η^2 Complexes of Cyclic Polyolefins: Crystal Structure of [$Mn(CO)_2(\eta^2$-$C_8H_8)(\eta$-$C_5H_5)$]†

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Treatment of [$Mn(CO)_2(thf)(\eta$-$C_5H_5)$] (thf = tetrahydrofuran) with cyclo-octatetraene produces [$Mn(CO)_2(\eta^2$-$C_8H_8)(\eta$-$C_5H_5)$], whose structure was determined by *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$, with four molecules in a unit cell of dimensions a = 10.813(7), b = 6.606(4), c = 17.164(9) Å, β = 94.68(5)°. The structure was solved by conventional techniques and refined by least squares to R 0.034 for 2 787 independent diffracted intensities. The molecule contains an η^2-cyclo-octatetraene ligand which possesses mirror symmetry and presents the convex face of a tub conformation towards the cyclopentadienyl ring. Nuclear magnetic resonance spectra show that the complex is non-fluxional below the temperature (*ca.* 75 °C) at which it decomposes to the dimanganese μ-cyclo-octatetraene complex [$\{Mn(CO)_2(\eta$-$C_5H_5)\}_2(\mu$-$C_8H_8)$]. The η^2-cyclo-octatetraene is readily displaced by phosphine ligands. Analogous η^2-olefin complexes of manganese are obtained from cycloheptatriene and cyclo-octa-1,3,6-triene.

PERHAPS the most distinctive feature of cyclo-octatetraene as a ligand in transition-metal chemistry is its versatility. The ability of the hydrocarbon to vary its mode of co-ordination to suit the requirements of a particular metal–ligand grouping is reflected in the wide variety of its complexes. Species are known in which cyclo-octatetraene is η^3-bonded {as in [$Nb(\eta^3$-$C_8H_8)_2(\eta^4$-$C_8H_8)$][$AsPh_4$][1]}, η^4-bonded {as in [$Fe(CO)_3$(1—4-η-C_8H_8)],[2] [$Os(CO)_3$(1,2,3,6-η-C_8H_8)],[3] and [Co(1,2,5,6-η-$C_8H_8)(\eta$-C_5H_5)][4]}, η^6-bonded {as in [$Mo(CO)_3$(1—6-η-C_8H_8)][5]}, or η^8-bonded {as in [$U(\eta$-$C_8H_8)_2$][6]}, and there are many in which two or three metal atoms are bridged by the hydrocarbon. There is not, however, any well authenticated complex of cyclo-octatetraene as an η^2 ligand. *X*-Ray diffraction has revealed that in catenated [$CuCl(C_8H_8)$] cyclo-octatetraene is bonded to copper substantially through one double bond, but there are indications of a weaker interaction with a second.[7] Again, [$Fe(CO)_2(C_8H_8)(C_5H_5)$]$^+$ may, on the basis of a ^{1}H n.m.r. spectrum, contain η^2-cyclo-octatetraene but the complex is unstable and incompletely characterised.[8] The invoking by us [9] and others [10] of a transient η^2 mode during reactions of co-ordinated cyclo-octatetraene prompted us to synthesise and investigate the chemistry of an η^2-cyclo-octatetraene complex. We describe here the chemistry of a complex which is shown unequivocally to contain cyclo-octatetraene co-ordinated in an η^2 mode, and also related complexes of η^2-cycloheptatriene and η^2-cyclo-octa-1,3,6-triene. Aspects of the work have appeared in a preliminary communication,[11] subsequent to which paramagnetic [$Nb(C_8H_8)(\eta$-$C_5H_5)_2$] has been reported, on the basis of its i.r. spectrum, to contain η^2-cyclo-octatetraene.[12]

RESULTS AND DISCUSSION

Photochemically induced substitution of a single carbonyl ligand of [$Mn(CO)_3(\eta$-$C_5H_5)$] has been achieved with a wide variety of ligands. The fact that mono- and di-olefins such as cyclo-octene and cyclo-octa-1,5-diene [13] are among these suggested that [$Mn(CO)_2(\eta^2$-$C_8H_8)(\eta$-$C_5H_5)$] (1) might be obtained as a stable complex. Although substitution of [$Mn(CO)_3(\eta$-$C_5H_5)$] can be achieved by u.v. irradiation in the presence of a ligand in a non-co-ordinating solvent, it is generally more efficient to irradiate the complex in a co-ordinating solvent such as tetrahydrofuran (thf) to produce [$Mn(CO)_2(thf)(\eta$-$C_5H_5)$], which is then treated with the ligand. This was found to be the case for each of the complexes described in this work.

The methods of preparation for [$Mn(CO)_3(\eta$-$C_5H_5)$] which are described in the literature usually require high pressures of carbon monoxide.[14] In order to facilitate our investigations we sought a synthesis of the compound directly from the now readily available [15] [$Mn_2(CO)_{10}$] and discovered that treating the carbonyl in boiling octane with dicyclopentadiene for *ca.* 3 d produced [$Mn(CO)_3(\eta$-$C_5H_5)$] in 70% yield and high purity.

