Reactivity of some "ladder" type complexes under conditions of metallation

T. Yu. Orlova,[a]* Yu. S. Nekrasov,[a] P. V. Petrovskii,[a] M. G. Ezernitskaya,[a]
T. V. Magdesieva,[b] S. V. Milovanov,[b] and K. P. Butin[b]

[a]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: yusnekr@ineos.ac.ru
[b]Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 5546

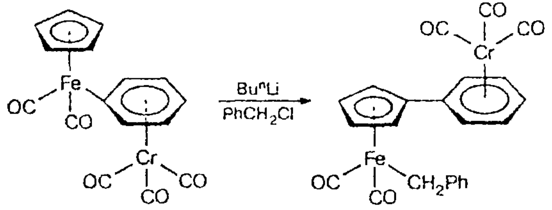
The behavior of binuclear "ladder" type complexes FpL, where Fp = $Cp(CO)_2Fe$, L = p-$MeC_6H_4Cr(CO)_3$ (4), $CH_2C_6H_5Cr(CO)_3$ (5), and p-$FpC_6H_4Cr(CO)_3$ (6), under conditions of metallation was studied. Unlike compounds 5 and 6, the σ-bound ligand L in compound 4 migrates from the iron atom to the cyclopentadienyl ring to give complexes $Me(CO)_2FeC_5H_4-C_6H_4(p\text{-}Me)Cr(CO)_3$. The electrochemical reduction potentials of the complexes 4—6 and the rearrangement products were measured. The migration activity of L is determined by the ease of reductive cleavage of the Fe—L bond and the susceptibility of the system to undergo intramolecular electron transfer from the Cp ligand to the aromatic ring.

Key words: "ladder" type complex, metallation, rearrangement, electrochemistry.

We have shown previously[1,2] that binuclear complexes with a bridging η^1,η^5-cyclopentadienyl ligand ("ladder" type complexes) Fp-η^1,η^5-$C_5H_4M(CO)_2R$ (Fp = $Cp(CO)_2Fe$; M = Fe, Mn; R = CO, Alk) are selectively metallated by Bu^nLi (THF, −78 °C) into the Cp ring. With allowance for this fact, a series of tri-, tetra-, penta-, and hexanuclear complexes have been synthesized from the binuclear complex Fp-η^1,η^5-$C_5H_4Mn(CO)_3$ (1).[2–6] However, metallation of binuclear complexes Fp-η^1,η^5-$C_5H_4(CO)_2FeR$ (2: R = Me or CH_2Ph), whose structures are similar to that of 1, and subsequent treatment of the products with FpI, used as an electrophilic agent, did not give the expected trinuclear complexes Fp-η^1,η^5-$C_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4(CO)_2FeR$. Instead, the reaction yielded compounds resulting from migration of the σ-bound organometallic fragment $C_5H_4(CO)_2FeR$ from the Fe atom to a C atom of the cyclopentadienyl ring. This rearrangement is accompanied by intramolecular replacement of the Li atom and formation of a new carbon-carbon bond in the coordination sphere of iron.[2] A similar rearrangement is observed in the metallation of the "ladder" type binuclear complex Fp-η^1,η^6-$C_6H_5Cr(CO)_3$ (3) with a bridging η^1,η^6-phenyl ligand[7] (Scheme 1).

To identify the main factors that determine the route of metallation (formation of "ladder" type polynuclear systems or rearrangements), in this work, we studied the behavior of analogs of binuclear complex 3, compounds FpL, where L = p-$MeC_6H_4Cr(CO)_3$ (4), $CH_2C_6H_5Cr(CO)_3$ (5), and p-$FpC_6H_4Cr(CO)_3$ (6), in reactions carried out under identical conditions (Bu^nLi, Me_2SO_4). We found that the migration of the coordinated ligand p-$MeC_6H_4Cr(CO)_3$ from the Fe atom into the cyclopentadienyl ring (Scheme 2) is typical only of complex 4, whereas metallation of compounds 5 and 6 follows the normal route.

Scheme 1



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Comparison of the electrochemical reduction potentials (E^{red}) of these complexes and those studied previously[8] (Table 1) shows that there is a relationship between the E^{red} value and the ability of the coordinated ligand to migrate. The rearrangement occurs for complexes with low reduction potentials.

