Iodine and cymantrenyl regioselective exchange in the η^5-$IC_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ complex under cross-coupling conditions

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The reaction of η^5-$IC_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ with $Me_3SiC{\equiv}CSiMe_3$ (2 : 1) in the presence of $Pd(MeCN)_2Cl_2$ afforded the $I(CO)_2Fe(C_5H_4—C_5H_4)Mn(CO)_3$ complex generated through migrations of the I atom from the Cp ring to the Fe atom and of the $C_5H_4Mn(CO)_3$ group from the Fe atom to the Cp ring.

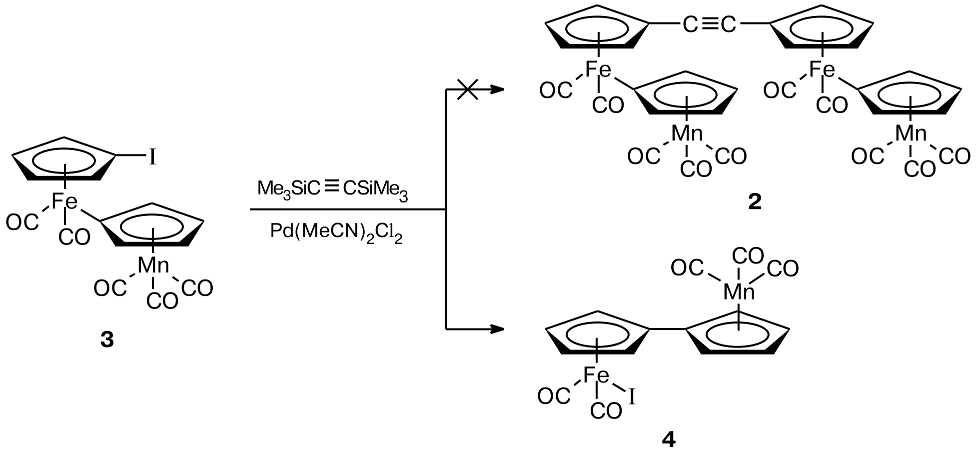
Key words: ladder complexes, rearrangement, iron and manganese cyclopentadienyl carbonyl complexes.

Earlier,[1] we have found that the binuclear η^5-$Cp(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ ladder complex (**1**) with the bridging η^1,η^5-cyclopentadienyl ligand was selectively metallated by *n*-butyllithium (THF, –78 °C) exclusively at the η^5-Cp ring. This made it possible to use this complex as a building block for the synthesis of tri-, tetra-, penta-, and hexanuclear systems containing the W, Mo, Ti, Zr, and other metal atoms in addition to the Fe and Mn atoms.[1—5]

The aim of the present study was to synthesize the tetranuclear μ-$(C{\equiv}C)[C_5H_4(CO)_2Fe$-$\eta^1,\eta^5$-$C_5H_4Mn(CO)_3]_2$ complex (**2**) by the cross-coupling reaction (Stille reaction) starting from 2 equiv. of η^5-$IC_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ (**3**) (which has been prepared earlier[2] by metallation of complex **1** with *n*-butyllithium followed by the reaction with C_3F_7I) and 1 equiv. of $Me_3SiC{\equiv}CSiMe_3$ in the presence of $Pd(MeCN)_2Cl_2$. However, the reaction afforded the η^5,η^5-$I(CO)_2Fe(C_5H_4—C_5H_4)Mn(CO)_3$ complex (**4**) instead of the expected compound **2** as a result of migrations of the I atom from the Cp ring to the Fe atom and of the $C_5H_4Mn(CO)_3$ group from the Fe atom to the Cp ring (Scheme 1).

Earlier,[6] the migration of the σ-cymantrenyl ligand from the Mo atom to the Cp ring has been observed upon thermal treatment of η^5-$Cp(CO)_3Mo$-η^1,η^5-

