(η-Cycloheptatriene)- and (η-Cycloheptatrienylium)-(η-cyclopentadienyl)manganese. Formation of Cyclic Triene Complexes by Photochemical Displacement of Three Carbonyl Groups from Tricarbonyl(η-cyclopentadienyl)manganese

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Cycloheptatrienes react photochemically with tricarbonyl(η-cyclopentadienyl)manganese or its derivatives to give neutral diamagnetic (η-cycloheptatriene)(η-cyclopentadienyl)manganese compounds *via* dicarbonyl(1—2-η-cycloheptatriene) intermediates. Trityl salts convert the cycloheptatriene derivatives into (η-cycloheptatrienylium)-(η-cyclopentadienyl)manganese salts which may be reduced back by lithium tetrahydridoaluminate. 7-Substituted cycloheptatrienes yield predominantly the *exo*-substituted complexes which resist such hydride abstraction but are convertible into other isomers by hydrogen migration on heating. (η-Cyclo-octatriene)- and (1—6-η-cyclo-octatetraene)-(η-cyclopentadienyl)manganese may be obtained similarly but are much less stable than their cycloheptatriene analogues.

THE ease of displacement of carbonyl by other ligands varies widely for different metal carbonyl derivatives.[1] Where stability prevents thermal substitution, photolysis has frequently proved effective [2] as for example in the tricarbonyl(η-cyclopentadienyl)manganese series with which the present paper is concerned. Involvement of photodissociation of a carbonyl group to form a co-ordinatively unsaturated intermediate, which can readily add a wide variety of ligands, was deduced from kinetic studies [2] and is accepted as the general mechanism of such reactions. Confirmation by matrix-isolation studies includes direct observation of the dicarbonyl species [3] postulated as an intermediate in the sequence (1). Further substitution according to (2) will be inhibited if the new ligand L is displaced in preference to carbon monoxide or if it causes too great an increase in the strength of the remaining Mn–CO bonds. Whereas such disubstitution has been achieved by prolonged irradiation with, for example, phosphines, phosphites,[4] and dimethyl sulphoxide,[5] examples of trisubstitution involving reaction (3) are rare and apparently confined to ligands whose donor and acceptor properties are most similar to those of CO. Thus, apart from exchange with labelled carbon monoxide,[6] direct replacement of all CO groups by phosphorus trifluoride has been achieved; [7] stepwise preparation of the tris(thiocarbonyl) derivative,[8] in which each carbonyl is replaced photochemically by cyclo-octene and this then thermally by CS, also involves step (3) (L = CS and L′ = *cis*-cyclo-octene).

$$[\mathrm{Mn(CO)_3(C_5H_5)}] \xrightarrow[-\mathrm{CO}]{h\nu} \begin{matrix}[\mathrm{Mn(CO)_2(C_5H_5)}]\\ \text{or}\\ [\mathrm{Mn(CO)_2(C_5H_5)(solvent)}]\end{matrix} \xrightarrow{\mathrm{L}} [\mathrm{Mn(CO)_2(C_5H_5)L}] \tag{1}$$

$$[\mathrm{Mn(CO)_2(C_5H_5)L}] \xrightarrow[-\mathrm{CO}]{h\nu} [\mathrm{Mn(CO)(C_5H_5)L}] \xrightarrow{\mathrm{L'}} [\mathrm{Mn(CO)(C_5H_5)(L)L'}] \tag{2}$$

$$[\mathrm{Mn(CO)(C_5H_5)L_2}] \xrightarrow[-\mathrm{CO}]{h\nu} [\mathrm{Mn(C_5H_5)L_2}] \xrightarrow{\mathrm{L'}} [\mathrm{Mn(C_5H_5)L_2L'}] \tag{3}$$

Our own success in converting tricarbonyl(η-methylcyclopentadienyl)manganese photochemically [9] into the tris(cyano) anion, $[\mathrm{Mn(CN)_3(C_5H_4Me)}]^{3-}$, encouraged us to seek further examples, notably with hydrocarbon ligands. Photochemical reactions of $[\mathrm{Mn(CO)_3(C_5H_5)}]$ with alkenes and with dienes have been extensively studied by Fischer and Herberhold and their co-workers.[10-12] Their detailed examination of the behaviour of a range of both conjugated and unconjugated dienes showed that initial displacement of one carbonyl group with the diene acting as a unidentate ligand tended to be followed by co-ordination of the second double bond to another manganese atom. Butadiene is apparently exceptional [12] in yielding monomeric $[\mathrm{Mn(CO)(C_4H_6)(C_5H_5)}]$ while cyclohexadiene gave [11] a little of the corresponding product together with much $[\mathrm{(H_5C_5)(OC)_2Mn(\mu\text{-}C_6H_8)Mn(CO)_2(C_5H_5)}]$. Trienes were not

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[1] R. J. Angelici, *Organometallic Chem. Rev.*, 1968, **3**, 173.

[2] W. Strohmeier, *Angew. Chem.*, 1964, **76**, 873; W. Strohmeier and F. J. Müller, *Chem. Ber.*, 1969, **102**, 3608 and refs. in these papers.

