Electrochemical Evidence for the Generation of New Sandwich Complexes of Iron; Cyclopentadienyl(arene)iron Anion and Cyclopentadienyl(cyclohexadienyl)iron Cation

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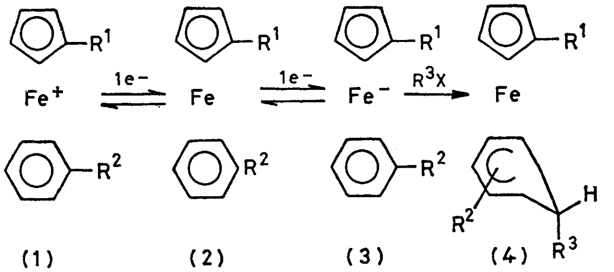
Summary Cyclopentadienyl(arene)iron cations may be successively reduced electrochemically to their corresponding radicals and anions, which react with electrophilic reagents leading to the substituted cyclohexadienyl(cyclopentadienyl)iron derivatives; the latter are electrochemically oxidized to the corresponding cations, isoelectronic with the well known ferricinium cation.

PARAMAGNETIC organometallic complexes have aroused great interest owing to their physical, chemical, and catalytic properties. In particular, several studies have reported the synthesis and reactivity of paramagnetic transition metal sandwich complexes during the last ten years.[1] We report here the redox properties of (η^5-cyclopentadienyl)(η^6-arene)iron and the (η^5-cyclopentadienyl)(η^5-cyclohexadienyl)iron derivatives and give electrochemical evidence for the formation of two new classes of complex: the (η^5-cyclopentadienyl)(η^6-arene)iron anions and the (η^5-cyclopentadienyl)(η^6-cyclohexadienyl)iron cations.

Dessy and his co-workers[2] and Nesmeyanov and his co-workers[3] reported some years ago the electrochemical behaviour of $[(C_5H_5)(C_6H_6)Fe]^+$ in non-aqueous media (two one-electron cathodic waves in dimethoxyethane or acetonitrile); both pointed out the reversibility of the first reduction step and the non-reversibility of the second one. More recently it was shown that, in aqueous media, the cyclopentadienyl(arene)iron derivatives generated by electrolysis of the corresponding cations are unstable and undergo either a decomposition or dimerization, depending on the acidity of the solution and on the nature of the ring substituents.[4]

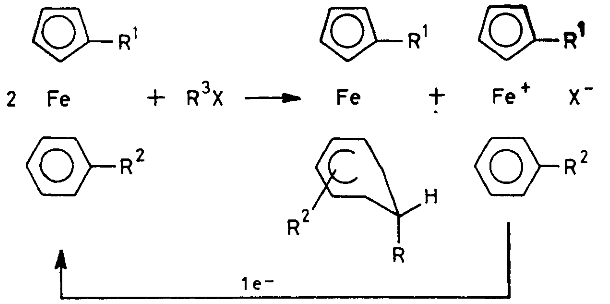
By contrast, we found that the electrochemical reduction of $[(\eta^5\text{-}C_5H_4R^1)(\eta^6\text{-}C_6H_5R^2)Fe]^+$ (**1**) in tetrahydrofuran (THF) affords, successively, the corresponding radical (**2**) and anion (**3**). We have used both of these complexes in the preparation of the (η^5-cyclopentadienyl)(η^5-cyclohexadienyl)iron derivatives (**4**) (Scheme 1).

Complex (**1**) in THF, with tetrabutylammonium hexafluorophosphate (0·2 M) as the supporting electrolyte, is reduced at mercury or platinum electrodes. Polarography shows two reduction waves [*e.g.* at $-1{\cdot}25$ and $-2{\cdot}13$ V *vs.* S.C.E. (standard calomel electrode) when $R^1 = R^2 =$ H]; both steps are mono-electronic as shown by coulometry. Cyclic voltammetry with mercury, platinum, or glassy carbon electrodes shows that the first stage is completely reversible even at a scan rate of 20 mV s^{-1}. It shows also



SCHEME 1.