η^2-*Cyclo-octatetraene.*—Ultraviolet irradiation of a thf solution of [$Mn(CO)_3(\eta$-$C_5H_5)$] generated red [$Mn(CO)_2(thf)(\eta$-$C_5H_5)$], which was stirred with cyclo-octatetraene at room temperature to give [$Mn(CO)_2(\eta^2$-$C_8H_8)(\eta$-$C_5H_5)$] (1) in 20% yield as orange crystals moderately stable in air but very oxygen-sensitive in solution. In addition, a small amount of red crystalline [$\{Mn(CO)_2(\eta$-$C_5H_5)\}_2(\mu$-$C_8H_8)$] (2) was obtained, arising from η^2 co-ordination of two olefinic bonds with manganese.

The two carbonyl stretching absorptions for (1) in the i.r. (1 971s, 1 915s cm^{-1}) are at considerably lower frequency than those of [$Mn(CO)_3(\eta$-$C_5H_5)$] (2 030s, 1 946s cm^{-1}), in accord with poor π-acceptor capacity of the olefinic bond relative to carbon monoxide. This is also reflected in the high lability of η^2-cyclo-octatetraene, discussed below. Evidence for the co-ordination of only one olefinic bond of cyclo-octatetraene to manganese in solution is provided by n.m.r. data, ruling out the possibility of additional co-ordination from the C_8H_8 ring and a shift of the cyclopentadienyl co-ordination in the direction of η^3-C_5H_5. The latter mode has recently been characterised in [$W(CO)_2(\eta^3$-$C_5H_5)(\eta^5$-$C_5H_5)$].[16] The ^{1}H n.m.r. spectrum of (1) displays a singlet for the cyclopentadienyl protons [τ 6.07 (5 H)] and resonances due to the unco-ordinated [τ 3.82 m (2 H),

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† Dicarbonyl(1—2-η-cyclo-octatetraene)(η-cyclopentadienyl)-manganese.

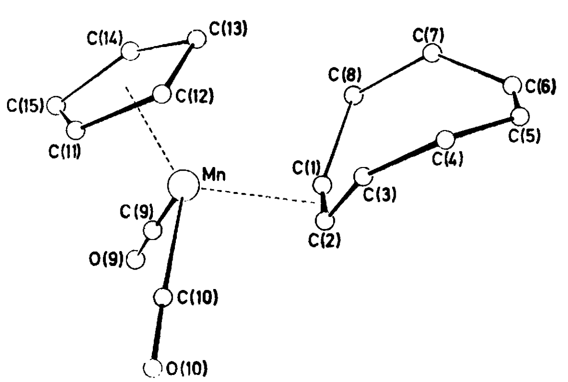


FIGURE 1 Molecular structure of $[Mn(CO)_2(\eta^2\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$ (1), showing the crystallographic numbering

4.49m (4 H)] and co-ordinated [τ 6.86m (2 H)] olefinic protons of η^2-C_8H_8. This conclusion is supported by the ^{13}C n.m.r. spectrum, which has a CO resonance at 234.9, a C_5H_5 resonance at 86.3, and resonances due to four pairs of equivalent ring-carbon atoms, three characteristic of unco-ordinated olefinic carbon (133.6, 126.8, 124.8) and one of co-ordinated olefinic carbon [56.9 p.p.m. (downfield of $SiMe_4$)].

η^2 Co-ordination of cyclo-octatetraene was established for (1) in the solid state by *X*-ray diffraction. The molecular geometry and atom-numbering system are shown in Figure 1 and the crystal packing arrangement in Figure 2, while Tables 1 and 2 summarise the results obtained. The manganese atom is in almost ideal octahedral co-ordination with the cyclopentadienyl ring occupying three facial sites, the two carbonyls one site each, and the remaining site occupied by a double bond of the tetraene [angles C(9)–Mn–C(10) 89°, C(9)–Mn–C(1,2) 94°, C(10)–Mn–C(1,2) 93°; where C(1,2) is the midpoint of the co-ordinated double bond C(1)–C(2)]. The molecule possesses a (non-crystallographic) plane of symmetry, which bisects the $Mn(CO)_2$ angle and passes through C(13) and the midpoints of the C(11)–C(15), C(1)–C(2), and C(5)–C(6) bonds. The mirror symmetry of the cyclo-octatetraene ligand is apparent in the torsion angles around the ring (Table 3), which also show the atom sequences C(8,1,2,3) and C(4,5,6,7) to be planar, and the sequences C(2,3,4,5) and C(6,7,8,1) to deviate slightly from planarity.

