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Journal of Organometallic Chemistry 690 (2005) 3340–3347
Journal of Organometallic Chemistry
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Reversible pyranyl complex formation and the mechanism of rearrangement to (η^5-6-oxocycloheptadienyl)$Mn(CO)_3$ complexes in the reaction of β-cyclomanganated 1,5-diarylpenta-1,4-dien-3-ones and alkynes; the crystal structure of [2,4-diphenyl-6-(2-phenylethenyl)pyranyl-η^5]tricarbonylmanganese

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Received 25 February 2005; accepted 5 April 2005
Available online 31 May 2005

Abstract

[1-Phenyl-2-[(*E*)-3-phenylprop-2-en-1-oyl-κ*O*]ethenyl-κ*C*^{1}]tetracarbonylmanganese (**1a**) reacts with PhCCH in CCl_4 at room temperature to form [2,4-diphenyl-6-(2-phenylethenyl)pyranyl-η^5]tricarbonylmanganese (**2a**), whose X-ray crystal structure is reported to complement that of its isomer [6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-1,2,3,4,5-η]tricarbonylmanganese (**3a**), previously obtained from the reaction under reflux; but for **1a** and PhCCPh the pyranyl complex cannot be isolated before rearrangement to the **3a** analogue occurs. More forcing reaction conditions for **1a** with Me_3SiCCH and for [1-(2-trifluoromethylphenyl)-2-[(*E*)-3-(2-trifluoromethylphenyl)prop-2-en-1-oyl-κ*O*]ethenyl-κ*C*^{1}]tetracarbonylmanganese (**1b**) with Me_3SiCCH and PhCCH give new analogues of **3a** where previously only **2a** analogues had been isolated.

The reaction in CCl_4 under reflux of PhCCH and the β-deuterio analogue of **1a**, [1-phenyl-2-[(*E*)-3-phenylprop-2-en-1-oyl-3d-κ*O*]ethenyl-κ*C*^{1}]tetracarbonylmanganese, gave deuteriated **3a** with *exo*-D at the α-carbon, C7. This is inconsistent with the Mn-mediated Ph migration mechanism originally proposed to accommodate the *endo* position of Ph in **3a**, and instead it implicates a cyclopropyl carbonyl-addition intermediate or a cyclopropyl acyl-substitution transition state in the key rearrangement step for **2a** → **3a**.

Keywords: Manganese; Alkyne; Cyclometallation; Crystal structure; Mechanism; Addition–elimination; Acyl substitution

1. Introduction

Following an early review [1] incorporating the coupling of alkynes with cyclomanganated aryl carbonyl compounds, we reported [2a] that reactions of alkynes with β-cyclomanganated chalcones in CCl_4 under reflux give (η^5-pyranyl)$Mn(CO)_3$ complexes. The reaction was more recently studied with β-cyclomanganated dienones (**1**) and shown [2b] to give not only pyranyl complexes (e.g., **2a**; Scheme 1) but also 6-oxocycloheptadienyl complexes (e.g., **3a**). The latter were suggested to be formed via an insertion intermediate (**4b** or **4c**) with metal coordination alternative to that in the assumed precursor **4a** (Scheme 2) of the pyranyl complex.

Reversible formation of the pyranyl complex was indicated by the observation that while **1a** with PhCCH gave only oxocycloheptadienyl complex **3a** as the isolable product after 24 h, the initial formation and then disappearance of some pyranyl complex **2a** was detected by IR monitoring during the course of the reaction. Another 24-h reaction which gave no pyranyl complex

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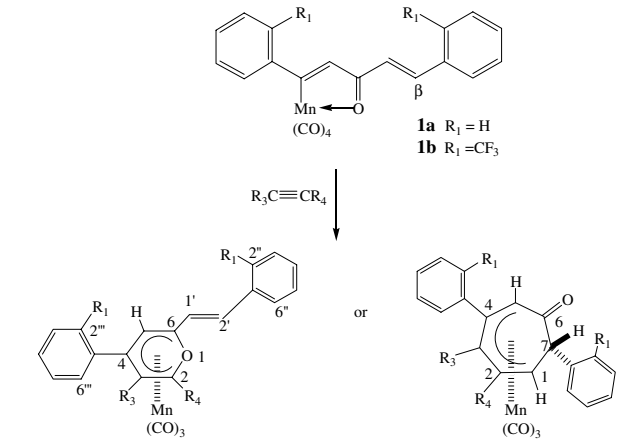
doi:10.1016/j.jorganchem.2005.04.015



2a $R_1 = R_3 = H$; $R_4 = Ph$ (from **1a** with PhCCH)
2b $R_1 = R_3 = H$; $R_4 = SiMe_3$ (from **1a** with Me_3SiCCH)
2c $R_1 = H$; $R_3 = R_4 = Ph$ (from **1a** with PhCCPh)

2d $R_1 = CF_3$; $R_3 = H$; $R_4 = Ph$ (from **1b** with PhCCH)
2e $R_1 = CF_3$; $R_3 = H$; $R_4 = SiMe_3$ (from **1b** with Me_3SiCCH)
2f $R_1 = CF_3$; $R_3 = R_4 = Ph$ (from **1b** with PhCCPh)

3a $R_1 = R_3 = H$; $R_4 = Ph$ (from **1a** with PhCCH)
3b $R_1 = R_3 = H$; $R_4 = SiMe_3$ (from **1a** with Me_3SiCCH)
3c $R_1 = H$; $R_3 = R_4 = Ph$ (from **1a** with PhCCPh)

