in $[Pd_2(S_7)_4]^{4-}$ and our two complexes are similar; that is, the S–S bond lengths and S–S–S bond angles are close to 2.0 Å and 109°, respectively. In association with $(Ph_4P)_2S_7$[47] and $(Ph_4P)(NH_4)S_7$,[48] which have the free S_7^{2-} ligand, different conformations of S_7^{2-} ligands are exhibited. Table V gives a comparison of their torsion angles and conformations. In the title complexes, there are two types of conformations observed in bridging two metal atoms. It is noted that in one conformation of the S_7^{2-} ligand of the title complexes one torsion angle is very large at 115 or 121°.

A bimetallic activation and reduction of N_2 has been suggested[21,22] as a possible pathway toward N_2 fixation. The substrate of N_2 between two metals may change from HN=NH (diazene) and H_2NNH_2 (hydrazine) as intermediates to NH_3 (ammonia). In nitrogen fixation, the oxidation state of the center Mo ion may change to a higher state when electrons flow to the substrate. The presence of the loosely coordinated H_2NNH_2 ligand between two sulfur-rich Mo(VI) centers linked by a S_7^{2-} chain may assure a concomitant reduction to ammonia after reduction of the Mo(VI) ion. The isolation of the title complexes implies that the intermediates may still bind to the center ion which is in a higher oxidation state after electrons flow to the substrate or intermediates. Further discussion remains for the future after the identification of the bridging ligand (H_2NNH_2 or NH=NH).

Acknowledgment. This research was supported by grants from the Structural Chemistry Research Laboratory of the Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, and the National Science Foundation of China.

Supplementary Material Available: Tables SI and SII, listing thermal parameters, the angles and distances of all non-hydrogen atoms, and torsion angles associated with the anions for both compounds, and a table listing the complete crystallographic data for both compounds (9 pages); tables of calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.

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Spin Crossover, Dimerization, and Structural Dynamics of Manganocenes Probed by Deuterium NMR Spectroscopy[†,1]

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The deuteriated manganocenes $(C_5D_5)_2Mn$ (**1**), $(C_5H_4CD_3)_2Mn$ (**2a**), and $(C_5D_4CH_3)_2Mn$ (**2b**) have been prepared and investigated by temperature- and concentration-dependent paramagnetic ^{2}H NMR spectroscopy. As compared to ^{1}H NMR, the spectral resolution is far better. This has allowed the detection of the elusive low-spin isomer of the most simple manganocene (in the form of **1**) in solution, the investigation of the spin crossover ($\Delta H° = 12.8$ kJ mol^{-1}, $\Delta S° = 84$ J mol^{-1} K^{-1}), and the formation of antiferromagnetic dimers which contain η^3,η^2-bridging and η^5-terminal Cps. The bridging Cps are involved in a rapid dynamic process so that the η^3 and η^2 fragments are indistinguishable down to 160 K. No interconversion of the bridging and the terminal Cps is visible up to 230 K, and no Cp exchange between monomeric and dimeric manganocene, up to 300 K. Similarly, two spin isomers and dimers have been observed for **2a** and **2b**. The averaged data for the equilibrium of the spin isomers are $\Delta H° \approx 17$ kJ mol^{-1} and $\Delta S° \approx 61$ J mol^{-1} K^{-1}, the energy barrier is $\Delta G^* \approx 46$ kJ mol^{-1}, and the lifetime of the spin isomers lies between 10^{-5} and 10^{-4} s. On the basis of selective deuteriation, the signal assignment shows unambiguously that all signals of the low-spin isomers have small shifts. Hence there is no reason to postulate the population of the $^2A_{1g}$ state in these manganocenes. The temperature dependence of the ^{2}H NMR signal shifts reflects the presence of the $^2E_{2g}$ and the $^6A_{1g}$ states only.

Manganocenes are the most attractive metallocenes as far as the magnetic properties are concerned. It has been shown with various techniques that they can have one or five unpaired electrons and that the spin crossover lies in an easily accessible temperature range when R in $(RCp)_2Mn$ is H, CH_3, and *t*-Bu.[2] The most recently used technique is NMR spectroscopy.[3] In this laboratory it proved to be very efficient in demonstrating that the spin state of manganocenes can be tuned by systematic variation of the number and/or the type of the substituents at the cyclopentadienyl ligands.[3c] The parent sandwich Cp_2Mn appeared to be particularly capricious because in THF the pure high-spin donor adduct Cp_2Mn(THF) formed, which was confirmed later by X-ray analysis.[4] By contrast, in toluene, spin crossover influenced the ^{1}H NMR signal shift but we were unable to detect the low-spin isomer. On decrease of the temperature, two additional ^{1}H NMR signals appeared that we ascribed to the formation of manganocene dimers and/or oligomers.

The situation seemed to become confusing when it was claimed[3d,f] that ^{1}H NMR studies disclose both spin isomers of Cp_2Mn but no dimer. Furthermore, the signal coalescence expected for rapid spin crossover did not occur.

This reflects upon the NMR method which had been used (i) to confirm the structure of manganocenes,[3b–f] (ii) to observe both the low- and high-spin species under slow-exchange conditions,[3d–f] (iii) to determine the lifetime of a spin isomer,[3e] (iv) to determine the thermodynamic parameters of the spin equilibrium,[3e,f] (v) to

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[†] Dedicated to Prof. Wolfgang Beck on the occasion of his 60th birthday.

(1) NMR Spectroscopy of Paramagnetic Complexes. 38. For part 37, see: Blümel, J.; Hebendanz, N.; Hudeczek, P.; Köhler, F. H.; Steck, A. *J. Am. Chem. Soc.*, in press. This contribution is part of the Diplomarbeit of B.S., TU München, 1986.

