ELSEVIER

Journal of Organometallic Chemistry 637–639 (2001) 823–826

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Note

Improved electrochemistry of multi-ferrocenyl compounds: investigation of biferrocene, terferrocene, bis(fulvalene)diiron and diferrocenylethane in dichloromethane using $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte

Nicole Camire [a], Ulrich T. Mueller-Westerhoff [b,*], William E. Geiger [a,*]

[a] *Department of Chemistry, University of Vermont, Burlington, VT 05405, USA*
[b] *Department of Chemistry, University of Connecticut, Storrs, CT 06269-3060, USA*

Received 2 February 2001; received in revised form 28 March 2001; accepted 8 April 2001

Abstract

Cyclic voltammetry in CH_2Cl_2 containing 0.1 M $[NBu_4][B(C_6F_5)_4]$ gives enhanced behavior for the oxidation of complexes containing two or more ferrocenyl groups, owing to better stabilities and solubilities of the multiply-charged oxidation products. The lower ion-pairing interaction of the anion $[B(C_6F_5)_4]^-$ with oligoferrocenyl multiply-charged cations leads to larger separations of the oxidation waves which may be exploited in studies of mixed-valent systems. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electrochemistry; Biferrocene; Bis(fulvalene)diiron; Perfluorophenyl borate; Supporting electrolyte; Cyclic voltammetry

1. Introduction

The facile and often simple electron-transfer (ET) properties of ferrocenyl groups are a major factor in their widespread usage in multimetallic mixed-valent, dendrimeric, and polymeric chemistries [1]. Electrochemical properties, especially $\Delta E_{1/2}$ values, [2] are routinely used to address the degree of electronic interactions between the ferrocenyl groups. Representative examples of this approach are readily found in both older [3–5] and more recent [6] literature.

Acetonitrile and dichloromethane are the two solvents most often used in these studies. Although both are excellent electrochemical solvents [7], each has drawbacks when applied to the oxidation reactions of multi-ferrocenyl compounds. Many of the neutral (Fe^{II}) complexes (e.g. bis(fulvalene)diiron, BFD, **3**) exhibit low solubilities in CH_3CN and some multiply-oxidized Fe^{III} cations exhibit follow-up reactions in this solvent, limiting the chemical reversibility of second [3], third [5], or even higher [8] oxidation waves of oligoferrocenyl systems. Although CH_2Cl_2 may overcome these problems, it has one important shortcoming arising from another solubility problem: because of its low polarity, many multiply-charged cations are poorly soluble in dichloromethane. This factor often gives rise to electrode passivation and/or stripping-type CV waves [9] which obscure the thermodynamic and mechanistic information ideally available in voltammetry experiments. A common experimental compromise is to use mixtures of CH_3CN and CH_2Cl_2 [5,8,9a,10], usually in a 1:1 ratio [11], in the hopes of moderating these solvent-based effects. Virtually all the literature experiments were conducted with a supporting electrolyte consisting of a tetraalkylammonium ($[NR_4]^+$) cation and an anion of either $[PF_6]^-$, $[BF_4]^-$ or $[ClO_4]^-$.

Large weakly-coordinating anions have provided a new way to approach solubilities of highly charged cations [12]. Usage of a tetrabutylammonium salt of

---

* Corresponding authors. Fax: +1-802-656-8705.
E-mail address: wgeiger@zoo.uvm.edu (W.E. Geiger).

