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Synthesis and characterization of complexes η^5,η^5-$(CO)_3Mn(C_5H_4$-$C_5H_4)(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ and μ-$(C{\equiv}C)[C_5H_4(CO)_2Fe$-$\eta^1,\eta^5$-$C_5H_4Mn(CO)_3]_2$

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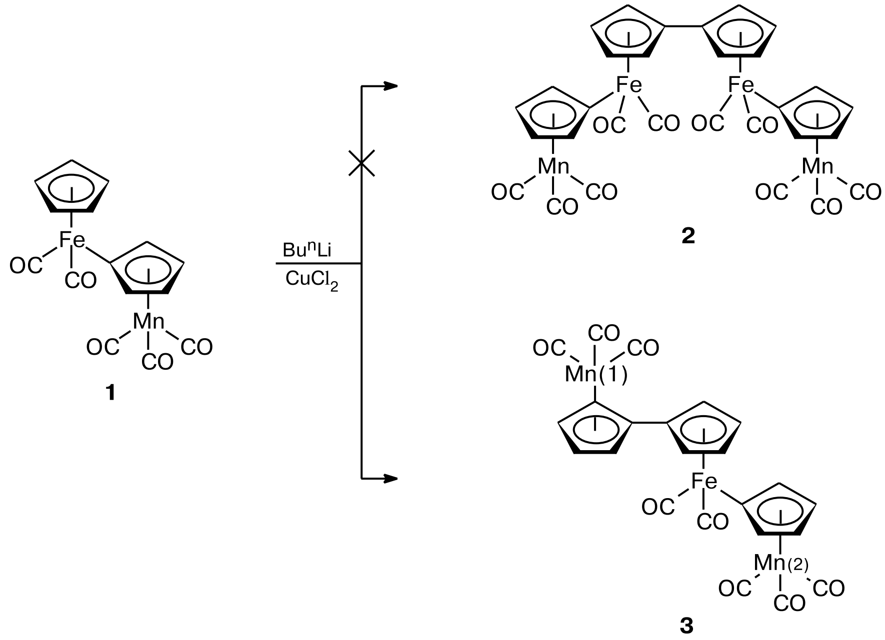
The complex η^5,η^5-$(CO)_3Mn(C_5H_4$-$C_5H_4)(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ was synthesized by the reaction of η^5-$Cp(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ with Bu^{n}Li (THF, −78 °C) and then with anhydrous $CuCl_2$. The complex μ-$(C{\equiv}C)[C_5H_4(CO)_2Fe$-$\eta^1,\eta^5$-$C_5H_4Mn(CO)_3]_2$ was prepared by the reaction of η^5-$IC_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ with $Me_3SnC{\equiv}CSnMe_3$ (2 : 1) in the presence of $Pd(MeCN)_2Cl_2$.

Key words: ladder complexes, iron and manganese cyclopentadienyl carbonyl complexes.

Previously,[1—5] using the ladder-type complex η^5-$Cp(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ (**1**) as a "building block," we have synthesized and characterized a series of new tri-, tetra-, penta-, and hexanuclear complexes containing Mo, W, Ti, Zr, and other elements in addition to the Fe and Mn atoms. In this work, we attempted to synthesize a symmetric complex η^5,η^5-$(C_5H_4$-$C_5H_4)[(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3]_2$ (**2**) by the oxidative coupling reaction between η^5-$LiC_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ and anhydrous $CuCl_2$. It is known[6] that dicymantrenyl was synthesized by this method from a lithium cymantrene derivative. However, we isolated trinuclear complex **3** instead of the expected complex **2** (Scheme 1).

It can be assumed that a radical $^{\bullet}C_5H_4(CO)_2FeC_5H_4Mn(CO)_3$ formed in this reaction favors the homolysis of the σ-Fe—C_5H_4 bond to form a radical $^{\bullet}C_5H_4Mn(CO)_3$. The subsequent recombination

