Tertiary Phosphine Adducts of Manganese(II) Dicyclopentadienide. Magnetic Studies and Structural Characterization of "Tilted" Cyclopentadienyl Rings

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Abstract: Adducts of manganese(II) dicyclopentadienide, $Mn(C_5H_5)_2$, and of $Mn(C_5H_4CH_3)_2$ with the unidentate tertiary phosphines PMe_3, PMe_2Ph, $PMePh_2$, and PEt_3 and with the chelating phosphine $Me_2PCH_2CH_2PMe_2$ (dmpe) have been synthesized. The structures of $(C_5H_5)_2Mn(PMe_3)$, $(C_5H_5)_2Mn(PMePh_2)$, and $(C_5H_5)_2Mn(dmpe)$ have been determined by X-ray crystallographic studies, and "tilted" planar cyclopentadienyl rings have been observed. Electron paramagnetic resonance spectra as well as magnetic susceptibilities have been determined.

It has long been known that manganese(II) dicyclopentadienide ($MnCp_2$) ($Cp = \eta^5\text{-}C_5H_5$) and its ring-substituted analogue $Mn(C_5H_4Me)_2$ show highly unusual magnetic properties.[1,2] In the solid state at room temperature, $MnCp_2$ is a polymer[3] with bridging C_5H_5 groups that exhibits antiferromagnetic behavior, presumably via intermolecular spin exchange. Above 432 K or when diluted in, e.g., $MgCp_2$, $MnCp_2$ adopts a high-spin ^6S state[1] whereas $Mn(C_5H_4Me)_2$ exists in a temperature-dependent equilibrium between high-spin and low-spin species.[4] Complete methylation of the cyclopentadienyl rings to give $Mn(C_5Me_5)_2$ results in a normal metallocene structure and an exclusively low-spin ground state.[5,6] This behavior is consistent with a significantly enhanced ligand field strength upon methylation of the cyclopentadienyl rings.

Tertiary phosphine adducts of manganese(II) dialkyls have been described recently,[7,8] and we now describe a similar series of adducts of $MnCp_2$ and $Mn(C_5H_4Me)_2$ which possess unusual geometric structures. It may be noted that adducts of $MnCp_2$ with ethers and amines have been made,[1] but none have been studied subsequently or structurally characterized.

Results and Discussion

The interaction of manganese(II) dicyclopentadienide with tertiary phosphines in toluene yields a series of unidentate adducts $Cp_2Mn(PR_3)$, $PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, PEt_3, and the bidentate adduct $Cp_2Mn(dmpe)$, dmpe = 1,2-bis(dimethylphosphino)ethane. Similar adducts of the methylcyclopentadienide $Mn(C_5H_4Me)_2$ can be made. Although $(C_5H_4Me)_2Mn(PMe_3)$ could be isolated at low temperature, it melted at ca. 0 °C and analytical data were not obtained. However, $(C_5H_4Me)_2Mn$-(dmpe) could be isolated and, as expected, was far more soluble than $Cp_2Mn(dmpe)$. The adducts and analytical data are listed in Table I. All compounds are colorless, air sensitive, and soluble in petroleum or toluene; they sublime in vacuo at ca. 70 °C.

Crystallographic Studies. The structures of the two monophosphine adducts $Cp_2Mn(PMe_3)$ (**1**) and $Cp_2Mn(PMePh_2)$ (**3**) and the diphosphine adduct $Cp_2Mn(dmpe)$ (**5**) have been determined by single-crystal X-ray diffraction methods. Diagrams of their molecular structures are presented in Figures 1–3,[9] while important bond lengths and angles are given in Tables II (**1** and **3**) and III (**5**). Full lists of bond lengths and angles have been deposited as supplementary material.

As expected, the structures of compounds **1** and **3** are very similar and may be described as having pseudotrigonal geometry if the Cp groups are each considered to occupy only one coordination site. (Following standard convention we represent each ring, for the purpose of geometry calculations, by its centroid,

Table I. Properties and Analytical Data for Phosphine Adducts of Manganese(II) Dicyclopentadienide

compd[a]	mp, °C	anal.[b]		
		% C	% H	% P
1, $Cp_2Mn(PMe_3)$	130–132	58.5 (59.8)	7.36 (7.28)	10.6 (11.9)
2, $Cp_2Mn(PMe_2Ph)$	79–81	66.2 (66.8)	6.45 (6.55)	9.5 (9.6)
3, $Cp_2Mn(PMePh_2)$	68–70	71.2 (71.7)	6.06 (6.01)	8.1 (8.0)
4, $Cp_2Mn(PEt_3)$	68–70	62.6 (63.4)	8.18 (8.30)	10.1 (10.2)
5, $Cp_2Mn(dmpe)$	174	57.1 (57.3)	7.67 (7.81)	18.5 (18.5)
6, $(C_5H_4Me)_2Mn(dmpe)$	108–110	59.1 (59.5)	8.21 (8.33)	17.2 (17.1)

[a] All compounds are colorless. [b] Required values are given in parentheses.

Table II. Selected Bond Lengths (Å) and Angles (deg) for $Cp_2Mn(PMe_3)$ (**1**) and $Cp_2Mn(PPh_2Me)$ (**3**)

Bond Lengths			
$Cp_2Mn(PMe_3)$		$Cp_2Mn(PPh_2Me)$	
Mn(1)–P(1)	2.577 (4)	Mn(1)–P(1)	2.613 (4)
Mn(1)–C(11a)	2.608 (7)	Mn(1)–C(1a)	2.481 (5)
Mn(1)–C(12a)	2.630 (7)	Mn(1)–C(2a)	2.501 (6)
Mn(1)–C(13a)	2.540 (7)	Mn(1)–C(3a)	2.492 (5)
Mn(1)–C(14a)	2.428 (6)	Mn(1)–C(4a)	2.501 (6)
Mn(1)–C(15a)	2.450 (6)	Mn(1)–C(5a)	2.492 (5)
Mn(1)–C(21a)	2.531 (7)	Mn(1)–C(1b)	2.567 (7)
Mn(1)–C(22a)	2.481 (6)	Mn(1)–C(2b)	2.374 (6)
Mn(1)–C(23a)	2.490 (7)	Mn(1)–C(3b)	2.391 (6)
Mn(1)–C(24a)	2.522 (8)	Mn(1)–C(4b)	2.613 (7)
Mn(1)–C(25a)	2.547 (7)	Mn(1)–C(5b)	2.724 (8)
Mn–Cp(cent 1)	2.237 (4)	Mn–Cp(cent 1)	2.195 (3)
Mn–Cp(cent 2)	2.198 (8)	Mn–Cp(cent 2)	2.237 (3)
Bond Angles			
Cp(cent 1)–Mn–Cp(cent 2)	142.3 (4)	Cp(cent 1)–Mn–Cp(cent 2)	142.2 (2)
Cp(cent 1)–Mn–P	108.0 (2)	Cp(cent 1)–Mn–P	110.5 (5)
Cp(cent 2)–Mn–P	109.5 (2)	Cp(cent 2)–Mn–P	106.7 (4)

