Journal of Organometallic Chemistry, 444 (1993) 179–183

JOM 23087

The redox behaviour of ferrocene derivatives

II *. 8-Ferrocenyl-2-hydroxytricyclo[7.3.1.$0^{2,7}$]tridecan-13-one and 2,2-dimethylpropylferrocene

Arnaldo Cinquantini, Giuliana Opromolla and Piero Zanello
Dipartimento di Chimica dell'Università di Siena, Pian dei Mantellini, 44, 53100 Siena (Italy)

Gianluca Giorgi
Centro Interdipartimentale di Analisi e Determinazioni Strutturali dell'Università di Siena, Via Mattioli 10, 53100 Siena (Italy)

(Received May 22, 1992)

Abstract

The electrochemical behaviour of 8-ferrocenyl-2-hydroxytricyclo [7.3.1.$0^{2,7}$] tridecan-13-one (**1**) has been examined in different non-aqueous solvents. It undergoes a one-electron oxidation to the corresponding monocation $[\mathbf{1}]^+$ at potential values slightly lower than that of unsubstituted ferrocene. $[\mathbf{1}]^+$ is stable under an inert atmosphere, but immediately decomposes upon exposure to air. Attempts to identify the relevant decomposition products failed. In a search for reactive sites in the 17-electron $[\mathbf{1}]^+$, an extended mass spectrometric study of the redox couple $\mathbf{1}/[\mathbf{1}]^+$ has been carried out. Their fragmentation pathways show that the skeleton of the ferrocenyl monocation is made labile by the primary loss of H_2O from the hydroxy group in the peripheral substituent, as well as by carbonyl-based fragmentations. Comparison with the electrochemical and mass spectral behaviour of the ferrocene molecule bearing the unreactive 2,2-dimethylpropyl substituent (**3**) supports the hypothesis that the high sensitivity of $[\mathbf{1}]^+$ to dioxygen arises from the fact that the removal of one electron makes the functional groups present in the lateral fused-rings assembly particularly reactive.

1. Introduction

Ferrocenes are redox-active molecules of interest in disciplines from organometallic biochemistry [2–6] to organometallic materials [7–10], and ferrocenium salts also exhibit pronounced antitumour activity [11].

We have recently started a programme to characterize the redox behaviour of ferrocene molecules, with particular interest in the chemical stability of their ferrocenium salts [1]. We report here a ferrocenium salt which is stable under an inert atmosphere, but unusually unstable in air. The relative unstability of metallocenes [12,13] and ferrocenium species [14] to dioxygen has been long recognized, but to our knowledge none decomposes as rapidly in air as the monocation of 8-ferrocenyl-2-hydroxytricyclo[7.3.1.$0^{2,7}$]tridecan-13-one ($[\mathbf{1}]^+$) does. The ferrocene parent **1** (Scheme 1), obtained by Claisen–Schmidt condensation of ferrocenecarboxaldehyde (**2**) with cyclohexanone [15], carries a bulky substituent which is labilized by removal of one electron, and could be responsible for the unusual reactivity towards dioxygen. Since mass spectrometric studies have shown that both the nature and the size of the substituents of the cyclopentadienyl rings as well as steric factors affect the fragmentation reactions of ferrocene complexes [16–18], we used this technique to test our hypothesis. 2,2-dimethylpropylferrocene (**3**), which bears an unreactive bulky substituent, was also used to compare and to contrast the unusual redox and mass spectrometric behaviour of the redox couple $\mathbf{1}/[\mathbf{1}]^+$.

Correspondence to: Professor P. Zanello.

* For Part I, see ref. 1.

0022-328X/93/$6.00

2. Results and discussion

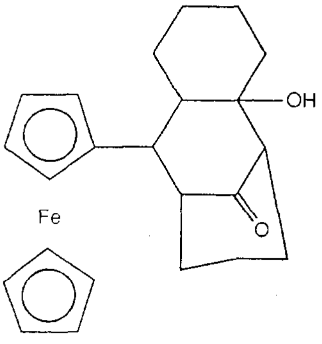
2.1. Electrochemical and spectral characterization of the redox couple *1* / *[1]*$^+$

Figures 1(a), (b) show the cyclic voltammetric responses given by **1** and its precursor **2** in acetonitrile solution. **1** undergoes reversible oxidation at potentials significantly less positive than **2**, indicating that the hydroxytricyclotridecanone fragment is significantly more electron-donating than the formyl substituent.