[3] P. S. Braterman and J. D. Black, *J. Organometallic Chem.*, 1972, **39**, C3.

[4] See, for example, W. Strohmeier and C. Barbeau, *Z. Naturforsch.*, 1962, **B17**, 848; S. S. Sandhu and A. K. Mehta, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 891; F. Le Moigne and R. Dabard, *J. Organometallic Chem.*, 1973, **60**, C14.

[5] W. Strohmeier and J. F. Guttenberger, *Z. Naturforsch.*, 1963, **B18**, 667.

[6] I. S. Butler and A. E. Fenster, *J. Organometallic Chem.*, 1973, **51**, 307; *cf.* W. Strohmeier and D. von Hobe, *Z. Naturforsch.*, 1963, **B18**, 770.

[7] T. Kruck and V. Krause, *Z. Naturforsch.*, 1972, **B27**, 302.

[8] A. E. Fenster and I. S. Butler, *Canad. J. Chem.*, 1972, **50**, 598; *cf.* N. J. Coville and I. S. Butler, *J. Organometallic Chem.*, 1974, **64**, 101.

[9] J. A. Dineen and P. L. Pauson, *J. Organometallic Chem.*, 1974, **71**, 91.

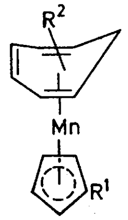
[10] E. O. Fischer and M. Herberhold, *Z. Naturforsch.*, 1961, **B16**, 841; E. O. Fischer, W. Bathelt, M. Herberhold, and J. Müller, *Angew. Chem. Internat. Edn.*, 1968, **7**, 634; W. Bathelt, M. Herberhold, and E. O. Fischer, *J. Organometallic Chem.*, 1970, **21**, 395; M. Herberhold and H. Brabetz, *Chem. Ber.*, 1970, **103**, 3896; M. Herberhold and C. R. Jablonski, *ibid.*, 1969, **102**, 767.

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

[12] H. P. Kögler and E. O. Fischer, *Z. Naturforsch.*, 1960, **B15**, 676; E. O. Fischer, H. P. Kögler, and P. Kuzel, *Chem. Ber.*, 1960, **93**, 3006.

examined although benzene did give [11] a very small yield of (η-benzene)(η-cyclopentadienyl) manganese, the product of complete carbonyl displacement.

As already briefly reported,[13] we find that cyclic trienes not only react with the tricarbonyl with complete CO substitution, but do so with remarkable efficiency. The (η-cycloheptatriene)(η-cyclopentadienyl)manganese derivatives, (I), so formed are air sensitive, but thermally stable, deep red crystalline solids. The analogous complex of cyclo-octa-1,3,5-triene is less thermally stable and (1—6-η-cyclo-octatetraene)(η-cyclopentadienyl)-manganese could only be kept at −78 °C (see Experimental). Most of the present work therefore concerns the cycloheptatriene series.



(I)

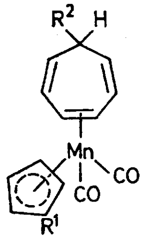
RESULTS AND DISCUSSION

Complete conversion of the tricarbonyl to the cycloheptatriene complex was achieved by irradiating in heptane solution for *ca.* 8 h. At intermediate stages i.r. examination (Table 1) revealed the presence of a new metal carbonyl species, apparently a dicarbonyl, which we believe to be the expected intermediate (II) and/or (III) in which the triene acts as a monofunctional ligand. However, when its concentration was near a maximum appreciable amounts of the tricarbonyl precursor were still present, and although the intermediate was much less air sensitive than the final product, we did not find a satisfactory method for its complete separation from the precursor in the mixture obtained either by irradiation or by treating dicarbonyl(η-cyclopentadienyl)-(tetrahydrofuran)manganese,[11] $[Mn(CO)_2(C_5H_5)(thf)]$, with cycloheptatriene. We believe nevertheless that its spectral identification is sufficiently certain and that formation of such a relatively stable intermediate may be significant in controlling the stereochemistry of products formed from substituted cycloheptatrienes.

Table 1

ν(CO) Bands (cm^{-1}) for monosubstituted species in n-heptane

$[Mn(CO)_2(C_5H_5)(1—2\text{-}\eta\text{-}1,3,5\text{-}C_7H_8)]$	1 965vs, 1 908vs
$[Mn(CO)_2(C_5H_4Me)(1—2\text{-}\eta\text{-}1,3,5\text{-}C_7H_8)]$	1 964vs, 1 908vs
$[Re(CO)_2(C_5H_5)(1—2\text{-}\eta\text{-}1,3,5\text{-}C_7H_8)]$	1 974vs, 1 906vs
$[Mn(CO)_2(C_5H_5)(1—2\text{-}\eta\text{-}1,3,5\text{-}C_8H_{10})]$	1 963vs, 1 904vs



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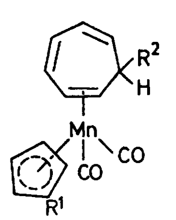
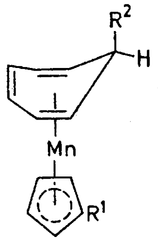
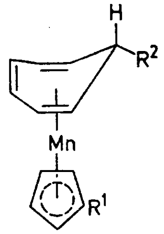