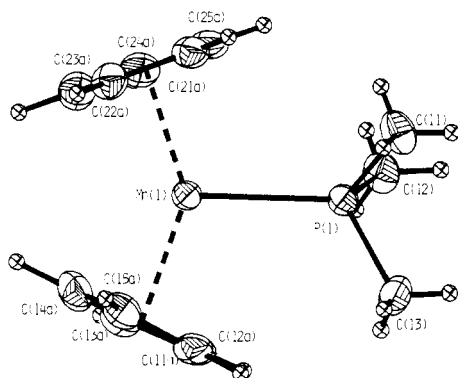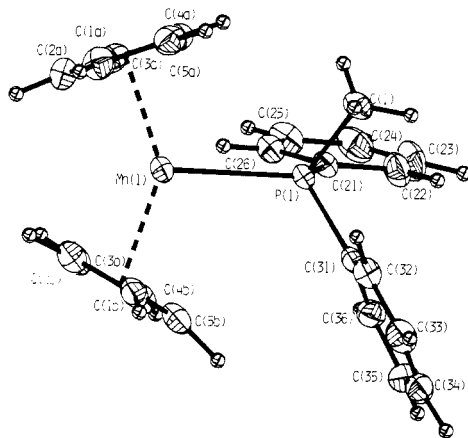[†] Imperial College of Science and Technology.
[‡] Queen Mary College.

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Figure 1. Structure of $Cp_2Mn(PMe_3)$.

Figure 2. Structure of $Cp_2Mn(PMePh_2)$.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $Cp_2Mn(dmpe)$ (5)

Mn–P(1)	2.674 (4)	Cp(cent)–Mn–Cp(cent)*	136.9 (2)
Mn–C(1)	2.655 (8)	P–Mn–P*	77.4 (2)
Mn–C(2)	2.742 (8)	Cp(cent)–Mn–P	105.6 (2)
Mn–C(3)	2.671 (8)		
Mn–C(4)	2.510 (8)		
Mn–C(5)	2.492 (6)		
Mn–C(cent)	2.334 (5)		

labeled hereafter as Cp(cent)). The differences in the shape and orientation of the phosphines in **1** and **3** do not result in any significant differences in distribution of angles in the "trigonal plane", so that the Cp(cent)–Mn–Cp(cent) angles are almost equal (142.3 (2)° in **1**, 142.1 (2)° in **3**). The Mn–P vector in both molecules is almost symmetrically disposed with respect to the two Mn–Cp(cent) vectors (108.1 (2)°, 109.6 (2)° in **1**; 110.6 (2)°, 106.8 (2)° in **3**), and all three vectors are virtually planar, the three angles summing to 360.0° (**1**) and 359.5° (**3**).

In compound **3** one of the Cp rings is symmtrically pentahapto bound, with Mn–C distances in the narrow range 2.481 (5)–2.501 (6) Å and orientationally fixed. Furthermore, the C–C distances are all equal within the limits of experimental error [1.381

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Figure 3. Structure of $Cp_2Mn(dmpe)$.

Table IV. Deviation of Atoms (Å) from the Least-Squares Plane of the Cp Rings for Compounds **1, 3,** and **5** and Their Angle of Tilt (deg)

atom	deviation	atom	deviation
	Compd 1		
(1) plane through ring 1a,		(2) plane through ring 1b,	
$7.8902X + 3.7716Y -$		$7.8075X + 2.9163Y -$	
$0.1503Z = -0.5778$		$1.0103Z = -0.5077$	
C(11a)	-0.0205	C(11b)	-0.0115
C(12a)	0.0253	C(12b)	0.0632
C(13a)	-0.0207	C(13b)	-0.0853
C(14a)	0.0074	C(14b)	0.0709
C(15a)	0.0086	C(15b)	-0.0372
$\tau = 6.13$		$\tau = 9.78$	
(3) plane through ring 2a,		(4) plane through ring 2b,	
$4.2784X + 13.0689Y -$		$4.2656X + 12.1027Y -$	
$2.2298Z = 5.2188$		$2.0324Z = 5.2539$	
C(21a)	-0.0024	C(21b)	-0.0043
C(22a)	-0.0038	C(22b)	-0.0035
C(23a)	0.0083	C(23b)	0.0109
C(24a)	-0.0097	C(24b)	-0.0138
C(25a)	0.0076	C(25b)	0.0106
$\tau = 1.87$		$\tau = 2.17$	
	Compd 3		
(1) plane through ring 1a,		(2) plane through ring 1b,	
$3.4932X - 5.2307Y +$		$7.4847X - 5.7012Y -$	
$14.8595Z = 4.5087$		$1.7074Z = 7.4535$	
C(1a)	0.0056	C(1b)	-0.0072
C(2a)	-0.0066	C(2b)	0.0064
C(3a)	0.0052	C(3b)	-0.0032
C(4a)	-0.0017	C(4b)	-0.0012
C(5a)	-0.0024	C(5b)	0.0052
$\tau = 0.31$		$\tau = 10.47$	
(3) plane through ring 1c, $7.3253X - 5.9320Y -$			
$1.2969Z = 7.4334$			
C(1c)	0.0111	C(4c)	0.0258
C(2c)	0.0044	C(5c)	-0.0222
C(3c)	-0.0191	$\tau = 9.27$	
	Compd 5		
$-0.0771X + 9.5581Y + 6.5675Z = 5.8444$			
C(1)	-0.0077	C(4)	0.0015
C(2)	0.0084	C(5)	0.0039
C(3)	-0.0061	$\tau = 7.29$	

^{a} The equations of the planes are of the form $AX + BY + CZ = D$, where X, Y, and Z are fractional coordinates. ^{b} τ is the angle of tilt of the Cp ring.

