Table IV. Solvation in Acetonitrile

radical	EA(R•) (eV)	E'_{red}(R•) (eV)	IP(R•) (eV)	E'_{ox}(R′) (eV)	$\Delta G°_{27}$[g] (kcal/mol)	$\Delta G°_{26}$[g] (kcal/mol)
$PhCH_2$	0.86[a]	3.31[c]	7.20[d]	5.47[c]	−56.5 (−57)[h]	−39.8
Ph_2CH	1.15[b]	3.60[c]	6.8[e]	5.09[c]	i	−39.3
9-fluorenyl	1.53[b]	3.98[c]	7.1[f]	5.50[c]	i	−36.2

[a] Reference 44. [b] Calculated from this work assuming $\Delta G°_{27}$ = −56 kcal mol. [c] Calculated assuming E'(SCE) = 4.74 eV (ref 45). [d] Reference 43. [e] Reference 47. Corrected for the difference between benzyl and diphenylmethyl measured in the same laboratory. [f] Reference 48. [g] Estimated uncertainty ±4 kcal mol^{-1}. [h] Reference 45. [i] Assumed to be −56 kcal mol^{-1}.

by treating the effect of substitution by phenyl or methyl as group contributions.

The decrease in the radical oxidation potentials caused by the presence of α-oxygen or nitrogen atoms was atributed to a three-electron-bonding interaction.

Analysis of the data as a whole suggested that the measured $E_{1/2}$ values were within 100 mV of the standard potential, $E°$. The values obtained were used to calculate other thermodynamic properties such as pK_a(RH), pK_R(ROH), and solvation free energies.

Steric versus Electronic Effects on the "Tilt" of the Cyclopentadienyl Rings in Adducts of Manganese Dicyclopentadienide. Molecular and Electronic Structure of Dicyclopentadienide Manganese Tetrahydrofuran

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Abstract: The crystal and molecular structure of the tetrahydrofuran adduct of manganese dicyclopentadienide has been determined. The C_5H_5 rings are planar, and the total "tilt" of both rings is only 3.9°. Comparison with the tilt in phosphine adducts of $(C_5H_5)_2Mn$ leads to the conclusion that the tilting of the rings in such high-spin $(C_5H_5)_2Mn(L)_n$ adducts is due to steric rather than electronic effects. Crystal data for $(C_5H_5)_2Mn(OC_4H_8)$: monoclinic, $C2/c$; a = 12.541 (1), b = 9.927 (1), c = 12.650 (1) Å; β = 125.58 (1)°; Z = 4; R = 0.025 for 111 parameters and 987 observed reflections.

The unusual properties of manganese dicyclopentadienide, $(C_5H_5)_2Mn$, and its adducts have been the subject of many investigations[1,2] since the first discovery of these compounds.[3,4] Recently Wilkinson, Hursthouse, and their co-workers discussed a series of phosphine and diphosphine adducts of $(C_5H_5)_2Mn$.[5] In these adducts the C_5H_5 rings are planar but "tilted" to a small but significant extent. Tilting occurs when the manganese–ring (centroid) vector and the normal to the plane of the ring through the manganese are not collinear but make a small angle with each other. There are two possible reasons for this tilting. The first is electronic. If $(C_5H_5)_2Mn$ is regarded as containing Mn^{2+} and two η^5-$C_5H_5^-$ ligands and η^5-$C_5H_5^-$ donates six electrons, then monoadducts of $(C_5H_5)_2Mn$ have 19 valence electrons and bisadducts have 21. Lauher and Hoffmann have analyzed the consequences of the presence of more than 18 valence electrons in $(\eta^5\text{-}C_5H_5)_2M(L)_n$ derivatives.[6] They attributed the tilted, slipped, or bent C_5H_5 rings in such complexes as $(C_5H_5)_2Mo(R)(NO)$ (R = I, CH_3, η^1-C_5H_5[7]) and $(C_5H_5)_2W(CO)_2$[8] to the population of orbitals having π-antibonding character. These orbitals are significantly and unsymmetrically localized on the C_5H_5 rings. However, as Wilkinson, Hursthouse, and co-workers pointed out,[5] a too rigid application of the model derived by Lauher and Hoffmann to the adducts of $(C_5H_5)_2Mn$ is unwise, because both $(C_5H_5)_2Mn$ and the adducts are essentially high spin at the temperature of the X-ray diffraction experiments that determined the structures. The bonding between C_5H_5 and Mn is very ionic,[1,3,9,10] and thus the covalent model of Lauher and Hoffmann may not be valid.