0022-328X/01/$ - see front matter
PII: S0022-328X(01)00956-1

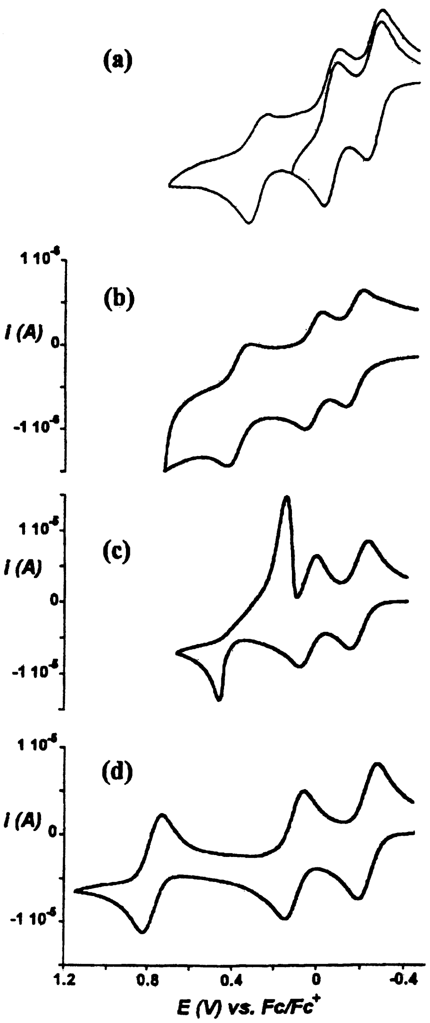


Fig. 1. CV scans at $\nu = 0.2$ V s^{-1} for terferrocene (**2**) in different nonaqueous solutions: (a) reproduction of scan from Ref. [5] in 1:1 CH_3CN:CH_2Cl_2/0.1 M $[NBu_4][PF_6]$; (b) 0.4 mM **2** in CH_3CN/0.1 M $[NBu_4][PF_6]$; (c) 0.4 mM **2** in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$; (d) 0.4 mM **2** in CH_2Cl_2/0.1 M $[NBu_4][B(C_6F_5)_4]$.

one of these anions, namely $[B\{C_6H_3(CF_3)_2\}_4]^-$, as a supporting electrolyte was first reported by Mann and co-workers in a study of the oxidative processes of several metal complexes [13]. Extension of this electrochemical approach to $[NR_4]^+$ salts of the tetrakis(pentafluorophenyl)borate anion, $[B(C_6F_5)_4]^-$, was recently shown to expand the options for electrochemistry in low-polarity solvents [14]. The purpose of the present communication is twofold: first, to demonstrate that the electrode behavior of multiply-oxidised oligoferrocenyl complexes in CH_2Cl_2/0.1 M $[NBu_4][B(C_6F_5)_4]$ is completely consistent with high solubilities and stabilities of the oxidation products, and: second, to point out the large increases in $\Delta E_{1/2}$ that may potentially arise when weakly ion-pairing anions like $[B(C_6F_5)_4]^-$ replace $[PF_6]^-$, $[BF_4]^-$ or $[ClO_4]^-$. The second point suggests that the $\Delta E_{1/2}$ values of mixed-valent systems can be systematically changed by altering the identity of the supporting electrolyte anion.

2. Results and discussion

Cyclic voltammetry (CV) results on terferrocene (TF, **2**) intended to illustrate the major points of this communication are collected in Fig. 1. The originally-reported [5] scan in 1:1 CH_3CN:$CH_2Cl_2 + 0.1$ M $[NBu_4][PF_6]$, reproduced in Fig. 1(a), shows all three oxidation waves for the ET sequence $TF^{0/1+/2+/3+}$. The poor chemical reversibility for the third oxidation wave suggests decomposition of the trication TF^{3+}, an effect also observed in pure CH_3CN (Fig. 1(b)). Oxidative behavior in pure CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ (Fig. 1(c)) is both reversible and well-behaved through the first and second waves, but strong adsorption of the trication is seen when the third wave is included. When, however, 0.1 M $[NBu_4][B(C_6F_5)_4]$ is used as the supporting electrolyte in CH_2Cl_2, all three oxidations are Nernstian, and give stable products which are apparently fully soluble (Fig. 1(d)). The $E_{1/2}$ values can be confidently measured (Table 1) as $E^1_{1/2} = -0.23$ V, $E^2_{1/2} = 0.11$ V, $E^3_{1/2} = 0.79$ V (vs. Fc). The persistence of TF^{3+} suggests that the heretofore spectrally elusive [5] trication might be amenable to physical characterization.

Table 1
$E_{1/2}$ values (V) vs. ferrocene and $\Delta E_{1/2}$ values (mV) for biferrocene (**1**), terferrocene (**2**), bis(fulvalene)diiron (**3**) and bis(ferrocenyl)ethane (**4**)

Compound	Solvent	S.E. anion [a]	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$\Delta E_{1/2}$ (2–1) (mV)	$\Delta E_{1/2}$ (3–2) (mV)	Ref.
1	CH_3CN	$[ClO_4]^-$	−0.09	0.24		330		[3]
1	CH_2Cl_2	$[B(C_6F_5)_4]^-$	−0.13	0.40		530		This work
2	CH_3CN/CH_2Cl_2	$[PF_6]^-$	−0.27	−0.05	0.36	220	380	[5]
2	CH_2Cl_2	$[B(C_6F_5)_4]^-$	−0.23	0.11	0.79	340	680	This work
3	CH_3CN	$[ClO_4]^-$	−0.27	0.32		590		[3]
3	CH_2Cl_2	$[B(C_6F_5)_4]^-$	−0.33	0.64		970		This work
4	CH_3CN	$[ClO_4]^-$	≈ −0.07	≈ −0.03		≈40		[3]
4	CH_2Cl_2	$[B(C_6F_5)_4]^-$	−0.08	0.10		180		This work

[a] In each case the cation of the supporting electrolyte is either $[NBu_4]^+$ or $[NEt_4]^+$.