Scheme 1



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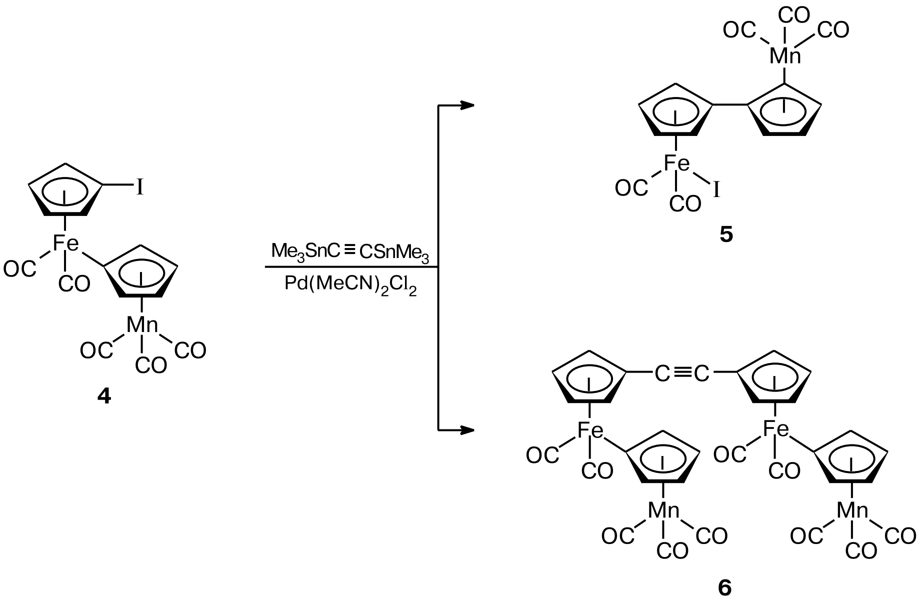
Scheme 2



of these radicals affords complex **3** as a yellow substance soluble in organic solvents (ether, benzene, chloroform, and others). Its structure was established by ^{1}H NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis.

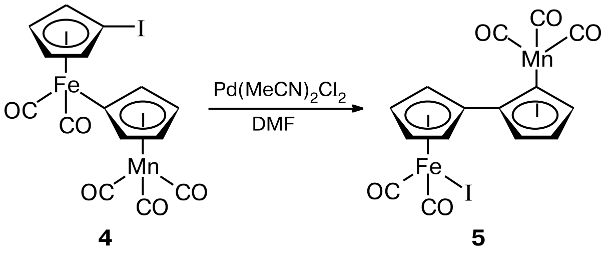
Earlier,[7] when performing cross-coupling of η^5-IC$_5$H$_4$(CO)$_2$Fe-η^1,η^5-C$_5$H$_4$Mn(CO)$_3$ (**4**) with Me$_3$SiC≡CSiMe$_3$ in the presence of Pd(MeCN)$_2$Cl$_2$, we isolated only complex **5** (product of rearrangement of the starting compound **4**) instead of the expected symmetric tetranuclear complex μ-(C≡C)[C$_5$H$_4$(CO)$_2$Fe-η^1,η^5-C$_5$H$_4$-Mn(CO)$_3$]$_2$ (**6**) (Scheme 2). Complex **6**, along with complex **5**, was synthesized by the same reaction replacing Me$_3$SiC≡CSiMe$_3$ by its Sn-containing analog Me$_3$SnC≡CSnMe$_3$ (Scheme 2).

Complex **6** is a yellow substance well soluble in organic solvents (ether, benzene, methylene chloride) and poorly soluble in hexane. Its structure was established by ^{1}H NMR spectroscopy, IR spectroscopy, and elemental analysis.

Complex **4** isomerizes to a regio-exchange product (**5**) in the presence of the Pd(MeCN)$_2$Cl$_2$ catalyst when the second reagent Me$_3$SiC≡CSiMe$_3$ or Me$_3$SnC≡CSnMe$_3$ (Scheme 3) is absent.

The IR spectra of the previously studied ladder complexes met the rigid local symmetry approximation. Hence, the spectra contain two bands (A′ + A″) for the Fe(CO)$_2$ group of local symmetry C_s and two bands (A$_1$ + E) for the Mn(CO)$_3$ group of symmetry 3_v. In the case of complex **3**, the bands can be assigned approximately on the basis of intensities and band shapes. The earlier established[8] regularities of a mutual electronic influence of the metal carbonyl moieties, resulting in shifts of the ν(CO) band relatively to its position in related mononuclear complexes depending on the donor or acceptor properties of adjacent metal carbonyl groups, should also be taken into account when assigning the bands.

