Photochemical reactions of transition metal organyl complexes with olefins
Part 10*. Light-induced formal [5 + 2] cycloadditions at manganese**

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Abstract

Tricarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-manganese (**1**) forms upon UV irradiation in THF at 208 K solvent stabilized dicarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-tetrahydrofurane-manganese (**2**). With butynedioic acid dimethyl ester (**3**) and diphenylacetylene (**5**) complex **2** yields tricarbonyl-η^5-1,2-dimethoxycarbonyl-4,6-dimethyl-cyclohepta-2,4-dien-1-yl-manganese (**4**) and tricarbonyl-η^5-4,6-dimethyl-1,2-diphenyl-cyclohepta-2,4-dien-1-yl-manganese (**6**) in a formal [5 + 2] cycloaddition. Addition of carbon monoxide and a 1,4-H shift completes the reaction. Propynoic acid methyl ester (**7**) forms the 2:1 adduct dicarbonyl-$\eta^{5:2}$-1,3-dimethyl-6-methoxycarbonyl-6-(*E*-2'-methoxycarbonylvinyl)-cyclohepta-2,4-dien-1-yl-manganese (**8**). The crystal and molecular structure of **8** was determined by X-ray structure analysis. The molecular structures of the complexes **4** and **6** were established by IR and NMR spectroscopy. Formation mechanisms of **4**, **6** and **8** are discussed. Crystal data for **8**: monoclinic space group $P2_1/c$, $a = 802.6(3)$, $b = 1136.6(1)$, $c = 1872.3(3)$ pm, $\beta = 93.14(2)°$, $V = 1.705$ nm^3, $Z = 4$.

Introduction

Since the discovery of the nickel catalysed tetramerisation of acetylene to cyclooctatetraene by Reppe *et al.* [2], cyclisations or cycloadditions catalysed or mediated by transition metals play an important role in the synthesis of organic ring systems [3–6]. Coordination of unsaturated hydrocarbons to transition metals allows pericyclic reactions, forbidden by the Woodward–Hoffmann rules [7, 8]. Although photochemically forbidden, conjugated dienes react with tricarbonyl-η^6-1,3,5-cycloheptatriene-chromium(0) in a formal [4 + 6] cycloaddition to give tricarbonyl-$\eta^{4:2}$-bicyclo[4.4.1]-undeca-2,4,7-triene-chromium(0) [9]. With alkynes or activated alkenes [2 + 6] cycloadditions were observed [10–13].

In contrast to the broad application of complexes with η^1 and η^3 coordinated enyl ligands for cyclisations and cycloadditions [14–17], the synthetic potential of the vinylogous pentadienyl complexes for the formation

of medium-sized rings has so far only been documented in a few papers. In this context we have shown that tricarbonyl-η^5-2,4-pentadien-1-yl-manganese and its derivatives react with conjugated dienes to give tricarbonyl-$\eta^{3:2}$-2,6-cyclononadien-1-yl-manganese complexes in a photochemically induced formal [4 + 5] cycloaddition [18–24]. Reductive cleavage of the 2,6-cyclononadien-1-yl ligands and isolation of cyclononadienes showed this synthesis to be an interesting route to nine-membered rings [25, 26], accessible only in low yields with classical organic reactions.

For the reactions of tricarbonyl-η^5-2,4-pentadien-1-yl-manganese with dienes there is good evidence for substitution of one CO by the 1,3-diene in a first step, and successive CC bond formation between η^5-2,4-pentadien-1-yl and 1,3-diene at manganese with a $\eta^{3:4}$-2,6,8-nonatrien-1-yl complex as intermediate. The surplus of two electrons of the η^2-1,3-diene ligand seems to be a basic condition for the formation of the first CC bond. Ring closure and recomplexation of CO completes the reaction.

By extension of this reaction principle to tricarbonyl-η^5-2,4-pentadien-1-yl-manganese and alkynes one may expect the formation of tricarbonyl-$\eta^{3:2}$-2,5-cyclo-

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**Dedicated to Professor Dr O.J. Scherer on the occasion of his 60th birthday.
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heptadien-1-yl-manganese complexes by a formal [2 + 5] cycloaddition. Due to the easier accessibility of tricarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-manganese (1) we will report about some of its reactions with three functionalised alkynes [27&.

