

β -Cyclomanganated 1,5-diphenylpenta-1,4-dien-3-ones and their reactions with alkynes: routes to η^5 -pyranyl– and η^5 -oxocycloheptadienyl–Mn(CO)₃ complexes

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Abstract

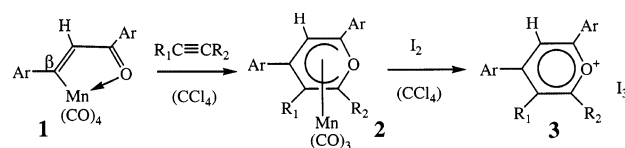
1,5-Diphenylpenta-1,4-dien-3-ones (**4**) are cyclometalated with benzylpentacarbonylmanganese to form [[1-phenyl-2-((*E*)-3-phenylprop-2-en-1-yl- κ O)]ethenyl- κ C¹]tetracarbonylmanganese derivatives (**5**). Coupling of **5** with alkynes in some cases gives [4-phenyl-2-(2-phenylethenyl)pyranyl- η^5]tricarbonylmanganese complexes (**6**) analogous to those previously reported for β -manganated chalcones, but in other cases an alternative cyclisation pathway subsequent to insertion of alkyne into the C–Mn bond leads to [6-oxo-4,7-diphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese complexes (**7**). The X-ray crystal structure determination is reported for one such compound, [6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7a**), derived from 1,5-diphenylpenta-1,4-dien-3-one and phenylacetylene. The 7-phenyl group is found to occupy the *endo* position, and a mechanism involving Mn-mediated aryl migration is suggested to explain this stereochemistry. The reaction of **7a** with ammonium cerium(IV) nitrate gives a low yield of 2-nitro-3,5,7-triphenylcyclohepta-2,4,6-trien-1-one (**9**), whose structure was established by X-ray crystal structure analysis. The pyranyl complexes (**6**) provide the corresponding pyrylium triiodide salts (**8**) when demetalated with iodine. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Manganese; Alkyne; Cyclometallation; Metallacycle; Crystal structures; Pyrylium salts

1. Introduction

We have reported the formation of derivatives of [[1-phenyl-2-phenylcarbonyl- κ O)]ethenyl- κ C¹]tetracarbonylmanganese (**1**) in the reaction of chalcones [(*E*)-1,3-diarylprop-2-en-1-ones] with benzylpentacarbonylmanganese [1a]. These β -cyclomanganated enones are alkenyl analogues of orthomanganated acetophenones, and like the latter [2] they undergo synthetically valuable reactions with alkenes [1a] and alkynes [1b], some of which involve cyclisation incorporating the unsaturated donor carbonyl function into a new ring. With alkynes, the donor carbonyl group is incorporated to form [η^5 -pyranyl]Mn(CO)₃ complexes (**2**; Scheme 1), which on treatment with iodine in carbon tetrachloride, provide pyrylium triiodide salts (**3**) [1b].

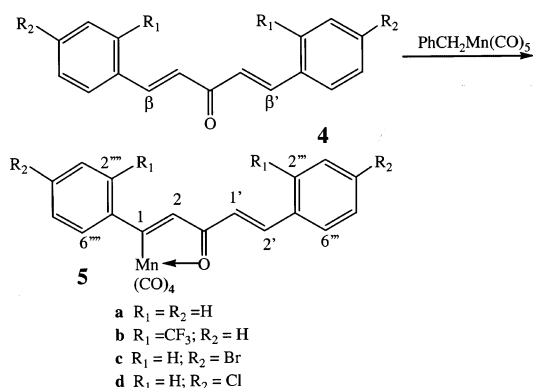
We now report on β -manganation of 1,5-diphenylpenta-1,4-dien-3-ones (**4a–d**; Scheme 2) and on preliminary studies of alkyne-coupling reactions of the β -manganation products (**5**). Of interest from a synthetic perspective was whether alkyne insertion into the C–Mn bond might result in subsequent alternative cyclisation pathways when the donor function (ArCH=CH–C=O) is potentially reactive at four unsaturated centres rather than the two in the donor group (ArC=O) of β -manganated chalcones.



Scheme 1. Syntheses from cyclomanganated chalcones and alkynes.

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Scheme 2. Cyclomanganation of 1,5-diarylpenta-1,4-dien-3-ones.

2. Experimental

2.1. General

Benzylpentacarbonylmanganese was prepared by the standard literature method [3]. Petroleum spirit (b.p. 60–80 °C) was redistilled and CCl_4 was of analytical grade. Other commercial reagents were used without purification. Cyclomanganation reactions and coupling reactions with alkynes were conducted under nitrogen, but subsequent workup was without any precautions to exclude air. There were no special precautions for the reactions with iodine or ammonium cerium(IV) nitrate. Preparative scale layer chromatography (referred to as PLC in the text) was performed on Merck Kieselgel 60 silica gel, and alumina (Brockmann activity II) was used for column chromatography. The composition of mixed solvents is expressed on a volume/volume basis.

NMR spectra were recorded on a Bruker AC300 instrument using CDCl_3 as solvent except for pyrylium triiodide salts for which $(\text{CD}_3)_2\text{CO}$ or $(\text{CD}_3)_2\text{SO}$ was used. Infrared spectra (in CH_2Cl_2 unless specified) were obtained on a Digilab FTS-45 FTIR instrument and FAB mass spectra on a VG ZAB 2HF instrument using a 2-nitrophenol matrix. UV spectra were recorded on a Uvikon 860 spectrophotometer.

2.2. Standard procedure for the preparation of (*E,E*)-1,5-diarylpenta-1,4-dien-3-ones [4a]

Ethanol (10 ml) and a solution of NaOH (2 g) in water (15 ml) were mixed in a flask immersed in crushed ice. A solution in Me_2CO (ca. 0.5 ml; 8 mmol) of the appropriate benzaldehyde (ca. 16 mmol) was added dropwise while stirring and maintaining the temperature at about 25 °C. After a further hour, the precipitate was collected and washed with water until the washings were neutral to litmus. The crude product was dried under vacuum and then recrystallised from EtOAc in 50–80% yield. NMR spectra indicated that

the recrystallised product was the pure (*E,E*)-isomer in all cases. Elemental analyses on the manganated products (see Section 2.3) provided confirmation of identity.

(*E,E*)-1,5-Diphenylpenta-1,4-dien-3-one (**4a**): m.p. 107 °C (lit. [4b] 112 °C). $^1\text{H-NMR}$: δ = 7.75 (d, 2H, J = 16.0 Hz, H1), 7.61 (m, 4H, H2', 6'), 7.42 (m, 6H, H3', 5', H4'), 7.09 (d, 2H, J = 16.0 Hz, H2). $^{13}\text{C-NMR}$: δ = 189.0 (s, C3), 143.4 (d, C1), 134.9 (s, C1'), 130.6 (d, C4'), 129.0 (d, C3', 5'), 128.5 (d, C2', 6'), 125.5 (d, C2).

(*E,E*)-1,5-Di-(2-trifluoromethylphenyl)penta-1,4-dien-3-one (**4b**): m.p. 131 °C. $^1\text{H-NMR}$: δ = 8.09 (dq, 2H, J = 15.8, 1.7 Hz, H1), 7.79 (d, 2H, J = 7.7 Hz, H6'), 7.73 (d, 2H, J = 7.7 Hz, H3'), 7.61 (t, 2H, J = 7.7 Hz, H4'), 7.51 (t, 2H, J = 7.7 Hz, H5'), 7.01 (d, 2H, J = 15.8 Hz, H2). $^{13}\text{C-NMR}$: δ = 188.3 (s, C3), 139.3 (d, C1), 133.7 (s, C1'), 132.2 (d, C4'), 129.9 (d, C5'), 128.9 (d, C2), 128.0 (d, C6'), 126.3 (d, J = 5.3 Hz, C3').

(*E,E*)-1,5-Di-(4-bromophenyl)penta-1,4-dien-3-one (**4c**): m.p. 211 °C. $^1\text{H-NMR}$: δ = 7.66 (d, 2H, J = 15.9 Hz, H1), 7.55 (d, 4H, J = 8.5 Hz, H3', 5'), 7.46 (d, 4H, J = 8.5 Hz, H2', 6'), 7.03 (d, 2H, J = 15.9 Hz, H2). $^{13}\text{C-NMR}$: δ = 188.4 (s, C3), 142.2 (d, C1), 133.7 (s, C1'), 132.3 (d, C3', 5'), 129.8 (d, C2', 6'), 125.8 (d, C2), 124.9 (s, C4').