3d $R_1 = CF_3$; $R_3 = H$; $R_4 = Ph$ (from **1b** with PhCCH)
3e $R_1 = CF_3$; $R_3 = H$; $R_4 = SiMe_3$ (from **1b** with Me_3SiCCH)
3f $R_1 = CF_3$; $R_3 = R_4 = Ph$ (from **1b** with PhCCPh)

Scheme 1. Products from reactions of cyclomanganated 1,5-diarylpenta-1,4-dien-3-ones with alkynes.

was that of **1b** with PhCCPh which furnished only **3f**. However, some other reactions were allowed to proceed only for the shorter time required for all of the manganated reactant to be consumed (ca. 4 h) and in these cases (e.g., **1a** with Me_3SiCCH; **1b** with PhCCH and Me_3SiCCH) only the pyranyl complexes (**2e**, **2b**, **2d**) were obtained. Reaction times in these cases were not extended to see if rearrangement to oxocycloheptadienyl complexes might occur over time. One of the aims of the present study was to fill these gaps in the original exploratory study and determine whether reversible pyranyl formation accompanied by rearrangement to oxocycloheptadienyl complex is general under appropriate conditions.

The second and major aim was to test the Mn-mediated phenyl migration mechanism (**4b** → **3a**) previously proposed [2b] to accommodate the stereochemistry of the oxocycloheptadienyl complex **3a** which is *endo* (7-Ph group towards the $Mn(CO)_3$ face of the oxocycloheptadienyl ring). A tracer study using **1a** labeled with D at the β-position now allows a distinction between this and an alternative rearrangement mechanism starting from **4c** previously considered [2b] and leads to a major mechanism reassessment.

2. Results and discussion

2.1. Product formation under modified reaction conditions

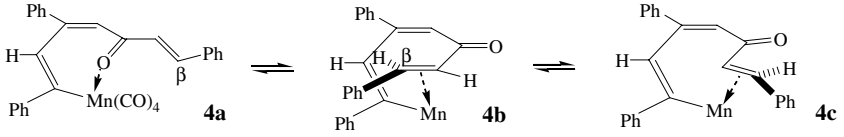
The following summary shows that both pyranyl and oxocycloheptadienyl complexes are formed from each of the manganated dienones **1a** and **1b** under appropriate conditions, and are isolable in all but one case (pyranyl complex from **1a** with PhCCPh). Over time, the rearrangement of pyranyl to oxocycloheptadienyl complex occurs routinely. It seems likely on mechanism grounds that the oxocycloheptadienyl complexes would all be *endo* as for **3a**, whose crystal structure has been determined [2b], but this is not proven; certainly chemical shift comparability for H7 within and between the **3a**–**c** and **3d**–**f** series suggests that all H7 are on the same (*exo*) face.

2.1.1. Reactions of [1-phenyl-2-[(E)-3-phenylprop-2-en-1-oyl-κO]ethenyl-κC^1]tetracarbonylmanganese (*1a*)

Phenylacetylene. Previously [2b] this reaction in CCl_4 under reflux gave only **3a** though there was IR evidence for the formation and disappearance of the pyranyl complex **2a**. Now the reaction in CCl_4 at room temperature for 28 h gives **2a**, isolated as dark red crystals, whose X-ray crystal structure is determined (see Sections 2.3 and 3.4) to complement that of the isomeric *endo*-oxocycloheptadienyl complex **3a** from the previous study [2b].

(*Trimethylsilyl*)*acetylene*. The unknown oxocycloheptadienyl complex **3b** was obtained from the reaction carried out now under more forcing conditions in heptane (b.p. 98 °C) under reflux for 24 h, along with an equivalent amount of the pyranyl complex **2b** already known [2b] from the reaction in CCl_4.

Diphenylacetylene. This reaction had not been studied previously but over 4 days at room temperature, formation and disappearance of **2c** in only a low concentration was observed with **3c** accumulating as the only isolable product.



Scheme 2. Alternative metal coordination modes in the insertion intermediate for **1a** and phenylacetylene.

*2.1.2. Reactions of [1-(2-trifluoromethylphenyl)-2-[(E)-3-(2-trifluoromethyl)phenylprop-2-en-1-oyl-κO]ethenyl-κC^1]tetracarbonylmanganese (**1b**)*

Phenylacetylene. Previously [2b] this reaction in CCl_4 gave only **2d** but in heptane under reflux over 24 h **3d** was obtained in 3:1 excess over **2d**.

(*Trimethylsilyl*)*acetylene*. The unknown oxocycloheptadienyl complex **3e** was obtained from the reaction carried out in heptane under reflux but even after 7 days there was still almost a two-fold excess of the pyranyl complex **2e**, already known [2b] from the reaction in CCl_4.

Diphenylacetylene. By contrast, this reaction had earlier [2b] yielded only **3f** after 24 h in CCl_4 under reflux. Here the same product was obtained along with an equivalent amount of the new pyranyl complex **2f** at 30 °C in heptane.

Conclusions from these results are first that the pyranyl complex is always formed but it rearranges to oxocycloheptadienyl complex over time, presumably through reversal to complex **4a** (Scheme 2). Second, there are reactivity differences with substituents, e.g., for **1a** with diphenylacetylene even at room temperature, the oxocycloheptadienyl complex **3c** is dominant from an early stage of the reaction, whereas for the sluggish reaction of **1b** with Me_3SiCCH the pyranyl complex **2e** is still dominant over **3e** after 7 days in heptane at 98 °C. As yet there are too few data to justify analysis of substituent effects.

