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The synthesis of binuclear half-open 1,1′-biferrocene: redox behavior and an interpretation of the ^{57}Fe Mössbauer data

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Abstract

Replacing the two Cp rings of 1,1′-biferrocene with pentadienyl ligands results in a cathodic shift of the redox potential for the ferrocene/ferrocenium couple and decreased quadrupole splitting in the Mössbauer spectrum and these findings can be accounted for by a change in the orbital population around the metal atom. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Half-open ferrocene; Half-open biferrocene; Redox behavior

1. Introduction

There is considerable interest in bridged metallocenes arising from the unusual properties of mixed-valence fulvalenyl bridged binuclear metallocenes and the potential for developing new types of catalysts involving electron transfer [1,2]. Moreover, the area of transition metal pentadienyl chemistry has received growing attention and one interesting aspect involves comparing electronic structural data for related open and closed metallocenes [3–7]. To date, it has been demonstrated that the (pentadienyl)iron systems are usually η^5 complexes with similar Fe–C distance exhibited in the cyclic counterpart ferrocene. However, the introduction of pentadienyl ligand in half-open (η^5-2,4-dimethylpentadienyl)-(η^5-cyclopentadienyl)iron and bis(η^5-2,4-dimethylpentadienyl)iron complexes results in drastic change in their redox potentials and ESR behavior [7]. Successive opening of one or both Cp rings of ferrocene results in cathodic shift of the redox potential, increased chemical lability, and vastly decreased *g* anisotropy in ESR spectra. As opposed to closed ferrocenium [8–10], ESR spectra of the half-open and open ferrocenium ions can be observed at room temperature [7]. In connection with our investigations on the electron transfer in mixed-valence biferrocenium cations [11], we became interested in the synthesis of binuclear half-open ferrocene (**1**).

2. Results and discussion

Compound **1** was prepared by a straightforward ‘one-pot’ procedure. Sodium cyclopentadienide was converted to fulvalene dianion **2** according to the procedure given by Mueller-Westerhoff et al. [12]. After the slow addition of a 1:1 mixture of K(2,4-C_7H_{11}) and **2** in THF to a slurry of $FeCl_2$ in THF solvent at -78°C under nitrogen was completed, the mixture was slowly warmed to room temperature and stirred for 1 h. The THF solvent was then removed under vacuum, and the product was extracted into hexane and filtered. The solvent was removed under vacuum and the red residue was chromatographed on neutral alumina (activity I) under N_2. The first band eluted with 50:1 hexane–THF solvent was a mixture of ferrocene, half-open ferrocene, and open ferrocene ($\sim 7\%$ yield). The second band was the desired compound **1** ($\sim 20\%$ yield) (see Section 3). A sample of bis(fulvalene)diiron was also obtained by further elution with benzene (Scheme 1).

This approach starts with simple material and is capable of being carried out without the isolation of any intermediates. Attempts to apply the substitution reaction on binuclear cyclopentadienyl-arene iron compound **3** to yield **1** were unsuccessful. However, ferrocene **5** was obtained from the cyclopentadienyl substitution reaction of (arene)iron cation **4** in 73% yield (Eq. (1)).

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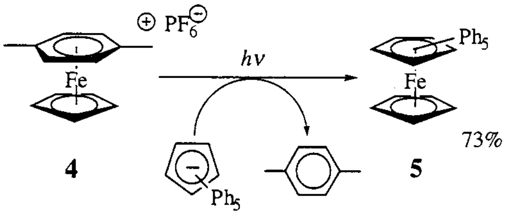


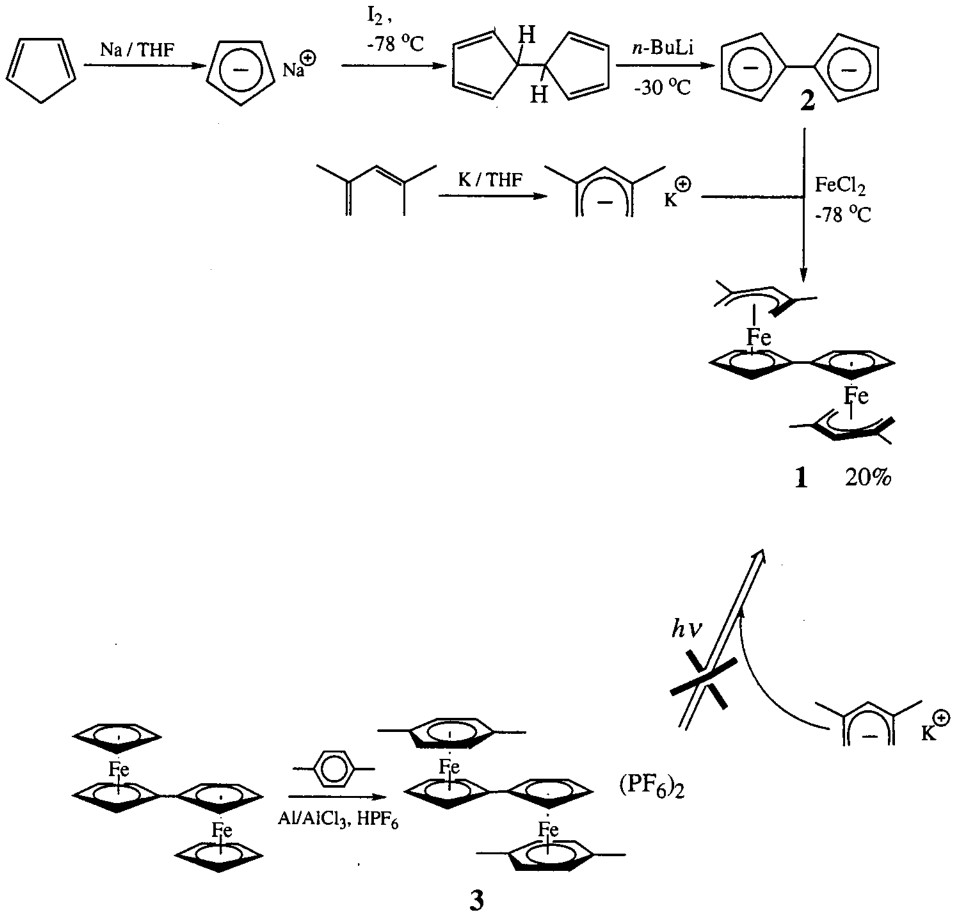
(1)

