Photochemical reaction of the heterometallic complex $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_3\}(CO)_{10}$ with triphenylphosphine

V. A. Maksakov, I. V. Slovokhotova, and S. P. Babailov*

Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4489. E-mail: maksakov@che.nsk.su

Photolysis of the heterometallic complex $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_3\}(CO)_{10}$ together with PPh_3 results in replacement of the CO groups by PPh_3 both at the Mn atom and in the Os_3 metallocycle to afford the complexes $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_2PPh_3\}(CO)_{10}$, $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_3\}(CO)_9PPh_3$, and $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_2PPh_3\}(CO)_9PPh_3$ (two isomers). The reaction is also accompanied by the partial removal of the $Mn(CO)_3$ group followed by the protonation of the cyclopentadienyl group and formation of triosmium clusters $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4R)(CO)_{10}$ (R = H, Et).

Key words: heterometallic Os_3Mn complexes, photochemical reaction, replacement of CO ligands by PPh_3.

Previously[1] we have studied the structure of the phosphine-containing heterometallic complexes $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_3\}(CO)_9PPh_3$ and $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_3\}(CO)_8(PPh_3)_2$ (three isomers), which have been synthesized by the reaction of $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_3\}(CO)_{10}$ (**1**) with PPh_3 using Me_3NO as the oxidant for the carbonyl groups. The spectral characteristics and the data of X-ray structural analysis give evidence that PPh_3 in all the complexes is coordinated to the osmium atom and the $Mn(CO)_3$ fragment does not participate in the reaction. We have found further that neither Me_3NO nor NH_2OH, commonly used[2] as the oxidants for the CO groups, do not oxidize carbonyl groups in $CpMn(CO)_3$ and its derivatives. As is well known,[3,4] the replacement of the CO groups in cymantrene is performed by thermal or photochemical reactions. The photochemical reactions are commonly conducted at room temperature, and this has the advantage that the thermally unstable reaction products can be synthesized.

This work is aimed at the study of the photochemical reaction of complex **1** with PPh_3 and the separation of some chiral reaction products in optically active form.

Results and Discussion

Our attempt to replace the CO groups at the manganese atom by PPh_3 in the heterometallic complex **1** during prolonged heating of its benzene solution with PPh_3 resulted in the formation of the compound $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_3\}(CO)_9PPh_3$ in the yield of 12%. In this complex one of the osmium atoms is coordinated with phosphine. Both the initial and final complexes decompose significally during reaction. Therefore, the reaction was carried out with the UV irradiation of a solution of complex **1** and PPh_3. When a quartz flask was used, a mixture of inseparable products of the complex decomposition formed. The irradiation of the reaction mixture in a Jena glass flask that absorbs radiation with wavelengths of <370 nm results in an increase in the reaction time and a decrease in the yield of the decomposition products. An optimal irradiation time is 30 h. During this time and at the 1 : 1 reactant ratio, ~2/3 of the starting complex reacts and the optimal yield of the reaction products is achieved. Analysis of the separated complexes showed that the CO groups located at both the manganese atom and the osmium atoms are replaced by phosphine during the photochemical reaction (Scheme 1).

Complex **3** was synthesized[1] by the reaction of **1** with PPh_3 in the presence of Me_3NO and structurally characterized.

The ^1H NMR and IR spectra of complex **2** indicate the presence of the $Mn(CO)_2PPh_3$ moiety. In the IR spectrum of **2**, as in the case of replacement of one CO group by PPh_3 in cymantrene,[4] the absorption bands of CO are shifted to the low-frequency region: 2035, 1958 cm^{-1} in the starting complex **1** and 1954, 1894 cm^{-1} in **2**. The cluster parts of the metal-carbonyl region of the IR spectra of cluster **2** and the starting complex **1**[5] are virtually the same. The proton signals of the phenyl groups of triphenylphosphine appear in the ^1H NMR

