Spin Equilibria and Thermodynamic Constants for $(C_5H_4R)_2Mn$, $R=H$ or Me , in Solid Solutions of Diamagnetic Diluents

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Graphical abstract:

Solid solutions of $(C_5H_4Me)_2Mn$ in $(C_5H_4Me)_2Fe$ disrupts the antiferromagnetic coupling in polymeric $(C_5H_4Me)_2Mn$ and leads to a spin equilibrium in the monomeric manganocenes.

Abstract.

The solid state structure of $(C_5H_4Me)_2Mn$ is determined and its solid state magnetism investigated. $(C_5H_4Me)_2Mn$ is a chain polymer, as is the parent $(C_5H_5)_2Mn$ (Bünder W.; Weiss, E. *Z. Naturforsch.* **1978**, 33b, 1237), and they exhibit very similar solid state magnetic susceptibilities that are modeled as an antiferromagnetically-coupled linear Heisenberg-chain of high-spin Mn(II) centers ($S = 5/2$) (König, E.; Desai, V. P.; Kanellakopulos, B.; Klenze, R. *Chem. Phys.* **1980**, 54, 109). Doping of these manganocenes into diamagnetic hosts such as $(C_5H_4Me)_2Fe$ and $(C_5H_5)_2Fe$, respectively, stabilizes the low-spin configuration ($S = 1/2$) relative to the high-spin configuration ($S = 5/2$). At higher temperatures the solid solutions of these manganocenes show spin-crossover behavior modeled by a Boltzmann distribution of spins to give $\Delta H^0 \approx 1.7 \text{ kcal mol}^{-1}$ and $\Delta S^0 \approx 5 \text{ cal (mol K)}^{-1}$ for the $LS \rightleftharpoons HS$ equilibria.

1. Introduction

Since the preparation of $(C_5H_5)_2Mn$, Cp_2Mn , by Wilkinson [1, 2] and Fischer [3] more than sixty years ago the molecular and electronic structure of manganocenes have attracted considerable interest, since their physical properties are rather unusual when compared to those of either Cp_2Cr or Cp_2Fe . Unlike the solid state sandwich structures of D_{5h} and D_{5d} symmetry, $(C_5H_5)_2Mn$ is a zig-zag chain polymer in the solid state in which a C_5H_5 group is a perpendicular bisector of a line that connects the η^5 -(C_5H_5)Mn fragments.[4] The polymeric structure accounts for its low solubility in aliphatic hydrocarbons that is easily disrupted, since Cp_2Mn is volatile and adopts a sandwich structure like the other first row metallocenes in the gas phase.[5, 6] When originally reported, the magnetic susceptibility data of Cp_2Mn was perplexing, until the polymeric solid state structure was determined, since a plot of the magnetic moment as a function of temperature showed that the individual Mn(II) centers are antiferromagnetically coupled in the temperature range 90-432 K above which it undergoes an abrupt phase transition to a pink form, where the magnetic moment is consistent with an isolated $S = 5/2$ paramagnet, i.e. high-spin (HS) Mn(II). Magnetic measurements showed that Cp_2Mn , magnetically diluted in Cp_2Mg , behaves as an isolated $S = 5/2$ paramagnet from 90 to 500 K.[7] Interestingly, the undiluted substituted derivative $(C_5H_4Me)_2Mn$ exhibits similar magnetic susceptibility behavior in the temperature range 200-400 K.[8] The gas phase electron diffraction data of $(C_5H_4Me)_2Mn$ have been interpreted as a mixture of two monomeric spin isomers, where the ratio of high-spin (Mn-C(ave)= 2.43 Å) to low-spin (Mn-C(ave)= 2.14 Å) is 60:40 at 373K.[9] This gas phase structural study supports the deductions of earlier gas phase photoelectron spectroscopy (PES) studies postulating that $(C_5H_4Me)_2Mn$