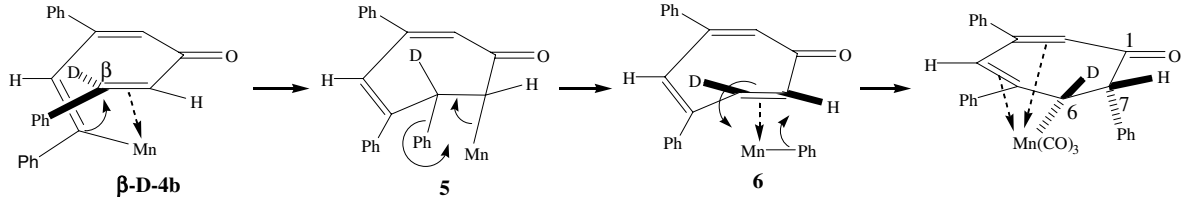
2.2. Deuterium isotopic labeling study for the mechanism of formation of oxocycloheptadienyl complex *3a*

We previously [2b] considered two possible mechanisms for formation of **3a** with the Ph group in the *endo* position, starting, respectively, with *syn* addition across the coordinated π-bond of intermediates **4b** or **4c**. These mechanisms are repeated here in Scheme 3 and 4 but now depicting β-deuterio-labeled **4b** and **4c** as obtained from PhCCH and the β-deuterio derivative of **1a.** The latter compound (β-**D-1a**, systematically named [1-phenyl-2-[(*E*)-3-phenylprop-2-en-1-oyl-3d-κ*O*]ethenyl-κC^1]-tetracarbonylmanganese) was synthesized in the present study (see Section 3.3 and Scheme 7) for the purpose of distinguishing between these mechanisms.

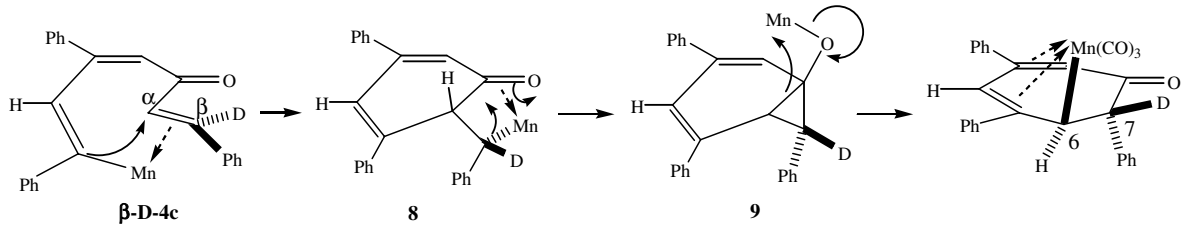
The metal-mediated phenyl migration mechanism (Scheme 3) was originally invoked to meet the stereochemical requirement that the Ph group finishes up on the same face as the coordinated Mn (*endo*) as would result if the Mn remains π-coordinated in **6** as it transfers Ph. If this mechanism operates the D label would be in the 6-position in **3a** as shown (Scheme 3).

The alternative mechanism originally considered [2b] was one (Scheme 4) in which the rearrangement occurs via initial alkene addition to form a 6-membered ring followed by ring expansion through addition of the manganated carbon in **8** to the ketone C=O, with subsequent elimination to reopen the cyclopropyl ring of **9**. An analogous (but 5- to 6-membered) ring-expansion addition–elimination mechanism through a cyclopropyl addition intermediate (with subsequent Pd hydride elimination) has been proposed for a palladiated precursor derived from *N*-allyl-*N*-(2-bromoallyl)-4-methylbenzenesulfonamide and $Pd(PPh_3)_4$ leading on to the 5-methylene-3,4-dihydropyridine *N*-(4-methylbenzenesulfonyl) derivative [3].

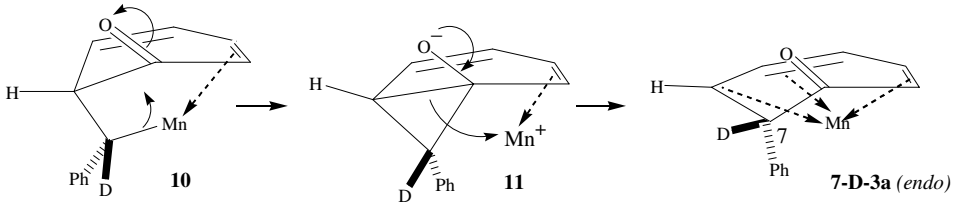
Here the Ph group does not migrate, rather the carbon atom with attached phenyl group (and H, or D as shown here) exchanges position to move adjacent to C=O. However it was originally considered that in the non-polar solvent, stabilisation of the alkoxide anion by coordination to Mn as shown in **8** and **9** would be re-



Scheme 3. Metal-mediated phenyl-migration mechanism (note here and elsewhere, other ligand coordinations to Mn are omitted for clarity).



Scheme 4. Carbonyl addition–elimination ring-expansion mechanism.

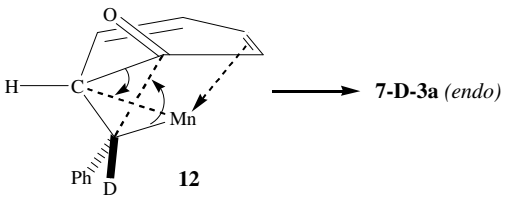


Scheme 5. Carbonyl addition–elimination ring-expansion mechanism with zwitterion intermediate (some substituents excluded for clarity).

quired and this would result in the movement of the metal to the face opposite Ph giving the *exo* isomer as shown (Scheme 4) rather than the observed *endo* product. The mechanism of Scheme 3 was therefore preferred [2b].