Wilkinson, Hursthouse, and co-workers suggested that the second possibility, steric repulsion, was more likely to be responsible for the observed tilting of the C_5H_5 rings.[5] The evidence was not clear-cut, as is often the case with steric arguments. The balance of various steric and electronic effects was obviously very close. It occurred to us that a detailed analysis of the structure of an adduct between $(C_5H_5)_2Mn$ and a donor that had fewer steric requirements than phosphines would be a useful way to resolve the problem of whether steric or electronic effects are the cause of the tilt. A donor in which the ligating atom was from group 16 would be particularly useful, and tetrahydrofuran, C_4H_8O (THF), appeared to be an ideal candidate. An unstable adduct between THF and $(C_5H_5)_2Mn$ was described by Wilkinson and co-workers in their first report on $(C_5H_5)_2Mn$, though it appeared

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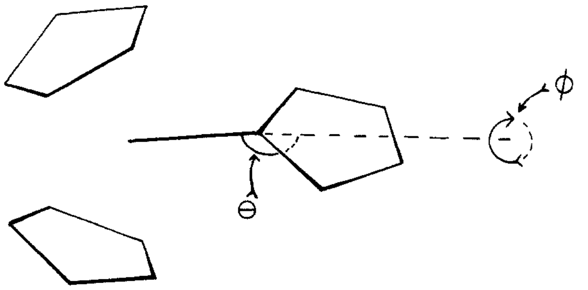

Figure 1. Definition of the angles θ and ϕ for $(C_5H_5)_2Mn(THF)$. A ϕ angle of zero is defined as the horizontal, i.e. at 90° to the plane defined by the Cp(1)–Mn–Cp(1′) vectors (see Table IV for definition of Cp(1) and Cp(1′)).

to have the formula $(C_5H_5)_2Mn(THF)_2$.[3] Two factors made THF an attractive donor to study. First, its steric bulk is small compared to a phosphine or diphosphine. Second, the angles θ and ϕ, as defined in Figure 1, would be a good measure of the ionic or covalent nature of the interaction between $(C_5H_5)_2Mn$ and THF. In a purely covalent adduct the angle θ would be expected to approach 125°, corresponding to donation of a pair of electrons from a tetrahedrally hybridized oxygen atom. A ϕ angle of 90° would maximize π-overlap of the second lone pair on the oxygen atoms with the b_2 or $1a_1$ orbitals (in C_{2v} symmetry) on the manganese.[6] On the other hand, in a purely ionic adduct there would be no electronic preference for particular θ or ϕ angles. Steric repulsions would be minimized by a θ angle of 180° and a ϕ angle of 0°. For a group 15 donor atom, a θ angle of 180° and a ϕ angle determined by steric constraints would be expected regardless of the amount of covalency in the Mn–L bond; in addition to $(C_5H_5)_2Mn(PMe_3)$[5] and $(C_5H_5)_2Mn(PMePh_2)$,[5] the structure of $[C_5H_4(CH_2)_3C_5H_4]Mn(NC_5H_3Cl_2\text{-}3,5)$[11] confirms this. We report here the molecular and electronic structure of $(C_5H_5)_2Mn(THF)$ and discuss the tilting of the C_5H_5 rings in adducts of $(C_5H_5)_2Mn$.