is a spin equilibrium molecule in gas phase while Cp_2Mn exists predominantly as the high-spin isomer with a small contribution from the low-spin isomer.[10] The original interpretation of the gas phase PES of Cp_2Mn has been revised recently by Green.[11] The revised interpretation, based on spin unrestricted DFT calculations, resolved some apparent contradictions in the original interpretation[12-14] and showed that the electron spectroscopy of open-shell metallocenes cannot be understood satisfactorily using a ferrocene-like model. The EPR studies of Ammeter and Maki have shown that Cp_2Mn and $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$ in frozen solution and diluted in a host of Cp_2M or $(\text{C}_5\text{H}_4\text{Me})_2\text{M}$ ($\text{M} = \text{Mg}, \text{Fe}, \text{Ru}$), respectively, behave as spin crossover molecules, in which the low-spin (LS) state is stabilized by about $0.5 \text{ kcal mol}^{-1}$. [15-18] The low-spin isomer ($^2\text{E}_{2g}$ in D_{5h} symmetry) is doubly degenerate and behaves as a dynamic Jahn-Teller molecule. The nature of the potential energy surface of the dynamic Jahn-Teller distortion depends upon the substituents on the Cp-ring and the host metallocene. In toluene solution, spin isomers and monomer-oligomer equilibria are present over the temperature range 160-400 K in the ^2H NMR spectra of $(\text{C}_5\text{D}_5)_2\text{Mn}$ and $(\text{C}_5\text{H}_4\text{CD}_3)_2\text{Mn}$. [19] In contrast to $(\text{C}_5\text{H}_5)_2\text{Mn}$ and $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$, $(\text{C}_5\text{Me}_5)_2\text{Mn}$ is low spin since the Mn-C(ave) distance is $2.11 \text{ \AA}$. [20] The magnetic moment in the solid state (5-550 K) shows it to be low-spin (see Supporting Information for details, Fig. S2) and its EPR spectrum in frozen glasses and solid solutions of $(\text{Me}_5\text{C}_5)_2\text{Fe}$ agree with the $^2\text{E}_{2g}$ ground state, consistent with the gas phase PES data. [21, 22] The electronic structure of Cp_2Mn in solid, solution, and gas phase is now clear. What is not clear, however, is the thermodynamic constants for the low spin-high spin equilibrium in solid solutions. This article describes a variable temperature magnetic susceptibility study of $(\text{C}_5\text{H}_5)_2\text{Mn}$ and $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$ in solid solutions of diamagnetic metallocenes that are consistent with the solid state EPR results and quantifies the thermodynamic constants for the spin-equilibrium.

2. Experimental Section

2.1 General Considerations. All reactions, product manipulations, and physical studies were carried out as previously described. [23-25] Magnetic measurements were conducted in a 7 T Quantum Design MPMS magnetometer utilizing a superconducting quantum interference device (SQUID). Between 10 and 25 mg of sample were sealed in evacuated quartz tubes held in place with $\sim 5 \text{ mg}$ of quartz wool. This method provided a very small and reliable container correction, typically *ca.* $-2 \times 10^{-5} \text{ emu/mol}$. The data were also corrected for the overall diamagnetism of the molecule using Pascal constants (see Supporting Information for details, Fig. S7). [26] For a more detailed description of the quartz tube technique for magnetic susceptibility studies see ref. [24].

2.2 Manganocenes. Cp_2Mn and $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$ were synthesized according to published procedures,[7, 8] and purified by sublimation and/or crystallization. $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$ was crystallized from diethyl ether at $-20\text{ }^\circ\text{C}$, while Cp_2Mn was crystallized from toluene at $-20\text{ }^\circ\text{C}$.

2.3 Dilution Experiments. To prepare magnetically diluted samples it was necessary to melt both compounds in the correct ratios at $200\text{ }^\circ\text{C}$ and to keep the melt at this temperature for 3 days. Subsequently the mixture was sublimed in oil pump vacuum onto a water cooled cold finger. This procedure was first used by Wilkinson and co-workers.[7, 8]

2.4 Crystallographic Details. The red-orange crystals were grown by slowly cooling of a saturated ether solution to $-20\text{ }^\circ\text{C}$. A crystal of appropriate dimensions was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker SMART 1K CCD diffractometer[27] at $151(2)\text{ K}$. Cell constants and an orientation matrix were obtained of the measured positions of reflections with $I > 10\sigma$ to give the unit cell. The systematic absences uniquely determined the space group in each case. An arbitrary hemisphere of data was collected at using the ω scan technique with 0.3° scans counted for 10 s per frame. Data were integrated using SAINT[28] and corrected for Lorentz and polarization effects. The data were analyzed for agreement and absorption using XPREP,[29] and an empirical absorption correction was applied based on comparison of redundant and equivalent reflections. The structures were solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions, but not refined. The structure was solved and refined using the software packages SHELXS-97 (structure solution) and SHELXL-97 (refinement).[30, 31] Dimethylmanganocene crystallizes in the primitive, acentric orthorhombic space group $P2_12_12_1$. The correct enantiomorph was identified by refining the Flack parameter as well as checking the R-value of the inverted structure.