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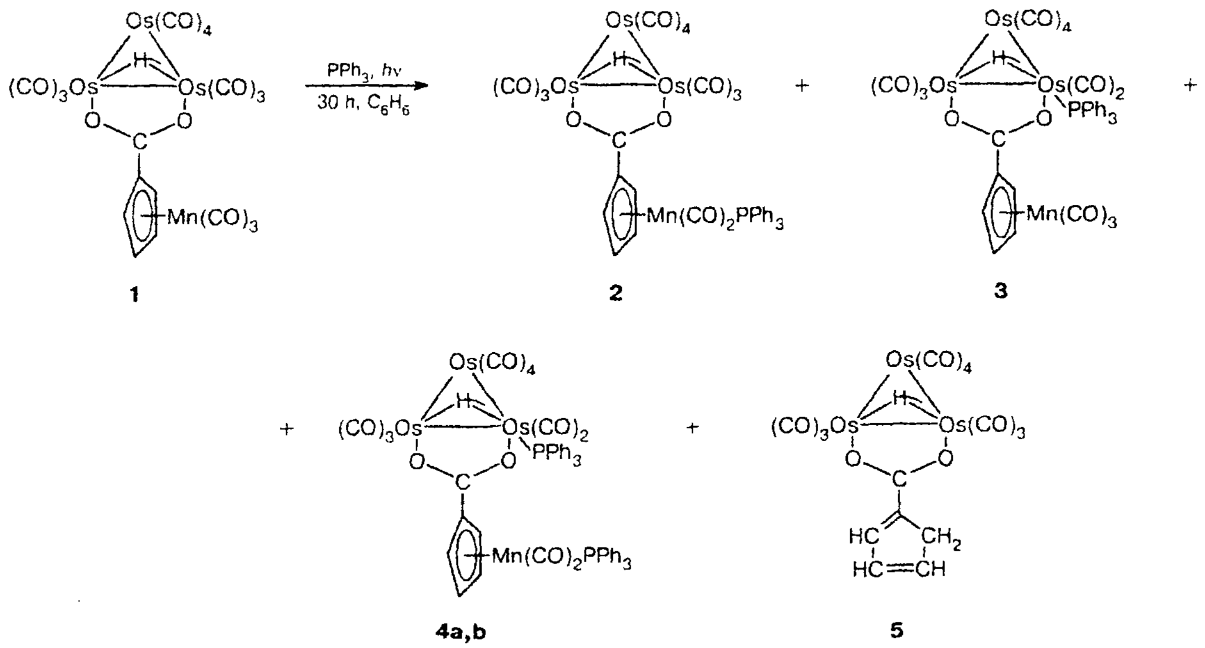
Scheme 1



spectrum of complex **2**. Two multiplet signals from the protons of the substituted Cp ring are somewhat shifted toward the strong field. Such a fact is usually attributed[6] to an increase in the electron density due to replacement of the CO groups by PPh_3. The chemical shift of the μ-H atom remains unchanged in fact. On the basis of the IR and ^1H NMR spectroscopic data one can conclude that the introduction of PPh_3 into the $Mn(CO)_3$ fragment does not distort the symmetry of the cluster group of the complex.

The isomeric complexes **4a** and **4b** differ somewhat in the R_f value upon separation on Silufol (R_f = 0.20 and 0.25 for **4a** and **4b**, respectively) and in color (**4b** has a less intense yellow color). Complex **4b** transforms into **4a** (slowly in the solid phase and much more rapidly in a solution). The mass spectra of **4a** and **4b** contain the same molecular ion with m/z = 1572 and correspond to a similar character of fragmentation: initially ten CO groups are removed (nine groups of the cluster fragment and one group coordinated to the manganese atom) and then the $Mn(CO)PPh_3$ fragment is eliminated. The IR spectra of the isomeric complexes **4a** and **4b** in the stretching vibrations region for the CO groups of the cluster fragment are typical[7] of the chiral clusters $(\mu\text{-}H)Os_3(\mu\text{-}O_2CR)(CO)_9L$. Additional absorption bands are present in this region (~1950, ~1890 cm^{-1}), which are characteristic[4,8] of the carbonyl groups of the $R{-}C_5H_4Mn(CO)_2PPh_3$ complexes. The signals from the phenyl protons are observed in the ^1H NMR spectra of both isomers, and the ratio of their integral intensities relative to the monosubstituted Cp rings (~8 : 1) indicates the presence of two PPh_3 ligands in each of the complexes **4a** and **4b**. The isomerism of complexes **4a** and **4b** manifests as the difference in the chemical shifts of the protons of the Cp rings and μ-H ligands. Each of the four protons of the substituted Cp ring in **4a** is observed in the spectrum as a distinct multiplet (δ 4.55, 4.44, 3.72 and 3.32). In the spectrum of **4b** and the starting complex **1**, the protons of the Cp ring manifest as two signals (δ 4.79 and 3.68). The signal of μ-H in the spectrum of **4a** (δ −9.27) is shifted relative to the similar signal in the spectrum of **1** by ~1 ppm to the weak field and has the J_{P-H} = 10 Hz. The signal of μ-H in the spectrum of **4b** (δ −12.63) is shifted by ~2 ppm to the strong field, and J_{P-H} = 15 Hz. The ^1H NMR spectrum of **4a** resembles in the chemical shifts and signal character the spectrum of complex **3**[1] in which the PPh_3 ligand occupies an equatorial position near one Os atom bound by the bridging ligand. This arrangement of PPh_3 results in its spatial interaction with the bulk fragment $[CpMn(CO)_2PPh_3]$ and inclination relative to the plane passing through the $[Os(CO)_4]$ group and the μ-H atom, which manifests in the non-equivalency of the signals from the Cp ring protons. The PPh_3 ligand in complex **4b** likely occupies a pseudo-equatorial position in the Os_3 metallocycle and is directed far from the $[CpMn(CO)_2PPh_3]$ fragment. This results in the shift of the signal of μ-H to the strong field and considerable increase in the J_{P-H} value.[9]