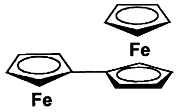
Removal of $[PF_6]^-$ from the solution in favour of $[B(C_6F_5)_4]^-$ exerts a profound influence on the $\Delta E_{1/2}$ values of the successive oxidations of **2** in CH_2Cl_2 (Table 1), with increases of 120 mV for $\Delta E_{1/2}$ (2–1) and 300 mV for $\Delta E_{1/2}$ (3–2) in the $[B(C_6F_5)_4]^-$ solution. The total separation of the three oxidation waves therefore increases from about 600 mV in $[PF_6]^-$ solutions to 1020 mV in $[B(C_6F_5)_4]^-$ solutions. When these experiments are performed in CH_3CN/0.1 M $[NBu_4][B(C_6F_5)_4]$, neither the chemical reversibility of the third oxidation wave nor the $\Delta E_{1/2}$ values are greatly altered compared to those observed in CH_3CN/0.1 M $[NBu_4][PF_6]$. These facts are strongly suggestive that the ion pairing effects of $[PF_6]^-$ with TF^{2+} and TF^{3+} in CH_2Cl_2 are virtually absent in the more polar CH_3CN.

Fractionally similar increases in $\Delta E_{1/2}$ are also seen for diferrocenyl-type complexes which have interacting ferrocenyl groups. Biferrocene (**1**, BF) has been electrochemically characterized a number of times in CH_2Cl_2 [15] and in CH_3CN [3,16] with reported average $\Delta E_{1/2}$ (2–1) values of 338 and 320 mV, respectively, when the electrolyte anion was $[ClO_4]^-$, $[PF_6]^-$ or $[BF_4]^-$. This value rises to 530 mV in CH_2Cl_2/0.1 M $[NBu_4][B(C_6F_5)_4]$ (Table 1). Similarly, the somewhat less-highly studied bis(fulvalene)diiron, BFD (**3**), displays an increase of $\Delta E_{1/2}$ (2–1) from 590 mV in either $CH_3CN/[ClO_4]^-$ or $CH_2Cl_2/[BF_4]^-$ to 970 mV in $CH_2Cl_2/[B(C_6F_5)_4]^-$ (Table 1).

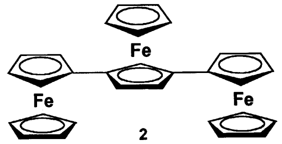
Ion-pairing effects have been probed for their relevance to the electronic properties of mixed-valence complexes [17]. The present data suggest, however, that such effects from anions (such as $[BF_4]^-$) commonly considered to be weakly ion-pairing may be more important than previously thought, at least in relatively low-polarity solvents. It is expected that physical studies (e.g. optical spectroscopy) of cationic mixed-valent systems with $[B(C_6F_5)_4]^-$ or related 'non-coordinating' counter-anions [12,18] will be helpful in furthering our understanding of the impact of media effects [19] on the electronic properties of this class of compounds.

An increase in $\Delta E_{1/2}$ values may prove to be particularly useful for complexes with more weakly-interacting ferrocenyl groups by diminishing the tendency of the mixed valent intermediate to disproportionate. For example, CV scans of bis(ferrocenyl)ethane, $[CpFe(C_5H_4)CH_2]_2$ (**4**) are unable to resolve the two individual oxidation processes (estimated to have $\Delta E_{1/2}$ (2–1) ca. 40 mV) [3] in a $CH_2Cl_2/[PF_6]^-$ electrolyte solution, whereas two well-resolved waves with $\Delta E_{1/2} = 180$ mV are observed in a $[B(C_6F_5)_4]^-$ electrolyte [20]. The apparent K_{disp} value for $\mathbf{4}^+$ in CH_2Cl_2 decreases from ca. 0.2 to 0.001 by taking advantage of the anion substitution.

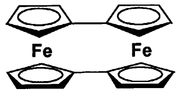
In summary, there are significant advantages in conducting ET studies of the multiple oxidations of oligoferrocenes by using very poorly ion-pairing anions of low nucleophilicity. There is every reason to anticipate that similar advantages will be observed for ET processes leading to cations and polycations of other oligo-building blocks [1d] such as the (dppe)Cp*Fe group [21].