Now, however, the finding that the D label finishes up in the 7-position of the deuteriated form of **3a** leads to rejection of Scheme 3 and acceptance of the basic skeletal change, though not the stereochemistry, of Scheme 4. The *endo* stereochemistry would require (Scheme 5) a zwitterionic alkoxide intermediate **11** in place of **9**, whose instability in the non-polar medium could be offset if Mn were to provide better stabilization through retention in a π-bonding mode (not shown in full in Scheme 5) on the bottom face, where it would be ideally positioned to attract the electron pair from the cyclopropyl σ-bond in the final forward ring-opening to the stable conjugated 1,2,3,4,5-η complex.

The instability of a bare alkoxide intermediate (**11**) in the non-polar aprotic solvent would be circumvented in a modified mechanism (Scheme 6) in which the rearrangement takes place by concerted acyl substitution at the carbonyl carbon rather than through the two-step addition–elimination sequence, with minimal negative charge transfer onto the carbonyl oxygen. Nucleophilic acyl substitution in esters by a concerted rather than two-step addition–elimination mechanism is well-established [4] if not common. Here, the substitution reaction is at a ketone carbonyl, a reaction known in organic chemistry only if the nucleophile is very strong like amide or alkoxide [5a] or if the leaving group is stabilized as a carbanion (e.g., as in β-diketones and trihalomethyl ketones [5b]). Perhaps in the acyl substitution transition state **12**, the CH leaving group may be stabilized as in a β-diketone through conjugation around the ring dienone system, but a key factor could be that the coordination of CH to Mn, the driving force for attainment of the high degree (η^5) of product stabilization through metal coordination, is already well developed in the acyl substitution transition state. The resulting *endo* stereochemistry may reflect this demand.



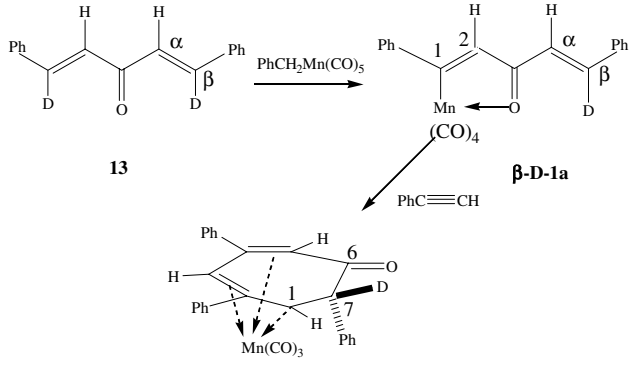
Scheme 6. Concerted acyl substitution ring-expansion mechanism avoiding zwitterion intermediate (some substituents excluded for clarity).

2.3. Structure of pyranyl complex *2a*

The structure of the pyranyl complex **2a** (see Fig. 1) consists of a $Mn(CO)_3$ "piano stool" moiety coordinating to a 2,4,6-substituted η^5-pyranyl ring. The five carbon atoms C(1)–C(5) are essentially co-planar, with the oxygen atom displaced such that the dihedral angle between the C(1)–O(1)–C(5) plane and the η^5-plane is 42.9(2)°.

The manganese atom is coordinated to the ring in an unsymmetrical manner, with the Mn–C(5) distance of 2.401(3) Å significantly longer than the other Mn–C bonds (2.127–2.189(3) Å). We note that in the only other reported η^5-pyranyl-manganese structure of this type, with 2,4-diphenyl-6-methyl substitution pattern, the equivalent asymmetry was also found [2a], though to a lesser extent. Whether this is a steric or electronic effect, or even a general one, cannot be concluded on the basis of these two examples.

The bond lengths around the ring system are not equal, with C(3)–C(4) being the longest, and C(4)–C(5) the shortest. The lengths do not correspond to a particular resonance form as the bonds do not give an alternating pattern. The oxygen atom in the pyranyl ring



Scheme 7. Deuterium labeling study.

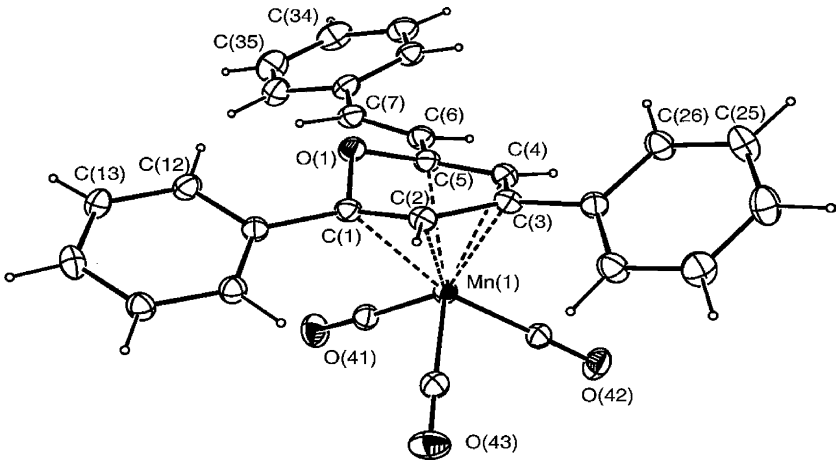


Fig. 1. The molecular structure of [2,4-diphenyl-6-(2-phenylethenyl)pyranyl-η^5]tricarbonylmanganese (**2a**).

has a shorter bond to C(5) compared to C(1), presumably related to the unsymmetrical placing of the manganese. The phenyl groups are not co-planar with the pyranyl ring, being at angles of 36° and 26° to the η^5-plane, which limits any extended π–electron interaction. Though the ethenyl group [C(6)–C(7)–C(31)] forms a smaller angle (14°) there is no evidence for delocalisation as the bond length of 1.334(5) Å for C(6)–C(7) corresponds to an unperturbed C=C double bond.