Thus, the principal difference between the **4a** and **4b** isomers consists in the spatial arrangement of the PPh_3 ligand relative to the Os_3 metallocycle.

Our attempt to synthesize the isomeric complexes **4a** and **4b** through the introduction of the second phosphine ligand into cluster **2** with the use of Me_3NO

resulted in the formation of only one isomer **4a**. This finding agrees with the fact[1,9] that in the triosmium clusters of the $(\mu\text{-H})Os_3(\mu\text{-X})(CO)_9PPh_3$ type prepared with the use of Me_3NO, phosphine is initially coordinated only in the equatorial position of one of the "bridging" osmium atoms.

Noteworthy, during photolysis of complex **1**, the elimination of the $Mn(CO)_3$ group and formation of the new compound $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_5)(CO)_{10}$ (**5**) occur along with replacement of various CO groups by phosphine. The scission of the Mn—Cp bond may occur through both homolytic and heterolytic pathways. Radical species capable of dimerization should arise during homolytic scission. When the reaction occurs according to Scheme 1, the formation of $Mn_2(CO)_{10}$ is probable because CO is accumulated in the solution due to the partial decomposition of the starting carbonyl complex. However, new compounds of this type were not found upon the separation of the reaction mixture. Therefore, the decay of complex **1** along the heterogeneous cleavage Mn—Cp bond seems to be more preferable. The $[C_5H_4]$ carbocycle acquires a negative charge, which is compensated by the addition of a proton from the reaction medium. An equilibrium mixture of three isomeric complexes whose ratio is determined by the nature of the substituents in the cyclopentadiene ring usually forms.[10,11] The ^1H NMR spectrum (Fig. 1, *a*) of the main separated complex **5** can be rationalized only on the assumption that the $-COO^-$ group is located in position 1 of the cyclopentadiene ring. The olefinic H atom arranged near the carboxylic group manifests in the weakest field whereas two other H atoms at the douple C=C bond have a lesser chemical shift. The signals from the H atoms of the CH_2 group manifest in the strong field typical of saturated hydrocarbons. The signal from μ-H in the ^1H NMR spectrum of compound **5** (δ −10.35) is typical of the bridging hydrogen atoms in the $(\mu\text{-H})Os_3(\mu\text{-}O_2CR)(CO)_{10}$ clusters.[7] The absorption bands of the stretching vibrations of the carbonyl groups in the $[Mn(CO)_3]$ fragment are absent from the IR spectrum of complex **5**, and the region of the stretching vibration of the carbonyl groups of the $[Os_3(CO)_{10}]$ fragment completely corresponds to the structure of compound **5**. The mass spectrum of **5** contains a peak from the molecular ion with m/z = 966 and the peaks corresponding to the loss of ten CO groups of the cluster.