TABLE 1

Atomic positional co-ordinates (fractional cell co-ordinates) for $[Mn(CO)_2(\eta^2\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$, complex (1), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	0.374 8(2)	−0.004 4(2)	0.422 9(1)
C(2)	0.383 5(2)	0.191 6(3)	0.453 7(1)
C(3)	0.431 7(2)	0.376 4(3)	0.418 0(1)
C(4)	0.539 3(2)	0.402 1(3)	0.385 7(1)
C(5)	0.637 7(2)	0.256 8(3)	0.372 5(1)
C(6)	0.629 3(2)	0.068 4(3)	0.343 2(1)
C(7)	0.520 1(2)	−0.048 8(3)	0.315 0(1)
C(8)	0.412 3(2)	−0.077 0(3)	0.346 4(1)
C(9)	0.154 3(2)	−0.115 2(3)	0.455 1(1)
C(10)	0.170 8(2)	0.235 3(3)	0.510 0(1)
C(11)	0.043 6(2)	0.324 2(3)	0.366 7(1)
C(12)	0.155 9(2)	0.379 0(3)	0.336 0(1)
C(13)	0.198 5(2)	0.212 8(3)	0.294 9(1)
C(14)	0.113 2(2)	0.053 7(3)	0.299 2(1)
C(15)	0.016 3(2)	0.123 1(4)	0.344 2(1)
H(1)	0.374 2(21)	−0.109 0(32)	0.460 4(13)
H(2)	0.387 2(20)	0.209 0(33)	0.509 8(12)
H(3)	0.384 1(21)	0.500 1(36)	0.427 2(13)
H(4)	0.559 4(22)	0.529 9(37)	0.373 7(13)
H(5)	0.715 9(24)	0.308 3(39)	0.383 7(14)
H(6)	0.710 4(22)	0.001 6(35)	0.335 0(13)
H(7)	0.533 2(20)	−0.123 1(31)	0.265 9(13)
H(8)	0.357 3(20)	−0.171 4(32)	0.319 6(12)
H(11)	0.002 7(21)	0.400 8(32)	0.397 6(14)
H(12)	0.197 4(26)	0.512 3(45)	0.345 3(16)
H(13)	0.272 3(26)	0.213 1(40)	0.271 0(15)
H(14)	0.116 2(25)	−0.072 0(44)	0.277 3(16)
H(15)	−0.049 4(24)	0.044 7(39)	0.355 5(14)
Mn	0.187 94(2)	0.126 83(4)	0.415 96(1)
O(9)	0.130 7(1)	−0.271 8(2)	0.478 9(1)
O(10)	0.159 4(1)	0.302 6(2)	0.571 1(1)

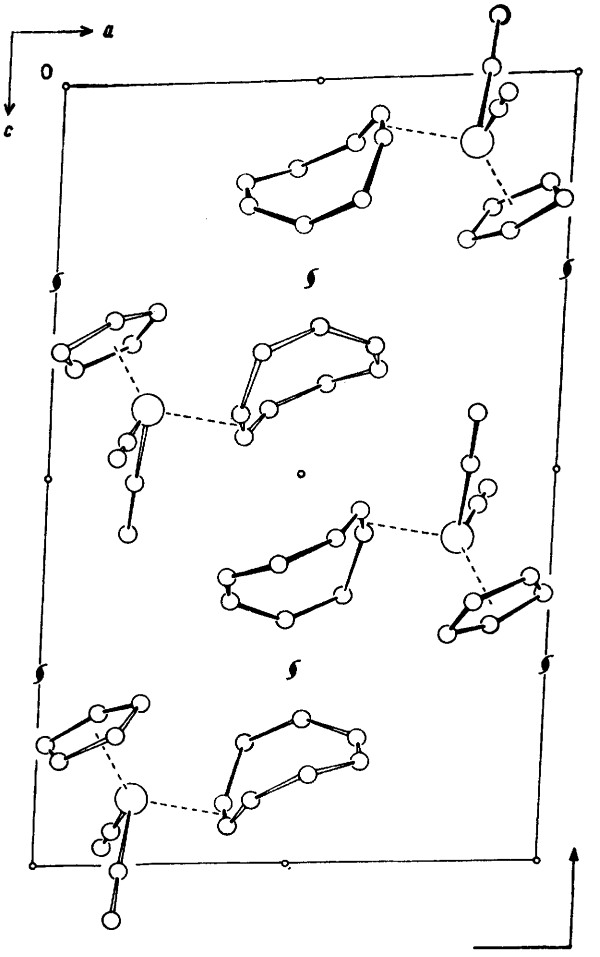


FIGURE 2 Contents of the monoclinic unit cell of (1) seen in projection down *b* towards the origin

The folds in the C_8 ring along C(3) · · · C(8) and C(4) · · · C(7) produce dihedral angles of *ca.* 143 and 147° respectively, and the Mn–C(1)–C(2) plane makes a dihedral angle of *ca.* 106° with the C(8,1,2,3) portion of the ring. The cyclo-octatetraene ligand thus presents the convex face of a tub conformation towards the cyclopentadienyl ring, with the plane of the C_5 ring effectively parallel to the plane of the atoms C(3,4,7,8); dihedral angle 1.7°. This conformation is therefore little distorted from that found for free cyclo-octatetraene in the solid state (C=C, 1.34; C–C, 1.54 Å; internal angles all 125°). The co-ordinated double bond in (1) is long [C(1)–C(2) 1.398 (2) Å], but the three free double bonds are normal (mean 1.34 Å). The mean single bond length is 1.47 Å and the ring internal angles are slightly opened (mean 129°).

