Organometallic Chemistry

Oxidation of (η^5-6-*exo*-cyclopentadienylcyclohexadienyl)-(η^5-cyclopentadienyl)iron by trityl hexafluorophosphate

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Oxidation of the cyclohexadienyl complex $Fe(\eta^5-C_5H_5)(1-5-\eta^5-6-exo-C_5H_5-C_6H_6)$ (2) by $(Ph_3C)PF_6$ (CH_2Cl_2, from −30 to +20 °C) occurs as two concurrent processes: elimination of an H atom from the cyclohexadienyl ligand and replacement of an H atom in the cyclopentadienyl ring by a CPh_3 fragment. A mixture of cationic complexes $[Fe(\eta^5-C_5H_5)(\eta^6-Ph-C_5H_5)]^+$ (1^+) and $[Fe(\eta^5-C_5H_4CPh_3)(\eta^6-Ph-C_5H_5)]^+$ (4^+) with PF_6^- anions is obtained. Deprotonation of the mixture of 1^+ and 4^+ complexes under the action of Bu^{t}OK in *m*-xylene followed by boiling of the reaction mixture gives phenylferrocene (7) as the product of η^6:η^5-interring haptotropic rearrangement.

Key words: alkylation; iron complexes, oxidation; interring haptotropic rearrangement.

The development of a convenient method for synthesis of $[Fe(\eta^5-C_5H_5)(\eta^6-Ph-C_5H_5)]^+$ (1^+) became necessary in the course of the systematic study of interring η^6:η^5-haptotropic rearrangements (IHR) of transition metal complexes with fused or nonfused aromatic ligands.[1,2] For this purpose, the oxidation of the iron η^5-cyclohexadienyl complex $Fe(\eta^5-C_5H_5)(1-5-\eta^5-6-exo-C_5H_5-C_6H_6)$ (2) was studied in the present work. The initial complex 2 was obtained by the previously described procedure[3] and characterized by the data of ^{1}H NMR and IR spectroscopy and mass spectrometry. This complex is a mixture of three isomers that differ in the position of the double bonds of the noncoordinated 6-*exo*-cyclopentadienyl fragment. A solid amorphous yellow mixture of products was obtained by the action of the oxidant $(Ph_3C)PF_6$ on this complex in CH_2Cl_2 in the temperature range from −30 to 20 °C followed by multiple precipitation. The fast atomic bombardment (FAB) mass spectrum of this mixture contains peaks of the molecular ions with *m/z* 506 $[M_1]^+$ (corresponding to 4^+) and 264 $[M_2]^+$ (corresponding to 1^+), a peak of the protonated molecular ion with *m/z* 507 $[M_1+H]^+$, a fragmentation peak with *m/z* 364 $[M_1-C_5H_5-Ph]^+$, and an intense peak with *m/z* 243 $[Ph_3C]^+$. These data allow us to propose that the cationic complex containing the CPh_3 fragment is one of the reaction products. This is confirmed by the ^{1}H NMR spectroscopy data. The spectrum of the mixture in acetone-d_6 contains a singlet at δ 5.16 corresponding to the nonsubstituted coordinated C_5H_5 ligand, two multiplets at δ 4.52 and 5.31 (AA′BB′ type spectrum) assigned to the substituted C_5H_4R ligand, and overlapping groups of signals in the regions of 5.8—6.1 and 6.4—6.9 ppm belonging to the coordinated arene and noncoordinated C_5H_5 group. The signals of the protons of the CPh_3 fragment appear as an intense multiplet centered at δ 7.32. Two overlapping multiplets

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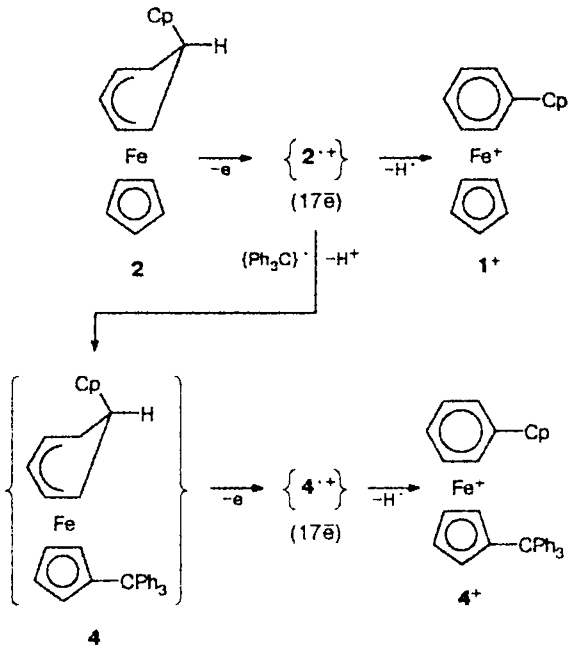
with the centers at δ 3.1 and 2.99 correspond to the methylenic protons in the noncoordinated cyclopentadienyl rings.

The data obtained suggest that complexes 1^+ and 4^+ (1.0 : 0.8) probably formed *via* Scheme 1, are the main reaction products.