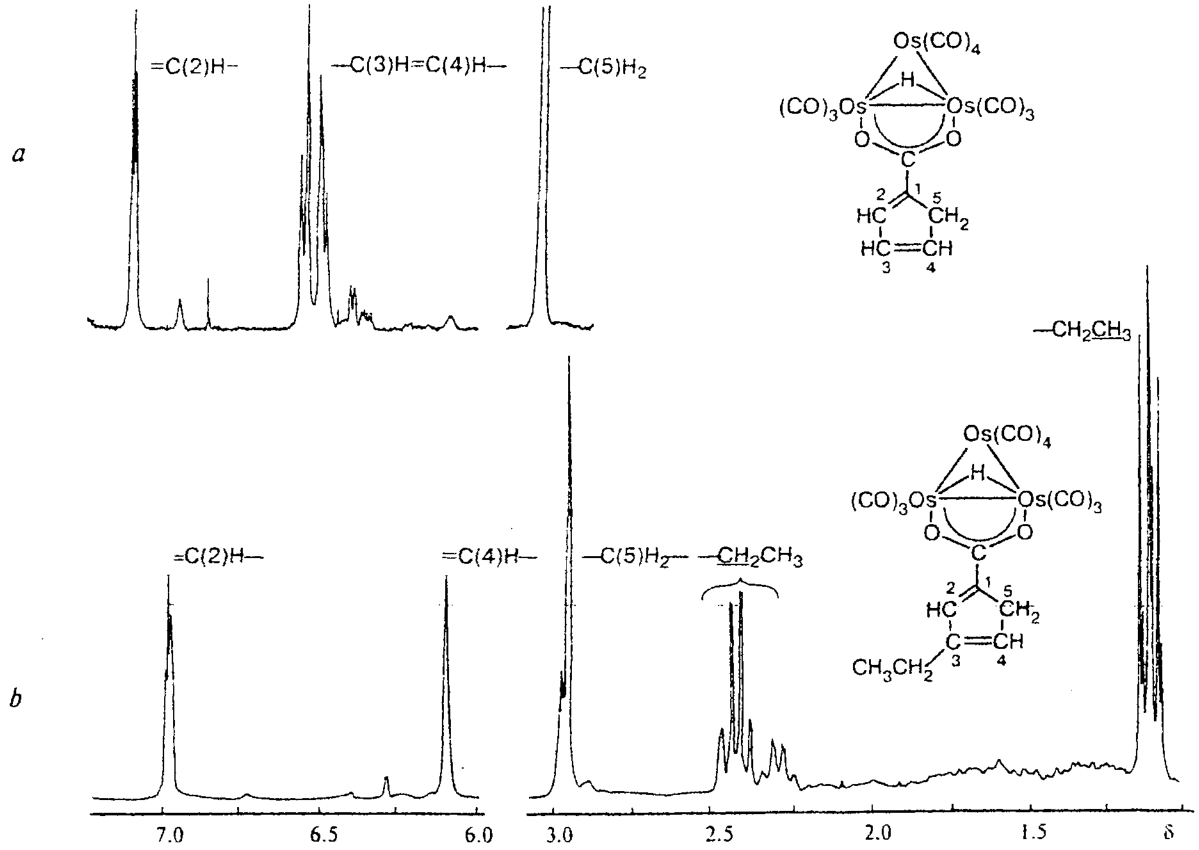


Fig. 1. Low-field region of the ^1H NMR spectra (250 MHz, $CDCl_3$, δ) of complex **5** (*a*) and a mixture of isomers of $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4\text{-3-Et})(CO)_{10}$ (*b*) (structural formula concerns the main isomer).

A small amount of the compound was also separated chromatographically. Its ^{1}H NMR spectrum can be treated as that of complex 5, in which the carboxyl group is in position 2 of the Cp ligand. However, we failed to characterize this product completely because of its small amount.

Elimination of the $Mn(CO)_3$ group during UV irradiation is likely typical of all complexes of the **1** type. The $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_3\text{-3-EtMn(CO)}_3\}(CO)_{10}$ complex looses the $Mn(CO)_3$ group due to the photochemical reaction leading to the formation of two new isomeric complexes $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4\text{-3-Et})(CO)_{10}$ (ratio ~3 : 1). The IR spectra in the region of stretching vibrations of the CO groups and the mass spectra of the isomeric complexes are identical. The differences are mainly observed in the chemical shifts of protons of the ethyl groups of 1,3-disubstituted cyclopentadienic ligands (Fig. 1, *b*). The formation of the isomers can be explained by the addition of a proton into positions 2 and 5 after the loss of the $[Mn(CO)_3]$ group of the complex.