(*E,E*)-1,5-Di-(4-chlorophenyl)penta-1,4-dien-3-one (**4d**): m.p. 186 °C. $^1\text{H-NMR}$: δ = 7.67 (d, 2H, J = 15.9 Hz, H1), 7.53 (d, 4H, J = 8.5 Hz, H3', 5'), 7.38 (d, 4H, J = 8.5 Hz, H2', 6'), 7.02 (d, 2H, J = 15.9 Hz, H2). $^{13}\text{C-NMR}$: δ = 188.3 (s, C3), 142.1 (d, C1), 136.5 (s, C4'), 133.3 (s, C1'), 129.6 (d, C2', 6'), 129.3 (d, C3', 5'), 125.8 (d, C2).

2.3. Standard procedure for the preparation of cyclomanganated (*E,E*)-1,5-diarylpenta-1,4-dien-3-ones

A solution of the diarylpenta-1,4-dien-3-one (**4**; 1 mmol) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (1.1 mmol) in petroleum spirit (20 ml) under nitrogen was heated under reflux. Upon completion of the reaction, as monitored by IR spectroscopy (ca. 3–4 h), the solvent was removed under vacuum. Dichloromethane (10 ml) and deactivated neutral alumina (4 g, activity II) were added to the residue. The mixture was stirred while the CH_2Cl_2 was removed under vacuum. The alumina with product adsorbed was transferred onto the top of a column (2 × 12 cm) of neutral alumina (activity II). Elution with CH_2Cl_2 –petroleum spirit (1:8) followed by solvent evaporation gave the product as a red oil which was crystallised from petroleum spirit. Yields given are for the chromatographically pure products prior to crystallisation, which, with the small quantities involved, resulted in significant losses.

[[1-Phenyl-2-((*E*)-3-phenylprop-2-en-1-oyl- κO)]-ethenyl- κC^1]tetracarbonylmanganese (**5a**): 81%; crystallised as small dark red crystals: m.p. 116 °C. Anal.

Found: C, 62.95; H, 2.98. Calc. for $C_{21}H_{13}O_5Mn$: C, 63.02; H, 3.27%. IR (cm^{-1}): $\nu(CO)$ 2082 (m), 1997 (vs, br), 1942 (s). 1H -NMR: δ = 7.72 (d, 1H, J = 16.1 Hz, H5), 7.59 (m, 2H, H2'', 6''), 7.45 (m, 8H, H2', 6', H3', 5', H4', H3'', 5'', H4''), 7.33 (s, 1H, H2), 6.99 (d, 1H, J = 16.1 Hz, H4). ^{13}C -NMR: δ = 251.2 (s, C1), 219.5 (s, CO), 214.1 (s, CO), 210.4 (s, CO), 203.9 (s, C3), 150.2 (s, C1'), 145.4 (d, C5), 134.6 (s, C1''), 133.9 (d, C2), 131.1 (d, C4''), 129.1 (d, C3'', 5''), 128.7 (d, C4'), 128.6 (d, C2'', 6''), 128.4 (d, C3', 5'), 125.3 (d, C2', 6'), 123.6 (d, C4).

[1-(2-Trifluoromethylphenyl)-2-((*E*)-3-(2-trifluoromethylphenyl)prop-2-en-1-oyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5b**): 85%; crystallised as small crimson crystals: m.p. 94 °C. Anal. Found: C, 51.81; H, 1.88. Calc. for $C_{23}H_{11}F_6O_5Mn$: C, 51.51; H, 2.07%. IR (cm^{-1}): $\nu(CO)$ 2088 (m), 1996 (vs, br), 1951 (s). 1H -NMR: δ = 8.05 (dq, 1H, J = 16.0, 1.7 Hz, H5), 7.77 (m, 3H, H3', H3'', H6''), 7.60 (m, 2H, H5', H4''), 7.52 (t, 1H, J = 7.6 Hz, H5''), 7.35 (m, 3H, H2, H4', H6'), 6.93 (d, 1H, J = 16.0 Hz, H4). ^{13}C -NMR: δ = 251.0 (s, C1), 219.0 (s, CO), 213.2 (s, CO), 204.2 (s, C3), 150.5 (s, C1'), 141.0 (d, C5), 135.4 (d, C2), 133.2 (s, C1''), 132.3 (d, C4''), 131.4 (d, C5'), 130.4 (d, C5''), 127.8 (d, C6''), 127.3 (d, C4), 126.4 (d, C3', C3''), 126.3 (d, C4'), 125.1 (d, C6').

[1-(4-Bromophenyl)-2-((*E*)-3-(4-bromophenyl)prop-2-en-1-oyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5c**): 87%; crystallised as small cherry-red crystals: m.p. 109 °C. Anal. Found: C, 45.47; H, 1.67. Calc. for $C_{21}H_{11}Br_2O_5Mn$: C, 45.20; H, 1.99%. IR (cm^{-1}): $\nu(CO)$ 2083 (m), 1998 (vs, br), 1944 (s). 1H -NMR: δ = 7.62 (d, 1H, J = 16.1 Hz, H5), 7.57 (d, 2H, J = 8.5 Hz, H3', 5'), 7.56 (d, 2H, J = 8.5 Hz, H3'', 5''), 7.44 (d, 2H, J = 8.5 Hz, H2'', 6''), 7.31 (d, 2H, J = 8.5 Hz, H2', 6'), 7.27 (s, 1H, H2), 6.97 (d, 1H, J = 16.1 Hz, H4). ^{13}C -NMR: δ = 250.2 (s, C1), 219.4 (s, CO), 213.8 (s, CO), 210.0 (s, CO), 203.5 (s, C3), 148.2 (s, C1'), 144.1 (d, C5), 134.2 (d, C2), 133.4 (s, C1''), 132.5 (d, C3'', 5''), 131.6 (d, C3', 5'), 129.9 (d, C2'', 6''), 126.8 (d, C2', 6'), 125.6 (s, C4''), 123.8 (d, C4), 122.9 (s, C4').

[1-(4-Chlorophenyl)-2-((*E*)-3-(4-chlorophenyl)prop-2-en-1-oyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5d**): 75%; crystallised as bright cherry-red crystals: m.p. 119 °C. Anal. Found: C, 54.01; H, 2.10. Calc. for $C_{21}H_{11}Cl_2O_5Mn$: C, 53.76; H, 2.36%. IR (cm^{-1}): $\nu(CO)$ 2083 (m), 2000 (vs, br), 1944 (s). 1H -NMR: δ = 7.65 (d, 1H, J = 16.1 Hz, H5), 7.52 (d, 2H, J = 8.5 Hz, H2'', 6''), 7.40 (m, 6H, H2', 6', H3', 5', H3'', 5''), 7.28 (s, 1H, H2), 6.95 (d, 1H, J = 16.1 Hz, H4). ^{13}C -NMR: δ = 250.1 (s, C1), 219.4 (s, CO), 210.0 (s, CO), 203.5 (s, C3), 148.5 (s, C1'), 144.0 (d, C5), 137.2 (s, C4''), 134.6 (s, C4'), 134.2 (d, C2), 133.0 (s, C1''), 129.7 (d, C3'', 5''), 129.5 (d, C3', 5'), 128.6 (d, C2'', 6''), 126.6 (d, C2', 6'), 123.8 (d, C4).

2.4. Coupling reactions with alkynes

This section is divided according to starting β -manganated compound in order to highlight product variations. In general, reactions were stopped once the manganese reactant had been consumed, as indicated by IR monitoring, but in some cases reactions were continued overnight (see individual cases for details).

