J|A|C|S
ARTICLES

Published on Web 03/02/2006

Use of Weakly Coordinating Anions to Develop an Integrated Approach to the Tuning of $\Delta E_{1/2}$ Values by Medium Effects

Frédéric Barrière*,† and William E. Geiger*

Contribution from the Department of Chemistry, University of Vermont,
Burlington, Vermont 05405

Received December 16, 2005; E-mail: william.geiger@uvm.edu

Abstract: An integrated approach to the control of $\Delta E_{1/2}$ values, and therefore comproportionation equilibria, through medium effects was delineated for multi-step redox reactions involving cationic products. $\Delta E_{1/2}$ values (defined as $E_{1/2}{}^{2+/1+} - E_{1/2}{}^{1+/0}$) of the two one-electron oxidations of bis(fulvalene)dinickel, **1**, were measured under 45 different conditions of solvent and supporting electrolyte. The smallest value, 212 mV, was found in anisole/0.1 M $[NBu_4]Cl$ and the largest, 850 mV, in CH_2Cl_2/0.02 M $Na[B(C_6H_3(CF_3)_2)_4]$. By systematically changing the solvent properties, the degree of ion-pairing strengths of the supporting electrolyte ions, and the concentration of the electrolytes, a set of ideal properties was found for maximizing $\Delta E_{1/2}$ values involving positively charged electrode products. Most importantly (i) the solvent must be of lower polarity and low donor strength and (ii) the supporting electrolyte must have a weakly coordinating anion (WCA). The contrast in ion-pairing tendencies of $\mathbf{1}^{2+}$ with WCAs (on the weak side) and halides (on the strong side) mimics that of dianions in THF, where longer chain tetraalkylammonium ions (weak ion pairing) contrast with alkali metal ions (strong ion pairing). The broad picture of medium effects is that of a "mirror image" of solvent and electrolyte properties that influence the tuning of $\Delta E_{1/2}$ values for multi-electron systems. Application was made both to the four-step oxidation process and to the two-step reduction process of the tetraferrocenyl complex $Ni(S_2C_2Fc_2)_2$, Fc = $Fe(C_5H_5)(C_5H_4)$, **2**. The two-electron process $\mathbf{2}^{0/2-}$ is observed either as a single two-electron voltammetric wave or as two well-separated one-electron waves, depending on the medium. The consequences of the present model for the interpretation of $\Delta E_{1/2}$ values in mixed-valence chemistry are discussed.

Introduction

Background and Goals. The fundamental importance of multi-step electron-transfer processes is widely recognized,[1] and the statistical, electrostatic, magnetic inductive, and electronic coupling factors influencing the $\Delta E_{1/2}$ values of successive one-electron processes (see eq 1) have been intensely studied.[2,3]

$$A \xrightleftharpoons{E_{1/2}(1)} B \xrightleftharpoons{E_{1/2}(2)} C$$

$$\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1) \qquad (1)$$

Another important factor, namely, the effect of the solvent/electrolyte medium, has been less systematically probed,[2f,j,k] except perhaps for cathodic processes involving organic anions and dianions. In that case, very large decreases in $\Delta E_{1/2}$ values[4] may occur when the supporting electrolyte cation is changed from weakly to strongly ion pairing and a lower-polarity solvent (dielectric constant, ϵ, of about 10 or less) is employed. An example of such a medium change is that of tetrabutylammo-

---

[†] Present address: Université de Rennes 1, UMR CNRS 6226 "Sciences Chimiques de Rennes" Groupe Matière Condensée et Systèmes Electroactifs (MaCSE), 35042 Rennes, France.

(1) For leading references, see: (a) Bard, A. J. *Pure Appl. Chem.* **1971**, *25*, 379. (b) Lowe, D. J.; Fisher, K.; Thomeley, R. N. F.; Vaughn, S.; Burgess, B. K. *Biochemistry* **1989**, *28*, 8460. (c) Anson, F. C.; Shi, C.; Steiger, B. *Acc. Chem. Res.* **1997**, *30*, 437. (d) Bryce, M. R.; Batsanov, A. S.; Finn, T.; Hansen, T. K.; Howard, J. A. K.; Kamenjicki, M.; Lednev, I. K.; Asher, S. A. *J. Chem. Soc., Chem. Commun.* **2000**, 295. (e) Hapiot, P.; Kispert, L. D.; Konovalov, V. V.; Savéant, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 6669. (f) Gileadi, E. *J. Electroanal. Chem.* **2002**, *532*, 181. (g) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *76*, 301. (h) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; Wiley-VCH: Weinheim, Germany, 1999. (i) Kaifer, A. E.; Gomez-Kaifer, M. *Supramolecular Electrochemistry*; Wiley-VCH: Weinheim, Germany, 1999. (j) Newkome, G. R.; He, E. F.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689. (k) Nguyen, P.; Gomez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515. (l) Evans, D. H.; Hu, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3983.

(2) The literature on this topic is extensive, being represented by: (a) Creutz, C. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley and Sons: New York, 1983; Vol. 30, p 1. (b) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107. (c) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121. (d) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439. (e) Barlow, S.; Marder, S. R. *Chem. Commun.* **2000**, 1555. (f) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655. (g) Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383. (h) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *33*, 273. (i) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178*, 431. (j) Crutchley, R. J. *Coord. Chem. Rev.* **2001**, *219−221*, 125 (see p 144). (k) Al-Noami, M.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **2004**, *43*, 1770. (l) Nelsen, S. F. *Chem.—Eur. J.* **2000**, *6*, 581. (m) Lambert, C.; Noell, G. *J. Chem. Soc., Perkin Trans. 2* **2002**, 2039. (n) Lindeman, S. V.; Rosokha, S. V.; Sun, D.; Kochi, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 843. (o) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637.

(3) Evans, D. H.; Lehmann, M. W. *Acta Chem. Scand.* **1999**, *53*, 765. In the present paper, $E_{1/2}$ is used in place of the formal potential, $E^{\circ\prime}$, of ref 3. The two values are equal if the diffusion coefficients of the oxidized and reduced forms of the redox couple are the same. For our model systems, $E_{1/2}$ values should closely approximate formal potentials. See also ref 17.

(4) For clarity of comparison, increased separations of voltammetric waves always give increased $\Delta E_{1/2}$ values in this paper, whether the redox processes involve oxidations to cations or reductions to anions. The oxidation process is treated as proceeding from the neutral compound **A** to the +1 and +2-charged species **B** and **C**, respectively. When reductions are introduced later in the text, they are also treated as originating from neutral compounds, but leading in that case to anionic products.

10.1021/ja058171x CCC: $33.50 © 2006 American Chemical Society

nium versus alkali metal ions in THF.[5a] Until the recent introduction of weakly coordinating anions (WCAs) in supporting electrolytes,[6,7] medium-based changes of comparable magnitude had not been observed for anodic reactions involving cationic products. Taking advantage of WCAs, we sought to identify the solvent/electrolyte conditions that maximize *anodic* $\Delta E_{1/2}$ values (for positively charged products) and compare them with those known to maximize *cathodic* $\Delta E_{1/2}$ values (for negatively charged products).[5] The present paper describes the results of such a study, part of which was communicated earlier.[8] Although our model systems have organometallic redox sites, the results are relevant to organic and inorganic redox reactions alike involving positively charged species. One of the outcomes is identification of a pattern for the influence of the medium on oxidative electron-transfer processes that is the mirror image of the long-established pattern for reductive electron-transfer reactions (involving anions),[5] allowing an integrated understanding of the influence of medium on $\Delta E_{1/2}$ values in nonaqueous solutions.

The starting point in the medium of anodic electrochemistry, especially for organometallic compounds, is $CH_2Cl_2/[NR_4][TA]$, where TA is one of the "traditional anions"[9] such as $[BF_4]^-$, $[PF_6]^-$, $[ClO_4]^-$, and, to a lesser extent, $[BPh_4]^-$. Dichloromethane and other halogenated hydrocarbons have low donor properties and correspondingly low nucleophilicities. There is increasing evidence, however, that the traditional anions may react as nucleophiles with radical cations and other electron-deficient compounds.[6,7,10,14d] WCAs, introduced in large part to avoid nucleophilic reactions with early transition metals,[12,13] are capable of minimizing or eliminating these reactions in electrogenerated cations and are fast becoming the electrolyte anion of choice in anodic molecular electrochemistry.[6−8,11,14] The high degree of charge delocalization in these anions makes them not only weak nucleophiles but also weakly ion pairing,[15] allowing for the first time an in-depth study of how anodic $\Delta E_{1/2}$ values are affected by ion pairing using "large" versus "small" anions on a scale comparable to that known for cathodic $\Delta E_{1/2}$ values using large $[NR_4]^+$ versus alkali metal ions. Cognizant of the important role played by solvent properties,[16] the present paper also takes into account both the polarity and donor/acceptor properties of the solvent. The results provide overall conceptual guidelines for manipulation of $\Delta E_{1/2}$ values and, thereby, the comproportionation reaction (eq 2), for which the value of K_{comp} is easily obtained from $\Delta E_{1/2}$ measurements[17] (eq 3).

$$A + C \leftrightarrows 2B;\ K_{comp} = [B]^2/[A][C] \qquad (2)$$

$$\log K_{comp} = 16.9\ \Delta E_{1/2} \text{ at 298 K } (\Delta E_{1/2} \text{ in V}) \qquad (3)$$

Choice of WCA Electrolyte Anions. The WCA anions employed in this study were tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$ (TFAB), and tetrakis[(3,5-trifluoromethyl)phenyl]borate, $[B(C_6H_3(3,5\text{-}CF_3)_2)_4]^-$ ($BArF_{24}$). Highly distributed negative charges make these anions among the least nucleophilic known.[13] Furthermore, their salts are generally well soluble in lower-polarity solvents, thereby minimizing adsorption problems with cationic electrode products. The particularly high solubility of $[BArF_{24}]^-$ salts[18] may be advantageous in providing a number of electrolyte salts, differing in counterion, that offer acceptable voltammetry conditions (see data below in 0.02 M $Na[BArF_{24}]$ in CH_2Cl_2).

