Migration of the η^1:η^6-$C_6H_5Cr(CO)_3$ ligand into the cyclopentadienyl ring during metallation of the η^5-$C_5H_5(CO)_2Fe$ η^1:η^6-$C_6H_5Cr(CO)_3$ binuclear complex

T. Yu. Orlova, V. N. Setkina, and P. V. Petrovskii*

*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085*

It was found that the η^1:η^6-$C_6H_5Cr(CO)_3$ ligand migrates into the cyclopentadienyl ring when the η^5-$C_5H_5(CO)_2Fe$ η^1:η^6-$C_6H_5Cr(CO)_3$ binuclear complex is metallated with Bu^{n}Li. Under the same conditions, no migration of the phenyl ligand in the η^5-$C_5H_5(CO)_2Fe$ η^1-C_6H_5 complex was observed.

Key words: migration, phenyl, complex.

It is known that during the metallation of the cyclopentadienyl ring in $Cp(CO)_2FeR$ type complexes (Cp = η^5-C_5H_5, R is the η^1-bonded ligand), the η^1-bonded ligand migrates in some cases (R = $SiMe_3$, COMe, POR'_2, *etc.*) into this ring.[1–3]

Previously we found that when $Cp(CO)_2FeCpm(CO)_2FeR$ staircase type complexes (Cpm = η^1:η^5-C_5H_4, R = Me, CH_2Ph, or $C_5H_4Mn(CO)_3$) were metallated with Bu^{n}Li and then treated with $Cp(CO)_2FeI$ in order to prepare tri- and tetranuclear complexes of the same type, products of the migration of the $Cpm(CO)_2FeR$ ligand into the cyclopentadienyl ring were formed.[4,5]

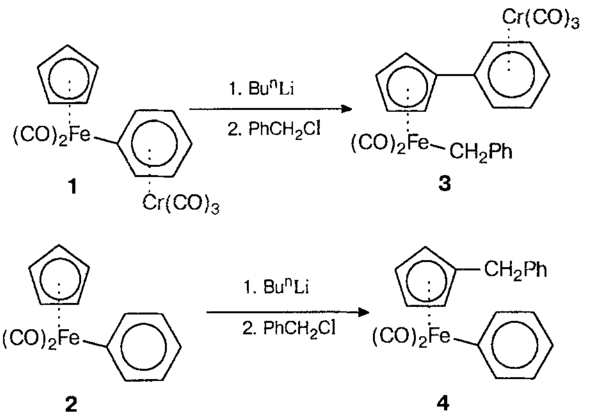
It was of interest to reveal the effect of coordination of the η^1-aromatic ligand to the carbonyl-metal group on the migration of this ligand.

To this end, $Cp(CO)_2Fe$ η^1:η^6-$C_6H_5Cr(CO)_3$ complex with the η^1:η^6-phenylchromotricarbonyl ligand (**1**) and $Cp(CO)_2FePh$ complex with the η^1-phenyl ligand (**2**) were compared in the metallation reaction under identical conditions.

When the binuclear complex **1** was metallated with Bu^{n}Li and then treated with $PhCH_2Cl$ as the electrophile, the η^1-$C_6H_5Cr(CO)_3$ ligand bonded to the Fe atom underwent anionic rearrangement into the Cp ring to yield compound **3**. In complex **2**, the phenyl group did not migrate into the Cp ring under the same conditions and complex **4** was the reaction product (Scheme 1).

Complexes **3** and **4** were characterized by spectroscopy (IR, ^{1}H NMR). The known reaction with iodine resulting in the cleavage of the η^1 bond was also used to confirm their structures. The reaction products, η^5-$C_5H_4Ph(CO)_2FeI$ (**5**) and η^5-$C_5H_4CH_2Ph(CO)_2FeI$ (**6**), were isolated and identified.

Scheme 1



Thus, the obtained data suggest that the observed migration of the η^1-phenylchromotricarbonyl ligand from the metal atom into the Cp ring occurs by the mechanism of intramolecular nucleophilic substitution; evidently, this is made possible by the clearly pronounced electron-acceptor character of the carbonyl-metal group.

