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Manganese complexes of the pentaphenylcyclopentadienyl ligand

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Abstract

The preparation and characterisation of $[Mn(\eta^5-C_5Ph_5)(CO)_3](1)$, $[Mn(\eta^5-C_5Ph_5)(CO)_2(PMe_2Ph)](2)$, and $[Mn(\eta^5-C_5(p-tol)_5)(CO)_3](3)$ are described; these complexes are the first reported fully characterised $C_5Ar_5^-$ derivatives of Group 7. Compounds (1) and (3) are reversibly oxidised at +0.98 and +0.89 V, respectively (versus Fc^{+/0}), significantly more positive than the oxidation of the analogous $[Mn(\eta^5-C_5H_5)(CO)_3]$. Single crystal X-ray diffraction studies of (1) and (2) (refined to $R_1(F)$ 0.0967, $wR_2(F^2)$ 0.2971 and $R_1(F)$ 0.0472, $wR_2(F^2)$ 0.1356, respectively) are also reported.

1. Introduction

The cyclopentadienyl ligand has become one of the most widely used ligands in organometallic chemistry, since the discovery and characterisation of ferrocene were reported in the early 1950s. Cyclopentadienyl complexes are known for all of the transition metal and main group metals and metalloids, as well as all of the lanthanoid and the more common actinide metals. Since the synthesis of the ligand precursors in 1925 [1,2] and the report of the first metal complex in 1964 [3], pentaphenylcyclopentadienyl derivatives of most elements of the Periodic Table have been reported. Although main group, first, second and third row transition metals and lanthanide complexes have been reliably reported, fully characterised complexes of Groups 5 and 7 are notably absent. [Mn(η^5 -C₅H₅)(CO)₃] is one of the prototypical "half-sandwich" complexes [4], and its derivatives have been used as gasoline additives and have some industrial catalytic applications.

We report here, the synthesis and characterisation of three pentaphenylcyclopentadienyl complexes of manganese, $(\eta^{5}$ -pentaphenylcyclopentadienyl)tricarbonylmanganese(I), $[Mn(\eta^{5}-C_{5}Ph_{5})(CO)_{3}]$ (1) (dimethylphenylphosphine)- $(\eta^{5}$ -pentaphenylcyclopentadienyl)dicarbonylmanganese(I),

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 $[Mn(\eta^5-C_5Ph_5)(CO)_2(PMe_2Ph)]$ (2), as well as the analogous penta-*p*-tolylcyclopentadienyl manganese complex, (η^5 -penta(*p*-tolyl)cyclopentadienyl)tricarbonylmanganese(I), $[Mn(\eta^5-C_5(p-tol)_5)(CO)_3]$ (3). Surprisingly, interpretations of the molecular structure of $[Mn(\eta^5-C_5H_5)(CO)_3]$ have been the subject of some ambiguity, the crystal structure of this simple molecule having been reported three times in the literature [5–7].



2. Results and discussion

Pale yellow crystals of $[Mn(\eta^5-C_5Ph_5)(CO)_3]$ (1) were prepared in yields of 38–68% by reaction of LiC₅Ph₅ with $[Mn(CO)_3(CH_3CN)_3]Br$, or $[Mn(CO)_5Br]$, or of C₅Ph₅Br with $[Mn(CO)_3(CH_3CN)_2Br]/Zn$ in refluxing tetrahydrofuran. Yellow $[Mn(\eta^5-C_5(p-tol)_5)(CO)_3]$ (3) was prepared similarly. The synthetic routes to (1) and (3) are remarkably different to the original syntheses of $[Mn(\eta^5-C_5H_5)(CO)_3]$,

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in which $[Mn(\eta^5-C_5H_5)_2]$ was reacted with carbon monoxide at elevated temperatures and pressures [4,8]. Reactions analogous to those used for the preparations of $[Mn(n^2 C_5Me_5(CO)_3$ and $[Mn(\eta^5-C_5Bz_5)(CO)_3]$ were also not suitable due to the very low solubility of C₅Ph₅H [9–12]. For instance, the purple radical, C₅Ph₅, generated from the mixture of C₅Ph₅Br, zinc dust and Mn₂(CO)₁₀ in refluxing tetrahydrofuran, was not sufficiently reactive to cleave the Mn-Mn bond even though the reaction was continued for four days. In most reactions involving $Mn_2(CO)_{10}$ as a precursor, metal-metal bond cleavage has been shown to be the initial step [13]. [Mn(CO)₃Br], [Mn(CO)₃-(CH₃CN)₃]Br and [Mn(CO)₃(CH₃CN)₂Br] are readily prepared and are the most commonly used precursors for substitution reactions as a consequence of the lability of the CH₃CN and Br⁻ ligands.