Choice of Solvents and Comments on Ion Pairing. The effect of the medium on $\Delta E_{1/2}$ is a complex function of solvent−solute and ion-pairing interactions. The most important solvent parameters,[19] namely, dielectric constant (ϵ), dipole moment (μ), donor number (DN), and acceptor number (AN), are listed in Table 1 for the 11 solvents chosen for this study. There is an extensive literature, some of which will be referred to below, of the influence of solvent on $E_{1/2}$ values. Crucial to the current work are the contrasting ion-pairing behaviors of salts in higher-polarity ($\epsilon > 20$) versus lower-polarity ($\epsilon < 10$) solvents. The latter facilitate ion pairing, not only through simple tight ion pairs but also through formation of triple ions and even higher aggregates and clusters.[20] Owing to this complexity,[21,22] we did

---

(5) (a) Swarc, M., Ed. *Ions and Ion Pairs in Organic Reactions*; Wiley-Interscience: New York, 1972; Vols. 1 and 2. (b) Fry, A. J.; Simon, J.; Tashiro, M.; Yamato, T.; Mitchell, R. H.; Dingle, T. W.; Williams, R. V.; Mahedevan, R. *Acta Chem. Scand.* **1983**, *B37*, 445. (c) Fry, A. J. *J. Electroanal. Chem.* **2003**, *546*, 35.

(6) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4687.

(7) LeSuer, R. J.; Geiger, W. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 248.

(8) Barrière, F.; Camire, N.; Geiger, W. E.; Mueller-Westerhoff, U. T.; Sanders, R. *J. Am. Chem. Soc.* **2002**, *124*, 7262.

(9) Fry, A. J. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; Chapter 15.

(10) Zoski, C. G.; Sweigart, D. A.; Stone, N. J.; Rieger, P. H.; Mocellin, E.; Mann, T. F.; Mann, D. R.; Gosser, D. K.; Doeff, M. M.; Bond, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 2109.

(11) D'Alessandro, D. M.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **2004**, 3950.

(12) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391 and references therein.

(13) (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 1181. (c) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

(14) (a) Gassman, P. G.; Deck, P. A. *Organometallics* **1994**, *13*, 1934. (b) Gassman, P. G.; Sowa, J. R., Jr.; Hill, M. G.; Mann, K. R. *Organometallics* **1995**, *14*, 4879. (c) Camire, N.; Geiger, W. E.; Mueller-Westerhoff, U. T. *J. Organomet. Chem.* **2001**, *637-639*, 823. (d) Camire, N.; Nafady, A.; Geiger, W. E. *J. Am. Chem. Soc.* **2002**, *124*, 7260. (e) Stoll, M. E.; Belanzoni, P.; Calhorda, M. J.; Drew, M. G. B.; Félix, V.; Geiger, W. E.; Gamelas, C. A.; Goncalves, I. S.; Romão, C. C.; Veiros, L. F. *J. Am. Chem. Soc.* **2001**, *123*, 10595. (f) Chávez, I.; Alvarez-Carena, A.; Molins, E.; Roig, A.; Maniukiewicz, W.; Arancibia, A.; Arancibia, V.; Brand, H.; Manríquez, J. M. *J. Organomet. Chem.* **2000**, *126*, 1059. (g) Nataro, C.; Campbell, A. N.; Ferguson, M. A.; Incarvito, C. D.; Rheingold A. L. *J. Organomet. Chem.* **2003**, *673*, 47. (h) Yandulov, D. V.; Schrock, R. R. *Can. J. Chem.* **2005**, *83*, 341.

(15) LeSuer, R. J.; Buttolph, C.; Geiger, W. E. *Anal. Chem.* **2004**, *76*, 6395.

(16) (a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; VCH Publishers: Weinheim, Germany, 2003. (b) Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*; John Wiley and Sons: New York, 1975.

(17) For a discussion of differences between standard and formal potentials, see: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; Wiley: New York, 2001; pp 52−53.

(18) (a) Brookhart, M.; Liu, Y.; Goldman, E. W.; Timmers, D. A.; Williams, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 927. (b) Buschmann, W. E.; Miller, J. S. *Inorg. Synth.* **2003**, *33*, 83.

(19) (a) Linert, W.; Fukuda, Y.; Camard, A. *Coord. Chem. Rev.* **2001**, *218*, 113. Acceptor numbers (AN) are taken from the Gutmann ^{31}P chemical shift data for $Et_3PO{-}SbCl_5$ in the appropriate solvent (see ref 16a, pp 23−24). Acceptor numbers have also been reported as AN_λ, based on solvatochromism data. There are a few cases in which dramatically different values are obtained using the two approaches. Of the solvents appearing in Figure 3, only CH_2Cl_2 falls into this category. Hence, both acceptor numbers for CH_2Cl_2 ($AN = 20.4$; $AN_\lambda = 12.6$) are included in the Figure. (b) A reviewer has pointed out that Drago's S′ solvent values may be used optimally to describe the nonspecific solvation effects assumed in the present work. Relevant references may be found in Mu, L.; Drago, R. S.; Richardson, D. E. *J. Chem. Soc., Perkin Trans. 2* **1998**, 159.

(20) Bockris, J. O.; Reddy, A. K. N. *Modern Electrochemistry*, 2nd ed. (Ionics); Plenum Press: New York, 1998; pp 314−315.

(21) For conductivity studies in dichloromethane, the reader is referred to the work of Songstad et al. See: (a) Sigvartsen, T.; Gestblom, B.; Noreland, E.; Songstad, J. *Acta Chem. Scand.* **1989**, *43*, 103. (b) Svorstoel, I.; Hoeiland, H.: Songstad, J. *Acta Chem. Scand., Ser. B* **1984**, *B38*, 885.

(22) For NMR approaches to this problem, see: Kumar, A. P. G.; Pregosin, P.; Goicoechea, J. M.; Whittlesey, M. K *Organometallics* **2003**, *22*, 2956 and references therein.

Table 1. Relevant Solvent Parameters[a]

	ϵ^T	μ(D)	DN	DN_λ	AN	AN_λ
toluene	2.38[23]	0.375		3.9		3.3
diethyl ether	4.27[20]	1.150	19.2	18.1	3.9	4.2
anisole	4.30[21]	1.380		7.9		7.6
tetrahydrofuran	7.52[22]	1.750	20.0	20.6	8.0	7.8
dichloromethane	8.93[25]	1.600	(0)	1.2	20.4	12.6
acetone	21.0[21]	2.880	17.0	17.0	12.5	14.0
benzonitrile	25.9[20]	4.180	11.9	12.0	15.5	13.8
acetonitrile	36.6[20]	3.924	14.1	13.2	18.9	18.9
nitromethane	37.3[20]	3.460	2.7	4.8	20.5	19.3
DMF	38.2[20]	3.820	26.6	25.1	16.0	16.1
DMSO	47.2[20]	3.960	29.8	30.1	19.3	17.6

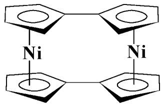
[a] ϵ^T is the dielectric constant at temperature T (°C); μ(D) is dipolar moment in Debye; DN and AN are the donor and acceptor numbers. For details and definitions, see: Linert, W.; Fukuda, Y.; Camard, A. *Coord. Chem. Rev.* **2001**, *218*, 113.

not attempt to quantify ion-pairing equilibrium constants. A recent conductivity study has shown that, in lower dielectric solvents, contact ion-pairing equilibrium constants are generally 1−2 orders of magnitude lower for TFAB salts compared to traditional anions, when the counterion is tetrabutylammonium.[15]

A second important aspect of solvent polarity is the relationship of ϵ to free energies of solvation. On the basis of the Born equation, a lower-polarity solvent is expected to more weakly solvate charged electrode products, leading to an increase in $\Delta E_{1/2}$ for successive one-electron couples.[23]

Choice of Model Systems. Two model systems were chosen for this study. A comprehensive set of medium variations was carried out on bis(fulvalene)dinickel, **1**.