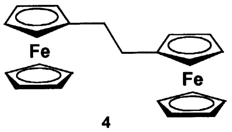
1



2



3



4

3. Experimental

Compounds **1**–**3** were synthesized, starting from CpNa, according to a literature procedure [22]. By using less than the stoichiometric amount of I_2 in the first step, the reaction was directed so as to provide all three compounds in acceptable yields. Crude **4** (claimed to have a purity of 98%) was purchased from Aldrich and used after extensive purification. Compound **4** was also prepared by a published procedure [23]. $[NBu_4][B(C_6F_5)_4]$ was prepared by metathesis of $Li[B(C_6F_5)_4]\cdot 2Et_2O$ (Boulder Scientific Co., Boulder, CO) with $[NBu_4]Cl$ as described previously [14] and recrystallized several times from CH_2Cl_2/Et_2O. Dichloromethane (Aldrich, Omnisolve) was first distilled after drying under CaH_2, and then by bulb-to-bulb transfer under static high vacuum conditions. Electrochemistry was conducted at ambient temperatures in a Vacuum Atmospheres drybox under nitrogen. Although the voltammetry experiments were begun only when the box atmosphere was no higher than 1 ppm in oxygen and water, this fairly rigorous precaution is not thought to be crucial to the electrode behavior described in the present study. Similar results were obtained in bench-top experiments conducted under nitrogen or argon. Glassy carbon working electrodes of 1 or 2 mm diameter were polished with 1 μm and then 0.25 μm diamond paste, rinsed with water and then acetone, and evacuated before putting them into the drybox. The experimental reference electrode was a AgCl-coated Ag wire isolated from the working electrode compartment by a fine frit. The reported potentials versus the ferrocene/ferrocenium couple used in this paper were obtained indirectly by adding decamethylferrocene [24] (Fc*) as an internal standard near the end of an experiment. The measured analyte potential was then referred to Fc by subtraction of 0.62 V if the supporting electrolyte anion was $[B(C_6F_5)_4]^-$, and 0.55 V for solutions containing $[PF_6]^-$. Since much of the older literature on ferrocenyl complexes uses potentials referenced to the aqueous SCE, we note that one must add 0.46 V to our reported values versus Fc for $[PF_6]^-$ experiments in order to reproduce the original literature values versus SCE and 0.49 V to obtain those against the less frequently used [5] SSCE (sodium SCE). All CV experiments used standard criteria [25] for characterization of diffusion control and reversibility of the oxidation processes.

Acknowledgements

We thank Richard W. Sanders (University of Connecticut) for synthetic help and gratefully acknowledge the partial contribution of $Li[B(C_6F_5)_4]\cdot 2Et_2O$ from Boulder Scientific Co. Research at the University of Vermont was supported by the National Science Foundation.

References

[1] (a) U.T. Mueller-Westerhoff, Angew. Chem. Int. Ed. Engl. 25 (1986) 702;
(b) D. Astruc, Electron Transfer and Radical Processes in Transition-Metal Chemistry, Ch. 2, VCH, New York, 1995;
(c) S. Barlow, D. O'Hare, Chem. Rev. (1997) 637;
(d) I. Cuadrado, M. Moran, C.M. Casado, B. Alonso, J. Losada, J. Coord. Chem. Rev. 193-195 (1999) 395;
(e) C. Valerio, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais, D. Astruc, J. Am. Chem. Soc. 119 (1997) 2588;
(f) P. Zanello, in: A. Togni, T. Hayashi (Eds.), Ferrocenes, Ch. 7, VCH, New York, 1995;
(g) K.E. Gonsalves, X. Chen, in: A. Togni, T. Hayashi (Eds.), Ferrocenes, Ch. 10, VCH, New York, 1995.

[2] In this paper the $\Delta E_{1/2}$ values are always defined as the more positive value minus the more negative value, e.g. $E^2_{1/2} - E^1_{1/2}$, so that all values are positive. The term $\Delta E_{1/2}$ (2–1) refers to $E^2_{1/2} - E^1_{1/2}$, that of $\Delta E_{1/2}$ (3–2) to $E^3_{1/2} - E^2_{1/2}$.

[3] W.H. Morrison Jr, S. Krogsrud, D.N. Hendrickson, Inorg. Chem. 12 (1973) 1998.

[4] D.E. Richardson, H. Taube, Coord. Chem. Rev. 60 (1984) 107.

[5] G.M. Brown, T.J. Meyer, D.O. Cowan, C. LeVanda, F. Kaufman, P.V. Roling, M.D. Rausch, Inorg. Chem. 14 (1975) 506.