(III)

In earlier work it had been shown that 7-substituted cycloheptatrienes react (thermally) with hexacarbonylchromium or its derivatives to give predominantly 7-*endo*-substituted complexes,[14] apparently maintaining the pseudo-equatorial orientation which the substituent adopts [15] in the free triene. This has also been found in the reaction of a substituted cycloheptatriene with a ruthenium carbonyl derivative.[16] Exceptions were the phenyl and cyano-derivatives which yielded mainly *exo*-substituted complex,[14] and we have recently shown by *X*-ray crystallography [17] that 7-phenylcycloheptatriene yields predominantly tricarbonyl(1—4-η-7-*exo*-phenylcycloheptatriene)iron when treated with enneacarbonyldi-iron. In the manganese series we have now treated both the cyclopentadienyl and the methylcyclopentadienyl complex with 7-phenyl-, 7-methyl-, and 7-t-butyl-cycloheptatriene in addition to the unsubstituted triene. In each case mixtures of the substituted complexes (IV) and (V) were obtained in which the *exo* : *endo* ratio was *ca.* 2 : 1. Arguing that a bulky substituent in the C_5H_5 moiety might further enhance this ratio, we treated tricarbonyl(η-t-butylcyclopentadienyl)manganese with 7-t-butylcycloheptatriene, only to observe in effect a change to predominant (4 : 1) *endo* orientation. On the available evidence no simple explanation can be suggested for these ratios. The products appear stable to further irradiation, alone or when mixed with free cycloheptatrienes bearing different substituents. The ratios are therefore not the result of photochemically induced exchange or isomerisation reactions but appear to be kinetically controlled and



(IV)



(V)

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[13] P. L. Pauson and J. A. Segal, *J. Organometallic Chem.*, 1973, **63**, C13.

[14] P. L. Pauson, G. H. Smith, and J. H. Valentine, *J. Chem. Soc.* (*C*), 1967, 1061; P. L. Pauson and K. H. Todd, *ibid.*, 1970, 2315.

[15] H. Günther, M. Görlitz, and H. H. Hinrichs, *Tetrahedron*, 1968, **24**, 5665; *cf.* W. E. Heyd and C. A. Cupas, *J. Amer. Chem. Soc.*, 1971, **93**, 6086.

[16] J. A. K. Howard, S. A. R. Knox, V. Riera, B. A. Sosinsky, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1974, 673.

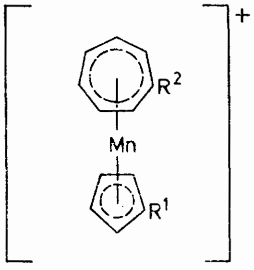
[17] J. A. D. Jeffreys, G. R. Knox, D. G. Leppard, P. L. Pauson, A. Pryde, and W. E. Watts, unpublished work.

possibly predetermined in the intermediate (II) or (III). Without knowledge of the detailed geometry preferred in this species it is not possible to assess the factors which determine the structure of the final product. In addition to the *endo*- and *exo*-7-substituted products at least one other isomer was formed in smaller amount from both 7-methyl- and 7-phenyl-cycloheptatriene. The evidence already cited shows that these must arise from the known photochemical rearrangement of the hydrocarbons prior to complex formation. In the case of the methyl derivative the ^{1}H n.m.r. spectrum unambiguously led to the assignment of the 1-methyl structure expected on this basis.

A number of related photochemical reactions have been attempted but with little success. Photolysis of tricarbonyl(η-cyclopentadienyl)rhenium with cycloheptatriene appeared to stop at the stage corresponding to intermediate (II) or (III). Tricarbonyl(η-cycloheptadienyl)manganese did not react with the triene beyond slight decomposition and tricarbonyl(η-cyclopentadienyl)manganese appeared to react only very slowly and gave no stable product when irradiated with 'hexamethyl(Dewar benzene)' (hexamethylbicyclo[2.2.0]hexadiene). Photolysis of tricarbonyl(η-toluene)chromium with cycloheptatriene, although carried out in toluene solution, resulted not in carbonyl but in hydrocarbon replacement yielding tricarbonyl(η-cycloheptatriene)chromium. Thermal displacement appears to be known only in the reverse sense (cycloheptatriene by arene) for chromium,[18] whereas both arene-molybdenum and -tungsten tricarbonyls suffer thermal displacement of arene by cycloheptatriene[19] and tricarbonyl(η-mesitylene)molybdenum suffers photochemical displacement even by butadiene.[12] Nevertheless the direction of the present exchange process is surprising in view of the greatly enhanced thermal and photo-lability[20] of cycloheptatriene compared to arenes linked to chromium (but not molybdenum) in exchange reactions of the type (4) where L* is the isotopically labelled hydrocarbon ligand L.

$$[\mathrm{Cr(CO)_3L}] + \mathrm{L}^* \longrightarrow [\mathrm{Cr(CO)_3L}^*] + \mathrm{L} \qquad (4)$$