2.4.1. Reactions of [[1-phenyl-2-(3-phenylpropenoyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5a**)

2.4.1.1. Coupling of 5a with trimethylsilylacetylene: preparation of [4-phenyl-2-(2-phenylethenyl)-6-trimethylsilylpyranyl- η^5]tricarbonylmanganese (6a). [[1-Phenyl-2-((*E*)-3-phenylprop-2-en-1-oyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5a**) (0.37 g, 0.92 mmol) and trimethylsilylacetylene (0.25 ml, 1.77 mmol) were dissolved in nitrogen-flushed CCl_4 and refluxed under nitrogen. When IR monitoring indicated that all **5a** had reacted (4 h), CCl_4 was removed under vacuum. To the residual oil, CH_2Cl_2 (10 ml) and deactivated neutral alumina (4 g) were added. The mixture was rotated (rotary evaporator) while the solvent was removed under vacuum. The alumina with product absorbed was then transferred to the top of a column (2 $\times$ 12 cm) of alumina. Elution with CH_2Cl_2 –hexane gave [4-phenyl-2-(2-phenylethenyl)-6-trimethylsilylpyranyl- η^5]tricarbonylmanganese (**6a**) as a red oil (0.34 g, 79%) which was crystallised from petroleum spirit as small black crystals: m.p. 121 °C. Anal. Found: C, 63.77; H, 4.76. Calc. for $C_{25}H_{23}O_4SiMn$: C, 63.82; H, 4.93%. IR (cm^{-1}): $\nu(CO)$ 2008 (vs), 1942 (s), 1930 (s). 1H -NMR: δ = 7.84 (d, 2H, J = 7.1 Hz, H2'', 6''), 7.47 (m, 8H, H3'', 5'', H4'', H2'', 6'', H3'', 5'', H4''), 6.88 (d, 1H, J = 15.6 Hz, H2'), 6.14 (d, 1H, J = 15.6 Hz, H1'), 5.21 (s, 1H, H5), 4.75 (s, 1H, H3), 0.32 (s, 9H, SiMe₃). ^{13}C -NMR: δ = 136.9 (s, C1'' or C1'''), 136.1 (s, C1'' or C1'''), 130.7 (d, C2'), 129.2 (d, C3'', 5''), 128.8 (d, C3'', 5''), 128.5 (d, C4'' or C4'''), 128.4 (d, C4'' or C4'''), 127.0 (d, C2'', 6''), 126.4 (d, C2'', 6''), 123.1 (d, C1'), 104.4 (s, C2), 99.3 (s, C4), 91.0 (d, C5), 88.0 (s, C6), 82.0 (d, C3), –2.1 (q, SiMe₃).

2.4.1.2. Coupling of 5a with phenylacetylene: preparation of [6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (7a). [[1-Phenyl-2-((*E*)-3-phenylprop-2-en-1-oyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5a**; 0.118 g, 0.29 mmol) and phenylacetylene (0.1 ml, 0.91 mmol) were refluxed overnight in nitrogen-saturated CCl_4 (20 ml). The solvent was removed under vacuum. PLC of the residual oil (Et_2O –petroleum spirit (1:3)) gave one major band. Removal of the band and extraction with CH_2Cl_2 followed by solvent removal under vacuum gave [6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7a**; 0.092

g, 66%) as a yellow oil which was crystallised by solvent diffusion (EtOAc–petroleum spirit) as bright yellow crystals, m.p. 190 °C. Anal. Found: C, 70.95; H, 3.95. Calc. for $C_{28}H_{19}O_4Mn$: C, 70.89; H, 4.04%. IR (cm^{-1}): $\nu(CO)$ 2030 (vs), 1967 (s), 1956 (s). 1H -NMR: δ = 7.72–7.20 (m, Ar–H), 6.64 (1H, dd, J = 2.2, 1.1 Hz, H3), 4.79 (1H, d, J = 1.1 Hz, H5), 3.97 (1H, dd, J = 3.5, 2.2 Hz, H1), 2.62 (1H, d, J = 3.5 Hz, H7). ^{13}C -NMR: δ = 191.0 (s, CO), 140.6 (s), 138.0 (s), 137.9 (s), 130.6 (d), 130.4 (d), 129.6 (d), 129.1 (d), 129.0 (d), 128.9 (d), 128.5 (d), 127.5 (d), 127.1 (d), 119.2 (s, C2 or C4), 113.5 (s, C2 or C4), 95.2 (d, C3), 76.0 (d, C5), 58.9 (d, C1), 47.2 (d, C7). This compound was further characterised by a single crystal X-ray structure determination.

2.4.2. Reactions of [1-(2-trifluoromethylphenyl)-2-((E)-3-(2-trifluoromethylphenyl)prop-2-en-1-oyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5b**)

2.4.2.1. Coupling of 5b with trimethylsilylacetylene: preparation of [4-(2-trifluoromethylphenyl)-2-(2-(2-trifluoromethylphenyl)ethenyl)-6-trimethylsilylpyranyl- η^5]tricarbonylmanganese (6b**).** [1-(2-Trifluoromethylphenyl)-2-((E)-3-(2-trifluoromethylphenyl)prop-2-en-1-oyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5b**) (0.172 g, 0.32 mmol) and trimethylsilylacetylene (0.09 ml, 0.64 mmol) were refluxed for 3 h in nitrogen-saturated CCl_4 . Carbon tetrachloride was removed under vacuum. PLC (petroleum spirit) of the residual oil gave one major band at R_f 0.2 which yielded [4-(2-trifluoromethylphenyl)-2-(2-(2-trifluoromethylphenyl)ethenyl)-6-trimethylsilylpyranyl- η^5]tricarbonylmanganese (**6b**) as a red oil (0.186 g, 96%) which was crystallised from warm petroleum spirit as small black crystals: m.p. 95 °C. Anal. Found: C, 54.14; H, 3.49. Calc. for $C_{27}H_{21}O_4F_6SiMn$: C, 53.47; H, 3.49%. IR (cm^{-1}): $\nu(CO)$ 2013 (vs), 1948 (s), 1930 (s). 1H -NMR: δ = 7.90 (d, 1H, J = 7.7 Hz, H6'''), 7.89 (d, 1H, J = 7.8 Hz, H3'''), 7.63 (m, 4H, H3'', H6'', H4'', H5''), 7.49 (t, 1H, J = 7.7, H4''), 7.36 (t, 1H, J = 7.6 Hz, H5''), 7.29 (dq, 1H, J = 15.4, 2.0 Hz, H2'), 6.03 (d, 1H, J = 15.4 Hz, H1'), 4.83 (s, 1H, H5), 4.62 (s, 1H, H3), 0.27 (s, 9H, $SiMe_3$). ^{13}C -NMR: δ = 135.4 (s, C6'''), 135.0 (s, C1'', C1'''), 132.7 (d, C6'' or C4''' or C5'''), 131.8 (d, C4''), 129.0 (d, C6'' or C4''' or C5'''), 127.7 (d, C5''), 127.1 (d, C1'), 127.0 (d, C6'' or C4''' or C5'''), 126.2 (d, J = 5.0 Hz, C3'', C3'''), 125.5 (d, C2'), 102.4 (s, C2), 97.4 (s, C4), 94.5 (d, C5), 88.7 (s, C6), 86.6 (d, C3), –2.4 (q, $SiMe_3$).

2.4.2.2. Coupling of 5b with phenylacetylene: preparation of [2-phenyl-4-(2-trifluoromethylphenyl)-6-(2-(2-trifluoromethylphenyl)ethenyl)pyranyl- η^5]tricarbonylmanganese (6c**).** [1-(2-Trifluoromethylphenyl)-2-((E)-3-(2-trifluoromethylphenyl)prop-2-en-1-oyl- κO)]ethenyl-

κC^1]tetracarbonylmanganese (**5b**) (0.30 g, 0.56 mmol) and phenylacetylene (0.14 ml, 1.27 mmol) were refluxed for 4 h in nitrogen-saturated CCl_4 . Analogous workup to that for **6a** gave [6-phenyl-4-(2-trifluoromethylphenyl)-2-(2-(2-trifluoromethylphenyl)ethenylpyranyl- η^5]tricarbonylmanganese (**6c**) as a red oil (0.24 g, 70%) which was crystallised from petroleum spirit as small red crystals: m.p. 142 °C. Anal. Found: C, 59.38; H, 2.75. Calc. for $C_{30}H_{17}O_4F_6Mn$: C, 59.03; H, 2.81%. IR (cm^{-1}): $\nu(CO)$ 2016 (vs), 1955 (s), 1934 (s). 1H -NMR: δ = 7.97 (d, 1H, J = 7.5 Hz, H6'''), 7.92 (d, 1H, J = 7.4 Hz, H3'''), 7.60 (m, 12H), 6.22 (d, 1H, J = 15.4 Hz, H1'), 5.38 (s, 1H, H5), 4.88 (s, 1H, H3). ^{13}C -NMR: δ = 135.7 (d, C6'''), 135.0 (s), 134.9 (s), 132.7 (d), 131.9 (d), 129.2 (d), 129.0 (d), 128.5 (d), 127.8 (d), 127.3 (d), 127.0 (d), 126.2 (d, J = 5.7 Hz, C3'', C3''') 124.6 (d), 123.3 (d, C2''', 6'''), 100.2 (s, C2), 94.8 (s, C4 or C6), 94.6 (s, C4 or C6), 86.2 (d, C3), 83.3 (d, C5).