Both (1) and (3) are air stable in solid and in solution. Their inertness parallels that of other substituted cyclopentadienyl complexes. The kinetic inertness of $[Mn(\eta^5-C_5RH_4)-(CO)_3]$ (R = H, Me) is well known; no carbonyl exchange with ¹⁴CO occurs in toluene at 32 °C over several weeks, no reaction occurs between PPh₃ and $[Mn(\eta^5-C_5H_5)-(CO)_3]$ even in refluxing decalin and substitution of CO is only possible either by ultraviolet irradiation or by using Me₃NO to actively remove CO [13].

Similarly, $[Mn(\eta^5-C_5Me_5)(CO)_3]$ undergoes monosubstitution either under ultraviolet irradiation or by oxidative substitution [12,14]. There are many reports of cyclopentadienyl manganese derivatives with one or more ligands substituted for CO [13,15]. Recently, a study on the monosubstitution of $[Mn(\eta^5-C_5R_5)(CO)_3]$ (R = H, Me or Et) in *n*-heptane solution under ultraviolet irradiation showed that the bulkier ligand, C5Et5, better stabilised the formation of the solvated intermediate, $[Mn(\eta^5-C_5R_5)(CO)_2-$ (*n*-heptane)] than did the other two ligands [16]. Substitution of one CO in $[Mn(\eta^5-C_5Ph_5)(CO)_3]$ (1) by PMe₂Ph was readily achieved by refluxing a THF solution in the presence of Me₃NO to give $[Mn(\eta^5-C_5Ph_5)(CO)_2(PMe_2Ph)]$ (2). Using an analogous procedure, it was possible to introduce a range of other substituents (including phosphines and isonitriles).

 $[Mn(\eta^5-C_5Ph_5)(CO)_3]$ (1) is not oxidised by reactants such as Br₂, I₂ or NOBF₄, even in the presence of CH₃CN. Recently, it has been found that monosubstitution of a carbonyl ligand proceeded smoothly when $[Ru(\eta^5-C_5Ph_5)(CO)_2Br]$ or $[Os(\eta^5-C_5Ph_5)(CO)_2Br]$ were reacted with other ligands in the presence of Me₃NO [17,18].

However, compounds (1) and (3) each undergo a reversible, one-electron cyclic voltametric oxidation in CH_2Cl_2 at 0.98 V for (1) and 0.89 V for (3) (both versus $Fc^{+/0}$).

$$[Mn(\eta^{5}-C_{5}Ar_{5})(CO)_{3}] \rightleftharpoons [Mn(\eta^{5}-C_{5}Ar_{5})(CO)_{3}]^{+} + e^{-t}$$

The reversibility of these oxidations confirms that complexes of the penta-*p*-tolylcyclopentadienyl ligand, $C_5(p-tol)_5^-$, are easier to oxidise than are those of the $C_5Ph_5^-$ ligand. These oxidation potentials are much higher than that for $[Mn(\eta^5-C_5H_5)(CO)_3]$ which undergoes a

Table 1 Selected average interatomic distances and angles in $[Mn(\eta^5-C_5Ph_5)(CO)_3]$

Atoms	Average dimension
$\overline{Mn-C(C_5)}$	2.16(1) Å
Mn–CO	1.78(1) Å
C–O	1.17(1) Å
$C-C$ (C_5 ring)	1.42(2) Å
$C(C_5)$ -ipso- $C(C_6)$	1.50(2) Å
CO-Mn-CO	90.3(5)°
Mn-C-O	175(1)°
C-C-C (C ₅ ring)	107.7(1)°

reversible oxidation at ca. 0.29 V [19]. In general, the value of the redox couple for a pentaphenylcyclopentadienyl complex is shifted 0.25–0.30 V more positively than that of its cyclopentadienyl analogue [20,21].

In addition, $[Mn(\eta^5-C_5H_5)(CO)_3]$ exhibits a second irreversible oxidation at 1.48 V detected in CF₃CO₂H at a platinum electrode [19], an electrochemically reversible reduction, coupled to a follow-up chemical reaction at -2.46 V [22] and a second irreversible reduction at -3.32 V observed in tetrahydrofuran at a platinum electrode [23]. The first reduction has been shown by preparative electrolysis to generate red $[Mn(\eta^5-C_5H_5)(CO)_3]^-$. However, chemical reduction of $[Mn(\eta^5-C_5H_5)(CO)_3]^-$ in HMPA yields predominantly first $[Mn(CO)_5]^-$ and then $[Mn(CO)_4]^{3-}$ by poorly defined ligand redistribution reactions [24]. We have observed no additional oxidations, nor corresponding reductions of $[Mn(\eta^5-C_5Ar_5)(CO)_3]$.