(6)–1.396 (6) Å], and the ring is accurately planar (see Table IV). The second ring, however, is both tilted with respect to the Mn–Cp(cent) vector and disordered over two orientations, separated by a twist angle of 37°, with occupancies of 0.65 and 0.35 (see Experimental Section). Each group of five carbon atoms at this site are accurately planar (Table IV), and their least-squares planes are almost coincident (interplanar angle = 1.9°). The Mn–C distances for the tilted ring system range from 2.336 (8)
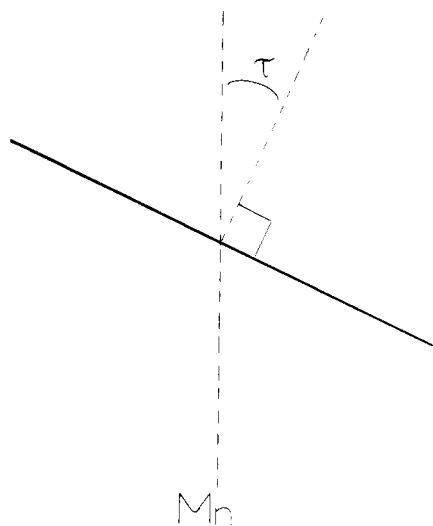
Figure 4. Definition of Cp ring tilt angle τ.

to 2.724 (8) Å, and the angle of tilt, τ, defined as the angle between the Mn–Cp(cent) vector and the ring normal (see Figure 4), is 10°. The C–C distances in these disordered rings vary more than in the fixed ring, but the differences are barely significant, and one must also regard them with suspicion since the closeness of the fractional atoms between the two images may have introduced further errors through correlation effects. More significantly, the small variations found do not fit in with any expected trends, e.g., C–C distance vs. Mn–C distance. It is not possible here to attach much significance to the relative orientations of the two rings, since the disorder at one of the sites will, of course, give two different relationships. However, it is worth noting that the most occupied ring position at the disordered site has an approximately staggered orientation with respect to the fixed ring.

In compound **1**, both Cp rings are orientationally disordered, although it is clear that the situation found in compound **3** is being echoed in **1**. For both ring positions, the best structure refinement was obtained for fractional occupancies of 0.75 and 0.25 (see Experimental Section), suggesting that the disordering of the two rings is correlated. Each group of five atoms is essentially planar (Table IV). For the two ring orientations at site 2 (*C2na*, *C2nb*), the planes are coincident (interplanar angle = 1.0°), but at site 1 (*C1na*, *C1nb*) the two planes are not quite coincident, giving an interplanar angle of 5.1°. In spite of this difference, we feel that it is valid to discuss this structure in terms only of the two rings present at 75% occupancy. In this case, we note that the two rings are close to being eclipsed, as opposed to the principally staggered configuration in **3**. The approximate mirror relationship that exists between the two rings does not hold for the PMe$_3$ group orientation, so that one methyl group lies closer to the "trigonal" Cp$_2$MnP plane than the other two.

Examination of the Mn–C distances for complex **1** indicates that ring 1 (*C1na*) [Mn–C 2.432 (6)–2.630 (7) Å] is tilted slightly and this is confirmed by calculation of the tilt angle τ (see above), which is 6.1°. Ring 2, however (*C2na*), gives a smaller range of Mn–C distances [2.485 (6)–2.549 (7) Å] and a small tilt angle, 1.9°. As with compound **3**, the spread of C–C ring distances is small [even for the more tilted ring (1.379 (7)–1.404 (7) Å] and shows no trend to which any significance can be attached.

Molecules of compound **5** which have crystallographic *C2* symmetry can be considered to have a pseudotetrahedral geometry if, as previously, the Cp rings are regarded as occupying one coordination site. The increase in formal coordination number compared with the "three-coordinated" monophosphine adducts is reflected in a number of the geometry parameters. First, all Mn–ligand contacts are greater here than in compounds **1** and **3**. Thus Mn–C distances are 2.492 (6)–2.742 (8) Å, with an average of 2.616 Å (the Mn–Cp(cent) distance is 2.334 Å), while the Mn–P distance of 2.674 (4) Å is 0.05–0.1 Å greater than in **1** and **3**. Second, the Cp(cent)–Mn(cent)–Cp angle is reduced

from 142° in **1** and **3** to 137° here in **5**. The Cp rings in this compound are fixed, but are in fact tilted, as can be seen from the spread of Mn–C distances and the angle, τ, of 7.3° between the Mn–Cp (centroid) vector and the ring normal. It is important to note also that the rings are accurately planar (Table IV) and that the small variation in C–C distances does not show any specific trend.

Having described the structures of these three compounds, it is interesting to consider the implications of the results, particularly the tilting of some of the Cp rings. Lauher and Hoffmann[10] have described the bonding in Cp$_2$ML$_n$ systems in detail and have explained the occurrence of tilted rings in the complexes Cp$_2$Mo(NO)L (L = Me,[11] Cp(η^1)),[12] in terms of electron counts in excess of 18. The distortion arises from occupancy of a molecular orbital formed by mixing of high-lying valence orbitals of the Cp$_2$M fragment with the nitrosyl π^* orbital, which is unsymmetrical with respect to the Mn–C$_5$ bonding. In principle, the Cp$_2$Mn(PR$_3$) and Cp$_2$Mn(PR$_3$)$_2$ complexes can also be classed as having excess electrons if the Cp$^-$ groups are considered to be six-electron donors, i.e., 19 e for the monophosphines and 21 e for the dmpe complex. Also the phosphines have π-acceptor orbitals that could mix in with the orbitals of the Cp$_2$Mn fragment. Thus, the Cp$_2$MnPR$_3$ molecules are structurally related to the model compound Cp$_2$Mo(CO), but with one more d electron, and the Cp$_2$Mn(dmpe) molecules are related to Cp$_2$Ti(CO)$_2$ or Cp$_2$W(CO)$_2$ but with three or one additional d electrons, respectively. However, it seems to us unwise to take any comparisons too far for the simple reason that in our manganese(II) complexes the metal exists in the spherical high-spin ^{6}S state, indicating that in the metal–ligand interactions covalency contributions are relatively small.

In this case, it is probable that the precise molecular structures adopted correspond to a delicate balance between fairly similar steric and electronic energies. It is interesting, therefore, to analyze the structures in terms of intramolecular, interligand interactions.