The unsubstituted cycloheptatriene complexes (I; R^{1} = H or Me, R^{2} = H) reacted very readily with triphenylmethyl hexafluorophosphate or tetrafluoroborate to yield the corresponding salts of the cations (VI; R^{1} = H or Me, R^{2} = H). The reverse reaction was effected with lithium tetrahydridoaluminate and deuteride, the latter giving the *exo*-labelled triene complex (IV; R^{2} = D). Addition of other nucleophiles to the cations (VI) appears more difficult. We failed to isolate the expected adducts of type (IV) from reaction of the salts with methyl- or phenyl-lithium, methylmagnesium iodide, or cyclopentadienylsodium. Neutral red products were formed, but were too unstable to be isolated from the reaction mixtures. Isolation of bicycloheptatrienyl following such thermal decomposition suggests that the nucleophiles had induced reductive coupling (*cf.* ref. 21) rather than addition.



(VI)

As expected[22] no tropylium complex (VI) was obtained when the only pure *exo*-substituted complex isolated in this work, the phenyl derivative (IV; R^{1} = Me, R^{2} = Ph), was treated with triphenylmethyl tetrafluoroborate. Cationic complexes substituted in the seven-membered ring were, however, readily obtained from the isomer mixtures, presumably by abstraction of the *exo*-hydrogen atom from the other isomers present. Those prepared in this way (see Experimental section) include the only previously known complex of this type, the (η-cyclopentadienyl)(η-methyltropylium)manganese cation (VI; R^{1} = H, R^{2} = Me) which Fischer and Breitschaft obtained[23] by the remarkable ring expansion which accompanies Friedel–Crafts acetylation of (η-benzene)(η-cyclopentadienyl)manganese.

It is already well established that hydrogen migration similar to that occurring in the hydrocarbons can occur in various metal derivatives of cycloheptatrienes including their 1—4-η tricarbonyliron,[16] 1—2:5—6-η pentane-2,4-dionatorhodium,[24] and 1—6-η tricarbonylchromium derivatives.[25] Where the stereochemistry is known it is the 7-*endo*-hydrogen atom which migrates and we have shown that this is possible in the (1—6-η-cycloheptatriene)(η-cyclopentadienyl)manganese series by heating the 7-*exo*-phenyl-substituted complex (IV; R^{1} = Me R^{2} = Ph) at 100 °C. While no pure isomer was isolated from the resulting mixture, the appearance of a multiplet centred at τ 10.24 assignable to 7-*exo* protons and the formation of cation (VI; R^{1} = Me, R^{2} = Ph) from the mixture represent conclusive evidence for the expected rearrangement; the gradual appearance of additional methyl n.m.r. signals demonstrates its stepwise character. Thermal instability of the complexes limits the useful heating time to *ca.* 10 h (at 100 °C) but equilibrium has probably been attained at this stage. The ^{1}H n.m.r. spectrum of the final

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[18] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3475, but *cf.* J. A. S. Howell, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 293 for failure of heptafulvene complexes to undergo analogous displacement.

[19] A. Pidcock and B. W. Taylor, *J. Chem. Soc. (A)*, 1967, 877.

[20] W. Strohmeier and D. von Hobe, *Z. Naturforsch.*, 1963, **B18**, 981; W. Strohmeier and H. Mittnacht, *Z. phys. Chem.*, 1962, **34**, 82; 1961, **29**, 339; *Chem. Ber.*, 1960, **93**, 2085.

[21] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3484.

[22] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc. (C)*, 1969, 2024; P. L. Pauson and K. H. Todd, *ibid.*, 1970, 2315.

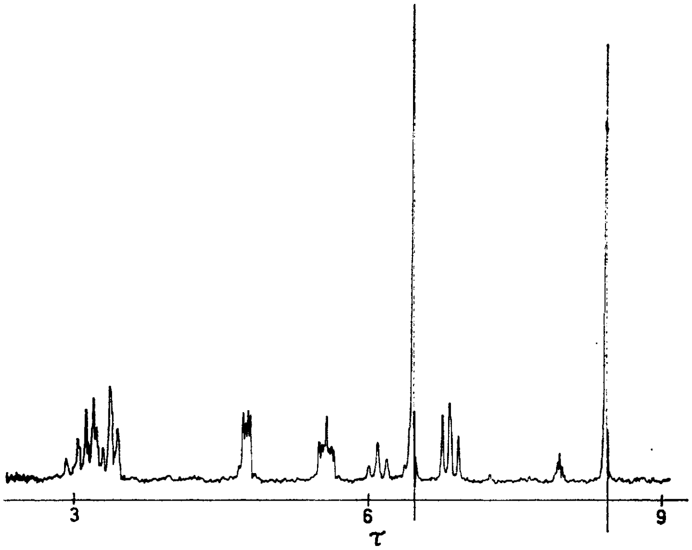
[23] E. O. Fischer and S. Breitschaft, *Chem. Ber.*, 1966, **99**, 2213.

[24] J. M. Brown and D. G. Coles, *J. Organometallic Chem.*, 1973, **60**, C31.