3. Results and Discussion

3.1 Solid State Crystal Structure of $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$. The solid state magnetic susceptibility of $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$ reported by Wilkinson implies that its solid state structure is polymeric like that of Cp_2Mn . [7] This inference is correct as shown in the ORTEP, Figure 1. Selected bond distances are given in the Figure caption.

Figure 1. ORTEP of $(C_5H_4Me)_2Mn$ (50% probability ellipsoids). Atom labels bearing $_3$ are symmetry related positions. All non-hydrogen atoms are refined anisotropically and the hydrogen atoms are placed in idealized positions using a riding model. Selected bond distances (Å): Terminal : Mn(1)-C(1) 2.468(2), Mn(1)-C(2) 2.437(2), Mn(1)-C(3) 2.379(2), Mn(1)-C(4) 2.379(2) , Mn(1)-C(5) 2.426(2), Mn-Cp(centroid) 2.10, Mn-C(ave) 2.418 ± 0.031 ; Bridging: Mn(1)-C(7) 2.997(2), Mn(1)-C(8) 3.313(2), Mn(1)-C(9) 2.997(2), Mn(1)-C(10) 2.416(2), Mn(1)-C(11) 2.409(2), Mn(1)-C(8 $_3$) 2.409(2), Mn(1)-C(9 $_3$) 2.518(2), Mn(1) $\cdots$ Mn(1 $_3$) 5.32.

Introducing one methyl group on the cyclopentadienyl ring does not change significantly the overall pattern in the bond lengths of the polymer chain in $(C_5H_4Me)_2Mn$ compared to $(C_5H_5)_2Mn$. However, the low temperature (-122 °C) diffraction data for $(C_5H_4Me)_2Mn$ yields much more precise bond lengths. The intra- and interchain distances between the manganese atoms are different in both metallocenes: The *intrachain* Mn $\cdots$ Mn distance is slightly shorter 5.32 Å vs. 5.38 Å, respectively, but the *interchain* Mn $\cdots$ Mn distances (6.46 Å and 8.63 Å) are substantially more asymmetric than in the parent molecule (7.89 Å and 7.36 Å),[4] although they both average to 7.65 and 7.63 Å, respectively. The Mn-C bond lengths in the terminal and bridging cyclopentadienyl rings follow a pattern that is informative. In the terminal ring, C(1)-C(5), the Mn-C distances follow a two short, three long pattern. Thus, the Mn(1)-C(3) and -C(4) are equal at 2.379(2) Å while the Mn(1)-C(5), -C(2), -C(4) average to 2.447 ± 0.016 Å. The global average of these five distances is 2.418 ± 0.031 Å. In the Cp_2Mn polymer the equivalent distance is 2.41(1) Å.[4] The seven Mn-C(bridge) distances factor into the following pattern: Mn(1)-C(10), -C(11), 2.435 ± 0.013 Å (ave), Mn(1)-C(7), -C(9) are equal at 2.997(2) Å, Mn-C(8) is 3.313(2) Å, a two short, two longer, and one very long pattern of distances. The two other distances,

Mn(1)-C(8_3) and Mn(1)-C(9_3), are equivalent to Mn(1_3)-C(8) and Mn(1_3)-C(9) by symmetry, are 2.409(2) and 2.518(2) Å, respectively. The C-C distances in the terminal and bridging rings average to 1.408(2) Å and 1.413(9) Å, and are not statistically different.

The pattern in the Mn-C distances suggests that the terminal ring may be classified as (η^5 -C₅H₄Me)Mn while the bridging ring is η^2 to one (η^5 -C₅H₄Me)Mn(1_3) fragment and either η^2 , η^4 -bonded to the other (η^5 -C₅H₄Me)Mn(1) fragment. Although this classification is artificial, it is helpful to see how the monomeric units in (C₅H₄Me)₂Mn are linked together in the polymeric chain by relatively long and presumably weak intermolecular η^2, η^4 -C₅H₄Me interactions, which rationalizes its the rather low sublimation temperature and good solubility in aromatic hydrocarbons.