[6] (a) See for example: D. Astruc, Acc. Chem. Res. 30 (1997) 383;
(b) P. Hudeczek, F.H. Köhler, P. Bergerat, O. Kahn, Chem. Eur. J. 5 (1995) 70;
(c) C.B. Hollandsworth, W.G. Hollis Jr, C. Slebodnick, P.A. Deck, Organometallics 18 (1999) 3610.

[7] D.T. Sawyer, A. Sobkowiak, J.L. Roberts Jr, Electrochemistry for Chemists, Ch. 7, 2nd ed., Wiley, New York, 1995.

[8] R. Rulkens, A.J. Lough, I. Manners, S.R. Lovelace, C. Grant, W.E. Geiger, J. Am. Chem. Soc. 118 (1996) 12683.

[9] (a) Some recent examples: B. Garcia, C.M. Casado, I. Cuadrado, B. Alonso, M. Moran, J. Losada, Organometallics 18 (1999) 2349;
(b) C. Ganter, C. Kaulen, U. Englert, Organometallics 18 (1999) 5444;
(c) Reference [1d].

[10] (a) T.-Y. Dong, P.-H. Ho, X.-Q. Lai, Z.-W. Lin, K.-J. Lin, Organometallics 19 (2000) 1096;
(b) T.-Y. Dong, W.-Y. Lee, P.-T. Su, L.-S. Chang, K.-J. Lin, Organometallics 17 (1998) 3323.

[11] A 1:14 ratio of $CH_3CN:CH_2Cl_2$ was used in reference [1d].

[12] C.A. Reed, Acc. Chem. Res. 31 (1998) 133.

[13] (a) M.G. Hill, W.M. Lamanna, K.R. Mann, Inorg. Chem. 30 (1991) 4687;
(b) A.R. Siedle, B. Hanggi, R.A. Newmark, K.R. Mann, T. Wilson, Macromol. Symp. 89 (1995) 299.

[14] R. LeSuer, W.E. Geiger, Angew. Chem. Int. Ed. Engl. 39 (2000) 248.

[15] (a) C. LeVanda, K. Bechgaard, D.O. Cowan, J. Org. Chem. 41 (1976) 2700;
(b) D.R. Talham, D.O. Cowan, Organometallics 6 (1987) 932;
(c) V.V. Dement'ev, F. Cervantes-Lee, L. Parkanyi, H. Sharma, K.H. Pannell, M.T. Nguyen, A. Diaz, Organometallics 12 (1993) 1983;
(d) A.B. Bocarsly, E.G. Walton, M.G. Bradley, M.S. Wrighton, J. Electroanal. Chem. 100 (1979) 283;
(e) L.F. Schneemeyer, M.S. Wrighton, J. Am. Chem. Soc. 101 (1979) 6496.

[16] (a) I. Motoyama, K. Suto, M. Katada, H. Sano, Chem. Lett. (1983) 1215;
(b) J.A. Baglio, G.S. Calabrese, E. Kamieniecki, R. Kershaw, C.P. Kubiak, A.J. Ricco, A. Wold, M.S. Wrighton, G.D. Zoski, J. Electrochem. Soc. 129 (1982) 1461;
(c) C. LeVanda, D.O. Cowan, K. Bechgaard, J. Am. Chem. Soc. 97 (1975) 980.

[17] (a) J.T. Hupp, Inorg. Chem. 29 (1990) 5010;
(b) W.S. Hammack, H.G. Drickamer, M.D. Lowery, D.N. Hendrickson, Chem. Phys. Lett. 132 (1986) 231.

[18] K. Seppelt, Angew. Chem. Int. Ed. Engl. 32 (1993) 1025.

[19] P. Chen, T.J. Meyer, Chem. Rev. 98 (1998) 1439.

[20] N. Camire, Unpublished work. The response of diferrocenylethane in CH_3CN has been described previously in Ref. [3] ($\Delta E_{1/2}$ (2–1) estimated as 40 mV based on differential pulse voltammetry scan).

[21] F. Paul, C. Lapinte, Coord. Chem. Rev. 178-180 (1998) 431.

[22] C. LeVanda, K. Bechgaard, D.O. Cowan, U.T. Mueller-Westerhoff, P. Eilbracht, G.A. Candela, R.L. Collins, J. Am. Chem. Soc. 98 (1976) 3181.

[23] U.T. Mueller-Westerhoff, M. Zhou, Synlett (1994) 975.

[24] Decamethylferrocene was used as the internal standard because the ferrocene potential is too close to that of some of the waves of the analytes.

[25] W.E. Geiger, in: P.T. Kissinger, W.R. Heineman (Eds.), Laboratory Methods in Electro-Analytical Chemistry, Ch. 23, 2nd ed., Marcel Dekker, New York, 1996.