Photochemical Reactions of Transition Metal Organyl Complexes with Olefins, 21[+]

Photolysis of Tricarbonyl(η^5-cyclohexadienyl)manganese in Tetrahydrofuran, Reactions with Cumulated Dienes

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Keywords: Manganese complexes / Organyl complexes / C–C coupling / [5+2] Cycloaddition / Cumulenes / Photochemistry

$[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**) forms highly reactive $[Mn(\eta^5\text{-}C_6H_7)(CO)_2(THF)]$ (**2**) upon UV irradiation in THF at 208 K. Solvent complex **2** reacts between 208 and 293 K with 1,1-disubstituted allenes C_3H_2RR' [R, R′ = CH_3, CH_3 (**A**); CH_3, C_6H_5 (**B**); C_2H_5, C_6H_5 (**C**); C_6H_5, C_6H_5 (**D**); OCH_3, $Si(CH_3)_3$ (**E**)] to four different types of complexes: The [5+2] cycloadduct $[Mn(\eta^{3:2}\text{-}C_9H_9RR')(CO)_3]$ (**3E**), rearranged [5+2] cycloadducts $[Mn(\eta^{3:2}\text{-}C_9H_9RR')(CO)_3]$ (**4B**, **4C**, **4D**), 1:2 adducts $[Mn(\eta^{3:2}\text{-}C_{12}H_{11}R_2R'_2)(CO)_3]$ (**5A–5E**), and the 1:3 adduct $[Mn\{\eta^{3:2:2}\text{-}C_{15}H_{13}(CH_3)_6\}(CO)_2]$ (**6A**). The constitutions of the products were established by IR and NMR spectroscopy, as well as by C,H elemental analysis and mass spectrometry. The crystal and molecular structure of **6A** was determined by X-ray structure analysis. A formation mechanism for the complexes is proposed.

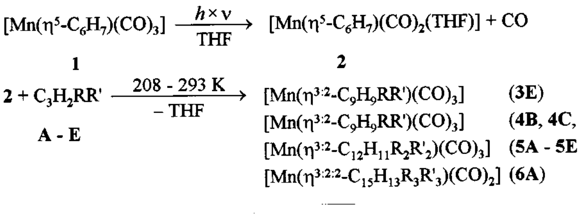
Introduction

Coordination of unsaturated hydrocarbons to transition metals allows pericyclic reactions, that are not allowed for the free hydrocarbons by the Woodward−Hoffmann rules.[2][3] Thus transition-metal-mediated cycloadditions of higher order play an important role in the synthesis of medium-sized carbocyclic and heterocyclic systems. Within the scope of our studies on photochemical reactions of transition metal organyl complexes with olefins we have already reported about light-induced [6+4] cycloadditions of conjugated dienes to tricarbonyl(η^6-1,3,5-cycloheptatriene)chromium(0)[4−9] and [6+2] cycloadditions of dienes to tricarbonyl(η^6-cycloocta-1,3,5,7-tetraene)chromium(0).[10]

Further significant advances have been made in recent years.[11−15] The related [6+2] cycloadditions of alkynes to trienes at chromium have also been described by different authors.[16−19] Furthermore we have shown that tricarbonyl(η^5-pentadienyl)manganese and its derivatives react with conjugated dienes to give tricarbonyl($\eta^{3:2}$-cyclonona-2,6-dienyl)manganese complexes in a photochemically induced formal [5+4] cycloaddition.[20−23] Also, photo-assisted cycloadditions of alkynes to η^5-dienyl ligands have been reported by us[24−28] and others.[29,30] In this respect, the role of cumulenes and heterocumulenes as partners in transition-metal-promoted cycloadditions has so far been described only in a few papers.[31,32] In the following we will discuss our studies upon the reactions of photochemically generated dicarbonyl(η^5-2,4-cyclohexadienyl)(tetrahydrofuran)manganese (**2**) with selected 1,1-disubstituted cumulenes.

Preparative Results

UV irradiation of tricarbonyl(η^5-2,4-cyclohexadienyl)manganese (**1**) at 208 K in THF generates in situ the thermally labile, solvent stabilized dicarbonyl(η^5-2,4-cyclohexadienyl)(tetrahydrofuran)manganese (**2**). After addition of 3-methyl-1,2-butadiene (**A**), 3-phenyl-1,2-butadiene (**B**), 3-phenyl-1,2-pentadiene (**C**), 1,1-diphenyl-1,2-propadiene (**D**), or 1-methoxy-1-trimethylsilyl-1,2-propadiene (**E**) to the THF solution of **2** at 208 K, the reaction mixture is allowed to warm up slowly to room temperature. Four different types of complexes are formed under these conditions depending on the substituents of the 1,1-disubstituted allenes. Only for **E** is the [5+2] cycloadduct $[Mn\{\eta^{3:2}\text{-}C_9H_9(OCH_3)Si(CH_3)_3\}(CO)_3]$ (**3E**) obtained. Dienes **B**, **C**, and **D** also yield 1:1 adducts with the general formula $[Mn(\eta^{3:2}\text{-}C_9H_9RR')(CO)_3]$ (**4B**, **4C**, **4D**) which are formed from the primary [5+2] cycloadduct by a 1,3 H-shift. All cumulenes used in this study generate 1:2 adducts $[Mn(\eta^{3:2}\text{-}C_{12}H_{11}R_2R'_2)(CO)_3]$ (**5A−5E**), and with **A** a 1:3 adduct $[Mn\{\eta^{3:2:2}\text{-}C_{15}H_{13}(CH_3)_6\}(CO)_2]$ (**6A**) is also obtained.



$$\underset{\mathbf{1}}{[Mn(\eta^5\text{-}C_6H_7)(CO)_3]} \xrightarrow[\text{THF}]{h\times\nu} \underset{\mathbf{2}}{[Mn(\eta^5\text{-}C_6H_7)(CO)_2(THF)]} + CO$$

$$\mathbf{2} + \underset{\mathbf{A - E}}{C_3H_2RR'} \xrightarrow[-\text{ THF}]{208 - 293\text{ K}} \begin{array}{ll} [Mn(\eta^{3:2}\text{-}C_9H_9RR')(CO)_3] & (\mathbf{3E}) \\ [Mn(\eta^{3:2}\text{-}C_9H_9RR')(CO)_3] & (\mathbf{4B, 4C, 4D}) \\ [Mn(\eta^{3:2}\text{-}C_{12}H_{11}R_2R'_2)(CO)_3] & (\mathbf{5A - 5E}) \\ [Mn(\eta^{3:2:2}\text{-}C_{15}H_{13}R_3R'_3)(CO)_2] & (\mathbf{6A}) \end{array}$$

	A	B	C	D	E
R =	CH_3	CH_3	C_2H_5	C_6H_5	OCH_3
R′ =	CH_3	C_6H_5	C_6H_5	C_6H_5	$Si(CH_3)_3$

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The reaction mixtures were separated by column and/or HPL chromatography. The complexes are isolated as yellow to red crystals (**4B**, **4C**, **4D**, **6A**) or oils (**3E**, **5A−5E**) in moderate to low yields depending upon the substituents R, R′.

^{1}H-NMR and ^{13}C-NMR Spectra

The ^{1}H-NMR-spectroscopic data of the products **3E−6A** are given in the Experimental Section. The assignments of the signals to the corresponding protons are based upon homo-decoupling experiments and H,H-COSY-90 spectra. The ^{1}H-NMR spectrum of the [5+2] cycloadduct **3E** shows 11 well-separated signals with the relative intensities 1:1:1:3:1:1:1:1:1:1:9 that prove the addition of one 1-methoxy-1-trimethylsilyl-1,2-propadiene (**E**) to the cyclohexadienyl ligand. The δ,*J* diagram (Figure 1) is in accord with a 6-methylenebicyclo[3.2.1]oct-3-en-2-yl ligand with methoxy and trimethylsilyl groups at the exocyclic sp^2-methylene carbon atom, formed by a [5+2] cycloaddition of the unsubstituted double bond of the cumulene **E** to the cyclohexadienyl ligand of **1**.