This classification scheme does not, however, address the question of why Cp₂Mn and (C₅H₄Me)₂Mn are polymers while all of the other known first row metallocenes are monomers in the solid state. From a molecular orbital perspective two d-orbitals (d_{xz} , d_{yz}) interact with the Cp-symmetry orbitals forming bonding and antibonding combinations that contain 4 and 2 electrons, respectively,[6, 32] and the non-bonding $d_{x^2-y^2}$, d_{xy} , d_{z^2} orbitals each contain one electron in the high spin isomer. From a crystal field perspective, high spin Mn(II) has no crystal field stabilization energy and both models rationalize weak Mn-Cp bonding. The average gas phase bond dissociation enthalpy, D, for Mn-Cp is 51 kcal mol⁻¹, some 9 kcal mol⁻¹ less than that of Cp₂Ni; although both metallocenes have two electrons in M-Cp antibonding orbitals.[33, 34] As the Mn-Cp bonds are the weakest of the known first-row transition metal metallocenes, reorganization of a monomer to form a polymer creates additional Mn-C and Mn ... C interactions and a lattice energy that compensates the loss of entropy. Although this proposition is qualitative, it provides a model from which the “odd” behavior of Cp₂Mn and (C₅H₄Me)₂Mn may be understood.

3.2 Solid State Magnetic Susceptibility Studies. (C₅H₄Me)₂Mn. Wilkinson reported the magnetic susceptibility of (C₅H₄Me)₂Mn from 200-365 K and demonstrated that the magnetic moment significantly increases upon melting, 334-336 K.[7] The data in quartz tubes,[24] reproduces the original study and extends the temperature range from 5 K to 400 K.[35] Up to 330 K the shape of the curve is similar to Cp₂Mn (see Supporting Information, Figure S3), but then increases by *ca.* 10 %, probably due to the breakdown of the chain-structure on melting. However, a spin-only value of high-spin Mn(II) is not observed, since the effective magnetic moment is 5.50 μ_B at 400 K. When the liquid is cooled, the effective magnetic moment curve retraces its path and, on supercooling, continues smoothly past the discontinuity at the melting point. The super-cooled liquid curve exactly overlaps the initial heating curve at *ca.* 220 K (Figure 2).

Figure 2. Magnetic moment (μ_B) vs. T of $(C_5H_4Me)_2Mn$.

Figure 3. $\chi(T)$ vs. T plot of $(C_5H_4Me)_2Mn$. The magnetic susceptibility is modeled as a Heisenberg linear chain. The averaged g -value is set to 2.0, since this is a very good approximation for the $S=5/2$ Mn^{2+} ion, and a Curie constant ($C= 0.019729$) was included in the fitting procedure (eq. 1) to account for paramagnetic impurities.

The magnetic behavior of Cp_2Mn was successfully modelled by König *et al.* using the approximation that the Mn atoms are antiferromagnetically-coupled linear Heisenberg-chain, including a Curie-Weiss constant to account for interchain interactions.[36]

$$\chi_m = \frac{Ng^2\mu_B S(S+1)}{3k(T-\Theta)} \frac{[1-u(y)]}{[1+u(y)]} + \frac{C}{T} \quad (\text{eq 1}),$$

where $u(y) = \coth\left(\frac{3}{2}y^{-1}\right) + \frac{2}{3}y$, and $y = \frac{3kT}{g^2 S(S+1)|J|}$, N is the Avogadro constant, k the Boltzmann constant, μ_B in the units of Bohr magneton, S the spin state, g the g -value, Θ the Curie-Weiss constant and C the Curie constant for the impurities.

