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Oxidatively induced coupling of fluorenyl ligands in 9-methylfluorenyliron complexes

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Abstract

Oxidation of zwitterionic 9-methylfluorenyliron complexes $[(\eta^6\text{-}9\text{-}CH_3C_{13}H_8)(\eta^5\text{-}C_5R_5)Fe]$ (R = H, (**I**) or CH_3 (**II**)) by $AgBF_4$ or $(C_5H_5)_2FeBF_4$ leads to binuclear dications $\{(\mu\text{-}\eta^6:\eta^6\text{-}9,9'\text{-}(CH_3)_2\text{-}9,9'\text{-}C_{13}H_8C_{13}H_8)[Fe(C_5R_5)]_2\}(PF_6)_2$ (R = H (**III**) or CH_3 (**IV**)) owing to coupling of two methylfluorenyl ligands at the 9 position. It was found that the presence of 9-methyl substituent in fluorenyl ligand plays an important role in determining the result of oxidation of **I** and **II**.

Keywords: Iron; Mössbauer spectroscopy

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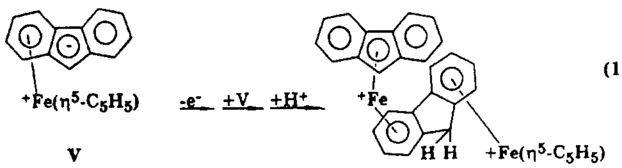
1. Introduction

There is great current interest in the development of new synthetic routes to organometallic compounds based on the reactions of transition metal odd-electron complexes. This methodology necessitates knowledge of regularities relating structures of 17- and 19-electron radicals and ion radicals with their reactivities, since even slight structural modifications can fully change the type of transformation [1,2]. As we have shown previously [3], chemical and electrochemical oxidation of (η^5-fluorenyl) (η^5-cyclopentadienyl)iron (**V**) leads to a binuclear complex with a bridging μ-$\eta^6:\eta^6$-fluorene ligand. Electro-oxidation of **V** and **II** was irreversible up to −70 °C as shown by CVA data and according to



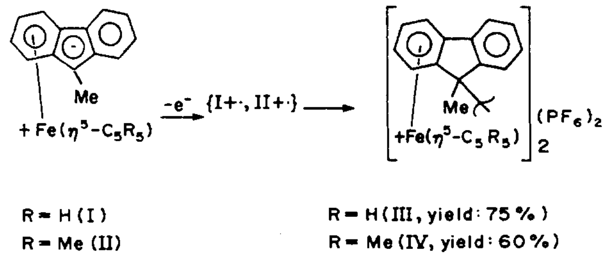
(1)

This work was aimed at elucidation of influence of methyl substituent at the 9 position of fluorenyl ligand on the outcome of oxidation of zwitterionic fluorenyl complexes **I** and **II**.

2. Results and discussion

Complexes **I** and **II** were generated in situ by deprotonation of the corresponding η^6-9-methylfluorene cations $[(\eta^6\text{-}9\text{-}CH_3C_{13}H_8)(\eta^5\text{-}C_5R_5)Fe]PF_6$ (R = H (**VI**) or CH_3 (**VII**)). Complexes **VI** and **VII** were prepared in their turn according to literature procedures from 9-methylfluorene and ferrocene [4] and from $FeBr(CO)_2\text{-}(\eta^5\text{-}C_5Me_5)$ [5] respectively.

Oxidation of **I** and **II** with $AgBF_4 \cdot$ 3dioxane gave **III** and **IV** respectively which were characterized by elemental analysis, Mössbauer spectroscopy, fast atom bombardment (FAB) mass spectroscopy and ^{13}C and ^1H NMR spectroscopy. On the basis of these data, **III** and **IV** were formulated as products of C(9)–C(9′) coupling of two fluorenyl ligands:



(2)

Complexes **III** and **IV** demonstrate in Mössbauer spectra only one unbroadened doublet, both the isotopic

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Table 1
The ^1H NMR spectra of **III**, **IV** and **VI** (solvent acetone-d^6: tetramethylsilane as the reference standard)

Compound	δ (ppm)				
	Cyclopentadienyl or CH_3 in pentamethylcyclo pentadienyl ring	9-H	9-Me	Coordinated six-membered ring	Non-coordinated six-membered ring
III	4.80 (s, 10H)	–	2.38 (s, 3H), 2.10(s)	5.26(m, 2H), 5.99(t, 2H), 6.21(t, 2H), 6.77(d, 2H)	7.69(t, 2H), 7.76(t, 2H), 7.94(m, 4H)
IV	1.77 (s, 30H)	–	2.18(s), 2.12(s)	6.70(d, 2H), 6.53(d, 2H), 6.16(m, 6H)	8.0(m, 2H), 7.78(m, 2H), 7.64(m, 6H)
VI	4.90 (s, 5H), {4.98 [a] (s, 5H)	4.67 (q, 1H, $J = 7.6$ Hz), (4.22 [a] (q, 1H, $J = 7.3$ Hz))	1.63 (d, 3H, $J = 7.6$ Hz), 1.99 [a](d, 3H, $J = 7.3$ Hz))	6.46–6.56 (m), 6.58 [a] (t), 6.95 [a](d), 7.09(d), 7.28(m)	7.55–7.67 (m, 2H), 7.77 (m, 1H), 8.15 (m, 1H)

[a] The signals of the 9-endo-Me isomer of the **VI** admixture.

shifts (IS) (**III**, 0.78 mm s^{-1}; **IV**, 0.786 mm s^{-1}; relative to sodium nitroprusside) and the quadrupole splitting constants (QSC) (**III**, 1.69 mm s^{-1}; **IV**, 1.32 mm s^{-1}) being very close to those of relative arenecyclopentadienyliron cations (compare with **VI** (IS, 0.78 mm s^{-1}; QSC, 1.76 mm s^{-1}) and **VII** (IS, 0.84 mm s^{-1}; QSC, 1.4 mm s^{-1}) [6,7].