Experimental Section

All operations were carried out under vacuum or argon. Solvents, including THF, were predried, stored over CH_3Li, and distilled under vacuum. Infrared spectra were measured on a Perkin-Elmer 683, NMR, on a Varian XL200, and ESR, on a locally modified version of the Varian E4 spectrometer. Magnetic moments in the solid state were measured by the Faraday method and in solution by the Gouy or Evans[12] method. The starting material $(C_5H_5)_2Mn$ was prepared according to the procedure described by Wilkinson and co-workers.[3] Crystals of $(C_5H_5)_2Mn(THF)$ were obtained by layering a saturated THF solution (40 cm^3) of $(C_5H_5)_2Mn$ with hexane (20 cm^3) and setting the mixture aside overnight. Large light brown crystals were thus obtained.

X-ray Crystallography. A crystal grown as described above was coated with Apiezon grease and sealed in a glass capillary under argon. The space group, symmetry, and cell dimensions were determined by a combination of photography and the centering of reflections with an Enraf-Nonius CAD4 diffractometer under the control of NRCCAD software.[13] Crystal data for $(C_5H_5)_2Mn(THF)$: $C_{14}H_{18}MnO$, MW = 257.26; monoclinic, $C2/c$; a = 12.541 (1), b = 9.927 (1), c = 12.650 (1) Å; β = 125.58 (1)°; Z = 4; $F(000)$ = 540 electrons; d_{calcd} = 1.33 Mg m^{-3}; Mo Kα radiation, λ = 0.710 73 Å; μ = 9.67 cm^{-1}; ω–2θ scan to a maximum 2θ of 50°, giving 1122 unique reflections of which 987 were observed according to the criterion that $I > 2.5\sigma(I)$. Refinement of 111 parameters gave a final R $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0.025, an R_w $(=(\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2})$ of 0.032, and a goodness of fit $(=\Sigma w(F_o - F_c)^2/(\text{number of reflections} - \text{number of parameters})$ of 1.161. Refinement minimized the function $\Sigma w(|F_o| - |F_c|)^2$ with w calculated from counting statistics. The maximum shift/error was 0.366. The C, O, and Mn atoms were refined anisotropically, and the H atoms, isotropically. A final difference Fourier map had a highest peak of 0.25 e $Å^{-3}$ and a deepest hole of –0.17 e $Å^{-3}$. For the refinement, the scattering factors for neutral C, H, Mn,

Table I. Fractional Atomic Coordinates for $(C_5H_5)_2Mn(THF)$

atom	x	y	z
Mn	0	0.10977 (4)	0.25
O	0	–0.11449 (17)	0.25
C(1)[a]	0.11182 (21)[b]	–0.19823 (22)	0.33716 (24)
C(2)	0.05918 (25)	–0.33839 (22)	0.31969 (23)
C(11)	0.09185 (24)	0.29261 (24)	0.1893 (3)
C(12)	0.06600 (24)	0.1834 (3)	0.11001 (24)
C(13)	0.14939 (25)	0.07972 (24)	0.1879 (3)
C(14)	0.22468 (22)	0.1250 (3)	0.3150 (3)
C(15)	0.18837 (24)	0.2573 (3)	0.3149 (3)
H(1A)	0.168 (3)	–0.188 (3)	0.3131 (24)
H(1B)	0.1514 (24)	–0.1664 (25)	0.4236 (25)
H(2A)	0.0299 (24)	–0.347 (3)	0.3732 (24)
H(2B)	0.125 (3)	–0.405 (3)	0.344 (3)
H(11)	0.054 (3)	0.374 (3)	0.162 (3)
H(12)	0.005 (3)	0.179 (3)	0.024 (3)
H(13)	0.161 (3)	–0.002 (3)	0.165 (3)
H(14)	0.282 (4)	0.080 (3)	0.383 (3)
H(15)	0.215 (3)	0.303 (3)	0.384 (3)

[a] For the numbering scheme, see Figure 2. [b] Estimated standard deviations relating to the least significant figures are given in parentheses.

