^1H, ^{13}C, and ^{19}F NMR study of products of the interaction of the η^5-cyclopentadienyldicarbonyliron(II) anion, $CpFe(CO)_2^-$, with pentafluorobenzoyl chloride

T. V. Magdesieva, I. I. Kukhareva, D. P. Krut'ko, G. A. Artamkina, K. P. Butin, and I. P. Beletskaya*

Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 939 5546

Interaction of the η^5-cyclopentadienyldicarbonyliron(II) anion with pentafluorobenzoyl chloride affords $C_6F_5COFe(CO)_2Cp$, $CpFe(CO)_2C_6F_4COFe(CO)_2Cp$, and $CpFe(CO)_2C_6F_4C_6F_4Fe(CO)_2Cp$. The reaction products are characterized by ^1H, ^{13}C and ^{19}F NMR spectra.

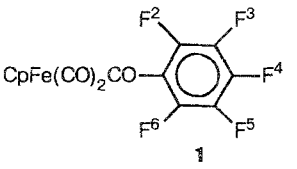
Key words: η^5-cyclopentadienyldicarbonyliron(II) ion, pentafluorobenzoyl chloride, arylation, aroylation; ^1H, ^{13}C, and ^{19}F NMR spectra.

Aryl and acyl derivatives of transition metals are of significant interest as intermediates in the carbonylation of aryl halides. To investigate the mechanism of metal carbonyl-catalyzed carbonylation of aryl halides, we synthesized the aroyl iron complex $C_6F_5COFe(CO)_2Cp$ (**1**). Earlier,[1] this complex was obtained in 17.5 % yield by the reaction of C_6F_5Li with the $CpFe(CO)_3^+$ cation. It should be pointed out that the $CpFe(CO)_3^+X^-$ complex, where $X^- = PF_6^-$, is also formed in a low (~12 %) yield.[2] We carried out the reaction of C_6F_5COCl with the η^5-cyclopentadienyldicarbonyliron anion.

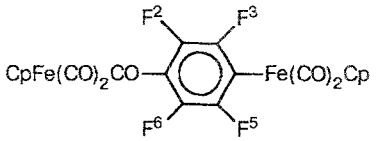
$$C_6F_5COCl + CpFe(CO)_2^- \longrightarrow \underset{\mathbf{1}}{C_6F_5COFe(CO)_2Cp} + Cl^-$$

However, in addition to aroyl complex **1** as the main reaction product, two minor products were isolated. The first product, 1-(η^5-cyclopentadienyldicarbonyliron)-4-[(η^5cyclopentadienyldicarbonyliron)carbonyl]tetrafluorobenzene, $CpFe(CO)_2C_6F_4COFe(CO)_2Cp$ (**2**), is the product of further nucleophilic substitution in the aromatic ring. The second rather unexpected product, is a dimer, 4,4'-bis(η^5-cyclopentadienyldicarbonyliron)octafluorodiphenyl $CpFe(CO)_2C_6F_4{-}C_6F_4Fe(CO)_2Cp$ (**3**), and the mechanism of its formation is obscure. The compounds obtained were identified on the basis of their spectral data (mass spectra, ^1H, ^{13}C, and ^{19}F NMR).

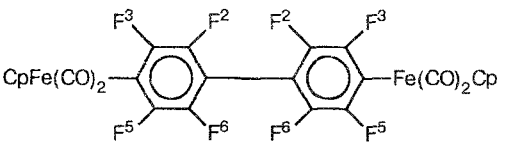
It is rather difficult to distinguish the $CpFe(CO)_2COAr$ and $CpFe(CO)_2Ar$ type compounds by mass spectrometry,[3] since the spectra of $CpFe(CO)_2COAr$ do not often contain the molecular ion peak. In addition, it has been reported,[3] that the characteristic peak with m/z 205 for the $[CpFe(CO)_2CO]^+$ fragment, which makes it possible to establish the presence of the acyl carbonyl group, is not always present in the spectra of $CpFe(CO)_2COAr$ either.



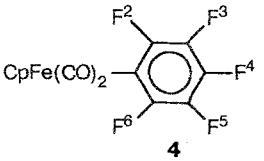
1



2



3



4

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 935—937, May, 1994.

In the mass spectra of compounds **1** and **2**, the molecular ion peak was only recorded for complex **1**, and it was of low intensity (*m/z* 372, I_{rel} = 0.3 %). Both compounds readily split the CO groups off, which accounts for the new signals that arise in their spectra. These signals correspond to $[M-CO]^+$, $[M-2CO]^+$, and $[M-3CO]^+$ fragments (*m/z* 344, 316, 288 and 502, 474, 446 for complexes **1** and **2**, respectively), and also to the $[M-5CO]^+$ fragment (*m/z* 390 for compound **2**).