TABLE 2

Bond distances and angles in $[Mn(CO)_2(\eta^2\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$, (1)

(*i*) Distances (Å)			
(*a*) Metal–carbon			
Mn–C(1)	2.193(2)	Mn–C(11)	2.152(2)
Mn–C(2)	2.202(2)	Mn–C(12)	2.168(2)
Mn–C(9)	1.783(2)	Mn–C(13)	2.167(2)
Mn–C(10)	1.790(2)	Mn–C(14)	2.153(2)
		Mn–C(15)	2.141(2)
(*b*) Carbonyl groups			
C(9)–O(9)	1.148(2)	C(10)–O(10)	1.155(2)
(*c*) Cyclo-octatetraene ring			
C(1)–C(2)	1.398(2)	C(5)–C(6)	1.342(3)
C(2)–C(3)	1.479(2)	C(6)–C(7)	1.461(3)
C(3)–C(4)	1.340(2)	C(7)–C(8)	1.337(3)
C(4)–C(5)	1.464(3)	C(8)–C(1)	1.484(2)
(*d*) Cyclopentadienyl ring			
C(11)–C(12)	1.410(3)	C(13)–C(14)	1.404(3)
C(12)–C(13)	1.403(3)	C(14)–C(15)	1.427(3)
		C(15)–C(11)	1.408(3)
(*ii*) Angles (°)			
C(9)–Mn–C(10)	88.8(1)	C(6)–C(7)–C(8)	130.3(2)
Mn–C(9)–O(9)	178.4(2)	C(7)–C(8)–C(1)	128.4(2)
Mn–C(10)–O(10)	179.0(2)	C(8)–C(1)–C(2)	128.2(2)
C(1)–C(2)–C(3)	128.5(1)	C(11)–C(12)–C(13)	108.4(2)
C(2)–C(3)–C(4)	128.5(2)	C(12)–C(13)–C(14)	108.3(2)
C(3)–C(4)–C(5)	130.4(2)	C(13)–C(14)–C(15)	107.6(2)
C(4)–C(5)–C(6)	129.6(2)	C(14)–C(15)–C(11)	107.7(2)
C(5)–C(6)–C(7)	130.1(2)	C(15)–C(11)–C(12)	107.9(2)
C(9)–Mn–C(1,2)	93.8 *	C(10)–Mn–C(1,2)	92.9 *

* C(1,2) is the midpoint of C(1)–C(2).

The n.m.r. data presented earlier for (1) are consistent only with a stereochemically rigid molecule at room temperature. It is evident that the rapid bond shift isomerisation [17] of free cyclo-octatetraene is quenched on co-ordination of the $[Mn(CO)_2(\eta\text{-}C_5H_5)]$ species to one olefinic bond. Efforts to induce a fluxional migration of the metal grouping about the C_8H_8 ring, such as occurs with $[Fe(CO)_3(\eta^4\text{-}C_8H_8)]$ [18] and $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$,[19] were thwarted by the decomposition of (1) above *ca.* 75 °C. The products are $[\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_2(C_8H_8)]$ (2) and cyclo-octatetraene.

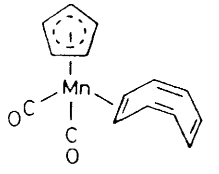
The dimanganese complex, also formed as a co-product in the synthesis of (1), is very unstable in solution. It decomposes to paramagnetic material which has prevented an n.m.r. spectrum being obtained. Since in the mass spectrum the heaviest ion corresponds only to $[Mn(CO)_2(C_8H_8)(C_5H_5)]^+$ the formulation relies heavily on analytical data and on the precedent established by the existence of the cyclo-octa-1,5-diene complex $[\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_2(C_8H_{12})]$ (3).[13] The i.r. spectrum of (2) has six terminal carbonyl stretching frequencies, indicating that isomers (2a) and (2b) are present in solution.

TABLE 3

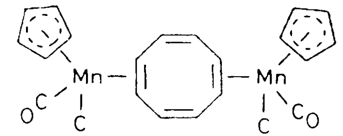
Torsion angles (°) in the C_8 ring

C(8)–C(1)–C(2)–C(3)	0.0	C(4)–C(5)–C(6)–C(7)	0.0
C(1)–C(2)–C(3)–C(4)	−50.0	C(5)–C(6)–C(7)–C(8)	−46.2
C(2)–C(3)–C(4)–C(5)	3.2	C(6)–C(7)–C(8)–C(1)	−3.8
C(3)–C(4)–C(5)–C(6)	45.7	C(7)–C(8)–C(1)–C(2)	50.1