(1)



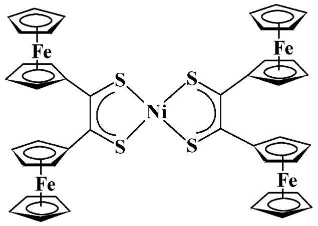
Smart and co-worker have shown that this compound undergoes two separate one-electron oxidations to isolable products, $\mathbf{1}^+$ and $\mathbf{1}^{2+}$ (eq 4).[24]

$$\mathbf{1} \underset{}{\overset{E_{1/2}(1)}{\rightleftharpoons}} \mathbf{1}^+ \overset{E_{1/2}(2)}{\rightleftharpoons} \mathbf{1}^{2+}$$

$$\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1) \tag{4}$$

The monocation $\mathbf{1}^+$ is formally a Class III (intrinsically delocalized) mixed-valent species[24d] in the Robin−Day classification system.[25] Since the charge in $\mathbf{1}^+$ is delocalized over the two nickelocenyl groups, it is not likely to be significantly redistributed by changes in the medium, a matter that might be of concern if the ion were on the Class II/Class III interface.[26] The delocalized charges also render the oxidized forms less sensitive to nucleophilic attack, which allowed measurement of $\Delta E_{1/2}$ values even in the presence of strong nucleophiles, such as halides. Furthermore, the oxidations occur at mild potentials, well within most solvent/electrolyte "windows". More broadly, **1** is part of the family of dimetallocenes for which $\Delta E_{1/2}$ values have so often been employed to indicate their mixed-valence classification.[27]

(2)



Measurements were also carried out on complex **2**,[28] for which the oxidizable ferrocenyl groups [$E_{1/2}(n)$, n = 1−4 (eq 5)] and the reducible nickel dithiolene center[29] [$E_{1/2}(m)$, m = 1−, 2− (eq 6)] offer significant variations from compound **1**.

$$\mathbf{2} \overset{E_{1/2}(1)}{\rightleftharpoons} \mathbf{2}^+ \overset{E_{1/2}(2)}{\rightleftharpoons} \mathbf{2}^{2+} \overset{E_{1/2}(3)}{\rightleftharpoons} \mathbf{2}^{3+} \overset{E_{1/2}(4)}{\rightleftharpoons} \mathbf{2}^{4+} \tag{5}$$

$$\mathbf{2} \overset{E_{1/2}(1-)}{\rightleftharpoons} \mathbf{2}^- \overset{E_{1/2}(2-)}{\rightleftharpoons} \mathbf{2}^{2-} \tag{6}$$

The four ferrocenyl redox sites provided a forum in which to use the basic principles delineated in the study of **1** to separate the multiple anodic processes of **2**. Furthermore, the two nickel dithiolene reductions provided a vehicle for evaluating how a mirrored version of these basic principles might be employed for the thermodynamic manipulation of multiple redox processes involving product *anions*. The overall goal of the present work was to provide an *integrated* solvent/electrolyte approach to medium-controlled manipulation of $\Delta E_{1/2}$ values for both positively and negatively charged redox products.

Experimental Section

Reagents. Compound **1**[24] was prepared by Dr. Eckhardt Schmidt at the University of Vermont and checked by ^{1}H NMR (Bruker, 500 MHz) and C,H elemental analysis (Robertson Laboratories). Compound **2** was provided by U. T. Mueller-Westerhoff. Although both of these samples are relatively stable in air, their solutions were always handled under an inert atmosphere, using Schlenck or drybox techniques. Tetrabutylammonium salts of $[BF_4]^-$, $[PF_6]^-$, and $[ClO_4]^-$ were prepared by standard metathesis reactions, recrystallized, and vacuum-dried. $[NBu_4]$-[TFAB] was prepared by metathesis of $[NBu_4]Br$ with $Li[B(C_6F_5)_4]$ etherate (Boulder Scientific Co.) in methanol and recrystallized from CH_2Cl_2/hexane or CH_2Cl_2/diethyl ether. A full description of this procedure has been published.[15] $[NBu_4][BArF_{24}]$ was prepared by metathesis of $[NBu_4]Br$ with $Na[B(C_6H_3(CF_3)_2)_4]$ (Boulder Scientific Co.) in methanol and recrystallized from dichloromethane/diethyl ether. Solvents were reagent grade. A number of them were dried and distilled from appropriate drying agents, including diethyl ether and anisole (from Na), THF (from K), CH_2Cl_2 (from CaH_2), acetone (from CaH_2), and CH_3CN (from CaH_2). Others (benzonitrile, DMF, and DMSO) were used as received after drying over type 4 Å molecular sieves.

---

(23) Refs 16b, p 160 ff. Nonspecific solvation is assumed for the models in the present study. A simple Born model has been shown to provide an adequate description of solvation effects in metallocene redox reactions. See: Ryan, M. F.; Richardson, D. E.; Lichtenberger, D. L.; Gruhn, N. E. *Organometallics* **1994**, *13*, 1190.

(24) (a) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 956. (b) Sharp, P. R.; Raymond, K. N.; Smart, J. C.; McKinney, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 753. (c) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009 (see data entry in Table 1 of this paper). (d) Clark, S. F.; Watts, R. J.; Dubois, D. L.; Connolly, J. S.; Smart, J. C. *Coord. Chem. Rev.* **1985**, *64*, 273.

(25) Robin, M. D.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(26) See ref 2l.

(27) Leading references may be found in ref 2.

(28) Mueller-Westerhoff, U. T.; Sanders, R. W. *Organometallics* **2003**, *22*, 4778.

(29) (a) McCleverty, J. *Progress in Inorganic Chemistry*; John Wiley and Sons: New York, 1968; Vol. 10, pp 49−221. (b) Wang, K. In *Progress in Inorganic Chemistry*; Karlin, K. D., Stiefel, E. I., Eds.; John Wiley and Sons: New York, 2003; Vol. 52, pp 267−314. (c) Zanello, P.; Grigiotti, E. In *Trends in Molecular Electrochemistry*; Pombeiro, A. J. L., Amatore, C., Eds.; Marcel Dekker: New York, 2004; pp 3−70.

Table 2. Redox Potentials versus Ferrocene$^{0/+}$ for **1** in 45 Different Media. Supporting Electrolyte Concentrations are 0.1 M unless Otherwise Noted. TFAB = [B(C$_6$F$_5$)$_4$]$^-$; BArF$_{24}$ = [B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$^-$; hept = heptyl; triflate = [CF$_3$SO$_3$]$^-$

solvent–electrolyte	$E_{1/2}$(2+/1+, V)	$\Delta E_{1/2}$ (mV)	$E_{1/2}$(1+/1, V)	Fc*–Fc (V)
toluene−[NBu$_4$][BF$_4$][a]	−0.301	409	−0.710	−0.430
Et$_2$O−[NBu$_4$][BArF$_{24}$]	+0.072	806	−0.734	−0.550
Et$_2$O−Na[BArF$_{24}$]	+0.034	798	−0.764	−0.583
anisole−[NBu$_4$][Cl]	−0.561	212	−0.773	
anisole−[NBu$_4$][PF$_6$]	−0.312	417	−0.729	−0.518
anisole−[NBu$_4$][TFAB]	+0.000	806	−0.736	−0.607
THF−[Nhept$_4$][Br]		234		
THF−[NBu$_4$][BF$_4$]	−0.380	343	−0.723	−0.413
THF−[NBu$_4$][triflate]	−0.373	354	−0.727	−0.438
THF−[NBu$_4$][ClO$_4$]	−0.358	363	−0.722	−0.423
THF−[NBu$_4$][PF$_6$]	−0.302	407	−0.709	−0.446
THF−[NBu$_4$][BPh$_4$]	−0.282	425	−0.707	−0.485
THF−Na[BArF$_{24}$]	−0.092	610	−0.702	−0.502
THF−[NBu$_4$][TFAB]	−0.113	595	−0.708	−0.484
THF−[NBu$_4$][BArF$_{24}$]	−0.113	598	−0.711	−0.521
CH$_2$Cl$_2$−[NBu$_4$][Cl]	−0.460	273	−0.733	−0.534
CH$_2$Cl$_2$−[Nhept$_4$][Br]		313		
CH$_2$Cl$_2$−[NBu$_4$][BF$_4$]		410		
CH$_2$Cl$_2$−[NBu$_4$][triflate]		410		
CH$_2$Cl$_2$−[NBu$_4$][ClO$_4$]		422		
CH$_2$Cl$_2$−[NBu$_4$][PF$_6$]	−0.228	480	−0.708	−0.548
CH$_2$Cl$_2$−[NBu$_4$][BPh$_4$]		517		
CH$_2$Cl$_2$−[NBu$_4$][BArF$_{24}$]		744		
CH$_2$Cl$_2$−[NBu$_4$][TFAB]	+0.026	753	−0.727	−0.614
CH$_2$Cl$_2$−[Li(Et$_2$O)$_n$][TFAB]		753		
CH$_2$Cl$_2$−Na[BArF$_{24}$][b]		850		
C$_6$H$_5$CN−[NBu$_4$][Cl]	−0.465	285	−0.750	−0.524
C$_6$H$_5$CN−[NBu$_4$][PF$_6$]	−0.229	474	−0.703	−0.530
C$_6$H$_5$CN−[NBu$_4$][TFAB]	−0.189	514	−0.703	−0.543
acetone−[NBu$_4$][Cl]	−0.502	262	−0.764	−0.451
acetone−[NBu$_4$][PF$_6$]	−0.253	441	−0.695	−0.487
acetone−[NBu$_4$][TFAB]	−0.209	489	−0.698	−0.504
acetone−[NEt$_4$][ClO$_4$][c]		410		
CH$_3$CN−[NBu$_4$][Cl]	−0.366	331	−0.697	−0.501
CH$_3$CN−[NBu$_4$][PF$_6$]	−0.223	459	−0.682	−0.507
CH$_3$CN−[NBu$_4$][TFAB]	−0.203	480	−0.683	−0.517
CH$_3$NO$_2$−[NBu$_4$][Cl]	−0.335	350	−0.685	−0.505
CH$_3$NO$_2$−[NBu$_4$][PF$_6$]	−0.198	485	−0.683	−0.510
CH$_3$NO$_2$−[NBu$_4$][TFAB]	−0.183	500	−0.683	−0.516
DMF−[NBu$_4$][Cl]	−0.435	298	−0.733	−0.475
DMF−[NBu$_4$][PF$_6$]	−0.289	407	−0.697	−0.478
DMF−[NBu$_4$][TFAB]	−0.284	415	−0.699	−0.493
DMSO−[NBu$_4$][Cl]	−0.415	337	−0.752	
DMSO−[NBu$_4$][PF$_6$]	−0.343	371	−0.714	−0.486
DMSO−[NBu$_4$][TFAB]	−0.325	393	−0.718	−0.493