In the IR spectra of both compounds, intense bands corresponding to the stretching vibrations of the CO-ligands bonded with the Fe atom, and a band for the acyl carbonyl group vibrations, are observed. The ν(CO) values observed coincide with the literature data[1,4] for aryl and aroyl cyclopentadienyldicarbonyliron complexes. However, the structure of the compounds under study cannot be unequivocally established by IR spectroscopy, and comparative analysis of ^1H, ^{13}C, and ^{19}F NMR spectra is necessary.

The parameters of the NMR spectra of the compounds obtained, as well as those of the aryl iron complex $CpFe(CO)_2C_6F_5$ (**4**) taken for comparison, are listed in Table 1.

^1H, ^{13}C and ^{19}F NMR spectra of complex **4** coincide well with the literature data.[5,6] In the carbonyl resonance area of the $^{13}C\{^1H\}$ NMR spectrum of complex **4**, a triplet is observed with the coupling constant $^4J_{C-F}$ = 4.6 Hz, which is due to the interaction of the ^{13}C nuclei in the carbonyl ligands with the ^{19}F nuclei in the *ortho*-position of the aryl ligand.

In the ^{19}F NMR spectrum of aroyl complex **1**, three multiplets with integral intensity ratios 2 : 1 : 2 are observed. They correspond to the *ortho*-, *para*-, and *meta*-F atoms in the pentafluorophenyl ring, which form an AA′MM′X spin system. The upfield shift of the signals of the *ortho*-F atoms relative to those in the spectrum of complex **4** is in keeping with the replacement of the $CpFe(CO)_2$-substituent by the $CpFe(CO)_2CO$-substituent. In the $^{13}C\{^1H\}$ NMR spectrum of complex **1** two singlets at δ 241.7 and 213.1 are observed, rather than triplets, which correspond to the acyl carbonyl and two CO-ligands, respectively. Thus, both coupling constants $^3J_{C-F}$ and $^5J_{C-F}$ for the carbon atoms of the carbonyl groups are less than 1 Hz.

The ^{19}F NMR spectrum of asymmetrical complex **2** is an AA′XX′ spin system, and the multiplet for fluorine atoms F(3) and F(5) in the *ortho*-positions relative to the $CpFe(CO)_2$-substituent is shifted downfield relative to the signals for F(2) and F(6). In the $^{13}C\{^1H\}$ NMR spectrum, there are three signals for carbonyl groups at δ 244.8, 214.0, and 213.7, which correspond to the acyl carbonyl, CO-ligands at the Fe atom directly bonded with the aromatic ring, and the carbonyl ligands at the Fe atom that is separated from this ring by the acyl group, respectively. In addition, in the $^{13}C\{^1H\}$ and ^1H NMR spectra of complex **2** two signals of equal intensity for nonequivalent cyclopentadienyl ligands are observed. Thus, the NMR spectral data allow unambiguous elucidation of the structures of the obtained complexes **1** and **2**.

The structure of compound **3** was established from mass spectral data, *viz.*, from the presence of peaks that correspond to the $[M-177]^+$ (*m/z* 473), $[M-177-CO]^+$ (*m/z* 445), and $[M-177-2CO]^+$ (*m/z* 417) fragments, as well as from the NMR spectral data (see Table 1).

In the ^1H and $^{13}C\{^1H\}$ NMR spectra of symmetrical compound **3**, there is one signal for each of the Cp- and carbonyl ligands at the Fe atoms directly bonded with the aromatic fluorosubstituted system. The presence of the $-C_6F_4C_6F_4-$ fragment in the complex is confirmed by the ^{19}F NMR spectrum, which contains two multiplets of equal intensity at δ −28.3 and −60.9, indicative of fluorine atoms in the *ortho*- (F(3) and F(5)) and *meta*- (F(2) and F(6)) positions relative to the $CpFe(CO)_2$-substituent. The absence of the mirror symmetry for the line splitting in these two multiplets unequivocally attests to the realization of an $(AA'XX')_2$ spin system.

The presence of compound **3** among the reaction products points to the fact that the processes that occur during the interaction of the η^5-cyclopentadienyldicarbonyliron anion with pentafluorobenzoyl chloride seem to be accompanied by the formation of radical species.