The ^{13}C-NMR spectrum of **3E** shows the expected 14 signals. IR, ^{1}H-NMR and ^{13}C-NMR data of **3E** fit well with a tricarbonyl{$\eta^{3:2}$-6-(1-methoxy-1-trimethylsilyl-methylene)bicyclo[3.2.1]oct-3-en-2-yl}manganese complex.

The reactions of **2** with 3-phenyl-1,2-butadiene (**B**), 3-phenyl-1,2-pentadiene (**C**) and 1,1-diphenyl-1,2-propadiene (**D**) yield the 1:1 adducts **4B**, **4C** and **4D**. The ^{1}H-NMR spectra of these complexes are similar with the exception of the substituent signals. The δ-*J* diagram (Figure 1) is in accordance with a 7-methylenebicyclo[3.2.1]oct-2-en-6-yl ligand with methyl and phenyl groups at the exocyclic sp^2-methylene carbon. Like in **3E** it is formed by a [5+2] cycloaddition of the unsubstituted double bond of the cumulene **B** to the cyclohexadienyl ligand followed by a H shift from position 7 to 2.

The ^{13}C-NMR data of **4B** supplement the information from the ^{1}H-NMR spectrum. The ^{1}H-NMR and ^{13}C-NMR spectra of **4C** and **4D** differ from those of **4B** only due to the signals of the substituents. Therefore related structures have to be considered.

All cumulenes used in this study form 2:1 adducts with **1**. The tricarbonyl complexes **5A−5E** show similar NMR spectra which differ only in the signals of the respective substituents. The δ,*J* diagram (Figure 1) is closely related to that of **4B** and it is in accordance with a 7-methylenebicyclo[3.2.1]oct-2-en-6-yl ligand with two methyl groups at the exocyclic sp^2-methylene carbon atom and a 3-methyl-2-butenyl group in 4^{endo} position.

The ^{13}C-NMR-spectroscopic data are also in accord with a $\eta^{3:2}$-4-(3-methyl-2-butenyl)-7-(1-methyl-ethylidene)bicyclo[3.2.1]oct-2-en-6-yl-ligand in **5A**.

The ^{1}H-NMR and ^{13}C-NMR spectra of **5B−5E** are, with the exception of the signals of the substituents, closely related to those of **5A**. Therefore, in all of them $\eta^{3:2}$-4-(2-propenyl)-7-(methylene)bicyclo[3.2.1]oct-2-en-6-yl-ligands, correspondingly substituted, are present.

The ^{1}H-NMR spectrum of **6A** shows the expected thirteen signals with single and six methyl signals with threefold intensities for a 1:3 adduct of **1** and **A**. Chemical shifts and signal patterns are closely related to those of **5A**, but due

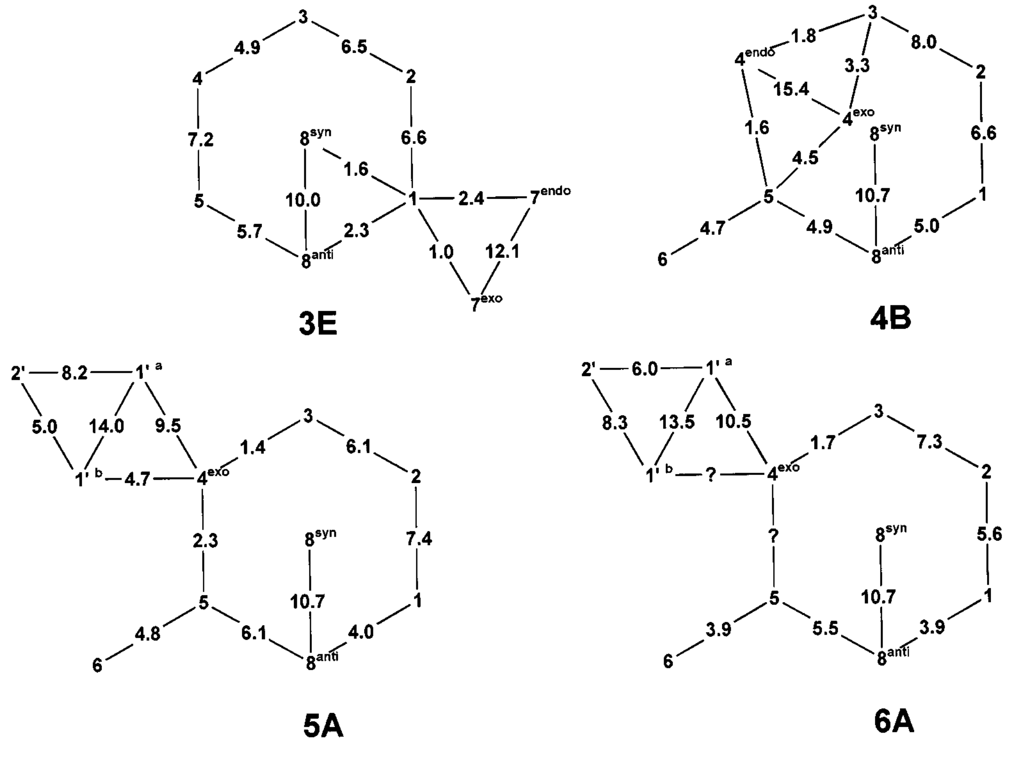


Figure 1. δ,*J* diagrams, showing geminal and vicinal coupling constants, of **3E**, **4B**, **5A** and **6A**

to the overlap of some signals it was not possible to determine all coupling constants. The assignment of the signals was facilitated by a ^{1}H,^{1}H COSY-90 NMR spectrum, and by the molecular structure of **6A** which was determined by X-ray structure analysis. Two doublets of an AB system at $\delta = 1.00$ and 0.56 ($J = 4.1$ Hz) are due to $1''E$-H and $1''Z$-H of the 2,4-dimethyl-3-methylenepenta-2,4-diyl group. The δ,J diagram (Figure 1) of the remaining 11 signals of single intensity is in accord with a 4-(3-methyl-2-butenyl)bicyclo[3.2.1]octa-2,6-dien-7-yl system.

The ^{13}C-NMR spectrum is also consistent with the structure of **6A**.

Crystal and Molecular Structure of 6A

Recrystallization of $[\mathrm{Mn}\{\eta^{3:2:2}\text{-}\mathrm{C}_{15}\mathrm{H}_{12}(\mathrm{CH}_3)_6\}(\mathrm{CO})_2]$ (**6A**) from *n*-pentane at 243 K yields red, rhombic crystals. The complex crystallizes in the triclinic space group $P\bar{1}$ with unit cell of $a = 804.8(2)$ pm, $b = 1201.5(4)$ pm, $c = 1222.1(3)$ pm, $\alpha = 61.01(2)°$, $\beta = 81.12(2)°$, $\gamma = 87.47(2)°$. Figure 2 shows an ORTEP projection of the molecule (selected bond lengths and angles are given in the caption). If the coordination sphere of complex **6A** is considered a distorted trigonal bipyramid, the centre of C6, C7 (M2) and C9 occupy the two axial positions. In the equatorial sites the centre of C2, C3 (M1), the centre of gravity of C14−C16 (M3), and C10 are located. The mean value of the six angles between axial and equatorial positions is 90.3° with an msd of 9.0°. For the three angles between equatorial sites the mean value is 119.9° with an msd of 9.5°. Alternatively the coordination sphere can be described as a distorted octahedron with C14−C16 occupying two coordination sites. However, the angle M1−Mn1−C10 with 111.7(5)° makes this description less suited for **6A**.