[a] The toluene−[Bu$_4$N][BF$_4$] electrolyte is of the 1{[Bu$_4$N][BF$_4$]}-3{toluene} stoichiometry. For details, see: Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 323. [b] The CH$_2$Cl$_2$−[Na][BArF$_{24}$] electrolyte is a saturated solution with a ca. 0.02 M salt concentration. [c] Data from ref 24c. $E_{1/2}$ potentials were reported versus SCE (+0.12 and −0.29 V).

Electrochemistry. A standard three-electrode configuration was used for voltammetry and coulometry experiments. The concentration of analyte was generally 1 mM. Unless otherwise noted, the concentration of supporting electrolyte was 0.1 M. The experimental reference electrode was a AgCl-coated Ag wire prepared by anodic electrolysis of the wire in 1 M HCl. All potentials in this paper are referred, however, to the ferrocene/ferrocenium reference couple.[30] This was accomplished by adding either ferrocene (FeCp$_2$) or decamethylferrocene (FeCp*$_2$) to the solution as an internal standard after recording the voltammetry of the analyte. Although the [FeCp$_2$]$^{0/+}$ couple is still favored as the international standard reference,[30a] the [FeCp*$_2$]$^{0/+}$ couple shows less potential change with electrolyte medium.[31] To have a set of data for conversion of $E_{1/2}$ versus [FeCp*$_2$]$^{0/+}$ to $E_{1/2}$ versus [FeCp$_2$]$^{0/+}$ under our experimental conditions, the differences in the two $E_{1/2}$ values were measured for most of the media used in this study. As given in Table 2, $E_{1/2}$ ([FeCp*$_2$]$^{0/+}$ − [FeCp$_2$]$^{0/+}$) varied from a low of −0.614 V in CH$_2$Cl$_2$/[NBu$_4$][TFAB] to a high of −0.413 V in THF/[NBu$_4$][BF$_4$] (accuracy ca. 0.005 V). Whereas these adjustment values were useful in converting individual $E_{1/2}$ values of the analyte to the ferrocene reference potential, it should be noted that the primary measurable of this paper, namely, the $\Delta E_{1/2}$ values, is independent of the adjustments. In a few cases in which an internal standard was not added to the solution, only the $\Delta E_{1/2}$ values are reported (see Tables 2 and 4).

The working electrodes were glassy carbon disks having a diameter of either 1 or 1.5 mm (Bioanalytical Systems), polished on a Buehler polishing cloth with Metadi II diamond paste, rinsed copiously with Nanopure water, and placed under vacuum for drying. A computer-interfaced PARC Model 273A potentiostat was employed, and experiments were carried out at ambient temperatures in the drybox.

---

(30) (a) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461. (b) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(31) (a) Ruiz, J.; Astruc, D. *C. R. Acad. Sci. Ser. II* **1998**, 21. (b) Noviandri, I.; Brown, K. N.; Fleming, D. S.; Gulyas, P. T.; Lay, P. A.; Masters, A. F.; Phillips, L. *J. Phys. Chem. B* **1999**, *103*, 6713. (c) Noviandri, I.; Bolskar, R. D.; Lay, P. A.; Reed, C. A. *J. Phys. Chem. B* **1997**, *101*, 6350. (d) Matsumoto, M.; Swaddle, T. W. *Inorg. Chem.* **2004**, *43*, 2724−2735. (e) Bashkin, J. K.; Kinlen, P. J. *Inorg. Chem.* **1990**, *29*, 4507. (f) Redepenning, J.; Castro-Naro, E.; Venkataraman, G.; Mechalke, E. *J. Electroanal. Chem.* **2001**, *498*, 192.

Table 3. $E_{1/2}$ (Volt vs Ferrocene$^{0/+}$) for **2** in Two Different Media. See Equation 5 for Designation of Redox Processes

solvent–electrolyte	$E_{1/2}(4)$	$E_{1/2}(3)$	$E_{1/2}(2)$	$E_{1/2}(1)$	$E_{1/2}(1-)$	$E_{1/2}(2-)$
$CH_2Cl_2-[NBu_4][PF_6]$	0.29	0.23	0.12	0.0	−0.68	−1.46
anisole−$Na[B(C_6H_3(CF_3)_2)_4]$	0.67[a]	0.47	0.23	0.0	−0.60	−0.77

[a] This process is complicated by product adsorption (see Figure 9).

Table 4. $\Delta E_{1/2}$ Values (mV) for **2** in Selected Electrolytes. TFAB = $[B(C_6F_5)_4]^-$; [BArF$_{24}$] = $[B(C_6H_3(CF_3)_2)_4]^-$

	oxidations $E_{1/2}(4) - E_{1/2}(1)$	reductions $E_{1/2}(1-) - E_{1/2}(2-)$
anisole−Na[BArF$_{24}$]	670[a]	183
THF−Na[BArF$_{24}$]	606	472
CH_2Cl_2−[NHept$_4$]Br		797
$CH_2Cl_2-[NBu_4][PF_6]$	292	759
CH_2Cl_2−[NBu$_4$][BArF$_{24}$]	522	770
CH_2Cl_2−[NBu$_4$][TFAB]	510	752
CH_2Cl_2−Na[BArF$_{24}$][b]	682	~40

[a] This process is complicated by product adsorption (see Figure 9). [b] The CH_2Cl_2−[Na][BArF$_{24}$] electrolyte is a saturated solution with a ca. 0.02 M salt concentration.

The redox couples described in this paper were, unless otherwise noted, essentially Nernstian, with no evidence of either slow charge transfer or of chemical follow-up reactions that were fast on the CV time scale. This simplified the $E_{1/2}$ measurements, which were obtained by three different voltammetric methods. Simple visualization of the CV peaks was satisfactory in many cases. Square wave voltammetry (SWV, frequencies of 10 Hz or higher) and differential pulse voltammetry (DPV, pulse height 10 mV) were employed when the $|\Delta E_{1/2}|$ values were less than about 110 mV. The precision of $\Delta E_{1/2}$ values is greater than 10 mV.

Results And Discussion

I. Medium Effects on $\Delta E_{1/2}$ of 1. A. Overview. $\Delta E_{1/2}$ values for the oxidation of **1** in 45 different media ranged from 212 to 850 mV (Table 2), representing an increase of almost 10^{11} in K_{comp} for the following reaction: $\mathbf{1}^{2+} + \mathbf{1} \rightleftharpoons 2\ \mathbf{1}^{+}$. The smallest $\Delta E_{1/2}$ values occurred in low-polarity solvents having low acceptor numbers and containing small electrolyte anions, such as halides. The largest $\Delta E_{1/2}$ values were also found in solvents of low polarity, in this case, those having low donor numbers and containing large WCAs in the supporting salt. The dominating effect of ion pairing in low-polarity solvents containing WCAs is well illustrated by the fact that $\Delta E_{1/2}$ values are similar in CH_2Cl_2 (up to 850 mV) and in Et_2O (800 mV), despite the large difference in donor numbers of these solvents (0 vs 19.2, respectively).

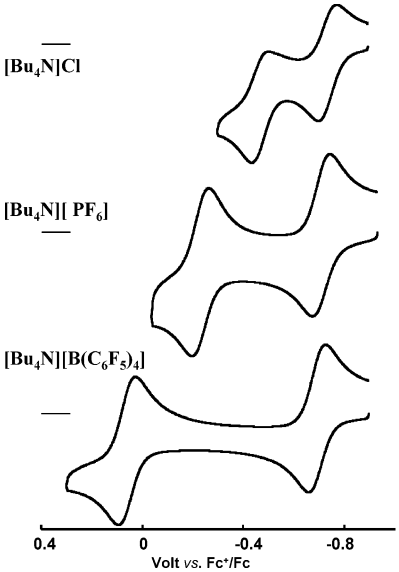


Figure 1. CV scans at $\nu = 0.1$ V/s of bis(fulvalene)dinickel **1** in CH_2Cl_2, 0.1 M $[Bu_4N]Cl$, $[Bu_4N][PF_6]$, or $[Bu_4N][B(C_6F_5)_4]$.