Scheme 1



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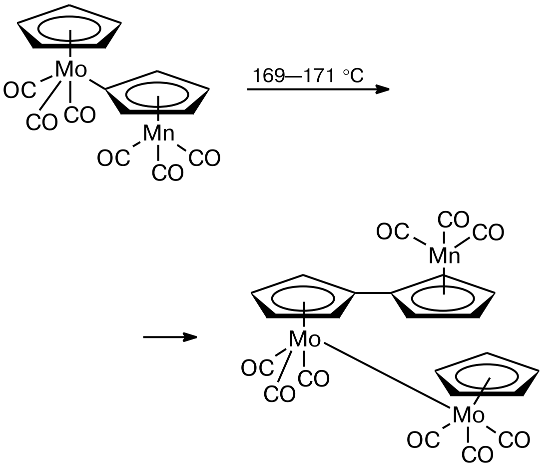
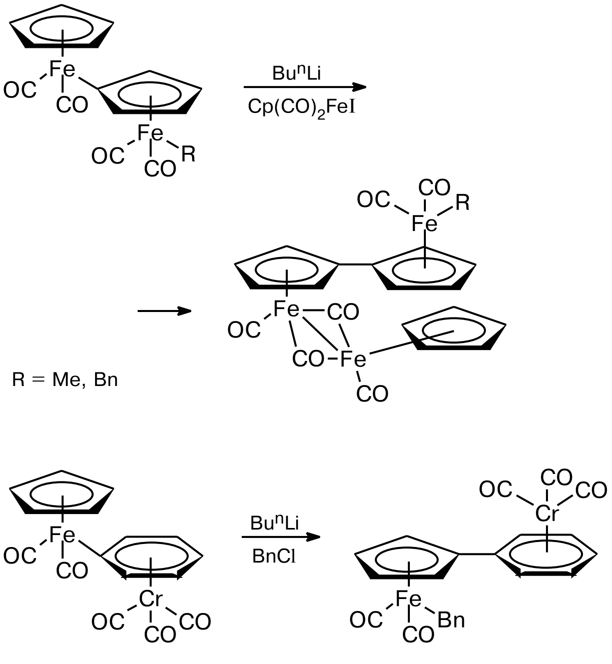
$C_5H_4Mn(CO)_3$ giving rise to the unsymmetrical η^5,η^5-$(CO)_3Mn(C_5H_4—C_5H_4)(CO)_3Mo—Mo(CO)_3\eta^5$-Cp dimer (Scheme 2).

Scheme 2



We have observed[1,7] the migration of the σ-$C_5H_4(CO)_2FeR$ (R = Me, Bn) and σ-$PhCr(CO)_3$ ligands from the Fe atom to the Cp ring on metallation of the η^5-$Cp(CO)_2Fe$-η^1,η^5-$C_5H_4(CO)_2FeR$ and η^5-$Cp(CO)_2Fe$-η^1,η^6-$PhCr(CO)_3$ complexes, respectively, with *n*-butyllithium (THF, –78 °C) (Scheme 3).

Scheme 3



In the study,[8] an attempt to synthesize the binuclear η^5,η^5-$Me(CO)_nM(C_5H_4—C_5H_4)TiCl_2$-$\eta^5$-Cp complexes (M = Fe, *n* = 2; M = Mo, W, *n* = 3) by cross-coupling starting from η^5-$IC_5H_4(CO)_nMMe$ and η^5-$Me_3SnC_5H_4TiCl_2$-η^5-Cp also resulted in the formation of $MeC_5H_4(CO)_nMI$ as products of the regioselective exchange of the iodine atom and the Me group. By analogy with the scheme of the regioselective exchange proposed in the cited study,[8] it can be assumed that the reaction under consideration involved reduction of the $Pd(MeCN)_2Cl_2$ catalyst to produce the η^5-$(C_5H_4PdI)(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ complex. This complex underwent intramolecular transmetallation accompanied by migrations of the I atom to the Fe atom and of the cymantrenyl group to the Pd atom. Subsequent reductive elimination afforded the final product **4**.

Dark-brown complex **4** is soluble in organic solvents (ether, benzene, chloroform, *etc.*) and insoluble in hexane. Its structure was established by ^1H and ^{13}C NMR and IR spectroscopy and mass spectrometry.

The IR spectrum of a solution of complex **4** in CH_2Cl_2 has four ν(CO) bands (Table 1). By analogy with the data on the similar ladder complexes, the bands at 2041 and 1998 cm^{-1} can be assigned to the antisymmetric and symmetric stretching vibrations of the CO groups at the Fe atoms, and the bands at 2023 and 1941 cm^{-1} can be assigned to the symmetric and degenerate stretching vibrations of the CO groups coordinated to the Mn atom. The stretching frequencies of the CO groups at each metal atom are identical with the ν(CO) frequencies in the spectra of the corresponding mononuclear $CpFe(CO)_2I$ (**5**) and $CpMn(CO)_3$ (**6**) complexes (see Table 1), *i.e.*, the mutual electronic influence of the metal carbonyl fragments is not transferred through the bridging dicyclopentadienyl ligand. Earlier,[9] we have observed an analogous effect in the $Me(CO)_2FeC_5H_4PhCr(CO)_3$ complexes.