The results obtained are consistent with the previously proposed[8] scheme of metallation of the "ladder" type binuclear complexes, which includes deprotonation of the cyclopentadienyl ligand, the transfer of an electron to the σ-bound aromatic ring, cleavage of the σ-bond, formation of radical species, and their recombination (Scheme 3). It is the occurrence of intramolecular electron transfer during this process that implies a correlation between the ease of reduction of the complex and its tendency to rearrange.

The absence of rearrangement in the case of complex 5, whose reduction potential is low and comparable with

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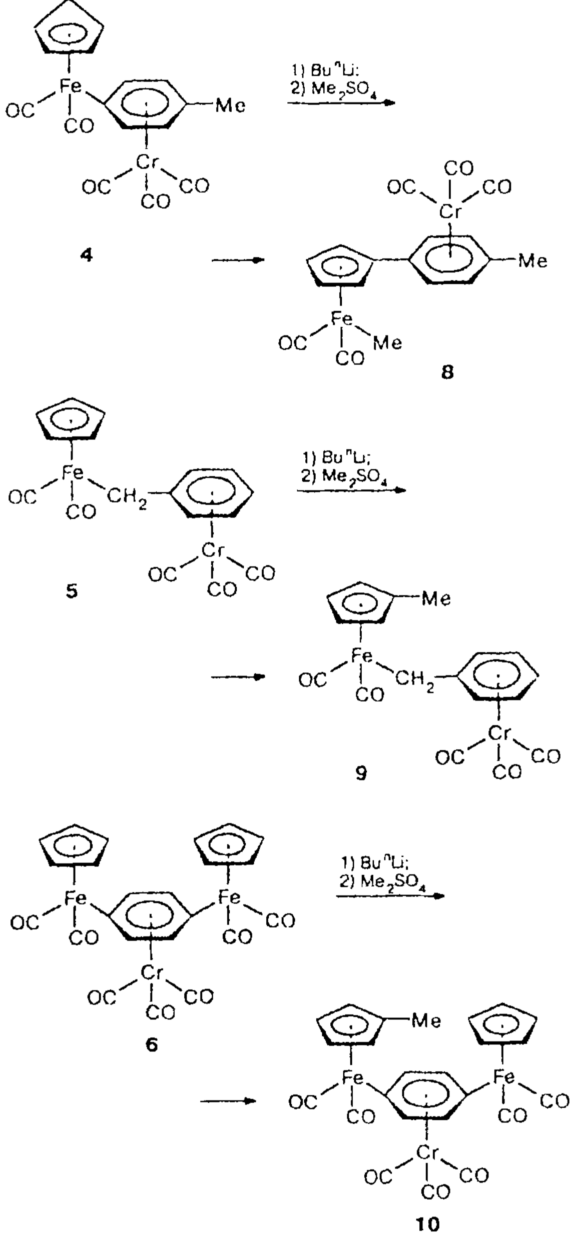
Scheme 2



that of complex **3**, can be explained by assuming that the methylene group hampers the electron transfer on the aromatic ligand. Thus, the reduction potential of a "ladder" type binuclear complex is one of the factors determining the route of metallation.

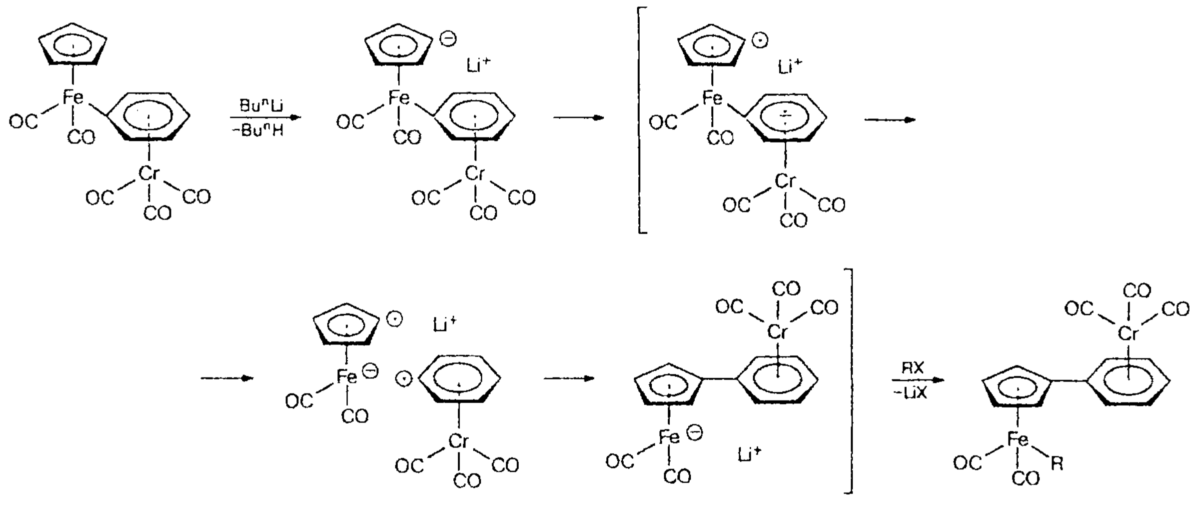
Table 1. Reduction potentials (E^{red}) of the complexes studied