The plane defined by Mn1, M1, M3, C10 (rmsd 2.69 pm) is cut by M2−Mn1 with 72.6° and by C9−Mn1 with 82.5°. While C2−C3 are virtually parallel to that plane (2.8°), C15−C16 are turned by 28.0° with respect to it. The Mn−C bond lengths of the hydrocarbon chelate ligand differ over a considerable range. For the coordinated sp^2-carbon atoms in the equatorial plane the distances lie between 212.2(3) pm (Mn1−C14) and 217.8(3) pm (Mn1−C3). For Mn1−C16 the distance is distinctly larger [236.5(3) pm] as a result of the steric bulk of the two methyl groups. The C−C double bond in axial position is less tightly coordinated according to Mn1−C6 237.2(3) pm and Mn1−C7 226.1(3) pm. As a consequence of the different extent of coordination the elongation of C2−C3 140.4(4) pm is larger than for C6−C7 with 137.4 (4). A comparable bonding situation has been already found for [$\eta^{3:2:2}$-1-(3-butene-1,2-diyl)-1,3-dimethyl-2,6-cyclononadiene]dicarbonylmanganese with even larger Mn−C distances for the axially coordinated C−C double bond.[20]

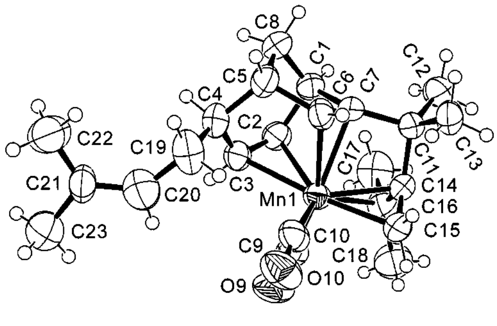


Figure 2. ORTEP projection of dicarbonyl{2,3,6,7,3″,4″,1″′-η-7-(2,4-dimethyl-3-methylenepenta-2,4-diyl)-4-(3-methyl-2-butenyl)-bicyclo[3.2.1]octa-2,6-diene}manganese (**6A**); selected bond lengths [pm] and bond angles [°]: Mn1−C2 213.4(3), Mn1−C3 217.8(3), Mn1−C6 237.2(3), Mn1−C7 226.1(3), Mn1−C9 176.8(3), Mn1−C10 177.9(4), Mn1−C14 212.2(3), Mn1−C15 214.6(3), Mn1−C16 236.5(3), C2−C3 140.4(4), C6−C7 137.4(4), C14−C15 142.6(4), C14−C16 141.5(4), O9−C9 116.2(3), O10−C10 116.3(3); C9−Mn1−C10 84.72(15), O9−C9−Mn1 175.7(3), O10−C10−Mn1 170.6(3), C16−C14−C15 116.3(3)

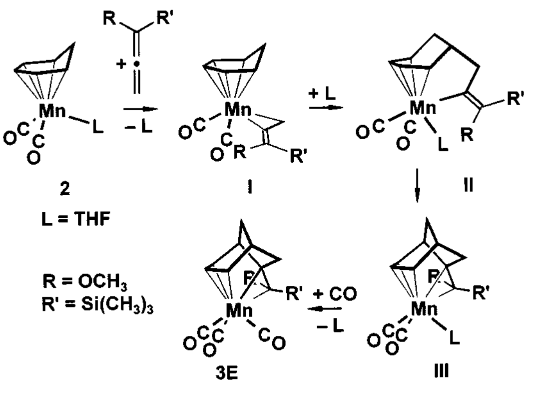
Discussion

Tricarbonyl(η^5-penta-2,4-dienyl)manganese complexes react photochemically with 1,3-dienes in a formal [5+4] cycloaddition to tricarbonyl($\eta^{3:2}$-cyclonona-2,6-dienyl)-manganese complexes. The expected analogous photochemical [5+2] cycloaddition of alkynes to tricarbonyl(η^5-penta-2,4-dienyl)manganese is not observed experimentally.[26] At 208 K in THF, photochemically generated, very reactive dicarbonyl(η^5-2,4-dimethylpenta-2,4-dienyl)(tetrahydrofuran)manganese adds diphenylacetylene or dimethyl butynedioate to yield in a first step the [5+2] cycloadducts with accordingly substituted $\eta^{3:2}$-cyclohepta-2,4-dienyl ligands. These unstable intermediates rearrange by manganese-mediated 1,4-H shifts and form substituted tricarbonyl(η^5-cyclohepta-2,4-dienyl)manganese complexes.

Similarly, irradiation of tricarbonyl(η^5-cyclohexa-2,4-dienyl)manganese (**1**) at 208 K in *n*-pentane in the presence of the cumulenes **A−E** causes within 30 minutes only complete decomposition of **1**. The IR spectra, measured during the UV irradiation in regular intervals show no new bands in the region of 2200−1600 cm^{-1} due to the formation of manganese complexes.

Dicarbonyl(η^5-cyclohexa-2,4-dienyl)(tetrahydrofuran)-manganese (**2**), photochemically generated at 208 K, reacts with the 1,2-dienes **A−E** when the solution is allowed to warm up to room temperature to four types of complexes. From the constitution of these products their formation can be proposed taking into account the results of other cycloadditions of higher order at metal centres. Prerequisite for a C−C bond formation is the simultaneous presence of reactive hydrocarbon ligands in the coordination sphere. Stable complexes are only formed when one of the ligands is endowed with uncoordinated π-bonds. Each C−C bond formation is accompanied by a loss of two metal−carbon bonds, and produces electronically and coordinatively unsaturated intermediates. Saturation is accomplished by coordination of n-donor or σ-donor-π-acceptor ligands. Metal-mediated C−C bond formation is closely related to reductive elimination, and coordination of olefins to metals centres, by which two metal−carbon bonds are generated, to oxidative addition reactions.

First step of the reaction between **2** and the cumulene **A−E** is the substitution of the weakly coordinated THF ligand (**I**) by the cumulene. For stereochemical reasons the hydrocarbons are coordinated through the unsubstituted double bond to the manganese centre. C−C bond formation between C-1 of the cyclohexadienyl and the terminal carbon atom of the coordinated cumulene leads to the dicarbonyl{$\eta^{4:1}$-1-(2-propen-1,2-diyl)cyclohexa-2,3-diene}manganese intermediates **II** probably stabilized by THF. The second C−C bond is formed between 5-C of the ring and 2-C of the 2-propen-1,2-diyl side chain, and the exocyclic, substituted double bond is coordinated to manganese (**III**). The result of the two C−C bond formations is a formal [5+2] cycloadduct of a cumulene to the cyclohexadienyl ligand. Substitution of the THF ligand by carbon monoxide, dissolved in the solution, completes the reaction of **2** with 1-methoxy-1-trimethylsilyl-1,2-propadiene (**E**) to give **3E**.

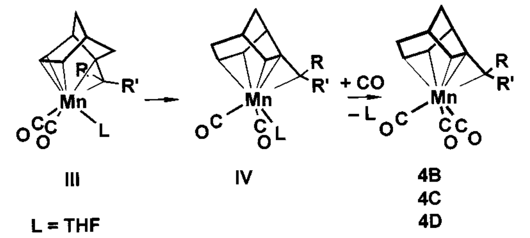


Scheme 1. Proposed formation of tricarbonyl{$\eta^{3:2}$-6-(1-methoxy-1-trimethylsilylmethylene)bicyclo[3.2.1]oct-3-en-2-yl}manganese (**3E**) via intermediates **I**−**III**

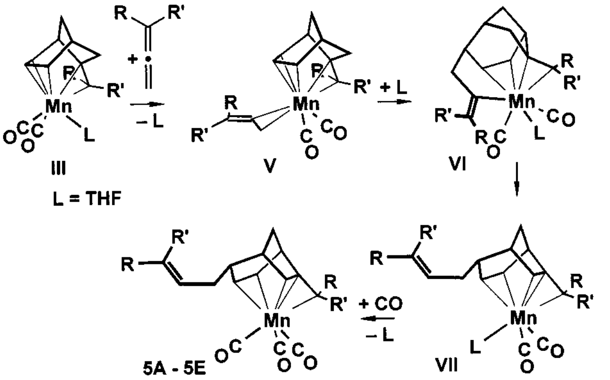
With regard to the substituents at the coordinated exocyclic double bond two isomers (*E*, *Z*) are possible. The spectroscopic data of **3E**, however, prove only the formation of one isomer. For stereochemical reasons the bulky $Si(CH_3)_3$ group is proposed to be in *E* position relative to C-5.

