Photochemical substitution of benzene in the iron cyclohexadienyl complex $[(\eta^5\text{-}C_6H_7)Fe(\eta\text{-}C_6H_6)]^+$

*D. A. Loginov, M. M. Vinogradov, Z. A. Starikova, P. V. Petrovskii, and A. R. Kudinov**

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5085. E-mail: arkudinov@ineos.ac.ru

The visible light irradiation of the $[(\eta^5\text{-}C_6H_7)Fe(\eta\text{-}C_6H_6)]^+$ cation (**1**) in acetonitrile resulted in the substitution of the benzene ligand to form the labile acetonitrile species $[(\eta^5\text{-}C_6H_7)Fe(MeCN)_3]^+$ (**2**). The reaction of **1** with Bu^tNC in MeCN produced the stable isonitrile complex $[(\eta^5\text{-}C_6H_7)Fe(Bu^tNC)_3]^+$ (**3**). The photochemical reaction of cation **1** with pentaphosphaferrocene $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$ afforded the triple-decker cation with the bridging pentaphospholyl ligand, $[(\eta^5\text{-}C_6H_7)Fe(\mu\text{-}\eta\text{:}\eta\text{-}cyclo\text{-}P_5)FeCp^*]^+$ (**4**). The latter complex was also synthesized by the reaction of cation **2** with $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$. The structure of the complex **[3]**PF_6 was established by X-ray diffraction.

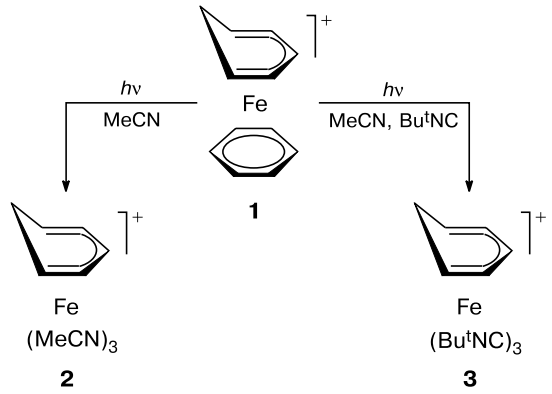
Key words: iron, sandwich compounds, triple-decker complexes.

The cationic fragment $[CpFe]^+$ has found wide use in organometallic chemistry for the synthesis of sandwich,[1] triple-decker,[2—6] and cluster[7] compounds. This cation is generated by visible light irradiation of a solution of the iron benzene complex $[CpFe(\eta\text{-}C_6H_6)]^+$ in dichloromethane. Recently, we have demonstrated[5,8—10] that under analogous conditions, the cobalt complex $[(\eta\text{-}C_4Me_4)Co(\eta\text{-}C_6H_6)]^+$ serves as a source of the $[(\eta\text{-}C_4Me_4)Co]^+$ moiety. The cationic (cyclohexadienyl)iron species $[(\eta^5\text{-}C_6H_7)Fe]^+$ is isolobal with $[CpFe]^+$ and $[(\eta\text{-}C_4Me_4)Co]^+$. Hence, it seemed probable that the $[(\eta^5\text{-}C_6H_7)Fe(\eta\text{-}C_6H_6)]^+$ complex (**1**) would also eliminate the benzene ligand under photochemical conditions. The present study was aimed at verifying this hypothesis.

Results and Discussion

Benzene in the $[(ring)M(\eta\text{-}C_6H_6)]^+$ complexes ((ring)M = CpFe or $(\eta\text{-}C_4Me_4)Co$) is known[8,11] to be easily replaced by acetonitrile molecules under visible light irradiation to form the corresponding acetonitrile derivatives $[(ring)M(MeCN)_3]^+$. The latter have found wide use as synthons for the synthesis of the $[(ring)M]^+$ moieties.[12—19] The acetonitrile complexes substantially differ in thermal stability. For instance, the iron complex $[CpFe(MeCN)_3]^+$ decomposes at a temperature above –40 °C, whereas the cobalt analog $[(\eta\text{-}C_4Me_4)Co(MeCN)_3]^+$ is stable even in boiling acetonitrile. We found that the visible light irradiation of a solution of iron cyclohexadienyl complex **1** in MeCN also affords the corresponding acetonitrile derivative