2.4.2.3. Coupling of 5b with diphenylacetylene: preparation of [6-oxo-4,7-di-(2-trifluoromethylphenyl)-2,3-diphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (7b**).** Reaction of [1-(trifluoromethylphenyl)-2-((E)-2-(trifluoromethylphenyl)ethenylcarbonyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5b**; 0.157 g, 0.29 mmol) and diphenylacetylene (0.1 g, 0.56 mmol) followed by workup and purification by PLC as described for **7a** gave [6-oxo-4,7-di-(2-trifluoromethylphenyl)-2,3-diphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7b**; 0.07 g, 35%) as a yellow oil which was crystallised by diffusion (EtOAc–petroleum spirit) as small yellow crystals, m.p. 130 °C. This compound was pure by NMR and was identified by spectral comparison with **7a**. IR (cm^{-1}): $\nu(CO)$ 2028 (vs), 1967 (s), 1952 (s). 1H -NMR: δ = 7.50 (m, Ar–H), 4.41 (1H, s, H5), 3.95 (1H, d, J = 3.7 Hz, H1), 3.27 (1H, d, J = 3.7 Hz, H7). ^{13}C -NMR: δ = 188.2 (s, C6), 139.3–125.6 (several signals: C-2,3,4, other Ar–C), 76.2 (d, C5), 66.5 (d, C1), 41.6 (d, C7).

2.4.3. Reaction of [1-(4-Chlorophenyl)-2-((E)-3-(4-chlorophenyl)prop-2-en-1-oyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5d**)

2.4.3.1. Coupling with phenylacetylene: preparation of [6-oxo-4,7-di-(4-chlorophenyl)-2-phenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (7c**).** Reaction of [1-(4-chlorophenyl)-2-((E)-3-(4-chlorophenyl)prop-2-en-1-oyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**5d**; 0.18 g, 0.38 mmol) and phenylacetylene (0.09 ml, 0.82 mmol) and workup and purification by PLC as described for **7a** above gave [6-oxo-4,7-di-(4-chlorophenyl)-2-phenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7c**; 0.04 g, 20%) as a yellow oil which was crystallised by solvent diffusion (EtOAc–petroleum spirit) as large yellow crystals, m.p. 194 °C.

Anal. Found: C, 62.09; H, 3.11. Calc. for $C_{28}H_{17}Cl_2O_4Mn$: C, 61.90; H, 3.15%. IR (cm^{-1}): $\nu(CO)$ 2032 (vs), 1968 (s), 1957 (s). 1H -NMR: δ = 7.66–7.16 (m, Ar-H), 6.57 (1H, dd, J = 2.2, 1.1 Hz, H3), 4.71 (1H, d, J = 1.1 Hz, H5), 3.88 (1H, dd, J = 3.6, 2.2 Hz, H1), 2.58 (1H, d, J = 3.6 Hz, H7). ^{13}C -NMR: δ 219.6 (s, $2 \times Mn(CO)$), 219.4 (s, $MnCO$), 190.4 (s, CO), 139.0 (s), 137.6 (s), 136.7 (s), 136.3 (s), 133.6 (s), 130.9 (d), 130.8 (d), 130.3 (d), 129.2 (d), 129.1 (d), 129.0 (d), 128.4 (d), 117.8 (s, C2 or 4), 113.6 (s, C2 or 4), 95.0 (d, C3), 75.5 (d, C5), 58.3 (d, C1), 46.5 (d, C7).

2.5. Preparation of pyrylium triiodide salts

2.5.1. 4-Phenyl-2-(2-phenylethenyl)-6-trimethylsilylpyrylium triiodide (**8a**)

[4-Phenyl-2-(2-phenylethenyl)-6-trimethylsilylpyranyl- η^5]tricarbonylmanganese (**6a**; 0.07 g, 0.15 mmol) and iodine (0.085 g, 0.67 mmol) were stirred in CCl_4 for 1 h. Solvent was removed under reduced pressure and ether was added to the residual oil to precipitate solid 4-phenyl-2-(2-phenylethenyl)-6-trimethylsilylpyrylium triiodide (**8a**) which was collected (0.073 g, 78%) and crystallised by solvent diffusion from MeCN–ether as small black crystals, m.p. 165 °C. Anal. Found: C, 37.62; H, 3.08%. Calc. for $C_{22}H_{18}SiI_3O$: C, 37.10; H, 3.26%. λ_{max} (nm) (relative absorbance intensities) in MeCN: 291 (100), 339 (41), 368 (31). 1H -NMR ($(CD_3)_2CO$): δ = 8.98 (1H, d, J = 2.0 Hz, H-3), 8.83 (1H, d, J = 2.0 Hz, H-5), 8.65 (1H, d, J = 16.2 Hz, H-2'), 8.49 (2H, d, J = 7.2 Hz, H-2'', 6'''), 8.10 (2H, dd, J = 7.8, 1.8 Hz, H-2'', 6''), 7.94 (4H, m, H-1', 3'', 4'', 5'''), 7.74 (3H, m, H-3'', 4'', 5''), 0.82 (9H, s, $Si(CH_3)_3$). ^{13}C -NMR ($(CD_3)_2CO$): δ = 190.0 (s, C-6), 175.6 (s, C-2), 162.3 (s, C-4), 148.1 (d, C-2'), 135.7 (d, C-4''), 135.1 (s, C-1''), 133.5 (s, C-1'''), 133.3 (d, C-4'''), 130.9 (d, C-3''', 5'''), 130.3 (d, C-2'', 3'', 5'', 6'', 2'', 6''), 126.0 (d, C-5), 119.8 (d, C-3), 119.7 (d, C-1'), -2.61 (q, $Si(CH_3)_3$).

2.5.2. 4-(2-Trifluorophenyl)-2-(2-(2-trifluoromethylphenyl)ethenyl)-6-trimethylsilylpyrylium triiodide (**8b**)

[4-(2-Trifluoromethylphenyl)-2-(2-(2-trifluoromethylphenyl)ethenyl)-6-trimethylsilylpyranyl- η^5]tricarbonylmanganese (**6b**; 0.08 g, 0.13 mmol) and iodine (0.069 g, 0.54 mmol) were stirred in CCl_4 for 1 h. Solvent was removed under reduced pressure and ether was added to the residual oil to precipitate solid 4-(2-trifluorophenyl)-2-(2-(2-trifluorophenylethenyl)-6-trimethylsilylpyrylium triiodide (**8b**) which was collected (0.093 g, 69%) and crystallised by solvent diffusion from MeCN–ether as small black crystals, m.p. 124 °C. This compound, pure by NMR, was identified by spectral comparison with **8a** and **8c**. λ_{max} (nm) (relative absorbance intensities) in MeCN: 290 (100), 333 (43), 361 (30). 1H -NMR ($(CD_3)_2CO$): δ = 8.83 (1H, d, J = 16.2 Hz, H-2'), 8.76 (1H, s, H-5), 8.72 (1H, s, H-3), 8.44

(1H, d, J = 7.6 Hz, H-6'''), 8.23 (1H, d, J = 8.3 Hz, H-6''), 8.16 (1H, d, J = 16.2 Hz, H-1'), 8.07 (m, H-3''-5'', H3'''-5'''), 0.83 (9H, s, $Si(CH_3)_3$). ^{13}C -NMR ($(CD_3)_2CO$): δ = 193.3 (s, C-6), 174.7 (s, C-2), 165.2 (s, C-4), 142.4 (d, C-2'), 134.5 (s, C-1''), 134.1 (d), 134.0 (d), 133.0 (d), 132.8 (d), 132.0 (d), 130.7 (d, C-5), 130.0 (s, C-1'''), 129.6 (d, C-6'''), 128.3 (d, J = 4.5 Hz, C-3'''), 127.6 (d, J = 5.2 Hz, C-3''), 125.0 (d, C-3), 123.2 (d, C-1'), -2.86 (q, $Si(CH_3)_3$).