In case of cumulenes with phenyl substituents (**B**, **C**, **D**) from **III** a manganese-mediated 1,3-H shift takes place which results in the THF stabilized dicarbonyl($\eta^{3:2}$-7-methylenebicyclo[3.2.1]oct-2-en-6-yl)manganese complexes **IV**. The exchange of THF by CO completes the reactions to **4B**, **4C** and **4D**. Again, only one regioisomer with the phenyl group in *Z* position relative to C-5 is observed for **4B**, and **4C**.

The formation of the 1:2 adducts **5A−5E** is explained by an analogous reaction sequence as for **3E** starting from **III**. Substitution of the THF ligand by a cumulene affords the intermediate **V**. C−C bond formation between C-4 of the 6-methylenebicyclo[3.2.1]oct-3-en-2-yl and the terminal carbon atom of the coordinated cumulene leads to the accordingly substituted dicarbonyl{$\eta^{2:2:1}$-4-(2-propen-1,2-diyl)-6-methylenebicyclo[3.2.1]oct-2-en}(tetrahydrofuran)manganese intermediates **VI**. By a 1,5-H shift (**VII**) and addition of carbon monoxide the tricarbonyl{2,3,6,7,1″-η-7-methylene-4-(2-propenyl)bicyclo[3.2.1]oct-2-en-6-yl}manganese complexes **5A−5E** result. Only one regioisomer is obtained for the products from unsymmetrically substituted 1,1-allenes (**5B**, **5C**, **5E**).

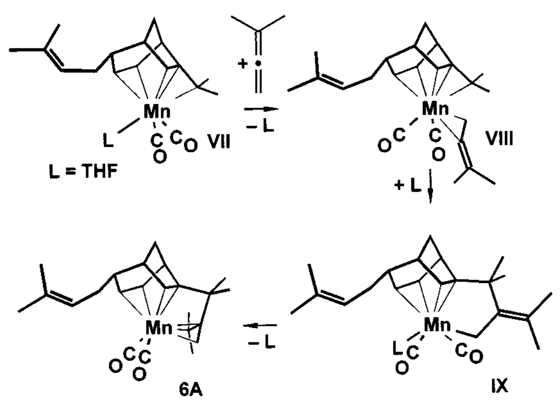


Scheme 2. Proposed formation of tricarbonyl{$\eta^{3:2}$-7-methylenebicyclo[3.2.1]oct-2-en-6-yl}manganese complexes **4B**, **4C**, **4D** by 1,3-H shift in intermediate **III**



Scheme 3. Proposed formation of tricarbonyl{2,3,6,7,1″-η-7-methylene-4-(2-propenyl)bicyclo[3.2.1]oct-2-en-6-yl}mangemese complexes **5A−5E** via intermediates **III** and **V**−**VII**

The ligand of **6A** consists of three cumulenes and cyclohexadienyl. A reasonable reaction sequence for **6A** starts from intermediate **VII**. Substitution of THF by **A** gives the cumulene complex **VIII** which rearranges by C−C bond formation between C-1 of the 1-methylethylidene group and C-2 of the 3-methyl-1,2-butadiene unit to intermediate **IX**, stabilized with THF. Finally the 2,4-dimethyl-3-methylenepenta-2,4-diyl side chain is η^3-coordinated to the manganese centre.



Scheme 4. Proposed formation of dicarbonyl{2,3,6,7,3″,4″,1‴-η-7-(2,4-dimethyl-3-methylenepenta-2,4-diyl)-4-(3-methyl-2-butenyl)-bicyclo[3.2.1]octa-2,6-diene}manganese (**6A**)

Experimental Section

All operations and reactions were carried out under dry, oxygen-free nitrogen by common Schlenk techniques. All solvents were purified by standard methods (*n*-pentane, *n*-hexane with CaH_2, THF with potassium, diethyl ether with sodium/benzophenone and CH_2Cl_2 with P_4O_{10}) and stored under nitrogen. Alumina, neutral (Macherey-Nagel GmbH and CO KG, Düren) for column chromatography was degassed under vacuum, deactivated with 4% of water and saturated with nitrogen. UV irradiations were carried out in a 180-mL Duran flask with cooling jacket, wrapped with aluminium foil, with a 150-W mercury lamp TQ 150 (Heraeus-Noblelight, Kleinostheim). The irradiation flask was cooled by a cryostat SK 80 D (Lauda) with methanol as cooling liquid. During the irradiation, nitrogen was bubbled through the solutions to ensure mixing and to remove some of the carbon monoxide from the solutions. HPLC was performed with an Abimed/Gilson appliance consisting of three pumps (type 303), a dynamic mixer (type 811), a high-grade steel column with pre-column (Abimed/Gilson, type Dynamax, l = 25 cm, d = 21.4 mm, silica gel Si 60, 8 µm) and a UV detector (type 116). − IR: Perkin-Elmer FT-IR 16 PC. − NMR: Bruker AC 200 (200.13 MHz for ^1H, 50.32 MHz for ^{13}C), Bruker AMX 400 (400.13 MHz for ^1H, 100.63 MHz for ^{13}C). Chemical shifts are given relative to TMS, calculated from the solvent as internal standard (C_6HD_5: $\delta_H = 7.20$, C_6D_6: $\delta_C = 128.0$ and CD_2Cl_2: $\delta_C = 54.0$). − C, H elemental analyses: Perkin−Elmer microanalyzer 240. The starting material tricarbonyl(η^5-cyclohexa-2,4-dienyl)manganese (**1**) was prepared from $[Mn(CO)_5Br]$ according to a literature procedure.[33][34] 3-Methyl-1,2-butadiene (**A**), 3-phenyl-1,2-butadiene (**B**), 3-phenyl-1,2-pentadiene (**C**), 1,1-diphenyl-1,2-propadiene (**D**) and 1-methoxy-1-trimethylsilyl-1,2-propadiene (**E**) were also prepared as described in literature.[35]

1. Photoreaction of Tricarbonyl(η^5-cyclohexadienyl)manganese (1) in Tetrahydrofuran: The irradiation flask was loaded with 250 mg (1.15 mmol) of $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**), dissolved in 180 mL of THF. The pale yellow solution was cooled to 208 K and irradiated with UV light. After a few minutes, the colour of the solution turned to red. After 45 minutes, the CO bands of **1** had nearly disappeared and the irradiation was stopped. Dicarbonyl(η^5-cyclohexa-2,4-dienyl)(tetrahydrofuran)manganese (**2**) was identified by IR spectroscopy according to two νCO bands at 1930 (s) und 1861 (s) cm^{-1}.

2. Reaction of Dicarbonyl(η^5-cyclohexa-2,4-dienyl)(tetrahydrofuran)manganese (2) with 3-Methyl-1,2-butadiene (A): To a THF solution of $[Mn(\eta^5\text{-}C_6H_7)(CO)_2THF]$ (**2**), freshly prepared from 250 mg (1.15 mmol) of $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**), 0.2 mL (3 mmol) of 3-methyl-1,2-butadiene (**A**) was added at 208 K. The reaction mixture was allowed to warm up to room temperature while a slight stream of nitrogen was bubbled through it. During this procedure the colour of the solution changed from carmine to yellow. The solvent was removed in vacuo and the brown, oily residue was dissolved in *n*-pentane and chromatographed at 253 K on alumina with *n*-pentane.