Complex	Formula	E^{red} /V
1	$FpC_5H_4Mn(CO)_3$	2.20
2	$FpC_5H_4(CO)_2FeCH_2Ph$	2.10
3	$FpC_6H_5Cr(CO)_3$	2.06
4	$FpC_6H_4(p\text{-}Me)Cr(CO)_3$	2.09
5	$FpCH_2C_6H_5Cr(CO)_3$	2.06
6	$FpC_6H_4(p\text{-}Fp)Cr(CO)_3$	2.18
7	$Me(CO)_2FeC_5H_4{-}C_6H_5Cr(CO)_3$	2.12
8	$Me(CO)_2FeC_5H_4{-}C_6H_4(p\text{-}Me)Cr(CO)_3$	2.08
11	FpPh	2.14

Since the reductive cleavage of the Fe—C σ-bond is the key step in the assumed reaction scheme, it is of interest to study the possibility of migration of the σ-bound $p\text{-}MeC_6H_4Cr(CO)_3$ fragment from the Fe atom into the cyclopentadienyl ring on treatment of complex **4** with a strong reducing reagent, for example, sodium amalgam. No rearrangement product was detected in the reaction mixture resulting from treatment of complex **4** with a large excess of sodium amalgam; instead, the following compounds were isolated and identified: $[C_6H_4(p\text{-}Me)Cr(CO)_3]_2$, $FpC_6H_4Me\text{-}p$, and $C_6H_5MeCr(CO)_3$. The composition of the reaction products does not rule out completely the possibility of rearrangement, since the isolated compounds could have resulted from reductive destruction of both the starting complex **4** and the rearrangement product **8**. Comparison of the E^{red} values of the initial complexes **3**, **4** and the corresponding rearrangement products **7**, **8** indicates that the latter are reduced at somewhat more cathodic potentials (see Table 1). However, this difference is so small (20—30 mV) that the use of a strong reducing reagent should destroy not only the starting complex but also the product of its rearrangement. Therefore, we attempted to induce the migration of the σ-bound ligand in complex **3** electrochemically by conducting electrolysis at a controlled potential. The formation of the rearrangement product **7** can be judged by the presence of a peak of its oxidation (+0.83 V), because no peaks for the starting complex **3** are manifested in this range of potentials.

Figure 1 presents cyclic voltammograms (CVA) of complexes **3** and **7**, and the CVA of complex **3** in the presence of benzyl chloride. It can be seen that the CVA pattern of the mixture (anodic region, repeated scanning) depends substantially on the cathodic potential. The more cathodic the region where the direction of the potential scanning is changed, the higher the probability of reduction of the rearrangement product and the larger the anodic peak at $E = -0.32$ V, which corresponds to the oxidation of the $(CO)_3CrC_6H_5{-}C_5H_4(CO)_2Fe^-$ anion. When the direction of scanning is changed at −2.05 V, the peak at $E = 0.32$ V can hardly be observed, but a small anodic peak, corresponding to the rearrangement product, is exhibited at $E = +0.83$ V. These results imply that if the electrochemically induced migration of the σ-bound ligand from the Fe atom into the Cp ring is possible, for this migration to occur the difference between the reduction potentials of the starting complex and the rearrangement product should be as great as possible.