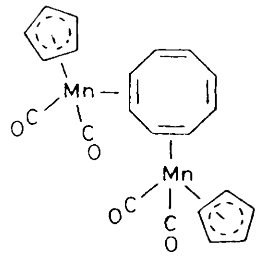
The η^2-cyclo-octatetraene ligand is highly labile. At room temperature (1) reacts with $P(OMe)_3$ or PPh_3 to provide the appropriate complex $[Mn(CO)_2(PR_3)(\eta\text{-}C_5H_5)]$ [20] quantitatively in under 2 h. In this behaviour (1) is comparable with the *cis*-cyclo-octene complex $[Mn(CO)_2(\eta^2\text{-}C_8H_{14})(\eta\text{-}C_5H_5)]$.[21] Attempts to protonate the C_8H_8 ring of (1) failed. However, treatment with $[CPh_3][BF_4]$ resulted in a shift of ν(CO) to higher frequency [2 022, 1 979s cm^{-1} (acetone)], consistent with the addition of CPh_3^+ to the C_8H_8 ring, but no complex could be isolated. Similar addition to $[Fe(CO)_3(\eta^4\text{-}C_8H_8)]$ has been reported.[22] It has been suggested that η^2-cyclo-octatetraene is involved in reactions where η^2-cyclo-octatetraene complexes undergo (*formally*) electrocyclic additions; *e.g.* with cyclo-octatetraene itself [9,23] and with electrophilic alkynes.[10] However, treatment of (1) with hexafluorobut-2-yne resulted only in decomposition to (2).



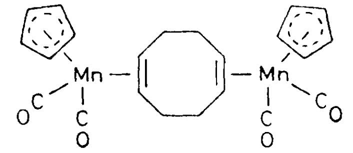
(1)



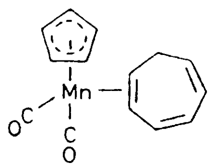
(2a)



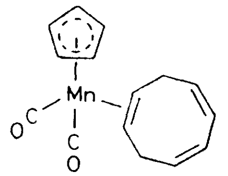
(2b)



(3)



(4)



(5)

η^2-Cycloheptatriene.—Addition of cycloheptatriene to a thf solution of $[Mn(CO)_2(thf)(\eta\text{-}C_5H_5)]$ gives, after chromatographic separation, yellow crystals of $[Mn(CO)_2(\eta^2\text{-}C_7H_8)(\eta\text{-}C_5H_5)]$ (4), identified by i.r., mass, and n.m.r. spectra. The complex is even more unstable than (1) in solution and was obtained in poor yield, in company with traces of a complex suggested to be the cycloheptatriene analogue of (2).

The frequencies (1 965s, 1 909s cm^{-1}) of the two carbonyl i.r. bands of (4) indicate that η^2-cycloheptatriene is a less effective π acceptor than η^2-cyclo-octatetraene. There are clearly two possible isomers for $[\mathrm{Mn(CO)_2(\eta^2\text{-}C_7H_8)(\eta\text{-}C_5H_5)}]$, in which the manganese is co-ordinated either to an olefinic bond adjacent to the ring methylene or to the central double bond. Nuclear magnetic resonance spectra reveal that the bonding is exclusively as in (4). There are seven chemical shifts in the ^{1}H n.m.r. spectrum, whereas at most five could be expected for the alternative isomer. In addition, the ^{13}C n.m.r. spectrum comprises the two carbonyl signals required by the asymmetry of (4) and six ring-carbon resonances; three (a further one obscured by solvent signals) due to unco-ordinated olefinic carbons (137.8, 131.0, 128.2), two to co-ordinated olefinic carbons (53.6, 52.6), and one to the methylenic carbon (34.0 p.p.m.).

The instability of (4) and its low yield of formation prohibited adequate investigation of its chemistry, so that we were unable to determine whether treatment with $[\mathrm{CPh_3}][\mathrm{BF_4}]$ afforded $[\mathrm{Mn(CO)_2(\eta^3\text{-}C_7H_7)(\eta\text{-}C_5H_5)}]^+$ or $[\mathrm{Mn(CO)_2(\eta^3\text{-}C_7H_8CPh_3)(\eta\text{-}C_5H_5)}]^+$.

η^2-Cyclo-octatriene.—Cyclo-octatriene, obtained by reduction of cyclo-octatetraene, exists as a mixture of cyclo-octa-1,3,6-triene, cyclo-octa-1,3,5-triene, and bicyclo[4.2.0]octa-2,4-diene. It was therefore not surprising that addition to $[\mathrm{Mn(CO)_2(thf)(\eta\text{-}C_5H_5)}]$ provided, after chromatography, four products. Three of these had i.r. spectra typical of dicarbonylmanganese complexes and the other, isolated in trace amounts, had the characteristics of an analogue of (2). Only one of the dicarbonyls was obtained in a significant yield (15%), yellow crystals formulated as $[\mathrm{Mn(CO)_2(\eta^2\text{-}C_8H_{10})(\eta\text{-}C_5H_5)}]$. Nuclear magnetic resonance spectra reveal that this is a complex (5) of cyclo-octa-1,3,6-triene. The ^{13}C n.m.r. spectrum contains one CO resonance and four ring-carbon resonances, two due to unco-ordinated olefinic carbons (134.1, 126.7), one to co-ordinated olefinic carbon (54.2), and one to methylenic carbon (31.2 p.p.m.), in accord with mirror symmetry for the co-ordinated hydrocarbon. The ^{1}H n.m.r. spectrum has signals at τ 4.32 s, br (4 H), 6.80 m (2 H), and 7.44 m (4 H). Double irradiation experiments showed that there was no discernible coupling between the co-ordinated (τ 6.80) and unco-ordinated (τ 4.32) olefinic protons, as required by (5) and in contrast to what would be expected of a complex of cyclo-octa-1,3,5-triene or bicyclo[4.2.0]octa-2,4-diene.