2.5.3. [2-Phenyl-4-(2-trifluoromethylphenyl)-6-(2-(2-trifluoromethylphenyl)ethenyl)pyrylium triiodide (**8c**)

[2-Phenyl-4-(2-trifluoromethylphenyl)-6-(2-(2-trifluoromethylphenyl)ethenyl)pyranyl- η^5]tricarbonylmanganese (**6c**; 0.107 g, 0.18 mmol) and iodine (0.089 g, 0.70 mmol) were stirred in CCl_4 for 1 h. Solvent was removed under reduced pressure and ether was added to the residual oil to precipitate solid [2-phenyl-4-(2-trifluoromethylphenyl)-6-(2-(2-trifluoromethylphenyl)ethenyl)pyrylium triiodide (**8c**) which was collected (0.123 g, 85%) and crystallised by solvent diffusion from MeCN–ether as small black crystals, m.p. 164 °C. Anal. Found: C, 38.28; H, 1.78. Calc. for $C_{27}H_{17}F_6I_3O$: C, 38.06; H, 2.01%. λ_{max} (nm) (relative absorbance intensities) in MeCN: 288 (100), 331 (43), 364 (34). 1H -NMR ($(CD_3)_2CO$): δ = 9.10 (1H, s, H-5), 8.86 (1H, dq, J = 15.8 Hz, H-2'), 8.72 (2H, d, J = 7.3 Hz, H-2''', 6'''), 8.71 (1H, s, H-3), 8.47 (1H, d, J = 7.7 Hz, H-2'''), 8.08 (11H, m, H-1', 2''-5'', 3'''-5''', 3''''-5'''''). ^{13}C -NMR ($(CD_3)_2CO$): δ = 172.4 (s, C-6), 170.3 (s, C-2), 168.4 (s, C-4), 142.0 (d, C-2'), 137.0 (d, C-4'''), 134.7 (s, C-1''), 134.2 (d), 134.1 (d), 133.1 (s, C1'''), 132.8 (d), 132.0 (d, C1'), 131.1 (d), 129.9 (d, C2''', C6''', C2''), 129.4 (s, C-1'''), 128.2 (d, J = 4.9 Hz, C-3'' or C-3'''), 127.6 (d, J = 5.4 Hz, C-3'' or C-3'''), 126.6 (s, J = 34.7 Hz, C-2'' or C-2'''), 123.2 (d, C-3), 122.8 (s, J = 28 Hz, C-2'' or C-2'''), 120.9 (d, C-5).

2.6. Reaction of [6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7a**) with ammonium cerium(IV) nitrate

[6-Oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7a**; 0.10 g, 0.21 mmol) and ammonium cerium(IV) nitrate (0.32 g, 0.58 mmol) were stirred in MeCN (20 ml) for 1 h. Acetonitrile was removed under vacuum. PLC of the residual oil (Et_2O –petroleum spirit (1:1)) gave one major band at R_f 0.7 which yielded a yellow oil (0.06 g). Crystallisation by the solvent diffusion method ($EtOAc$ –pentane) gave a very small quantity of yellow crystals of 2-nitro-3,5,7-triphenylcyclohepta-2,4,6-trien-1-one (**9**): m.p. 200 °C. This compound was characterised by a single crystal X-ray structure determination (see below).

Table 1
Selected bond lengths (Å) and bond angles (°) for **7a**

<i>Bond lengths</i>			
Mn(1)–C(2)	2.295(3)	Mn(1)–C(3)	2.182(3)
Mn(1)–C(4)	2.183(3)	Mn(1)–C(5)	2.178(3)
Mn(1)–C(6)	2.178(3)	Mn(1)–C(8)	1.815(3)
Mn(1)–C(9)	1.813(3)	Mn(1)–C(10)	1.815(3)
C(1)–C(11)	1.515(4)	C(1)–C(7)	1.523(4)
C(1)–C(2)	1.532(4)	C(2)–C(3)	1.408(4)
C(3)–C(4)	1.428(4)	C(3)–C(31)	1.504(4)
C(4)–C(5)	1.422(4)	C(5)–C(6)	1.436(4)
C(5)–C(51)	1.502(4)	C(6)–C(7)	1.474(4)
C(7)–O(7)	1.224(3)		
<i>Bond angles</i>			
C(9)–Mn(1)–C(8)	91.90(13)	C(9)–Mn(1)–C(10)	85.40(13)
C(8)–Mn(1)–C(10)	95.56(12)	C(11)–C(1)–C(7)	112.5(2)
C(11)–C(1)–C(2)	113.9(2)	C(7)–C(1)–C(2)	105.6(2)
C(3)–C(2)–C(1)	122.1(2)	C(2)–C(3)–C(4)	120.0(2)
C(5)–C(4)–C(3)	125.0(2)	C(4)–C(5)–C(6)	126.4(2)
C(5)–C(6)–C(7)	129.6(3)	O(7)–C(7)–C(6)	122.2(3)
O(7)–C(7)–C(1)	123.6(2)	C(6)–C(7)–C(1)	114.1(2)

Table 2
Selected bond lengths (Å) and bond angles (°) for **9**

<i>Bond lengths</i>			
O(1)–C(1)	1.261(8)	O(2)–N(1)	1.217(8)
O(3)–N(1)	1.234(8)	N(1)–C(2)	1.467(9)
C(1)–C(7)	1.442(9)	C(1)–C(2)	1.453(9)
C(2)–C(3)	1.366(9)	C(3)–C(4)	1.419(9)
C(3)–C(21)	1.495(9)	C(4)–C(5)	1.350(9)
C(5)–C(6)	1.433(8)	C(5)–C(31)	1.485(9)
C(6)–C(7)	1.366(9)	C(7)–C(41)	1.483(9)
<i>Bond angles</i>			
O(2)–N(1)–O(3)	124.1(7)	O(2)–N(1)–C(2)	116.9(7)
O(3)–N(1)–C(2)	119.0(7)	O(1)–C(1)–C(7)	119.7(7)
O(1)–C(1)–C(2)	118.4(7)	C(7)–C(1)–C(2)	121.8(6)
C(3)–C(2)–C(1)	134.4(6)	C(3)–C(2)–N(1)	116.7(6)
C(1)–C(2)–N(1)	108.8(5)	C(2)–C(3)–C(4)	123.7(6)
C(5)–C(4)–C(3)	130.6(7)	C(4)–C(5)–C(6)	125.7(6)
C(7)–C(6)–C(5)	132.3(7)	C(6)–C(7)–C(1)	125.6(7)

2.7. X-ray crystal structure determinations

The compounds **7a** and **9** were characterised by single-crystal X-ray crystallography. For each, the space group and crystal quality were established by precession photography. Accurate cell parameters and intensity data were collected by ω -scans on a Siemens P4 diffractometer with Mo–K α radiation $\lambda = 0.7107$ Å at -130 °C. The structures were solved by Patterson methods (**7a**) or direct methods (**9**) and routinely developed. Refinement was full-matrix least-squares based on F^2 , using the SHELX programs [5].

2.7.1. Crystal structure of [6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7a**)

Crystal data: C₂₈H₁₉MnO₄, MW 474.37, hexagonal, space group $P6_1$, a 10.233(2), c 37.509(5) Å, V 3401(1)

Å³, D_{calc} 1.389 g cm^{−3} for $Z = 6$, $F(000)$ 1464, $\mu(\text{Mo} - \text{K}\alpha)$ 0.61 mm^{−1}. Yellow hexagonal-block shaped crystal from EtOAc–pentane, $1.1 \times 1.0 \times 0.7$ mm. A total of 2379 data were collected in the range $2 < 2\theta < 50^\circ$, 2025 unique, 1890 with $I > 2\sigma(I)$, corrected for absorption based on ψ -scans. All non-H atoms were treated anisotropically, phenyl-H atoms and H(1) were included in calculated positions, while H(2), H(4) and H(6) were located as the three highest peaks in a penultimate difference map and were refined with a constrained C–H distance and tied U_{iso} . Refinement converged with R_1 0.0248 (2σ -data), R_1 0.0270, wR_2 0.0609, Goodness-of-fit F^2 0.999 (all data), no final feature $> |0.38|$ e Å^{−3}. That $P6_1$ was the correct polarity space group was confirmed by a Flack x parameter of 0.01(2). Selected bond parameters are given in Table 1.