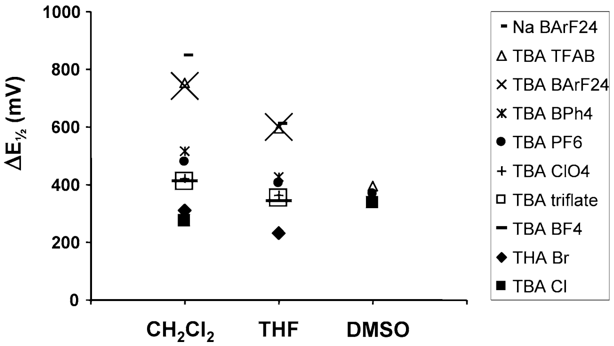


Figure 2. Schematic representation of the available tuning window of $\Delta E_{1/2}$ values for complex **1** as a function of the supporting salt in dichloromethane, tetrahydrofuran, and dimethylformamide.

Scheme 1

$$\text{Red} - e^- \leftrightarrows [\text{Ox}]^+ \qquad E_{1/2}(1)$$
$$[\text{Ox}]^+ + A^- \leftrightarrows [\text{Ox}]A \qquad K_{11}$$

B. Role of Electrolyte Anion. With any of the solvents utilized, the $\Delta E_{1/2}$ values invariably increase as one moves from smaller to larger electrolyte anions, A^-. The CVs of **1** in CH_2Cl_2 (Figure 1) are representative, with $\Delta E_{1/2}$ increasing from 273 mV ($A^- = Cl^-$) to 480 mV ($A^- = [PF_6]^-$) to 753 mV (A^- = TFAB). Switching A^- from Cl^- to TFAB results in an overall change of 480 mV in $\Delta E_{1/2}$, reflecting an increase of 1.3×10^8 in K_{comp}. The increase arises almost completely from the positive shift in $E_{1/2}(2)$, for the change in $E_{1/2}(1)$ is rather small (ca. 30 mV or less). This is qualitatively explained by an electrostatic model in which the greater positive charge of the dication accentuates ion-pairing effects, which decrease owing to charge-to-size ratios in the order $Cl^- > [PF_6]^- >$ TFAB. Equation 7 describes the modified $E_{1/2}$ when ion pairing of $[\text{Ox}]^+$ by the electrolyte anion is taken into account (Scheme 1).

$$E_{1/2} = E_{1/2}(1) - (RT/F)\ln(1 + K_{11}[A^-]) \qquad (7)$$

The CH_2Cl_2 data with different anions are shown graphically in Figure 2. Remarkably, the $\Delta E_{1/2}$ values obtained with traditional anions are closer to those seen with halide ions than with WCA anions. Whereas this trend (halide < $[PF_6]^-$ < $[TFAB]^-$) holds for all the solvents studied, it becomes less exaggerated in solvents of higher dielectric constant or greater donor strength. This is illustrated in Figure 2, wherein the $\Delta E_{1/2}$ spreads for the three types of anions are seen to decrease from 480 mV in CH_2Cl_2 to 361 mV in THF to 56 mV in DMSO.

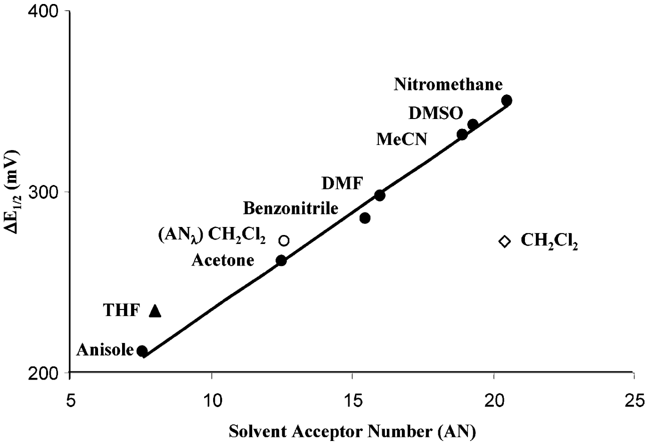


Figure 3. Correlation between the measured $\Delta E_{1/2}$ value of **1** in 0.1 M $[NBu_4]Cl$ and the acceptor number (AN) of the solvent. (▲) THF 0.1 M $[N(hept)_4]Br$ is not included in the regression analysis. For description of AN versus AN_λ, see ref 19. All ● values are AN, except for anisole, for which only the AN_λ value was available. For dichloromethane, both the AN value (◇) and AN_λ (○) value are shown. See discussion in text of ref 19. When CH_2Cl_2 is excluded from the regression analysis, R^2 is 0.9929.

Although the $\Delta E_{1/2}$ value in DMSO is markedly smaller than that in CH_2Cl_2 in the presence of $[NBu_4][TFAB]$ (393 vs 753 mV), it is actually *larger* in DMSO with $[NBu_4]Cl$ as electrolyte (337 vs 273 mV). Qualitatively, this comparison shows the dominance of solvation in high-polarity solvents and of ion pairing in low-polarity solvents.

C. Role of Solvent Donor/Acceptor Properties. Assuming that none of the three redox states of **1** undergoes specific solvation,[32] the solvent properties which influence its $\Delta E_{1/2}$ values must arise from nonspecific forces.[16,33] Considering first the solvent donor strength, the smaller $\Delta E_{1/2}$ in THF/$[NBu_4][TFAB]$ (595 mV) compared to that in CH_2Cl_2/$[NBu_4][TFAB]$ (753 mV) might be attributed to the increasingly stronger solvation of the analyte by the strong donor THF (DN = 20 vs 0 for CH_2Cl_2) as the products increase in positive charge. However, the solvent donor effect is unlikely to dominate $\Delta E_{1/2}$ for the large, charge-delocalized, oxidation products $\mathbf{1}^+$ and $\mathbf{1}^{2+}$. Commensurate with the absence of a strong accepting analyte, no meaningful correlation of $\Delta E_{1/2}$ with the solvent DN is found.

There is a significant correlation, however, of $\Delta E_{1/2}$ with solvent *acceptor* strength when $[NBu_4]Cl$ is the electrolyte, owing to the strong ion-pairing ability of chloride (Figure 3). With perhaps one exception, there is a linear dependence of $\Delta E_{1/2}$ on AN, with greater values being observed for more strongly accepting solvents. The increase of $\Delta E_{1/2}$ is attributed to increased solvation of chloride, thereby decreasing ion-pairing effects.

D. Role of Supporting Electrolyte Cation. To this point, the ion pairing of the countercation C^+ with the electrolyte anion has not been specifically taken into account. Clearly, however, since C^+ competes with $[Ox]^+$ for ion pairing with A^- (Scheme 2), changes in C^+ may have an effect on the measured $E_{1/2}$ by changing the affinity of A^- for $[Ox]^+$.

This is well illustrated by the increase of $\Delta E_{1/2}$ in CH_2Cl_2 containing saturation-limited 0.02 M $Na[BArF_{24}]$ (850 mV) compared to that having 0.10 M $[NBu_4][BArF_{24}]$ (744 mV).

Scheme 2

$$\begin{array}{llll} \mathrm{Red} - e^- & \leftrightarrows & [\mathrm{Ox}]^+ & E_{1/2}(1) \\ [\mathrm{Ox}]^+ + A^- & \leftrightarrows & [\mathrm{Ox}]A & K_{11} \\ C^+ + A^- & \leftrightarrows & CA & K_{CA} \end{array}$$

Scheme 3

$$\begin{array}{llll} [\mathrm{Ox}]^+ + A^- & \leftrightarrows & [\mathrm{Ox}]A & K_{11} \\ [\mathrm{Ox}]^{2+} + A^- & \leftrightarrows & \{[\mathrm{Ox}]A\}^+ & K_{21} \\ [\mathrm{Ox}]^{2+} + 2A^- & \leftrightarrows & [\mathrm{Ox}]A_2 & K_{22} \end{array}$$

Although some of this difference arises from the alteration in electrolyte concentrations, the major factor is the comparatively stronger ion pairing of $[BArF_{24}]$ with sodium rather than the oxidized forms of **1** (decreasing the concentration of a $[NBu_4]^+$ solution from 0.10 to 0.02 M results in an increase of less than 60 mV in $\Delta E_{1/2}$, vide infra). The resulting $\Delta E_{1/2}$ value obtained for **1** in CH_2Cl_2/0.02 M $Na[BArF_{24}]$ is the largest measured in the present study. The size of the "competitive ion-pairing" effect is likely to be largest in low-donor solvents, such as CH_2Cl_2, which poorly solvate small cations, thereby increasing their availability to A^-. The lithium ether solvate salt $[Li(Et_2O)_n][TFAB]$ does not show the same effect when compared with its tetrabutylammonium counterpart $[NBu_4][TFAB]$. In that case, $\Delta E_{1/2}$ is virtually unchanged at 753 mV, owing apparently to a strong lithium/ether interaction. Overall, however, competitive ion-pairing effects should be considered as one of the factors influencing solvent/supporting electrolyte design to maximize or minimize $\Delta E_{1/2}$ values (see section F).