Both in (4) and (5) can be seen a tendency for co-ordination of manganese to an olefinic bond with adjacent methylenic carbons. This may be in part due to an ability of these *sp*^{3}-hybridised carbons to accommodate the angular changes resulting from co-ordination of the olefinic bond.

Ultraviolet irradiation of $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_5)}]$ in toluene in the presence of cycloheptatriene or cyclo-octatetraene has been reported to effect complete carbonyl substitution and formation of $[\mathrm{Mn(\eta\text{-}C_5H_5)(\eta^6\text{-}C_7H_8)}]$ or $[\mathrm{Mn(\eta\text{-}C_5H_5)(\eta^6\text{-}C_8H_8)}]$ respectively.[24] Both the solvent, *via* an intermediate $[\mathrm{Mn(\eta\text{-}C_5H_5)(\eta^6\text{-}C_6H_5Me)}]$, and u.v. radiation source, which was more powerful than that used by us, could play a role in this more extensive substitution.

EXPERIMENTAL

Synthetic Studies.—Infrared spectra were recorded using a Perkin-Elmer 257 spectrometer with calcium fluoride cells of 1.0 mm path length and calibrated *via* the 1 601 cm^{-1} absorption of polystyrene. Proton n.m.r. spectra were obtained on either Varian Associates HA100 or JEOL PS100 instruments and ^{13}C n.m.r. spectra on a JEOL PFT100 instrument. Mass spectra were produced on an AEI MS 902 spectrometer operating at 70 eV. Reactions were performed in a nitrogen atmosphere using deoxygenated solvents which were dried immediately before use by distillation from calcium hydride or lithium aluminium hydride. Chromatography was on silica gel columns. Cyclic polyolefins were distilled before use. The u.v. radiation source was a 250-W mercury lamp.

Preparation of $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_5)}]$.—Dicyclopentadiene (25 g, 192 mmol) and $[\mathrm{Mn_2(CO)_{10}}]$ (10 g, 25.6 mmol) were heated in n-octane (300 cm^3) at reflux for 70 h. Octane and some dicyclopentadiene were then removed at reduced pressure and the residue dissolved in dichloromethane and filtered to remove a manganese dioxide precipitate. The filtrate was evaporated under reduced pressure to leave a yellow oil which, on addition of hexane and cooling to -30 °C, gave yellow crystals. After removal of the crystals second and third crystallisations were effected. The combined product was then sublimed (30 °C, 10^{-1} Torr) * onto a water-cooled probe as pure $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_5)}]$ (7.3 g, 70%), identified by comparison of its i.r. [ν(CO) 2 027s, 1 946s cm^{-1}] and ^{1}H n.m.r. (τ 6.07s) spectra with literature data.[25]

Reactions of $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_5)}]$.—(a) *With cyclo-octatetraene.* A thf solution (80 cm^3) of $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_5)}]$ (0.5 g, 2.5 mmol) was subjected to u.v. radiation for 2 h, generating a red solution of $[\mathrm{Mn(CO)_2(thf)(\eta\text{-}C_5H_5)}]$. Cyclo-octatetraene (2.5 g, 24 mmol) was then added and the mixture stirred, without irradiation, for 1 h. Removal of solvent under reduced pressure and chromatography of the residue in hexane, eluting with dichloromethane–hexane (1 : 9), gave yellow and orange bands. The first contained unreacted $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_5)}]$ and the second $[\mathrm{Mn(CO)_2(\eta^2\text{-}C_8H_8)(\eta\text{-}C_5H_5)}]$ (1), obtained from hexane as orange crystals [136 mg (20%); m.p. 67—69 °C; ν(CO) 1 971s, 1 915s cm^{-1} (hexane); ^{1}H n.m.r. τ 3.82 m (2 H), 4.49 m (4 H), 6.07 s (5 H), 6.86 m (2 H) ([^{2}H$_6$]benzene); ^{13}C n.m.r. 234.9, 133.6, 126.8, 124.8, 86.3, 56.9 p.p.m. (downfield of SiMe$_4$)([^{2}H$_8$]toluene); Found: C, 64.4; H, 4.6%. *M*, 280. $\mathrm{C_{15}H_{13}MnO_2}$ requires C, 64.3; H, 4.6%. *M*, 280]. Elution with dichloromethane–hexane (1 : 2) developed a red band which gave rise to $[\{\mathrm{Mn(CO)_2(\eta\text{-}C_5H_5)}\}_2(\mathrm{C_8H_8})]$ (2), obtained from dichloromethane–hexane as red crystals {5 mg (0.5%); m.p. 106—110 °C; ν(CO) 1 979s, 1 970s, 1 959(sh), 1 954s, 1 916s, 1 911s cm^{-1} (hexane); Found: C, 57.5; H, 4.0%. *M*, 280 $[\mathrm{Mn(CO)_2(C_8H_8)(C_5H_5)}^+]$. $\mathrm{C_{22}H_{18}Mn_2O_4}$ requires C, 57.9; H, 4.0%. *M*, 456}.