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Table I. ^{13}C NMR Data[a] for Deuteriated Cyclopentadienyl Anions

compd	C1	C2/5[b]	C3/4[b]	Cα
$[C_5H_5]^-$	102.41	102.41	102.41	
$[C_5D_5]^-$	102.22	102.22	102.22	
	22.9	*22.9*	*22.9*	
	(190)	(190)	(190)	
$[CD_3C_5H_4]^-$	112.95	103.19	101.05	14.31
				18.9
$[CH_3C_5H_4]^-$	112.82	102.96	100.70	15.02
$[CH_3C_5D_4]^-$	112.82	102.74	100.52	15.02
		22.5	*22.0*	
		(220)	(180)	

[a] Shifts in ppm; $^1J(^{13}C-^2H)$ in Hz in italics; $^1\Delta^{13}C(^2H)$ in ppb in parentheses. [b] The assignment follows that deduced for $(MeCp)_2Fe$[9a] and $(t\text{-}BuCp)_2Fe$.[9b]

measure the activation parameters of the spin crossover at the coalescence of the NMR signals,[3e] (vi) to determine the electron spin delocalization,[3b,c,e] and (vii) to determine the molecular ground state.[3d-f] For some of these points the results depend markedly on the signal assignment. Thus it turned out[3c,e] that Switzer et al.[3b] had mistaken the CH_3 signal of $(C_5H_4CH_3)_2Mn$ for one of the two ring proton signals because no other substituted manganocene was available for comparison and the signal integration had been performed at 310 K where the signals suffered from distorsions owing to the rapid interchange of the low- and high-spin species. This did not affect Switzer's main conclusions. However, the electron spin delocalization, which in turn was the argument for an $^2A_{1g}$ state being populated besides the $^2E_{2g}$ and the $^6A_{1g}$, had to be revised.[3e] Surprisingly, when Cozak et al. repeated[3f] their earlier work,[3d] they retained the previous signal assignment without giving any experimental proof and they also repeated Switzer's reasoning in detail.

^{2}H NMR spectroscopy promised to be the method of choice for establishing the spin crossover and the concurrent intermolecular interaction of the manganocenes in solution because it has been shown that on passing from proton to deuterium NMR spectroscopy the half-widths of the metallocene signals are reduced by a factor of roughly 40.[5a] This improvement has allowed the observation of signals which may not be detected by ^{1}H NMR spectroscopy.[5b,c] We have therefore synthesized the deuteriated manganocenes $(C_5D_5)_2Mn$ (**1**), $(C_5H_4CD_3)_2Mn$ (**2a**), and $(C_5D_4CH_3)_2Mn$ (**2b**) and investigated them by variable-temperature ^{2}H NMR spectroscopy.

Results and Discussion

Deuteriated Ligands [Cp-*d*$_5$]$^-$, [MeCp-*d*$_3$]$^-$, and [MeCp-*d*$_4$]$^-$. Among several methods for the base-catalyzed deuteriation of cyclopentadiene[6] we have selected and slightly modified the method of Lambert et al.,[6f] which resembles that of McLean et al.[6a] When the H/D exchange was performed with $NaOD/D_2O/DMSO$, the cyclopentadiene could be recovered by phase separation. This simplified the repeated deuteriation and reduced the losses due to the volatility and the dimerization of cyclopentadiene. Reaction with sodium hydride gave [Cp-*d*$_5$]$^-$; the yield starting from C_5H_6 was 60%.

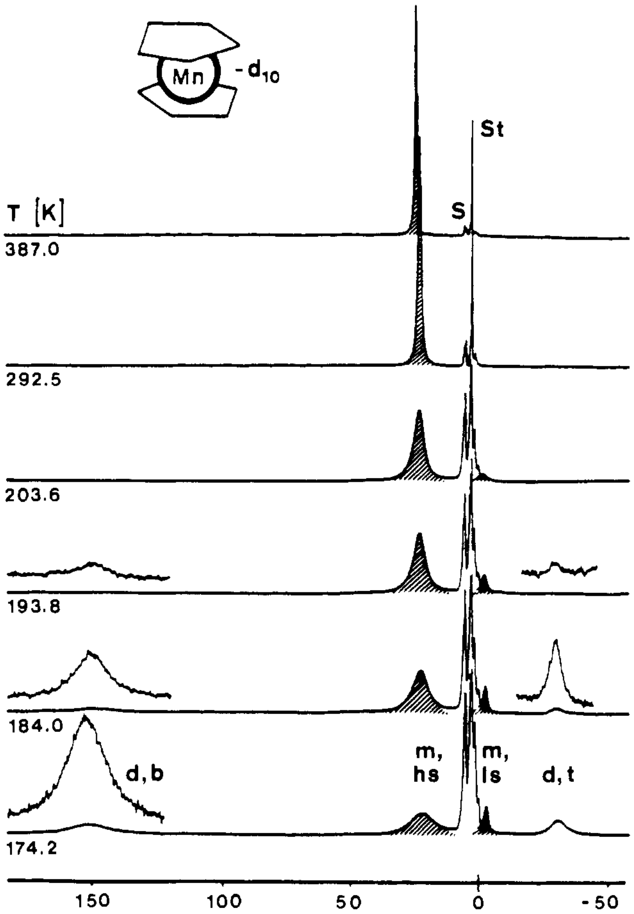

Figure 1. Temperature-dependent ^{2}H NMR spectra of a 0.2 mol % solution of Cp_2Mn-d_{10} in toluene (top two spectra) and toluene/pentane (4/1). Key: S = solvent signals; St = standard (Cp_2Fe-d_{10}); m = monomeric, d = dimeric, hs = high-spin, ls = low-spin Cp_2Mn-d_{10}; b = bridging, t = terminal ligand (cf. text for details). The scale (ppm) is relative to TMS and does not indicate paramagnetic signal shifts.

The selective deuteriation of $(MeCp)_2Fe$[7] (which is restricted to the protons of the five-membered ring) is not applicable to the analogous manganocene. We have therefore reacted Cp$^-$ with $(CD_3O)_2SO_2$ and [Cp-*d*$_5$]$^-$ with $(CH_3O)_2SO_2$. After distillation of the reaction mixture the resulting methylcyclopentadienes were obtained as THF solutions appropriate for the deprotonation with NaH. The corresponding anions formed in yields up to 95% starting from Cp$^-$. In our hands, dimethyl sulfate as the alkylating reagent[8a] led to less polymethylated cyclopentadienes than methyl iodide, which has also been used for specific deuteriation.[8b]

The anions were characterized by ^{13}C NMR spectroscopy partly in comparison with the nondeuteriated analogues. Table I contains the signal shifts, the one-bond carbon–deuterium couplings and, as far as a mixture of the deuteriated and the nondeuteriated compound was investigated, the one-bond deuterium-induced intrinsic ^{13}C NMR isotope shifts, $^1\Delta^{13}C(^2H)$. The isotope shifts are similar to those of methylated aromatic compounds,[9b,10] and

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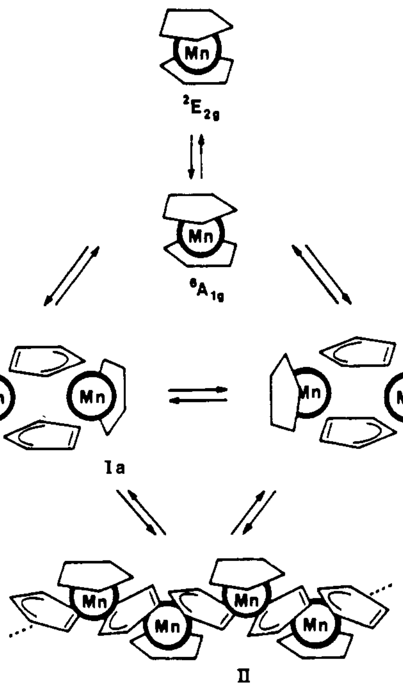

Figure 2. Equilibria proposed for manganocene dissolved in toluene.