2.1. Crystal structure determinations

2.1.1. $[Mn(\eta^5 - C_5 Ph_5)(CO)_3]$ (1)

An air-stable crystal of $[Mn(\eta^5-C_5Ph_5)(CO)_3]$ (1) was grown by slow vapour diffusion of pentane into a dichloromethane solution of (1) and the crystal structure was determined at room temperature. A single crystal X-ray diffraction study of (1) was undertaken for comparison with that of (2). Compound (1) crystallises in the monoclinic space group $P2_1/n$ (#14). The crystal structure of (1) consists of discrete molecules in the solid state and no intermolecular contacts of significance were observed in the solid. The closest intermolecular contact is 3.46 Å between C(33) on molecule (x, y, z) and C(34) on molecule (-x, -y, -z). The closest intermolecular non-bonding approaches to manganese are greater than 4 A. Final atomic positional coordinates, with estimated standard deviations, bond lengths and angles and anisotropic thermal parameters are deposited.¹ Selected interatomic bond distances and angles, with standard

¹ The atomic coordinates and thermal parameters have been submitted as supplementary material for deposition at the Cambridge Crystallographic Data Centre with deposition number CCDC 284608 (see Deposition of crystallographic data).



Fig. 1. ORTEP [39] illustration of $[Mn(\eta^5-C_5Ph_5)(CO)_3]$ (1), viewed perpendicular to the C_5 ligand plane, showing the atom numbering scheme.

deviations derived from the refinement, are given in Table 1. The atomic nomenclature is defined in Fig. 1. Figs. 1 and 2 illustrate the molecular geometry viewed along, and perpendicular to, the normal to the C_5 plane of the $C_5Ph_5^-$ ligand, respectively.

2.1.2. The $[Mn(\eta^5 - C_5 Ph_5)(CO)_3]$ molecule

Coordination by the η^5 -pentaphenylcyclopentadienyl group and the three carbonyl groups creates a "threelegged piano stool" environment about the manganese atom. The Mn-(C₅ centroid) distance is 1.784 Å and the average Mn-C distance of 2.16 Å may be compared with the mean of nearly 147 structures of $[Mn(C_5R_5)(CO)_3]$ compounds of 1.775(1) and 2.142(2) Å. The Mn-CO distances (1.74(1), 1.77(1)) and (1.83(1)) Å) are indistinguishable and may be compared, for example, with the mean bond length of 1.784(2) in the $[Mn(C_5R_5)(CO)_3]$ compounds. The C=O bond lengths in (1) are the same within experimental error. The Mn-(C₅ centroid) distance is relatively long; there being only 42 compounds with Mn-(C5 centroid) distances of 1.785 Å or longer. There appears to be no simple correlation between Mn-(C₅ centroid) distance and other parameters - whilst many of these 42 compounds do have bulky cyclopentadienyl ligands and the longest Mn-(ring centroid) distance reported to date is the exceptionally long (at R = 0.0979) 1.912 Å of $[{Os_3(\mu-H)(CO)_8(PPh_3)_2}(\mu-O_2C-\{(\eta^5-C_5H_4)Mn(CO)_3\}]^2)$ [25], that of [Mn(η^5 -C₅H₅)(CO)₃] is 1.794 Å.

The C₅ nucleus of the pentaphenylcyclopentadienyl ligand is planar to within 0.014 Å. The C–C bond lengths of the C₅ ring range from 1.39(2) to 1.46(1) Å, the average C–C bond length being 1.42 Å, which is consistent with C₅Ph₅ rings in other metal complexes. The *ipso*-carbon atoms of each of the phenyl rings are displaced slightly from the C₅ plane by between 0.09 and 0.20 Å, with the average distance being 0.16 Å. The *ipso*-carbon atoms of all phenyl rings are on the opposite side of the C₅ plane to the manganese atom. The phenyl rings are all also planar to within a mean deviation from the plane of 0.02 Å and are canted at between 46.2° and 61.9° (average 51.6°) to the C₅ ring in a paddle wheel arrangement. The average angle between the planes of adjacent phenyl rings of the C₅Ph₅⁻ ligand is 54.9°.

2.1.3. $[Mn(\eta^5 - C_5 Ph_5)(CO)_2(PMe_2 Ph)]$ (2)

 $[Mn(\eta^5-C_5Ph_5)(CO)_2(PMe_2Ph)](2)$ also crystallises in the monoclinic space group $P2_1/n$ (#14). The crystal structure of (2) consists of discrete molecules in the solid state and no

² This distance is a considerable outlier in Mn–(C₅ centroid) distances, d, of [Mn(η^{5} -C₅R₅)(CO)₃] compounds – the next 7 longest distances are in the range 1.812 $\leq d \leq 1.823$ Å.



Fig. 2. ORTEP [39] illustration of $[Mn(\eta^5-C_5Ph_5)(CO)_3]$ (1), viewed parallel to the C_5 ligand plane, showing the atom numbering scheme.