The results of the present study demonstrated that cross-coupling cannot be used for coupling of binuclear ladder complexes. However, the regioselective exchange, which occurs under mild conditions to form a new car-

Table 1. Frequencies (ν(CO)/cm^{-1}) and their assignments in the IR spectra of solutions of complexes **1** and **4**—**10** in CH_2Cl_2

Complex	$Fe(CO)_2$		$M(CO)_3$*	
1	2032	1978	2003	1916
4	2041	1998	2023	1941
5	2041	1996	—	—
6	—	—	2025	1940
7	2012	1957	1957	1877
8	2038	1986	2005	1917
9	2017	1967	1959	1881
10	2016	1964	1958	1880

* M = Mn or Cr.

bon—carbon bond, is of interest by itself and can be used for synthetic purposes.

Taking into account that halogen-containing derivatives of cyclopentadienyl carbonyl complexes of transition metals serve as the starting compounds in a number of procedures used for oligomerization of organometallic systems, we synthesized new halogen-containing binuclear complexes.

Metallation of complex **1** or η^5-Cp(CO)$_2$Fe-η^1,η^6-BnCr(CO)$_3$ (**7**) with *n*-butyllithium (THF, –78 °C) followed by the reaction of the lithium derivative with CCl_4 or C_3F_7I [10] gave rise to the η^5-ClC$_5$H$_4$(CO)$_2$Fe-η^1,η^5-C$_5$H$_4$Mn(CO)$_3$ (**8**), η^5-ClC$_5$H$_4$(CO)$_2$Fe-η^1,η^6-BnCr(CO)$_3$ (**9**), and η^5-IC$_5$H$_4$(CO)$_2$Fe-η^1,η^6-BnCr(CO)$_3$ (**10**) complexes, respectively.

Complexes **8—10** were obtained as yellow crystalline compounds soluble in usual organic solvents. These complexes were characterized by elemental analysis, IR and ^{1}H NMR spectroscopy, and mass spectrometry. In the IR spectra of binuclear complexes **8—10** (see Table 1), the stretching frequencies of the CO groups at the iron atom are slightly increased ($\Delta\nu$ = 6—8 cm^{-1}) compared to those in the spectra of the corresponding unsubstituted complexes due to the electron-withdrawing effect of the halogen atom in the cylcopentadienyl ligand, whereas the stretching frequencies of the CO groups at the manganese or chromium atoms remain virtually unchanged. The nature of the halogen atom has no effect on the ν(CO) frequencies.

Experimental

All reactions were carried out under dry argon. The IR spectra were recorded in CH_2Cl_2 on a Nicolet Magna IR 750 IR Fourier-transform spectrometer (resolution was 2 cm^{-1}). The ^{1}H and ^{13}C NMR spectra (in C_6H_6) were measured on a Bruker AMX-400 spectrometer (400.13 and 100.61 MHz, respectively). The electron-impact mass spectra were obtained on a Kratos MS 890 instrument; the energy of ionizing electrons was 70 eV; the temperature of the ionization chamber was 200 °C.

Tetrahydrofuran was distilled over sodium benzophenone ketyl under Ar immediately before use, and DMF was dried by distillation over CaH_2.

The Cp(CO)$_2$FeC$_5$H$_4$Mn(CO)$_3$ and Cp(CO)$_2$FeBnCr(CO)$_3$ complexes were prepared according to known procedures.[11,12]

Reaction of the IC$_5$H$_4$(CO)$_2$FeC$_5$H$_4$Mn(CO)$_3$ complex (3) with Me$_3$SiC≡CSiMe$_3$ in the presence of Pd(MeCN)$_2$Cl$_2$. Bis(trimethylsilyl)acetylene Me$_3$SiC≡CSiMe$_3$ (0.085 g, 0.5 mmol) was added to a solution of IC$_5$H$_4$(CO)$_2$FeC$_5$H$_4$Mn(CO)$_3$ (0.5 g, 1 mmol) and Pd(MeCN)$_2$Cl$_2$ (0.012 g, 0.05 mmol) in DMF (20 mL). The mixture was stirred at ~20 °C for 24 h. Then diethyl ether and a 50% aqueous KF solution were successively added. The reaction mixture was stirred for 30 min by passing Ar through the solution. The ethereal layer was separated, washed with water, dried over $MgSO_4$, and filtered. After the removal of the solvent, the residue was chromatographed successively on silica gel (40 : 100) and Silufol plates, and product **4** was eluted with a 1 : 1 hexane—benzene mixture. An attempt to isolate the reaction product by reprecipitation with hexane from benzene resulted in decomposition of **4**.