The most noteworthy feature to arise from this analysis is that in all three compounds, **1**, **3**, and **5**, for those rings that are tilted, the direction of tilt is such that the "front" sides of the rings, that is, the sides nearest to the phosphine ligands, are being pushed away from the metal. This immediately suggests that the tilting might be a result of steric repulsions between the two types of ligand; note also that this direction of tilt is opposite to that found in the Mo nitrosyls.[11,12] However, close examination of individual contacts does not lead to a clear-cut solution. While it is true that in each compound carbon atoms at the front ends of the tilted rings do make "close" contacts with the phosphines, e.g., C-(13)···C(11a) = 3.46 Å, C(13)···C(13b) = 3.44 Å, P(1)···C(11a) = 3.56 Å, P(1)···C(12a) = 3.51 Å for compound **1**, C(31)···C(5b) = 3.38 Å, P(1)···C(5b) = 3.50 Å, P(1)···C(1c) = 3.47 Å for compound **3**, and P(1)···C(3) = 3.60 Å, P(1)*···C(1) = 3.55 Å, P(1)*···C(2) = 3.66 Å for compound **5** (where P(1)* is the atom generated by the twofold axis running through the molecule), there are also equally close contacts involving the symmetrically bound ring (*Cna*) in compound **3**, e.g., P(1)···C(4a) = 3.41 Å.

It is also interesting to consider at this point the structure of a titanium analogue of compound **5**, (C$_5$H$_4$Me)$_2$Ti(dmpe).[13] This also has tilted Cp rings, but the tilt is now opposite to that found in the Mn^{II} compounds. However, any detailed comparison is hampered by the fact that the C$_5$H$_4$Me methyl groups are on the far sides of the Cp rings, i.e., distal to the phosphine binding, and it is possible that the tilting here may be due to Me···Me repulsions.

Clearly the examination of individual and varying atom···atom interligand interactions does not allow one to arrive at a complete assessment of the steric situation; only a comprehensive

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Table V. Field Strengths of Experimental and Computed Transitions for $Cp_2Mn(PEt_3)^a$

transitions	Y	Z	X	Y	X	off axis	off axis	Z	Y	Z	X	Y
found	73	130		203		281	349	412	620	777	921	1067	1203
calcd	74	125	195	224	272				609	770	936	1121	1152

a Transitions: Found (calcd), mT^{-1}. Calculated field strengths for $D = 0.72$ cm^{-1}, $\lambda = 0.17$.

Table VI. Crystal Data and Details of Structure Analysis

|	Crystal Data		
compd	$Cp_2Mn(PMe_3)$ (1)	$Cp_2Mn(PPh_2Me)$ (3)	$Cp_2Mn(dmpe)$ (5)
formula	$C_{13}H_{19}MnP$	$C_{23}H_{23}MnP$	$C_{16}H_{26}MnP_2$
formula wt	261.2	385.3	335.3
crystal system	monoclinic	monoclinic	tetragonal
a/Å	8.243 (1)	9.080 (1)	13.892 (2)
b/Å	15.303 (1)	10.161 (1)	13.892
c/Å	11.476 (2)	21.769 (3)	9.050 (3)
β/deg	108.04 (1)	100.66 (1)	
U/Å^3	1376	1974	1747
temp/K	295	295	295
space group	$P2_1/c$	$P2_1/c$	$P4n2$
Z	4	4	4
Dc/(g cm^{-3})	1.26	1.30	1.28
	Data Collection		
θ scan width/deg	$0.8 + 0.35 \tan \theta$	$0.8 + 0.35 \tan \theta$	$0.8 + 0.35 \tan \theta$
θ_{min}, θ_{max}/deg	1.5, 28	2.0, 27	1.5, 25
total data	3785	4808	1876
total unique	3306	4297	1540
total obsd ($F_o > 3\sigma F_o$)	2195	2909	1252
	Refinement		
no. of parameters	294	343	123
weight parameter g	0.00025	0.0004	0.0005
R	0.0421	0.0400	0.0360
R_w	0.0408	0.0416	0.0353

"integration" of all steric interaction energies will suffice. In our view, the features demonstrated by the structures of these compounds are worthy of further study, particularly in view of the variable electronic behavior shown by related molecules. Accordingly, we have commenced such an analysis using our recently developed steric interactions program[14] and will report on our findings subsequently.

Electron Paramagnetic Resonance Spectra. The X-band EPR spectra of the unidentate phosphine adducts 1-4 were measured in toluene glasses at liquid nitrogen temperatures. All the spectra showed an intense feature at ca. 130 mT, weaker resonances at ca. 75 and 200 mT, and several high-field bands out to 1200 mT; hyperfine structures due to ^{55}Mn ($I = ^5/_2$, 100% abundance) were evident in the low-field region. A representative spectrum is given in Figure 5. These spectra are characteristic of rhombically distorted $S = ^5/_2$ species and are similar to EPR spectra of other such molecules, notably tetrahedral manganese(II) alkyls of stoichiometry $MnR_2(PR_3')_2$[8] and certain biologically active Fe^{III} compounds such as ferrichrome A, ferrirubin, and transferrin.[15]

The spectra may be analyzed in terms of the spin Hamiltonian:

$$\mathcal{H} = \beta gBS + D[S_z^2 - (1/3)S(S + 1) + \lambda(S_x^2 - S_y^2)] + ASI$$

where D is a zero-field splitting parameter and λ is a symmetry parameter that can vary from 0 for an axial geometry to $^1/_3$ for maximum possible rhombic symmetry. The g-tensor was assumed to be isotropic and equal to 2.0, as is typical for $^6S_{5/2}$ ground states.[16] Initial assignments of observed resonances to specific transitions were made using the D-B plot method,[15a] and final
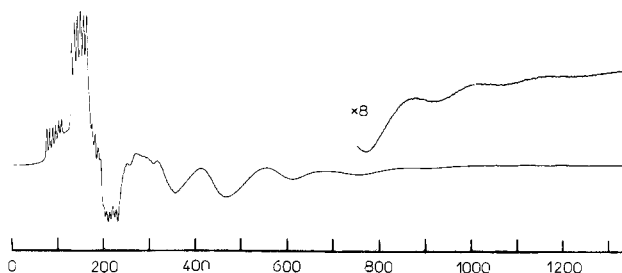
Figure 5. Electron paramagnetic resonance spectrum of $Cp_2Mn(PEt_3)$ in toluene glass at 77 K; scale in mT.

refinements of D and λ were performed by using the iterative least-squares program MNES.[16]

The ca. 1:4 relative intensity of the band at 75 mT to the band at 130 mT in each spectrum is diagnostic of λ values near 0.20; this latter value is also consistent with the resonance positions at ca. 200 mT. The appearance of bands out to 1200 mT is indicative of D values greater than 0.5 cm^{-1}. Although a completely unambiguous assignment of D and λ values could not be made, taking $D = 0.72$ cm^{-1} and $\lambda = 0.17$ gives a satisfactory accounting of the observed spectra. A listing of observed and calculated transition field stengths is given in Table V.