[25] M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *J.C.S. Perkin II*, 1972, 1141.

mixture suggests that the 2-phenyl derivative predominates and apparently none of the intermediates does so after shorter periods of heating.

The n.m.r. spectra of the cycloheptatriene complexes were well resolved as exemplified for (IV; R^1 = Me, R^2 = Ph) in the Figure. They show the increased chemical-shift differences of the 'olefinic' protons compared to the parent hydrocarbons which are familiar from the tricarbonyl(η-cycloheptatriene)chromium series [22,26] and are therefore readily interpretable as detailed in Table 2. The structure of (η-7-*exo*-phenylcycloheptatriene)(η-1-methylcyclopentadienyl)manganese, (IV; R^1 = Me, R^2 = Ph), has been fully confirmed by preliminary results of a full *X*-ray crystallographic study.[27]



^{1}H N.m.r. spectrum of (η-7-*exo*-phenylcyclohepta-1,3,5-triene)(η-methylcyclopentadienyl)manganese, (IV; R^1 = Me, R^2 = Ph)

TABLE 2

^{1}H N.m.r. data (τ) [a] for complexes (I)

R^2	R^1	$H^{3,4}$	$H^{2,5}$	$H^{1,6}$	H^7 *endo*	H^7 *exo*	C_5 ring	R^2	R^1
H	H	4.42	5.60	7.40	7.60	9.96	6.38 (s)		
H	Me	4.49	5.66	7.49	*ca.* 7.50	9.96	6.48		8.42 (s)
7-*exo*-D	H	4.40	5.58	7.41	7.59		6.35 (s)		
7-*exo*-Me	H	4.43	5.69	6.90	*b*		6.34 (s)	10.80 (d)	
7-*endo*-Me	H		5.53	7.29		10.22	6.33 (s)	8.89 (d)	
1-Me	H		5.61	7.69		9.91 (dd)	6.36 (s)	8.05 (s)	
7-*exo*-Me	Me	4.53	5.74	7.00	*b*		6.45 (s)	10.79 (d)	8.39 (s)
7-*endo*-Me	Me		5.60	7.36		10.20		8.88 (d)	8.36 (s)
1-Me	Me		5.67	7.80		9.90 (dd)		8.05 (s)	8.49 (s)
7-*exo*-Ph [c]	Me	4.79	5.60	7.85	6.12 (t)		6.46 (s)	3.21	8.42 (s)
7-*endo*-Ph	Me	4.57	5.60	7.40			6.46 (s)	*b*	8.46 (s)
7-*exo*-Bu^t	Me	4.51	5.71	7.20	*b*		6.43 (s)	9.85 (s)	8.39 (s)
7-*endo*-Bu^t	Me	4.65	5.50	7.52		11.13 (t)	6.43 (s)	9.06 (s)	8.39 (s)
7-*exo*-Bu^t	Bu^t	*b*	5.70	7.07	*b*		6.30 (t), 6.64 (t)	9.82 (s)	8.89 (s) [d]
7-*endo*-Bu^t	Bu^t	4.56	5.49	7.45		11.04 (t)	5.95 (t), 6.75 (t)	9.02 (s) [d]	8.98 (s) [d]

[a] Solutions in $C_6D_5CD_3$. All resonances were multiplets unless shown otherwise. [b] Obscured or otherwise unassignable. [c] See also the Figure; the peak at τ 7.95 is due to incompletely deuteriated solvent. [d] Tentative assignment.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 grating instrument and were calibrated against deuterium chloride. ^{1}H N.m.r. spectra were obtained on a Perkin-Elmer R14 spectrometer at 100 MHz, mass spectra on an A.E.I. MS9 spectrometer. Photochemical reactions were conducted in a vessel of *ca.* 200 cm^3 capacity using a water-cooled 500 W Hanovia 6744 medium-pressure lamp and a silica-glass liner. All reactions and purification procedures were carried out under an atmosphere of dry oxygen-free nitrogen and all solvents were deoxygenated before use.

(η-*Cyclohepta*-1,3,5-*triene*)(η-*cyclopentadienyl*)*manganese*, (I; R^1 = R^2 = H).—A stirred solution of distilled cycloheptatriene (3.0 g) and tricarbonyl(η-cyclopentadienyl)-manganese (2.0 g) in n-heptane (or toluene) (200 cm^3) was irradiated at room temperature for *ca.* 8 h. During this time a slow colour change from pale yellow to deep red occurred. The reaction was monitored by i.r. spectroscopy and when all ν(CO) absorptions had disappeared the solution was filtered through Kieselguhr and then evaporated. The resulting solid was dried *in vacuo* (0.01 Torr) * for 1 h and then sublimed on to a water-cooled probe at 60°C (0.01 Torr) giving the *product* as red-black needles (1.8 g, 87%) (Found: C, 67.8; H, 6.3%; *M* 212.0410. $C_{12}H_{13}Mn$ requires C, 67.9; H, 6.2%; *M* 212.0398).