2.4. Summary

The synthetic and spectral monitoring work in this and the previous paper [2b] shows the generality of the reaction of alkynes with cyclomanganated dienones initially to form pyranyl complexes but accompanied by a slower rearrangement to oxocycloheptadienyl complexes. The deuterium labeling study supports a rearrangement mechanism in which the pyranyl complex reverts to its ring-opened precursor (**4a**) which then, through the alternative metal coordination mode (**4c**), cyclises to a 6-membered ring system which rearranges with ring expansion through a 3-membered ring carbonyl addition intermediate (**10** → **11** → **3**; Scheme 5) or acyl substitution transition state (**12** → **3**; Scheme 6) to give the *endo*-oxocycloheptadienyl complex.

3. Experimental

3.1. Spectral

Infrared spectra (dichloromethane) were recorded on a Digilab FTS-45 FTIR spectrometer. Electrospray mass spectra were recorded on a Fisons Instruments VG Platform II instrument with samples prepared in a dilute sodium methoxide solution in methanol to aid ionisation ($[M + MeO]^-$ parent ions) for negative ion mode operation [6].

NMR spectra ($CDCl_3$ as solvent) were recorded on Bruker Avance DRX 300 or 400 instruments; extensive signal overlaps with the large numbers of aryl hydrogen and carbon atoms prevent complete individual signal assignment in some cases.

3.2. Synthetic

Reagents, solvents and purification methods are described largely in the previous paper [2b]. Petroleum spirit was the fraction of b.p. 60–80 °C.

Preparations of cyclomanganated dienones **1a** and **1b** have been described [2b] and their coupling reactions with alkynes (typically 0.2 mmol **1** and 0.6 mmol alkyne in 10 mL solvent) have been carried out as earlier under nitrogen [2b]. Solvent and reaction duration are indicated below in individual cases; reaction temperatures other than room temperature (20–25 °C) were either controlled with an oil bath, or as the boiling point of solvent for reactions under reflux (76 °C in CCl_4, 98 °C in heptane). Reactions were monitored by IR spectroscopy and were sometimes interrupted before completion to obtain pyranyl complexes, or for long sluggish reactions, to limit decomposition. Yields stated should be considered in this context.

Pyranyl complexes **2** were normally recrystallised from dichloromethane/petroleum spirit mixtures by cooling to −20 °C, and oxocycloheptadienyl complexes **3** from ethyl acetate/petroleum spirit by vapour diffusion.

3.2.1. *[2,4-Diphenyl-6-(2-phenylethenyl)pyranyl-η^5] tricarbonylmanganese (**2a**)*

[1-Phenyl-2-[(*E*)-3-phenylprop-2-en-1-oyl-κ*O*]ethenyl-κC^1]tetracarbonylmanganese **1a** with phenylacetylene in carbon tetrachloride at room temperature over 28 h yielded **2a**, separated on an alumina column using 1:8 v/v dichloromethane/petroleum spirit, and crystallised as dark red needles (27%). Anal. Found: C, 70.94; H, 4.10. $C_{28}H_{19}O_4Mn$ Calc.: C, 70.89; H, 4.04%. IR:

ν(CO) 2015 (vs), 1956 (s), 1934 (s) cm^{-1}. ESMS (MeOH, NaOMe; −20 V) *m/z* 505 (100%; $[M + MeO]^-$). ^1H NMR: δ 7.91 (2H, d, 1H, $J = 7.6$ Hz, ArH), 7.56–7.31 (13H, m, Ar–H), 7.11 (1H, d, $J = 15.6$ Hz, H2′), 6.32 (1H, d, $J = 15.6$ Hz, H1′), 5.72 (1H, s, H3), 5.06 (1H, s, H5). ^{13}C NMR: δ 222.2 (s, metal carbonyl), 137.1(s), 136.5 (s), 136.5 (s), 130.0 (d, C2′), 129.6 (d), 129.2 (d), 129.0 (d), 128.7 (d), 128.4 (d), 127.4 (d), 127.0 (d), 123.8 (d, C1′), 123.4 (d), 101.1 (s, C2), 97.2 (s, C4), 94.6 (s, C6), 82.4 (d, C3), 81.2 (d, C5).