These Hamiltonian parameters may be compared with those found in the distorted tetrahedral Mn^{II} alkyls $MnR_2(PR_3)_2$, where $D = 0.55$ cm^{-1} and $\lambda = 0.28$.[8] The zero-field splitting parameters, D, show that cyclopentadienyl ligands affect the ligand field to a greater extent than σ-alkyl groups; this is consistent with the expected increase in metal–ligand bonding. The λ values show that the $Cp_2Mn(PR_3)$ molecules are rhombically distorted, but to a lesser degree than in the tetrahedral $MnR_2(PR_3')_2$ complexes.

The high-spin $^6S_{5/2}$ ground states indicated for the $Cp_2Mn(PR_3)$ compounds by EPR spectra at -196 °C are consistent with the solid-state magnetic moment of $Cp_2Mn(PEt_3)$ at room temperature; $\mu = 5.7$ μ_B. Susceptibility measurements in solution were

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Table VII. Atomic Parameters for $Cp_2Mn(PMe_3)$ (**1**)

	x	y	z
	atom coordinates, $\times 10^4$		
Mn(1)	1469 (1)	2142	1828
P(1)	3548 (1)	841 (1)	2423 (1)
C(11)	5474 (4)	988 (3)	3678 (3)
C(12)	4373 (4)	518 (2)	1200 (3)
C(13)	2791 (5)	−185 (2)	2855 (4)
C(11a)	−784 (5)	1128 (3)	2311 (4)
C(12a)	−904 (5)	937 (3)	1095 (4)
C(13a)	−1471 (5)	1697 (3)	455 (4)
C(14a)	−1590 (5)	2385 (4)	1220 (5)
C(15a)	−1153 (5)	2012 (3)	2393 (5)
C(11b)	−1269 (8)	2356 (6)	2041 (8)
C(12b)	−785 (8)	1484 (7)	2575 (8)
C(13b)	−911 (8)	966 (7)	1576 (7)
C(14b)	−1028 (8)	1418 (7)	351 (8)
C(15b)	−1421 (8)	2213 (7)	694 (7)
C(21a)	3856 (5)	3206 (3)	2797 (4)
C(22a)	2290 (5)	3663 (3)	2503 (4)
C(23a)	1558 (6)	3691 (3)	1190 (4)
C(24a)	2688 (5)	3216 (3)	656 (4)
C(25a)	4106 (5)	2940 (3)	1674 (4)
C(21b)	3193 (8)	3394 (7)	2795 (8)
C(22b)	1829 (8)	3696 (7)	1849 (8)
C(23b)	2243 (8)	3420 (7)	817 (8)
C(24b)	3544 (8)	3017 (6)	1108 (7)
C(25b)	4240 (8)	2995 (6)	2319 (8)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
	anisotropic temperature factors,[a] $A^2 \times 10^3$					
Mn(1)	51	50	54	−1	15	2
P(1)	56	54	53 (1)	1 (1)	20 (1)	6 (1)
C(11)	74 (1)	116 (1)	58 (1)	0 (1)	11 (1)	23 (1)
C(12)	89 (1)	89 (1)	62 (1)	−10 (1)	27 (1)	16 (1)
C(13)	104 (1)	64 (1)	141 (1)	29 (1)	50 (1)	20 (1)
C(11a)	69 (1)	75 (1)	80 (1)	−5 (1)	36 (1)	−11 (1)
C(12a)	67 (1)	92 (1)	67 (1)	−10 (1)	10 (1)	−24 (1)
C(13a)	67 (1)	102 (1)	78 (1)	3 (1)	−5 (1)	−9 (1)
C(14a)	67 (1)	100 (1)	107 (1)	5 (1)	21 (1)	18 (1)
C(15a)	71 (1)	96 (1)	106 (1)	4 (1)	47 (1)	7 (1)
C(11b)	63 (1)	76 (1)	62 (1)	12 (1)	21 (1)	11 (1)
C(12b)	66 (1)	72 (1)	72 (1)	3 (1)	21 (1)	−4 (1)
C(13b)	62 (1)	69 (1)	65 (1)	0 (1)	25 (1)	−5 (1)
C(14b)	95 (1)	92 (1)	99 (1)	−10 (1)	10 (1)	2 (1)
C(15b)	69 (1)	69 (1)	59 (1)	−7 (1)	4 (1)	8 (1)
C(21a)	70 (1)	59 (1)	89 (1)	−20 (1)	20 (1)	−10 (1)
C(22a)	87 (1)	61 (1)	80 (1)	−18 (1)	16 (1)	0 (1)
C(23a)	88 (1)	80 (1)	88 (1)	12 (1)	20 (1)	6 (1)
C(24a)	84 (1)	89 (1)	92 (1)	20 (1)	34 (1)	−4 (1)
C(25a)	65 (1)	71 (1)	71 (1)	5 (1)	21 (1)	−16 (1)
C(21b)	81 (1)	74 (1)	85 (1)	−5 (1)	14 (1)	−13 (1)
C(22b)	74 (1)	63 (1)	74 (1)	0 (1)	9 (1)	0 (1)
C(23b)	87 (1)	74 (1)	75 (1)	9 (1)	27 (1)	−2 (1)
C(24b)	75 (1)	69 (1)	68 (1)	13 (1)	23 (1)	−18 (1)
C(25b)	70 (1)	62 (1)	68 (1)	4 (1)	14 (1)	−13 (1)

	x	y	z	U
	hydrogen atom coordinates, $\times 10^4$, and isotropic temperature factors, $A^2 \times 10^3$, for $Cp_2Mn(PMe_3)$ (**1**)			
H(111)	6181 (9)	524 (8)	3828 (8)	72 (1)
H(112)	5929 (9)	1427 (8)	3508 (9)	67 (1)
H(113)	5109 (9)	1125 (8)	4440 (8)	69 (1)
H(121)	3393 (9)	420 (8)	567 (8)	73 (1)
H(122)	5230 (9)	39 (8)	1403 (8)	77 (1)
H(123)	4805 (9)	919 (8)	1009 (9)	66 (1)
H(131)	3574 (9)	−627 (8)	2919 (8)	75 (1)
H(132)	1993 (9)	−401 (8)	2114 (8)	74 (1)
H(133)	2497 (9)	−98 (8)	3510 (8)	72 (1)
H(11a)	−466 (9)	696 (9)	3031 (9)	95 (1)
H(12a)	−635 (9)	336 (9)	775 (9)	95 (1)
H(13a)	−1783 (9)	1738 (9)	−529 (9)	95 (1)
H(14a)	−1930 (9)	3024 (9)	964 (9)	95 (1)
H(15a)	−1098 (9)	2332 (9)	3194 (9)	95 (1)
H(21a)	4675 (9)	3105 (9)	3657 (9)	86 (1)
H(22a)	1731 (9)	3921 (9)	3102 (9)	86 (1)
H(23a)	404 (9)	3965 (9)	677 (9)	86 (1)
H(24a)	2340 (9)	3063 (8)	−278 (9)	86 (1)
H(25a)	5114 (9)	2587 (9)	1571 (9)	86 (1)