Experimental

All procedures were carried out under exclusion of air and moisture in purified dry nitrogen using standard Schlenk techniques. Tetrahydrofurane was dried by successive distillation from calcium hydride and potassium. It was stored over molecular sieves. The other solvents were dried with sodium/benzophenone or phosphorous pentoxide.

UV irradiations were carried out in a 400 ml vessel of Duran with a cooling jacket, wrapped with aluminium foil. A 150 W mercury lamp TQ 150 (Heraeus-Noblelight, Kleinostheim) was used as UV source. During the photo reactions nitrogen was bubbled through the solutions in order to mix and to remove the carbon monoxide from the solutions.

For column chromatography neutral alumina (Macherey & Nagel, Düren) was heated in vacuum at 413 K and deactivated with 5% of water saturated with nitrogen.

Tricarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-manganese (1) was prepared according to the literature [28]. All other reagents were commercial products. Butynedioic acid dimethyl ester (Fluka, purum, $\approx 98\%$) and propynoic acid methyl ester (Janssen, $\approx 99\%$) were freshly distilled in vacuum.

(i) Photo reaction of tricarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-manganese (1) in tetrahydrofurane

The irradiation vessel was loaded with 350 mg (1.50 mmol) of [Mn(CO)$_3$(η^5-C$_7$H$_{11}$)] (1) dissolved in 350 ml THF. The bright yellow solution was irradiated at 208 K with UV light. After 10 min the colour had turned to red. After 120 min the CO bands of 1 had disappeared and the irradiation was stopped. The colour of the solution was carmine. Dicarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-tetrahydrofurane-manganese (2) was identified by IR spectroscopy according to two ν(CO) bands (1927s, 1854s cm^{-1}).

(ii) Thermal reaction of dicarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-tetrahydrofurane-manganese (2) with butynedioic acid dimethyl ester (3)

To a THF solution of [Mn(CO)$_2$(η^5-C$_7$H$_{11}$)(thf)] (2), freshly prepared from 350 mg (1.50 mmol) of [Mn(CO)$_3$(η^5-C$_7$H$_{11}$)] (1), 1.5 ml (9.1 mmol) butynedioic acid dimethyl ester (3) were added at 208 K. The cold reaction mixture was allowed to warm up to room

temperature while a slight stream of nitrogen was bubbled through it. The solvent was removed in high vacuum; the red, oily residue was dissolved in pentane and chromatographed with pentane and pentane/ether (1/1) on Al$_2$O$_3$ at 233 K. The first zone contains the starting complex 1, the second zone tricarbonyl-η^5-1,2-dimethoxycarbonyl-4,6-dimethyl-cyclohepta-2,4-dien-1-yl-manganese (4), which crystallised from pentane as yellow sphere-like aggregates of fine needles. Yield 96 mg isolated 12%. IR: ν(CO) 2033vs, 1978s, 1955vs, ν(COCH$_3$) 1744m, 1716m cm^{-1}. ^{1}H NMR: 253 K, CD$_2$Cl$_2$: 1-COOCH$_3$, 2-COOCH$_3$, 3.64, 3.83, 3-H 5.91, 4-CH$_3$ 2.10, 5-H 4.41, 6$_{anti}$-H 3.13, 6$_{syn}$-CH$_3$ 0.88, 7$_{anti}$-H 2.33, 7$_{syn}$-H 0.04 ppm. Anal. Calc. for MnC$_{16}$H$_{17}$O$_7$ (376.25): C, 51.08; H, 4.55. Found: C, 51.0; H, 4.6%.

