were calculated, were not varied during the refinement, and were all given a fixed isotropic temperature factor of 5.0 Å^2. The methylene hydrogen atoms on C37, C43, C44, C38, and C45 (C45′) were not included in the refinement. The final conventional residual index ($R = \sum||F_o| - |F_c||/\sum|F_o|$) was 0.048 with a corresponding weighted index ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.065, and the function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$. The atomic scattering factors were those from Ref. 10.

Acknowledgment. X-ray diffraction studies were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division, under Contract No. W-7405-Eng-82. Synthetic studies received support from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 90885-93-1; 2, 14694-95-2; 6, 109086-50-2.

Supplementary Material Available: Tables of least-squares planes, bond lengths, bond angles, fractional coordinates of hydrogen atoms, and anisotropic thermal parameters of non-hydrogen atoms (5 pages); a list of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

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Electronic Ground States and Isotropic Proton NMR Shifts of Manganocene and Its Derivatives

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Received January 16, 1987

A crossover enthalpy of $\Delta H° = 21 \pm 5$ kJ/mol ($\Delta S° = 100 \pm 20$ J/(mol K)) for the slow spin exchange involving the $^6A_{1g}{}^2E_{2g}$ ground state of manganocene was found by paramagnetic NMR spectroscopy. A theoretical expression was derived which accounts for the average isotropic NMR shift in rapid exchanging molecules. In the case of dimethylmanganocene a fit with the experimental data was found for $\Delta H° = 20$ kJ/mol ($\Delta S° = 20$ J/(mol K)) assuming an hyperfine spin coupling of 16 MHz for the thermally populated upper state of the complex. Both the molecular spin crossover enthalpies and the ring proton coupling constants found by NMR are consistent with a molecular $^2A_{1g}$ state dominated isotropic shift for dimethyl-, diethyl-, and tetraethylmanganocene. Hence, the large isotropic shift observed for the annular protons in the substituted complexes is explained by the rapid molecular exchange with the $^2A_{1g}$ state. Results show that for manganocene the slow exchange permits the observation of separate resonances as expected for the more populated $^2E_{2g}$ and $^6A_{1g}$ states. No resonance or evidence of an exchange with the $^2A_{1g}$ state was found between −90 and 110 °C for this complex.

Introduction

Generally, in paramagnetic transition-metal complexes the isotropic nuclear magnetic shifts of the ligand depends on the metal–ligand bonding and magnetic anisotropy. For metallocenes, spin density on the cyclopentadienyl rings will cause the carbon and its attached protons to experience a strong paramagnetic shift under nuclear magnetic resonance (NMR) experimental conditions. Most often the isotropic NMR shift is due either to spin density at the atom itself (contact interaction) or anisotropy originating from the neighboring metal center (dipolar interaction).

The molecular structure of several paramagnetic coordination compounds and organometallic metallocenes have been studied by proton and carbon NMR spectroscopy.[1] For the metallocenes of the transition series, the hyperfine coupling resulting from contact spin interaction can easily be obtained from the isotropic shift. Paramagnetic NMR has also been shown to be useful for the study of molecular dynamics. A good example of this is the diamagnetic/paramagnetic equilibrium for the $Ni(PPh_2Me)_2Br_2$ complex.[2] Variable-temperature NMR studies have shown that Ni(II) complexes have exchange-averaged isotropic shifts proportional to the mole fraction of thermally populated electronic state.[3,4] Moreover, it has been shown that there is generally good agreement between the experimental and the theoretically predicted NMR bandwidths or isotropic shifts for fast exchanging ligands. This type of theoretical treatment of the isotropic NMR shifts is valid when each state follows the Curie law and is graphically significant for segments where the exchange-averaged shift is important relative to that of each state.[4]

These are 3d^5 Mn(II) compounds with low enough crossover energies to allow for significantly populated doublet and sextet electronic ground states at experimentally accessible temperatures.[5-9] Their NMR spectra

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reflect this and show the ligands are undergoing exchange between paramagnetic environments. Moreover, the variable-temperature region examined for ring-substituted manganocenes covers both linear and nonlinear shift regions. Recently, detail studies of the NMR properties of manganocene, $(\eta^5\text{-}C_5H_5)_2Mn$, and its alkyl ring derivatives have been reported.[10-12] It seemed to us that the ligand isotropic shifts did not concord with the structural data gather till now from solution magnetic susceptibility measurements. In this paper we wish to give a complete account of the proton NMR spectra with respect to the configuration or spin crossover properties of manganocene, dimethylmanganocene, $(\eta^5\text{-}C_5H_4(CH_3))_2Mn$, diethylmanganocene, $(\eta^5\text{-}C_5H_4(C_2H_5))_2Mn$, and tetraethylmanganocene, $(\eta^5\text{-}C_5H_3(C_2H_5)_2)_2Mn$.