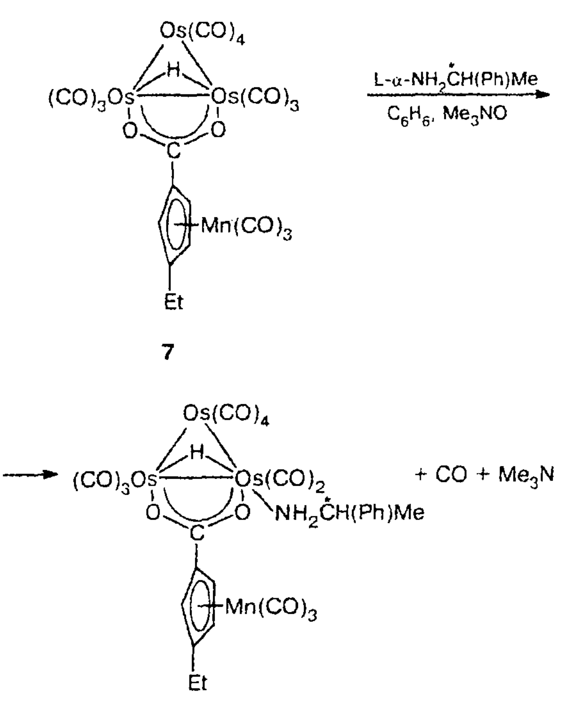
Complexes **3** and **4** are chiral, and we were able to separate them in the optically active form as enantiomers through, *e.g.*, diastereoisomeric complexes, by the introduction of an optically active ligand instead of PPh_3 coordinated in the Os_3 metallocycle. However, we failed to divide the diastereoisomers obtained by the reaction of complex **1** with L-α-$NH_2C^*H(Ph)Me$. For this reason, the ethyl group was previously introduced into the Cp ring of complex **1** in order to divide diastereoisomeric complexes **6** obtained according to Scheme 2.

If we succeeded in dividing the diastereoisomers **6a** and **6b**, we could easily obtain enantioisomeric complexes **7** by a simple replacement of the L-α-$NH_2C^*H(Ph)Me$ fragment in each complex by the CO group.

The presence of two doublet signals from the μ-H ligands in a strong field of the ^{1}H NMR spectrum (δ −9.91, J_{H-H} = 3.5 Hz and δ −10.05, J_{H-H} = 5.5 Hz) indicates the formation of two diastereomeric complexes **6**. A weak splitting of the signals from μ-H in the diastereoisomers occurs on one of the diastereotopic H atoms in the NH_2 groups. All the other signals (except for the clear triplet from the $\underline{CH_3}CH_2$ group) are either broadened or seen as complex multiplets because of the superposition of the signals from protons, which are somewhat different in their chemical shifts in the two diastereoisomeric complexes. Unfortunately, the introduction of the ethyl group into the Cp ring of complex **1**, did not result in better division of diastereoisomers and did not allow the Os_3Mn complexes to be obtained in the optically active form. Replacement of L-α-phenylethylamine in **6** by ethyl ester of L-α-alanine also did not give a desirable result.

Thus, both the $[Mn(CO)_3]$ and $[Os_3(CO)_{10}]$ fragments are reactive in the photochemical reaction of complex **1** with PPh_3 unlike the similar thermal reaction and the process using of Me_3NO.[1] The elimination of the $Mn(CO)_3$ fragment in complexes **1** or **7** followed by the addition of a proton to the negatively charged Cp ring occurs simultaneously with replacement.

Scheme 2



6a,b

Experimental

All reactions were carried out in as-distilled solvents in an argon atmosphere. A TLC on Silufol UV-254® plates was used to analyze the reaction mixtures and separate the reaction products. Photochemical reactions were performed in a Jena glass flask by irradiating the reaction solutions with a DRT-240 lamp at a ~25 cm distance.

The IR spectra were recorded on a Specord IR-75 spectrometer in cyclohexane and ^{1}H NMR spectra on Tesla BS-576 and Bruker DPX-250 instruments with Me_4Si as the internal standard. The mass spectra (EI, 70 eV) were recorded on an MX-1310 spectrometer. The molelular masses of the Os-containing compounds and their fragments were calculated for ^{192}Os isotope. Yields of the products are presented based on the reacted starting complexes.

Ethylcymantrene[3] and $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_3\}(CO)_{10}$ (**1**)[5] complex were synthesized according to known procedures.

1-Carboxy-3-ethylcyclopentadienyltricarbonylmanganese (1,3-ethyl(carboxy)cymantrene). A 0.6 *M* solution (28 mL) of *n*-butyllithium in *n*-hexane was added dropwise over 35 min to a solution of 3.1 g (1.3 · 10^{-2} mol) of ethylcymantrene in 80 mL THF with stirring and cooling to −40°C. Then the reaction mixture was stirred for 20 min without cooling and poured on dry ice. In 2 h the solvent was removed in a vacuum, 160 mL of water was added to the precipitate, and the solution obtained was passed through a column with silica gel and acidified with concentrated HCl. The precipitate formed was filtered off and washed with water. After recrystallization from *n*-hexane, 1.75 g (48%) of light yellow product with m.p. 106—108 °C (from hexane) was obtained. ^{1}H NMR (100 MHz, acetone-d_6, δ): 1.18 (t, 3 H, CH_3); 2.38 (q, 2 H, CH_2); 5.03 (s, 1 H, CH, Cp); 5.45 (m, 2 H, 2 CH, Cp). The melting point and parameters of the ^{1}H NMR spectrum are similar to those for 1,3-ethyl(carboxy)cymantrene prepared according to another procedure.[12]