Table II. Distances in $(C_5H_5)_2Mn(THF)$ (Å)

Mn–O	2.226 (2)[a]	Mn–C(13)	2.435 (2)
Mn–C(11)[b]	2.498 (2)	Mn–C(14)	2.438 (2)
Mn–C(12)	2.462 (2)	Mn–C(15)	2.478_5 (2_1)[c]
C(11)–C(12)	1.382 (4)	C(14)–C(15)	1.390 (4)
C(12)–C(13)	1.387 (4)	C(15)–C(11)	1.368 (4)[d]
C(13)–C(14)	1.383 (4)		
O–C(1)	1.440 (2)	C(2)–C(2′)	1.505 (5)
C(1)–C(2)	1.500 (3)		
Mn–ring (centroid)	2.163 (2)	Mn–ring (plane)	2.162 (1)

[a] Estimated standard deviations relating to the least significant figure are given in parentheses. [b] For the numbering scheme, see Figure 2. [c] Average Mn–C distances 2.462 (2) Å. [d] Average C–C distances 1.382 (4) Å.

Table III. Angles in $(C_5H_5)_2Mn(THF)$ (deg)

C(11)–C(12)–C(13)[a]	107.7_5 (2_3)[b]
C(12)–C(13)–C(14)	107.9 (2)
C(13)–C(14)–C(15)	107.7 (2)
C(14)–C(15)–C(11)	108.1 (2)
C(15)–C(11)–C(12)	108.5 (2)
O–C(1)–C(2)	105.9 (2)
C(1)–C(2)–C(2′)	102.8 (2)
C(1)–O–C(1′)	109.5 (2)
ring (centroid)–Mn–ring (centroid)	138.1 (2)
ring (plane)–Mn–ring (plane)	142.0 (2)

[a] For the numbering scheme, see Figure 2. [b] Estimated standard deviations relating to the least significant figure are given in parentheses.

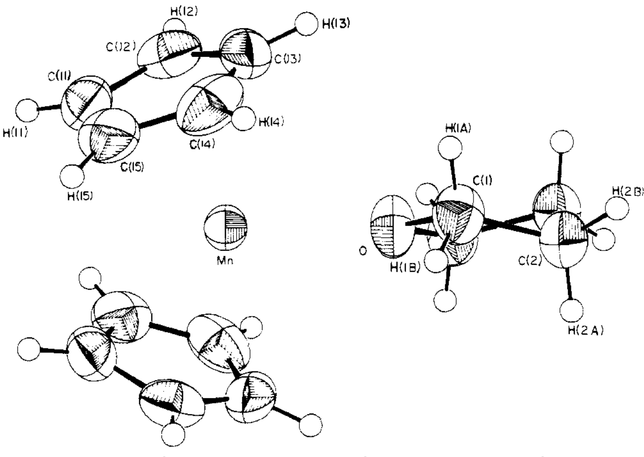

Figure 2. Molecular structure and numbering scheme of $(C_5H_5)_2Mn(THF)$.

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Table IV. Least-Squares Planes in $(C_5H_5)_2Mn(THF)$ and Distances (Å) of Relevant Atoms from the Planes

Plane 1. C(11)–C(15)[a]			
$11.757X + 3.228Y - 8.172Z = 4.559$[b]			
C(11)	0.004 (4)	H(11)	0.04 (4)
C(12)	-0.004 (4)	H(12)	-0.03 (3)
C(13)	0.005 (4)	H(13)	0.06 (4)
C(14)	-0.002 (4)	H(14)	-0.03 (4)
C(15)	-0.001 (4)	H(15)	-0.10 (4)
Mn	-2.162 (1)		
Plane 1′. C(11′)–C(15′)			
$11.757X + 3.228Y - 8.172Z = 0.473$			
distances of atoms from the plane are the same as for plane 1 but with the opposite sign			
Plane 2. Mn, O, C(1), C(1′), C(2), C(2′)			
$-10.360X + 0.000Y + 11.878Z = 2.969_5$			
Mn	0.000 (1)	O	0.000 (2)
C(1)	0.123 (4)	C(2)	-0.215 (4)
C(1′)	-0.123 (4)	C(2′)	0.215 (4)
Plane 3			
$1.697X + 0.000Y + 9.198Z = 2.299$			
Mn	0.000 (1)	O	0.000 (2)
Cp(1)[c]	0.000 (5)	Cp(1′)	-0.000 (5)
dihedral angle, planes 1 and 1′			142.0 (2)
dihedral angle, planes 2 and 3			63.5 (1)