Table 2

intermolecular contacts of significance were observed in the solid. The closest intermolecular contact is 3.332(5) Å between O(1) on molecule (x, y, z) and C(41) on molecule (1/2 - x, 1/2 + y, 1/2 - z). The closest intermolecular nonbonding approaches to manganese are greater than 4 Å. Final atomic positional coordinates, with estimated standard deviations, bond lengths and angles and anisotropic thermal parameters are deposited.³ Selected interatomic bond distances and angles, with standard deviations derived from the refinement, are given in Table 2. The atomic nomenclature is defined in Fig. 3. Figs. 3 and 4 illustrate the molecular geometry viewed along, and perpendicular to, the normal to the C₅ plane of the C₅Ph₅⁻ ligand, respectively.

The Mn–(C₅ centroid) distance is 1.809 Å and the average Mn–C(C₅) distance of 2.178(4) Å are both slightly longer than those of (1). The Mn–(C₅ centroid) distance is at the upper end of such distances in [Mn(C₅R₅)(CO)₃] compounds, with only 8 compounds with longer Mn–(C₅ centroid) distances. It is easily the longest such distance in [Mn(η^5 -C₅R₅)(CO)₂(PX₃)] (X \neq M, P) compounds, as are, therefore, the Mn–C(C₅) distance of [Mn(C₅R₅)(CO)₃] compounds contracts on phosphine substitution, but has increased in this case. The Mn–CO distances (1.757(4), 1.773(4) Å) are indistinguishable and similar to those in (1), but relatively long

Selected average interatomic distances and angles in $[Mn(\eta^5-C_5Ph_5)-(CO)_2PMe_2Ph](2)$

Atoms	Average dimension
$Mn-C(C_5)$	2.178(4) Å
Mn–P	2.264(1) Å
Mn–CO	1.765(4) Å
C–O	1.158(4) Å
$C-C$ (C_5 ring)	1.427(5) Å
$C(C_5)$ -ipso- $C(C_6)$	1.492(5) Å
CO–Mn–CO	91.2(2)°
Mn–C–O	178.9(3)°
$C-C-C$ (C_5 ring)	108.0(3)°

for $[Mn(\eta^5-C_5R_5)(CO)_2(PX_3)]$ (X \neq M, P) compounds. As in (1), the C=O bond lengths in (2) are the same within experimental error. The Mn–P distance of 2.264(1) Å is again easily the longest in the 31 $[Mn(\eta^5-C_5R_5)(CO)_2-(PX_3)]$ (X \neq M, P) compounds reported to date (range 2.126 $\leq d \leq 2.359$, mean 2.215 Å). These distances easily exceed those of the $[Mn(\eta^5-C_5R_5)(CO)_2(PX_3)]^+$ (X \neq M, P) cations, which are included in the above analyses.

The C₅ nucleus of the pentaphenylcyclopentadienyl ligand is planar to within 0.006 Å. The C–C bond lengths of the C₅ ring range from 1.415(5) to 1.432(5) Å, the average C–C bond length being 1.427(5) Å, which is consistent with C₅Ph₅ rings in other metal complexes. The *ipso*-carbon atoms of each of the phenyl rings are displaced slightly from the C₅ plane by between 0.158 and 0.268 Å, with the average distance being 0.202 Å. This is a greater displacement than in [Mn(η^5 -C₅Ph₅) (CO)₃] (mean 0.161 Å). The *ipso*-carbon atoms of all phenyl rings are on the opposite side of the C₅ plane to the manganese atom. The phenyl rings are all also planar to within a mean deviation from the plane of

³ The atomic coordinates and thermal parameters have been submitted as supplementary material for deposition at the Cambridge Crystallographic Data Centre with deposition number CCDC 284609 (see Deposition of crystallographic data).

⁴ 41 observables from 31 compounds, ranges: Mn–(C₅ centroid) 1.744 $\leq d \leq 1.791$, mean 1.774 Å; Mn–C(C₅) 2.113 $\leq d \leq 2.211$, mean 2.140 Å.



Fig. 3. ORTEP [39] illustration of $[Mn(\eta^5-C_5Ph_3)(CO)_2PMe_2Ph]$ (2), viewed perpendicular to the C₅ ligand plane, showing the atom numbering scheme.



Fig. 4. ORTEP [39] illustration of $[Mn(\eta^5-C_5Ph_5)(CO)_2PMe_2Ph]$ (2), viewed parallel to the C_5 ligand plane, showing the atom numbering scheme.

0.012 Å and are canted at between 47.06° and 56.87° (average 51.5°) to the C₅ ring in a paddle wheel, or propeller, arrangement. The average angle between the planes of adjacent phenyl rings of the $C_5Ph_5^-$ ligand is 52.6°.