3.2.2. [2,3-Diphenyl-4-(2-trifluoromethylphenyl)-6-(2-(trifluoromethylphenyl)ethenyl)pyranyl-η^5] tricarbonylmanganese (**2f**)

[1-(2-Trifluoromethylphenyl)-2-[(*E*)-3-(2-trifluoromethylphenyl)prop-2-en-1-oyl-κ*O*]ethenyl-κC^1]tetracarbonylmanganese (**1b**) with diphenylacetylene in heptane at 30 °C over 48 h and chromatography on a silica layer (1:3 v/v ethyl acetate/petroleum spirit as eluent) yielded apart from some unreacted starting material the previously characterized [2b] **3f** (9%) as well as the new pyranyl complex **2f** as a yellow oil (13%), characterized by spectral properties only. IR: ν(CO) 2020 (vs), 1962 (s), 1935 (s) cm^{-1}. ESMS (MeOH, NaOMe; −20 V) *m/z* 717 (100%; $[M + MeO]^-$), 685 (50%, $[M - H]^-$). ^1H NMR: δ 8.22 (1H, d, $J = 7.6$ Hz, H3‴), 7.72 (3H, m, H3‴, H6″, H6‴), 7.67 (1H, t, $J = 7.7$ Hz, H5‴), 7.56 and 7.54 (each 1H, t, $J = 8$ Hz, H5″, H4‴), 7.43 (1H, t, $J = 7.5$ Hz, H4″), 7.2-7.0 (11H, m, H2′, $2 \times C_6H_5$), 6.29 (1H, d, $J = 15.4$ Hz, H1′), 4.93 (1H, s, H5). ^{13}C NMR: δ 220.6 (s, metal carbonyl), 138.9 (d, C6‴), 136.7 (s), 133–126 (multiple overlapping signals including 132.9, 132.8, 132.2, 132.0, 129.4, 128.8, 128.5, 128.3, 127.9, 127.7, 127.4, 127.1, 126.7, 126.4, 126.0; aryl and alkenyl *C*H), 104.7 (s, C2), 104.2 (s, C6), 102.9 (s, C4), 84.4 (s, C3), 82.1 (d, C5).

3.2.3. [6-Oxo-4,7-diphenyl-2-trimethylsilylcyclohepta-1,4-dienyl-1,2,3,4,5-η]tricarbonylmanganese (**3b**)

[1-Phenyl-2-[(*E*)-3-phenylprop-2-en-1-oyl-κ*O*]ethenyl-κC^1]tetracarbonylmanganese **1a** with (trimethylsilyl)acetylene under reflux in heptane over 24 h and chromatography on a silica layer (2:3 v/v ethyl acetate/petroleum spirit as eluent) yielded equal amounts of the previously characterized [2b] **2b** (29%) and the new oxocycloheptadienyl complex **3b**, assumed to be the *endo* isomer, as a yellow oil (29%), characterized by spectral properties only. IR: ν(CO) 2031 (vs), 1974 (s), 1947 (s) cm^{-1}. ESMS (MeOH, NaOMe; −20V) m/z 469 (79%, $[M-H]^-$), 397 (100%, $[M - SiMe_3]^-$). ^1H NMR: δ 7.61–7.14 (10H, m, Ar–H), 6.01 (1H, m, H3), 4.83 (1H, m, H5), 3.44 (1H, m, H1), 2.52 (1H, d, $J = 3.4$ Hz, H7), 0.39 (9H, s, $SiCH_3$). ^{13}C NMR: δ 220.5 (s, metal carbonyl), 188.5 (C6), 140.8 (s), 138.2 (s), 130.4 (d), 129.8 (d), 129.2 (d), 129.2 (d), 129.1 (d), 127.7 (d), 122.7 (d, C4), 106.4 (s, C2), 99.1 (d, C3), 76.3 (d, C5), 67.6 (d, C1), 48.6 (d, C7), −1.2 (SiC).

3.2.4. [6-Oxo-2,3,4,7-tetraphenylcyclohepta-1,4-dienyl-1,2,3,4,5-η]tricarbonylmanganese (**3c**)

[1-Phenyl-2-[(*E*)-3-phenylprop-2-en-1-oyl-κ*O*]ethenyl-κC^1]tetracarbonylmanganese (**1a**) was reacted with diphenylacetylene in heptane at 30 °C over 96 h during which period only minor peaks corresponding to **2c** (2017, 1957, 1934 cm^{-1}) were observed as **1a** disappeared and **3c** accumulated. Chromatography on an alumina column (1:3 v/v ether/petroleum spirit as eluent) yielded as a yellow-orange band only **3c** (30%), again assumed to be the *endo* isomer by analogy with **3a**. IR: ν(CO) 2028 (vs), 1969 (s), 1948 (s) cm^{-1}. ESMS (MeOH, NaOMe; −20 V) *m/z* 581 (10%; $[M + MeO]^-$), 549 (100%, $[M - H]^-$). ^1H NMR: δ 7.51–6.83 (20H, m, Ar–H), 4.67 (1H, m, H5), 3.92 (1H, m, H1), 2.82 (1H, d, $J = 3.6$ Hz, H7). ^{13}C NMR: δ 220.8 (s, metal carbonyl), 191.4 (C6), 141.2 (s), 140.7 (s), 138.1 (s), 137.1 (s), 132.4 (d), 131.2 (d), 130.1 (d), 129.9 (d), 129.3 (d), 128.7 (d), 128.2 (d), 128.1 (d), 128.0 (d), 127.9 (d), 127.6 (d), 127.1 (d), 121.9 (s, C4), 116.4 (s, C2), 114.7 (s, C3), 79.7 (d, C5), 63.8 (d, C1), 47.3 (d, C7).