Experimental Section

Preparation and characterization of the studied compounds is given in detail elsewhere.[11] The tetraethyl derivative was isolated as an impurity during the synthesis of diethylmanganocene. The doubly substituted cyclopentadienyl ligand was identified as the 1,2-ring isomer product from the more easy to handle ferrocene analogue $(\eta^5\text{-}C_5H_3(C_2H_5)_2)_2Fe$: ^1H NMR (C_6D_6) δ 3.85 (m, ring), 3.80 (m, ring), 2.28 (q, ^3J = 7.5 Hz, CH_2), 1.10 (t, ^3J = 7.5 Hz, CH_3); ^{13}C NMR (C_6D_6) δ, 88.5 (substituted C), 67.9 and 66.6 (CH), 20.7 (CH_2), 15.1 (CH_3); MS, $[M]^+$ m/z 298 (relative intensity 100). This air-stable iron complex was prepared by $FeCl_2$ exchange with the manganese complex.[9] After repeated thin-layer chromatography, the NMR spectrum of the Fe(II) product did not change, indicating the purity of the isomer employed was acceptable for our NMR study of the Mn(II) complex. Anal. Calcd for $C_{18}H_{26}Mn$: C, 72.71; H, 8.81; Mn, 18.48. Found: C, 72.22; H, 8.85; Mn, 19.79.

The proton NMR experiments were carried out on a Varian 200-MHz or a Bruker WP400 instrument. Saturated toluene-d_8 solutions placed in 5-mm (o.d.) NMR tubes filled with nitrogen were used for manganocene and dimethylmanganocene. The oily ethyl derivatives were 10% (v/v). Solution magnetic susceptibility was measured by the Evans NMR method and corrected for toluene density variation.[13]

The variable-temperature proton NMR spectra of manganocene and its dimethyl, diethyl, and tetraethyl derivatives were recorded between −90 and 110 °C. The paramagnetic NMR shifts were measured relative to the solvent toluene-d_7 impurity and transposed relative to Me_4Si by using 2.31 ppm. The shifts are given in magnetic field $\Delta H/H$ units with values increasing upfield.

Data reduction and error analysis were carried out for the linear relations. In all cases the linear correlation coefficients were better than 0.90. The mean deviation of the experimental shifts from the linear $\Delta H/H$ equation given below was ±200 to ±500 ppm K and ±1 to ±6 ppm for the slopes and intercepts at the origin, respectively. An in-depth analysis for the fitness of the calculated shifts from eq 3b was judged not to be necessary. The errors or precision of the experimental shifts can be assessed from the band widths at half-height given in parentheses ($w_{1/2}$ in hertz) following the given paramagnetic shifts.

Results and Discussion

On the basis of temperature-dependent NMR spectra, the spin exchanges for the studied compounds can be classified as slow or fast on the NMR time scale. In this respect we found that manganocene undergoes a slow exchange and its derivatives a rapid exchange in toluene between −90 and 110 °C.

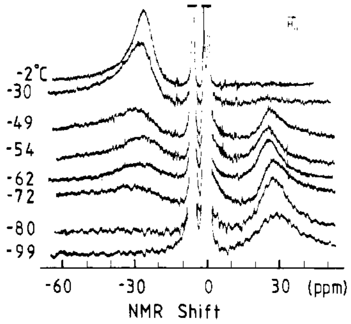

Figure 1. Proton NMR spectra (200 MHz) of $(\eta^5\text{-}C_5H_5)_2Mn$ in toluene-d_8 at selected temperatures.

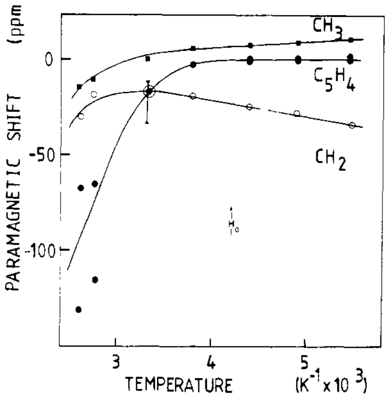

Figure 2. Paramagnetic proton NMR shift vs. the inverse temperature for $(\eta^5\text{-}C_5H_4C_2H_5)_2Mn$ in toluene-d_8.

For manganocene, the exchange rate remained slow over the full experimental temperature range. At −54 °C there are two well-resolved resonances of equal intensity; see Figure 1. A linear temperature dependence for both resonances between −90 and 110 °C was found. The following linear correlations were found in the low (lt) and high temperature (ht) regions:[11] $\Delta H/H$(lt) = (2200 (ppm K) T^{-1} + 15 (ppm)) and $\Delta H/H$(ht) = ($-800T^{-1}$ − 25) (hyperfine coupling constants, A_h(lt) = −0.279 MHz (−0.100 G) and A_h(ht) = 0.0087 MHz (0.0031 G)).