2.1.4. The $[Mn(\eta^5 - C_5 Ph_5)(CO)_2(PMe_2Ph)]$ molecule A similar "three-legged piano stool" environment about the manganese atom results from coordination by the η^5 pentaphenylcyclopentadienyl group, the two carbonyl groups and the phosphine. The most remarkable feature of the structure is the near parallel orientations of the C_5 and the PMe₂Ph phenyl planes. The angle between the phosphine phenyl and C_5 planes is only 7.55°, a consequence of the need to minimise intramolecular interferences between the phosphine methyl and cyclopentadienyl phenyl substituents. This steric pressure is also reflected in the slightly longer Mn-(C_5 centroid) distance in (2) by comparison with (1), and the considerably longer dimensions than in all [Mn(η^5 - C_5R_5) (CO)₂(PX₃)] (X \neq M, P) compounds reported to date.

With the chiral $C_5Ph_5^-$ phenyl propeller, and the chirality at the manganese atom, molecule (2) is diastereotopic in the solid state. However, the phenyl propellers and the phosphine substituents appear to rotate freely on the NMR time-scale at room temperature in solution, as there are no unexpected multiplicities in the ¹H, ¹³C or ³¹P NMR spectra, and, unlike [Ru(η^5 -C₅Ph₅)(CO)₂(PPh₃)Br] [26], the diastereomers are not resolved in solution.

3. Conclusions

Manganese derivatives of C₅Ar₅⁻ ligands are readily accessible in high yield from easily available starting materials. The compounds $[Mn(\eta^5-C_5Ar_5)(CO)_3]$ undergo reversible one-electron oxidations at potentials more positive than the cyclopentadienyl analogue. Substitution of one of the CO ligands by P- and C-donor ligands is conveniently effected via the intermediacy of Me₃NO. The Mn-(C₅ centroid) distances of $[Mn(\eta^5-C_5Ph_5)(CO)_3]$ and $[Mn(n^{5}-C_{5}Ph_{5})(CO)_{2}(PMe_{2}Ph)]$ are relatively long for compounds of these types. In particular, the Mn-ligand distances in $[Mn(\eta^5-C_5Ph_5)(CO)_2(PMe_2Ph)]$ are considerably longer than those reported for $[Mn(\eta^5-C_5R_5)(CO)_2(PX_3)]$ $(X \neq M, P)$ compounds to date. Although the phosphine and cyclopentadienyl phenyl substituents of $[Mn(\eta^5 C_5Ph_5(CO)_2(PMe_2Ph)$] adopt configurations minimising steric interferences in the solid state, these substituents appear to be freely rotating (on the NMR time-scale) in solution at room temperature.

4. Experimental

All manipulations were performed at atmospheric pressure under an atmosphere of dinitrogen by using conventional Schlenk techniques. Chlorobenzene (Merck) was dried, distilled and stored over calcium hydride. Tetrahydrofuran (thf) (Merck) was pre-dried over sodium wire and distilled from sodium benzophenone ketyl. *n*-Hexane (BDH) was distilled from sodium wire. Dichloromethane (Ajax) was distilled from calcium hydride. C₅Ph₅Br [27], and C₅(*p*-MeC₆H₄)₅Br [28] were prepared as described previously. Mn₂(CO)₁₀ (Aldrich), PMe₂Ph (Fluka) and 'BuNC (Aldrich) were used as received. [Mn(CO)₅Br], [Mn(CO)₃(CH₃CN)Br]₂ and [Mn(CO)₃(CH₃CN)₃]Br were prepared according to literature procedures [29–31]. Trimethylamine *N*-oxide dihydrate (Aldrich) was dehydrated by sublimation prior to use. Flash silica (240–400 mesh) was obtained from Merck. Melting points were recorded on a Reichert hot platform in air and are uncorrected. ¹H and ¹³C NMR spectra were recorded on Bruker AC200F (¹H NMR 200.13 MHz, ¹³C NMR 50.33 MHz) or Bruker AMX400 (¹H NMR 400.21 MHz) spectrometers. The spectra were referenced internally to TMS or to residual solvent resonances (CD₂Cl₃, ¹H δ 5.30 ppm, ¹³C δ 53.8 ppm). ³¹P NMR spectra were recorded on a Bruker AMX400 spectrometer operating at 162.0 MHz and were referenced to external neat trimethylphosphite (taken to be δ 140.85 ppm from 85% H₃PO₄). Electron impact mass spectra were obtained using a Kratos MS 9 geometry mass spectrometer with a direct insertion probe, a 280 °C source temperature, 70 eV ionisation voltage and 4 kV acceleration voltage.

Melting points were determined using a Gallenkamp melting point apparatus in air and are uncorrected.

Elemental analyses were carried out by one of the following departments: the Australian Microanalytical Service in Melbourne, the Microanalytical Service at the Australian National University or at the JEAF in The University of Sydney.

Infrared spectra were recorded on a Digilab FTS-40 infrared spectrophotometer either as a solution or as a suspension in a potassium bromide matrix. The resolution used was 4 cm^{-1} and the number of scans was 16.