E. Effect of Electrolyte Concentration. The relationship between changes in the $\Delta E_{1/2}$ value (i.e., $\Delta\Delta E_{1/2}$) and the concentration of a single supporting electrolyte is given in eq 8.[3] This equation assumes that the only ion-pairing reactions are those of Scheme 3, involving 1:1 and 1:2 cation:anion salts, which in the present case would be $[\mathbf{1}][A]$, $\{[\mathbf{1}][A]\}^+$, and $[\mathbf{1}][A]_2$.

$$\Delta\Delta E_{1/2} = (RT/F)\ln\{(1 + K_{11}[A])^2/(1 + K_{21}[A] + K_{21}K_{22}[A]^2)\} \quad (8)$$

The second and third of these are recognized as the ion-paired salts of the dication $\mathbf{1}^{2+}$ with either one or two anions, respectively.

The difficulty of this analysis is exacerbated by the fact that higher aggregates (such as $[Ox_2A]^+$), which are almost surely present in the low-polarity solvents under investigation,[5a,21] are not accounted for in eq 8. Thus, we restricted our investigation of $\Delta\Delta E_{1/2}$ versus [A] to the utilitarian question of how changes in voltammetry level electrolyte concentrations are likely to affect $\Delta E_{1/2}$. For these measurements, a medium which supports a large $\Delta E_{1/2}$ value for **1**, namely, CH_2Cl_2 / $[NBu_4][TFAB]$, was chosen, and the electrolyte concentration was varied from 0.02 to 0.67 M. The former is the lowest concentration used in the present study, and the latter approaches the practical limit of electrolytes in organic solvents. As shown in Figure 4, over the entire concentration range, a change of only 52 mV is seen in $\Delta E_{1/2}$, with the larger value occurring at the lower electrolyte concentration. In light of the very large $\Delta\Delta E_{1/2}$ values shown in this paper, which accompany changes in the chemical makeup of solvent and electrolyte ions, manipulation of the supporting

---

(32) That is, the solvent acts as a continuum and does not form coordinate bonds with the analyte.

(33) Popovych, O.; Tomkins, R. P. T. *Nonaqueous Solution Chemistry*; John Wiley & Sons: New York, 1981; Chapter 3.

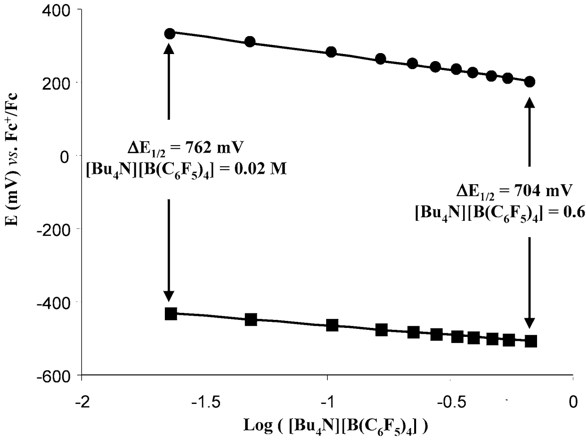


Figure 4. Redox potential of **1** as a function of log([NBu$_4$][B(C$_6$F$_5$)$_4$]). (■) $E_{1/2}$(1); (●) $E_{1/2}$(2).

electrolyte concentration may not seem to be important. Lowering of $\Delta\Delta E_{1/2}$ by 59 mV represents, however, an increase of an order of magnitude in K_{comp}, which may be of practical value in some applications.

F. Ideal Medium Properties to Maximize $\Delta E_{1/2}$ and $\Delta\Delta E_{1/2}$ for Electrogenerated Cations. Maximizing $\Delta E_{1/2}$ for redox processes involving positively charged products requires a medium with the following properties: (i) a lower-polarity solvent (preferably of low donor strength) to minimize solvation of analyte cations, (ii) a weakly coordinating electrolyte anion to minimize ion pairing, (iii) a small electrolyte countercation to enhance competitive ion pairing with the supporting salt anions, and (iv) a low concentration of the supporting electrolyte. The nucleophilic properties of the solvent must also be kept in mind, again favoring solvents of low donor number. Properties (i) and (ii) have the largest effects on $\Delta E_{1/2}$ values, with property (i) being crucial to effecting the largest *changes* in $\Delta E_{1/2}$, that is, $\Delta\Delta E_{1/2}$. Properties (iii) and (iv) help to refine $\Delta E_{1/2}$ changes on a more modest scale. Taken together, properties (i) to (iv) are seen as moving toward a goal of maximum "nakedness" of the most highly charged analytes.

II. Application to Polycations: Oxidation of 2. The $E_{1/2}$ values for the six one-electron transfer processes of **2** (see eqs 5 and 6) in two different media are given in Table 3. Oxidation of **2** presents two challenges often encountered with multi-step anodic reactions in low-polarity solvents, namely, poorer product solubilities for the more highly oxidized forms and small $\Delta E_{1/2}$ values if the redox sites are not strongly interacting.[8,14c,34] The differential pulse voltammograms of Figure 5 show how the four ferrocenyl-based oxidations of **2** become spread out in CH$_2$Cl$_2$ as the supporting electrolyte is changed. Expressed as $E_{1/2}(4) - E_{1/2}(1)$, this value goes from 292 mV in [NBu$_4$][PF$_6$] to 510 mV in [NBu$_4$][TFAB] to 682 mV in Na[BArF$_{24}$], an increase of almost 400 mV in changing from a traditional anion to a WCA electrolyte. This degree of control in the $E_{1/2}$ spacing of multielectron oxidations provides the basis for increased flexibility in the characterization of members of the electron-transfer sequence.[28] $\Delta E_{1/2}$ values for **2** in a number of different media are collected in Table 4.

III. Ideal Medium Properties to Maximize $\Delta E_{1/2}$ for Electrogenerated Anions: A "Mirror Image". There is a sizable organic electrochemical literature addressing various medium effects on the $\Delta E_{1/2}$ values of multi-step *reductions* of neutral compounds to the corresponding *anions*.[5] By analogy to the present work, the medium properties which maximize the $\Delta E_{1/2}$ values for *anionic* products are (i) a lower-polarity solvent (preferably of low acceptor number) to minimize solvation of analyte anions, (ii) a weakly coordinating electrolyte cation to minimize ion pairing, (iii) a small electrolyte counteranion to enhance competitive ion pairing with the supporting salt cations, and (iv) a low concentration of the supporting electrolyte.

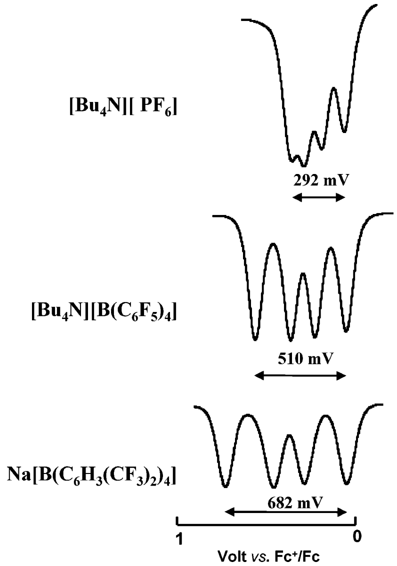


Figure 5. Differential pulse voltammograms (pulse height = 25 mV, scanning positive) of tetraferrocenyl(nickel dithiolene) **2** in CH$_2$Cl$_2$, 0.1 M [Bu$_4$N][PF$_6$], 0.1 M [Bu$_4$N][B(C$_6$F$_5$)$_4$], and 0.02 M Na[B{C$_6$H$_3$(CF$_3$)$_2$}$_4$]. The potential difference indicated represents $\Delta E_{1/2} = E_{1/2}(4) - E_{1/2}(1)$; see eq 5.

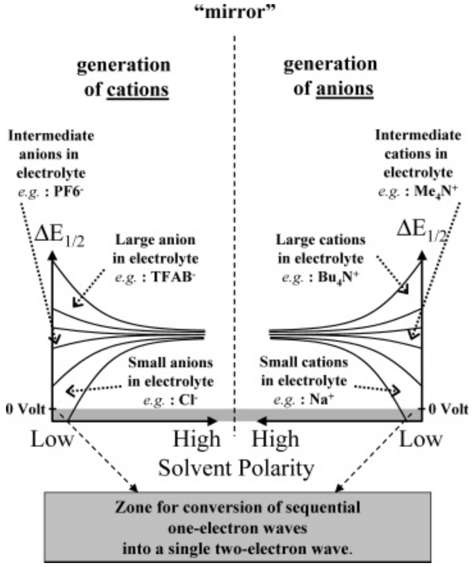


Figure 6. Mirror image model of electrolyte effects on $\Delta E_{1/2}$.