Experimental

The reactions were carried out under argon. IR spectra were recorded on a Zeiss UR-20 instrument, ^{1}H NMR spectra were recorded on a Bruker WP-200-SY instrument (200.13 MHz), and mass spectra were obtained on a Kratos MS 890 instrument. THF was distilled from benzophenone ketyl under argon. $Cp(CO)_2FePh$ and $Cp(CO)_2Fe\{\eta^1$:η^6-$C_6H_5Cr(CO)_3\}$ were prepared according to the procedures reported previously.[6,7]

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Reactions of complex 1 with Bu^nLi and $PhCH_2Cl$. 1.7 mL (2.55 mmol) of a 1.5 *M* Bu^nLi solution in hexane was added at −78 °C to a solution of 0.37 g (1 mmol) of **1** in 50 mL of THF. The reaction mixture was stirred for 1.5 h, then 1 mL of $PhCH_2Cl$ was added, and the mixture was stirred for 1 h at −78 °C. Then the mixture was slowly heated to room temperature. The solvent was removed, the residue was chromatographed on Al_2O_3 (activity II according to Brockmann), and complex **3** was eluted with benzene; the yield was 0.06 g (14 %). The product was purified by reprecipitation with heptane from benzene (1:1), m. p. 143—145 °C. IR (CH_2Cl_2), $\nu(CO)/cm^{-1}$: 1895, 1955, 1970, and 2010; ^1H NMR (C_6D_6), δ: 7.18—7.14 (m, Ph); 4.54 (m, 5 H, Ph); 4.52 (t, 2 H, C_5H_4); 4.27 (t, 2 H, C_5H_4); 2.7 (s, 2 H, CH_2). MS, *m/z* : 416 [M^+—3 CO].

0.1 g of I_2 in 3 mL of CH_2Cl_2 were added to 0.05 g of **3**. The mixture was kept for 20 h at 20 °C, then it was washed with an aqueous solution of $Na_2S_2O_3$, dried with Na_2SO_4, and chromatographed on Al_2O_3; the product was eluted with benzene. ^1H NMR (C_6D_6), δ for compound **5**: 7.18—7.07 (m, Ph); 4.61 (t, 2 H, C_5H_4); 4.24 (t, 2 H, C_5H_4).

Reaction of complex 2 with Bu^nLi and $PhCH_2Cl$. 2 mL (3.2 mmol) of a 1.6 *M* Bu^nLi solution in hexane was added at −78 °C to the solution of 0.25 g (1 mmol) of **2** in 50 mL of THF. The reaction mixture was stirred for 1 h, then 1 mL of $PhCH_2Cl$ was added, and the mixture was stirred for 1 h at −78 °C. Then the mixture was slowly heated to room temperature. The solvent was removed, the residue was chromatographed on Al_2O_3, and complex **4** was eluted with heptane; the yield was 0.25 g (70 %). The product was purified by low-temperature recrystallization from hexane. IR (CH_2Cl_2), $\nu(CO)/cm^{-1}$: 1961 and 2019. ^1H NMR (C_6D_6), δ: 7.03—7.83 (m, Ph); 4.09 (t, 2 H, C_5H_4); 4.53 (t, 2 H, C_5H_4); 2.76 (s, 2 H, CH_2).

0.1 g of I_2 in 3 mL of CH_2Cl_2 was added to 0.03 g of **4**. The mixture was kept for 18 h at 20 °C, then it was washed with an aqueous solution of $Na_2S_2O_3$, dried with Na_2SO_4, and chromatographed on Al_2O_3; the product was eluted with benzene. ^1H NMR (C_6D_6), δ for compound **6**: 7.27—7.08 (m, Ph); 4.64 (t, 2 H, C_5H_4); 4.27 (t, 2 H, C_5H_4); 3.77 (s, 2 H CH_2).

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