Electrochemical experiments were performed using a BAS 100W Electrochemical Analyser. The sample cell was fitted with a plastic top that could be sealed almost air-tight. A three-electrode configuration was used. The working electrode was a BAS glassy carbon disc (3 mm diameter) which was polished with an alumina (0.25 mm grade) suspension on a velvet polishing cloth, then rinsed with distilled water and acetone, and then dipped in the solvent of use for one minute before each cyclic voltammogram was recorded. The auxiliary electrode was a platinum wire (0.5 mm diameter, 4 cm length) which did not need cleaning between voltammograms but was cleaned by rinsing with 5 M aqueous HNO₃, distilled water and the solvent used prior to each set of experiments. The reference electrode was a BAS Ag/AgCl/NaCl (3 M) electrode with a vycor frit. All samples were thoroughly degassed with high purity argon (CIG) which was passed through a scrubber and a drying tower to remove any traces of oxygen and water, respectively. All potentials are quoted relative to the ferrocenium/ferrocene redox couple, which was observed at ca. 500 mV against the reference electrode [Ag/AgCl/NaCl (3 M)]. Samples were prepared as approximately 1 mM solutions with tetra-(*n*-butyl)ammonium tetrafluoroborate (TBATFB ca. 0.1 M) as the supporting electrolyte. TBATFB was prepared either from aqueous HBF₄ (35% v/v, Merck) and $(n-C_4H_9)$ NOH (40% w/w, Aldrich) or by recrystallisation of TBATFB (Aldrich) three times from ethyl acetate/diethyl ether in air, then drying in vacuo. Full iR (100%) compensation was employed in each scan. Except as otherwise stated, all measurements were carried out in dichloromethane

solution with 0.1 M TBATFB as the supporting electrolyte and a scan rate of 100 mV s^{-1} .

4.1. Preparation of $[Mn(\eta^{5}-C_{5}Ph_{5})(CO)_{3}]$ (1)

4.1.1. Method A: reaction of $[Mn(CO)_3(CH_3CN)_3]Br$ with LiC_5Ph_5

A solution of LiC₅Ph₅ (1.0 mmol) in tetrahydrofuran (10 mL) was added to a solution of [Mn(CO)₃(CH₃CN)₃]Br (0.34 g, 1.0 mmol) in tetrahydrofuran (10 mL). The solution was refluxed with stirring for 16 h, then the solvent was removed under reduced pressure. The orange/yellow solid was extracted into CH₂Cl₂, and chromatographed on a hexane/alumina column under N₂. Elution with CH₂Cl₂/hexane (1:3) gave a light yellow band which was collected. The solvent was removed under vacuum to yield [Mn- $(\eta^5-C_5Ph_5)(CO)_3$](1) as a pale yellow solid (0.40 g, 68%).

4.1.2. Method B: reaction of $[Mn(CO)_5Br]$ with LiC_5Ph_5

A solution of LiC_5Ph_5 (1.0 mmol) in tetrahydrofuran (10 mL) was added to a solution of [Mn(CO)₅Br] (0.27 g, 1.0 mmol) in tetrahydrofuran (10 mL) and the resultant solution was refluxed with stirring for 16 h. The product was purified chromatographically as in Method A (0.22 g, 38%).

4.1.3. Method C: reaction of $[Mn(CO)_3(CH_3CN)_2Br]$ with C_5Ph_5Br and Zn

mixture $[Mn(CO)_3(CH_3CN)_2Br]$ (0.15 g, Α of 0.50 mmol), C₅Ph₅Br (0.26 g, 0.50 mmol) and zinc dust (0.033 g, 0.50 mmol) in tetrahydrofuran (15 mL) was refluxed with stirring for 16 h. The product was purified chromatographically as in Method A (0.17 g, 59%). M.p. 287-289 °C. Anal. Calc. for C38H25MnO3: C, 78.08; H, 4.31. Found: C, 78.0; H, 4.3%. ¹H NMR (ppm, 200 MHz, CD₂Cl₂): δ 7.06 (br, m, 25 H, Ar-*H*). IR v_{max} (cm⁻¹, KBr): 3060 w, 2007 vs, 1934 vs, 1923 vs, 1503 w, 1445 w, 746 w, 739 w, 699 m sh, 665 m, 636 m, 559 w, v_{max} (CO) (cm⁻¹, CH₂Cl₂): 2015 s, 1934 s. MS (EI) (m/z%): 584 (M⁺, 12), 528 $(M^+ - 2CO, 17), 500 (M^+ - 3CO, 100), 446$ $(C_5Ph_5H^+, 33).$