Controlled potential coulometry at the voltage corresponding to the anodic step of **1** ($E_w = +0.7$ V) indicates the consumption of one electron per molecule. At the same time, the starting pale-yellow solution turns to green. The final solution displays a cyclic voltammetric response complementary to that illustrated in Fig. 1(a). These findings indicate the chemical reversibility of the **1**/[**1**]$^+$ redox change under dinitrogen (see below).

Analysis [19] of the cyclic voltammograms relevant to the oxidation of **1** with a scan rate v varying from 0.02 V s^{-1} to 20.48 V s^{-1}, confirms that the one-electron removal is not complicated by subsequent chemical reactions. The ratio i_{pc}/i_{pa} is constant and equal to unity, the product $i_{pa}\,v^{-1/2}$ remains substantially constant, and the peak-to-peak separation increases progressively from 70 mV to 214 mV.

The departure of this last parameter from the value of 59 mV expected for an electrochemically reversible electron transfer is, in principle, attributable to reorganization within the complex **1** and/or the solvent, which raises the barrier to electron-transfer, slowing down the relevant rate, and also to uncompensated solution resistances. Since, under the present experimental conditions, the one-electron oxidation of ferrocene is known to involve minimal structural reorganization, [20–22], and displays a similar trend of ΔE_p with scan rate, the removal of one electron from **1** should also cause minimal geometrical rearrangement [23–25].



Scheme 1.

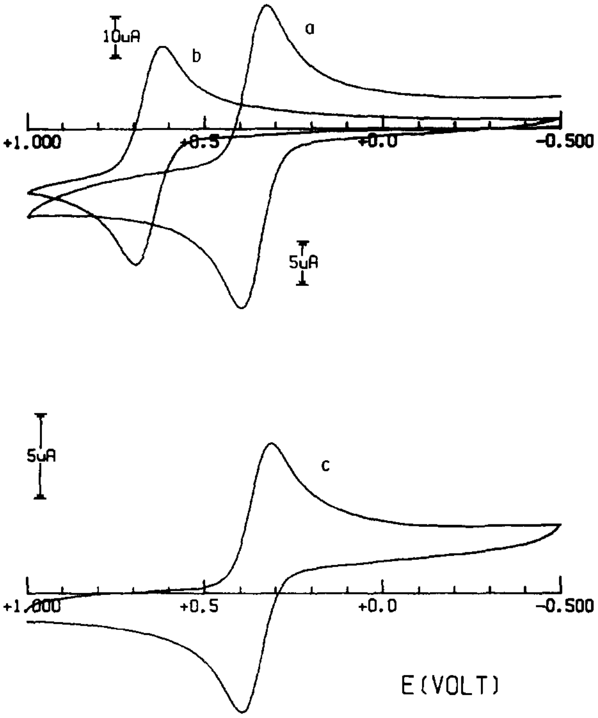


Fig. 1. Cyclic voltammograms recorded at a platinum electrode on MeCN solutions containing [NEt_4][ClO_4] (0.2 mol dm^{-3}) and (a) **1** (1.3×10^{-3} mol dm^{-3}), (b) **2** (2.5×10^{-3} mol dm^{-3}), (c) [**1**] [BF_4] (2.3×10^{-3} mol dm^{-3}). Scan rate 0.05 V s^{-1}.

The monocation [**1**]$^+$ can thus be easily prepared either by macroelectrolysis or by chemical oxidation with mild oxidizing agents such as $NOBF_4$, $AgPF_6$, and $[(C_5H_5)_2Fe]^+$. Oxidation of an orange-yellow solution of **1** by $NOBF_4$ in a 1 : 1 ratio affords a green solution which rapidly turns brown on standing in air. The final solution exhibits no redox activity of any kind. Under dinitrogen, the green solution is indefinitely stable. Evaporation of the solvent leaves a green residue which gives rise to the voltammetric pattern shown in Fig. 1(c), clearly due to [**1**]$^+$, when dissolved in acetonitrile solution.

The UV-visible spectrum of **1** in acetonitrile exhibits a d–d transition band at 449 nm ($\epsilon = 108$ M^{-1} cm^{-1}) and a charge-transfer band at 217 nm ($\epsilon = 10400$ M^{-1} cm^{-1}). Upon oxidation, the ligand field transition shifts to 630 nm ($\epsilon = 361$ M^{-1} cm^{-1}), whereas the adsorption in the UV region remains almost unchanged ($\lambda_{max} = 218$ nm, $\epsilon = 34600$ M^{-1} cm^{-1}).

We have been unable to obtain direct chemical information on the solvent-dependent decomposition of [**1**]$^+$ in air. We therefore performed an extended mass spectrometric investigation on the components of the redox couple **1**/[**1**]$^+$.