(iii) Thermal reaction of dicarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-tetrahydrofurane-manganese (2) with diphenylacetylene (5)

To a THF solution of [Mn(CO)$_2$(η^5-C$_7$H$_{11}$)(thf)] (3), freshly prepared from 350 mg (1.50 mmol) of [Mn(CO)$_3$(η^5-C$_7$H$_{11}$)] (1), 630 mg (3.6 mmol) diphenylacetylene (5) in 2 ml THF were added at 208 K. The reaction mixture was treated and worked up according to (ii). The first zone contains the starting complex 1, the second zone tricarbonyl-η^5-4,6-dimethyl-1,2-diphenyl-cyclohepta-2,4-dien-1-yl-manganese (6), which was isolated from pentane as an orange–yellow crystal powder. Yield 70 mg isolated 11%. IR ν(CO) 2014vs, 1954s, 1934s cm^{-1}. ^{1}H NMR: 253 K, CD$_2$Cl$_2$: 1,2-C$_6$H$_5$ 7.59 (o), 7.36 (o, p), 7.10 (m, m) 7.00 (p), 3-H 5.61, 4-CH$_3$ 2.10, 5-H 4.15, 6$_{anti}$-H 3.40, 6$_{syn}$-CH$_3$ 1.03, 7$_{anti}$-H 2.49, 7$_{syn}$-H 0.51 ppm. Anal. Calc. for MnC$_{24}$H$_{21}$O$_3$ (412.37): C, 69.91; H, 5.13. Found: C, 70.8; H, 5.3%.

(iv) Thermal reaction of dicarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-tetrahydrofurane-manganese (2) with propynoic acid methyl ester (7)

To a THF solution of [Mn(CO)$_2$(η^5-C$_7$H$_{11}$)(thf)] (2), freshly prepared from 350 mg (1.50 mmol) of [Mn(CO)$_3$(η^5-C$_7$H$_{11}$)] (1), 0.5 ml (6 mmol) of propynoic acid methyl ester (7) was added at 208 K. When the reaction mixture was treated according to (iii), the colour of the solution turned from carmine to orange red. The solvent was removed in high vacuum, the red, oily residue was dissolved in pentane and chromatographed on an Al$_2$O$_3$ column with pentane and pentane/ether (5/1) at 233 K. The first zone contains 1, the second zone dicarbonyl-$\eta^{5:2}$-1,3-dimethyl-6-methoxycarbonyl-6-(E-2'-methoxycarbonylvinyl)-cyclohepta-2,4-dien-1-yl-manganese (8), which was isolated after crystallisation from pentane in the form of garnet red platelets. Yield 157 mg isolated 28%. IR ν(CO) 1980vs, 1920s; ν(COOCH$_3$) 1741w, 1724w cm^{-1}. ^{1}H NMR: 253 K, CD$_2$Cl$_2$: 1-CH$_3$ 2.19, 2-H 5.59, 3-CH$_3$ 2.47, 4-H 4.75,

5-H 2.97, 6-COOCH$_3$ 3.64, 7$_{syn}$-H 1.55, 7$_{anti}$-H 2.65, 1'-H, 2'-H 5.30, 5.20, 2'-COOCH$_3$ 3.65 ppm. MS, $E_i = 0.2$ A; 30 V; 200 °C QT; 180 °C: $m/z = 374$ $(M^+/<1\%)$; 318 $(M^+ - 2CO/100\%)$. *Anal.* Calc. for MnC$_{17}$H$_{19}$O$_6$ (374.27): C, 54.56; H, 5.12. Found: C, 54.0; H, 5.3%.

Instrumentation

IR spectra were obtained from pentane solutions in cells with CaF$_2$ windows and a 0.2 mm path length in the region 2200–1600 cm^{-1} with an IR spectrometer model 881 (Perkin Elmer). ^{1}H and ^{13}C NMR spectra were recorded with an AMX 40 pulse-FT-NMR spectrometer (Bruker, Karlsruhe) at 400.13 and 100.13 MHz. Mass spectra were measured with a Finnigan-MAT 90. C and H elemental analyses were performed with a microanalyser model 240 (Perkin Elmer).

X-ray crystal structure of dicarbonyl-η$^{5:2}$-1,3-dimethyl-6-methoxycarbonyl-6-(E-2'-methoxycarbonylvinyl)-cyclohepta-2,4-dien-1-yl-manganese (8)

Intensity data collection and lattice constants refinement were done on a P4/V diffractometer (Siemens). Crystal data are given in Table 1, together with other information about data collection and structure determination. The atomic coordinates of the non-hydrogen atoms are given in Table 2. The structure was solved using direct methods and subsequent difference

TABLE 1. Crystal data of dicarbonyl-η$^{5:2}$-1,3-dimethyl-6-methoxycarbonyl-6-(E-2'-methoxycarbonylvinyl)-cyclohepta-2,4-dien-1-yl-manganese (8)