Focusing on the two dominant effects of (i) solvent and (ii) analyte−electrolyte ion pairing, and keeping in mind that ion-pairing effects are maximized in low-polarity solvents, an integrated picture emerges, summarized graphically in Figure 6, of how the medium influences $\Delta E_{1/2}$ values for both cationic and anionic electron-transfer products. In this figure, the ordinate is the $|\Delta E_{1/2}|$ value of a multi-step electron-transfer process involving formation of either cations (on left) or anions (on right). The abscissa employs the qualitative notion of "solvent polarity scale" and is meant to be dominated by solvent dielectric constant but cognizant of solvent donor−acceptor properties.[16a] For both cations and anions, the greatest differences in $\Delta E_{1/2}$ occur in low-polarity solvents with electrolyte counterions that differ considerably in size/charge ratios. The ion-pairing differences are mitigated for both types of analytes in higher-polarity solvents, which minimize the ion-pairing effects. Drawn in this way, the medium effects on $\Delta E_{1/2}$ take on a mirror image relationship for multi-step electron-transfer reactions to either cations or anions.

One of the most interesting consequences of Figure 6 is the relatively small dependence of $\Delta E_{1/2}$ on solvent properties when intermediate-sized electrolyte counterions are present, whether the products carry a positive or negative charge. Since the traditional anions (e.g., $[PF_6]^-$) and smaller tetraalkylammonium cations, such as $[NMe_4]^+$, fall into this category, media containing these electrolyte ions will not display more than minor solvent changes in $\Delta E_{1/2}$.

IV. Application of Mirror Image Model to Inorganic Polyanions: Reduction of 2. Most of the electrochemical ion-pairing studies of organic anions have been conducted in higher-polarity solvents (e.g., CH_3CN, DMF, DMSO) which, as indicated above, minimize ion-pairing effects, thus limiting electrolyte-induced $\Delta E_{1/2}$ changes. In this light, and in order to apply the mirror image model to a transition-metal complex, we investigated medium effects on the cathodic reduction of **2**, which possesses a square-planar nickel dithiolene center that is expected to have two reversible one-electron reductions (eq 6).[29] The results are collected in Tables 3 and 4.

Measured in CH_2Cl_2 containing $[NBu_4][BArF_{24}]$, a $\Delta E_{1/2}$ value of 770 mV was observed, in qualitative agreement with expectations based on a plethora of data on substituted nickel dithiolenes, for which large $\Delta E_{1/2}$ values (900−1000 mV) have been reported for these oxidation states[29] (note that $\Delta E_{1/2}$ is redefined here as being $E_{1/2}(1-) - E_{1/2}(2-)$), so that more positive $\Delta E_{1/2}$ values again indicate more highly separated waves). Consistent with the mirror image model, the electrolyte $Na[BArF_{24}]$, which *maximized* $\Delta E_{1/2}$ between positively charged electrode products, resulted here in a *minimized* $\Delta E_{1/2}$ ($\Delta E_{1/2}$ is close to zero; see Figure 7). Thus in CH_2Cl_2, a decrease of over 700 mV is realized in switching from $[NBu_4]^+$ to Na^+ as the electrolyte cation. Then, keeping the supporting electrolyte unchanged (as $Na[BArF_{24}]$), increasing the solvent donor strength gives rationale and progressive increases in $\Delta E_{1/2}$ to 183 mV in anisole (DN = 7.9) and to 472 mV in THF (DN = 20). There is a linear correlation (Figure SM1) of $\Delta E_{1/2}$ with solvent *donor* strength that is the mirror image of the correlation between solvent *acceptor* strength for oxidations when Cl^- is the electrolyte anion (section C). We note also that the strong ion pairing of Na^+ with $\mathbf{2}^{2-}$ is not minimized by competitive ion pairing with the weakly ion-pairing $[BArF_{24}]^-$ counteranion.

The one-electron versus two-electron stoichiometry of the cathodic waves for **2** was conveniently determined by comparison of their voltammetric heights to those of the anodic waves, which are all one-electron processes. Assignment of the single cathodic wave in $CH_2Cl_2/Na[BArF_{24}]$ as the two-electron process of eq 9 is supported by CV scans, such as those shown in Figure 8, which give results for **2** in both this medium (bottom) and in $CH_2Cl_2/[NBu_4][PF_6]$ (top). Strong ion pairing of the dianion $\mathbf{2}^{2-}$ to one or two sodium atoms is possible.

$$\mathbf{2} + 2e^- + m\mathrm{Na}^+ \leftrightarrows \mathrm{Na}_m[\mathbf{2}]^n \qquad (9)$$

with $m = 1$ and $n = -1$ or $m = 2$ and $n = 0$.

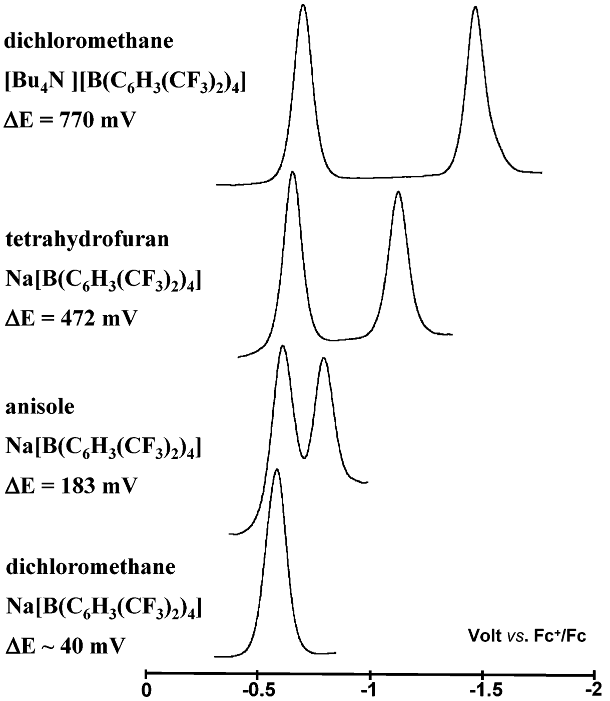


Figure 7. Differential pulse voltammograms (pulse height = 25 mV) of tetraferrocenyl(nickel dithiolene) **2** in 0.1 M $CH_2Cl_2-[Bu_4N][B\{C_6H_3(CF_3)_2\}_4]$, 0.1 M tetrahydrofuran−$Na[B\{C_6H_3(CF_3)_2\}_4]$, 0.1 M anisole−$Na[B\{C_6H_3(CF_3)_2\}_4]$, and $CH_2Cl_2-Na[B\{C_6H_3(CF_3)_2\}_4]$ saturated (0.02 M). The potential difference indicated represents $\Delta E_{1/2} = E_{1/2}(1-) - E_{1/2}(2-)$; see eq 6.

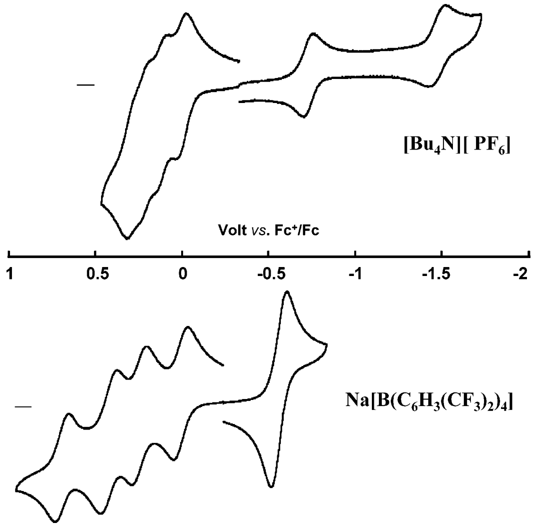


Figure 8. CV scans at $\nu = 0.1$ V/s of tetraferrocenyl(nickel dithiolene) (**2**) in CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$ and 0.02 M $Na[B\{C_6H_3(CF_3)_2\}_4]$ over the full potential range (oxidation and reduction).

Support for the direct involvement of the sodium cation in the obtaining of a two-electron stoichiometry was provided by addition of a drop of CH_3CN to the $CH_2Cl_2-Na[BArF_{24}]$ solution, which resulted in the instant recovery of the pair of one-electron waves ($\Delta E_{1/2} = 512$ mV) owing to the diminution of the sodium ion-pairing ability by acetonitrile.

Although these data confirm the mirror image model and show that the reduction of **2** can be manipulated between one-electron and two-electron stoichiometries, they do not address mechanistic aspects of the single two-electron wave. The most important voltammetric finding is that the shape of the two-electron wave is similar to that of a one-electron wave under the same conditions, a point that is confirmed by examination of the first one-electron oxidation wave for **2**$^{0/+}$. That is, in a CV scan in CH_2Cl_2/Na[BArF$_{24}$] at 0.1 V s^{-1}, the ΔE_p value for **2**$^{0/2-}$ was 99 mV, compared to a value of 89 mV for **2**$^{0/+}$. The DPV width at half-height was 105 mV, compared to 100 mV for **2**$^{0/+}$. Both of these measurements indicate that "potential inversion",[3,35] in which $E_{1/2}(2-) > E_{1/2}(1-)$, has not occurred.[36] Rather, the two one-electron processes are simply separated by the very small $\Delta E_{1/2}$ of ca. 40 mV.[37] In terms of gross medium effects, the change of about 730 mV in $\Delta E_{1/2}$ for the reduction of **2** compares well to the approximately 640 mV change observed for the oxidation of **1**, giving strong support to the mirror image model delineated above.[38] Consistent with the mirror image concepts discussed above, the $\Delta E_{1/2}$ for these reductions was further increased using an even larger electrolyte cation and a more strongly ion-pairing counteranion. Thus a $\Delta E_{1/2}$ value of 797 mV was measured in CH_2Cl_2/[N(heptyl)$_4$]Br.