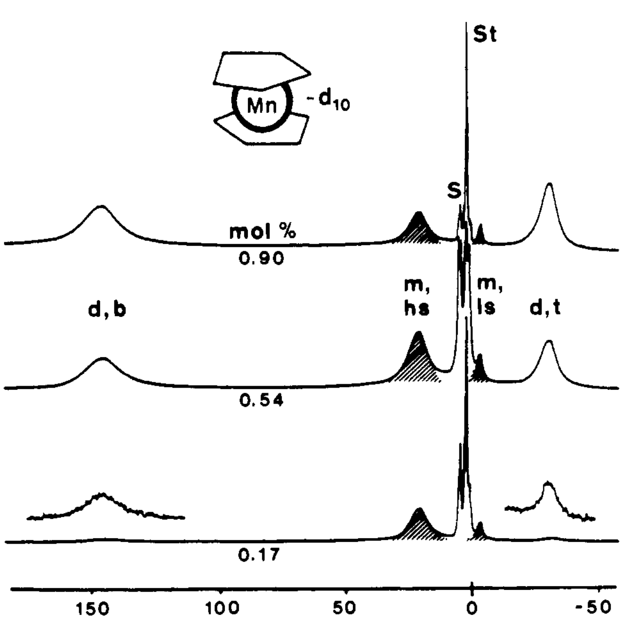

Figure 3. Concentration-dependent ^{2}H NMR spectra of Cp_2Mn-d_{10} in toluene at 188.4 K. Symbols are as in Figure 1.

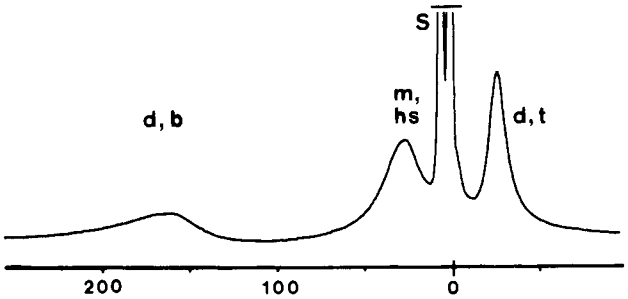

Figure 4. ^{1}H NMR spectrum of Cp_2Mn in toluene-d_8 (saturated solution) at 210 K. Symbols are as in Figure 1.

the CD couplings correspond to what is expected from the CH couplings of similar anions[11] after multiplying with the gyromagnetic ratios $\gamma(^2H)/\gamma(^1H)$.

Perdeuteriomanganocene. Following published routes[2b,12] Cp_2Mn-d_{10} and the selectively deuteriated 1,1′-methylmanganocenes described below were synthesized in yields up to 64% by reaction of the ligand anions with manganese(II) chloride. The analysis of the mass spectra gave a deuterium content of 93–94% for the five-membered ring positions (and 98% for the methyl groups).

It was clear from our earlier work that the investigation of the spin crossover of Cp_2Mn, in particular the detection of the elusive low-spin isomer, is difficult because it requires low temperature and solvents like toluene. The problems are low solubility and broad resonances with bad signal-to-noise ratio. They could be overcome by investigating Cp_2Mn-d_{10} because its ^{2}H NMR signal is 38 times narrower than the ^{1}H NMR signal of Cp_2Mn.[5a] Thus it was possible to study Cp_2Mn-d_{10} over a range 227.5 down to 159.5 K; a series of selected spectra is shown in Figure 1. Above 210 K only one manganocene signal is seen near 25 ppm with a half-width at a given temperature, W_T, that increases from $W_{387} \approx 30$ Hz to $W_{212} \approx 150$ Hz. Below 210 K three new signals appear, a narrow one and two broad ones. At 184 K, for instance, the shifts on the TMS scale are −1.48 ppm ($W = 59$ Hz), 154.5 ppm ($W = 440$ Hz), and −29.5 ppm ($W = 195$ Hz). The two unshaded manganocene signals in Figure 1 have an intensity ratio of approximately 1/1 (as long as the signal-to-noise is good), and they increase on the expense of the shaded signals when the temperature is lowered.

This behavior is best understood with the equilibria shown in Figure 2. Thus association occurs on lowering the temperature, with the simplest product being the dimer I. Further reaction with Cp_2Mn forms chains with bridging η^3,η^2-Cp ligands.[13] The two unshaded signals in Figure 1 are therefore assigned to $[Cp_2Mn$-$d_{10}]_n$.[14] A more detailed assignment is possible when a $(\eta^5\text{-Cp})Mn(\eta^3\text{-Cp})(\eta^2\text{-Cp})$ fragment is regarded as a $CpMn^{II}$ half-sandwich, which should have typical Cp proton resonances in the range −15 to −65 ppm.[15] Therefore we attribute the unshaded signal near −30 ppm (Figure 1) to the terminal Cp of structure I[14] in Figure 2. The fact that, down to 160 K, only one signal (near 150 ppm) rather than two is observed for the bridging Cp must be due to dynamic averaging visualized by the equilibrium Ia ⇄ Ib in Figure 2. On the other hand, a possible interconversion of terminal and bridging Cps in dimeric manganocene and an exchange of Cps between monomeric and dimeric manganocene could not be observed in the NMR spectra up to 230 K. The formation of manganocene dimers in solution was confirmed by concentration-dependent measurements. From a series of spectra with four concentrations at three temperatures (supplementary material) three have been selected in Figure 3. Evidently the intensity of the dimer signals increases with increasing concentration at a given temperature as expected whereas that of the shaded signals decreases.

The behavior of the shaded signals in Figure 1 and 3 is characteristic of a high-spin/low-spin equilibrium of monomeric manganocene. At low temperature one signal is present for each spin isomer. The narrower and less shifted one is attributed to the low-spin isomer. This is in accord with our results on 1,1′-

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[13] Bünder, W.; Weiss, E. *Z. Naturforsch., B: Chem. Sci.* **1978**, *33*, 1235.