Scheme 3



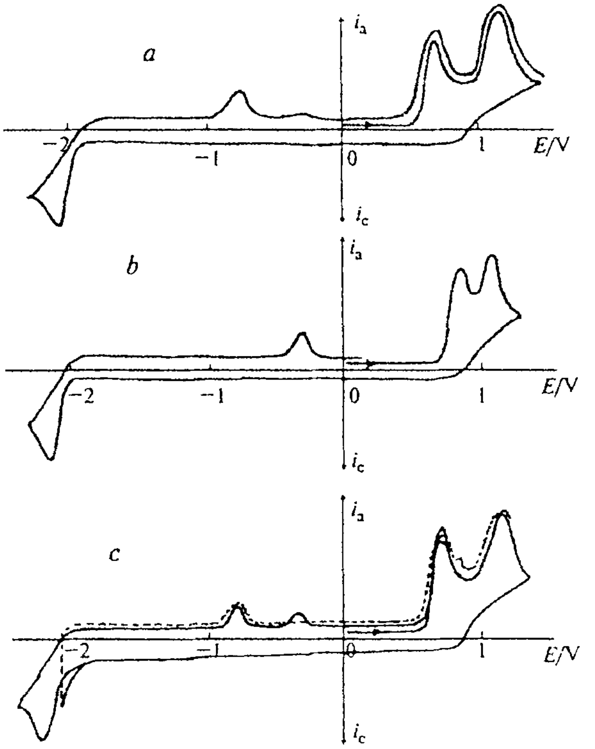


Fig. 1. Cyclic voltammograms of the complexes $Cp(CO)_2Fe(\eta^1,\eta^6-C_6H_5)Cr(CO)_3$ (3), $C = 5\cdot10^{-4}$ mol L^{-1} (*a*); $(CO)_2C_6H_5CH_2Fe(C_5H_4-C_6H_5)Cr(CO)_3$ (7), $C = 5\cdot10^{-4}$ mol L^{-1} (*b*); $Cp(CO)_2Fe(\eta^1,\eta^6-C_6H_5)Cr(CO)_3$ (3), $C = 5\cdot10^{-4}$ mol L^{-1}, in the presence of 10^{-3} mol L^{-1} of $PhCH_2Cl$ (*c*) (in MeCN/0.05 *M* Bu_4NBF_4 at a Pt electrode, Ag/AgCl/KCl, 20 °C).

Experimental

All the experiments were carried out under Ar. Complexes **4—6** were prepared by known procedures.[9,10] THF was distilled over sodium benzophenone ketyl directly prior to the experiment. IR spectra were recorded in CH_2Cl_2 on a Nicolet Magna JR 750 FT IR spectrometer (resolution 2 cm^{-1}). ^{1}H NMR spectra were measured in C_6D_6 on a Bruker WP-200-SY spectrometer (200 MHz). Electrochemical measurements were carried out on a SVA-1B-M volammetric system using stationary and rotating platinum electrodes in anhydrous MeCN at 20 °C with a 0.05 *M* solution of Bu_4NBF_4 as the supporting electrolyte. Platinum served as the auxiliary electrode, and a silver chloride electrode served as the reference electrode. Oxygen was removed from the cell by passing a stream of dry Ar. Voltammetric curves were recorded by the method of cyclic voltammetry at potential sweep rates of 50, 100, 200, and 500 mV s^{-1}. The velocity of electrode rotation varied from 480 to 3450 rpm. The ohmic losses were taken into account. Acetonitrile of the "pure" grade was purified by the known procedure.[8]

Reaction of complex 4 with Bu^{n}Li followed by alkylation with Me_2SO_4. A 1.49 *M* hexane solution of Bu^{n}Li (1 mL, 1.5 mmol) was added at −78 °C to a solution of compound **4** (0.26 g, 0.6 mmol) in 30 mL of THF. The reaction mixture was stirred for 1 h, then Me_2SO_4 (1 mL) was added, and the mixture was stirred for an additional 15 min at −78 °C. Then the temperature was gradually raised to room temperature, the solvent was removed, and the residue was chromatographed on Al_2O_3 (Brockman activity II). Complex **8** was eluted with a 1 : 1 benzene—hexane mixture. Yield 0.03 g (20%); 0.1 g of the starting complex **4** was recovered. IR, ν(CO)/cm^{-1}: 2009, 1966, 1953, 1892. ^{1}H NMR, δ: 4.83 (m, 2 H, Ph); 4.48 (m, 2 H, Ph); 4.3 (t, 2 H, Cp); 4.10 (t, 2 H, Cp); 1.63 (s, 3 H, $CH_3C_6H_4$); 0.30 (s, 3 H, CH_3Fe).