1st Fraction: $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**).

2nd Fraction: Yellow zone, tricarbonyl{2,3,6,7,1″-η-4-(3-methyl-2-butenyl)-7-(1-methylethylidene)bicyclo[3.2.1]oct-2-en-6-yl}manganese (**5A**) with traces of other carbonyl complexes. After purification by HPL chromatography with *n*-hexane as eluent, 105 mg (26%) of **5A**, yellow oil. − IR (*n*-pentane): ṽ (CO) = 2005 (s), 1932 (vs), 1922 (vs) cm^{-1}. − ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ = 5.32 (m, J = 8.2, 5.0, 1.4, 1.4 Hz, 1 H, 2′-H), 3.82 (ddd, J = 6.1, 2.3, 1.4 Hz, 1 H, 3-H), 2.94 (ddd, J = 14.0, 9.5, 8.2 Hz, 1 H, $1'^{A}$-H), 2.89 (d, J = 4.8 Hz, 1 H, 6-H), 2.72 (ddd, J = 14.0, 5.0, 4.7 Hz, 1 H, $1'^{B}$-H), 2.64 (dddd, J = 9.5, 4.7, 2.3, 1.4 Hz, 1 H, 4-H), 2.45 (dd, J = 7.4, 4.0 Hz, 1 H, 1-H), 2.30 (dd, 7.4, 6.1 Hz, 1 H, 2-H), 1.99 (s, 3 H, 1″*E*-CH_3), 1.97 (dddd, J = 6.1, 4.8, 2.3, 2.3 Hz, 1 H, 5-H), 1.76 (d, J = 1.4 Hz, 3 H, 3′-CH_3), 1.69 (d, J = 1.4 Hz, 3 H, 3′-CH_3), 1.57 (ddd, J = 10.7, 6.1, 4.0 Hz,1 H, 8^{anti}-H), 1.28 (s, 3 H, 1″*Z*-CH_3), 1.21 (d, J = 10.7 Hz, 1 H, 8^{syn}-H). − ^{13}C NMR (50.32 MHz, C_6D_6, 298 K): δ = 226.0 (s, *C*O), 225.3 (s, *C*O), 224.5 (s, *C*O), 133.2 (s, C-3′), 122.9 (d, J = 157 Hz, C-2′), 99.4 (d, J = 158 Hz, C-3), 90.4 (s, C-7 or C-1″), 88.0 (s, C-7 or C-1″), 66.6 (d, J = 166 Hz, C-2), 59.0 (d, J = 119 Hz, C-4), 49.6 (d, J = 165 Hz, C-6), 42.7 (t, J = 132 Hz, C-1′), 39.7 (d, J = 141 Hz, C-1), 35.1 (t, J = 131 Hz, C-8), 33.5 (d, J = 154 Hz, C-5), 27.3 (q, J = 129 Hz, 1″*E*-CH_3), 25.9 (q, J = 126 Hz, 3′-CH_3), 25.6 (q, J = 126 Hz, 3′-CH_3), 18.1 (q, J = 125 Hz, 1″*Z*-CH_3). − $C_{19}H_{23}MnO_3$ (354.33): calcd. C 64.41, H 6.54; found C 64.02, H 6.52.

3rd Fraction: Yellow solution, dicarbonyl{2,3,6,7,3″,4″,1‴-η-7-(2,4-dimethyl-3-methylenepenta-2,4-diyl)-4-(3-methyl-2-butenyl)-bicyclo[3.2.1]octa-2,6-diene}manganese (**6A**). Removal of the solvent and crystallization from *n*-pentane at 243 K yielded 55 mg (12%) of **6A**. Red, rhombic crystals, suitable for X-ray diffraction analysis. − IR (*n*-pentane): ṽ (CO) = 1956 (vs), 1900 (vs) cm^{-1}. − ^1H NMR (200.13 MHz, C_6D_6, 298 K): δ = 5.56 (m, J = 8.3, 6.0, 1.4, 1.4 Hz, 1 H, 2′-H), 3.54 (dd, J = 3.9, 1.5 Hz, 1 H, 6-H), 3.44 (ddd, J = 7.3, 2.3, 1.7 Hz, 1 H, 3-H), 3.16 (ddd, J = 13.5, 10.5, 6.0, Hz, 1 H, $1'^{A}$-H), 2.95 (ddd, J = 13.5, 8.3, ? Hz, 1 H, $1'^{B}$-H), 2.95 (m, J = 10.5, 1.7, ? Hz, 1 H, 4-H), 2.52 (ddd, J = 5.6, 3.9, 1.5 Hz, 1 H, 1-H), 2.20 (s, 3 H, CH_3), 2.19 (dd, J = 7.3, 5.6 Hz, 1 H, 2-H), 1.88 (s, 3 H, CH_3), 1.85 (m, J = 5.5, 3.9, 2.3, ? Hz, 1 H, 5-H), 1.80 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.35 (ddd, J = 9.4, 5.5, 3.9 Hz, 1 H, 8^{anti}-H), 1.26 (s, 3 H, CH_3), 1.00 (d, J = 4.1 Hz, 1 H, 1‴*E*-H), 0.99 (d, J = 9.4 Hz, 1 H, 8^{syn}-H), 0.56 (d, J = 4.1 Hz, 1 H, 1‴*Z*-H), 0.36 (s, 3 H, CH_3). − ^{13}C NMR (50.32 MHz, CD_2Cl_2 298 K) δ = 237 (s, br., 2 C, *C*O), 133.0 (s, C-3′), 123.9 (d, J = 144 Hz, C-2′), 96.8 (d, J = 167 Hz, C-3), 93.7 (s, C-7), 76.2 (d, J = 154 Hz, C-6), 74.4 (s, C-3″), 65.2 (s, C-4″), 56.8 (d, J = 126 Hz, C-4), 46.7 (t, J = 129 Hz, C-1′), 42.8 (d, J = 166 Hz, C-2), 42.0 (d, J = 138 Hz, C-1), 37.4 (d, J = 147 Hz, C-5), 36.0 (s, C-2″), (t, J = 129 Hz, C-8), 32.9 (t, J = 158 Hz, C-1‴), 30.3 (q, J = 130 Hz, 2 C, *C*H_3), 27.7 (q, J = 129 Hz, *C*H_3), 26.9 (q, J = 130 Hz, *C*H_3), 26.1 (q, J = 130 Hz, *C*H_3), 18.4 (q, J = 130 Hz, *C*H_3). − MS (70 eV); *m*/*z* (%): 337.8 (100) [M^+ − 2 CO], 283.9 (12.67) [M^+ − 2 CO, − Mn], 269.9 (53.47) [M^+ − 2 CO, − C_5H_8], 201.9 (59.39) [M^+ − 2 CO, − 2 C_5H_8]. − $C_{23}H_{31}MnO_2$ (394.44): calcd. C 70.04, H 7.92; found C 69.98, H 8.03.

3. Reaction of Dicarbonyl(η^5-cyclohexa-2,4-dienyl)(tetrahydrofuran)manganese (2) with 3-Phenyl-1,2-butadiene (B): To a THF solution of $[Mn(\eta^5\text{-}C_6H_7)(CO)_2THF]$ (**2**), freshly prepared from 250 mg (1.15 mmol) of $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**), 0.2 mL (1.5 mmol) of 3-phenyl-1,2-butadiene (**B**) was added at 208 K. After warming up to room temperature, the solvent was removed in vacuo and the residue was separated by HPLC with *n*-hexane.

1st Fraction: $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**).