[a] The temperature factor exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

Table VIII. Atomic Parameters for $Cp_2Mn(PPh_2Me)$ **3**

|	x	y	z
	atom coordinates, $\times 10^4$		
Mn(1)	7361	−349	2658
P(1)	6403 (1)	178 (1)	3691
C(1)	4376 (3)	373 (3)	3615 (1)
C(21)	7146 (3)	1749 (2)	4015 (1)
C(22)	6851 (4)	2210 (3)	4582 (1)
C(23)	7456 (4)	3406 (4)	4819 (2)
C(24)	8299 (4)	4154 (3)	4486 (2)
C(25)	8562 (4)	3714 (3)	3931 (2)
C(26)	8008 (3)	2517 (3)	3698 (1)
C(31)	6829 (3)	−967 (2)	4342 (1)
C(32)	6030 (3)	−2131 (3)	4324 (1)
C(33)	6358 (4)	−3041 (3)	4794 (2)
C(34)	7503 (4)	−2822 (3)	5281 (1)
C(35)	8342 (3)	−1692 (3)	5304 (1)
C(36)	7995 (3)	−766 (3)	4839 (1)
C(1a)	5778 (4)	−220 (3)	1602 (2)
C(2a)	7026 (4)	560 (3)	1575 (1)
C(3a)	6980 (3)	1626 (3)	1969 (1)
C(4a)	5697 (3)	1524 (3)	2230 (1)
C(5a)	4956 (3)	374 (3)	1999 (1)
C(1b)	8630 (5)	−2597 (4)	2893 (3)
C(2b)	9029 (5)	−1943 (4)	2377 (2)
C(3b)	9915 (4)	−834 (4)	2614 (2)
C(4b)	10059 (5)	−846 (5)	3271 (3)
C(5b)	9278 (5)	−1933 (5)	3440 (3)
C(1c)	9728 (7)	−1299 (6)	3486 (4)
C(2c)	8793 (6)	−2390 (6)	3245 (4)
C(3c)	8644 (7)	−2394 (7)	2603 (4)
C(4c)	9468 (7)	−1412 (7)	2423 (4)
C(5c)	10109 (7)	−657 (6)	2961 (4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
	anisotropic temperature factors,[a] $\text{Å}^2 \times 10^3$					
Mn(1)	49	51	45	−2	9	10
P(1)	40	50	43	−1	7	8
C(1)	45 (1)	83 (1)	75 (1)	8 (1)	10 (1)	14 (1)
C(21)	50 (1)	49 (1)	52 (1)	−6 (1)	5 (1)	12 (1)
C(22)	82 (1)	67 (1)	70 (1)	−14 (1)	20 (1)	11 (1)
C(23)	113 (1)	88 (1)	77 (1)	−36 (1)	19 (1)	17 (1)
C(24)	76 (1)	67 (1)	108 (1)	−31 (1)	−2 (1)	7 (1)
C(25)	59 (1)	61 (1)	93 (1)	−9 (1)	−1 (1)	−2 (1)
C(26)	52 (1)	56 (1)	61 (1)	−6 (1)	3 (1)	4 (1)
C(31)	41 (1)	50 (1)	48 (1)	−2 (1)	12 (1)	7 (1)
C(32)	56 (1)	57 (1)	63 (1)	−5 (1)	7 (1)	−1 (1)
C(33)	75 (1)	54 (1)	89 (1)	6 (1)	22 (1)	−3 (1)
C(34)	89 (1)	67 (1)	67 (1)	20 (1)	24 (1)	22 (1)
C(35)	71 (1)	72 (1)	65 (1)	4 (1)	−5 (1)	12 (1)
C(36)	53 (1)	61 (1)	63 (1)	3 (1)	1 (1)	3 (1)
C(1a)	85 (1)	67 (1)	66 (1)	−12 (1)	−12 (1)	−3 (1)
C(2a)	80 (1)	85 (1)	53 (1)	6 (1)	8 (1)	8 (1)
C(3a)	66 (1)	63 (1)	61 (1)	17 (1)	−7 (1)	−10 (1)
C(4a)	68 (1)	59 (1)	53 (1)	1 (1)	−3 (1)	10 (1)
C(5a)	51 (1)	79 (1)	67 (1)	11 (1)	−5 (1)	−7 (1)
C(1b)	68 (1)	63 (1)	74 (1)	13 (1)	25 (1)	15 (1)
C(2b)	57 (1)	43 (1)	78 (1)	−1 (1)	16 (1)	−4 (1)
C(3b)	47 (1)	49 (1)	68 (1)	−16 (1)	9 (1)	−2 (1)
C(4b)	63 (1)	82 (1)	68 (1)	−10 (1)	9 (1)	23 (1)
C(5b)	68 (1)	84 (1)	82 (1)	−1 (1)	20 (1)	26 (1)
C(1c)	47 (1)	43 (1)	60 (1)	−2 (1)	14 (1)	0 (1)
C(2c)	48 (1)	44 (1)	52 (1)	−7 (1)	5 (1)	3 (1)
C(3c)	60 (1)	61 (1)	55 (1)	−6 (1)	8 (1)	17 (1)
C(4c)	58 (1)	71 (1)	69 (1)	−6 (1)	12 (1)	16 (1)
C(5c)	50 (1)	59 (1)	60 (1)	15 (1)	14 (1)	5 (1)

	x	y	z	U
	hydrogen atom coordinates, $\times 10^4$, and isotropic temperature factors, $\text{A}^2 \times 10^3$			
H(11)	4127 (9)	511 (9)	4031 (8)	89 (1)
H(12)	3818 (9)	−429 (9)	3465 (8)	109 (1)
H(13)	4090 (9)	997 (9)	3355 (8)	71 (1)
H(22)	6239 (9)	1694 (9)	4814 (8)	82 (1)
H(23)	7279 (9)	3561 (9)	5251 (8)	99 (1)
H(24)	8805 (9)	5046 (9)	4676 (8)	109 (1)
H(25)	9154 (9)	4242 (9)	3704 (8)	102 (1)
H(26)	8210 (9)	2212 (9)	3325 (7)	51 (1)
H(32)	5232 (9)	−2270 (9)	4000 (7)	68 (1)
H(33)	5697 (9)	−3837 (9)	4725 (8)	99 (1)
H(34)	7684 (9)	−3440 (9)	5616 (7)	73 (1)