(b) *With cycloheptatriene.* In a manner identical to that described in (a), cycloheptatriene (5 g, 54 mmol) and $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_5)}]$ (1 g, 4.9 mmol) provided yellow crystalline $[\mathrm{Mn(CO)_2(\eta^2\text{-}C_7H_8)(\eta\text{-}C_5H_5)}]$ (4) [75 mg (6%); m.p. 58—60 °C; ν(CO) 1 965s, 1 909s cm^{-1} (hexane); ^{1}H n.m.r.

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

τ 3.17 m (1 H), 3.92 m (2 H), 4.28 m (1 H), 6.22 s (5 H), 6.47 m (1 H), 6.89 m (1 H), 7.30 m (1 H), 8.80 m (1 H) ([$^2H_8$]-toluene); ^{13}C n.m.r. 235.5, 233.9, 137.8, 131.0, 128.2, 84.0, 53.6, 52.6, 34.0 p.p.m. ($CDCl_3$)] and *ca.* 3 mg of yellow powder identified as [{$Mn(CO)_2(\eta\text{-}C_5H_5)\}_2(C_7H_8)$] on the basis of its i.r. spectrum [ν(CO) 1 957s, 1 899s (both v br) cm^{-1} (CH_2Cl_2)].

(c) *With cyclo-octatriene.* As in (a), cyclo-octatriene (0.65 g, 6 mmol) and [$Mn(CO)_3(\eta\text{-}C_5H_5)$] (0.25 g, 1.2 mmol) gave yellow crystalline [$Mn(CO)_2(\eta^2\text{-}C_8H_{10})(\eta\text{-}C_5H_5)$] (5) [53 mg (15%); m.p. 87—89 °C; ν(CO) 1 964s, 1 906s cm^{-1} (hexane); ^1H n.m.r. τ 4.32 s, br (4 H), 6.20 s (5 H), 6.80 m (2 H), 7.44 m (4 H) ([$^2H_6$]benzene); ^{13}C n.m.r. 228.9, 134.1, 126.7, 84.3, 54.2, 31.2 p.p.m. ($CDCl_3$); Found: C, 63.8; H, 5.8%. *M*, 282. $C_{15}H_{15}MnO_2$ requires C, 63.8; H, 5.3%. *M*, 282] and a trace of yellow oil identified tentatively as containing [{$Mn(CO)_2(\eta\text{-}C_5H_5)\}_2(C_8H_{10})$] from its i.r. spectrum [ν(CO) 1 971m, 1 960s, 1 915m, 1 909s, 1 903s cm^{-1} (hexane)].

Reaction of [$Mn(CO)_2(\eta^2\text{-}C_8H_8)(\eta\text{-}C_5H_5)$] (1) *with* PPh_3.—Triphenylphosphine (56 mg, 0.2 mmol) and (1) (60 mg, 0.2 mmol) were stirred together in dichloromethane (30 cm^3) at room temperature for 2 h. Evaporation of solvent, chromatography, and crystallisation of the material from the one yellow band then gave 33 mg (35%) of yellow crystalline [$Mn(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$], identified by comparison of its i.r. and ^1H n.m.r. spectra with literature data.[20]

X-Ray Data Collection and Structure Determination.—Pale orange crystals of [$Mn(CO)_2(\eta^2\text{-}C_8H_8)(\eta\text{-}C_5H_5)$] (1) were grown from hexane solution and a prismatic crystal of dimensions 0.15 × 0.31 × 0.57 mm was selected for mounting in a Lindemann-glass capillary tube in an atmosphere of nitrogen. This was used to collect 3 269 diffracted intensities in the range $2.9 < 2\theta < 60°$ on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[26] Three check reflections were remeasured every 40 reflections, and analysis of their intensity variation gave no evidence of crystal decay during the 85 h of exposure to *X*-rays. Only the 2 787 reflections for which $I > \sigma(I)$, where $\sigma(I)$ is the estimated error based on counting statistics, were used in the solution and refinement of the structure.