Applying König's approach to $(C_5H_4Me)_2Mn$ gives the values $J/k = -14.5$ K ($J = -42.3$ cm⁻¹) and $\theta = -9.9$ K, which are comparable to the ones obtained for Cp_2Mn ($J/k = -14.0$ K ($J = -40.8$ cm⁻¹); $\theta = -5$ K)[36] as anticipated from their very similar crystal structures (Figure 1). The fit in Figure 3 is good but not perfect, perhaps due to the approximate treatment of the three-dimensional problem that is relevant for polymeric $(C_5H_4Me)_2Mn$, since the manganese atoms are not strictly linear but they form a zig-zag chain. In addition, it does not account for the underlying spin equilibrium that introduces an admixture of the $S = 1/2$ spin isomer.[15]

3.3 Solid Solution Magnetic Susceptibility Experiments. Our initial experiment was to repeat Wilkinson's classic experiment of diluting Cp_2Mn into Cp_2Mg and using a SQUID magnetometer to measure the χ -values, rather than the Gouy balance used in the original experiments.[7, 8] As initially reported by Wilkinson[7, 8] magnetically dilute solid solutions are prepared by melting both metallocenes in the correct ratios followed by sublimation of the resulting mixture.

Figure 4. μ_{eff} and $1/\chi$ vs. T plot for 10 mole-% Cp_2Mn doped into the diamagnetic host Cp_2Mg .

The plot in Figure 4 clearly demonstrates that a 10% solid solution of Cp_2Mn in Cp_2Mg behaves as an isolated paramagnet with a magnetic moment $5.92 \mu_B$ expected for high spin Mn(II) over the temperature range of 5-300 K, as observed by Wilkinson.[7, 8] Thus, Cp_2Mg with a Mg-C distance of $2.34 \text{ \AA}$ in gas phase,[37] provides an ideal host for Cp_2Mn , with a Mn-C distance of $2.38 \text{ \AA}$ in gas phase, that is, the lattices are matched. Ammeter's EPR studies are consistent with the bulk magnetic susceptibility measurements.[16, 17] Furthermore Ammeter's extensive temperature dependent EPR studies demonstrated that the spin state at a given temperature is determined by the metal-to-ring distance of the host lattice. Diluting $(\text{C}_5\text{H}_5)_2\text{Mn}$ in, for example Cp_2Fe , where the Fe-C distance in gas phase is $2.06 \text{ \AA}$, favors exclusively low-spin Mn(II) at 4 K, which converts at higher temperatures to high-spin Mn(II) consistent with a thermal ${}^6\text{A}_{1g}/{}^2\text{E}_{2g}$ equilibrium. The diamagnetic ferrocene host lattice imposes an environment[38] on the isolated Cp_2Mn molecules that stabilizes the low-spin isomer at low temperature where the Mn-C distance (low spin) is close to that of the Fe-C distances in ferrocene. Although the EPR data give electronic structural information, these measurements cannot easily give thermodynamic values, however, bulk physical property measurement, such as magnetic susceptibility data as a function of temperature, can provide these data from which the thermodynamic constants may be obtained.

Wilkinson and Ammeter did not study the behavior of $(\text{C}_5\text{H}_5)_2\text{Mn}$ in $(\text{C}_5\text{H}_5)_2\text{Fe}$ by solid state susceptibility studies. To evaluate the concentration dependence of the SCO, two different concentrations are prepared (5 and 10 mole-%). The mixture is melted together at 200°C over a period of 3 days and subsequently the mixture is sublimed in oil pump vacuum onto a water cooled cold finger. Figure 5 shows that the electronic ground state at temperatures below 100 K is ${}^2\text{E}_{2g}$ (low-spin) consistent with Ammeter's EPR studies.[15] Figure 5 also shows a significant concentration dependence on the SCO. Although the concentration of Cp_2Mn is 5 mole% in the $(\text{C}_5\text{H}_5)_2\text{Fe}$ host, the concentration influences the temperature at which the molecules start converting to HS (5% at 140 K, 10% at 120 K). In addition, the higher the concentration of Cp_2Mn , the lower is the temperature of the spin crossover and the maximum value of μ_{eff} at 300 K. Even in the most dilute solid solution, the effective magnetic moment of $5.1 \mu_B$ is less than that observed in Cp_2Mg at 300 K. This presumably means that even in the 5% sample, the $(\text{C}_5\text{H}_5)_2\text{Mn}$ molecules are not completely magnetically isolated and some $\text{Mn}\cdots\text{Mn}$ interactions (either inter- or intra-molecular) exist, or that some of the isolated Cp_2Mn molecules are still low spin due to restraints presented by the host lattice.

Figure 5. Influence of different doping concentrations of Cp_2Mn in solid solutions of Cp_2Fe on the spin-crossover behavior.