[a] For the numbering scheme, see Figure 2. [b] The equations of the planes are of the form $AX + BY + CZ = D$ where X, Y, and Z are in angstroms. [c] Cp(1) is the centroid of the C_5 ring.

and O were taken from ref 14 and were corrected for anomalous dispersion. Because of the small value of the absorption coefficient, no correction was applied; an extinction parameter was included in the refinement. The programs used in the calculations were the NRCVAX System implemented on a Wicat Systems microcomputer.[15]

The positional parameters obtained from the refinement are given in Table I, and the distances, angles, and important mean planes derived from the positional parameters, in Tables II–IV, respectively. Tables of thermal parameters and of $|F_o|$ and F_c are available as supplementary material. The numbering scheme is shown in Figure 2.

Results and Discussion

It should be noted first that the crystal used in the diffraction experiment was of excellent quality, and a corresponding good data set was collected. This is reflected in the low R value (2.5%) obtained in the final refinement. All of the hydrogen atoms were located in a difference Fourier map, and they were refined individually. There was no evidence of any disorder in the C_5H_5 rings or in the THF, as is clear from the thermal ellipsoids shown in Figure 2.

The structure consists of well-separated molecules of $(C_5H_5)_2Mn(THF)$, the shortest intermolecular contact being 2.66 Å between the hydrogen atoms H(1B) on the α-carbon atoms of the THF ligands of two adjacent molecules, which are related by a center of symmetry (see Figures 2 and 3). The $(C_5H_5)_2Mn(THF)$ molecule lies on a twofold axis of symmetry. The C_5 ring is accurately planar, and within rather larger limits of accuracy, the five hydrogen atoms lie in the same plane (see Table IV). The ring is very regular, with an average C–C distance of 1.382 (4) Å and C–C–C angle of 108.0 (2)°. The C(11)–C(15) distance of 1.368 (4) Å deviates slightly from the other four distances, which average 1.385 (4) Å with a spread of only 0.007 Å. The C(11)–C(15) distance is within the 3σ error limit of the average; however, its deviation from the average makes a discussion of the ionicity of the $Mn-C_5H_5$ interaction based on the C–C distances unwarranted.

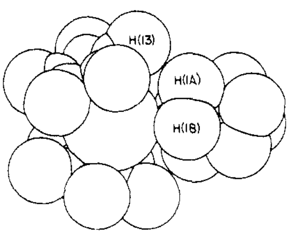

Figure 3. Space-filling model of $(C_5H_5)_2Mn(THF)$. The atoms are drawn with the covalent radii for Mn (1.30 Å), O (0.89 Å), and C (0.92 Å) and the van der Waals radius for H (2.00 Å).