Crystal data. $C_{15}H_{13}MnO_2$, $M = 280.2$, Monoclinic, $a = 10.813(7)$, $b = 6.606(4)$, $c = 17.164(9)$ Å, $\beta = 94.68(5)°$, $U = 1\,222(1)$ Å^3, D_m not measured, $Z = 4$, $D_c = 1.53$ g cm^{-3}, $F(000) = 576$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 9.9$ cm^{-1}. Space group, $P2_1/c$ (no. 14).

The structure was solved by heavy-atom methods and was refined with anisotropic thermal parameters for all non-hydrogen atoms. Electron-density difference syntheses revealed the positions of all hydrogen atoms, and these were refined with independent isotropic thermal parameters, using full-matrix least squares.[27] The H-atom positional parameters have been included in Table 1, but as the C–H distances are not of any chemical interest they have been omitted from Table 2. Weights were applied according to the scheme $w = 1.350/[\sigma^2(F_o) + 0.0003(F_o)^2]$, where $\sigma(F_o)$ is the standard deviation calculated from counting statistics, and this gave a satisfactory weight analysis. Refinement converged at *R* 0.034 (*R'* 0.034), and in the final cycle the mean shift-to-error ratio was 0.0005. A final difference synthesis showed no peaks >0.5 or <-0.5 e Å^{-3}.

Positional parameters are in Table 1, bond lengths and angles in Table 2, and some torsion angles in Table 3. No correction for *X*-ray absorption was applied [$\mu(\text{Mo-}K_\alpha) < 10$ cm^{-1}]. Atomic scattering factors were the analytic types of ref. 28 for molybdenum, carbon, and oxygen, and those of ref. 29 for hydrogen. All computational work was carried out with the SHELX system of programs [27] on the ICL system 4 computers of the South-Western Universities Computer Network. Observed and calculated structure factors, and all thermal parameters, are listed in Supplementary Publication No. SUP 22909 (20 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

REFERENCES

[1] L. J. Guggenberger and R. R. Shrock, *J. Amer. Chem. Soc.*, 1975, **97**, 6693.

[2] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 2084.

[3] M. I. Bruce, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1969, 987.

[4] F. S. Mathews and W. N. Lipscomb, *J. Phys. Chem.*, 1959, **63**, 845.

[5] J. S. McKechnie and I. C. Paul, *J. Amer. Chem. Soc.*, 1966, **88**, 5927.

[6] A. Zalkin and K. N. Raymond, *J. Amer. Chem. Soc.*, 1969, **91**, 5667.

[7] N. C. Baenziger, G. F. Richards, and J. R. Doyle, *Inorg. Chem.*, 1964, **3**, 1529.

[8] A. Cutler, D. Ehntholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, *J. Amer. Chem. Soc.*, 1976, **98**, 3495.

[9] A. P. Humphries and S. A. R. Knox, *J.C.S. Dalton*, 1978, 1514.

[10] R. E. Davis, T. A. Dodds, T. H. Hseu, J. C. Wagnon, T. Devon, J. Tancrede, J. S. McKennis, and R. Pettit, *J. Amer. Chem. Soc.*, 1974, **96**, 7562.

[11] I. B. Benson, S. A. R. Knox, R. F. D. Stansfield, and P. Woodward, *J.C.S. Chem. Comm.*, 1977, 404.

[12] C. P. Verkade, A. Westerhof, and H. J. de Liefde Meizer, *J. Organometallic Chem.*, 1978, **154**, 317.

[13] E. O. Fischer and M. Herberhold, *Experientia*, 1964, **9**, 259.

[14] 'Organometallic Syntheses,' eds. J. J. Eisch and R. B. King, Academic Press, London, 1964, vol. 1, p. 111, and refs. therein.

[15] R. B. King, J. C. Stokes, and T. F. Korenowski, *J. Organometallic Chem.*, 1968, **11**, 641.

[16] G. Huttner, H. H. Brintzinger, L. G. Bell, P. Friedrich, V. Bejenke, and D. Neugebauer, *J. Organometallic Chem.*, 1978, **145**, 329.

[17] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 671.

[18] F. A. Cotton and D. L. Hunter, *J. Amer. Chem. Soc.*, 1976, **98**, 1413.

[19] F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Amer. Chem. Soc.*, 1974, **96**, 7926.

[20] J. Müller and K. Fenderl, *J. Organometallic Chem.*, 1969, **19**, 123.

[21] R. J. Angelici and W. Loewen, *Inorg. Chem.*, 1967, **6**, 682.

[22] B. F. G. Johnson, J. Lewis, and J. W. Quail, *J.C.S. Dalton*, 1975, 1252.

[23] A. H. Connop, F. G. Kennedy, S. A. R. Knox, R. M. Mills, G. H. Riding, and P. Woodward, *J.C.S. Chem. Comm.*, 1980, 518.

[24] P. L. Pauson and J. A. Segal, *J.C.S. Dalton*, 1975, 2387.

[25] F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **1**, 175.

[26] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[27] G. M. Sheldrick, SHELX '76; a system of programs for crystallographic computations, Cambridge, 1976.

[28] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[29] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.