that the second reduction step is highly reversible at a scan rate of 200 mV s^{-1}, but only slightly reversible at a scan rate of 20 mV s^{-1}. A thin-layer linear-potential-sweep voltammogram shows that the first electron-transfer reaction is still completely reversible even at a scan rate of 1 mV s^{-1}; the second one is completely irreversible at a scan rate of 10 mV s^{-1}. This indicates that the first mono-electronic reduction of (**1**) affords the stable radical (**2**), while the reduction of (**2**) affords the chemically unstable anion (**3**). This anion decomposes into cyclopentadienide anion, arene, and metallic iron. All these results were confirmed by bulk electrolyses which enabled us to isolate (**2**) but not (**3**). In spite of the instability of the anion (**3**, $R^1 = R^2 = H$) we were able to use this new species for the synthesis of the complexes (**4**),† which could be prepared by the electrolysis of a solution of (**1**) at the level of the second reduction step (consumption of 2 F/mol) in the presence of electrophiles [CO_2, H^+, or R^3X (R^3 = Me or Ph, X = I)]. They could also be prepared by the electrochemical reduction of (**1**) at the first mono-electronic cathodic wave; in this case 2 F/mol are also required for the complete reaction which is consistent with Scheme 2.



SCHEME 2.

The absence, in the i.r. spectra of the complexes (**4**), of an absorption at *ca.* 2770 cm^{-1}, except for (**4**, $R^2 = R^3 = H$), is consistent with a structure in which the tetrahedral carbon bears R^3 in the *exo* position.[5]

Two molecules of (**2**) react with one molecule of RX to give (**4**) and (**1**).[6] The mechanism of this sequence is identical to that of the reaction of cobaltocene with RX in which the radical process was established unequivocally (Scheme 3).[7] The electron transfer between the radical

$$(\eta^5\text{-}C_5H_5)_2Co + RX \rightarrow [(\eta^5\text{-}C_5H_5)_2Co]^+ + (RX)^{\cdot -}$$

$$(RX)^{\cdot -} \rightarrow R^{\cdot} + X^-$$

$$(\eta^5\text{-}C_5H_5)_2Co + R^{\cdot} \rightarrow (\eta^4\text{-}C_5H_5R)(\eta^5\text{-}C_5H_5)Co$$

SCHEME 3.

metallocene [*i.e.* $(\eta^5\text{-}C_5H_5)_2Co$ or $(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Fe$] and RX is the key step and depends on the reaction potentials. The very cathodic oxidation potential of $(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Fe$ promotes such an electron transfer and then a radical mechanism probably takes place instead of a nucleophilic addition which gives (**5**) directly.

The electrochemical behaviour of (**4**) is very dependent on the substituents. All of the complexes (**4**) studied, in THF, with $Bu_4N^+PF_6^-$ as the supporting electrolyte, are oxidized at mercury or platinum electrodes between +0·1 and +0·5 V *vs.* S.C.E. depending on the nature of the substituents.‡ The unsubstituted derivative ($R^1 = R^2 = R^3 = H$) in which the *exo*-substituent on the tetrahedral carbon is hydrogen gives a two-electron non-reversible oxidation wave. Electrolysis at the level of this anodic wave affords quantitatively, after consumption of 2 F/mol, the corresponding cation (**1**). This is similar to the results we obtained in the isoelectronic cyclopentadienyl(cyclopentadiene)cobalt series[8] and is fully consistent with Scheme 4.

$$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_7)Fe \rightarrow [(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Fe]^+ + H^+ + 2e^-$$

SCHEME 4.

When the *exo* group in (**4**) is not hydrogen, the polarogram shows a mono-electronic anodic wave. Cyclic voltammetry shows that this oxidation step is fully reversible even at the very low scan rate of 10 mV s^{-1}. Electrolysis in THF produces, after consumption of 1 F/mol, a green solution which exhibits the same polarogram as the initial material, except that the anodic wave becomes cathodic. This is consistent with Scheme 5.

$$(\eta^5\text{-}C_5H_4R^1)(\eta^5\text{-}C_6H_5R^2,R^3)\,Fe \overset{-1e^-}{\rightleftharpoons} (\eta^5\text{-}C_5H_4R^1)(\eta^5\text{-}C_6H_5R^2,R^3)Fe^+$$

(**5**)

SCHEME 5.

Complex (**5**) is isoelectronic with the well known ferricinium cation, but unlike the latter it is not chemically very stable at room temperature, our attempts to separate (**5**)

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† The structures of the derivatives (**4**) were established by comparing their spectroscopic and electrochemical characteristics with those of complexes prepared by the standard method.[5]

‡ All the complexes (**4**) also show a two-electron reduction wave at about −2·7 V *vs.* S.C.E.

from the large amount of the electrolyte support being unsuccessful.

The preliminary results we report here show that in the series of the cyclopentadienyl(arene)iron complexes, as in the ferrocene series,[9] complexes in which the central metallic atom is surrounded by 17, 18, 19, or 20 electrons could exist.

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