Next, the spectra for dimethyl-, diethyl-, and tetraethylmanganocene have similar features. In all cases, broad bandwidths and no Curie isotropic shifts near room temperature indicated a rapid molecular exchange on the NMR time scale for these molecules. The temperature dependence of the shifts for diethylmanganocene is shown in Figure 2. This dependence is typical for all the alkyl derivatives studied. In summary, there is a linear lt region and an abrupt downfield shift above ca. 40 °C for each resonance.

Precise determination of the linear correlation between −90 and −10 °C for the ring protons in the substituted complexes was made from the $\Delta H/H$ vs. T^{-1} plots. Hence, the linear coefficient at lt for the two resolved cyclopentadienyl resonances are as follows: for dimethylmanganocene, $\Delta H/H$(lt) = ($700T^{-1}$ − 4) and ($2000T^{-1}$ − 8); for diethylmanganocene, $\Delta H/H$(lt) = ($1000T^{-1}$ − 4) and ($1800T^{-1}$ − 7); for tetraethylmanganocene, $\Delta H/H$(lt) = ($1000T^{-1}$ − 4) and ($1700T^{-1}$ − 7). The coupling constants for dimethylmanganocene, A_h(lt) = −0.090 (−0.032 G) and −0.256 MHz (−0.093 G), were calculated from the slopes of these plots. For the latter two complexes the mean couplings are −0.178 (−0.064 G) and −0.172 MHz (−0.061

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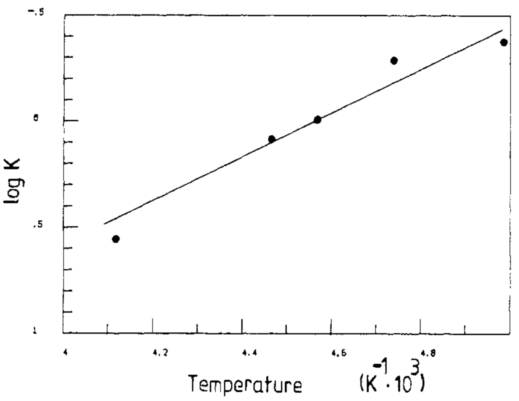

Figure 3. Equilibrium constant vs. the inverse temperature for the spin-exchange process observed by NMR for $(\eta^5\text{-}C_5H_5)_2Mn$ in toluene-d_8.

G), respectively. The adherence to the Curie law in this temperature region is indicative of either a slow spin exchange or a negligible contribution to the shift from other weakly populated electron excited states. Finally, exchange broadening ($w_{1/2} > 5000$ Hz) made detection of the ring resonance impossible in some spectra (200 MHz) recorded near 30 °C. The spectra of the dimethylmanganocene complex will be used in the following discussion as a bench mark for the substituted derivatives.

Other weak signals (integral less than 5% that of the complex) attributable to impurities in the complex solutions did not show the same temperature dependence as the former resonances. For example, manganocene had three overlapping resonances near −155 ppm and a series of other signals between 5 and 25 ppm which were prevalent between −64 and 36 °C. The low-field resonance has equally been observed at low temperature by Köhler and co-workers for manganocene.[12] However, these resonances were equally observed in our work for the substituted products and under the experimental conditions used (maximum radio frequency power 400 MHz) the low-field resonance integrals were less than 1% that of the ring resonances shown in Figure 1.

Before the NMR results are discussed, it should be pointed out that the Mn(II) complexes have a low crossover energy barrier between several electronic states. The high-spin $^6A_{1g}$ sextet state ($S = {}^5/_2$) has one unpaired electron in each of its five 3d orbitals ($a_{1g}{}^1$, $e_{2g}{}^2$, $e_{1g}{}^2$); there are two low spin doublet states ($S = {}^1/_2$): $a_{1g}{}^2$, $e_{2g}{}^3$ for the $^2E_{2g}$ state and $e_{2g}{}^4$, $a_{1g}{}^1$ for the $^2A_{1g}$ state. Photoelectronic, electron paramagnetic resonance, gas-phase structure determination, and bulk magnetic studies have shown the presence of a spin equilibrium in manganocene and dimethylmanganocene, with $^2E_{2g}$ and $^6A_{1g}$ as the only well-identified states.[5-7,14-16] Nevertheless, some authors have argued in favor of the importance of the nearby $^2A_{1g}$ state to explain the observed NMR and photoelectronic spectra of dimethylmanganocene.[5-7,14-16] The ordering of the energy level for these states is $^2E_{2g} < {}^6A_{1g} < {}^2A_{1g}$.

NMR Spectra of Manganocene. The proton spectrum for manganocene is best described by assuming the complex is undergoing a two-site exchange. The total NMR integral for the ring resonance considered was found to be constant within experimental error, and a third site exceeding 10% population is unlikely. In order to characterize this exchange, the enthalpy was determined. The integral ratios of the resonances are given in Table I between −30 and −72 °C where the two resonances are well-defined as shown in Figure 1. The probable error on the measured shifts varies between 3 and 5 ppm ($0.29w_{1/2}$). The integral ratio given in the table corresponds to the equilibrium constant K given by eq 1. Figure 3 shows the plot for the experimental log K vs. the inverse temperature used to calculate the enthalpy.