Scheme 1



$[(\eta^5\text{-}C_6H_7)Fe(MeCN)_3]^+$ (**2**) (Scheme 1).* This complex is moderately stable in MeCN at 0 °C but rather rapidly decomposes at room temperature, which is accompanied by a change of the color from purple to brown. We failed to characterize complex **2** by ^1H NMR spectroscopy because, in addition to low stability, this complex has no characteristic signals of high intensity. This reaction in the presence of Bu^tNC produced the tris(isonitrile) complex $[(\eta^5\text{-}C_6H_7)Fe(Bu^tNC)_3]^+$ (**3**). It should be noted that in the case of the $[CpFe]^+$ moiety, the bis(isonitrile) complex $[CpFe(Bu^tNC)_2(MeCN)]^+$ is formed under analogous conditions as the only species.[11] Unlike complex **2**, complex **3** is stable at room temperature and was

* All cationic complexes were isolated as salts with the PF_6^- anion (anions are omitted in the schemes).

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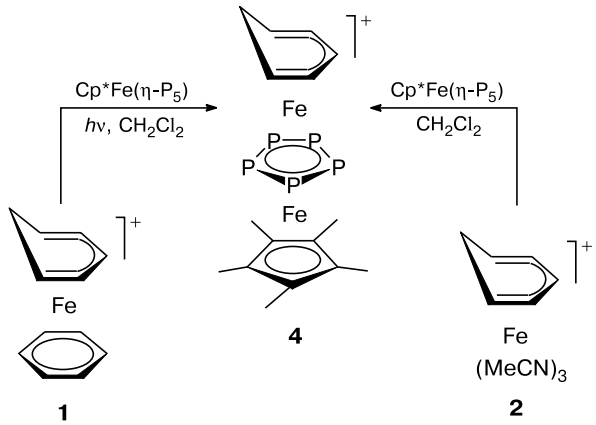
characterized by ^{1}H NMR spectroscopy and X-ray diffraction.

Interestingly, the reaction of benzene complex **1** with bipyridyl, like the analogous reaction of $[CpFe(\eta\text{-}C_6H_6)]^+$ with *o*-phenanthroline,[1] leads to the replacement of all organic ligands at the iron atom to form the $[Fe(bipy)_3]^{2+}$ dication.

Earlier, it has been demonstrated[3,9] that the visible light irradiation of the iron and cobalt benzene complexes $[(ring)M(\eta\text{-}C_6H_6)]^+$ in the presence of pentaphosphaferrocene $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$ affords triple-decker complexes with the bridging pentaphospholyl ligand $[(ring)M(\mu\text{-}\eta\text{:}\eta\text{-}cyclo\text{-}P_5)FeCp^*]^+$. The analogous reaction of cyclohexadienyl complex **1** with $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$ in dichloromethane produced the triple-decker cation $[(\eta^5\text{-}C_6H_7)Fe(\mu\text{-}\eta\text{:}\eta\text{-}cyclo\text{-}P_5)FeCp^*]^+$ (**4**) (Scheme 2).

Scheme 2



This reaction affords the target product in low yield (12%) because of a low reaction rate. A qualitative comparison allows the conclusion that the rate of displacement of benzene in the $[(ring)M(\eta\text{-}C_6H_6)]^+$ cations decreases in the following series: CpFe > $(\eta\text{-}C_4Me_4)$Co > > $(\eta^5\text{-}C_6H_7)$Fe. Complex **4** was synthesized in higher yield (28%) by the reaction of acetonitrile derivative **2** (prepared immediately before the reaction) with pentaphosphaferrocene in CH_2Cl_2. The triple-decker structure