Table 1 lists electrochemical data obtained by cyclic voltammetry for **1** and some other relevant compounds **6**–**8** (Chart 1). Like the closed biferrocene [13], half-open biferrocene **1** also undergoes two successive one-electron oxidation to yield the mono- and then the dication. From the first $E_{1/2}$ value, half-open biferrocene **1** is oxidized easier than ferrocene and half-open ferrocene. As a substituent, the half-open ferrocenyl group clearly acts as net electron donor. A substituent effect can be calculated for the half-open ferrocenyl group (δ_{Fc}) by:

$$\delta_{Fc} = E_{1/2}(Fc_2^{+,0}) - E_{1/2}(Fc^{+,0}) = 0.22 - 0.16 = 0.06 \text{ V}$$

It has been demonstrated that the magnitude of the peak-to-peak separation ($\Delta E_{1/2}$ in Table 1) gives an indication of the interaction between two Fe sites [14–16]. Comparing the magnitude of $\Delta E_{1/2}$ between biferrocene **8** and half-open biferrocene **1** reveals that the magnitude of interaction between two Fe sites in **1** is smaller. Thus, the interaction between the two Fe sites is sensitive to the nature of the η^5-2,4-dimethyl-pentadienyl moiety. It must be the effect of ring opening on the electronic structure. A simple correlation of the MOs of closed and open ferrocenes reported by Gleiter et al. suggested [5] that the Fe 3d orbitals is strongly coupled to pentadienyl ligand in the open ferrocenes.

A primary driving force for the ^{57}Fe Mössbauer spectroscopic studies of compound **1** has been needed to increase the understanding of the bonding. ^{57}Fe Mössbauer spectrum was run at 300 K for **1**. In this case, one quadrupole-split doublet is observed. The resulting fitting parameters are given in Table 1. It is clear from the date summarized in Table 1 that the difference between half-open ferrocene **6** and half-open biferrocene **1** lies in the fact that the latter compound shows a smaller value of ΔE_Q (quadrupole splitting). Appropriate molecular orbital descriptions of the bonding in ferrocene, half-open ferrocene, and open ferrocene have been worked out by Gleiter and co-workers al. [5] and Ernst et al. [17] and account for related observations arising



Scheme 1.

Table 1
Cyclovoltammetric data and Mössbauer fitting parameters

Compound	$E_{1/2}$ [a]	Characteristics (°C)	$\Delta E_{1/2}$ [b]	K_c [c]	δ [d]	ΔE_Q [e]
Ferrocene	0.42	Rev, 25			0.542	2.453
6 [f]	0.222	Rev, 20			0.474	1.946
7	0.114	Irrev, 20			0.498	1.516
8	0.33	Rev, 25	0.32	2.65×10^5	0.520	2.360
	0.65	Rev, 25				
1	0.16	Rev, 25	0.20	2.45×10^3	0.290	1.912
	0.36	Semirev, 25				

[a] Half-wave potential referenced to Ag | AgCl.

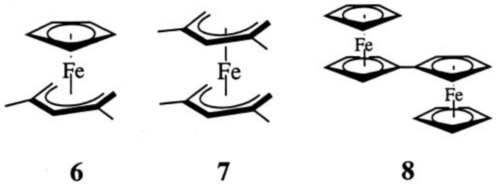
[b] Peak separation between half-wave potentials.

[c] Disproportionation equilibrium constant of (**2**, **2**) + (**3**, **3**) = 2(**2**, **3**) in which the abbreviations (**3**, **3**), (**2**, **3**) and (**2**, **2**) denote the dioxidized salt, the monooxidized salt and the neutral compound, respectively.

[d] Isomer shift referenced to iron-foil in mm s^{-1}.

[e] Quadrupole splitting in mm s^{-1}.

[f] From Ref. [7], solvent dimethoxyethane/$(C_4H_9)_4NClO_4$.



(Chart 1)

from the ^{57}Fe Mössbauer and ESR studies. Ernst suggested [17] that the d_{xy} and $d_{x^2-y^2}$ (e_2 set) electron density gives a positive contribution to ΔE_Q and the d_{xz} and d_{yz} (e_1 set) electron density gives a negative contribution. Thus, the observed decrease in the ΔE_Q going from ferrocene to open ferrocene is seen.

3. Supplementary information

The physical properties of **1** are as follows. ^{1}H-NMR (C_6D_6, ppm): − 0.56 (d, 4H, *endo*-CH_2), 1.76 (s, 12H, -CH_3), 2.50 (d, 4H, *exo*-CH_2), 4.02 (t, 4H, Cp), 4.07 (t, 4H, Cp), 5.06 (s, 2H, –CH). MS: M^+ at m/z 420. M.p.: 116–117°C.

Acknowledgements

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