An analogous reaction of cycloheptatriene and tricarbonyl(η-cyclopentadienyl)rhenium showed evidence [ν(CO) (in heptane) at 1 974vs and 1 906vs cm^{-1}] of monosubstitution but no product of complete carbonyl displacement could be isolated.

(η-*Cyclohepta*-1,3,5-*triene*)(η-*methylcyclopentadienyl*)-*manganese*, (I; R^1 = Me, R^2 = H).—This complex (3.3 g, 84%) was similarly obtained from tricarbonyl(η-methylcyclopentadienyl)manganese (3.8 g) (Found: C, 68.7; H, 6.7%; *M* 226.0557. $C_{13}H_{15}Mn$ requires C, 69.0; H, 6.7%; *M* 226.0555).

(1—6-η-*Cyclo-octatetraene*)(η-*cyclopentadienyl*)*manganese*.—A stirred solution of freshly distilled cyclo-octatetraene (2.2 g) and [$Mn(CO)_3(C_5H_5)$] (1.5 g) was irradiated in n-heptane for 7 h. The resulting red solution was filtered through Kieselguhr into a flask cooled to −78 °C. The solution was reduced to *ca.* 25 cm^2 at and below room temperature and was then cooled to −78 °C causing crystallis-

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* 1 Torr = (101 325/760) Pa.

[26] M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 2037.

[27] J. A. D. Jeffreys, personal communication.

ation. The mother liquor was removed leaving red crystals which were kept at −78 °C as the material is thermally unstable. A ^{1}H n.m.r. spectrum was obtained at *ca.* 0 °C by filling the tube at −196 °C and warming it up quickly just before measurement: τ (in $C_6D_5CD_3$) 4.66 (m, 2 H, H^{3,4}), 5.04 (m, 4 H, H^{2,5} and H^{1,6}), 5.22 (m, 2 H, H^{7,8}), and 6.46 (s, 5 H, C_5H_5).

(η-*Cyclo-octa*-1,3,5-*triene*)(η-*cyclopentadienyl*)*manganese*.—This was obtained similarly and could be crystallised at low temperature, but melted on warming above −30 °C. Since the *complex* is appreciably more thermally stable than the cyclo-octatetraene analogue it could be purified by rapid distillation at 10^{-3} Torr (Found: *M* 226.0550. $C_{13}H_{15}Mn$ requires *M* 226.0555); τ (in $C_6D_5CD_3$) 4.62 (m, 2 H, H^{3,4}), 5.11 (m, 4 H, H^{2,5} and H^{1,6}), 6.46 (s, 5 H, C_5H_5), 8.23 (m, 2 H, *endo*-H^{7}), and 10.35 (m, 2 H, *exo*-H^{7}).

(η-7-exo-*Phenylcyclohepta*-1,3,5-*triene*)(η-*methylcyclopentadienyl*)*manganese*, (IV; R^1 = Me, R^2 = Ph).—Tricarbonyl(η-methylcyclopentadienyl)manganese (2.0 g) and 7-phenylcyclohepta-1,3,5-triene (4.5 g) were irradiated in n-heptane (200 cm^3) for 10 h. The resulting red solution was evaporated and the excess of phenylcycloheptatriene (now partially isomerised) was distilled from the product at *ca.* 40 °C under high vacuum. ^{1}H N.m.r. integration of the methyl resonances of the solid residue gave the proportions 54% 7-*exo*-phenyl (IV; R^1 = Me, R^2 = Ph), 31% 7-*endo*-phenyl (V; R^1 = Me, R^2 = Ph), and 15% rearranged phenyl (*exo* : *endo* ratio 63 : 37). This material was dissolved in n-heptane (50 cm^3), filtered through Kieselguhr, and evaporated until crystallisation commenced. After allowing to stand for a few minutes the *product* (0.7 g) was collected. By cooling the mother liquor to −78 °C a second fraction (0.4 g) was obtained (yield 40%). The product was further purified by sublimation at 80 °C (10^{-4} Torr) (Found: C, 75.5; H, 6.3%; *M* 302.0858. $C_{19}H_{19}Mn$ requires C, 75.5; H, 6.3%; *M* 302.0868). Attempts to crystallise the 7-*endo*-phenyl complex from the remaining solution were not successful but after evaporation the resulting residue did react with $[Ph_3C][PF_6]$ in CH_2Cl_2 to give a salt (see below).

The Mixture of (η-*Cyclopentadienyl*)(η-7-exo-, (η-7-endo-, *and* (η-1-*methyl-cyclohepta*-1,3,5-*triene*)*manganese*, (I; R^1 = H, R^2 = Me).—This was obtained similarly from 7-methylcyclohepta-1,3,5-triene (2.6 g) and $[Mn(CO)_3(C_5H_5)]$ (2.0 g) as a red *oil* (1.6 g, 72%) after distillation at 10^{-3} Torr. The same reaction was also carried out using $[Mn(CO)_3(C_5H_4Me)]$. Isomer proportions from ^{1}H n.m.r. were: C_5H_5 complex, 50% 7-*exo*-methyl, 21% 7-*endo*-methyl, and 29% 1-methyl (*exo* : *endo* ratio 7 : 3); C_5H_4Me complex, 42% 7-*exo*-, 25% 7-*endo*-, and 33% 1-methyl (*exo* : *endo* ratio 63 : 37).