V. Solubilities of Redox Products. One practical consideration, not specifically considered above, involves the consequences of medium changes on the solubilities of electrode products. Poor product solubilities may lead to electrode adsorption effects that may not be desirable.[14c] We found that more conventional nickel dithiolene complexes, such as $[Ni(S_2C_2(CN_2)_2)]^-$ and $[Ni(S_2C_2(Ph_2)_2)]^-$, gave only anodic stripping waves when cathodically reduced in low-polarity solvents that have strongly ion-pairing cations, such as CH_2Cl_2/Na[BArF$_{24}$]. In this light, the ferrocenyl moieties of **2** are seen to play a significant role even in its *reduction* reactions by increasing the solubility of the sodium salt of **2**$^{2-}$ in CH_2Cl_2. Multiply charged anions will generally display poor solubilities in dichloromethane in the absence of large lipophilic cations, such as $[NBu_4]^+$. The extent to which smaller tetraalkylammonium ions, such as $[NMe_4]^+$, may be used in CH_2Cl_2 deserves attention, and such studies are now possible owing to the increased solubilities of their TFAB and [BArF$_{24}$]$^-$ salts. Finally, regarding solubility limits for the *oxidation* products of **2**, we note that even the [BArF$_{24}$]$^-$ salt of **2**$^{4+}$ precipitates on glassy carbon in anisole ($\epsilon = 4.3$, Figure 9).

Conclusions

Systematic changes in solvents and supporting electrolytes allow the orderly tuning of $\Delta E_{1/2}$ values for sequential one-electron redox processes in nonaqueous solutions. The maximum tuning window (i.e., largest $\Delta\Delta E_{1/2}$ values) occurs in lower-polarity solvents, which accentuate ion-pairing differences. The present data allow formulation of a model for medium effects on $\Delta E_{1/2}$ values of electrogenerated cations that is the mirror image of that of electrogenerated anions (Figure 6). The precise properties of solvent and electrolyte needed to achieve the largest values of $\Delta E_{1/2}$ are complementary, requiring for cations (or *anions*) (i) a lower polarity solvent of low donor number (or low *acceptor number*), (ii) a weakly ion-pairing electrolyte anion (or *cation*), (iii) a strongly ion-pairing electrolyte countercation (or *counteranion*), and (iv) a diminished concentration of supporting electrolyte.

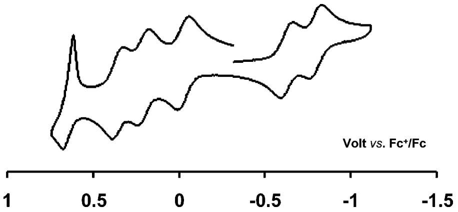


Figure 9. CV scans at $\nu = 0.06$ V/s of tetraferrocenyl(nickel dithiolene) **2** in 0.1 M anisole−Na[B{$C_6H_3(CF_3)_2$}$_4$] over the full potential range (oxidation and reduction).

Although the trends in $\Delta E_{1/2}$ are all explicable in terms of basic physical solution chemistry, the magnitudes of the changes are to us surprisingly large, as exemplified by a $\Delta E_{1/2}$ increase of almost 640 mV for the two oxidations of **1** when the medium is changed from anisole/0.1 M [NBu$_4$]Cl ($\Delta E_{1/2} = 212$ mV) to CH_2Cl_2/Na[BArF$_{24}$] ($\Delta E_{1/2} = 850$ mV). Restricting the medium changes to $[NBu_4]^+$ salts in CH_2Cl_2, $\Delta E_{1/2}$ increases by almost 350 mV when the anion is changed from $[BF_4]^-$ ($\Delta E_{1/2} = 410$ mV) to [TFAB]$^-$ ($\Delta E_{1/2} = 753$ mV). These enormous changes make it possible to exert significant control over the comproportionation thermodynamics of redox reactions.

Comparison of the three families of anions (halide, traditional, and WCA) for the oxidation of **1** in CH_2Cl_2 was particularly noteworthy. The large diminution of $\Delta E_{1/2}$ when weakly coordinating anions are replaced with halide ions (by ca. 480 mV) is easily reconciled by our understanding of the ion-pairing tendencies of large versus small anions. It was surprising, however, in light of the customary "innocent" perception[9,39,40] of the anions $[PF_6]^-$, $[BF_4]^-$, triflate, and $[ClO_4]^-$ that the $\Delta E_{1/2}$ lowering was also quite large in that case (average of 323 mV), placing the traditional anions closer to halides than to WCAs in their effect on the $\Delta E_{1/2}$ values of **1**.

Applying changes in electrolyte anions to the anodic voltammetry of **2**, the potential spread of the four ferrocenyl-based oxidations increased from 292 mV as measured in CH_2Cl_2/[NBu$_4$][PF$_6$] to 522 mV by changing the anion to [BArF$_{24}$]$^-$ and to 682 mV in CH_2Cl_2/Na[BArF$_{24}$]. The mirror image medium effect, when applied to the two nickel dithiolene-based reductions of **2** in CH_2Cl_2/[C][BArF$_{24}$] gave a single voltammetric 2e$^-$ wave ($\Delta E_{1/2}$ of ca. 40 mV) with $C^+ = Na^+$, as opposed to two well-separated one-electron reductions ($\Delta E_{1/2}$

---

(34) In the limit of two noninteracting redox centers, $\Delta E_{1/2}$ is predicted to be 36 mV at 298 K, based on statistical factors. See: (a) Ammar, F.; Savéant, J. M. *J. Electroanal. Chem.* **1973**, *47*, 115. (b) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(35) (a) Smith, W. H.; Bard, A. J. *J. Electroanal. Chem.* **1977**, *76*, 19. (b) Andrieux, C. P.; Savéant, J. M. *J. Electroanal. Chem.* **1974**, *57*, 27. (c) Ahlberg, E.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1981**, *103*, 844. (d) Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063.

(36) Potential inversion would give voltammetric wave shapes generally narrower than those of Nernstian one-electron processes, including $\Delta E_p < 60$ mV (CV), and widths at half-height less than 90 mV (differential pulse voltammetry and square wave voltammetry. See: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; Wiley: New York, 2001.

(37) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(38) The largest $\Delta E_{1/2}$ value for reduction of **2** (797 mV) was found in CH_2Cl_2 containing the large tetraheptylammonium cation and the small bromide anion.

(39) (a) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Solvents*; Marcel Dekker: New York, 1970; p 23. (b) Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L., Jr. *Electrochemistry for Chemists*, 2nd ed.; John Wiley & Sons: New York, 1995; Chapter 7.

(40) For early references to the search for noncoordinating anions, see ref 13a as well as: (a) Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1181. (b) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1025.

= 770 mV) with $C^+ = [NBu_4]^+$. In other work, the oxidative medium effect has been applied to manipulate the two-electron processes of $[Rh_2Fv(CO)_2(LL')]^{0/2+}$ (L = L′ = CO; LL′ = dppm) and $[Rh_2Fv(COD)_2]^{0/2+}$ (Fv = fulvalendiyl, dppm = diphenylphosphinomethane, COD = 1,5-cyclooctadiene) from either two separate one-electron waves to a single two-electron wave.[41]

Important influences on the $\Delta E_{1/2}$ separation of multi-step electron-transfer processes, not considered in the present analysis, are the structures and bonding of the redox-active compound and electrode products. These factors will no doubt modify the effect of medium on $\Delta E_{1/2}$,[42] and the present work provides a framework for such studies.

Finally, a comment on the relevance of the present findings to the area of mixed-valence chemistry is warranted. A widespread practice is to use $\Delta E_{1/2}$ values as a primary marker concerning electronic communication between redox centers, and there have been some efforts made to define $\Delta E_{1/2}$ ranges which support assignment to the different Robin−Day mixed-valent types.[2] The fact that $\Delta E_{1/2}$ values can be changed by many hundreds of millivolts for an individual compound, just by changing the medium, based both on the present work and on earlier studies,[6,8,11] does not invalidate that approach. It shows, however, that only when the medium is the same, or changes in the medium are taken into quantitative account, can differences in $\Delta E_{1/2}$ values be meaningfully compared for different compounds. Even given these controls and corrections, spectroscopic and/or structural data must be available to support the mixed-valent assignment.[2d]

Acknowledgment. We are grateful to the National Science Foundation (CHE-0092702 and CHE-0411703) for support of this work. We thank U.T. Mueller-Westerhoff for a sample of **2** and for helpful conversations.

Supporting Information Available: A figure showing linear correlation between the $\Delta E_{1/2}$ value of **2** measured in reduction and the donor number of the solvent, with $Na[B\{C_6H_3(CF_3)_2\}_4]$ as the supporting electrolyte salt. This material is available free of charge via the Internet at http://pubs.acs.org.

JA058171X

---

(41) Nafady, A.; Chin, T. T.; Geiger, W. E. *Organometallics*, in press.

(42) For traditional models addressing the relationship between solvation energies and delocalization of charges in cations, see ref 16b, pp 319 ff.