TABLE 1. Significant mass spectral data for **1**

m/z (relative abundances, %)
393 (31.5), 392 (100), 390 (6.6), 374 (25.1), 326 (2.8), 296 (16.4), 295 (73.2), 294 (12.1), 293 (4.9), 230 (6.0), 229 (36.8), 227 (3.0), 200 (4.5), 199 (24.3), 197 (2.2), 187 (4.8), 186 (40.0), 121 (21.0), 56 (5.6)

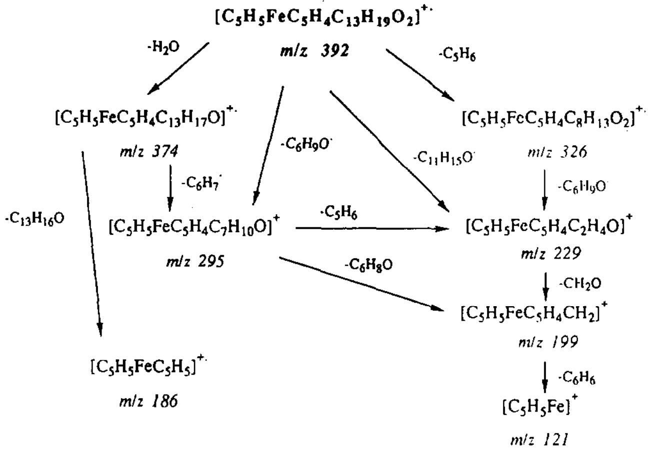
2.2. Mass spectrometric behaviour of the redox couple 1/[1]$^+$

The significant mass spectral data for **1** are reported in Table 1. The molecular ion (m/z 392) is also the base peak. The main fragmentation pathways, confirmed by collision-induced dissociation (CID) spectra and high-resolution mass data (Table 2), are shown in scheme 2.

The molecular ion fragments mainly by loss of H_2O, C_5H_6, $C_6H_9O^{\cdot}$ and $C_{11}H_{15}O$, yielding product ions at m/z 374, 326, 295 and 229 respectively. Further losses of C_5H_6 and $C_6H_9O^{\cdot}$ are observed by the ions at m/z 295 and 326 respectively. Typical fragmentations of the ferrocene moiety (m/z 186, 56) are also present.

The mass spectrum of deuterium-labelled **1** (base and molecular peak at m/z 393) shows fragment peaks at m/z 374, 295 and 229, indicating that the C=O group in the peripheral substituent is involved only in the loss of CH_2O from the ion at m/z 229 and of C_6H_8O from the ion at m/z 295, producing the ion $[C_5H_5FeC_5H_4CH_2]^+$ (m/z 199). This is also present in the mass spectra of alkyl [16] and acyl [26] derivatives of ferrocene, as well as in spiroferrocenophanes [27].

The mass spectrum of **1** does not show the cleavage of the metal-unsubstituted cyclopentadienyl bond. This can be ascribed to the poor interaction between the iron and the oxygen atoms in the gas phase [18], as happens in the solid state. In fact, in the crystal of **1** the Fe ··· O(=C) and Fe ··· O(H) distances are 5.87 Å and 6.14 Å respectively [15]. For the same reason, the migration of the OH group to the metal is not observed. This also excludes the direct participation of the metal in the dehydration process [17], for which we propose a 1,4-elimination mechanism usually observed in aliphatic, alicyclic and aromatic alcohols [28].



Scheme 2. Main fragmentation pathways for compound **1**.

TABLE 2. High-resolution mass spectral data for **1**

Ion	Observed mass (μ)	Error (μ^{-3})
$[C_{23}H_{28}O_2Fe]^{+\cdot}$	392.1441	−0.2
$[C_{23}H_{26}OFe]^{+\cdot}$	374.1321	1.2
$[C_{18}H_{22}O_2Fe]^{+\cdot}$	326.0957	1.2
$[C_{17}H_{19}OFe]^+$	295.0796	−1.0
$[C_{12}H_{13}OFe]^+$	229.0324	−0.8
$[C_{11}H_{11}Fe]^+$	199.0197	1.3
$[C_{10}H_{10}Fe]^{+\cdot}$	186.0121	1.1
$[C_5H_5Fe]^+$	120.9750	−0.9

However, the oxidation state of the metal seems to affect the extent of the fragmentation reactions. The mass spectrum of $[\mathbf{1}]^+$ is time dependent. At the beginning of the ionization process, the molecular and base peak is again at m/z 392. The relative intensity of the dehydrated monocation $[M-H_2O]^{+\cdot}$ (m/z 374) is 82%. Nevertheless, the intensity of the molecular ion $[M]^{+\cdot}$ rapidly decreases with time, while that of the ion $[M-H_2O]^{+\cdot}$ increases. After about 3 min, the relative intensities of the ions $[M]^{+\cdot}$ and $[M-H_2O]^{+\cdot}$ are 11% and 100% respectively. In addition, the height of the peak at m/z 199, arising from carbonyl-based fragmentations, reduces from 24% to 8%.