[14] The unshaded signals in Figure 1 are in accord with structures I *and* II in Figure 2. However, it is unlikely that we observe $[Cp_2Mn]_n$ with $n > 2$ because (i) the concentration of an oligomer depends on the nth power of the concentration of Cp_2Mn, which is very low (0.2 mol %), and (ii) the solubility of $[Cp_2Mn]_n$ should decrease rapidly with n. Therefore, we consider only the dimer throughout this work.

[15] Köhler, F. H.; Hebendanz, N.; Müller, G.; Thewalt, U.; Kanellakopulos, B.; Klenze, R. *Organometallics* **1987**, *6*, 115. Note that we have changed the sign convention for the paramagnetic shifts since.

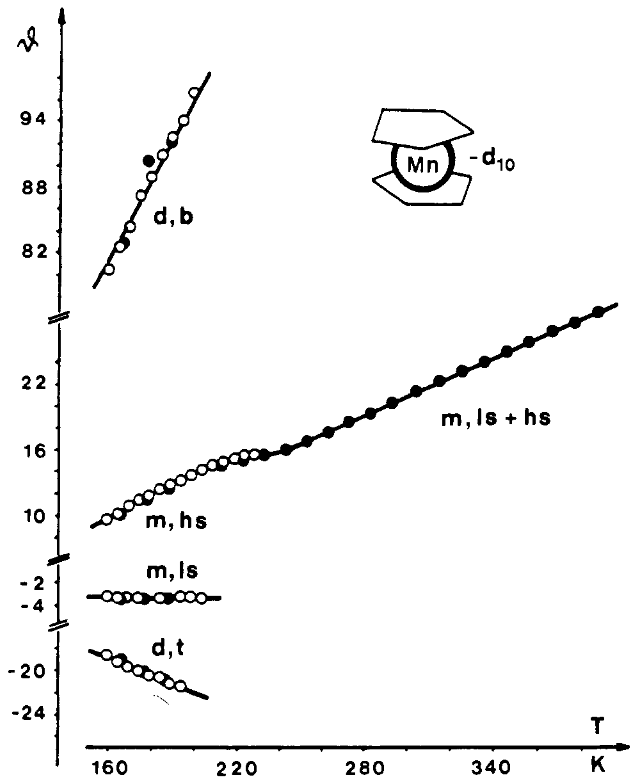

Figure 5. Temperature dependence of the reduced paramagnetic ^2H NMR signal shifts ϑ in ppm of Cp_2Mn-d_{10}. Key: 0.2 mol % solution in toluene/pentane (4/1) (○); 0.2 mol % solution in toluene (●); m = monomeric, d = dimeric, hs = high-spin, ls = low-spin; b = bridging, t = terminal ligand.

dialkylated manganocenes[3e] and with the fact that the ratio of the high-spin/low-spin signal intensities increases with the temperature (Figure 1) whereas it is independent of the overall concentration of the manganocene (Figure 3).

It is evident from Figure 4 that, under our conditions, it is virtually impossible to detect the low-spin Cp_2Mn isomer by ^1H NMR spectroscopy. Depending on the temperature, either the signals are too broad or the equilibrium concentration (vide infra) is unfavorable. By contrast, the signals of dimeric manganocene are clearly seen also by ^1H NMR spectroscopy although more detailed studies are not satisfactory. Cozak et al.[3d,f] have neglected the signal near 150 ppm (possibly after improper excitation of the resonance), and they have taken the signal near −30 ppm for the low-spin isomer of Cp_2Mn whereas it actually belongs to the dimer. Part of their work must therefore be revised.

The temperature-dependent ^2H NMR studies of Cp_2Mn-d_{10} are summarized in Figure 5 (tables with respective shifts and line widths are given in the supplementary material). For convenience we use the reduced shifts $\vartheta = \delta^{para}(T/298)$, which, in simple cases, should follow the Curie law and be constant with the temperature T. Such a case is low-spin Cp_2Mn-d_{10} whereas the high-spin isomer deviates slightly for reasons that are not yet clear. Above 210 K the signal of the low-spin isomer merges with that of the high-spin isomer thereby perturbing its ϑ/T curve until above 280 K almost pure high-spin isomer is present.[16]

The ϑ/T curves of the dimer signals strongly deviate from parallels to the T-axis. They are characteristic of a decrease of the magnetic moment with the temperature, i.e. antiferromagnetism. In fact, antiferromagnetic coupling should be mediated by the bridging Cps of dimeric manganocene and for polymeric manganocene this has been established by solid-state magnetic measurements.[2q]

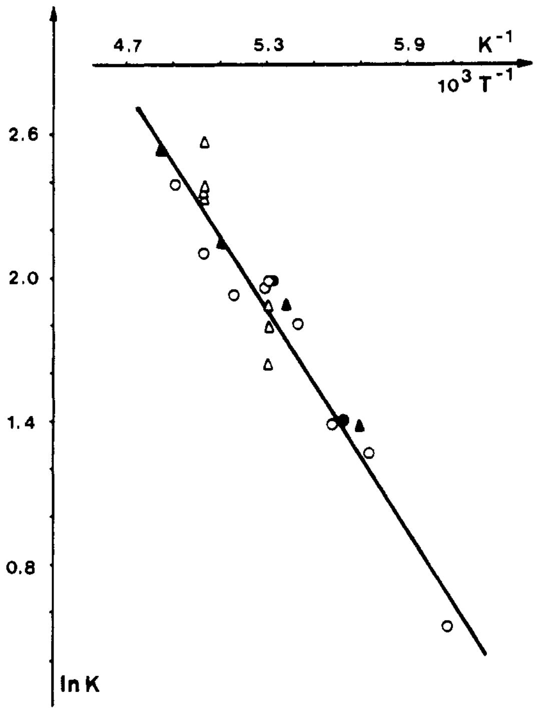

Figure 6. log K vs $1/T$ plot for the spin crossover of Cp_2Mn-d_{10}. Key: 0.2 mol % in toluene/pentane (○); 0.2 mol % in toluene (●); 0.17, 0.26, 0.39, and 0.54 mol % in toluene (△); 0.9 mol % in toluene (▲).