3.2.5. [6-Oxo-2-phenyl-4,7-di(2-trifluoromethylphenyl) cyclohepta-1,4-dienyl-1,2, 3,4,5-η]tricarbonylmanganese (**3d**)

[1-(2-Trifluoromethylphenyl)-2-[(*E*)-3-(2-trifluoromethylphenyl)prop-2-en-1-oyl-κ*O*]ethenyl-κC^1]tetracarbonylmanganese (**1b**) was reacted with phenylacetylene in heptane under reflux over 24 h. Chromatography on a silica layer (1:3 v/v ether/petroleum spirit as eluent) gave two bands from which were obtained the known [2b] pyranyl complex **2d** (17%) identified by IR [2014 (vs), 1934 (s, br) cm^{-1}] and the new, presumably *endo*, oxocycloheptadienyl complex **3d** (52%). Anal. Found: C, 59.25; H, 2.65. $C_{30}H_{17}O_4Mn$ Calc.: C, 59.03; H, 2.81%. IR: ν(CO) 2033 (vs), 1973 (s), 1960 (s) cm^{-1}. ESMS (MeOH, NaOMe; −20 V) *m/z* 641 (100%; $[M + MeO]^-$), 609 (10%, $[M - H]^-$). ^1H NMR: δ 7.85–7.41 (13H, m, Ar–H), 6.40 (1H, m, H3), 4.61 (1H, m, H5), 4.04 (1H, m, H1), 2.94 (1H, d, $J = 2.9$ Hz, H7). ^{13}C NMR: δ 219.7 (s, metal carbonyl), 187.8 (C6), 138.9–125.5 (overlapping aryl and CF_3 signals), 120.9 (d, C4), 112.0 (s, C2), 97.8 (d, C3), 77.0 (d, C5), 61.0 (d, C1), 41.8 (d, C7).

3.2.6. [6-Oxo-2-trimethylsilyl-4,7-di(2-trifluoromethylphenyl)cyclohepta-1,4-dienyl-1,2,3,4,5-η]tricarbonylmanganese (**3e**)

[1-(2-Trifluoromethylphenyl)-2-[(*E*)-3-(2-trifluoromethylphenyl)prop-2-en-1-oyl-κ *O*]ethenyl-κC^1]tetracarbonylmanganese (**1b**) was reacted with (trimethylsilyl) acetylene in heptane under reflux over 7 days. Chromatography on a silica layer (1:1 v/v dichloromethane/

petroleum spirit as eluent) gave two bands from which were obtained the known [2b] pyranyl complex **2e** (36%) identified by IR [2017 (vs), 1958(s), 1936 (s) cm^{-1}] and ESMS [637 (32%, $[M + MeO]^-$)], and the new presumably *endo* oxocycloheptadienyl complex **3e**, a yellow oil (20%) crystallised by vapour diffusion (ethyl acetate/petroleum spirit): Anal. Found: C, 53.78; H, 3.41. $C_{30}H_{17}O_4Mn$ Calc.: C, 53.47; H, 3.49%. IR: *v*(CO) 2030 (vs), 1972 (s), 1949 (s) cm^{-1}. ESMS (MeOH, NaOMe; −20 V) *m/z* 565 (100%; $[M - SiMe_3 + H + MeO]^-$), 533 (28%, $[M - SiMe_3]^-$). ^1H NMR: δ 7.79–7.41 (8H, m, Ar–H), 5.75 (1H, m, H3), 4.68 (1H, m, H5), 3.50 (1H, m, H1), 2.88 (1H, d, $J = 2.9$ Hz, H7), 0.35 (9H, s, $SiCH_3$). ^{13}C NMR: δ 219.7 (s, metal carbonyl), 184.8 (C6), 138.8 (s), 136.4 (s), 132.6 (d), 132.4 (d), 131.0 (d), 129.6 (d), 127.2 (d), 126.9 (q, $^1J_{CF} = 5.3$ Hz, CF_3), 125.8 (d, $^2J_{CF} = 13.3$ Hz, *C*-CF_3), 125.4 (q, $^1J_{CF} = 5.6$ Hz, CF_3), 124.1 (C4), 122.2 (d, $^2J_{CF} = 13.3$ Hz, *C*–CF_3), 104.1 (C2), 102.0 (C3), 77.3 (C5), 70.7 (C1), 43.2 (C7), −1.6 ($SiCH_3$).

3.3. Deuterium-labeling study (Scheme 7)

Ethanol (10 mL) and a solution of sodium hydroxide (2 g) in water (15 mL) were mixed in a flask immersed in crushed ice. A mixture of acetone (ca. 0.36 mL; 4.9 mmol) and benzaldehyde-formyl-d (Aldrich 98 at.%; 1.0 mL, 9.8 mmol) was added dropwise with stirring over 10 min. After a further 1 h without cooling, the precipitate was collected under vacuum in a sintered glass funnel and washed with water until the washings were neutral to litmus. The crude product was dried under vacuum and recrystallized from ethyl acetate to give 1,5-diphenylpenta-1,4-dien-3-one-1,5-d2 as pale lemon needles (**13**; 0.84 g; 73%). ^1H NMR spectral data matched those [2b] of **1a** except for the absence of the β-proton signal at δ 7.75, and with the α-proton signal (δ 7.10) now a broad singlet.

This compound (**13**; 500 mg, 2.1 mmol) and benzylpentacarbonylmanganese (660 mg, 2.3 mmol) were reacted to completion under reflux over 5 h in petroleum spirit (b.p. 60–80 °C) in a nitrogen atmosphere (Schlenk flask). The solvent was removed and the product chromatographed on an alumina column using 1:8 v/v dichloromethane/petroleum spirit as eluent. The product [[1-phenyl-2-(E)-3-phenylprop-2-en-1-oyl-3-d-κ*O*]ethenyl-κC^1]tetracarbonylmanganese (β-**D-1a**) was obtained as the main fraction (390 mg, 46%). NMR data matched those of the protio analogue **1a** except for the absence of the β-proton signal (δ 7.72 in **1a** [2b]) and the now broad singlet signal from the adjacent α-proton (δ 6.99); the other singlet α-proton signal (δ 7.33; H2 using the numbering in Scheme 7) was retained.