Figure 6. μ_{eff} and $1/\chi$ vs. T plot of 5 mole-% $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$ doped into the diamagnetic host lattice $(\text{C}_5\text{H}_4\text{Me})_2\text{Fe}$.

Repeating the dilution experiments by doping 5 mole% of $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$ in $(\text{C}_5\text{H}_4\text{Me})_2\text{Fe}$ yields the results shown in Figure 6. The effective magnetic moment, μ_{eff} , increases linearly from 2.05 B.M (5 K) to 2.39 B.M. (250 K), when the magnetic moment increases rapidly reaching 2.66 B.M. (300 K). Thus, at temperatures below 200 K, the $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$ molecules are essentially low spin. Unfortunately, $(\text{C}_5\text{H}_4\text{Me})_2\text{Mg}$ is a liquid at room temperature,[39] and therefore $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn}$ in $(\text{C}_5\text{H}_4\text{Me})_2\text{Mg}$ is not a solid solution at this temperature.

3.4 Thermodynamics of the SCO by solid state magnetic susceptibility studies.

Extracting thermodynamic data from solid state susceptibility measurements is, in general, rather complicated. In most cases, the non-interacting-molecules approach is not valid, because the interaction between the different spin-carriers in the assembly has to be included, that is, the cooperativity has to be

modeled.[40] However, in the case of diluted samples the simple thermodynamic model of non-interacting molecules may be applied and a Boltzmann distribution model used to fit the solid state magnetic susceptibility data, using the following equations:

$$\chi_{l.s.} = \frac{0.125 g_{l.s.}^2 S(S+1)}{T}, \quad \chi_{h.s.} = \frac{0.125 g_{h.s.}^2 S(S+1)}{T}, \quad \text{where} \quad \chi_m = \frac{1}{K+1} (K \chi_{h.s.} + \chi_{l.s.}),$$

$$K = e^{\frac{\Delta H^0 - T \Delta S^0}{RT}}, \quad \text{and} \quad \Delta G = \Delta H - T \Delta S = -RT \ln K.$$

Figure 7 shows the $\chi(T)$ vs. T plot of 10 mole-% Cp_2Mn diluted in Cp_2Fe and the corresponding fit to the Boltzmann distribution model as outlined above. The other plots are shown in Supporting Information (Figures S5 and S6), and Table 2 summarizes the resulting thermodynamic data.

Figure 7. $\chi(T)$ vs. T plot for a 10 mole-% solid solution of Cp_2Mn in Cp_2Fe . The full line represents a fit to a Boltzmann distribution model (see text). The fit is good ($R=0.99$) and gives the values of $\Delta H^0 = 1.57 \pm 0.1$ kcal/mol and $\Delta S^0 = 7.3 \pm 0.2$ cal/(mol K).

The thermodynamics for the low-spin $\rightleftharpoons$ high-spin equilibria for $(C_5H_5)_2Mn$ and $(C_5H_4Me)_2Mn$ in diamagnetic solid solutions is shown in Table 2a. These values may be compared with the values obtained from 2H NMR spectroscopy in PhMe- d_8 solution for monomeric $(C_5D_5)_2Mn$ and the various deuterium isotopologues of $(C_5H_4Me)_2Mn$, shown in Table 2b. In general, the ΔH^0 and ΔS^0 values obtained in toluene solution are somewhat more positive than those obtained from solid solutions of Cp_2Mn and $(C_5H_4Me)_2Mn$. The enthalpy changes in both phases favor the low-spin isomer by about 1.5 to 3.5 kcal mol $^{-1}$. The change in enthalpy values obtained in PhMe solution are greater than those in the solid solution by approximately a factor of 2, but both solutions show that the low-spin isomer, with the shorter Mn-C bond distance, is enthalpically favored by around 2 kcal mol $^{-1}$. The entropy change is positive and these values in solution are also larger than those in the solid solution by a factor of approximately 3. This difference presumably reflects the greater restriction to the degrees of freedom the manganocenes experience in the solid solutions. These comparisons reinforce the notion that the role of the host metallocene not only forces the manganocenes to be monomeric and magnetically dilute but the host lattice also restricts the motion of the individual isolated molecules.