Scheme 3



The IR spectrum of a solution of complex **3** exhibits six ν(CO) bands in the region of stretching vibrations of the CO groups (Table 1). Since the CpFe(CO)$_2$ moiety is bound with two electron-withdrawing substituents

Table 1. Frequencies (ν(CO)/cm^{-1}) and their assignment in the IR spectra of complexes **1**, **3**, **6**, and **7** in CH$_2$Cl$_2$

Complex	Fe(CO)$_2$	Mn(CO)$_3$
1	2032, 1978	2003, 1916
3	2043, 1993	2006, 1921, 2032, 1950
6	2029, 1976	2003, 1918
7	—	2025, 1940

$C_5H_4Mn(CO)_3$, the ν(CO) frequencies for the $Fe(CO)_2$ group should be higher than the corresponding frequencies for complex **1** containing only one $C_5H_4Mn(CO)_3$ group. Therefore, the bands at 2043 and 1993 cm^{-1} can be assigned to antisymmetric and symmetric vibrations of the $Fe(CO)_2$ group, respectively. It seems more difficult to assign other ν(CO) bands to vibrations of particular $Mn(CO)_3$ moieties. The $Mn(CO)_3$ groups are nonequivalent. One moiety, namely, $C_5H_4Mn(CO)_3$, is bound through a σ-bond to the Fe atom of the electron-releasing moiety $Cp(CO)_2Fe$, and another moiety is bound through the σ-bond with the Cp ring of the $C_5H_4(CO)_2Fe—C_5H_4Mn(CO)_3$ moiety, which is a weak acceptor with respect to the Cp ring. Therefore, it can be assumed that the bands at 2006 and 1921 cm^{-1} are attributed to the ν(CO) vibrations of a moiety bound with the Fe atom and close to the corresponding frequency of complex **1**, whereas the bands at 2032 and 1950 cm^{-1} can be assigned to ν(CO) of the $Mn(CO)_3$ group bound with the Cp ligand. These bands should be compared with ν(CO) in $CpMn(CO)_3$ (**7**): their frequencies increase (by 7—10 cm^{-1}) under the influence of the withdrawing substituent in the Cp ring.

The IR spectrum of a solution of complex **6** in CH_2Cl_2 contains four bands of stretching vibrations ν(CO): the bands at 2029 and 1976 cm^{-1} are assigned to antisymmetric and symmetric stretching vibrations of the CO groups at the Fe atom, and the bands at 2003 and 1918 cm^{-1} are attributed to symmetric and degenerate stretching vibrations of the CO groups coordinated to the Mn atom. The ν(CO) frequencies in tetranuclear complex **6** and in dinuclear complex **1** virtually coincide (see Table 1), *i.e.*, the mutual electronic influence of the metal carbonyl moieties is not transmitted through the a bridging ligand $C_5H_4C{\equiv}CC_5H_4$.

The published data[9] show that for the similar in structure dinuclear complex μ-(C≡C)$[C_5H_4(CO)_2FeMe]_2$ the frequencies of stretching vibrations of the CO groups at the Fe atom (ν(CO) = 2013 and 1960 cm^{-1}) are close to ν(CO) of the Fe atom in the mononuclear complex $Cp(CO)_2FeMe$ (ν(CO) = 2010 and 1955 cm^{-1} in CCl_4).[10]

Experimental

All reactions were carried out under dry argon.

IR spectra were recorded in CH_2Cl_2 on a Nicolet Magna IR 750 FTIR spectrometer with a resolution of 2 cm^{-1}. ^1H NMR spectra (C_6D_6) were obtained on a Bruker AMX-400 spectrometer (400.13 MHz).

Electron impact mass spectra were measured on a Kratos MS 890 instrument at an electron energy of 70 eV and a temperature in the ionization chamber of 200 °C.

X-ray fluorescence spectra were recorded on a VRA-30 spectrometer. Anhydrous $CuCl_2$ was prepared by heating dihydrate $CuCl_2 \cdot 2H_2O$ in an anhydrous hydrogen chloride flow at 140—150 °C; THF was distilled above sodium benzophenone ketyl in argon prior to use; DMF was distilled above CaH_2; CH_2Cl_2 was distilled above P_2O_5. Complexes $Cp(CO)_2FeC_5H_4Mn(CO)_3$ [11] and $IC_5H_4(CO)_2FeC_5H_4Mn(CO)_3$ [2] were synthesized according to known procedures.