4.2. Preparation of $[Mn(\eta^5 - C_5 Ph_5)(CO)_2(PMe_2 Ph)]$ (2)

PPhMe₂ (0.22 mL, 0.70 mmol) and trimethylamine oxide (0.045 g, 0.60 mmol) were added to a solution of [Mn(C₅Ph₅)(CO)₃] (0.295 g, 0.51 mmol) in tetrahydrofuran (30 mL) and the resulting reaction mixture was heated at reflux for 16 h. The solvent was removed in vacuo to afford an orange oil and the crude product was purified by column chromatography on alumina eluting with CH₂Cl₂/hexane (20/80 v/v). The product was recrystallised from CH₂Cl₂/hexane to give [Mn(η^5 -C₅Ph₅)(CO)₂(PMe₂Ph)] (**2**) as an orange crystalline solid (0.285 g, 81%). M.p. 287–289 °C. *Anal.* Calc. for C₄₅H₃₆MnOP: C, 77.80; H, 5.22. Found: C, 77.4; H, 4.9%. ¹H NMR (CDCl₃): δ 7.55–6.75 (br m, 30H, (C₆H₅)C₅ and P(C₆H₅)), 1.59 (br s, 6H, 2 × PCH₃) ppm.

³¹P{¹H} NMR (CDCl₃): δ 45.86 (s) ppm. I.R. (KBr): v 1850 (vs), 1918 (vs) cm⁻¹.

4.3. Preparation of $[Mn(\eta^5-C_5(p-tol)_5)(CO)_3]$ (3)

4.3.1. Method A: reaction of $[Mn(CO)_3(CH_3CN)_3]Br$ with $LiC_5(p-tol)_5$

A solution of $\text{LiC}_5(p\text{-tol})_5$ (0.87 mmol) in tetrahydrofuran (10 mL) was added to a solution of $[\text{Mn}(\text{CO})_3\text{-}(\text{CH}_3\text{CN})_3]\text{Br}$ (0.30 g, 0.86 mmol) in tetrahydrofuran (10 mL). The resultant solution was refluxed with stirring for 16 h, then the solvent was removed under reduced pressure. The orange/yellow solid was extracted into CH₂Cl₂, and chromatographed on a hexane/alumina column under N₂. Elution with CH₂Cl₂/hexane (1:5) gave a light yellow band which was collected. The solvent was then removed to yield $[\text{Mn}(\eta^5\text{-}\text{C}_5(p\text{-tol})_5)(\text{CO})_3]$ (3) as a pale yellow solid (0.19 g, 34%).

4.3.2. Method B: reaction of $[Mn(CO)_3(CH_3CN)_3]$ Br with $C_5(p-tol)_5$ Br and Zn

Tetrahydrofuran (15 mL) was added to a solid mixture of $[Mn(CO)_3(CH_3CN)_3]Br (0.34 \text{ g}, 1.0 \text{ mmol}), C_5(p-tol)_5Br (0.59 \text{ g}, 1.0 \text{ mmol})$ and zinc dust (0.075 g, 1.1 mmol). The resultant solution was refluxed with stirring for 16 h. The product was purified chromatographically as in Method A (0.45 g, 69%).

M.p. 255–257 °C. Anal. Calc. for $C_{43}H_{35}MnO_3$: C, 78.89; H, 5.39. Found: C, 78.1; H, 5.2%. ¹H NMR (ppm, 200 MHz, CD₂Cl₂): δ 7.09–6.83 (m, 20H, Ar-H) 2.26– 2.17 (m, 15H, CH₃). IR v_{max} (cm⁻¹, KBr): 3020 w, 2922 w, 2008 vs, 1932 vs, 1926 vs, 1520 m, 1187 w, 1020 w, 838 w, 820 w, 805 w, 728 w, 666 m, 630 m, 538 m sh. MS (EI) (*m*/*z*%): 654 (M⁺, 4.4), 598 (M⁺ – 2CO, 2), 570 (M⁺ – 3CO, 100), 526 (C₅Ph₅H⁺, 34).

4.4. Structure determinations

[Mn(η^{5} -C₅Ph₅)(CO)₃] (1): a yellow blade like crystal having approximate dimensions of 0.47 × 0.20 × 0.12 mm was attached to a thin glass fibre, and mounted on an Enraf-Nonius CAD4 diffractometer employing graphite monochromated Mo K α radiation. Primitive monoclinic cell constants were obtained from a least-squares refinement using the setting angles of 25 reflections in the range $16.02 < 2\theta < 24.24^{\circ}$. Diffraction data were collected at a temperature of 21 ± 1 °C using ω scans to a maximum 2θ value of 49.9°. The intensities of three representative reflections measured every 60 min, decreased by 53.2% and a polynomial correction factor was accordingly applied to the data. An analytical absorption correction was applied and the data were also corrected for Lorentz and polarisation effects.

All calculations were undertaken with the TEXSAN [32] crystallographic software package. Neutral atom scattering factors were taken from Cromer and Waber [33]. Anomalous dispersion effects were included in Fcalc [34] and the

values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [35]. The values for the mass attenuation coefficients were those of Creagh and Hubbell [36]. The structure was solved in the space group $P2_1/n$ (#14) by heavy-atom Patterson methods [37] and expanded using Fourier techniques [38]. In general non-hydrogen atoms were modelled anisotropically, however C(3), C(5), C(17), C(18), C(30) and C(35) were refined with isotropic thermal parameters. Hydrogen atoms were included in the model at calculated positions with group thermal parameters. ORTEP projections of the molecule are provided in Figs. 2 and 3 [39].