Photochemical reaction of the complex of $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_3\}(CO)_{10}$ with PPh_3. A solution of a mixture of cluster **1** (180 mg, $1.64 \cdot 10^{-4}$ mol) and PPh_3 (43 mg, $1.64 \cdot 10^{-4}$ mol) in benzene (16 mL) was irradiated with UV light for 30 h. The solvent was evaporated in a vacuum, and the solid residue was separated on Silufol, the eluent hexane—benzene (3 : 1). Five fractions were separated. The first fraction (8 mg, 8%) is a yellow crystalline substance, 1,1,1,1,2,2,2,3,3,3-decacarbonyl-1,2-μ-hydrido-1,2-μ,η^2-(*O*,*O*′)-(1-carboxycyclopentadien)triangulotriosmium (**5**). IR, ν/cm^{-1}: 2114 w, 2076 s, 2063 s, 2028 s, 2016 s, 1989 s, 1983 m (CO); 1540 w ($-CO_2$). ^{1}H NMR (250 MHz, $CDCl_3$, δ): 7.07 (m, 1 H, H(2)); 6.52 (m, 1 H, H(3)); 6.49 (m, 1 H, H(4)); 3.03 (m, 2 H, H(5)); −10.34 (s, 1 H, μ-H). MS, *m/z*: 966 $[M]^+$, 938, 910, 882, 854, 826, 798, 770, 742, 714, 686 [M − *n* CO] (*n* = 1—10; I_{rel} = 30—100%). The second fraction (32 mg, 18%) is unreacted starting cluster **1**.

The third fraction was additionally separated on Silufol, the eluent hexane—ether (1 : 1). Two compounds were obtained. The first (28 mg, 17%) is a yellow crystalline substance 1,1,1,1,2,2,2,3,3,3-decacarbonyl-1,2-μ-hydrido-1,2-μ,η^2-(*O*,*O*′)-(carboxycyclopentadienyltriphenylphosphinedicarbonylmanganese)triangulotriosmium (**2**). IR, ν/cm^{-1}: 2111 w, 2075 s, 2063 s, 2024 s, 2016 s, 2010 sh, 1987 w, 1981 w, 1951 m, 1894 m, 1889 sh (CO); 1545 w ($-CO_2$). ^{1}H NMR (100 MHz, $CDCl_3$, δ): 7.3 (m, 15 H, PPh_3); 4.85 (m, 2 H, Cp); 3.77 (m, 2 H, Cp); −10.25 (s, 1 H, μ-H). Found (%): C, 32.36; H, 1.52; Os, 43.20. $C_{36}H_{20}O_{14}Os_3P$. Calculated (%): C, 32.44; H, 1.50; Os, 42.81. The mass spectrum contains a molecular ion $[M]^+$ with *m/z* = 1338 (I_{rel} = 18%) and peaks of various intensities (from 16 to 100%) corresponding to the loss of 11 CO groups. All the physicochemical characteristics of the second compound (12 mg, 14%) obtained upon additional chromatographic separation of the third fraction correspond completely to the respective data for complex **3** synthesized and characterized by us earlier.[1]

The fourth fraction (10 mg, 5%) is a yellow crystalline substance, 1,1,1,1,2,2,3,3,3-nonacarbonyl-2-triphenylphosphine-1,2-μ-hydrido-1,2-μ,η^2-(*O*,*O*′)-(carboxycyclopentadienyltriphenylphosphinedicarbonylmanganese)triangulotriosmium (**4a**). IR, ν/cm^{-1}: 2095 m, 2056 s, 2039 w, 2019 vw, 2012 sh, 2002 s, 1997 sh, 1980 sh, 1972 m, 1950 m, 1948 sh, 1929 w, 1889 m (CO); 1545 w ($-CO_2$). ^{1}H NMR (100 MHz, CCl_4, cyclohexane-d_{12}, δ, *J*/Hz): 7.54—7.20 (m, 30 H, 2 PPh_3); 4.55 (m, 1 H, Cp); 4.44 (m, 1 H, Cp); 3.72 (m, 1 H, Cp); 3.32 (m, 1 H, Cp); −9.27 (d, μ-H, J_{P-H} = 10 Hz). Found (%): C, 40.97; H, 2.44; Os, 35.90. $C_{53}H_{35}MnO_{13}Os_3P_2$. Calculated (%): C, 40.60; H, 2.23; Os, 36.42. The mass-spectrum contains a peak from a molecular ion $[M]^+$ with *m/z* = 1572 (I_{rel} = 18%).