2nd Fraction: Yellow solution, tricarbonyl{$\eta^{3:2}$-7-(1-phenylethylidene)bicyclo[3.2.1]oct-2-en-6-yl}manganese (**4B**). After crystallization from *n*-pentane, **4B** was isolated as yellow needles 16 mg (4%). − IR (*n*-pentane): ṽ (CO) = 2007 (s), 1936 (vs), 1922 (s) cm^{-1}. − ^1H NMR (200.13 MHz, C_6D_6, 298 K): δ = 7.61 (d, J = 7.2 Hz, 2 H, *o*-Ph), 7.24 (t, J = 7.2 Hz, 2 H, *m*-Ph), 7.01 (t, J = 7.2 Hz, 1 H, *p*-Ph), 3.66 (dddd, J = 8.0, 3.3, 2.0, 1.8 Hz, 1 H, 3-H), 2.80 (ddd, J = 6.6, 5.0, 1.3 Hz, 1 H, 1-H), 2.70 (dd, J = 4.7, 1.3 Hz, 1 H, 6-H), 2.64 (m, J = 15.4, 4.5, 3.3, 1.5 Hz, 1 H, 4^{exo}-H), 2.39 (dd, J = 8.0, 6.6 Hz, 1 H, 2-H), 2.07 (ddd, J = 15.4, 1.8, 1.6 Hz, 1 H,

4^{endo}-H), 1.99 (m, *J* = 4.9, 4.7, 4.5, 2.0, 1.6 Hz, 1 H, 5-H), 1.53 (dddd, *J* = 10.7, 5.0, 4.9, 1.5 Hz, 1 H, 8^{anti}-H), 1.49 (s, 3 H, CH_3), 0.90 (d, *J* = 10.7 Hz, 1 H, 8^{syn}-H). − ^{13}C NMR (50.32 MHz, C_6D_6, 298 K): δ = 224 (s, br., 3 C, *C*O), 147 (s, 1 C, *ipso*-Ph), 130 (d, 2 C, *o*-Ph), *m*-, *p*-Ph (covered by solvent signals), 97.3 (s, 1 C, 7-C or 1′-C), 95.4 (d, *J* = 162 Hz, 1 C, 3-C), 93.8 (s, 1 C, 7-C or 1′-C), 64.4 (d, *J* = 161 Hz, 1 C, 2-C), 59.4 (d, *J* = 166 Hz, 1 C, 6-C), 46.2 (t, *J* = 129 Hz, 1 C, 4-C), 41.3 (t, *J* = 129 Hz, 1 C, 8-C), 35.4 (d, *J* = 136 Hz, 1 C, 1-C), 34.2 (d, *J* = 149 Hz, 1 C, 5-C), 28.7 (q, *J* = 130 Hz, 1 C, CH_3). − $C_{19}H_{17}MnO_3$ (348.28): calcd. C 65.52, H 4.92.

3rd Fraction: Yellow solution, tricarbonyl{2,3,6,7,1″-η-4-(3-phenyl-2-butenyl)-7-(1-phenylethylidene)bicyclo[3.2.1]oct-2-en-6-yl}manganese (**5B**), yellow oil, 40 mg (7%). − IR (*n*-pentane): ṽ (CO) = 2008 (s), 1940 (vs), 1920 (vs) cm^{-1}. − ^1H NMR (200.13 MHz, C_6D_6, 298 K): δ = 7.30−7.15 (m, 5 H, Ph-H), 7.10−6.90 (m, 5 H, Ph-H), 5.58 (m, *J* = 9.0, 5.5, 1.5 Hz, 1 H, 2′-H), 3.63 (ddd, *J* = 8.0, 2.3, 1.0 Hz, 1 H, 3-H), 3.05 (m, *J* = 14.7, 9.0, ? Hz, 1 H, $1'^{A}$-H), 3.03 (dd, *J* = 4.8, 1.0 Hz, 1 H, 6-H), 2.73−2.55 (m, 2 H, $1'^{B}$-H and 4-H), 2.47 (dd, *J* = 6.1, 5.3, 1.0 Hz, 1 H, 1-H), 2.39 (s, 3 H, CH_3), 2.33 (dd, *J* = 8.0, 6.1 Hz, 1 H, 2-H), 2.09 (s, 3 H, CH_3), 2.00 (ddd, *J* = 6.3, 4.8, 2.3 Hz, 1 H, 5-H), 1.71 (ddd, *J* = 10.9, 6.3, 5.3 Hz, 1 H, 8^{anti}-H), 1.23 (d, *J* = 10.9 Hz, 1 H, 8^{syn}-H). − ^{13}C NMR (50.32 MHz, C_6D_6, 298 K): δ = 229.0 (s, 1 C, *C*O), 226.0 (s, 1 C, *C*O), 218.7 (s, 1 C, *C*O), 143.9 (s, 1 C, *ipso*-Ph), 142.1 (s, 1 C, *ipso*-Ph), *o*-, *m*-, *p*-Ph (covered by solvent signals), 138.8 (s, 1 C, 3′-C), 125.2 (d, *J* = 160 Hz, 1 C, 2′-C), 99.6 (d, *J* = 159 Hz, 1 C, 3-C), 90.7 (s, 1 C, 7-C or 1′′-C), 90.1 (s, 1 C, 7-C or 1′′-C), 70.3 (d, *J* = 169 Hz, 1 C, 2-C), 58.8 (d, *J* = 120 Hz, 1 C, 4-C), 50.9 (d, *J* = 168 Hz, 1 C, 6-C), 42.5 (t, *J* = 131 Hz, 1 C, 1′-C), 39.3 (d, *J* = 143 Hz, 1 C, 1-C), 35.9 (t, *J* = 128 Hz, 1 C, 8-C), 34.4 (d, *J* = 148 Hz, 1 C, 5-C), 27.8 (q, *J* = 128 Hz, 1 C, CH_3), 25.8 (q, *J* = 127 Hz, 1 C, CH_3). − $C_{29}H_{27}MnO_3$ (478.47): calcd. C 72.80, H 5.69; found C 71.0, H 6.09.

4. Reaction of Dicarbonyl(η⁵-cyclohexa-2,4-dienyl)(tetrahydrofuran)manganese (2) with 3-Phenyl-1,2-pentadiene (C): To a THF solution of $[Mn(\eta^5\text{-}C_6H_7)(CO)_2THF]$ (**2**), freshly prepared from 250 mg (1.15 mmol) of $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**), 0.2 mL (1.5 mmol) of 3-phenyl-1,2-pentadiene (**C**) was added at 208 K. After warming up to room temperature, the solvent was removed in vacuo and the residue was separated by HPLC with *n*-hexane.

1st Fraction: $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**).

2nd Fraction: Yellow solution, tricarbonyl{$\eta^{3:2}$-7-(1-phenylpropylidene)bicyclo[3.2.1]oct-2-en-6-yl}manganese (**4C**). After crystallization from *n*-pentane, 25 mg (6%) of **4C**, orange red crystals. − IR (*n*-pentane): ṽ (CO) = 2006 (vs), 1934 (s), 1923 (vs) cm^{-1}. − ^1H NMR (200.13 MHz, C_6D_6, 298 K): δ = 7.59 (d, *J* = 7.0 Hz, 2 H, *o*-Ph), 7.23 (t, *J* = 7.0 Hz, 2 H, *m*-Ph), 7.10 (t, *J* = 7.0 Hz, 1 H, *p*-Ph), 3.67 (m, *J* = 8.0, 3.4, 2.0, 1.8 Hz, 1 H, 3-H), 3.03 (ddd, *J* = 6.3, 5.6, 1.3 Hz, 1 H, 1-H), 2.79 (dd, *J* = 4.9, 1.3 Hz, 1 H, 6-H), 2.65 (m, *J* = 15.4, 4.5, 3.4, 1.5 Hz, 1 H, 4^{exo}-H), 2.32 (dd, *J* = 8.0, 6.6 Hz, 1 H, 2-H), 2.23 (dq, *J* = 14.4, 7.2 Hz, 1 H, CH_2), 2.10 (m, *J* = 15.4, 2.0, 1.5 Hz, 1.5 Hz, 1 H, 4^{endo}-H), 2.02 (m, *J* = 4.9, 4.8, 4.5, 1.8, 1.5 Hz, 1 H, 5-H), 1.59 (m, *J* = 10.7, 5.6, 4.8, 1.5, 1.5 Hz, 1 H, 8^{anti}-H), 1.17 (dq, *J* = 14.4, 7.2 Hz, 1 H, CH_2), 0.97 (d, *J* = 10.7 Hz, 1 H, 8^{syn}-H), 0.80 (t, *J* = 7.2 Hz, 3 H, CH_3). − MS (70 eV); *m*/*z* (%): 362.0 (0.94) $[M^+]$, 334.0 (6.90) $[M^+ - CO]$, 306.0 (9.37) $[M^+ - 2\ CO]$, 278.0 (100) $[M^+ - 3\ CO]$, 223.0 (10.11) $[M^+ - 3\ CO, - Mn]$. − $C_{20}H_{19}MnO_3$ (362.31): calcd. C 66.30, H 5.29; found C 66.38, H 5.27.