Table I. Paramagnetic NMR Data for the Cyclopentadienyl Ring Protons of Manganocene and Tetraethylmanganocene

	shifts, H/H (ppm)		resonance integral		
complex[a]	C_5H_5 ($^6A_{1g}$)	C_5H_5 ($^2E_{2g}$)	ratio[b]	total	temp, °C
$(\eta^5\text{-}C_5H_5)_2Mn$	−28			72	−2
	−29 (1900)	25	3.56	83	−30
	−32	26	1.22	71	−49
	−28	26	0.98	74	−54
	−26	26	0.51	77	−62
	−32	27 (3800)	0.43	84	−72
		28		77	−80
		29		86	−99

complex[a]	shifts, H/H (ppm) C_5H_3	resonance integral total
$(\eta^5\text{-}C_5H_3(C_2H_2)_2)_2Mn$[c]	−20 (1000), −42 (2000)	90
	0 (ca. 4000)[d]	27
	−1.8 (ca. 200), 1.0 (ca, 400)[d]	−17
	0 (<320), 2.0 (ca. 320)[d]	−50
	0 (ca. 200), 3.0 (ca. 400)	−76

[a] In $C_6D_5CD_3$ solvent. The paramegnetic shifts for dimethyl- and diethylmanganocene are given in ref 5. Bandwidths at half-height, $w_{1/2}$, are given in parentheses (Hz). For the ring-substituted complex, some bandwidths could not be measured because of overlapping and exchange broadening especially evident for the ethyl resonances at −17 °C. [b] Ratio = $^6A_{1g}/^2E_{2g}$ resonance. [c] Spectra for this compound were recorded on a 400-MHz instrument. [d] Overlapping resonances.

$$(\eta^5\text{-}C_5H_5)_2Mn\ (lt) \overset{K}{\rightleftharpoons} (\eta^5\text{-}C_5H_5)_2Mn\ (ht) \tag{1}$$

Hence, the two-site-exchange assumption seems justified for the interpretation of the NMR spectra of manganocene. The energy found is $\Delta H° = 21 \pm 5$ kJ/mol and $\Delta S° = 100 \pm 20$ J/(mol K). This is double the enthalpy value reported for the doublet/sextet exchange in dimethylmanganocene.[17] The molecular spin states corresponding to each limit spectra was checked by measuring the solution magnetic susceptibility. The effective magnetic moments of 5.50 μ_B at 100 °C and 1.99 μ^B at −80 °C correspond fairly well to the expected values for the molecular spin states $S = {}^5/_2$ and $S = {}^1/_2$, respectively.

NMR Spectra of Dimethylmanganocene. Switzer and co-workers[17] have underlined the unusually low-field position for the ring protons in the dimethyl derivative compared to that of manganocene. They also interpreted the susceptibility for this complex in terms of a thermally populated sextet state and pointed out the disparities of the NMR shifts with the bulk magnetic properties. In their study Köhler and co-workers[12] have reported the NMR shifts and thermodynamic properties of some mono- and polyalkylated ring derivatives of manganocene including dimethyl- and diethylmanganocene. Also, this group assumes that the large downfield isotropic shift observed for certain substituted complexes is due to an equilibrium with the more populated $^6A_{1g}$ molecular state.

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The chemical assignments adopted in this paper for the resonances have previously been discussed.[11]

The spin crossover enthalpies reported so far in solution and for the solid have been determined by bulk susceptibility measurements mainly. For dimethylmanganocene the experimentally determined susceptibility, μ^2(exptl), has been equated to the weighed average susceptibility of the doublet and sextet states.[17] Hence, these values are for spin exchange without discrimination with regards to the molecular states, i.e. E_{2g} or A_{1g}. The equilibrium and equation are described in eq 2, where μ(doublet) and μ(sextet) are the effective magnetic moments and X and (1 - X) are the mole fractions for both spins, respectively.

$$\underset{X}{(\eta^5\text{-}C_5H_4(CH_3))_2\text{Mn (doublet)}} \rightleftharpoons \underset{(1-X)}{(\eta^5\text{-}C_5H_4(CH_3))_2\text{Mn (sextet)}} \qquad (2a)$$

$$\mu^2(\text{exptl}) = X\mu^2(\text{doublet}) + (1 - X)\mu^2(\text{sextet}) \qquad (2b)$$