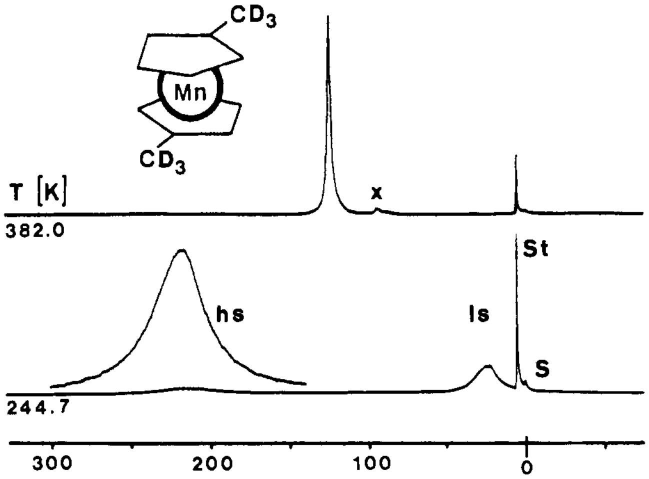

Figure 7. ^2H NMR spectra of a 7.09 mol % solution of $(C_5H_4CD_3)_2Mn$ in toluene at the temperatures indicated. Key: S = solvent; St = standard (C_6D_6); X = impurity of a higher methylated manganocene; hs = high-spin, ls = low-spin isomer. Top: hs/ls-averaged signal. The scale is in ppm.

The thermodynamic parameters of the spin crossover were determined from the ^2H NMR signal intensities of low- and high-spin Cp_2Mn-d_{10} via the equilibrium constant K. The plot in Figure 6 (details are given in the supplementary material) yields $\Delta H° = 12.8 \pm 0.8$ kJ mol^{-1} and $\Delta S° = 84 \pm 4$ J mol^{-1} K^{-1}. This means that the equilibrium is shifted more to the high-spin isomer as compared to 1,1′-monoalkylated manganocenes.[3e] The result fits well into the general trend according to which the high-spin isomer is favored when the electron-releasing power of the substituents on Cp is lowered. The earlier (much higher) $\Delta H°$ and $\Delta S°$ values for Cp_2Mn[3f] are based on an erroneous signal assignment as mentioned above. The maximum signal broadening was used as the criterion for the coalescence temperature. It was easier to observe for the high-spin than for the low-spin isomer and occurred near 212 K.

Deuteriated 1,1′-Dimethylmanganocenes. The compounds $(C_5H_4CD_3)_2Mn$ (**2a**) and $(C_5D_4CH_3)_2Mn$ (**2b**) were prepared as described for Cp_2Mn-d_{10} in the previous section. As can be seen in Figures 7 and 8, they yield very simple ^2H NMR spectra with narrow signals at high temperature. Besides that, the spectra show

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(16) With the thermodynamic data obtained below 1% low-spin isomer is calculated at 283 K.

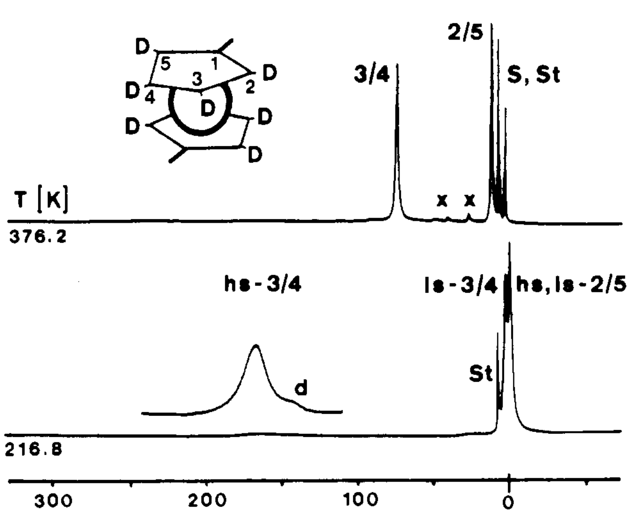

Figure 8. ^{2}H NMR spectra of a 4.27 mol % solution of $(C_5D_4CH_3)_2Mn$ in toluene at the temperatures indicated (cf. legend of Figure 7). Toluene-d_8 and benzene-d_6 have been used as standards at high and low temperatures, respectively. Top: hs/ls-averaged signals. d = dimer (cf. Figure 10).

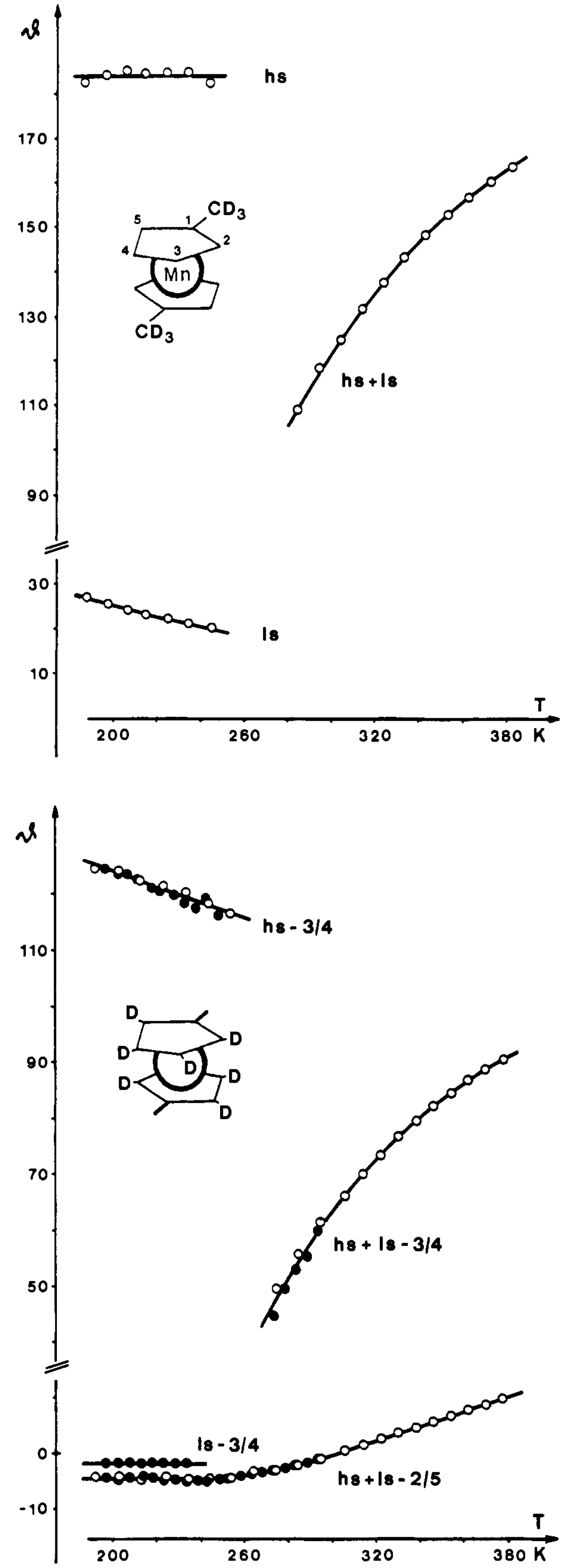

Figure 9. Temperature dependence of the reduced paramagnetic ^{2}H NMR signal shifts ϑ in ppm of (top) a 7.27 mol % solution of **2a** in toluene and (bottom) 4.27 mol % (○) and 9.41 mol % (●) solutions of **2b** in toluene. Only results for monomeric species are shown.