X-ray fluorescence spectrometry demonstrated that the *K*α-line intensity ratio of the characteristic spectra of iron and manganese corresponds to the atomic ratio of unity. M.p. 128—129 °C. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2041, 2023, 1998, 1941. ^{1}H NMR (C_6D_6), δ: 3.86 (t, 2 H, *J* = 2.2 Hz); 3.96 (t, 2 H, *J* = 2.4 Hz); 4.24 (t, 2 H, *J* = 2.4 Hz); 4.34 (t, 2 H, *J* = 2.4 Hz). ^{13}C NMR (C_6D_6), δ: 81.19; 82.18; 82.64; 82.72; 91.93; 95.91; 213.71; 224.47. MS, *m/z* : 506 [M]$^+$.

Synthesis of complexes 8—10 (general procedure). A solution of Bu^{n}Li (2—3-fold excess, 3—5 mmol) in hexane was added to a solution of the starting complex **1** or Cp(CO)$_2$FeBnCr(CO)$_3$ (1—2 mmol) in THF (50 mL). The reaction mixture was stirred at –78 °C for 1—1.5 h and then CCl_4 or C_3F_7I (1 mL) was added. The reaction mixture was stirred at –78 °C for 30 min and gradually warmed to ~20 °C. The solvent was evaporated and the residue was chromatographed on Al_2O_3 (Brockmann activity II), the product being eluted with a 1 : 1 benzene—hexane mixture. Halogen-containing derivatives **8—10** were obtained in yields from 20 to 40%.

η^5-Chlorocyclopentadienyldicarbonyliron-η^1,η^5-cyclopentadienylmanganesetricarbonyl ClC$_5$H$_4$(CO)$_2$FeC$_5$H$_4$Mn(CO)$_3$ (8). The yield was 32%. Found (%): C, 43.42; H, 1.95; Cl, 1.95. $C_{15}H_8O_5ClFeMn$. Calculated (%): C, 43.42; H, 1.90; Cl, 1.90. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2038, 2005, 1986, 1917. ^{1}H NMR (C_6D_6), δ: 3.72 (t, 2 H, C_5H_4); 4.06 (t, 2 H, C_5H_4); 4.23 (t, 2 H, C_5H_4); 4.43 (t, 2 H, C_5H_4). MS, *m/z*: 414 [M]$^+$.

η^5-Chlorocyclopentadienyldicarbonyliron-η^1,η^6-benzylchromiumtricarbonyl ClC$_5$H$_4$(CO)$_2$FeBnCr(CO)$_3$ (9). The yield was 23%. Found (%): C, 46.34; H, 2.56; Cl, 8.30. $C_{17}H_{11}O_5ClFeCr$. Calculated (%): C, 46.43; H, 2.50; Cl, 7.98. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2017, 1967, 1959, 1881. ^{1}H NMR (C_6D_6), δ: 2.18 (s, 2 H, CH_2); 3.55 (t, 2 H, C_5H_4); 3.95 (t, 2 H, C_5H_4); 4.35 (H, Ph); 4.75 (m, 4 H, Ph). MS, *m/z*: 438 [M]$^+$.

η^5-Iodocyclopentadienyldicarbonyliron-η^1,η^6-benzylchromiumtricarbonyl IC$_5$H$_4$(CO)$_2$FeBnCr(CO)$_3$ (10). The yield was 40%. Found (%): C, 38.41; H, 2.09. $C_{17}H_{11}O_5IFeCr$. Calculated (%): C, 38.30; H, 2.07. IR (CH_2Cl_2), ν/cm^{-1}: 2016, 1964, 1958, 1880. ^{1}H NMR (C_6D_6), δ: 2.18 (s, 2 H, CH_2); 3.63 (t, 2 H, C_5H_4); 4.09 (t, 2 H, C_5H_4); 4.37 (1 H, Ph); 4.76 (m, 4 H, Ph). MS, *m/z*: 530 [M]$^+$.

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