Several studies have shown that the isotropic NMR shift, for rapidly exchanging molecules, is also related to the mole fraction of paramagnetic state.[3,18,19] Substituting μ^2 in eq 2b for the paramagnetic NMR shift, $\Delta H/H$, for each spin state yields eq 3a. Furthermore, if the shifts for each state taken independently are assumed to have a linear T^{-1} dependence and X is replaced by the equilibrium constant or free energy dependent term, $K = \exp^{-\Delta G/RT}$, then eq 3b can be written. The paramagnetic shifts are given by $\Delta H/H(\text{lt}) = P(\text{lt})T^{-1} + A$ and $\Delta H/H(\text{ht}) = P(\text{ht})T^{-1} + B$, where P represents the slope and A and B are the intercepts determined graphically. This assumption seems reasonable given the linear dependence observed for both states in manganocene and at lt for the alkyl derivatives. Subtracting or referencing the paramagnetic shift relative to A and B gives the isotropic shift. However, these parameters help in fitting the theoretical curve and are kept here. Also, the temperature-dependent shifts are not identified with any of the molecular electronic states for now and are referred to as the lt and ht states.

$$\Delta H/H(\text{exptl}) = X[\Delta H/H(\text{lt})] + (1 - X)[\Delta H/H(\text{ht})] \qquad (3a)$$

$$H/H(\text{exptl}) = [1 + (\exp^{-\Delta G/RT})]^{-1}[(P(\text{lt})T^{-1} + \text{A}) - (P(\text{ht})T^{-1} + B)] + (P(\text{ht})T^{-1} + B) \qquad (3b)$$

Equation 3b is comparable to the theoretical expression given by Horrocks and McGarvey which they successfully applied to Ni(II) complexes undergoing rapid structural or chemical exchange.[3,20] This is evident when the ht state is assumed to be diamagnetic or $P(\text{ht}) = 0$. Moreover, for contact shifts the slope can be replaced by the general expression $-A_h[(g^2\beta^2/g_H\beta_H)(S(S + 1)/3k)]$, where A_h (in G) is the hyperfine spin-nucleus coupling constant for each molecular state and the other terms have their usual meaning.[21-23] This expression was used to calculate the coupling constants given in this paper.

Solving 3b for P(ht) requires variable-temperature NMR data of at least the lt region and knowledge of the free energy for the spin exchange process. The linear portion of the curve associated with dimethylmanganocene was used in our calculations (see captions for Figures 4 and 5).

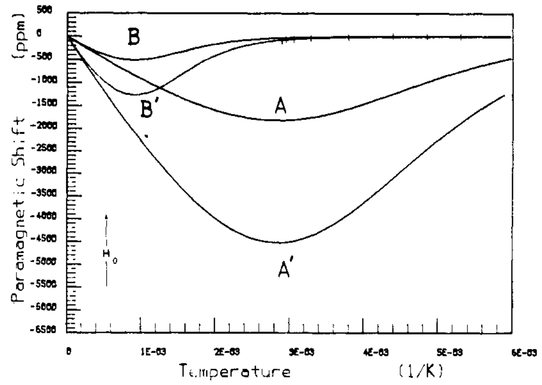

Figure 4. Ring proton NMR shifts following eq 3b. The experimently observed shift region is indicated by the vertical bars. In all cases the slope $P(\text{lt}) = 2000$ ppm K and $A = B = -4$ ppm. Curves A and A′ are for the same energy, $\Delta H° = 7.5$ kJ/mol and $\Delta S° = 24$ J/(mol K), but different slopes, $P(\text{ht}) = -1.0 \times 10^5$ and -2.5×10^5 ppm K, respectively. Similarly, curves B and B′ are for $\Delta H° = 20$ kJ/mol and $\Delta S° = 20$ J/(mol K), while $P(\text{ht}) = -1.0 \times 10^5$ and -5.0×10^5 ppm K, respectively.

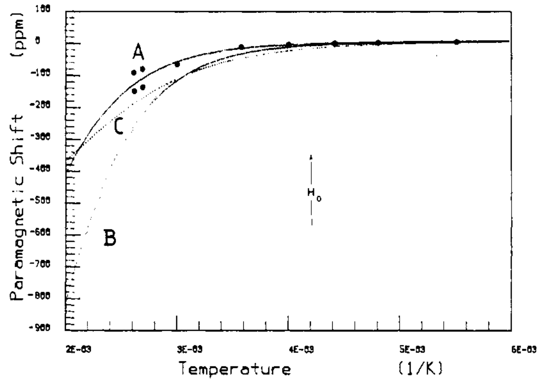

Figure 5. Theoretical (line) and experimental (dots) ring proton NMR shifts for $(\eta^5\text{-}C_5H_4CH_3)_2Mn$. The experimental resonances are split due to the ring substituent. For all calculations in eq 3b, $P(\text{lt}) = 2000$ ppm K and $A = B = -4$ ppm. Curve A: $\Delta H° = 20$ kJ/mol, $\Delta S° = 20$ J/(mol K), and $P(\text{ht}) = -1.0 \times 10^5$ ppm K. Curve B: same as curve A except $P(\text{ht}) = -5.0 \times 10^5$ ppm K. Curve C: $\Delta H° = 15$ kJ/mol, $\Delta S° = 20$ kJ/(mol K), and $P(\text{ht}) = -0.8 \times 10^5$ ppm K.