β-**D-1a** (184 mg, 0.46 mmol) and PhCCH (180 μL, 1.64 mmol) were heated in CCl_4 under reflux for 24 h. After solvent removal the residue was chromatographed on an alumina column using 1:1 v/v dichloromethane/petroleum spirit as eluent. The orange-yellow band provided (Scheme 7) *endo*-[6-oxo-2,4,7-triphenylcyclohepta-1,4-dienyl-7-d-1,2,3,4,5-η]tricarbonylmanganese (**7-D-3a**, 22 mg, 10%): δ 2.64 (trace of signal only, residual H7), 3.97 (IH, m, H1), 4.80 (1H, m, H5), 6.64 (1H, m, H3), 7.3–7.8 (15H, Ar–H).

Table 1
Selected bond parameters for [2,4-diphenyl-6-(2-phenylethenyl)pyranyl-η^5]tricarbonylmanganese (**2a**)

Bond lengths (Å)			
Mn(1)–C(1)	2.189(3)	Mn(1)–C(2)	2.127(3)
Mn(1)–C(3)	2.131(3)	Mn(1)–C(4)	2.177(3)
Mn(1)–C(5)	2.401(3)	Mn–CO (av.)	1.812(3)
C(1)–O(1)	1.428(3)	C(5)–O(1)	1.387(3)
C(1)–C(2)	1.408(4)	C(2)–C(3)	1.416(4)
C(3)–C(4)	1.438(3)	C(4)–C(5)	1.392(4)
C(5)–C(6)	1.454(4)	C(6)–C(7)	1.334(4)
Bond angles (°)			
O(1)–C(1)–C(2)	117.5(3)	C(1)–C(2)–C(3)	118.5(3)
C(2)–C(3)–C(4)	114.3(3)	C(3)–C(4)–C(5)	121.2(3)
C(4)–C(5)–O(1)	119.2(3)	C(1)–O(1)–C(5)	107.1(2)

3.4. Structure of [2,4-diphenyl-6-(2-phenylethenyl) pyranyl-η^5]tricarbonylmanganese (**2a**)

2a was characterised by single-crystal X-ray crystallography. Accurate cell parameters and intensity data were collected by ω-scans on a Siemens SMART diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å) at −105 °C. The structure was solved by Direct Methods and routinely developed. Refinement was full-matrix least-squares based on F^2, using the SHELX programs [7] running under the WinGX suite of programmes [8].

Crystal data: $C_{28}H_{19}MnO_4$, M 474.37, monoclinic, $P2_1/c$, *a* 14.165(4), *b* 12.397(4), *c* 13.581(4) Å, β 109.91(1)°, *U* 2242.3 $Å^3$, D_c 1.405 g cm^{-3} for *Z* 4, *F*(0 0 0) 976, μ(Mo Kα) 0.621 mm^{-1}. Red prismatic crystals from CH_2Cl_2, $0.68 \times 0.44 \times 0.15$ mm^3. A total of 28,026 reflections with $2° < 2\theta < 50°$ were collected, 4552 unique (R_{int} 0.0332), 3772 with $I > 2\sigma(I)$, corrected for absorption ($T_{max, min}$ 1.000, 0.863). All non-H atoms anisotropic, H atoms in calculated positions. Refinement converged with R_1 0.0464 (2σ data), wR_2 0.1305 (all data), GoF 1.137, largest residual feature 1.0 e $Å^{-3}$. The structure is illustrated in the Fig. 1, and the Table 1 lists selected bond parameters.

4. Supplementary material

Full details of the structure determination have been deposited with the Cambridge Crystallographic Data Centre as CCDC 263330. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

(fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

Acknowledgements

We thank Dr. J. Wikaira, University of Canterbury, for collection of X-ray intensity data.

References

[1] L. Main, B.K. Nicholson, Adv. Metal-Org. Chem. 3 (1994) 1.
[2] (a) W. Tully, L. Main, B.K. Nicholson, J. Organomet. Chem. 507 (1996) 103–115;
(b) W. Tully, L. Main, B.K. Nicholson, J. Organomet. Chem. 633 (2001) 162–172.
[3] C-W. Lee, K.S. Oh, K.S. Kim, K.H. Ahn, Org. Lett. 2 (2000) 1213.
[4] A. Williams, Acct. Chem. Res. 22 (1989) 387–392.
[5] (a) J. March, Advanced organic chemistry, third ed., Wiley, New York, 1985, pp. 567–568;
(b) J. March, Advanced Organic Chemistry, third ed., Wiley, New York, 1985, pp. 566–567.
[6] W. Henderson, J.S. McIndoe, B.K. Nicholson, P.J. Dyson, J. Chem. Soc., Dalton Trans. (1998) 519.
[7] (a) G.M. Sheldrick, SHELXS-97, University of Gottingen, Gottingen, Germany, 1997;
(b) G.M. Sheldrick, SHELXL-97, University of Gottingen, Gottingen, Germany, 1997.
[8] L.J. Farrugia, WinGX, Version 1.64.05, University of Glasgow, UK;
L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.