Table VIII (*Continued*)

	x	y	z	U
hydrogen atom coordinates, $\times10^4$, and isotropic temperature factors, $\text{Å}^2 \times 10^3$				
H(35)	9164 (9)	−1469 (9)	5655 (8)	100 (1)
H(36)	8640 (9)	5 (9)	4875 (8)	101 (1)
H(1a)	5544 (9)	−1004 (9)	1400 (7)	72 (1)
H(2a)	7813 (9)	337 (9)	1367 (8)	116 (1)
H(3a)	7597 (9)	2228 (9)	2042 (8)	78 (1)
H(4a)	5351 (9)	2108 (9)	2511 (7)	58 (1)
H(5a)	4114 (9)	82 (9)	2117 (7)	60 (1)
H(1b)	8204 (9)	−3598 (9)	2883 (8)	83 (1)
H(2b)	8751 (9)	−2258 (9)	1921 (8)	83 (1)
H(3b)	10313 (9)	−141 (9)	2347 (8)	83 (1)
H(4b)	10787 (9)	−196 (9)	3568 (8)	83 (1)
H(5b)	9401 (9)	−2393 (9)	3888 (8)	83 (1)
H(1c)	9946 (9)	−1010 (9)	3938 (9)	81 (1)
H(2c)	8052 (9)	−2916 (9)	3498 (9)	81 (1)
H(3c)	7706 (9)	−2870 (9)	2329 (9)	81 (1)
H(4c)	9796 (9)	−1330 (9)	1989 (9)	81 (1)
H(5c)	10690 (9)	266 (9)	3019 (9)	81 (1)

[a] The temperature factor exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

not accurately reproducible, and gave moments significantly below the spin-only value. We attribute this behavior to the presence of reversible equilibria (see below) that are dependent on the concentration of free phosphine.

$$Cp_2Mn(PR_3) \rightleftharpoons Cp_2Mn + PR_3$$

$$Cp_2Mn(PR_3) + PR_3 \rightleftharpoons Cp_2Mn(PR_3)_2$$
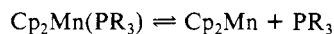
Nevertheless, the EPR and solid-state susceptibility data indicate an exclusively high-spin electronic configuration for all the $Cp_2Mn(PR_3)$ monoadducts.

It was noted during the above studies that addition of excess phosphine to the EPR samples caused significant changes in the spectra. The resonances due to the $Cp_2Mn(PR_3)$ complexes disappeared, and were replaced by a broad featureless signal centered on $g_{eff} = 2$. These signals were attributed to Cp_2Mn-$(PR_3)_2$ species, but compounds of this stoichiometry could not be isolated for unidentate phosphines (cf. behavior noted in ref 7 for the dialkyls). The assignment was confirmed, however, when frozen toluene solutions of the bidentate phosphine adducts, $Cp_2Mn(dmpe)$ and $(C_5H_4Me)_2Mn(dmpe)$, also showed broad, featureless signals at $g = 2$.

Although such spectra can be accounted for assuming $S = {}^5/_2$, the D and λ values necessary would have to be very small ($D \approx \lambda \approx 0$). We believe these values to be chemically unreasonable, since symmetry considerations lead us to expect that the Hamiltonian parameters for high-spin $Cp_2Mn(PR_3)_2$ should be generally similar to those of high-spin $Cp_2Mn(PR_3)$ and $MnR_2(PR_3')_2$ species. We propose instead that there is a high-spin–low-spin equilibrium present, with the EPR signal at −196 °C arising from a $S = {}^1/_2$ species. The broadness of the resonance may be attributed to exchange operating at this temperature. Unfortunately, spectral changes resulting from mobility of the solvent prevented a temperature-variation study of the EPR signal, and a susceptibility study in solution by the Evans' method gave irreproducible results, presumably due to reversible phosphine dissociation. However, the magnetic moment in the solid state is 5.6 μ_B and therefore the spin equilibrium, if it exists, must be established well below 25 °C. A largely high-spin configuration at room temperature would also be consistent with the observed crystallographic bond lengths. A variable-temperature magnetic susceptibility study should clarify this point.

Reactions. Manganese(II) dicyclopentadienide reacts with various ligands,[17] such as CO[18] or P(OR)$_3$,[19] to give compounds

of stoichiometry $CpMnL_3$, but although adducts may well be formed as the first step in the reaction, none have been characterized. Although $CpMn(PMe_3)_3$ is known,[19] it cannot be synthesized by the reaction between $MnCp_2$ and neat PMe_3 or excess PMe_3 in toluene under hydrogen (10 atm) at temperatures up to 130 °C. However, we have EPR evidence for an adduct with t-BuNC as an initial stage in the reaction to give $CpMn(CN$-t-$Bu)_3$.

Other first-row transition-metal compounds, Cp_2V, Cp_2Cr, and $(C_5Me_5)_2Mn$ (which is low spin), show no evidence of reaction with PMe_3; the only other neutral phosphine adduct is $(C_5H_4Me)_2Ti(dmpe)$, whose structure is similar to that of $Cp_2Mn(dmpe)$.[13]

Experimental Section

Microanalyses were performed by Pascher, Bonn. Melting points in sealed tubes are uncorrected.

Spectrometers: NMR, Perkin-Elmer R32 (90 MHz), JEOL FX 90Q; EPR, Varian E12 (X-band); IR, Perkin-Elmer 683.

Magnetic moments were determined in the solid state by the Gouy method and in solution by a modification of the Evans' method.[20]

All operations were carried out in vacuo or under purified argon. Solvents were distilled from sodium and sodium benzophenone under nitrogen. The petroleum used had bp 40–60 °C.

Adducts of Manganese(II) Dicyclopentadienide. These were all prepared by using essentially the same procedure now given for the trimethylphosphine complex.

To an orange solution of $MnCp_2$[1] (0.9 g, 4.8 mmol) in toluene (50 cm^3) at room temperature was added PMe_3 (0.5 cm^3, 5 mmol). After stirring for 1 h, the pale yellow solution was evaporated in vacuo. The residue was then extracted with toluene (2 × 40 cm^3), and the solution was concentrated to 40 cm^3 and cooled to −20 °C to give colorless prisms (yield 1.0 g, 80%).

The dmpe adduct was isolated similarly, but the adducts of PMe_2Ph, $PMePh_2$, and PEt_3 were crystallized from petroleum.