Also, the NMR shifts A and B were determined by extrapolation to $T^{-1} = 0$. As predicted from the Curie law both values are similar and close to the chemical shift of the free ligand. Hence, $A = B = -4$ ppm was used for the evaluation of eq 3. This leaves P(ht) as the only iterative parameter for a given set of $\Delta H°$ and $\Delta S°$.

The theoretical and experimental NMR shift dependence for dimethylmanganocene were compared. The plot obtained by using the energy values reported by Switzer for this complex is depicted in Figure 4. This should correspond to the predicted shift for the $^6A_{1g}/^2E_{2g}$ crossover exchange. Curves A and A′ show the influence of P(ht) on the shift. Similar results were obtained for the energy reported by Köhler, $\Delta H° = 11$–13 kJ/mol and $\Delta S° = 40$–50 J/(mol K). In all cases it was impossible to fit the curves to the experimental data regardless of the slope P(ht). We therefore began to explore $\Delta H°$ and $\Delta S°$ values different from those reported[12,17] with a view that the second exited state ($^2A_{1g}$ mentioned by Switzer et al.[17]) may be making a significant contribution to $\Delta H/H$(exptl).

We found that curves for standard free energies, $\Delta G°$ greater than 14 kJ/mol could be fitted. The 7.5–13 kJ/mol enthalpy range gave satisfactory results for $\Delta S° < 0$ only. Since the enthropy is expected to be positive for the type of exchange envisaged, this path was not pursued.

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The energy dependence for eq 3b is also shown in Figure 4. As example, curves A and B represent the temperature dependence of the shift for two energies; $\Delta H° = 7.5$ ($\Delta S° = 24$ J/(mol K)) and 20 kJ/mol ($\Delta S° = 20$ J/(mol K)), respectively. It can be seen for a given P(ht), two curves have similar slopes, but the "well's" minima are at different temperatures. For curve A this minimum is at low temperature for a possible fit. If P(ht) increases negatively, this will equally increase the slopes of the "well" and results in larger isotropic shifts. This can be seen in curves A′ and B′ calculated with the same parameters as curves A and B, respectively, except the slopes were increased 2.5 and 5 times, respectively.

For shifts corresponding to $\Delta H° > 14$ kJ/mol and $\Delta S° > 0$ ($\Delta G° > 14$ kJ/mol) it was found that large enthalpies yield correspondingly large P(ht) slopes. For example, fits for enthalpies around 25 kJ/mol gave P(ht) on the order of -1.0×10^7 ppm K ($A_h = 1260$ MHz (450 G)). Hence, a practical solution for the theoretical curves was sought for the smallest possible enthalpy and P(ht). Figure 5 shows the best fit found: $\Delta H° = 20$ kJ/mol, $\Delta S° = 20$ J/(mol K), and $P(\text{ht}) = -1.0 \times 10^5$ ppm K. It can be seen from curves A and B that the shifts are very sensitive to changes of P(ht) in the experimental temperature region even though, as we will see further, the complex is still mainly in the lt spin state. Curve C shows that for a standard free energy, $\Delta G° < 14$ kJ/mol, the theoretically predicted shift is displaced to low fields at low temperatures and at high fields at high temperatures.

In summary, acceptable fits were found for $\Delta H°$ between 15 and 20 kJ/mol and for $\Delta S°$ between 0 and 20 J/(mol K), giving a standard free energy ($\Delta G°$) near 14 kJ/mol. The P(ht) slopes ranged from -1.0×10^5 to -2.5×10^5 ppm K for different combinations of the energies. Hence, the hyperfine coupling constant at the ring protons in dimethylmanganocene is expected to be between 13 and 32 MHz (4.5 and 11.3 G).

Molecular States and Isotropic Shifts. The negative ring proton couplings observed at lt for manganocene and its derivatives contrasts with the positive values reported for the 3d^5 $^2E_{2g}$ spin state of ferrocenium, 0.470 MHz (0.168 G), and dimethylferricenium, 0.454 MHz (0.162 G)8 cations.[24] As for the Fe(III) complexes an important downfield dipolar shift is also expected at the ring protons of the Mn(II) complexes because of the large **g** tensor anisotropy.[5,14] However, the net upfield position of the observed shift at lt is indicative of a positive ($A_h < 0$) contact shift relative to the dipolar shift. Hence, the sign of the hyperfine coupling for manganocenes in the $^2E_{2g}$ state is definitely negative though a positive contribution from the dipolar shift is expected. A similar result as been found for some polysubstituted ferricinium complexes.[25]