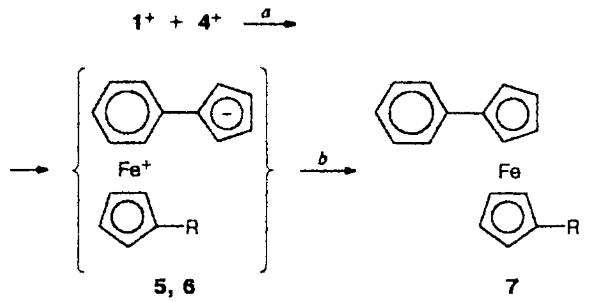
Scheme 1



The possibility of the generation of cation $2^{\cdot+}$ is confirmed by the data of cyclic voltammetry, according to which the one-electron oxidation of complex 2 (E_{ox} = 0.33 V) is an electrochemically reversible process and gives the relatively stable 17-electron radical cation $2^{\cdot+}$. We believe that complex 1^+ is formed due to the elimination of an H atom from the six-membered cycle, and cation 4^+ is formed by the subsequent replacement of an H atom in the coordinated cyclopentadienyl ring by a trityl radical and the elimination of hydrogen (see Scheme 1). 17-Electron complex 2^+ is an electronic analog of ferrocenium, and radical substitution of hydrogen similar to that observed by us for cation 2^+ are well known for ferrocenium salts.[4]

Despite the fact that complex 1^+ was not isolated in the individual state,* we studied the deprotonation of a mixture of complexes 1^+ and 4^+ by potassium *tert*-butylate in *m*-xylene. This process followed by heating was performed in a sealed evacuated system to prevent the decomposition and action of traces of air oxygen. Boiling of the green solution obtained was accompanied by noticeable decomposition and resulted in the formation of phenylferrocene (7), the product of η^6:η^5-IHR (Scheme 2). Attempts to isolate the products of the rearrangement of complex 6 failed.

Scheme 2



R = H (5, 7), Ph_3C (6)

Reagents and conditions: *a*. Bu^tOK, *m*-xylene; *b*. *m*-xylene, boiling, 48 h.

In order to reveal the general character of the radical replacement of the H atom in the cyclopentadienyl ring in the 17-electron iron (cyclohexadienyl)cyclopentadienyl complexes, we are performing a detailed study of the oxidation reactions of this type compound with a known (6-*exo*- or 6-*endo*-) orientation of the substituent. The results will be presented elsewhere.

Experimental

All reactions were carried out in an atmosphere of purified argon and in anhydrous solvents. ^1H and ^{13}C NMR spectra were recorded on Varian VXR-400 and Bruker WP-200SY spectrometers. Mass spectra were recorded on a Kratos Koncept instrument by the FAB method. The energy of the bombarding atoms (Cs) was 8 keV and 2-nitrobenzyl alcohol was used as the matrix. Electrochemical measurements were performed on a PI-50-1 potentiostat in CH_2Cl_2. A hanging mercury drop was used as the working electrode, a platinum mesh was the accessory electrode, and SCE was used as the reference electrode. The potential scanning rate was 200 mV s^{-1}, and $Bu^n_4NBF_4$ was used as the supporting electrolyte.

Oxidation of the complex Fe(η^5-C_5H_5)(1-5-η^5-6-*exo*-C_5H_5—C_6H_6) (2) was performed according to the procedure described previously[5] both at room temperature and at −30 °C. The compound $(Ph_3C)PF_6$ (0.540 g, 1.39 mmol) was added to a solution of complex 2 (0.370 g, 1.4 mmol) in CH_2Cl_2. Water (10 mL) was added to the reaction mixture 2.5 h later, and the organic solutions were combined and dried with $MgSO_4$. After removal of CH_2Cl_2 *in vacuo*, the product obtained was precipitated four times from $CHCl_3$ with ether, and a mixture of complexes 1^+ and 4^+ (1.0 : 0.8) was isolated. The total yield based on the calculation of the $1^+/4^+$ ratio (from the ^1H NMR spectrum) was 0.780 g (60%).

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* Complexes 1^+ and 4^+ cannot be separated chromatographically due to the elimination of the Cp and CPh_3 substituents upon contact with the sorbent (Al_2O_3, SiO_2) lasting 20—30 min.

Reaction of a mixture of complexes 1^+ and 4^+ with Bu^tOK. A mixture of complexes 1^+ and 4^+ (0.200 g, 0.2 mmol, $1^+/4^+$ = 1.0 : 0.8) in *m*-xylene (10 mL) was placed in a Schlenk-type vessel and degassed *in vacuo*. Bu^tOK (0.030 g, 0.27 mmol) was added to the suspension obtained, and the system was sealed off *in vacuo*. After shaking at 20 °C, the solution became dark green. The reaction mixture was boiled for 48 h until an orange color appeared. After cooling, the reaction vessel was opened in air, the *m*-xylene was removed *in vacuo*, and the dry residue was treated several times with cold heptane. The heptane extracts were combined and concentrated. The dry residue was chromatographed on a column (15×200 mm) with Al_2O_3 (II Brockmann activity). The first colorless fraction was eluted with petroleum ether, After removal of the solvent, this fraction gave triphenylmethane (0.03 g, 90%).* The second yellow fraction was eluted with a benzene—petroleum ether (1 : 2) mixture to obtain (after removal of the solvent and recrystallization from heptane) phenylferrocene 7 (0.04 g, 37%). The ^{1}H NMR spectrum and m.p. of compound 7 agree entirely with the published data.[6,7]

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* The yield of triphenylmethane is calculated per initial complex 4^+ that is present in a mixture of 1^+ and 4^+.