[1,2-Bis(dimethylphosphino)ethane]manganese Bis(methylcyclopentadienide). To a solution of $Mn(C_5H_4Me)_2$[2] (1 g, 4.7 mmol) in petroleum (50 cm^3) was added dmpe (0.7 g, 4.7 mmol). After stirring for a few minutes a white precipitate formed which was collected and washed with petroleum (50 cm^3). The residue was then extracted with toluene (50 cm^3), and the solution was concentrated to 25 cm^3 and cooled to −20 °C to give white plates of the complex. On concentration of the petroleum solutions, a further crop of crystals could be obtained (yield 1.19 g 60%).

The PMe_3 analogue was made in a similar manner but was thermally unstable.

X-ray Crystallography. Data Collection, Structure Solution, and Refinement. Crystals of all three compounds were sealed in Lindemann capillaries under argon. Orientation matrices and associated cell di-

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Table IX. Atomic Parameters for $Cp_2Mn(dmpe)$ (5)

	x	y	z
	atom coordinates, $\times 10^4$		
Mn(1)	1834	6834	2500
P(1)	2175 (1)	8618 (1)	1523 (1)
C(11)	2504 (3)	8809 (4)	−408 (5)
C(12)	1340 (3)	9619 (3)	1833 (6)
C(13)	3252 (3)	9029 (3)	2494 (6)
C(1)	2673 (4)	5391 (4)	1074 (6)
C(2)	2731 (4)	6124 (4)	32 (6)
C(3)	1769 (4)	6372 (3)	−363 (5)
C(4)	1167 (4)	5818 (3)	448 (5)
C(5)	1717 (4)	5212 (3)	1340 (5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
	anisotropic temperature factors,[a] $\mathring{A}^2 \times 10^3$					
Mn(1)	32	32	32	0	0	−3
P(1)	40 (1)	33	42	7	−2	−1
C(11)	60 (1)	72 (2)	45 (1)	16 (1)	−3 (1)	−20 (1)
C(12)	66 (2)	44 (1)	99 (2)	5 (1)	−3 (1)	18 (1)
C(13)	56 (1)	36 (1)	50 (1)	5 (1)	−12 (1)	−13 (1)
C(1)	72 (2)	54 (1)	77 (2)	−26 (1)	−26 (1)	14 (1)
C(2)	86 (2)	64 (2)	73 (2)	−29 (1)	29 (2)	−25 (1)
C(3)	110 (2)	44 (1)	43 (1)	−11 (1)	−6 (1)	7 (2)
C(4)	76 (2)	58 (1)	54 (1)	−6 (1)	−4 (1)	2 (1)
C(5)	92 (2)	43 (1)	50 (1)	−7 (1)	−1 (1)	4 (1)

	x	y	z	U
	hydrogen atom coordinates, $\times 10^4$ and isotropic temperature factors, $\mathring{A}^2 \times 10^3$			
H(111)	2008 (3)	8427 (4)	−1116 (5)	78 (2)
H(112)	3226 (3)	8549 (4)	−599 (5)	78 (2)
H(113)	2472 (3)	9569 (4)	−651 (5)	78 (2)
H(121)	750 (3)	9567 (3)	1060 (6)	73 (2)
H(122)	1713 (3)	10293 (3)	1669 (6)	73 (2)
H(123)	1065 (3)	9588 (3)	2947 (6)	73 (2)
H(131)	2993 (15)	9276 (15)	3493 (16)	51 (2)
H(132)	3505 (15)	9568 (15)	2024 (16)	52 (2)
H(1)	3138 (15)	5085 (16)	1544 (16)	57 (2)
H(2)	3266 (15)	6432 (16)	−415 (17)	60 (2)
H(3)	1545 (16)	6907 (15)	−1135 (17)	66 (2)
H(4)	447 (16)	5813 (15)	367 (16)	63 (2)
H(5)	1458 (15)	4691 (15)	2036 (16)	57 (2)

[a] The temperature factor exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

mensions and intensity data were obtained by using an Enraf-Nonius CAD4 and graphite monochromatized Mo Kα radiation (λ = 0.71069 Å), following procedures previously described in detail.[21] Crystal data and intensity measurement parameters are listed in Table VI. The structures were solved via standard heavy-atom methods and refined by using full-matrix least squares,[22] with scattering factors based on pa-

rameters given in ref 23. The structure solutions and refinements were straightforward except in the case of compound $Cp_2Mn(PMePh_2)$, 3, where one of the two Cp rings was disordered, and $Cp_2Mn(PMe_3)$, 1, where both rings showed disorder. For the case of compound 3 the disordered ring was represented by two images, with occupancies of 0.65 and 0.35 giving the best refinement. For compound 1, both rings showed disorder, and in each case occupancy factors of 0.75 and 0.25 gave the best refinement.

All non-hydrogen atoms were refined normally with anisotropic thermal parameters (including those with fractional occupancy), while hydrogen atoms were treated in various ways. For compound 3, phenyl and methyl hydrogens and those on the "rigid" Cp group were located in a difference map and the derived coordinates freely refined, along with individual isotropic thermal parameters. Hydrogen atoms on the carbons of the disordered ring were generated in chemically sensible positions and while the coordinates were freely refined, each group of five hydrogens were given a common, refined, isotropic thermal parameter. For compound 1, the phosphine methyl hydrogens were freely refined, but those on the disordered Cp rings were treated as for compound 3. For compound 5, the methyl hydrogens were constrained to form a trigonal top with C–H = 1.08 Å, and each group of three hydrogens assigned a common, refined, isotropic thermal parameter. Methylene and Cp hydrogens, however, were experimentally located and refined with individual isotropic thermal parameters. Final atomic positional and thermal parameters are given in Tables VII (1), VIII (3), and IX (5). Least-squares refinement parameters and results are summarized in Table VI. The weighting scheme used for all refinements was of the form λ = $1/[\sigma^2(F_o) + g(F_o)^2]$. Lists of F_o/F_c values have been deposited as supplementary material.

Note Added in Proof. A 3,5-dichloropyridine adduct of a manganese(II) metallocenophane has recently been described (Weed, J. T.; Rettig, M. F.; Wing, R. M. *J. Am. Chem. Soc.* **1983**, *105*, 6510–6511) and preliminary work indicating that Cp_2Mn binds two molecules of 3,5-dichloropyridine is mentioned.

Registry No. 1, 88635-41-0; 2, 88635-42-1; 3, 88635-43-2; 4, 88635-44-3; 5, 88635-45-4; 6, 88635-46-5; $MnCp_2$, 1271-27-8; $Mn(C_5H_4Me)_2$, 32985-17-4.

Supplementary Material Available: Full lists of bond lengths and angles and Tables of F_o/F_c values (34 pages). Ordering information is given on any current masthead page.

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