The angles θ and ϕ, which show the nature of the interaction between $(C_5H_5)_2Mn$ and THF, have the values 180° (by symmetry) and 26.5°, respectively. These indicate a very ionic interaction, the nature of which is further illuminated by the magnetic properties of the adduct. We experienced great difficulty in obtaining coherent and reproducible magnetic data for $(C_5H_5)_2Mn(THF)$ in the solid state. At 20 °C a value of 5.89 μ_B was found by the Faraday method. This value is suspect because, as already noted by Wilkinson, $(C_5H_5)_2Mn(THF)$ loses THF very readily in vacuo.[3,9] Since we were obliged to dry the crystals used for the measurement by pumping on them, it is probable that the samples were a mixture of $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mn(THF)$ and may have contained free THF as well. At 19 °C $(C_5H_5)_2Mn$ has a magnetic moment of 5.97 μ_B[3] (5.71 μ_B[16]) in the solid state. For our purposes it was vital to know the magnetic state of $(C_5H_5)_2Mn(THF)$ at 20 °C since the electronic arguments of Lauher and Hoffmann apply to the spin-paired state that would be present in the covalent molecule.[9,10,17–19] We therefore resorted to a variety of methods for determining the magnetic moment in THF solution. The Gouy method gave a value of 5.84 μ_B; the Evans NMR method gave 5.92 μ_B. The spin-only value for five unpaired electrons is 5.92 μ_B. The ESR spectrum of $(C_5H_5)_2Mn$ in frozen THF solution at −160 °C showed only an extremely broad and featureless signal centered at $g = 2.007$. This result is in accord with previous work[19,20] and is consistent with the presence of more than one unpaired electron on the paramagnetic center.

Köhler and co-workers reported that when $(C_5H_5)_2Mn$ was dissolved in THF it showed a signal at 1240 ppm (relative to $(\eta^5-C_5H_5)_2Fe$) in the ^{13}C NMR spectrum.[1] There was considerable displacement of the THF signals as well. From the shifts it was concluded that $(C_5H_5)_2Mn(THF)$ had a pure high-spin state. Three basic structures were suggested for the adduct, one of which was the one found in the present work. We found that the THF signals in the ^{13}C NMR were shifted to 146.4 and 90.3 ppm, compared to 67.4 and 25.3 ppm in pure THF. In the ^1H NMR we observed a very broad signal at −8.92 ppm, asssigned to C_5H_5. The THF signals appeared at 6.45 and 2.85 ppm, compared to 3.58 and 1.73 ppm in pure THF.

From the above measurements we conclude that $(C_5H_5)_2Mn(THF)$ does indeed have the $^6A_{1g}$ state with five unpaired electrons at 20 °C, the temperature at which the crystal structure was determined. This shows that the bonding in $(C_5H_5)_2Mn(THF)$ is very ionic and the electronic arguments of Lauher and Hoffmann[6] are not directly applicable.

The tilt angle, defined as the difference between the Cp(1) centroid–Mn–Cp(2) centroid angle (138.1 (1)°) and the Cp(1) plane–Mn–Cp(2) plane angle (142.0 (1)°), is 3.9 (1)°. Here, Cp refers to the C_5 ring. This corresponds to a τ angle, as defined by Wilkinson and Hursthouse,[5] of 1.95° per ring. The tilt direction is such as to open up the space at the back of the Mn atom (i.e.

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the rings are tilted *toward* the THF ligand). The tilt direction is clearly indicated by the unequal distances from manganese to the ring carbon atoms. The longest, Mn–C(11) (2.498 (2) Å), is to the carbon atom furthest away from the THF ligand (see Figure 2 and Table II). There are then two intermediate Mn–C distances, averaging 2.470 (2) Å, to C(12) and C(15), the carbon atoms adjacent to C(11). Finally, there are two short distances, averaging 2.436 (2) Å, to C(13) and C(14), the carbon atoms closest to the THF ligand. There is no slippage of the rings; the Mn–Cp (centroid) distance (2.163 (2) Å) and the Mn–Cp (plane) distance (2.162 (1) Å) are identical.

Wilkinson, Hursthouse, and co-workers noted that tilt angles of 3° or less are common in $(C_5R_5)_2M(L)_n$ derivatives, and these tilts are usually caused by steric strain behind the metal atom where the two rings abut one another.[5,21] The small tilt observed here is of the same type. Since $(C_5H_5)_2Mn(PMe_3)$ has a tilt of 8 or 12° (two independent molecules) *away* from the PMe_3 ligand, in the opposite direction to that of $(C_5H_5)_2Mn(THF)$, and since both molecules have the same electronic structure, the tilts must be due to steric, not electronic forces.