traces of higher methylated manganocenes,[17] which would be hard to detect by elementary analysis or ^{1}H NMR spectroscopy. The selective deuteriation allows one to unequivocally distinguish the signals of the Cp and the methyl group. It confirms our earlier assignment[3e] and the surprising fact that the signal of the methyl group is considerably more shifted than those of the Cp.[18] This definitely rules out the signal assignment for some alkylated manganocenes that was put forward repeatedly[3b,d,f] and that was the basis of conclusions concerning the ground state of manganocenes (see below). The assignment of D2/5 and D3/4 follows the arguments given earlier.[3e]

The reduced signal shifts of the methyl group show a temperature dependence (Figure 9) which is very similar to that found by ^{1}H NMR spectroscopy.[3e] This is contrasted by the signals of the five-membered ring. They could not be followed over an extended temperature range by ^{1}H NMR owing to excessive broadening whereas ^{2}H NMR was straightforward and gave the result shown in the lower part of Figure 9. A puzzling feature is that at low temperature the signal of D2/5, unlike that of D3/4, does not split as could be expected for slowly interconverting spin isomers. The reason is the low concentration[19] of the high-spin isomer and the small shift difference[20] of the signals of both spin isomers. Thus, for D2/5 the coalescence temperature is much lower than that for D3/4 (265 K) and below coalescence the high-spin isomer is not sufficiently populated to be detected. This phenomenon is known for diamagnetic dynamic molecules as hidden partner exchange.[21]

The spin crossover was analyzed quantitatively with three independent sets of parameters obtained from the CD_3 and D3/4 signals of **2a** and **2b**, respectively. The results are collected in Table II together with those obtained by ^{1}H NMR spectroscopy for comparison. The coalescence temperatures were determined from the maximum broadening of the coalescing signals of spectra that were recorded in 2 K steps. As expected, they depend on the separation $\Delta\delta$ of the signals of the two spin isomers. The ΔH° and ΔS° values were obtained from the signal areas of the two spin isomers below coalescence or from the signal shifts above coalescence as follows. From the ϑ/T curves (Figure 9) the ϑ-values of the two spin isomers were extrapolated for a given T, transformed to δ-values, and compared to the weighted average

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(17) As mentioned for the ligand synthesis, Cps having more than one methyl group may form. This leads to e.g. isomers of $(MeCp)Mn(Me_2Cp)$ and $(Me_2Cp)_2Mn$.

(18) Details including the reason for these anomalous signal shifts have been given in ref 3e.

(19) Using the data of Table I, a concentration of 8.4% at 220 K is calculated for the high-spin isomer; it decreases rapidly with temperature.

(20) Below 230 K and above 340 the ϑ/T curve of D2/5 in Figure 9 is essentially that of the low-spin and the high-spin isomer, respectively. Extrapolation yields a splitting of ca. 260 Hz at 220 K. This is about 20 times smaller as compared to D3/4.

(21) (a) Anet, F. A. L.; Basus, V. J. *J. Magn. Reson.* **1978**, *32*, 339. (b) Okzawa, N.; Sorensen, T. S. *Can. J. Chem.* **1978**, *56*, 2737.

Table II. Spin Crossover Data for 1,1-Dimethylmanganocenes at the Coalescence Temperatures

	$(C_5H_4CD_3)_2Mn^a$	$(C_5H_4CD_3)Mn^b$	$(C_5D_4CH_3)_2Mn^a$	$(C_5H_4CH_3)_2Mn^{a,c}$
T^d (K)	270	270	265	310
$\Delta H°$ (kJ mol^{-1})	16.8	15.3	18.9	11.6
$\Delta S°$ (J mol^{-1} K^{-1})	60.5	57.7	66.0	44.0
ΔP^e	−0.10	0.06	−0.31	0.40
$\Delta\delta^f$ (kHz)	5.65	5.65	4.03	35.20
$\Delta G^{\neq g}$ (kJ mol^{-1})	45.4	44.9	46.2	49
τ^h (10^{-5}s)	5	5	8	1

[a] Data from the comparison of the extrapolated signal shifts of the low- and high-spin isomer with the weighted average shift. [b] Data from signal integration. [c] Data from ref 3e. [d] Coalescence temperature. [e] Population difference of the high- and low-spin states. [f] Shift difference of the signal for the high- and low-spin isomers extrapolated from the ϑ/T curves in Figure 9. [g] Energy barrier on passing from the low- to the high-spin isomers. [h] Lifetime of a spin isomer.

signal shift actually measured at this temperature. The signal areas or shifts were transformed to $\Delta H°$ and $\Delta S°$ using standard procedures (supplementary material). Within the error limits the agreement of $\Delta H°$ and $\Delta S°$ of **2a** evaluated by the two methods is good. On the other hand, the precision of the data is not sufficient to establish a deuterium isotope effect on the spin crossover, which becomes apparent in the unusually large primary isotope shifts.[5a,22]

Our result is at variance with $\Delta H° = 20$ kJ mol^{-1} and $\Delta S° = 20$ J mol^{-1} K^{-1} that has been reported for $(C_5H_4CH_3)_2Mn$.[3f] It implies that high-spin 1,1-dimethylmanganocene should be unobservable by NMR spectroscopy below 250 K (because a population lower than 10^{-3} is calculated) whereas Figures 7 and 8 show that the high-spin isomer is clearly visible even at much lower temperature. These values are unrealistic possibly because, for the evaluation procedure, Curie behavior was assumed[3f] for all shifts, which is unjustified (cf. Figure 9).

Also given in Table II are the population difference ΔP and the signal shift difference $\Delta\delta$ of the high- and low-spin isomers. They were used to calculate[23] the energy barriers $\Delta G^{\neq}$ of the spin crossover and the lifetime τ of the spin isomers. The $\Delta G^{\neq}$ values are rather similar, while τ reflects the respective coalescence temperature.