The fifth fraction (10 mg, 5%) is a light yellow unstable crystalline substance, $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_2PPh_3\}(CO)_9PPh_3$ (**4b**). IR, ν/cm^{-1}: 2092 m 2066 s, 2039 vs, 2009 vs, 2000 sh, 1976 m, 1968 sh, 1955 m, 1988 m (CO); 1546 w ($-CO_2$). ^{1}H NMR (CCl_4, cyclohexane-d_{12}, δ): 7.48—7.26 (m, 30 H, 2 PPh_3); 4.79 (m, 2 H, Cp); 3.68 (m, 2 H, Cp); −12.63 (d, μ-H, J_{P-H} = 15 Hz). The mass spectrum contains a peak from a molecular ion $[M]^+$ with *m/z* = 1572 (I_{rel} ≈ 12%).

$(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_5)(CO)_{10}$ (5). A solution of cluster **1** (42 mg, $3.65 \cdot 10^{-5}$ mol) in benzene (12 mL) was irradiated with UV light for 9 h. The solution was filtered and evaporated in a vacuum, and a precipitate was separated on Silufol, the eluent hexane—benzene (4 : 1). A yellow crystalline substance (27 mg, 64%) was obtained. All the physicochemical characteristics of the compound synthesized are similar to the corresponding data for complex **5** obtained earlier according to Scheme 1.

Reaction of $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_2PPh_3\}(CO)_{10}$ (2) with PPh_3 together with Me_3NO. To a solution of a mixture of complex **2** (56 mg, $5.2 \cdot 10^{-5}$ mol) and PPh_3 (68 mg, $3.6 \cdot 10^{-4}$ mol) in benzene (30 mL) a solution of $Me_3NO \cdot 2H_2O$ (6 mg, $7.0 \cdot 10^{-5}$ mol) in MeOH (3 mL) was added dropwise with stirring over 1 h. Then the solution was passed through a column with silica gel (Silikagel 100/160 μ) and the precipitate was separated on Silufol, the eluent hexane—benzene (2 : 1). A yellow crystalline substance (42 mg, 65%) was obtained. The ^{1}H NMR and IR spectra of the compound separated are identical in fact to the corresponding spectra of complex $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_4Mn(CO)_2PPh_3\}(CO)_9PPh_3$ (**4a**).

1,1,1,1,2,2,2,3,3,3-Decacarbonyl-1,2-μ-hydrido-1,2-μ,η^2-(*O*,*O*′)-(1-carboxy-3-ethylcyclopentadienyltricarbonylmanganese)triangulotriosmium (7b). To a suspension of $Os_3(CO)_{11}NCMe$ (150 mg, $1.6 \cdot 10^{-4}$ mol) in acetonitrile (70 mL) with stirring, a solution of $Me_3NO \cdot 2H_2O$ (59 mg, $5.3 \cdot 10^{-4}$ mol) in MeOH (6 mL) was added dropwise over 1 h. The reaction mixture was kept for 1 h, passed through a column with silica gel (Silikagel 100/160 μ), washed off by benzene, and evaporated in a vacuum. The precipitate was dissolved in 25 mL of THF, and 1,3-ethyl(carboxy)cymantrene (123 mg, $4.3 \cdot 10^{-4}$ mol) was added and refluxed for 1 h. The reaction mixture was evaporated in a vacuum and separated on a column with silica gel (Silikagel 40/100 μ), collecting the fraction of bright yellow color (R_f ~0.55). A yellow crystalline complex $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_3\text{-3-}EtMn(CO)_3\}(CO)_{10}$ (**7**) (120 mg, 68%) was obtained. IR, ν/cm^{-1}: 2113 w, 2077 vw, 2066 s, 2028 vs, 2016 s, 2011 sh, 1983 m, 1954 sh, 1949 s (CO); 1549 w ($-CO_2$). ^{1}H NMR (250 MHz, $CDCl_3$, δ, *J*/Hz): 5.10 (m, 2 H, H(2), H(5), Cp); 4.58 (m, 1 H, H(4), Cp); 2.25 (q, 2 H, $\underline{CH_2}CH_3$, *J* = 7); 1.12 (t, 3 H, $CH_2\underline{CH_3}$, *J* = 7); −10.32 (s, μ-H). The mass spectrum contains a peak from a molecular ion $[M]^+$ with *m/z* = 1132 (I_{rel} = 55%) and the peaks of the relative intensity from 35 to 100% corresponding to the loss of 11 CO groups.