Similarly obtained in high yield were the mixtures of (η-7-exo- and (η-7-endo-*t-butylcyclohepta*-1,3,5-*triene*)(η-*methylcyclopentadienyl*)*manganese*, (IV and V; R^1 = Me, R^2 = Bu^t), and of (η-7-exo- and (η-7-endo-*t-butylcyclohepta*-1,3,5-*triene*)(η-*t-butylcyclopentadienyl*)*manganese*, (IV and V; R^1 = R^2 = Bu^t) (Found: *M* 324.1625. $C_{20}H_{29}Mn$ requires *M* 324.1649). Isomer proportion from ^{1}H n.m.r.: C_5H_4Me, 63% 7-*exo*-t-butyl, 37% 7-*endo*-t-butyl; $C_5H_4Bu^t$, *ca.* 20% 7-*exo*- and *ca.* 80% 7-*endo*-t-butyl.

Photolysis of (η-*Cyclopentadienyl*)(η-*methylcycloheptatriene*)*manganese Isomers with Excess of Cycloheptatriene*.—A solution of the distilled isomeric methylcycloheptatriene complexes (0.5 g) and cycloheptatriene (10 cm^3) in n-heptane (200 cm^3) was irradiated for 48 h. Evaporation and distillation of the residue gave a red oil the ^{1}H n.m.r. spectrum of which showed both that exchange of the C_7 rings had not taken place and that the 7-*exo*- : 7-*endo*-methyl ratio was unchanged.

Thermal Rearrangement of (η-7-exo-*Phenylcyclohepta*-1,3,5-*triene*)(η-*methylcyclopentadienyl*)*manganese*, (IV; R^1 = Me, R^2 = Ph).—The complex (0.07 g) in [$^2H_8$]toluene (0.5 cm^3) was heated in a n.m.r. tube to 100 °C for 10 h and the ^{1}H n.m.r. spectrum was recorded periodically. At the end of this period the sample started to deteriorate and no further change was observed. Initially, in addition to the methyl resonance at τ 8.42, two weaker signals appeared at τ 8.46 and 8.48. A third signal started to appear at τ 8.62 and, whereas the first two signals did not develop appreciably, grew with time at the cost of the initial resonance. The final spectrum showed a multiplet at τ 10.24 assigned to the 7-*exo* proton, confirming that sigmatropic shifts had occurred. The reaction was repeated using 0.3 g of complex in a sealed tube but all attempts to isolate the solid product failed. However, the ^{1}H n.m.r. spectrum after distillation, though complex, led to tentative assignment of the major component of the product as the 2-phenylcycloheptatriene complex.

(η-*Cycloheptatrienylium*)(η-*cyclopentadienyl*)*manganese Hexafluorophosphate*, (PF_6^- salt of VI; R^1 = R^2 = H).—A solution of triphenylmethyl hexafluorophosphate (2.0 g) in a minimum of dry dichloromethane was added to a suspension of (η-cycloheptatriene)(η-cyclopentadienyl)manganese (1.1 g) in CH_2Cl_2 (30 cm^3) at −78 °C. The resulting suspension was allowed to warm to room temperature and was stirred for 10 min. The solution was then reduced to *ca.* 20 cm^3 and the product (1.6 g) was collected, washed with ethanol (6 cm^3) and diethyl ether (3 × 6 cm^3), and finally dried *in vacuo*. Addition of diethyl ether to the mother liquor gave a second batch of product (0.1 g) (total yield 92%). Recrystallisation was effected using acetone–ethanol or –diethyl ether (Found: C, 40.6; H, 3.4; P, 8.8. $C_{12}H_{12}F_6MnP$ requires C, 40.5; H, 3.4; P, 8.7%); τ [in $(CD_3)_2CO$] 2.90 (s, 7 H, C_7H_7) and 5.05 (s, 5 H, C_5H_5).

(η-*Cycloheptatrienylium*)(η-*methylcyclopentadienyl*)*manganese Hexafluorophosphate*, (PF_6^- salt of VI; R^1 = Me, R^2 = H).—This salt (0.33 g, 88%) was obtained similarly from (η-cycloheptatriene)(η-methylcyclopentadienyl)manganese (0.23 g) (Found: C, 42.5; H, 4.0; P, 8.3. $C_{13}H_{14}F_6MnP$ requires C, 42.2; H, 3.8; P, 8.4%); τ [in $(CD_3)_2CO$] 3.00 (s, 7 H, C_7H_7), 5.14 (s, 4 H, C_5H_4), and 8.00 (s, 3 H, Me).

(η-*Cycloheptatrienylium*)(η-*methylcyclopentadienyl*)*manganese Tetrafluoroborate*, (BF_4^- salt of VI; R^1 = Me, R^2 = H).—This salt (4.3 g, 93%) was obtained similarly from (η-cycloheptatrienyl)(η-methylcyclopentadienyl)manganese (3.3 g) (Found: C, 50.1; H 4.5. $C_{13}H_{14}BF_4Mn$ requires C, 50.0; H, 4.5%).