One important indication of the steric forces at work in $(C_5H_5)_2Mn(THF)$ is the rotation angle ϕ, which is 26.5°. Inspection of a space-filling model (Figure 3) shows that the THF molecule is rotated about the ϕ axis so that the hydrogen H(1A) atoms of its α-carbon atoms fit into the spaces between the hydrogen atoms of the C_5H_5 rings. The shortest intramolecular nonbonded contact is between H(13), attached to the forward carbon atom C(13) of the C_5H_5 ring, and H(1A) and measures 2.59 Å. The C_5H_5 rings are staggered 35° with respect to one another; the fully staggered angle is 36°. The Mn–Cp (centroid) distance of 2.163 (2) Å is shorter than those in $(C_5H_5)_2Mn(PMe_3)$ and $(C_5H_5)_2Mn(PMe_2Ph)$, which are similar and average 2.217 (4) Å.[5] It is interesting to compare the data of $(C_5H_5)_2Mn(THF)$ with those of $(C_5H_4(CH_2)_3C_5H_4)Mn(NC_5H_3Cl_2\text{-}3,5)$, which has a θ angle of 176.7°, a ϕ angle of close to zero, a staggering of the rings of 36°, and an average Mn–Cp (centroid) distance of 2.14 Å.[11] Weed, Rettig, and Wing attribute the staggering of the rings to the minimization of nonbonded contacts between the carbon atoms of the ring and the nitrogen of the $NC_5H_3Cl_2\text{-}3,5$ ligand; the shortest such contact is 3.18 Å.[11] In $(C_5H_5)_2Mn(THF)$ the shortest ring-carbon to THF-oxygen distance is C(13)–O and measures 3.09 Å. It is a moot point whether the C–O or the H–H contacts determine the stagger of the rings in $(C_5H_5)_2Mn(THF)$.

The Mn–O distance of 2.226 (2) Å is the same as that found in $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2[Mn(THF)_2]$ (2.227 (3) Å).[22] This is the only other Mn(II)–THF complex that has been structurally characterized, and it also contains high-spin Mn(II). The Mn–O distance in $(C_5H_5)_2Mn(THF)$ is very long, even longer than the sum of the ionic radii of Mn^{2+} and O^{2-}, which is 2.20 Å, again indicating an ionic interaction. Accordingly, the THF ligand should be very little disturbed from its uncoordinated geometry. Surprisingly, the only data on THF are from an electron diffraction study performed in 1941; it gives C–O as 1.43 (3) Å, C–C as 1.54 (2) Å, and C–O–C as 111 (2)°.[23] The error limits are too large for a comparison to be useful. The THF molecule in $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2[Mn(THF)_2]$ has a $C_\alpha\text{–}C_\beta\text{–}C_{\beta'}$ angle that is 5° smaller than observed here, but the C–C distances are significantly (0.05 Å) longer in $(C_5H_5)_2Mn(THF)$. This may indicate that the THF–Mn interaction is even more ionic in $(C_5H_5)_2Mn(THF)$ than in $[(\eta^5\text{-}C_5H_5)_2Ti(\eta\text{-}Cl)_2]_2[Mn(THF)_2]$. It is clear from the data that the arrangement of the three ligands about the manganese in $(C_5H_5)_2Mn(THF)$ is controlled by steric factors alone.

Conclusion

The tilt of the C_5H_5 rings in $(C_5H_5)_2Mn(THF)$ is toward the THF ligand, whereas it is away from the PMe_3 ligand in $(C_5H_5)_2Mn(PMe_3)$. Both molecules contain high-spin Mn(II) and have similar and very ionic electronic structures. Therefore, the cause of the tilt in these molecules, and by implication in all bis(cyclopentadienide) derivatives of high-spin Mn(II), is steric strain and not electronic effects.

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Supplementary Material Available: Figure of molecular structure and numbering scheme for $(C_5H_5)_2Mn(THF)$ and table of thermal parameters (2 pages); listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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