Table 1. Parameters of ^{19}F, ^{13}C, and ^1H NMR spectra

Compound	$\delta^{19}F^a$			$J_{^{13}CO-^{19}F}$/Hz	$\delta^{13}C^a$			δ^1H^a,
	F(2), F(6)	F(4)	F(3), F(5)		CO	—CO—[b]	Cp	Cp
1	−72.4	−80.1	−83.4	$^3J_{C-F}<1$, $^5J_{C-F}<1$	213.1 (s)	241.7 (s)	86.9	4.04
2	−72.3		−29.7	$^3J_{C-F}<1$, $^3J_{C-F}<1$, $^4J_{C-F}=4.7$	213.7 (s), 214.0 (t)	244.8 (s)	84.9 86.8	3.93 4.18
3	−60.9		−28.3	$^4J_{C-F}=4.5$	213.1 (t)		84.9	3.8
4	−29.3	−82.7	−85.6	$^4J_{C-F}=4.6$	213.8 (t)		84.8	3.9

[a] Solvent is C_6D_6, 303 K, δ ^1H and δ ^{13}C were measured relative to TMS (internal standard), δ ^{19}F were measured relative to CF_3COOH (external standard). [b] Acyl carbonyl group.

Experimental

IR spectra were recorded on a UR-20 instrument (in vaseline oil). ^1H, ^{13}C, and ^{19}F NMR spectra were registered on a Varian VXR-400 spectrometer with working frequency for protons 400 MHz. Mass spectra (EI) were obtained on an MX-1321-A instrument at 70 eV. R_f values are given for TLC on SiO_2-precoated Silufol plates.

Synthesis of compounds 1, 2, and 3. To obtain a solution of $CpFe(CO)_2^-K^+$ (*cf.* Ref. 7), 0.177 g (0.5 mmol) of $[CpFe(CO)_2]_2$ was reduced by a $NaK_{2.8}$ alloy (0.12 mL) in THF for 1.5 h in an argon atmosphere. The mixture obtained was added dropwise, using a syringe previously filled with argon, to a solution of 0.46 g (2 mmol) of C_6F_5COCl in 5 mL of THF with stirring over 1 h at −90 °C. Stirring was continued for an additional 0.5 h, and then the temperature of the mixture was gradually increased to 20 °C. The reaction mixture was chromatographed on a column (silica gel, 40/100 μ). The gradient elution from hexane to benzene (up to 100 % of C_6H_6) afforded (in order of elution) compounds **3**, **1**, and **2**, R_f (hexane–benzene, 1:1) 0.42, 0.23, and 0.05, respectively.

4,4′-Bis(η^5-cyclopentadienyldicarbonyliron)octafluorodiphenyl, $CpFe(CO)_2C_6F_4C_6F_4Fe(CO)_2Cp$ (3). Yield is 0.049 g (7.6 %). MS, *m/z* (I_{rel} (%)): 473 $[M-177]^+$ (1.8), 453 $[M-177-20]^+$ (3.4), 445 $[M-177-CO]^+$ (3), 417 $[M-177-2CO]^+$ (2.7), 297 $[M-325-CO]^+$ (4), 213 $[M-235-2CO-Fe]^+$ (26.6), 193 $[M-325-2CO-Fe-20]^+$ (70), 173 $[M-325-2CO-Fe-40]^+$ (82.7), 148 (28).

(η^5-Cyclopentadienyldicarbonyliron)carbonylpentafluorobenzene, $C_6F_5COFe(CO)_2Cp$ (1). Yield is 0.15 g (40 %). MS, *m/z* (I_{rel} (%)): 372 $[M]^+$ (0.3), 344 $[M-CO]^+$ (39), 316 $[M-2CO]^+$ (50), 288 $[M-3CO]^+$ (36), 268 $[M-3CO-20]^+$ (79), 195 $[M-177]^+$ (50), 121 (100).

1-(η^5-Cyclopentadienyldicarbonyliron)-4-[(η^5-cyclopentadienyldicarbonyliron)carbonyl]tetrafluorobenzene, $CpFe(CO)_2C_6F_4COFe(CO)_2Cp$ (2). Yield is 0.059 g (11 %). Found (%): C, 48.70; H, 2.27. $C_{21}H_{10}F_4Fe_2O_5$. Calculated (%): C, 47.50; H, 1.90. MS, *m/z* (I_{rel} (%)): 502 $[M-CO]^+$ (42), 474 $[M-2CO]^+$ (24), 446 $[M-3CO]^+$ (25), 390 $[M-5\,CO]^+$ (100), 121 (39).

References

1. P. M. Treichel and R. L. Shubkin, *Inorg. Chem.*, 1967, **6**, 1328.
2. P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 1966, **5**, 1177.
3. R. B. King, *J. Am. Chem. Soc.*, 1968, **90**, 1417.
4. R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, 1964, **2**, 15.
5. M. I. Bruce, *J. Chem. Soc. A*, 1968, **7**, 1459.
6. I. R. Batler, W. E. Lindsell, and M. Y. K. Thomas, *J. Organomet. Chem.*, 1984, **262**, 59.
7. J. E. Ellis and E. A. Flom, *J. Organomet. Chem.*, 1975, **99**, 263.

Received July 9, 1993