Table 2a. Thermodynamic quantities obtained for low-spin $\rightleftharpoons$ high-spin equilibria in solid solutions

Compounds	ΔH^0 / kcal mol $^{-1}$ ^a	ΔS^0 / e.u. ^a	$\Delta G^0(298K)$ / kcal mol $^{-1}$
5% Cp_2Mn in Cp_2Fe	1.65 $\pm$ 0.1	5.4 $\pm$ 0.2	0.04
10% Cp_2Mn in Cp_2Fe	1.57 $\pm$ 0.1	7.3 $\pm$ 0.2	-0.6
5% $(C_5H_4Me)_2Mn$ in $(C_5H_4Me)_2Fe$	1.89 $\pm$ 0.1	2.4 $\pm$ 0.2	1.17

^a Fixed parameters: $S_{h.s.} = 5/2$, $S_{l.s.} = 1/2$, $g_{h.s.} = 2.0$. $g_{l.s.}$ values are taken from EPR spectroscopy and are 2.29 for Cp_2Mn and 2.32 for $(C_5H_4Me)_2Mn$. [15]

Table 2b. Thermodynamic quantities from solution NMR spectra^a

Metallocene	Method	ΔH^0 / kcal mol $^{-1}$	ΔS^0 / e.u.	$\Delta G^0(298K)$ / kcal mol $^{-1}$
$(C_5D_5)_2Mn$	NMR	3.06	20.1	-2.93
$(C_5H_4CD_3)_2Mn$	NMR	3.84	14.1	-0.58

$(C_5D_4CH_3)_2Mn$	NMR	4.52	15.8	-0.29
$(C_5H_4CH_3)_2Mn$	NMR	2.77	10.5	-0.36

^a average values for two methods; extrapolation and integration (ref. [19])

The only other substituted manganocenes that have been studied in solution and in solid state are shown in Table 2c, and they follow the general trends in ΔH and ΔS noted above.

Table 2c. Thermodynamic properties for the low-spin $\rightleftharpoons$ high-spin equilibrium for various manganocenes

Metallocene	Method	ΔH^0 / kcal mol ⁻¹	ΔS^0 / e.u.	$\Delta G^0(298K)$ / kcal mol ⁻¹
$(C_5H_4CMe_3)_2Mn$	χ (solid) ^a	3.1	14.9	-1.4
	χ (solution) ^b	2.0	10.5	-1.2
	UV-Vis ^b	3.7	13.9	-0.5
	NMR ^c	9.6-12.0	2.6-3.2	
$[1,3-(Me_3C)_2C_5H_3]_2Mn$	χ (solid) ^a	3.8	12.1	0.2
	UV-Vis ^a	2.7	11.2	-0.7

^a Ref. [41], ^b Ref. [17], ^c Ref. [19]

4. Conclusion

The crystal structure of $(C_5H_4Me)_2Mn$ is a polymer in the solid state, in which each of the terminal $(\eta^5-C_5H_4Me)Mn$ groups is connected to each other by $\eta^2, \eta^4-C_5H_4Me$ bridging groups aligned so as to form a one-dimensional zig-zag polymer chain. The solid state structure is similar to that of the parent manganocene, $(C_5H_5)_2Mn$ reported several years ago, as is the magnetic susceptibility data. The magnetic susceptibility data on dilute solid solutions of $(C_5H_4Me)_2Mn$ in $(C_5H_4Me)_2Fe$, 5-mole%) shows that the manganocene is a spin equilibrium molecule, when magnetically dilute, and the low-spin isomer is enthalpically favored but the high-spin isomer is entropically favored, so that $\Delta G(298 K)$ for the LS $\rightleftharpoons$ HS is 1.17 kcal mol⁻¹. The low-spin d⁵ isomer is enthalpically more stable than the high-spin isomer by about 2 kcal mol⁻¹ and their Gibbs free energies are essentially equal. The important concept

that emerges from this study is that the classification of Cp_2Mn as an “ionic metallocene” does not originate from thermodynamics but kinetic properties; the high-spin d^5 isomer is kinetically labile. Thus the free energy content of the isomers, ΔG^0 , is nearly identical, but their rates of ligand substitution are different.[42] Accordingly, Cp_2Fe , d^6 low-spin, is kinetically inert, but Cp_2Mn , d^5 high-spin, is kinetically labile, which results in the classification of the former as “covalent” and the latter as “ionic”.[7]

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