2.7.2. Crystal structure of

2-nitro-3,5,7-triphenylcyclohepta-2,4,6-trien-1-one (**9**)

Crystal data: C₂₅H₁₇NO₃, MW 379.40, monoclinic, space group $P2_1/n$, a 9.483(7), b 10.393(7), c 19.320(12) Å, β 90.32(1)°, V 1904(2) Å³, D_{calc} 1.323 g cm^{−3} for $Z = 4$, $F(000)$ 792, $\mu(\text{Mo} - \text{K}\alpha)$ 0.09 mm^{−1}. Yellow needle-shaped crystal from EtOAc–pentane, $0.56 \times 0.21 \times 0.12$ mm. A total of 2669 data were collected by ψ -scans in the range $2 < 2\theta < 45^\circ$, 2491 unique, 1175 with $I > 2\sigma(I)$, not corrected for absorption. All non-H atoms were treated anisotropically, with H atoms included in calculated positions. Refinement converged with R_1 0.0774 (2σ -data), wR_2 0.1909, Goodness-of-fit on F^2 1.033 (all data), no final feature $> |0.29|$ e Å^{−3}. Selected bond parameters in given in Table 2.

3. Results and discussion

3.1. Cyclomanganation of

1,5-diarylpenta-1,4-dien-3-ones (**4**)

The bright red β -cyclomanganation products (**5**) are formed from 1,5-diarylpenta-1,4-dien-3-ones (**4**) and benzylpentacarbonylmanganese with comparable ease to those (**1**) formed [1a] from simple chalcones, and they appear to be equally stable in air.

With the dienone system of **4**, there exists the possibility with excess benzylpentacarbonylmanganese of successive manganations leading to β, β' -dicyclomanganated products in which the carbonyl oxygen acts as a dual donor. Adams and coworkers have prepared such a compound from dimethyl acetylenedicarboxylate and Mn₂(CO)₁₀ [6]. However, there was no indication of a dimanganation product from **4a** even over prolonged periods for reactions in which benzylpentacarbonylmanganese was used in greater than two-fold excess.

3.2. Coupling with alkynes

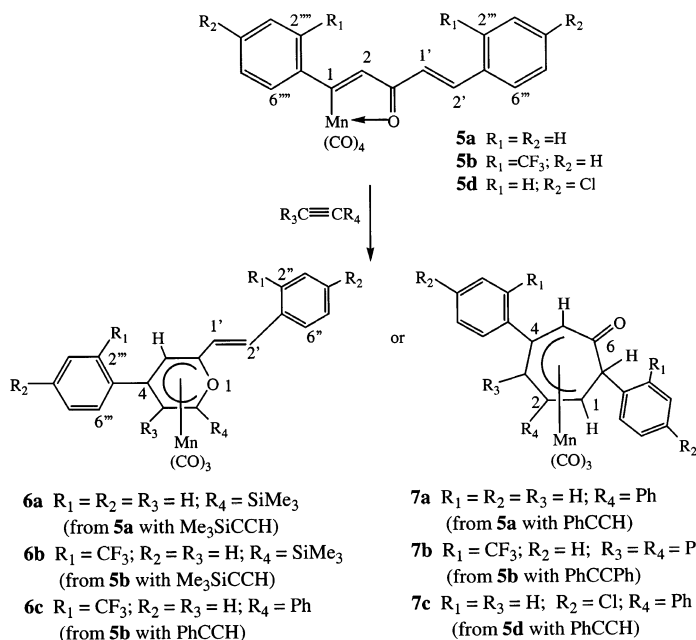
The reaction of the cyclomanganated dienones (**5**) with alkynes in some cases gives [4-phenyl-2-(2-phenylethenyl)pyranyl- η^5]tricarbonylmanganese derivatives (**6**), analogous to those (**2**) obtained from simpler β -manganated chalcones (**1**) [1b], but in other cases novel seven-membered ring complexes [6-oxo-4,7-diphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7**) were formed (Scheme 3). Various cycloheptadienyl complexes of manganese have been prepared previously from $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ or $\text{PhMn}(\text{CO})_5$ and cycloheptatriene [7], or by addition of nucleophiles to [(cycloheptatriene) $\text{Mn}(\text{CO})_3$] $^+$ ions [8], but the present route appears to be the first for manganese where the ring is built up in situ, and also the only one to give a ring incorporating a C=O group. Direct reaction of $\text{Mn}_2(\text{CO})_{10}$ with tropone does not give a corresponding species [9]. However, substituted (η^4 -tropone) $\text{Fe}(\text{CO})_3$ complexes have long been known, syntheses involving co-oligomerisation of alkynes and CO [10]. The same route is involved in the formation of the η^4 cobalt complex (hexachlorotropone-1,2,5,6- η) CoCp [11]. A chromium η^6 -tropone complex has been structurally characterised [12].

Whether it is the six- or seven-membered ring species which is formed can be established spectroscopically. Both **6** and **7** give the same type of three-band carbonyl region infrared spectrum, but the absorptions of the pyranyl complexes are consistently at lower frequencies by ca. 20 cm^{-1} than those of the oxocycloheptadienyl complexes. This suggests that there is stronger net electron donation from the η^5 -system in the pyranyl

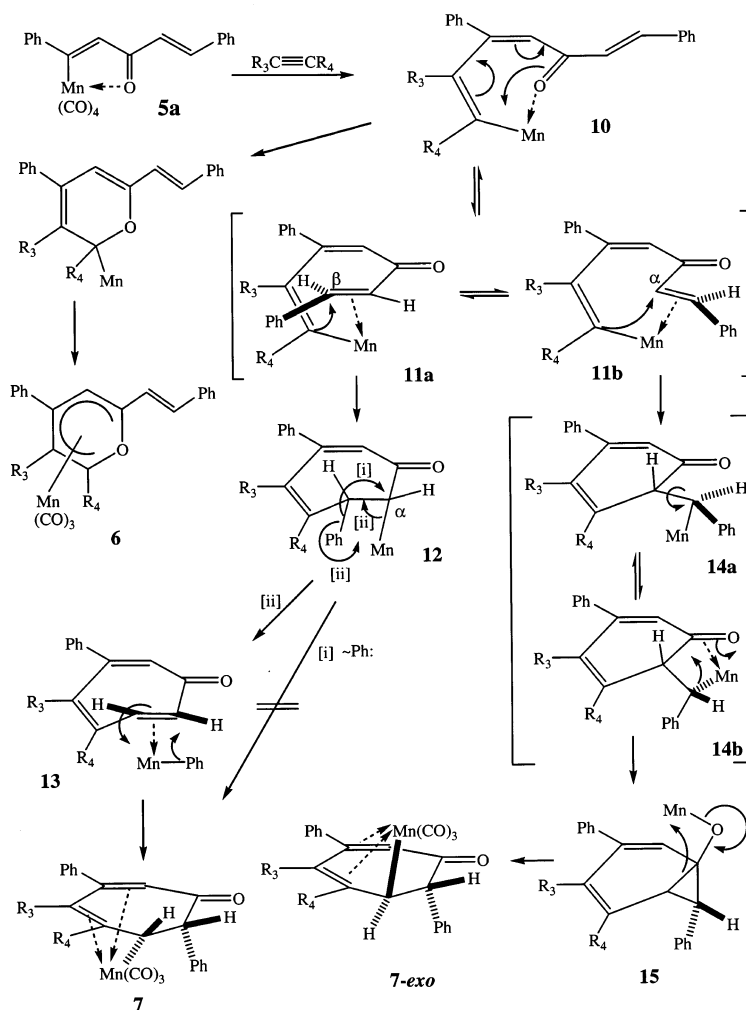
ligand than from the oxocycloheptadienyl ligand, as is consistent with the structures which show that the average $\text{Mn}-\text{C}(\eta^5)$ distances are, respectively, 2.188(3) and 2.203 (1) Å.