The ion $[M-H_2O]^{+\cdot}$ further fragments to $[C_5H_5FeC_5H_4C_{12}H_{17}]^{+\cdot}$ (theoretical 346.1384, measured 346.1373) by loss of CO. This process is not observed for **1**.

In the mass spectra measured at 20 eV, the trend in relative intensities of the $[M]^{+\cdot}$ and $[M-H_2O]^{+\cdot}$ ions is the same as observed at 70 eV.

To establish further the role of the substituent of the cyclopentadienyl ring on the reactivity of the 17-electron ferrocenium ions, a comparison with the 2,2-dimethylpropyl-substituted ferrocenium $[\mathbf{3}]^+$ was made. The alkyl chain is inert but electron removal in the parent falls at about the same potential as $[\mathbf{1}]^+$ (see Table 3).

In the mass spectrum of $[\mathbf{3}]^+$ the intensities of the molecular ion (m/z 256) as well as those of the main fragments ($[M-C_2H_5]^+$ (m/z 225), $[M-C_5H_9]^+$ (m/z 185)) are invariant with the time.

It seems reasonable that the reactive carbonyl and hydroxy groups in the three fused peripheral rings may be responsible for the unusual behaviour of $[\mathbf{1}]^+$. It is

TABLE 3. Formal electrode potentials (in volts and peak-to-peak separation in millivolts, at 0.05 V s^{-1}) for the ferrocenyl complexes **1**–**3**, in different non-aqueous solvents

Complex	$E^{\circ\prime}$	ΔE_p	Solvent
1	+0.36	70	MeCN [a]
	+0.44	70	CH_2Cl_2 [b]
	+0.52	90	THF [b]
2	+0.66	78	MeCN [a]
	+0.73	78	CH_2Cl_2 [b]
	+0.77	82	THF [b]
3	+0.32	78	MeCN [a]
	+0.37	80	CH_2Cl_2 [b]
	+0.51	98	THF [b]
$[Fe(C_5H_5)_2]$	+0.38	70	MeCN [a]
	+0.44	72	CH_2Cl_2 [b]
	+0.54	100	THF [b]
$[Fe(C_5Me_5)_2]$	−0.12	70	MeCN [a]
	−0.10	76	CH_2Cl_2 [b]

[a] Supporting electrolyte $[NEt_4][ClO_4]$ (0.2 mol dm^{-3}). [b] Supporting electrolyte $[NBu_4][ClO_4]$ (0.2 mol dm^{-3}).

likely that the dehydration process is the first step in the fast complete decomposition upon exposure to air. Samples from our oxidation of $[\mathbf{1}]^+$ show no peaks attributable either to ferrocene (m/z 186) or to iron-cyclopentadienyl (m/z 121) fragmentations.

2.3. Electrochemical characterization of the 3/[3]$^+$ redox couple

The cyclic voltammogram of **3** in acetonitrile solution displays an anodic step which involves a chemically reversible one-electron removal as determined by controlled potential coulometry. On changing from **3** to $[\mathbf{3}]^+$, the golden-yellow solution turns indigo.

3. Experimental details

8-ferrocenyl-2-hydroxytricyclo [7.3.1.0^{2,7}] tridecan-13-one (**1**) was prepared according to the literature method [15]. Deuterium-labelling at the –OH position was obtained by dissolving **1** in CD_3OD and $CDCl_3$ (Fluka, NMR grade) and allowing the solution to stay at room temperature for some days.

The materials and apparatus used for electrochemistry have been described elsewhere [1]. Potential values are referred to the saturated calomel electrode (SCE).

Mass spectra were measured on a double-focusing VG 70-250S mass spectrometer operating in the electron ionization mode at 70 eV, emission current 0.2 mA, with a source temperature of 180°C and an accelerating voltage of 8 kV. The resolution was 2000 M/ΔM (10% of valley def.). The samples were introduced via the direct inlet system at room temperature. Collision-induced dissociation spectra were obtained by computer-controlled B/E and B^2/E linked scans. Argon was introduced as activating gas in the collision cell situated in the first free region until the intensity of the main beam was reduced to 50% of its original value. Data acquisition and analysis of the spectra were performed with a VG 11-250J data system equipped with a Digital PDP 11/83 minicomputer. High-resolution mass measurements were performed at resolution 8000 M/ΔM against perfluorokerosene standard (Fluka) under the control of the data system.