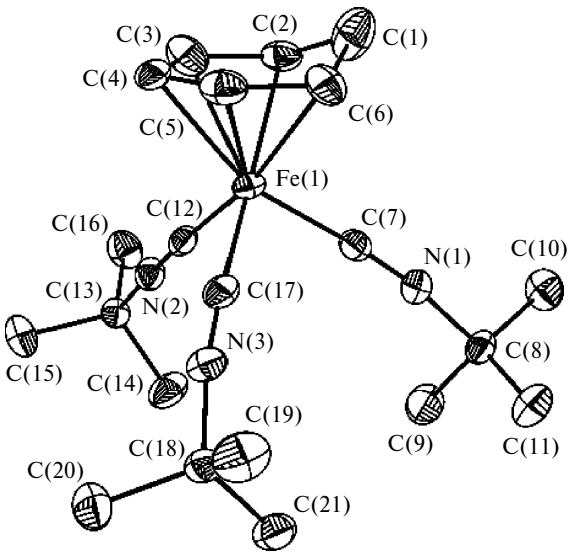


Fig. 1. Structure of cation **3** (displacement ellipsoids are drawn at the 50% probability level).

of complex **4** was established by ^{1}H and ^{31}P NMR spectroscopy. Earlier, we have demonstrated[6] that ^{31}P NMR spectroscopy is highly informative of the triple-decker structure of the $[(ring)M(\mu\text{-}\eta\text{:}\eta\text{-}cyclo\text{-}P_5)FeCp^*]^+$ complexes because the μ-pentaphospholyl ligand is characterized by the strong upfield shift of the ^{31}P signal ($\Delta\delta$ = 140—180 ppm) compared to the corresponding signal in the spectrum of the sandwich compound $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$. For cation **4**, $\Delta\delta \approx 160$ ppm.

The structure of the isonitrile complex **[3]**PF_6 was established by X-ray diffraction (Fig. 1, Table 1). The folding angle of the cyclohexadienyl ligand (dihedral angle between the planes through the C(2)C(3)C(4)C(5)C(6) and C(1)C(2)C(6) atoms) is 33.9°. The bonds between the carbon atoms of this ligand and the iron atom are substantially different in length. In particular, the Fe(1)—C(2) and Fe(1)—C(6) distances (aver., 2.147 Å) are longer than the Fe(1)—C(4) distance (2.107(2) Å). Only one iron complex with the unsubstituted cyclohexadienyl ligand, $(\eta^5\text{-}C_6H_7)Fe[(PPh_2CH_2)_3BPh]$,[20] is stored in the Cambridge Structural Database. The distance from the iron atom to the plane of the cyclohexadienyl ligand in this

Table 1. Selected bond lengths (*d*) and bond angles (ω) in cation **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Fe(1)—C(2)	2.157(2)	Fe(1)—C(12)	1.861(2)	C(5)—C(6)	1.403(3)	C(7)—Fe(1)—C(12)	89.77(7)
Fe(1)—C(3)	2.152(2)	Fe(1)—C(17)	1.852(2)	C(1)—C(6)	1.473(3)	C(7)—Fe(1)—C(17)	90.00(8)
Fe(1)—C(4)	2.107(2)	C(1)—C(2)	1.475(3)	C(7)—N(1)	1.161(2)	C(12)—Fe(1)—C(17)	90.40(8)
Fe(1)—C(5)	2.114(2)	C(2)—C(3)	1.381(3)	C(12)—N(2)	1.155(2)		
Fe(1)—C(6)	2.136(2)	C(3)—C(4)	1.409(3)	C(17)—N(3)	1.156(2)		
Fe(1)—C(7)	1.849(2)	C(4)—C(5)	1.402(3)				

complex (1.655 Å) is somewhat longer than the corresponding distance in complex **3** (1.625 Å), which is, apparently, associated with the difference in the steric and electronic effects in $[(PPh_2CH_2)_3BPh]^-$ and Bu^{t}NC.

To conclude, we established the ability of complex **1** to exchange benzene for other ligands under visible light irradiation. Hence, this complex can be considered as a promising synthon of the cationic species $[(\eta^5\text{-}C_6H_7)Fe]^+$.

Experimental

The reactions were carried out under argon with the use of anhydrous solvents purified according to standard procedures. The operations associated with the isolation of the reaction products were carried out in air. The starting compounds $[Fe(\eta\text{-}C_6H_6)_2](PF_6)_2$ [21] and Cp*Fe(η-cyclo-P_5) [6] were synthesized according to known procedures. The complex [**1**]PF_6 was synthesized by Nesmeyanov—Volkenau's method[22] with the use of THF as the solvent (see below). The irradiation was carried out in a Schlenk tube with a diameter of 15 mm using mercury luminescent lamps with a total power of 650 W. The Schlenk tube and the lamps were placed in a vessel cooled with running water and lined on the inside with aluminum foil. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz for ^{1}H and 161.98 MHz for ^{31}P).