Formula	C$_{17}$H$_{19}$MnO$_6$
M (C$_{17}$H$_{19}$MnO$_6$)	374.3 g mol^{-1}
Crystal size (mm)	0.1×0.2×0.2
Crystal system	monoclinic
Space group	$P2_1/c$
a (pm)	802.6(3)
b (pm)	1136.6(1)
c (pm)	1872.3(3)
β (°)	93.14(2)
V (nm^3)	1.705
Z	4
ρ_{calc} (g cm^3)	1.458
Radiation	Mo Kα
Wavelength, λ (pm)	0.71073
T (K)	291
Absorption coefficient (mm^{-1})	0.303
Scan type	ω
Scan range (ω) (°)	1.20°
Reflexions collected	5222
Independent reflexions	3804
Observed reflexions	1965
No. parameters	218
R	6.94
R_w	5.32

TABLE 2. Atomic coordinates and equivalent isotropic displacement coefficients U_{eq} (pm^2×10^{-2}) defined as one third of the trace of the orthogonalized U_{ij} tensor of dicarbonyl-η$^{5:2}$-1,3-dimethyl-6-methoxycarbonyl-6-(E-2'-methoxycarbonylvinyl)-cyclohepta-2,4-dien-1-yl-manganese (8)

	x	y	z	U_{eq}
Mn1	0.0837(2)	0.1160(1)	0.1545(1)	3.0(1)
O8	−0.0781(7)	−0.1115(5)	0.1182(2)	6.2(1)
O9	0.2999(7)	−0.0182(5)	0.2580(2)	6.3(1)
O13	0.4946(6)	0.0195(5)	0.0997(3)	5.2(1)
O14	0.3096(6)	−0.1065(5)	0.0480(2)	4.6(1)
O21	0.0211(7)	0.3792(5)	−0.0430(2)	6.8(1)
O22	0.2892(6)	0.4038(5)	−0.0058(2)	5.4(1)
C1	0.1657(9)	0.2967(6)	0.2011(3)	2.9(2)
C2	0.0365(10)	0.2394(6)	0.2355(3)	3.3(2)
C3	−0.1167(9)	0.2038(6)	0.2016(4)	3.6(2)
C4	−0.1469(9)	0.2069(6)	0.1257(3)	3.4(2)
C5	−0.0466(9)	0.2354(5)	0.0719(3)	3.3(2)
C6	0.1205(9)	0.2978(6)	0.0709(3)	3.1(2)
C7	0.1421(8)	0.3798(6)	0.1368(3)	3.7(2)
C8	−0.0157(10)	−0.0228(6)	0.1332(3)	3.9(2)
C9	0.2171(10)	0.0362(6)	0.2164(3)	3.6(2)
C10	0.3354(9)	0.3131(6)	0.2425(3)	4.9(2)
C11	0.2469(9)	0.2007(6)	0.0857(3)	3.3(2)
C12	0.2260(9)	0.0871(6)	0.0599(3)	3.3(2)
C13	0.3616(10)	0.0007(7)	0.0722(3)	3.7(2)
C14	0.4307(10)	−0.2005(7)	0.0596(4)	5.7(3)
C21	0.1339(10)	0.3632(6)	−0.0009(3)	4.2(2)
C22	0.3197(12)	0.4678(8)	−0.0702(4)	8.3(2)
C30	−0.2542(9)	0.1622(6)	0.2497(3)	5.9(2)

Fourier calculations. After the refinement of the arrangement of the heavier atoms using anisotropic displacement coefficients, a difference Fourier map revealed the positions of 14 out of 19 H atoms. We included these atoms in the refinement with fixed attributes to F_c. Some of the C atoms with neighboring H atoms not located showed some unusual features of anisotropic displacement ellipsoids. After refinement with the concerning H atoms in the calculated positions a much more probable result was achieved. Used programs: Siemens SHELXTL PLUS (VMS), XANADU.