Reaction of η^5-cyclopentadienyltricarbonyliron-η^1,η^5-cyclopentadienyltricarbonylmanganese, $Cp(CO)_2FeC_5H_4Mn(CO)_3$ (1), with Bu^{n}Li and anhydrous $CuCl_2$. An 0.8 *M* solution of Bu^{n}Li (6 mL, 4.6 mmol) in hexane was added at −78 °C to a solution of $Cp(CO)_2FeC_5H_4Mn(CO)_3$ (0.9 g, 2.3 mmol) in THF (50 mL). The mixture was stirred for 1.5 h at −78 °C, after which anhydrous $CuCl_2$ (0.6 g) was added. The mixture was stirred at −78 °C for 3 h, then the temperature was increased to ~20 °C, and CH_2Cl_2 was added. The resulting mixture was washed with water until a greenish color disappeared, and the CH_2Cl_2 layer was separated from water, dried above $MgSO_4$, and filtered. The solvent was removed, the residue was chromatographed on Al_2O_3 (II activity grade according to Brockmann), and η^5-cymantrenylcyclopentadienyldicarbonyliron-η^1,η^5-cyclopentadienyltricarbonylmanganese (**3**) was eluted with ethyl acetate. Complex **3** (0.1 g) was isolated in 10% yield based on the reacted complex **1**. Complex **3** was finally purified by TLC (Silufol, ethyl acetate—hexane, 1 : 2). Found (%): C, 47.08; H, 2.13. $C_{23}H_{12}FeMn_2O_8$. Calculated (%): C, 47.42; H, 2.06. As established by X-ray fluorescence spectrometry, the ratio of intensities of the K_α lines in the characteristic spectra of the iron and manganese corresponds to an atomic ratio of 1 : 2. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2043, 2032, 2006, 1993, 1950, 1921. ^1H NMR (C_6D_6), δ: 3.89 (t, 2 H, CpFe, *J* = 2.2 Hz); 4.05 (t, 2 H, CpFe, *J* = 2.2 Hz); 4.15 (t, 2 H, CpMn(2), *J* = 2.0 Hz); 4.32 (t, CpMn(2), 2 H, *J* = 2.0 Hz); 4.88, 4.97 (both t, 2 H each, CpMn(1), *J* = 2.2 Hz). MS, *m/z*: 526 [M – 2 CO]; 478 [M – 3 CO]; 470 [M – 4 CO]; 120 $[C_5H_4Fe]$; 148 $[C_5H_5MnCO]$.

Reaction of the complex η^5-iodocyclopentadienyldicarbonyliron-η^1,η^5-cyclopentadienyltricarbonylmanganese, $IC_5H_4(CO)_2FeC_5H_4Mn(CO)_3$ (4), with $Me_3SnC{\equiv}CSnMe_3$ in the presence of $Pd(MeCN)_2Cl_2$. $Pd(MeCN)_2Cl_2$ (0.0011 g, 0.04 mmol) was added to a solution of $IC_5H_4(CO)_2FeC_5H_4Mn(CO)_3$ (0.4 g, 1 mmol) and $Me_3SnC{\equiv}CsnMe_3$ (0.14 g, 0.4 mmol) in DMF (30 mL). The mixture was stirred for 24 h at ~20 °C. Then ether and a 50% solution of KF were added, and Ar was bubbled through the reaction mixture for 30 min. The solution was washed with water, and the ether layer was separated, dried above $MgSO_4$, and filtered. The solvent was removed, and the residue was chromatographed on silica gel (40 : 100) eluting η^5-cymantrenylcyclopentadienyldicarbonyliodoiron (**5**) with a benzene—hexane (1 : 1) mixture, whereas μ-acetylene-bis(cyclopentadienyldicarbonyliron-η^1,η^5-cyclopentadienyltricarbonylmanganese) (**6**) was eluted with benzene. The yield of complex **5** was 0.1 g (28% based on the reacted complex **4**). The yield of complex **6** was 0.015 g (3%). Found (%): C, 49.30; H, 2.26. $C_{32}H_{16}Fe_2Mn_2O_{10}$. Calculated (%): C, 49.10; H, 2.04. X-ray fluorescence spectrometry found that the ratio of intensities of the K_α lines in the characteristic spectra of iron and manganese corresponds to an atomic ratio of 1 : 1. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2029, 2003, 1976, 1918. ^1H NMR (C_6D_6), δ: 3.60, 3.92 (both t, 4 H each, CpFe, *J* = 2.2 Hz); 4.24, 4.34 (both t, 4 H each, CpMn, *J* = 2.2 Hz).

Reaction of the complex $IC_5H_4(CO)_2FeC_5H_4Mn(CO)_3$ (4) with $Pd(MeCN)_2Cl_2$. Complex $Pd(MeCN)_2Cl_2$ (0.002 g, 0.008 mmol) was added to $IC_5H_4(CO)_2FeC_5H_4Mn(CO)_3$ (**4**) (0.07 g, 0.1 mmol) in DMF (3 mL). The mixture was stirred for 24 h at ~20 °C, after which ether was added, and the mixture was washed with water, dried above $MgSO_4$, and filtered. The solvent was removed, and the residue was chromatographed on a Silufol plate eluting a product $I(CO)_2Fe(C_5H_4—C_5H_4)Mn(CO)_3$ (**5**) with a benzene—hexane (1 : 1) mixture. The resulting product was chromatographically identical to that synthesized previously.[7]

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