Reaction of complex 4 with Bu^{n}Li followed by alkylation with MeI. A 1.49 *M* hexane solution of Bu^{n}Li (1 mL, 1.5 mmol) was added at −78 °C to a solution of compound **4** (0.25 g, 0.6 mmol) in 30 mL of THF. The reaction mixture was stirred for 1 h at −78 °C, then MeI (1 mL) was added, and the mixture was stirred for an additional 15 min at −78 °C. Then the temperature was gradually raised to room temperature, the solvent was removed, and the residue was chromatographed on Al_2O_3 (Brockman activity II). Complex **8** was eluted with a 1 : 1 benzene—hexane mixture. Yield 0.04 g (23%); 0.1 g of the starting complex **4** was recovered.

Reaction of complex 5 with Bu^{n}Li followed by alkylation with Me_2SO_4. A 1 *M* hexane solution of Bu^{n}Li (1.6 mL, 1.8 mmol) was added at −78 °C to a solution of complex **5** (0.25 g, 0.6 mmol) in 30 mL of THF. The reaction mixture was stirred for 75 min at −78 °C, then Me_2SO_4 (1 mL) was added, and the mixture was stirred for an additional 15 min at −78 °C. Then the temperature was gradually raised to room temperature, the solvent was removed, and the residue was chromatographed on Al_2O_3 (Brockman activity II). Complex **9** was eluted with a 1 : 1 benzene—hexane mixture. Yield 0.05 g (19%). The product was reprecipitated from benzene with heptane. IR, ν(CO)/cm^{-1}: 2007, 1957, 1877. ^{1}H NMR, δ: 4.40 (m, 5 H, Ph); 3.83 (t, 2 H, Cp); 3.75 (t, 2 H, Cp); 2.78 (s, 2 H, CH_2); 2.05 (s, 3 H, CH_3).

Reaction of complex 6 with Bu^{n}Li followed by alkylation with Me_2SO_4. A 1.4 *M* hexane solution of Bu^{n}Li (0.45 mL, 0.6 mmol) was added at −78 °C to a solution of compound **6** (0.18 g, 0.3 mmol) in 30 mL of THF. The reaction mixture was stirred for 75 min at −78 °C, then Me_2SO_4 (1 mL) was added, and the mixture was stirred for an additional 15 min at −78 °C. Then the temperature was gradually raised to room temperature, the solvent was removed, and the residue was chromatographed on Al_2O_3 (Brockman activity II). Complex **10** was eluted with benzene. Yield 0.02 g (14%). IR, ν/cm^{-1}: 2031, 2016, 1978, 1959, 1934, 1852. ^{1}H NMR, δ: 5.73 (d, 2 H, Ph); 4.87 (d, 2 H, Ph); 4.23 (t, 2 H, Cp); 3.93 (t, 2 H, Cp); 3.94 (s, 5 H, Cp); 1.45 (s, 3 H, CH_3).

Reaction of complex 4 with Na/Hg followed by alkylation with Me_2SO_4. Compound **4** (0.1 g, 0.25 mmol) was added at −78 °C to 1.4% Na/Hg in 20 mL of THF. The reaction mixture was stirred for 1 h at this temperature, then the solution was separated from sodium amalgam, Me_2SO_4 (0.4 mL) was added, and the mixture was stirred for an additional 1.5 h at −78 °C. Then the temperature was gradually raised to room temperature, the solvent was removed, and the residue was chromatographed on Al_2O_3 (Brockman activity II). The products were eluted with hexane and then with benzene. The complexes FpC_6H_4Me-*p*, $C_6H_5MeCr(CO)_3$, and $[C_6H_4(p\text{-Me})Cr(CO)_3]_2$ were identified by chromatography on Silufol plates (comparison with authentic sample) and by ^{1}H NMR spectroscopy.

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