Discussion

Tricarbonyl-η^5-2,4-pentadien-1-yl-manganese complexes react upon UV irradiation in pentane with conjugated dienes in formal [5+4] cycloadditions to give tricarbonyl-η$^{3:2}$-2,6-cyclononadien-1-yl-manganese complexes. In contrast, tricarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-manganese (1) shows no reactivity toward alkynes under similar conditions, although an analogous [5+2] cycloaddition to tricarbonyl-η$^{3:2}$-2,5-cycloheptadien-1-yl-manganese complexes would be quite likely.

When 1 is irradiated in THF at 208 K an electronically and coordinatively unsaturated 16-electron complex is formed by loss of carbon monoxide. This complex is stabilised in solution by weak coordination of a solvent molecule and dicarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-yl-tetrahydrofurane-manganese (2) results.

A similar reaction is well known and has been thoroughly studied for tricarbonyl-η^5-cyclopentadienyl-manganese [29–32]. In contrast, there have been no indications so far for the formation of solvent stabilised pentadienyl complexes like 2. Powell and co-workers reported in 1984 that tricarbonyl-η^5-2,4-pentadien-1-yl-manganese does not form a corresponding dicarbonyl complex with THF [33]. Probably the reaction temperature of 273 K was still too high for this thermally very labile complex. Even dicarbonyl-η^5-cyclopentadienyl-tetrahydrofurane-manganese, although thermally less sensitive, is only stable below 253 K.

Complex 2 reacts thermally with butynedioic acid dimethyl ester (3) and diphenylacetylene (5) to give the tricarbonyl-η^5-2,4-cycloheptadien-1-yl-manganese complexes 4 and 6; propynoic acid methyl ester (7) forms the 2:1 adduct 8 (Scheme 1).

The ^{1}H NMR spectra of the complexes 4 and 6 are very similar with the exception of the substituent signals, so closely related molecular structures have to be considered. Reaction of the 2,4-dimethyl-2,4-pentadien-1-yl ligand and butynedioic acid dimethyl ester (3) or diphenylacetylene (5) yields by formation of one CC bond 1,2-disubstituted 4,6-dimethyl-1,4,6-heptatrien-1-yl ligands, by formation of a second CC bond the 5,6-disubstituted formal [5 + 2] cycloadducts 1,3-dimethyl-1,5-cycloheptadien-1-yl ligands.

Complex 4 shows nine signals with the intensities 1:1:3:3:1:1:3:3:1 which do not correspond with either ligand mentioned earlier. One doublet (δ 5.91, J = 1.0

Hz) and a multiplet (δ 4.41 J = 2.6, 1.9, 1.0 Hz) are observed in the olefinic region. Three singlets with threefold intensities (3.83, 3.64, 2.10) correspond to two methoxycarbonyl and one methyl group. The remaining signals, a doublet of threefold intensity, (δ 0.88, J = 6.5 Hz), a quartet with three further splittings (δ 3.13, J = 2.6, 6.5, 8.2, 12.1 Hz) a doublet of a double doublet (δ 2.33, J = 1.9, 8.2, 12.2) and a double doublet (δ 0.04, J = 12.1, 12.2 Hz) are coupled to each other and correspond to an aliphatic ethylidene and an adjacent aliphatic methylene group. Such groups are to be expected, when the originally formed 1,3-dimethyl-5,6-dimethoxycarbonyl-2,5-cycloheptadien-1-yl ligand rearranges by an 1,4-H shift to 1,2-dimethoxycarbonyl-4,6-dimethyl-2,4-cycloheptadien-1-yl. On this basis all the observed signals of 4 can be assigned without any contradictions (see 'Experimental'). The small coupling constant J_{56} = 2.6 indicates a torsion angle between 5-H and 6-H close to 90°.

Similarly for 6 a 1,2-diphenyl-4,6-dimethyl-2,4-cycloheptadien-1-yl ligand has to be concluded on the basis of the ^{1}H NMR spectrum. Instead of the dimethoxycarbonyl singlets four multiplets are observed in the phenyl region with relative intensities of 2:3:4:1, which are assigned according to their splittings to the protons of two chemically different phenyl groups. The phenyl groups cause some upfield shifts of the other signals due to electronic reasons and smaller couplings between 5-H and 6_{syn}-H, 7_{syn}-H, respectively.