Besides the ^2H NMR signals of the two spin isomers additional signals were found for **2a** and **2b** at low temperatures (Figure 10). At a given temperature their intensities increased much faster with the concentration than those of the two spin isomers. This parallels our findings for Cp_2Mn-d_{10} and shows that **2a** and **2b** form MeCp-bridged dimers in solution (cf. Figure 2). For **2a** it is unclear which of the two shaded signals in Figure 10 belongs to the bridging and to the terminal ligand, respectively. The shaded signals of **2b** were assigned tentatively by analogy to the signal shifts of dimeric Cp_2Mn-d_{10}.

The ^2H NMR results presented here disclose an error in our earlier assignment of the ^1H NMR signals of $(MeCp)_2Mn$.[3e] The shaded signals in Figure 10 show that dimeric $(C_5H_4CH_3)_2Mn$ like **2a** and **2b** should have three signals roughly 10–50 ppm at low frequency from that of D3/4 of the high-spin isomer. These signals will hardly be resolved in the ^1H NMR spectrum, and their combined intensity will be big when a high concentration is chosen as in our earlier work. We were therefore misled to assign as H2/5 of the high-spin isomer what must be actually attributed to the dimer. Instead the signal of H2/5 is hidden by other signals not far from 0 ppm, as proven for **2b** in Figures 8 and 9. This is another instructive example for the superiority of ^2H NMR spectroscopy. Anyway, the signal in question has not been used previously to derive quantitative results.

Ground States of Manganocenes. As mentioned above, there is general agreement for quite some time now that manganocenes can exist in both the $^6A_{1g}$ (e_{2g}^2, a_{1g}, e_{1g}^2) and the $^2E_{2g}$ (a_{1g}^2, e_{2g}^3) states[2f,i,l,q,3b–f,24,25] although considerable differences in the population result when the Cp substituents or the host lattice is varied. Also conceivable is a $^2A_{1g}$ (e_{2g}^4, a_{1g}) state, which has been suggested to explain the He I photoelectron spectrum of Cp_2Mn.[2g] In a second PE study $^6A_{1g}$ was favored for Cp_2Mn (at high temperature) and a mixture of $^2E_{2g}$ and $^6A_{1g}$ for $(C_5H_4CH_3)_2Mn$.[2h] The situation is similar to that of isoelectronic ferrocenium ions, which have been investigated more thoroughly. Stebler et al.[26] have reviewed the pertinent studies and performed inelastic neutron scattering experiments. They conclude that it is unclear in how far the $^2A_{1g}$ state determines the properties of ferrocenium ions. For manganocenes the most convincing indication of the $^2A_{1g}$ state seemed to be the ^1H NMR work of Switzer et al.[3b] They, and later Cozak et al.,[3f] argued that the unusually large signal shifts of the Cp protons of $(C_5H_4CH_3)_2Mn$ could be best understood when the $^2A_{1g}$ state contributes to the electron spin delocalization. However, the present work shows that their signal assignment was incorrect and that all signals of the low-spin isomers have small shifts (Figures 1, 3, 5, and 7–9). Thus, the shifts do not establish the participation of the $^2A_{1g}$ state.

Besides this, a thermally accessible $^2A_{1g}$ state should become apparent in the temperature dependence of the NMR signal shifts. The reason is that in going from $^2E_{2g}$ to $^2A_{1g}$ the electron spin delocalization should change and the signal shifts of the low-spin

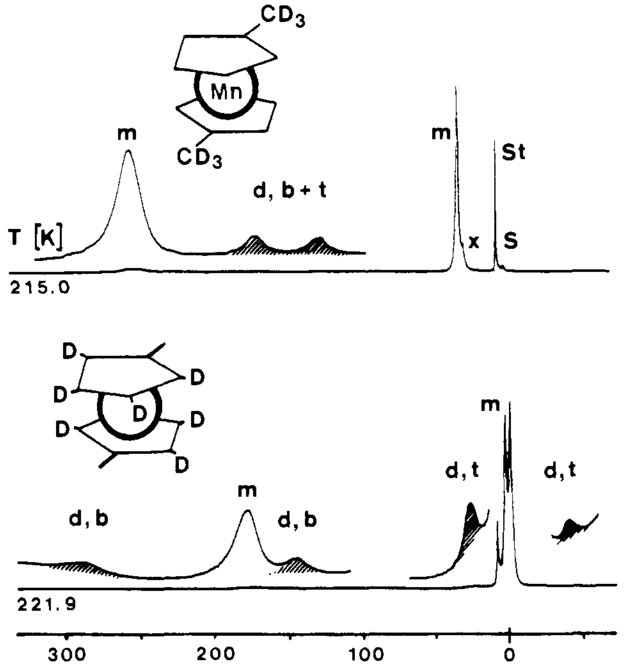

Figure 10. ^2H NMR spectra of a 7.09 mol % solution of $(C_5H_4CD_3)_2Mn$ in toluene (top) and a 9.41 mol % solution of $(C_5D_4CH_3)_2Mn$ (bottom) in toluene at the temperatures indicated. The unshaded signals belong to the monomers (m; cf. Figures 7 and 8 for assignment), and the shaded signals belong to the dimers (d). Key: b = bridging, t = terminal ligand; S = solvent, St = standard (C_6D_6); x = impurity of a higher methylated manganocene.

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(23) Shanan-Atidi, H.; Bar-Eli, K. H. *Chem. Phys.* **1970**, *74*, 961.

(24) Ammeter, H.; Zoller, L.; Bachmann, J.; Baltzer, P.; Gamp, E.; Bucher, R.; Deiss, E. *Helv. Chim. Acta* **1981**, *64*, 1063.

(25) Warren, K. D. *Inorg. Chem.* **1975**, *14*, 2279.

(26) Stebler, A.; Furrer, A.; Ammeter, H. *Inorg. Chem.* **1984**, *23*, 3493.

manganocenes should no longer follow the Curie law; i.e., they should not give parallels to the T axis in a ϑ/T diagram. The ^{2}H NMR data of Cp_2Mn-d_{10} in Figure 5 show that there is no evidence for the population of the $^2A_{1g}$ state. When a manganocene is substituted, it is no longer suitable for an unequivocal conclusion of this kind because then the degeneracy of the e_{2g} levels is lifted so that a deviation from the Curie law is introduced even if all three electrons stay in the orbitals that are derived from the e_{2g} set.[27] Hence, the fact that two signal shifts of the deuteriated low-spin 1,1-dimethylmanganocenes (Figure 9) deviate from the Curie law does not prove the $^2A_{1g}$ state either.