In previously studied simple cycloheptadienyl manganese complexes without the oxo group, carbonyl stretching frequencies more closely match those of six-membered ring species with η^5 donors, such as the pyranyl complexes (**6**) and cyclohexadienyl $\text{Mn}(\text{CO})_3$ [8]. In such cycloheptadienyl species both non-coordinated carbon atoms are sp^3 , permitting a marked folding of the seven-membered ring so that the η^5 section can bond efficiently and achieve $\text{Mn}-\text{C}$ distances similar to those in smaller ring compounds. By contrast, similar folding of the ligand in **7a** to allow optimum bonding is restricted by the presence of the sp^2 carbon of the ketone group. Restriction to folding will be enhanced by the preference of the ketone CO to remain conjugated to the dienyl π -system; the structure below shows the $\text{C}(5)-\text{C}(6)-\text{C}(7)-\text{O}(7)$ torsion angle is only 7.6° . It is clear that electron-withdrawal from the π -system by the conjugated ketone carbonyl will contribute to the reduction in ligand donor ability towards the metal.

Possible routes to **6** and **7** are outlined in Scheme 4, which for clarity does not include the variety of possible alkene and carbonyl coordinations to the metal. Regiospecific insertion of the alkyne into the $\text{Mn}-\text{C}$ bond of the cyclomanganated substrate (**5a** in Scheme 4 for simplicity) would give a seven-membered metallocyclic intermediate (**10**). As outlined in our previous paper [1b] and based on the proposal by Booth and Hargreaves [13], the pyranyl ring of **6** may be formed



Scheme 3. Reactions of cyclomanganated 1,5-diaryl-penta-1,4-dien-3-ones with alkynes.



Scheme 4. Pathways to **6** and **7** (ligand coordinations to Mn, where shown, are indicated by broken arrows, but most are omitted for clarity).

from **10** by rearrangement of the π -system (see electron-pair movements indicated in **10**) as the enone oxygen bonds to the manganese carbon, the remaining two π -bonds then coordinating to the metal.

Routes to **7** have been considered which derive (Scheme 4) from the alternative σ -vinyl- η^2 -alkene complexes **11a** and **11b**, formed after dissociation of the enone oxygen atom from manganese in **10** by rotation of the exocyclic C=C bond into a position where it can coordinate to the metal. Insertion of the coordinated C=C bond into the C-Mn bond would bring about ring-closure, from **11a** to form **12** or from **11b** to form **14**. Such insertion of a coordinated C=C group into the Mn-C bond has been invoked for some [5 + 2] cycloaddition reactions [14], and is analogous to the intermolecular alkene insertion reactions at aryl-Mn bonds of orthomanganated ketones [2a]. Similar coupling of η^1, η^2 carbon fragments is well known in the Heck reaction of aryl or vinyl halides with alkenes, and in a variety of other palladium-promoted reactions [15].

From **12**, formation of product **7** requires Ph and Mn to exchange places on the β and α carbons. A direct 1,2-migration from C_β to C_α with inversion of configuration at C_α would be feasible for the top face (*exo*) substituent at C_β but this is H, not Ph, and there is no product derived from H migration. In any case, if Ph did migrate (arrow [i] in structure **12**) inversion at C_α would leave Ph *exo* in the product. This raises the possibility that phenyl migration may be mediated on the *endo* face by Mn-Ph bonding, perhaps through Mn insertion into the C_β -Ph bond as indicated by [ii] via the Mn-Ph intermediate **13**. Insertion of *endo* C-H into adjacent η^5 -coordinated Mn to form Mn-H intermediates is established as the basis for thermally induced hydrogen migrations in tricarbonylcyclohexadienylmanganese [16]. Similar hydrogen migrations are mediated by other π -complexed metals, for instance in tricarbonylcycloheptatrienechromium systems in which the sequential character of hydrogen migration has been rationalised by Pauson as Cr-assisted *endo*-H migration

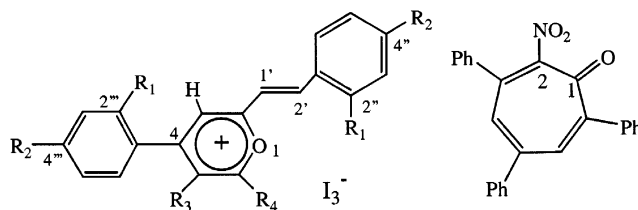
without formation of a discrete Cr–H intermediate [17]. By contrast, as far as we are aware, corresponding metal-mediated *endo*-aryl migrations are unknown. In the current system, the *endo* C–Ph bond is the only one accessible to the σ -bonded Mn for insertion in **12**, and collapse of **13** to **7** would be favoured over reversion to **12** by the stabilisation afforded by conjugated π -coordination in **7**. At this stage, an *endo*-Mn-mediated phenyl migration, whether or not through a discrete metal–aryl bonded intermediate, seems to be the most likely explanation for the *endo* stereochemistry of the phenyl group in **7**.

A mechanism which circumvents the requirement for Ph migration is one in which the α and β carbons (the β with the phenyl group attached) ultimately exchange positions. Initiated by the reverse orientation of insertion of the π -bond in **11b** into the C–Mn bond, this could be achieved via the sequence through **14** and **15**. However, by this pathway, as is clear from structures **14a/14b** and **15**, the original stereochemistry of the enone system translates into an *exo* orientation for the phenyl group in the product (designated **7-exo** in Scheme 4), whereas it is *endo* in **7**. Unless the metal promotes a configurational inversion somewhere on the pathway, it appears that this α,β -interchange route to **7** cannot apply.

A further puzzle in this initial study is the question of product preferences in these reactions as a function of alkyne substituent, for instance, why **5a** with phenylacetylene gives the oxocycloheptadienyl complex **7a** whereas with trimethylsilylacetylene it gives the pyranil complex **6a**. One observation of possible relevance is that in the phenylacetylene case there was IR evidence at early stages of the reaction for the formation of some of the pyranil complex of type **6**, suggesting that some of it may initially be formed reversibly. With trimethylsilylacetylene by contrast, only the pyranil complex **6** was formed so if its formation is reversible, this does not result in product redistribution to the **7** analogue. Further study with a wider range of substituents is needed to explain reactivity patterns.

3.3. Reaction of pyranil complexes (**6**) with iodine to form pyrylium triiodide salts

In cases where pyranil complexes were isolated, they behaved normally in their reaction with iodine to form pyrylium triiodide salts (**8**), the presence of the styryl substituent on the pyranil ring (in place of a phenyl group in the case of the pyranil complexes formed from β -manganated chalcones; Scheme 1 [1b]) having no influence on the course of the reaction. As for their pyranil complex precursors, these pyrylium salts have potential for synthetic modification centred on the alkene function. Given the enormous variety of heterocyclic structures that can be obtained by reaction of pyrylium salts with various reagents [18], there is potential application of these reactions in organic synthesis.



8a $R_1 = R_2 = R_3 = H$; $R_4 = SiMe_3$

8b $R_1 = CF_3$; $R_2 = R_3 = H$; $R_4 = SiMe_3$

8c $R_1 = CF_3$; $R_2 = R_3 = H$; $R_4 = Ph$

9

3.4. Reaction of [6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7a**) with ammonium cerium(IV) nitrate

The potential for organic synthesis of oxidative demetallation of the $(\eta^5\text{-cycloheptadienyl})Mn(CO)_3$ complexes reported here has been only tentatively explored so far. Significantly, reaction with I_2 , which was successful in the demetallation of pyranil complexes [1b] to form stable pyrylium salts, did not demetallate **7a**. However, when the strong oxidant ammonium cerium(IV) nitrate was used, the tropone **9**, in which ring-nitration has accompanied demetallation, was formed amongst a mixture of products. This suggests untapped potential in the use of moderate oxidants and electrophiles for the synthesis of cycloheptatrienone derivatives from **7**.

3.5. Crystal structures of **7a** and **9**

The structure of [6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7a**) is shown in Fig. 1, with the numbering scheme used for the structural discussion. The molecule is an unusual example from the well-known class of $(\eta^5\text{-dienyl})Mn(CO)_3$ complexes, with the dienyl fragment coming from a seven-membered ring related to tropone. The five carbon atoms which are bonded to the manganese atom form a very slightly puckered plane (maximum deviation 0.09 Å) which is 1.608(1) Å away from Mn(1). The individual Mn–C bonds vary from 2.178(3) to 2.295(3).