The ^{1}H NMR spectrum of complex 8 shows eleven well separated signals with the relative intensities of 1:1:1:3:3:1:1:3:3:1. According to their chemical shifts and coupling constants they are easily assigned to the protons of the $\eta^{5:2}$-1,3-dimethyl-6-methoxycarbonyl-6-(E-2'-methoxycarbonylvinyl)-cyclohepta-2,4-dien-1-yl ligand, proved by X-ray structure analysis.

Four signals appear in the olefinic region. The signal at lowest field at δ 5.59 ppm is assigned to 2-H. By the weak $^4J_{24}$ coupling with 1.1 Hz it is split into a doublet. The double doublet at δ 4.75 ppm ($^3J_{45}$ = 11.2, $^4J_{41}$ = 1.1 Hz) represents 4-H. An AB spin system at δ 5.20, 5.30 ppm with ^3J = 12.6 Hz corresponds to the exocyclic protons 1'-H, 2'-H. In the high field region in addition to four singlets of threefold intensity for the methyl and methoxycarbonyl groups, two double doublets at δ 2.97 ppm (^3J = 11.2, ^4J = 2.1 Hz) and at δ 2.65 ppm (^2J = 12.4, ^4J = 2.1 Hz) and a doublet at δ 1.55 ppm (^2J = 12.4 Hz) are observed. They can be assigned to 5-H, 7_{anti}-H and 7_{syn}-H (Fig. 1).

[Mn(CO)$_2$($\eta^{5:2}$-C$_{15}$H$_{19}$O$_4$)] (8) crystallizes monoclinic in the space group $P2_1/c$ with the cell constants a = 802.6(3), b = 1136.6(1), c = 1872.3(3) pm and β = 93.14(2)°. Selected bond lengths and angles are given in Table 3. Figure 2 shows an ORTEP plot of the molecular structure.
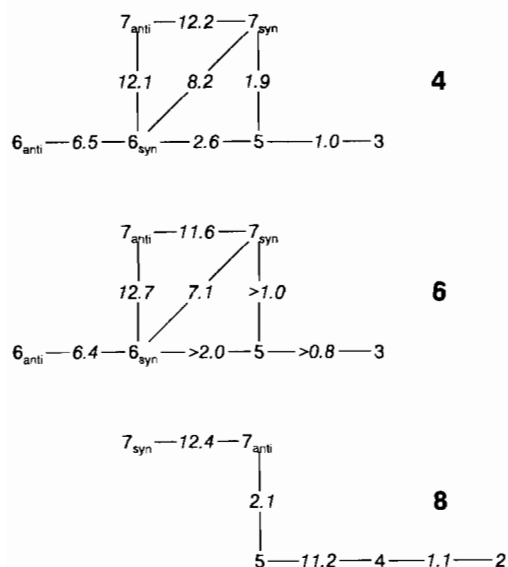

R = COOCH$_3$ 3
C$_6$H$_5$ 5
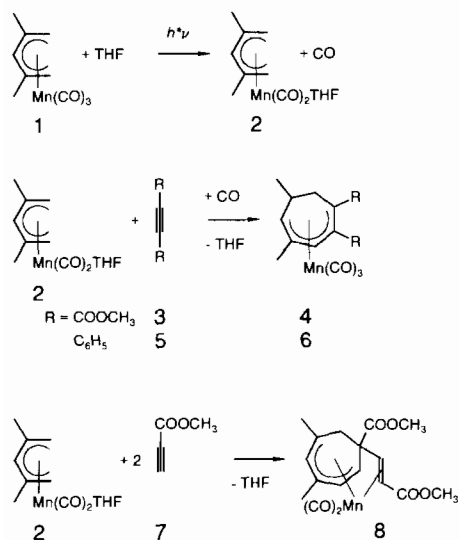
Scheme 1.

Fig. 1. Coupling constants diagrams of the complexes **4**, **6** and **8**.

