Me_5Cp)_2Mn$ system.

Conclusions

Our magnetic studies of decamethylmanganocene indicate that permethylation of the Cp ring results in exclusively low-spin behavior, in contrast to other manganocenes where high-spin states are thermally populated. From this result we conclude that the ligand field strength of the Cp ring is significantly enhanced by the complete replacement of the hydrogens with electron-donating methyl groups. The low-spin configuration of $(Me_5Cp)_2Mn$ renders it inert toward ring displacement and hydrolysis but the complex does undergo reversible oxidation and reduction to give low-spin 16- and 18-electron species for which no analogues exist in the other manganocenes. Further studies on other first-row transition-metal decamethylmetallocenes are now in progress.

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Substituent Effects in the Electroreduction of Porphyrins and Metalloporphyrins[1]

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Abstract: Electron affinities and electron transfer reactivities of selected mesotetraphenylporphyrin (TPP) moieties have been investigated by controlled potential coulometry, polarography, and cyclic voltammetry. The effect of β-pyrrole substituents (OEt, Cl, Br, SCN, CN, NO_2) on the electroreduction of TPP was remarkably large, accounting for polarographic half-wave potential ($E_{1/2}$) shifts as great as 0.35 V per substituent, which correlated linearly with Hammett's σ_p^-. Polysubstitution of cyano groups had an additive effect on $E_{1/2}$ shifts, but polysubstitution of bromine did not. Insertion of electroreducible cations, such as Mn(III), Fe(III), and Co(II), did not affect the magnitude of the substituent shifts observed on TPP per se. Substituent effects on the $E_{1/2}$ of the inserted metal were invariably smaller. Thus, the effect of β substitution on metalloporphyrins provides a simple diagnostic criterion for distinguishing between electron transfer implicating the central cation vs. electrons inserted into the porphyrin ligand.

A renaissance of interest in the electrochemistry of porphyrins and metalloporphyrins was engendered in the mid-1960s by several papers published in this journal.[5-8] An appreciable number of subsequent studies have been devoted to the electrooxidation–reduction of pyrrole-substituted porphyrins and of phenyl-substituted tetraphenylporphyrins and corresponding metalloporphyrins.[9-20] Classical literature on naturally occurring porphyrins contains indications that substituents affect redox behavior,[21] as indeed expected on theoretical considerations. Typically, electron-releasing substituents induce cathodic shifts of the reduction potentials whereas electron-withdrawing substituents exert the opposite effect. However, these potential shifts tend to be small in the case of natural porphyrins. Recently, several papers[16-18] have been devoted to the electrochemistry of synthetic phenyl-substituted tetraphenylporphins. Qualitatively, the same trends were observed as with the natural porphyrins, yielding Hammett-Taft linear free energy relationships. In metalloporphyrins, substituents on the porphyrin ligand have been reported to have little or no effect on the reduction potential of the inserted cation.[17b,22] To clarify the effect of substituents on the electroreduction of porphyrins, we decided to investigate pyrrole substitution with strong electron-withdrawing groups.[15] The relevant macrocycles are identified in Figure 1. Results are presented and discussed in this paper, including potential shifts as large as 1 V, which are unprecedented. Based on these

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