This testifies to the d^6-electron configuration of iron in **III** and **IV**. FAB mass spectroscopy data also confirm the structures proposed. Thus, in the spectrum of **IV**, three intense peaks corresponding to basic fragment ions were observed: $\{[(CH_8C_{13}H_8)_2Fe_2(C_5H_5)_2]PF_6\}^+$ (745), $[(CH_3C_{13}H_8)_2Fe_2(C_5H_5)_2]^+$ (479) and $[(CH_3C_{13}H_8)Fe(C_5H_5)]^+$ (300).

The ^1H and ^{13}C NMR spectroscopy data for **III** and **IV** are presented in Tables 1 and 2. Both **III** and **IV** demonstrate two methyl singlets in the ^1H NMR spectrum. In our opinion this is stipulated by the existence of **III** and **IV** as a mixture of two diastereomeric meso (*RS*, *SR*) and racemic (*RR*, *SS*) forms.

Thus oxidation of zwitterions **I** and **II** proceeds as dimerization of ligand-to-ligand type of corresponding cation radicals ($\mathbf{I}^{\cdot+}$) and ($\mathbf{II}^{\cdot+}$). The whole process can be considered as oxidatively induced coupling of two fluorenyl moieties at the 9 position, this transformation being responsible for irreversibility of electrochemical oxidation of **I** and **II**. The results obtained demonstrate a very important role played by the 9-methyl substituent in determining the outcome of oxidation of **I** and **II** since the oxidation of the relative zwitterion **V** which has no substituent at the 9 position proceeds in a quite different route (see Eq. (1)). The reasons for this difference are being clarified at the present time.

3. Experimental details

All reactions were performed in an purified argon atmosphere. The solvents used were purified over sodium–benzophenone ketyl. The ^1H and ^{13}C NMR spectra were recorded on Brucker WP-200 SY and Varian VXR-400 instruments. FAB mass spectra were taken with a Kratos Concept instrument (energy of bombarding atoms, 8 keV; 2-nitrobenzyl alcohol as matrix). Brockman II activity degree alumina was used for chromatography. Mössbauer spectra were recorded with a conventional Mössbauer spectrometer. The source was ^{57}Co–Cr at room temperature; the samples were at

Table 2
The ^{13}C NMR spectra of **III**, **IV** and **VI** (solvent, acetone-d^6; tetramethylsilane as the reference standard)

Compound	δ (ppm)					
	Cyclopentadienyl ring	Me in C_5Me_5 ring	C(9)	Me at C(9)	Coordinated six-membered ring	Non-coordinated six-membered ring
III	78.12	–	58.04	20.22	79.82, 83.64, 84.12, 87.70, 101.9, 119.94	122.93, 127.11, 130.58, 131.12, 138.40, 149.02
IV	91.57	15.56	79.01, 66.04	23.25,	82.42, 84.59, 89.90, 91.62, 100.31, 113.3	123.26, 124.57, 130.82, 131.44, 134.68, 150.92
VI	79.35, 78.20 [a]	–	45.08, 43.40 [a]	20.35, 17.10 [a]	79.22 [b], 81.34, 81.73, 85.36 86.64, 87.01 87.43, 87.59, 104.71 105.5, 113.26, 114.80	123.67 [b], 123.72, 125.98, 126.37, 129.56, 129.66, 131.81, 131.84, 131.87, 137.62, 150.77, 151.21

[a] The signals of the 9-endo-Me isomer of **VI**.

[b] Resonances of both the 9-exo-Me and the 9-endo-Me isomers of **VI** are given.

liquid-nitrogen temperature. The IS values were obtained with reference to sodium nitroprusside. The Mössbauer spectra were fitted to lorentzians with a common program.

Complexes **II** and **VII** were obtained as reported earlier [8]. Complex **VI** was prepared from 9-methylfluorene by the method of Nesmeyanov et al. [4].

3.1. Oxidation of I and II with $AgBF_4$

Zwitterions **I** and **II** were generated by the action of ^{t}Bu OK (0.06g, 0.5 mmol) on 0.45 mmol of corresponding η^6-9-methylfluorene complexes **VI** and **VII** in tetrahydrofuran (25 ml). The mixture was stirred at room temperature for 1.5–2 h. 0.22 g (0.47 mmol) of $AgBF_4 \cdot$ 3dioxane was added to dark-green coloured solutions which in about 1 min became yellow–brown. The reaction mixtures were treated with NH_4PF_6 solution (0.08 g, 0.55 mmol) in 15 ml of H_2O. The solutions were filtered off from the metal silver precipitated and were concentrated under reduced pressure at 40–50 °C until oily precipitates formed. The latter were extracted with chloroform and chromatographed on alumina column (30 × 100 mm) in the same solvent as eluent. Two yellow bands were sequentially eluted. The minor bands appearing first correspond to η^6-9-methylfluorene complexes **VI** and **VII** whereas the main less mobile bands belong to dimers **III** and **IV**. After removal of chloroform in vacuo and reprecipitation from $CHCl_3$–Et_2O, mixtures of the following complexes were obtained: 75% **III**, 5% **VI**; 60% **IV**, 8% **VII**. Anal. of **III** Found: H, 3.50; C, 50.46. $C_{38}H_{32}F_{12}Fe_2P_2$ (3) Calc.: H, 3.60; C, 51.33%.

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