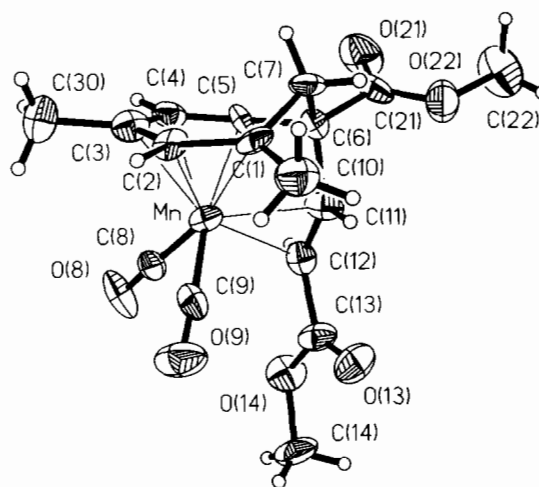Fig. 2. ORTEP plot of dicarbonyl-$\eta^{5:2}$-1,3-dimethyl-6-methoxy-carbonyl-6-(*E*-2'-methoxycarbonylvinyl)-cyclohepta-2,4-dien-1-yl-manganese (**8**).

TABLE 3. Selected bond lengths (pm) and bond angles (°) of dicarbonyl-$\eta^{5:2}$-1,3-dimethyl-6-methoxycarbonyl-6-(*E*-2'-methoxy-carbonylvinyl)-cyclohepta-2,4-dien-1-yl-manganese (**8**)

Bond lengths (pm)

Mn1–C1	231.3(10)	C3–C30	153.7(11)
Mn1–C2	211.6(9)	C4–C5	136.2(11)
Mn1–C3	212.6(9)	C5–C6	151.8(11)
Mn1–C4	216.2(10)	C6–C7	154.9(10)
Mn1–C5	227.0(9)	C6–C21	154.5(10)
Mn1–C6	261.9(9)	C6–C11	151.4(11)
Mn1–C8	180.2(9)	C11–C12	138.6(10)
Mn1–C9	178.2(9)	C12–C13	148.6(11)
Mn1–C11	211.9(9)	C13–O13	118.2(10)
Mn1–C12	218.4(9)	C13–O14	134.3(10)
Mn1–M1[a]	163.3(9)	O14–C14	145.3(10)
Mn1–M2[b]	203.7(9)	C21–O21	118.2(10)
C1–C2	141.1(11)	C21–O22	133.7(11)
C1–C7	153.3(10)	O22–C22	143.9(10)
C1–C10	154.1(11)	C8–O8	115.4(10)
C2–C3	141.2(11)	C9–O9	117.2(9)
C3–C4	142.9(10)		

Bond angles (°)

C1–C2–C3	124.8(6)	C7–C1–C2	125.6(6)
C2–C3–C4	122.4(6)	C6–C11–C12	123.2(6)
C3–C4–C5	131.8(7)	C8–Mn1–C9	86.6(5)
C4–C5–C6	132.7(6)	C11–C12–C13	119.9(6)
C5–C6–C7	109.3(5)	Mn1–C8–O8	178.6(6)
C5–C6–C11	104.0(5)	Mn1–C9–O9	177.6(7)
C5–C6–C21	109.8(6)	M1–Mn1–M2	108.4(5)
C7–C6–C11	104.3(5)	M1–Mn1–C8	122.6(5)
C7–C6–C21	113.2(5)	M1–Mn1–C9	129.0(5)
C11–C6–C21	115.6(6)	M2–Mn1–C8	104.3(5)
C1–C7–C6	105.0(5)	M2–Mn1–C9	101.7(5)

[a] M1 centre of gravity of C1–C5. [b] M2 centre of C11, C12.

Complex **8** is unsymmetrical and has a distorted pseudo tetrahedral coordination sphere, when the centre of gravity of C1–C5 (M1), the centre of C11, C12 (M2), C8 and C9 are considered. The atoms C1–C5 of the substituted $\eta^{5:2}$-6-vinyl-2,4-cycloheptadien-1-yl chelate ligand form a plane (rmsd = 5.25 pm) in which also C6 (4.9 pm) and C30 (9.6 pm) are located; the distance of Mn1 to this plane measures 160.9 pm, the line Mn1–M1 cuts the plane at 80.1°. In contrast to the η^5-pentadienyl complexes [34], the distances of Mn1 to C1–C5 vary between 231.3(10) and 211.6(9) pm. The largest distances are found for C1 and C5 due to the strain caused by the chelation of the coordinated vinyl group, which shows distances of 211.9(9) and 218.4(9) pm to Mn1. The strain within the ligand is also the reason for the deviation of some CCC angles at C6 from the ideal value of 109.5°.