References

1 P. Zanello, G. Opromolla, M. Casarin, M. Herberhold and P. Leitner, *J. Organomet. Chem.*, *443* (1993) 199.
2 P. D. Beer, *Chem. Soc. Rev.*, *18* (1989) 409.
3 A. Harada, Y. Hu, S. Yamamoto and S. Takahashi, *J. Chem. Soc., Dalton Trans.* (1988) 729, and references cited therein.
4 M. D. Lowery, R. J. Wittebort, M. Sorai and D. N. Hendrickson, *J. Am. Chem. Soc.*, *112* (1990) 4214.
5 J. Saji, K. Hoshino and A. Aoyagui, *J. Am. Chem. Soc.*, *107* (1985) 6865.
6 J. C. Medina, I. Gay, Z. Chen, L. Echegoyen and G. W. Gokel, *J. Am. Chem. Soc.*, *113* (1991) 365.
7 M. H. Desbois, J. Guilin, J.-P. Mariot, F. Varret and D. Astruc, *J. Chem. Soc., Chem. Commun.*, (1985) 447, and references cited therein.
8 W. T. Yap, E. A. Blubaugh, R. A. Durst and C. K. Chiang, *J. Electrochem. Soc.*, *136* (1989) 2588, and references cited therein.
9 C. Zou and M. S. Wrighton, *J. Am. Chem. Soc.*, *112* (1990) 7578, and references cited therein.
10 J. S. Miller, A. J. Epstein and W. M. Reiff, *Acc. Chem. Res.*, *21* (1988) 114.
11 P. Köpf-Maier and H. Köpf, *Chem. Rev.*, *87* (1987) 1137.
12 H. Kojima, S. Takahashi and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, (1973) 230.
13 F. Bottomley, D. E. Paez and P. S. White, *J. Am. Chem. Soc.*, *104* (1982) 5651.
14 J. K. Bashkin and P. J. Kinlen, *Inorg. Chem.*, *29* (1990) 4507.
15 R. E. Bozak, M. Hadi, S. Husebye, K. M. -Moe and D. Shaieb, *Acta Chem. Scand.*, *A42* (1988) 454.
16 D. T. Roberts, Jr., W. F. Little and M. M. Bursey, *J. Am. Chem. Soc.*, *89* (1967) 6156.
17 Yu. S. Nekrasov, V. F. Sizoi, D. V. Zagorevskii and N. I. Vasyukova, *Org. Mass Spectrom.*, *14* (1979) 22.
18 Yu. S. Nekrasov and D. V. Zagorevskii, *Org. Mass Spectrom.*, *26* (1991) 733.
19 E. R. Brown and J. R. Sandifer, in B. W. Rossiter and J. F. Hamilton (eds.), *Physical Methods of Chemistry. Electrochemical Methods*, Vol. 2, Wiley, New York, 1986, Chap. 4
20 P. Seiler and J. D. Dunitz, *Acta Crystallogr.*, *B35* (1979) 1068.
21 M. R. Churchill, A. G. Lander and A. L. Rheingold, *Inorg. Chem.*, *20* (1981) 849.
22 S. J. Geib, A. L. Rheingold, T. Y. Dong and D. N. Hendrickson, *J. Organomet. Chem.*, *312* (1986) 241.
23 P. Zanello, in I. Bernal (ed.), *Stereochemistry of Organometallic and Inorganic Compounds*, Vol. 4, Elsevier, Amsterdam, 1990, p. 181.

24 P. Zanello, in I. Bernal (ed.), *Stereochemistry of Organometallic and Inorganic Compounds*, Vol. 5, Elsevier, Amsterdam, in press.
25 P. Zanello, *Struct. Bonding (Berlin), 79* (1992) 101.
26 V. Rapic and N. Filipovic-Marinic, *Org. Mass Spectrom., 20* (1985) 688.
27 J. Mirek, S. Rachwal, T. Gorecki, B. Kawalek, P. Milart and E. Szneler, *J Organomet. Chem.*, 344 (1988) 363.
28 H. Budzikiewicz, C. Djerassi and H. Williams, in *Interpretation of Mass Spectra of Organic Compounds*, Holden-Day, San Francisco, CA, 1964.