Outstanding is the twofold increase in the magnitude of the ring proton hyperfine spin coupling constant upon substitution of manganocene. Substitution of a cyclopentadienyl proton usually does not affect as much the isotropic proton shifts or coupling constants.[26] However, large coupling at the protons have been reported for several sandwich-type compounds having in common at least one unpaired electron in a 3d metal orbital of a_1 representation: bis(cyclopentadienyl)vanadium(II), 2.33 MHz;[27] bis(cyclopentadienyl)chromium(II), 3.92 MHz;[27] bis(benzene)vanadium(I), 3.16 MHz;[28] (cycloheptatrienyl)(cyclopentadienyl)vanadium(0), 5.0 (Cp) and 12.0 MHz (COT);[29] (benzene)(cyclopentadienyl)chromium(0), 6.58 (Cp) and 13.0 MHz (arene);[30] (cyclopentadienyl)(cycloheptatrienyl)chromium(I), 6.05 (Cp) and 10.1 MHz (COT);[30] bis(benzene)chromium(I), 9.69 MHz;[31] bis(benzene)vanadium(0), 11.2 MHz.[28]

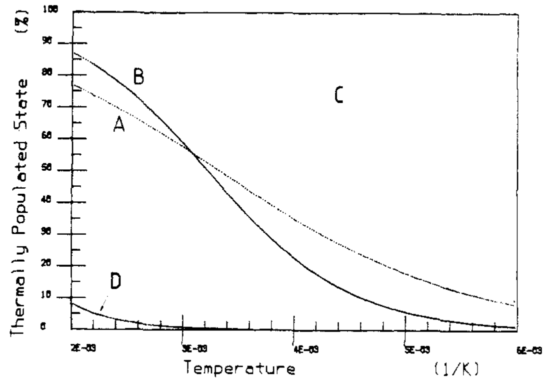

Figure 6. Percentage of thermally populated electronic ground state following spin exchange energies reported for (η^5-$C_5H_4Me)_2Mn$ ($\Delta H° = 7.5$ kJ/mol and $\Delta S° = 25$ J/(mol K) (curve A) and $\Delta H° = 13$ kJ/mol and $\Delta S° = 42$ J/(mol K) (curve B)) and the energy found by NMR in this work for (η^5-$C_5H_5)_2Mn$ ($\Delta H° = 21$ kJ/mol and $\Delta S° = 100$ J/(mol K) (curve C)) and (η^5-$C_5H_4Me)_2Mn$ ($\Delta H° = 20$ kJ/mol and $\Delta S° = 20$ J/(mol K) (curve D)).

Also noteworthy is the larger energy found from eq 3b for the crossover energy of dimethylmanganocene, which is double that reported for the $^2E_{2g}/^6A_{1g}$ spin exchange. For a better understanding of this result, the population curves of the ht spin states were determined for different experimental values of the enthalpy. The computer-drawn curves are represented as a percentage ht population, $[100 - (100/(1 + K)]$, in Figure 6. On the basis of the previous reported magnetic susceptibility results, it is expeced that ca. 100% of manganocene and 50% of its methyl derivative should be high spin at 36 °C.[8,9,14,17]

Curves A and B are for the experimentally found enthalpies reported by Switzer and Köhler for dimethylmanganocene. As expected, both curves show near 36 °C approximately equal populated states. Next, curve C shows that manganocene is 98% in the ht state as expected for the spin equilibrium of the $^6A_{1g}/^2E_{2g}$ states. Moreover, it can be gathered from the spectra that the ring proton shifts due to both states are of similar magnitude but of opposite signs (Table I). This result is important in assessing the relative contribution of each state to the observed average shifts discussed further. At ca. 36 °C in the fast exchange limit the $^6A_{1g}$ and $^2E_{2g}$ contact shifts will tend to cancel each other.

Finally, for the crossover enthalpy determined from eq 3b for the $^2E_{2g}/^2A_{1g}$ equilibration for dimethylmanganocene, curve D shows the observed low field shift is attributable to 0.4% of the $^2A_{1g}$ state at 36 °C. This can be explained by the unusually efficient coupling mechanism of the a_{1g} orbitals. The relative decreasing contribution of each state to the average shift is then $^2A_{1g} \gg {}^6A_{1g} \simeq {}^2E_{2g}$. Hence, at lt the $^2E_{2g}$ state predominates the isotropic shifts of the studied complexes. At ht the less

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populated $^2A_{1g}$ state dominates the isotropic shifts when the complex is undergoing rapid exchange. In agreement with our findings a $^2A_{1g}/^2E_{2g}$ energy separation of approximately 24 kJ/mol has been estimated by Anderson and Rai in the dimethylferricinium complex.[23] Extended Hückel molecular orbital calculations made by the same authors also predict the a_{1g} spin coupling can be as high as 7 MHz at the ferricinium protons. Accordingly, both molecular orbital calculation and NMR results have led Switzer et al. to predict a coupling of 9 MHz for the ht NMR related spin state in dimethylmanganese. Solodovnikov and co-workers[25] account for the reversal in spin coupling observed in polyalkylated ferricinium complexes by the increase importance upon substitution of the thermally accessible $^2A_{1g}$ ground state on the NMR shift.