Conclusion

Manganocenes turn out to be attractive compounds not only because their spin state in solution can be tuned by substitution, the solvent, and the temperature but also because they form antiferromagnetic Cp-bridged dimers. These dimers represent the first step from solvated monomers to polymeric crystalline[13] manganocene. They have not been detected by EPR spectroscopy,[2i,1] they will influence susceptibility measurements of manganocenes in solution at low temperature,[2i,3b] and it is questionable whether they can be detected by solid-state mangnetic measurements. For the chemist who wants to tailor a specific manganocene, ^{1}H and the more powerful ^{2}H NMR spectroscopy is an efficient method to check the approach.

Experimental Section

All reactions and the NMR measurements were carried out under exclusion of oxygen and moisture using the Schlenk tube technique and NMR tubes with ground-glass joints and stoppers. The glassware was flame dried in vacuo, and the solvents were dried by standard methods and saturated with inert gas. The 70-eV EI mass spectra were obtained with a Varian MAT 311A spectrometer, the NMR spectra of the manganocenes with a Bruker CXP 200 instrument, and all other NMR spectra with a Jeol JNM GX 270 spectrometer. The ligand anions were measured as 2.5 M solutions in THF at 20 °C, the solvent with $\delta(^{13}C2/5)$ 25.80 was used as an internal standard, and the digital resolution was 0.49 Hz. For the ^{2}H NMR spectra of the manganocenes the Bruker BVT 1000 temperature control unit was used and the temperature was measured with a Lauda R42 resistance thermometer. Cp_2Fe-d_{10} was used as an internal standard for Cp_2Mn-d_{10}, and C_6H_6 ($\delta(^1H)$ 7.15) was used for the deuteriated 1,1-dimethylmanganocenes. The δ_T^{para} values of the latter were calculated relative to $(C_5H_4CH_3)_2Fe$ with $\delta(^1H)$ 4.0 and 1.8 for C_5H_4 and CH_3, respectively.

Decadeuteriomanganocene (1). Cyclopentadiene-d_6 was prepared by following the method of Lambert and Finzel[6f] with some modifications. A 13.24-g (0.2-mol) sample of freshly prepared cyclopentadiene was cooled to 0 °C, 17 mL of dimethyl sulfoxide and 17 mL of a 4 M solution of NaOD in D_2O[28] were added dropwise, and the mixture was stirred vigorously for 50 min. After the mixture was standing for 5 min, three phases formed, the two lower of which were rejected, and another sample of DMSO/NaOD/D_2O with the composition indicated above was added to the remaining phase. The procedure was repeated four times, the phases were separated, the top phase was distilled at 380–280 mbar using a 20-cm Vigreux column, and the product was collected at −78 °C. Yield: 8.88 g (61.5%). A deuterium content of 94.3% was found by mass spectroscopy. MS [*m/z* (%)]: 73 (5), 72 (100) [$C_5D_6^+$], 71 (37) [$C_5D_5H^+$], 70 (45) [$C_5D_5^+$, $C_5D_4H_2^+$], 69 (12) [$C_5D_4H^+$], 66 (5.5) [$C_5D_3^+$].

A solution of 8.68 g (0.12 mol) of cyclopentadiene-d_6 in 50 mL of THF was cooled to 0 °C. After the addition of 3.70 g (0.15 mol) of NaH, the mixture was stirred for 1 h and refluxed for 2 h; then the solid was separated and washed twice with THF. The combined fractions gave 59.7 mL of a 1.97 M solution of C_5D_5Na in THF (yield 98%). Following Wilkinson's procedure,[2b,12] 10.2 mL (20 mmol) of the solution and 1.9 g (15 mmol) of $MnCl_2$ gave 1.01 g (52%) of Cp_2Mn-d_{10}. The deuterium content of 94.7% (mass spectroscopy) corresponds to that found for the ligand precursor. MS [*m/z* (%)]: 195 (96.6) [M^+], 194 (53.6) [$M^+ - 1$], 193 (14.3) [$M^+ - 2$], 192 (2.2) [$M^+ - 3$].

1,1′-Bis(trideuteriomethyl)manganocene (2a) and 1,1′-Dimethyloctadeuteriomanganocene (2b). In a modification of McLean's method,[8a] a solution of 5 mL (52 mmol) of $(CD_3O)_2SO_2$ in 100 mL of THF was held at 0 °C while 15.3 mL of a 2.62 M solution of CpNa in THF was added dropwise under stirring. The mixture was distilled at 140 mbar using a 20-cm Vigreux column, and the product was collected together with THF at −78 °C. The solution was brought to 0 °C, 1.26 g (53 mmol) of NaH was added, the mixture was stirred at 0 °C for 1 h and then refluxed for 2 h. Workup as described for C_5D_5Na gave 130 mL of a 0.28 M solution of $(C_5H_4CD_3)Na$ in THF (yield 90% relative to $C_5H_5^-$).

Similarly, 7.1 mL of $(CH_3O)_2SO_2$ in 120 mL of THF, 30.6 mL of a 1.96 M of C_5D_5Na in THF, and 1.55 g (65 mmol) of NaH gave 135 mL of a 0.42 M solution of $(C_5D_4CH_3)Na$ in THF (yield 95% relative to $C_5D_5^-$).

Further reaction of 7 mmol of $C_5H_4CD_3^-$ or $C_5D_4CH_3^-$ with 1.0 g (5 mmol) of $MnCl_2$ gave 490 mg of $(C_5H_4CD_3)_2Mn$ (yield 64%) or 480 mg of $(C_5D_4CH_3)_2Mn$ (yield 62%). The deuterium content estimated from the mass spectra was better than 98 or 93%. MS [*m/z* (%)]: **2a**, 221 (67.4) [M^+], 220 (40.5) [$M^+ - 1$], 219 (10.2) [$M^+ - 2$], 218 (1.7) [$M^+ - 3$]; **2b**, 219 (40.5) [M^+], 218 (4.0) [$M^+ - 1$].

Acknowledgment. This work has been generously supported by the Fonds der Chemischen Industrie.

Supplementary Material Available: Tables III–XIX, containing the temperature-dependent signal shifts, the half-widths, and the data relevant for the determination of the thermodynamic parameters, and Figure 11, showing thermodynamic plots (22 pages). Ordering information is given on any current masthead page.

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[27] More details concerning this reasoning are given in: (a) Köhler, F. H.; Geike, W. A. *J. Magn. Reson.* **1983**, *53*, 297. (b) Köhler, F. H.; Geike, W. A. *J. Organomet. Chem.* **1987**, *328*, 35.

[28] Meyer, R. J.; Pietsch, E. H. E. In *Gmelins Handbuch der anorganischen Chemie*; Verlag Chemie: Weinheim, Germany, 1965; Syst.-Nr. 21, Suppl. 2, p 821.