(η-*Cyclopentadienyl*)(η-*methylcycloheptatrienylium*)*manganese Tetrafluoroborate*, (BF_4^- salt of VI; R^1 = H, R^2 = Me).—This salt [23] (0.95 g, 46%) was obtained similarly from the isomeric (η-cyclopentadienyl)(η-methylcycloheptatriene)-manganese mixture (1.5 g) (Found: C, 49.9; H, 4.5. $C_{13}H_{14}BF_4Mn$ requires C, 50.0; H, 4.5%); τ [in $(CD_3)_2CO$] 2.99 (br. s, 6 H, C_7H_6), 5.07 (s, 5 H, C_5H_5), and 7.02 (s, 3 H, Me).

(η-*Methylcyclopentadienyl*)(η-*phenylcycloheptatrienylium*)-*manganese Hexafluorophosphate*, (PF_6^- salt of VI; R^1 = Me, R^2 = Ph).—This salt was similarly obtained in fair yield from either the residue of the mother liquor after crystallisation of (η-7-*exo*-phenylcycloheptatriene)(η-methylcyclopentadienyl)manganese or from the thermally rearranged 7-*exo*-phenyl complex (Found: C, 51.1, 51.2; H, 4.0, 4.1. $C_{19}H_{18}F_6MnP$ requires C, 51.1; H, 4.1%), τ [in $(CD_3)_2CO$] 1.92 (m, 2 H, *m*-Ph), 2.42 (m, 3 H, *o*- and *p*-Ph), 2.64 (m, 2 H of C_7H_6), 2.94 (m, 4 H of C_7H_6), 5.17 (br. s, 4 H, C_5H_4), and 8.09 (s, 3 H, Me).

Reaction of (η-7-exo-*Phenylcycloheptatriene*)(η-*methylcyclopentadienyl*)*manganese*, (IV; R^1 = Me, R^2 = Ph), *with Triphenylmethyl Tetrafluoroborate*.—The manganese complex (0.30 g) in dichloromethane solution was treated with $[Ph_3C][BF_4]$ (0.35 g) in a minimum of CH_2Cl_2. No immediate reaction occurred but the initial red colour slowly faded presumably as a result of oxidation. No salt could be isolated on addition of diethyl ether.

Attempts to Prepare the (1—7-η-*Cyclo-octatrienylium*)(η-*cyclopentadienyl*)*manganese Cation*.—Addition of excess of 65% hexafluorophosphoric acid to the cyclo-octatetraene complex in diethyl ether initially gave a white precipitate, but this decomposed rapidly and could not be isolated. Reaction of the cyclo-octatriene complex with $[Ph_3C][PF_6]$ in CH_2Cl_2 also did not lead to the required product.

Reduction of the (η-*Cycloheptatrienylium*)(η-*cyclopentadienyl*)*manganese Cation*, (VI; R^1 = R^2 = H), *with Lithium Tetrahydridoaluminate*.—The tetrafluoroborate salt (1.0 g) was suspended in dry tetrahydrofuran (50 cm³) and $Li[AlH_4]$ (0.07 g) was added in portions. The suspension was stirred vigorously for 1.5 h and then the solvent was removed. (η-Cycloheptatriene)(η-cyclopentadienyl)manganese (0.23 g, 32%) was sublimed from the residue and identified by comparison of its ^1H n.m.r. spectrum with that of an authentic sample. A similar reaction with $Li[AlD_4]$ gave (η-7-exo-*deuteriocyclohepta*-1,3,5-*triene*)(η-*cyclopentadienyl*)*manganese*, (IV; R^1 = H, R^2 = D) (Found: *M* 213.0408. $C_{12}H_{12}DMn$ requires *M* 213.0460).

Reaction of the (η-*Cycloheptatrienylium*)(η-*cyclopentadienyl*)*manganese Cations*, (VI; R^1 = H or Me, R^2 = H), *with Organometallic Reagents*.—Addition of methyl- or phenyllithium or of methylmagnesium iodide or sodium cyclopentadienide to a stirred suspension of one of the tetrafluoroborate salts in thf, either initially at −78 °C or at room temperature, led to formation of a red solution. After destroying the excess of reagent, the solvent was evaporated and the residue was sublimed at 80 °C and 10^{-3} Torr, giving a colourless solid which was identified (i.r., ^1H n.m.r., and m.p.) as bicycloheptatrienyl. The residue lost its red colouration during the sublimation suggesting that thermal decomposition had occurred.

Irradiation of Tricarbonyl(η-*toluene*)*chromium with Cycloheptatriene*.—Tricarbonyl(η-toluene)chromium (1 g) and cycloheptatriene (2 g) were irradiated in toluene (200 cm³). The initial yellow solution rapidly darkened to deep red. After 7 h the solution was filtered and evaporated and the residue was crystallised from benzene–n-heptane giving tricarbonyl(η-cycloheptatriene)chromium in high yield. This was identified by comparison of its i.r. spectrum with that of an authentic sample and by its reaction with $[Ph_3C][BF_4]$.

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