[(η^5-Cyclohexadienyl)(η-benzene)iron] hexafluorophosphate, [(η^5-C_6H_7)Fe(η-C_6H_6)]PF_6 ([1]PF_6). Tetrahydrofuran (10 mL) was added to a mixture of $[Fe(\eta\text{-}C_6H_6)_2](PF_6)_2$ (1 g, 1.99 mmol) and $NaBH_4$ (84 mg, 2.21 mmol). The reaction mixture was stirred with cooling (at a temperature from −30 to 0 °C) for 2 h. The solvent was removed *in vacuo* and the solid residue was extracted with dichloromethane. The precipitate that formed after the addition of diethyl ether was filtered off and washed with diethyl ether. The complex [**1**]PF_6 was obtained as an orange solid in a yield of 577 mg (81%). Found (%): C, 39.59; H, 3.45. $C_{12}H_{13}F_6FeP$. Calculated (%): C, 40.26; H, 3.66. ^{1}H NMR (acetone-d_6), δ: 1.09 (d, 1 H, C_6H_7); 3.58 (m, 2 H, C_6H_7); 4.98 (m, 2 H, C_6H_7); 6.44 (s, 6 H, C_6H_6); 7.14 (m, 1 H, C_6H_7) (*cf.* lit. data[23]).

[(η^5-Cyclohexadienyl)tris(*tert*-butylisocyanide)iron] hexafluorophosphate, [(η^5-C_6H_7)Fe(Bu^{t}NC)$_3$]PF_6 ([3]PF_6). A solution of the complex [**1**]PF_6 (100 mg, 0.28 mmol) and Bu^{t}NC (0.1 mL, 0.89 mmol) in acetonitrile (5 mL) was irradiated for 6 h. The solvent was removed *in vacuo*. The residue was dissolved in a small amount of dichloromethane (2—3 mL) and eluted through a short (3—5 cm) alumina column. The yellow fraction was concentrated to ~2 mL and then diethyl ether (10 mL) and petroleum ether (10 mL) were successively added. The yellow precipitate that formed was filtered off and twice reprecipitated with diethyl ether from dichloromethane. The complex [**3**]PF_6 was obtained as a yellow solid in a yield of 103 mg (75%). Found (%): C, 47.82; H, 6.47; N, 7.92. $C_{21}H_{34}F_6FeN_3P$. Calculated (%): C, 47.64; H, 6.47; N, 7.94. ^{1}H NMR (acetonitrile-d_3), δ: 1.51 (s, 27 H, Bu^{t}NC); 2.54 (m, 1 H, C_6H_7); 2.87 (m, 2 H, C_6H_7); 4.90 (m, 2 H, C_6H_7); 6.34 (m, 1 H, C_6H_7).

Reaction of the complex [1]PF_6 with bipyridyl. A solution of the complex [**1**]PF_6 (80 mg, 0.22 mmol), bipyridyl (108 mg, 0.69 mmol), and NH_4PF_6 (40 mg, 0.25 mmol) in acetonitrile (5 mL) was irradiated for 5 h. The solvent was removed *in vacuo*. The residue was successively washed with diethyl ether and water to remove excess bipyridine and NH_4PF_6. The crude product was dried *in vacuo* and reprecipitated with diethyl ether from acetonitrile. The $[Fe(bipy)_3](PF_6)_2$ complex was obtained as a purple solid in a yield of 125 mg (69%). Found (%): C, 44.25; H, 2.90; N, 10.31. $C_{30}H_{24}F_{12}FeN_6P_2$. Calculated (%): C, 44.24; H, 2.97; N, 10.32. ^{1}H NMR (acetone-d_6), δ: 7.58 (t, 1 H); 7.73 (d, 1 H); 8.27 (t, 1 H); 8.84 (d, 1 H).