Photochemical decomposition of complex 7. A solution of complex **7** (55 mg, $4.9 \cdot 10^{-5}$ mol) in benzene was irradiated by UV light for 10 h. The reaction mixture was filtered, a solution was evaporated in a vacuum, and the residue was separated on Silufol 2DC-Alufolien, Kieselgel 60 F_{254}, the eluent hexane—benzene (2 : 1). After threefold elution, two fractions were separated which significantly superimpose (R_f ~0.75). Isomeric complexes $(\mu\text{-H})Os_3(\mu\text{-}O_2CC_5H_4\text{-3-}Et)(CO)_{10}$ (21 mg, 43%) were obtained. IR of a mixture, ν(CO)/cm^{-1}: 2113 w, 2075 s, 2063 s, 2028 vs, 2015 s, 1988 sh, 1981 m. ^{1}H NMR of a mixture of isomers (250 MHz, $CDCl_3$, δ, *J*/Hz): 6.98 (m, 1 H, H(2), Cp); 6.09 (m, 1 H, H(4), Cp); 2.97—2.95 (m, 2 H, $C(5)H_2$, Cp); 2.43 (qd, 2 H, $\underline{CH_2}CH_3$, *J* = 7.5, *J* = 0.20); 2.29 (qm, 2 H, $\underline{CH_2}CH_3$, *J* = 7.5); 1.11 (t, 3 H, $\underline{CH_3}CH_2$, *J* = 7.5); 1.10 (t, 3 H, $\underline{CH_3}CH_2$, *J* = 7.5); −10.36 (s, 1 H, μ-H). Mass spectrum contains a peak from a molecular ion $[M]^+$ with *m/z* = 994 (I_{rel} = 45%) and the peaks of the relative intensity from 30 to 100% corresponding to the loss of 10 CO groups.

1,1,1,1,2,2,3,3,3-Nonacarbonyl-2-(α-1-phenyl-1-aminoethane)-1,2-μ-hydrido-1,2-μ,η^2-(*O,O′*)-(1-carboxy-3-ethylcyclopentadienyltricarbonylmanganese)triangulotriosmium (6a,b). To a solution of 120 mg ($1.03 \cdot 10^{-4}$ mol) of complex 7 and 100 mg ($8.2 \cdot 10^{-4}$ mol) of L-α-phenylethylamine in 25 mL of benzene 20 mg ($1.35 \cdot 10^{-4}$ mol) of $Me_3NO \cdot 2H_2O$ in 3 mL of absolute MeOH was added dropwise with stirring over 1.5 h. The reaction mixture was deposited on a column with silica gel (Silikagel 100/160 μ), washed with benzene, and evaporated in a vacuum, and the residue was separated on Silufol, the eluent hexane—benzene (3 : 1). A second fraction of yellow color with R_f ~0.25 was separated. A mixture of diastereoisomers $(\mu\text{-H})Os_3\{\mu\text{-}O_2CC_5H_3\text{-3-EtMn(CO)}_3\}(CO)_9NH_2C^*H(Ph)Me$ (**6a,b**) (66 mg, 51%) as a yellow oil-like substance slowly decomposing in air was obtained. IR of a mixture, ν/cm^{-1}: 2098 m, 2057 s, 2025 s, 2017 vs, 2010 s, 2002 s, 1992 sh, 1983 w, 1976 w, 1954 m (CO); 1544 w (—CO_2). ^{1}H NMR of a mixture (250 MHz, $CDCl_3$, δ, *J*/Hz): 7.45 (m, 5 H, Ph); 5.13 (m, 2 H, Cp); 4.53 (m, 1 H, Cp); 3.76 (m, 3 H, $\underline{NH_2}$—$\underline{CH}$); 2.21 (m, 2 H, $\underline{CH_2}CH_3$); 1.68 (m, 3 H, Ph—CH—$\underline{CH_3}$); 1.06 (m, 3 H, $\underline{CH_3}CH_2$); −9.91 (d, 1 H, μ-H, *J* = 3.5); −10.05 (d, 1 H, μ-H, *J* = 5.5).

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