3rd Fraction: Yellow solution, tricarbonyl{2,3,6,7,1″-η-4-(3-phenyl-2-pentenyl)-7-(1-phenylpropylidene)bicyclo[3.2.1]oct-2-en-6-yl}manganese (**5C**), 60 mg (10%), yellow oil. − IR (*n*-pentane): ṽ(CO) = 2008 (vs), 1940 (vs), 1920 (vs) cm^{-1}. − ^1H NMR (200.13 MHz, C_6D_6, 298 K): δ = 7.12−7.20 (m, 5 H, Ph-H), 7.00−6.90 (m, 5 H, Ph-H), 5.58 (dd, *J* = 9.5, 5.5 Hz, 1 H, 2′-H), 3.64 (ddd, *J* = 7.8, 2.0, 1.5 Hz, 1 H, 3-H), 3.29 (dq, *J* = 14.3, 7.2 Hz, 1 H, CH_2) 2.98 (ddd, *J* = 13.9, 9.5, 9.0 Hz, 1 H, $1'^{A}$-H), 2.98 (d, *J* = 4.9 Hz, 1 H, 6-H), 2.53−2.68 (m, 2 H, $1'^{B}$-H and 4-H), 2.26−2.48 (m, 5 H, 1-H, 2-H, CH_2), 1.98 (ddd, *J* = 5.5, 4.9, 2.0 Hz, 1 H, 5-H), 1.71 (ddd, *J* = 10.7, 5.5, 5.0 Hz, 1 H, 8^{anti}-H), 1.23 (d, *J* = 10.7 Hz, 1 H, 8^{syn}-H), 1.03 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3). − $C_{31}H_{31}MnO_3$ (506.53): calcd. C 73.51, H 6.17.

5. Reaction of Dicarbonyl(η⁵-cyclohexa-2,4-dienyl)(tetrahydrofuran)manganese (2) with 1,1-Diphenyl-1,2-propadiene (D): To a THF solution of $[Mn(\eta^5\text{-}C_6H_7)(CO)_2THF]$ (**2**), freshly prepared from 250 mg (1.15 mmol) of $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**), 0.3 mL (1.5 mmol) of 1,1-diphenyl-1,2-propadiene (**D**) was added at 208 K. After warming up to room temperature, the solvent was removed in vacuo and the residue was separated by HPLC with *n*-hexane/CH_2Cl_2 (50:1).

1st Fraction: $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**).

2nd Fraction: Yellow solution, tricarbonyl{$\eta^{3:2}$-7-(1,1-diphenylmethylene)bicyclo[3.2.1]oct-2-en-6-yl}manganese (**4D**). After crystallization from *n*-pentane/CH_2Cl_2 (5:1), 15 mg (3%) of **4D** was isolated as red crystals. − IR (*n*-pentane): ṽ (CO) = 2010 (s), 1945 (vs), 1921 (vs) cm^{-1}. − ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ = 7.81 (d, br, 2 H, *o*-Ph), 7.20 (m, 4 H, *o*-, *m*-Ph), 7.10 (t, *J* = 7.2 Hz, 1 H, *p*-Ph), 6.97 (t, *J* = 7.2 Hz, 2 H, *m*-Ph), 6.87 (t, *J* = 7.2 Hz, 1 H, *p*-Ph), 3.80 (dd, *J* = 8.2, 3.4 Hz, 1 H, 3-H), 3.57 (d, *J* = 4.8, 1 H, 6-H), 2.97 (dd, *J* = 8.2, 6.1 Hz, 1 H, 2-H), 2.71 (m, *J* = 14.7, 3.4, 3.4, 1 H, 4^{exo}-H), 2.21 (ddd, *J* = 6.1, 4.8, 1 H, 1-H), 2.15 (m, *J* = 5.5, 4.8, 3.4 Hz, 1 H, 5-H), 2.12 (d, *J* = 14.75 Hz, 1 H, 4^{endo}-H), 1.60 (ddd, *J* = 10.8, 5.5, 4.8 Hz, 1 H, 8^{anti}-H), 0.90 (d, *J* = 10.8 Hz, 1 H, 8^{syn}-H). − MS (70 eV); *m*/*z* (%): 409.8 (< 1) $[M^+]$, 381.9 (4.21) $[M^+ - CO]$, 353.9 (4.51) $[M^+ - 2\ CO]$, 325.9 (100) $[M^+ - 3\ CO]$, 272.0 (23.29) $[M^+ - 3\ CO, - Mn]$. − $C_{24}H_{19}MnO_3$ (410.35): calcd. C 70.25, H 4.67.

3rd Fraction: Yellow solution, tricarbonyl{2,3,6,7,1″-η-4-(3,3-diphenyl-2-propenyl)-7-(1,1-diphenyl-methylene)bicyclo[3.2.1]oct-2-en-6-yl}manganese (**5D**). After crystallization from *n*-hexane at 243 K, 35 mg (5%) of **5D**, red needles.− IR (*n*-pentane): ṽ (CO) = 2010 (s), 1942 (vs), 1920 (vs) cm^{-1}. − ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ = 7.79 (d, *J* = 7.2 Hz, 2 H, *o*-Ph), 7.44 (d, *J* = 7.2 Hz, 3 H, *o*-Ph), 7.32 (d, *J* = 7.2 Hz, 3 H, *o*-Ph), 7.28−7.01 (m, 8 H, *m*-Ph), 6.98 (t, *J* = 7.2 Hz, 3 H, *p*-Ph), 6.90 (t, *J* = 7.2 Hz, 1 H, *p*-Ph), 6.24 (dd, *J* = 9.0, 5.8 Hz,1 H, 2′-H), 3.83 (ddd, *J* = 8.0, 2.5, 1.5 Hz, 1 H, 3-H), 3.26 (dd, *J* = 6.1, 3.8 Hz, 1 H, 6-H), 3.25 (ddd, *J* = 14.1, 10.0, 9.0 Hz, 1 H, $1'^{A}$-H), 2.83 (dd, *J* = 8.0, 6.1 Hz, 1 H, 2-H), 2.80 (ddd, *J* = 14.1, 5.8, 4.1 Hz, 1 H, $1'^{B}$-H), 2.68 (m, *J* = 10.0, 4.1, ? Hz, 1 H, 4-H), 2.32 (dd, *J* = 6.1, 3.4, Hz, 1 H, 1-H), 2.18 (m, *J* = 6.1, 2.5, ? Hz, 1 H, 5-H), 1.66 (ddd, *J* = 10.9, 3.4, ? Hz, 1 H, 8^{anti}-H), 1.10 (d, *J* = 10.9 Hz, 1 H, 8^{syn}-H). − MS (70 eV); *m*/*z* (%): 518.2 (58.17) $[M^+ - 3\ CO]$, 464.2 (29.77) $[M^+ - 3\ CO, - Mn]$, 271.1 (76.81) $[M^+ - 3\ CO, - Mn, - C_3H_3(C_6H_5)_2]$, 193.0 (100) $[M^+ - 3\ CO, - Mn, - C_3H_2(C_6H_5)_2, - C_6H_5]$. − $C_{39}H_{31}MnO_3$ (602.61): calcd. C 77.73, H 5.19; found C 77.07, H 5.07.