The coordinated exocyclic CC double bond is twisted by 44.5° out of the favourable orientation, parallel to the plane C1–C5, as consequence of chelation strain. For the same reason the distance of Mn1 to C6 measures only 261.9(9) pm, much less than the sum of the van der Waals radii of carbon and manganese.

Prerequisite for the formation of complexes **4**, **6** and **8** from [Mn(CO)$_2$(η^5-2,4-C$_7$H$_{11}$)(thf)] (**3**) and alkynes is the thermal substitution of the weakly coordinated THF in **2** and the η^2-coordination of the alkynes to the manganese atom. Formation of a CC bond in **9** between the two ligands leads to the correspondingly substituted dicarbonyl-$\eta^{1:4}$-4,6-dimethyl-1,4,6-hepta-trien-1-yl-manganese (**10**) (Scheme 2). This 16-electron intermediate is probably stabilized by a THF ligand. A second CC bond completes the formal [2 + 5] cy-cloaddition of alkynes to the pentadienyl in the co-ordination sphere of manganese. On the basis of the
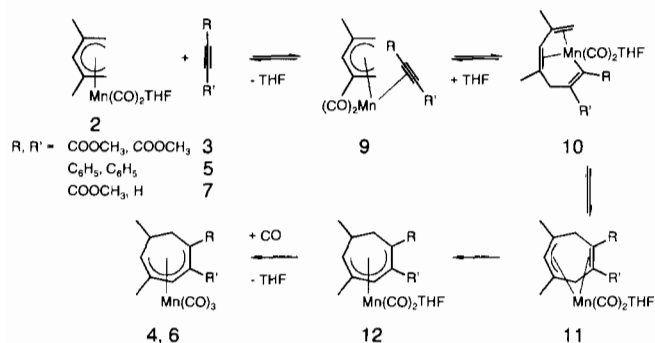
Scheme 2.
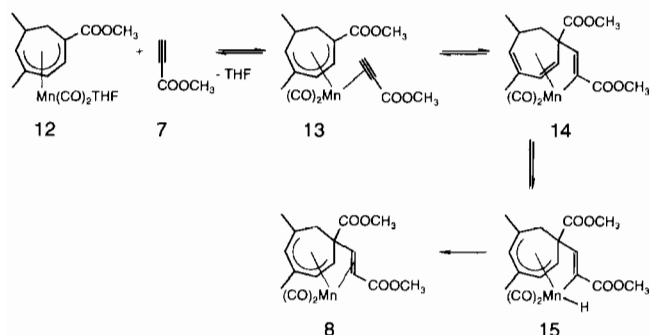
Scheme 3.

experimental results not totally to be excluded is a simultaneous formation of both CC bonds.

The intermediates **11** with $\eta^{3:2}$-coordinated 2,5-cycloheptadien-1-yl ligands are not stable with respect to an 1,4-H shift mediated by manganese and formation of η^5-2,4-cycloheptadien-1-yl complexes. Substitution of THF by carbon monoxide, liberated by partial decomposition yields **4** and **6**.

With propynoic acid methyl ester (**7**) as alkyne, THF is substituted in **10** by a second molecule of **7**. CC bond formation yields intermediate **14**. For the formation of **8** a hydrogen migration from C6 to C2′ is necessary, which occurs probably via the hydrido complex **15** (Scheme 3).

The different reactivities of the intermediates **12**, CO addition in the case of the alkynes **3** or **5** and addition of a second alkyne when **7** is used as component, depends obviously upon the degree of substitution of the alkynes. The fourfold substituted cycloheptadienyl ligands prevent the coordination of a second molecule of the disubstituted alkynes **3** or **5**. Interestingly, with **7** the third CC bond is formed from the unsubstituted carbon atom of the alkyne ligand to C1 with the methoxycarbonyl substituent and not to the unsubstituted C5. The CC bond formation in the coordination sphere of manganese is controlled by sterical as well as by electronic effects.

Further experiments with alkynes bearing sterically demanding acceptor substituents are in progress, to elucidate their sterical and electronic effects in the reactions with pentadienyl complexes.

Supplementary material

Further details about the crystal structure determination may be obtained under the deposit number CSD 57973 from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen 2, Germany.

Acknowledgements

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