4.5. Crystal data for $[Mn(\eta^5 - C_5 Ph_5)(CO)_3]$ (1)

Formula C₃₈H₂₅MnO₃, *M* 584.52, monoclinic, space group *P*2₁/*n* (#14), *a* 16.929(4), *b* 8.928(2), *c* 20.054(4) Å, β 106.04(2), *V* 2913.0(11) Å³, *D*_c 1.333 g cm⁻³, *Z* 4, crystal size 0.47 by 0.20 by 0.12 mm, colour yellow, habit blade, temperature 294(2) K, λ (Mo Kα) 0.71073 Å, μ (Mo Kα) 0.4900 mm⁻¹, *T* (Analytical)_{min,max} 0.8984, 0.9489, 2 θ _{max} 49.98, *hk1* range -20 19, -1 10, -1 10, *N* 4061, *N*_{ind} 3167-(*R*_{merge} 0.0738), *N*_{obs} 2058(*I* > 2 σ (*I*)), *N*_{var} 344, residuals⁵ *R*₁(*F*) 0.0967, *wR*₂(*F*²) 0.2971, GoF(all) 1.274, $\Delta \rho_{min,max}$ -1.516, 1.455 e⁻Å⁻³.

 $[Mn(\eta^5-C_5Ph_5)(CO)_2(PMe_2Ph)]$ (2): a yellow blade like crystal having approximate dimensions of $0.28 \times 0.25 \times$ 0.11 mm was attached to a thin glass fibre, and mounted on a Rigaku AFC7R diffractometer employing graphite monochromated Cu Ka radiation from a rotating anode generator. Primitive monoclinic cell constants were obtained from a least-squares refinement using the setting angles of 21 reflections in the range $68.01 < 2\theta < 91.99^{\circ}$. Diffraction data were collected at a temperature of 21 ± 1 °C using ω -2 θ scans to a maximum 2θ value of 130.2°. Omega scans of several intense reflections made prior to data collection, had an average width at halfheight of 0.18°, and scans of $(1.73 + 0.35 \tan \theta)^\circ$ were made at a speed of 16.0°/min (in omega). The weak reflections $(I \le 15.0\sigma(I))$ were rescanned up to 10 times. Stationary background counts were recorded on each side of the reflection, with a 2:1 ratio of peak to background counting time. The intensities of three representative reflections measured every 150 reflections, did not change significantly during the data collection. An analytical absorption correction was applied and the data were also corrected for Lorentz and polarisation effects.

All calculations were undertaken with the TEXSAN [32] crystallographic software package. Neutral atom scattering factors were taken from Cromer and Waber [33]. Anomalous dispersion effects were included in Fcalc [34] and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [35]. The values for the mass attenuation coefficients were those of Creagh and Hubbell [36]. The structure was solved

in the space group $P2_1/n$ (#14) by direct methods [40] and expanded using Fourier techniques [38]. Non-hydrogen atoms were modeled with anisotropic thermal parameters and hydrogen atoms were included in the model at calculated positions with group thermal parameters. ORTEP projections of the molecule are provided in Figs. 1 and 2 [39].

4.6. Crystal data for $[Mn(\eta^5-C_5Ph_5)(CO)_2(PMe_2Ph)]$ (2)

Formula C₄₅H₃₃MnO₂P, *M* 691.62, monoclinic, space group *P*2₁/*n*(#14), *a* 15.251(4), *b* 13.804(3), *c* 17.682(4) Å, *β* 106.39(2), *V* 3571.2(15) Å³, *D_c* 1.286 g cm⁻³, *Z* 4, crystal size 0.28 by 0.25 by 0.11 mm, colour yellow, habit blade, temperature 294(2) K, λ (Cu Kα) 1.5418 Å, μ (Cu Kα) 3.714 mm⁻¹, *T*(Analytical)_{min,max} 0.420, 0.698, 2 θ _{max} 130.20, *hk1* range 0 17, 0 16, -20 19, *N* 6028, *N*_{ind} 6027 (*R*_{merge} 0.05469), *N*_{obs} 4016(*I* > 2 σ (*I*)), *N*_{var} 443, residuals⁶ *R*₁(*F*) 0.0472, *wR*₂(*F*²) 0.1356, GoF(all) 1.189, $\Delta \rho$ _{min,max} -0.383, 0.495 e⁻Å⁻³.

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⁶ $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^{1/2}$ all reflections $w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.0P]$ where $P = (F_o^2 + 2F_c^2)/3$.

⁵ $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^{1/2}$ all reflections $w = 1/[\sigma^2(F_o^2) + (0.10P)^2 + 15.0P]$ where $P = (F_o^2 + 2F_c^2)/3$.

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