[(η^5-Cyclohexadienyl)iron](μ-η:η-pentaphospholyl)-[(η-pentamethylcyclopentadienyl)iron] hexafluorophosphate, [(η^5-C_6H_7)Fe(μ-η:η-*cyclo*-P_5)FeCp*]PF_6 ([4]PF_6). ***Method A.*** Dichloromethane (10 mL) was added to a mixture of the complex [**1**]PF_6 (38 mg, 0.11 mmol) and pentaphosphaferrocene Cp*Fe(η-*cyclo*-P_5) (44 mg, 0.13 mmol). The reaction mixture was irradiated for 6 h, concentrated to ~2 mL, and eluted through a silica gel column (10×1 cm) with a 10 : 1 CH_2Cl_2/Me_2CO mixture. The dark-gray fraction was collected, the solvent was removed *in vacuo*, and the residue was twice reprecipitated with diethyl ether from CH_2Cl_2. The complex [**4**]PF_6 was obtained as a gray solid in a yield of 8 mg (12%). Found (%): C, 30.84; H, 3.54. $C_{16}H_{22}F_6Fe_2P_6$. Calculated (%): C, 30.71; H, 3.54. ^{1}H NMR (acetone-d_6), δ: −0.36 (d, 1 H, C_6H_7); 1.21 (s, 15 H, Cp*); 2.21 (m, 1 H, C_6H_7); 2.46 (m, 2 H, C_6H_7); 3.44 (m, 2 H, C_6H_7); 6.14 (m, 1 H, C_6H_7). ^{31}P NMR (acetone-d_6), δ: −142.7 (sept, 1 P, PF_6^-); −3.3 (s, 5 P, *cyclo*-P_5).

Method B. A solution of the complex [**1**]PF_6 (80 mg, 0.22 mmol) in acetonitrile (3 mL) was irradiated for 4 h. The solvent was removed *in vacuo*, a solution of Cp*Fe(η-*cyclo*-P_5) (77 mg, 0.22 mmol) in CH_2Cl_2 (3 mL) was added to the residue, and the reaction mixture was stirred for ~24 h. The product was isolated as described above. The yield was 39 mg (28%).

X-ray diffraction study of the complex [3]PF_6. Yellow plate-like crystals with the composition $C_{21}H_{34}F_6FeN_3P$, which were grown by slow diffusion in a two-layer system consisting of a solution of the complex in CH_2Cl_2 and a Et_2O/petroleum ether mixture, are monoclinic. The unit cell parameters are a = 9.6038(6) Å, b = 19.0125(12) Å, c = 14.5770(9) Å, β = 105.2580(10)°, V = 2567.8(3) Å^3, space group $P2_1/n$, Z = 4, d_{calc} = 1.369 g cm^{-3}. A total of 28448 reflections were collected on a Bruker SMART APEX2 CCD diffractometer at 100 K (Mo-K_α radiation, $2\theta_{max}$ = 60.00°) from a single crystal of dimensions 0.45×0.23×0.20 mm. After merging of equivalent reflections, the data set consisted of 7483 independent reflections (R_{int} = 0.0434), which were used for the structure solution and refinement. An absorption correction (μ = 0.706 mm^{-1}) was applied with the use of the APEX2 program (T_{max} and T_{min} are 0.8717 and 0.7418, respectively).[24] The structure was solved by direct methods. All nonhydrogen atoms were located in difference electron density maps and refined based on F^2_{hkl} with anisotropic displacement parameters. All hydrogen atoms were positioned geometrically and refined using a riding model with U(H) = $n\cdot U$(C), where U(C) are the equivalent thermal parameters of the parent carbon atoms; n = 1.2 for the CH and CH_2 groups and n = 1.5 for the Me groups. The final R factors were as follows: R_1 = 0.0398 (calculated based on F_{hkl} for 5633 reflections with c $I > 2\sigma(I)$), wR_2 = 0.0982 (calculated based on F^2_{hkl} for a total of 7483 reflections), 289 parameters were refined, GOOF = 0.999. All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[25] The atomic coordinates, displacement parameters, and complete data on the geometric parameters were deposited with the Cambridge Structural Database.

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