NMR of Other Ring-Substituted Manganocenes. It can be assumed that substituted manganocene complexes with similar NMR properties are undergoing the same type of rapid exchange as identified here for dimethylmanganocene. Hence, following eq 3b the 16 ppm (mean) shift difference separating the two monoalkylated ring resonances in diethylmanganocene and dimethylmanganocene is the result of either or both a decrease in the $P(^2A_{1g})$ slope or a decrease in the $^2A_{1g}$ population due to a greater crossover enthalpy. First, the crossover energies for dimethyl-, diethyl-, diisopropyl-, and di-*tert*-butylmanganocene are expected to be identical within experimental error.[12] Also, in general metallocenes in the $^2A_{1g}$ state have isotropic **g** tensors.[32] Hence, variation of the energy can be ruled out as well as any dipolar contribution resulting from the **g** tensor. So the observed shift difference in these complexes can be accounted for by the change in $P(^2A_{1g})$ slope. A 20 ppm shift difference corresponds to a coupling constant change of –0.5 MHz (at 25 °C). This variation is quite significant but represents only 3% of the $^2A_{1g}$ coupling at the ring proton in dimethylmanganocene. Hence, the following decreasing order in hyperfine ring proton coupling can be made, at 117 °C, by using the mean shifts reported for the monoalkyl derivatives: methyl > ethyl > isopropyl > *tert*-butyl.[11,12]

We have here deliberately omitted considering the $^2E_{2g}$ and $^6A_{1g}$ states because of their relatively small population-coupling product. Further evidence for the existence of large $^2A_{1g}$ coupling in substituted complexes is the 44–55 ppm shift separation observed for the H(2,5) and H(3,4) ring protons. Since a significant dipolar contribution to the shift can be eliminated ($^2A_{1g}$ state), differences in spin coupling is more likely to account here for the degenerate ring resonances.

Generally, increase substitution on the cyclopentadienyl ligand results in an increase $^2E_{2g}$ to $^6A_{1g}$ or $^2A_{1g}$ crossover enthalpy. For example, the magnetic susceptibility and solution NMR results for $(\eta^5\text{-}C_5Me_5)_2Mn$, $(\eta^5\text{-}C_5Me_4H)_2Mn$, and $(\eta^5\text{-}C_5Me_4Et)_2Mn$ indicate that these complexes are exclusively in the $^2E_{2g}$ state at room temperature.[12,14] Hence, the energy term should equally be considered with the coupling when the NMR shifts of mono- and polyalkylated derivatives are compared. For example, the mean isotropic shift is 73 ppm (117 °C) less for the ring protons in tetramethylmanganocene compared to that of dimethylmanganocene.[12] This difference is 59 ppm (90 °C) for tetraethyl- and diethylmanganocene.[11]

Hence, the study of the paramagnetic properties for manganocene derivatives based on homologation of their NMR spectra at a given temperature is impossible without first checking the spin state inbalance. Hence, it is not surprising to find that assignment of the methylene *versus* ring proton resonance by means of spectra homolation alone for the methyl derivative with that of the ethyl or *tert*-butyl derivative do not agree.[11,12] Also important in understanding the metal–ligand spin delocalization mechanisms in paramagnetic metallocenes, our results underline the importance of considering not only the energy gap ($\Delta H°$) separating two states but also the exchange rate or activation energy barrier for a proper interpretation of the isotropic shift. These properties are readily accessible by variable-temperature NMR spectroscopy.

Acknowledgment. We are grateful to the "programme de formation de chercheur et d'action concertée du Québec" (FCAC, No. EQ2094) and to the National Science and Engineering Research Council of Canada (NSERC, No. A1527) for their financial assitance.

Registry No. $(\eta^5\text{-}C_5H_5)_2Mn$, 73138-26-8; $(\eta^5\text{-}C_5H_3(C_2H_5)_2)_2Mn$, 109064-68-8; $(\eta^5\text{-}C_5H_3(C_2H_5)_2)_2Fe$, 109064-69-9; $(\eta^5\text{-}C_5H_4(CH_3))_2Mn$, 32985-17-4; $(\eta^5\text{-}C_5H_4(C_2H_5))_2Mn$, 101923-26-6.

Supplementary Material Available: A calculation of the hyperfine spin coupling, A_h, for $(\eta^5\text{-}C_5H_5)_2Mn$ (Annexe I), slope (P) (linear part) of the plots for the ring proton shift vs. $1/T$ curve and the corresponding hyperfine coupling constant (A_h) for the studied complexes (Table II), a computer printout giving the percentage of thermally populated spin state (%) as a function of the inverse temperature (K^{-1}) for curves A, B, C, and D of Figure 6 (Table III; A, B, C, and D, respectively; the values were calculated by using the equilibrium constant dependent expression: [100 – 100/(1 + K)]) (6 pages). Ordering information is given on any current masthead page.

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