The C–C distances in the C(1)–C(5) dienyl unit are in the range 1.408(4)–1.436(4) Å, being shorter, as expected, than the uncoordinated single $sp^2\text{--}sp^2$ bond C(6)–C(7) (1.474(4) Å) and the $sp^2\text{--}sp^3$ bonds C(1)–C(2) and C(1)–C(7) which are 1.532(4) and 1.523(4) Å, respectively. C(1) and C(7) are twisted out of the plane of the ligand, away from the manganese atom and the phenyl substituent on C(1) is *endo*. The three phenyl rings on C(1), C(3) and C(5) form dihedral angles of 83, 34 and 54°, respectively, with the least-squares plane through C(2)–C(6).

There appear to be four other structure determinations of (heptadienyl) $Mn(CO)_3$ complexes [8,19–21]. As

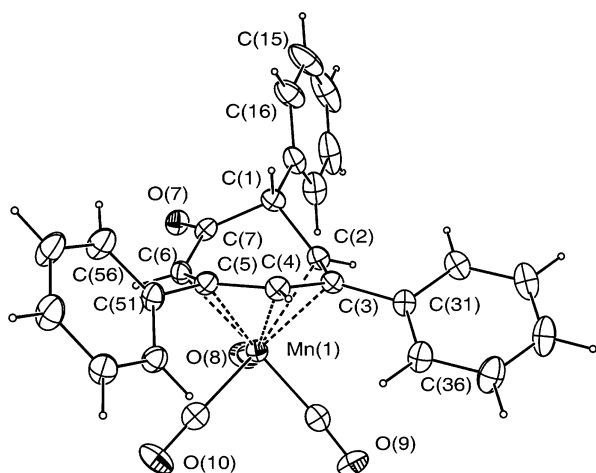


Fig. 1. Structure of [6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese (**7a**).

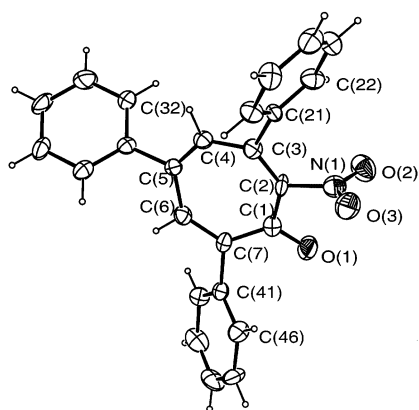


Fig. 2. Structure of 2-nitro-3,5,7-triphenylcyclohepta-2,4,6-trien-1-one (**9**).

mentioned in the case above (Section 3.2), these differ from **7a** in that in each of them the two non-coordinated carbon atoms are sp^3 and flexible, whereas the ring in **7a** is less puckered because of the ketone group.

The determination of the structure of **9** was carried out primarily for identification since spectroscopic methods did not provide full characterisation. The compound is the 2-nitro-tropone (2-nitro-3,5,7-triphenylcyclohepta-2,4,6-trien-1-one) as shown in Fig. 2. The seven-membered ring is significantly concave, bent about a line joining C(3) to the mid-point of the C(6)–C(7) bond such that C(3) is 0.14 Å below the least-squares plane and C(1) is 0.16 Å above it. The formal double C=C bonds C(2)–C(3), C(4)–C(5) and C(6)–C(7) average 1.360(8) Å, while the remaining C–C bonds of the seven-membered ring average 1.437(8) Å. The plane of the NO₂ group is at 88° to the least-squares plane of the central ring, while the three phenyl groups at C(3), C(5) and C(7) are twisted by 61, 52 and 51°, precluding extensive conjugation with the ring. With the exception of the non-planarity of the seven-

membered ring, these parameters closely match those of a series of aryl-substituted tropones investigated as possible colchicine analogues [22].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 168095 for **7a** and 168096 for **9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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References

- [1] (a) W. Tully, L. Main, B.K. Nicholson, *J. Organomet. Chem.* 503 (1995) 75; (b) W. Tully, L. Main, B.K. Nicholson, *J. Organomet. Chem.* 507 (1996) 103.
- [2] (a) L.H.P. Gommans, L. Main, B.K. Nicholson, *J. Chem. Soc. Chem. Commun.* (1987) 761 (alkene coupling); (b) L. Liebeskind, J.R. Gasdaska, J.S. McCallum, S.J. Tremont, *J. Org. Chem.* 54 (1989) 669 (Me₃NO-promoted alkyne coupling); (c) N.P. Robinson, L. Main, B.K. Nicholson, *J. Organomet. Chem.* 364 (1989) C37 (thermally promoted alkyne coupling); (d) L. Main, B.K. Nicholson, *Adv. Met.-Org. Chem.* 3 (1994) 1 (a review covering developments up to 1991); (e) R.C. Cambie, M.R. Metzler, P.S. Rutledge, P.D. Woodgate, *J. Organomet. Chem.* 429 (1992) 41 (see also p. 59 and references therein; reactions of manganated diterpenoid carbonyl compounds).
- [3] R.D. Closson, J. Kozikowski, T.H. Coffield, *J. Org. Chem.* 22 (1957) 598; see also M.I. Bruce, M.J. Liddell, G.N. Pain, *Inorg. Synth.* 22 (1989) 598.
- [4] A.I. Vogel, *Practical Organic Chemistry*, 3rd ed., Longman, London, 1956 (a) p. 717 and (b) p. 718.
- [5] (a) G.M. Sheldrick, *SHELXS-86*, University of Göttingen, Göttingen, Germany, 1986; (b) G.M. Sheldrick, *SHELXL-93*, University of Göttingen, Göttingen, Germany, 1993.
- [6] (a) R.D. Adams, *Chem. Soc. Rev.* (1994) 335; (b) R.D. Adams, L. Chen, W. Wu, *Organometallics* 12 (1993) 3431 (see also p. 4112).
- [7] (a) R.B. King, M.N. Ackermann, *Inorg. Chem.* 13 (1974) 637; (b) J.C. Burt, S.A.R. Knox, R.J. McKinney, F.G.A. Stone, *J. Chem. Soc. Dalton Trans.* (1977) 1.
- [8] E.D. Honig, M. Quin-jin, W.T. Robinson, P.G. Williard, D.A. Sweigart, *Organometallics* 4 (1985) 871 (and references therein).

- [9] M.J. Barrow, O.S. Mills, F. Haque, P.L. Pauson, *Chem. Commun.* (1971) 1239.
- [10] (a) D.L. Smith, L.F. Dahl, *J. Am. Chem. Soc.* 84 (1962) 1743;
(b) J.A.S. Howell, A.D. Squibb, Z. Goldschmidt, H.E. Gottlieb, A. Almadhoun, I. Goldberg, *Organometallics* 9 (1990) 80 (and references therein).
- [11] K. Suenkel, *J. Organomet. Chem.* 391 (1990) 247.
- [12] M.J. Barrow, O.S. Mills, *J. Chem. Soc. D* (1971) 119.
- [13] B. Booth, R.G. Hargreaves, *J. Chem. Soc. A* (1970) 308.
- [14] C. Wang, J.B. Sheridan, H.-J. Chung, M.L. Cote, R.A. Lalancette, A.L. Rheingold, *J. Am. Chem. Soc.* 116 (1994) 8966.
- [15] (a) R.F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, 1985;
(b) J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, Chichester, 1995.
- [16] W. Lamanna, M. Brookhart, *J. Am. Chem. Soc.* 102 (1980) 3490.
- [17] M.L. Foreman, G.R. Knox, P.L. Pauson, K.H. Todd, W.E. Watts, *J. Chem. Soc. Perkin Trans. 2* (1972) 1141.
- [18] A.T. Balaban, A. Dinculescu, G.N. Dorofeenko, G.W. Fischer, A.V. Koblik, V.V. Mezheritskii, W. Schroth, in: A.R. Katritzky (Ed.), *Pyrylium Salts: Syntheses, Reactions and Physical Properties (Advances in Heterocyclic Chemistry, Supplement 2)*, Academic Press, New York, 1982.
- [19] R.C. Bush, R.A. Jacobson, R.J. Angelici, *J. Organomet. Chem.* 323 (1987) C27.
- [20] M. Wieser, K. Sunkel, C. Robl, W. Beck, *Chem. Ber.* 127 (1992) 1369.
- [21] S. Lee, Y.K. Chung, T.-S. Woon, W. Shin, *J. Organomet. Chem.* 486 (1995) 135.
- [22] J.M. Gulbis, M.F. Mackay, M.G. Banwell, J.N. Lambert, *Acta Crystallogr. C* 48 (1992) 332 (and references therein).