6. Reaction of Dicarbonyl(η⁵-cyclohexa-2,4-dienyl)(tetrahydrofuran)manganese (2) with 1-Methoxy-1-trimethylsilyl-1,2-propadiene (E): To a THF solution of $[Mn(\eta^5\text{-}C_6H_7)(CO)_2THF]$ (**2**), freshly prepared from 250 mg (1.15 mmol) of $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**), 0.3 mL (1.5 mmol) of 1-methoxy-1-trimethylsilyl-1,2-propadiene (**E**) was added at 208 K. After warming up to room temperature, the solvent was removed in vacuo and the residue was separated by HPLC with *n*-hexane as eluent.

1st Fraction: [Mn(η^5-C_6H_7)(CO)$_3$] (**1**).

2nd Fraction: Yellow solution, tricarbonyl{$\eta^{3:2}$-6-(1-methoxy-1-trimethylsilylmethylene)bicyclo[3.2.1]oct-3-en-2-yl}manganese (**3E**). After removal of the solvent, 50 mg (12%) of **3E**, yellow oil. − IR (*n*-pentane): $\tilde{\nu}$ (CO) = 2006 (w), 1999 (s), 1924 (w), 1912 (vs) cm^{-1}. − ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ = 4.71 (ddd, J = 6.5, 4.9, 1.1 Hz, 1 H, 3-H), 4.39 (m, J = 6.6, 6.5, 2.7, 1.0 Hz, 1 H, 2-H), 4.01 (ddd, J = 7.2, 4.9, 2.7 Hz, 1 H, 4-H), 3.59 (s, 3 H, OCH_3), 3.28 (dddd, J = 7.2, 5.7, 1.3, 1.0 Hz, 1 H, 5-H), 2.31 (m, J = 6.6, 2.4, 2.3, 1.6 Hz, 1 H, 1-H), 1.73 (ddd, J = 12.1, 2.7, 1.3 Hz, 1 H, 7^{exo}-H), 1.35 (dddd, J = 12.1, 2.4, 1.1, 1.0 Hz, 1 H, 7^{endo}-H), 0.98 (ddd, J = 10.0, 2.7, 1.6 Hz, 1 H, 8^{syn}-H), 0.54 (m, J = 10.0, 5.7, 2.3, 1.0 Hz, 1 H, 8^{anti}-H), 0.43 [s, 9 H, Si(CH_3)$_3$]. − ^{13}C NMR (50 MHz, C_6D_6, 298 K): δ = 229.1 (s, *C*O), 225.2 (s, *C*O), 223.2 (s, *C*O), 128.3 (s, 6-C), 97.0 (d, J = 163 Hz, 3-C), 79.2 (s, 1′-C), 73.3 (d, J = 161 Hz, 2-C), 57.8 (q, J = 144 Hz, O*C*H$_3$), 56.7 (d, J = 168 Hz, 4-C), 47.2 (t, J = 136 Hz, 7-C), 37.6 (t, J = 131 Hz, 8-C), 37.46 (d, J = 140 Hz, 1-C or 5-C), 37.3 (d, J = 140 Hz, 1-C or 5-C), 1.6 [q, J = 120 Hz, 3 C, Si(*C*H$_3$)$_3$]. − $C_{16}H_{21}MnO_4Si$ (360.37): calcd. C 53.33, H 5.87; found C 53.93, H 6.04.

3rd Fraction: Yellow solution, tricarbonyl{2,3,6,7,1″-η-4-(3-methoxy-3-trimethylsilyl-2-propenyl)-7-(1-methoxy-1-trimethylsilylmethylene)bicyclo[3.2.1]oct-2-en-6-yl}manganese (**5E**). After crystallization from *n*-pentane at 243 K 75 mg (13%) of **5E**, yellow crystals. − IR (*n*-pentane): $\tilde{\nu}$ (CO) = 2000 (s), 1920 (vs, br.) cm^{-1}. − ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ = 5.15 (dd, J = 9.6, 5.4 Hz, 1 H, 2′-H), 4.01 (ddd, J = 7.8, 2.2, 1.6 Hz, 1 H, 3-H), 3.80 (s, 3 H, OCH_3), 3.52 (ddd, J = 5.5, 4.6, 2.2 Hz, 1 H, 1-H), 3.35 (s, 3 H, OCH_3), 3.09 (ddd, J = 14.3, 9.8, 9.6 Hz, 1 H, 1′^{A}-H), 2.81 (ddd, J = 14.3, 5.4, 3.5 Hz, 1 H, 1′^{B}-H), 2.75 (dd, J = 7.8, 5.5 Hz, 1 H, 2-H), 2.65 (m, J = 9.8, 3.5, 1.6, 1.4 Hz, 1 H, 4-H), 2.56 (d, J = 5.1 Hz, 1 H, 6-H), 2.21 (dd, J = 6.0, 5.1 Hz, 1 H, 5-H), 1.73 (m, J = 11.1, 6.0, 4.6, 1.4 Hz, 1 H, 8^{anti}-H), 1.34 (d, J = 11.1 Hz, 1 H, 8^{syn}-H), 0.47 [s, 9 H, Si(CH_3)$_3$], 0.28 [s, 9 H, Si(CH_3)$_3$]. − MS (70 eV); *m/z* (%): 501.6 (4.12) [M$^+$], 417.7 (100) [M$^+$ − 3 CO], 385.7 (69.23) [M$^+$ − 3 CO, − OCH$_3$], 355.7 (10.02) [M$^+$ − 3 CO, − 2 OCH$_3$], 281.8 (12.99) [M$^+$ − 3 CO, − 2 OCH$_3$, − Si(CH$_3$)$_3$]. − $C_{23}H_{35}MnO_5Si_2$ (502.64) calcd. C 54.96, H 7.02; found C 55.20, H 6.94.

7. X-ray-Structural Analysis of Dicarbonyl{2,3,6,7,3″,4″,1‴-η-7-(2,4-dimethyl-3-methylenepenta-2,4-diyl)-4-(3-methyl-2-butenyl)-bicyclo[3.2.1]octa-2,6-diene}manganese (6A):[36] $C_{23}H_{31}MnO_2$, M = 394.42 g × mol^{-1}, triclinic space group $P\bar{1}$, a = 804.8(2), b = 1201.5(4), c = 1222.1(3) pm, α = 61.01(2), β = 81.12(2), γ = 87.47(2)°, V = 1.0206(5) nm^3, Z = 2, ρ(calcd.) = 1.283 g × cm^{-3}. Crystal size 0.01 × 0.45 × 0.45 mm. Using a P4 diffractometer (Siemens), radiation Mo-K_α, graphite monochromator, wavelength λ = 71.073 pm, ω-scan type, 5259 reflections were collected in the θ range 4.16° to 26.50° at T = 293 K. After data reduction, 4157 unique reflections (R_{int} = 0.0123) were obtained. The structure was solved by direct methods using SHELXS-97[37] and refined by full-matrix least squares against F^2 with SHELXL-97.[38] 271 parameters were refined to R_1 [$I > 2\sigma(I)$] 0.0547, wR_2 [$I > 2\sigma(I)$] 0.0811.

Acknowledgments

Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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Received October 28, 1998
[I98373]