ACCOUNTS
of chemical research

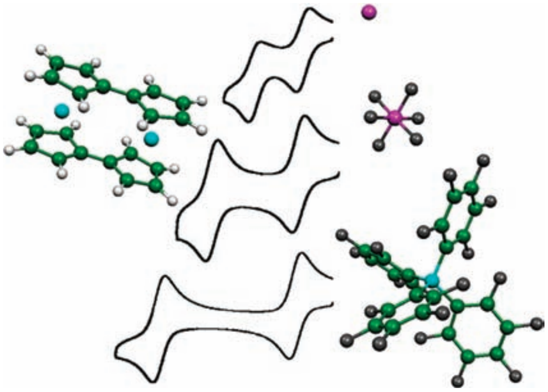
Organometallic Electrochemistry Based on Electrolytes Containing Weakly-Coordinating Fluoroarylborate Anions

WILLIAM E. GEIGER*,† AND FRÉDÉRIC BARRIÈRE‡

†Department of Chemistry, University of Vermont, Burlington, Vermont 05445,
‡Université de Rennes 1, UMR CNRS 6226, Equipe MaCSE, France

RECEIVED ON JANUARY 5, 2010

CONSPECTUS



Electrochemistry is a powerful tool for the study of oxidative electron-transfer reactions (anodic processes). Since the 1960s, the electrolytes of choice for nonaqueous electrochemistry were relatively small (heptaatomic or smaller) inorganic anions, such as perchlorate, tetrafluoroborate, or hexafluorophosphate. Owing to the similar size-to-charge ratios of these "traditional" anions, structural alterations of the electrolyte anion are not particularly valuable in effecting changes in the corresponding redox reactions. Systematic variations of supporting electrolytes were largely restricted to cathodic processes, in which interactions of anions produced in the reactions are altered by changes in electrolyte cations. A typical ladder involves going from a weakly ion-pairing tetraalkylammonium cation, $[N(C_nH_{2n+1})_4]^+$, with $n \geq 4$, to more strongly ion-pairing counterparts with $n < 4$, and culminating in very strongly ion-pairing alkali metal ions.

A new generation of supporting electrolyte salts that incorporate a weakly coordinating anion (WCA) expands anodic applications by providing a dramatically different medium in which to generate positively charged electrolysis products. A chain of electrolyte anions is now available for the control of anodic reactions, beginning with weakly ion-pairing WCAs, progressing through the traditional anions, and culminating in halide ions.

Although the electrochemical properties of a number of different WCAs have been reported, the most systematic work involves fluoro- or trifluoromethyl-substituted tetraphenylborate anions (fluoroarylborate anions). In this Account, we focus on tetrakis(perfluorophenyl)borate, $[B(C_6F_5)_4]^-$, which has a significantly more positive anodic window than tetrakis[(3,5-bis(trifluoromethyl)phenyl)]borate, $[BArF_{24}]^-$, making it suitable in a larger range of anodic oxidations.

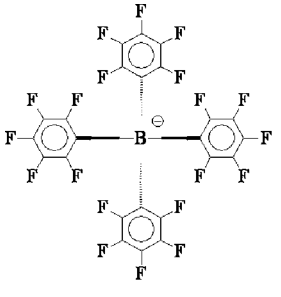
These WCAs also have a characteristic of specific importance to organometallic redox processes. Many electron-deficient organometallic compounds are subject to nucleophilic attack by the traditional family of electrolyte anions. With a view to testing the scope of the much less nucleophililic WCAs in providing a benign electrolyte anion for the generation of organometallic cation radicals, we carried out a series of studies on transition metal sandwich and half-sandwich compounds. The model compounds were chosen both for their fundamental importance and because their radical cations had been neither isolated nor spectrally characterized, despite many previous electrochemical investigations with traditional anions. The oxidation of prototypical organometallic compounds, such as the sandwich-structured ruthenocene and the piano-stool structured $Cr(\eta^6\text{-}C_6H_6)(CO)_3$, $Mn(\eta^5\text{-}C_5H_5)(CO)_3$, $Re(\eta^5\text{-}C_5H_5)(CO)_3$, and $Co(\eta^5\text{-}C_5H_5)(CO)_2$, gave the first definitive in situ characterization of their radical cations. In several cases, the kinetic stabilization of the anodic products allowed the identification of dimers or unique dimer radicals having weak metal−metal bonds and provided new preparative options for organometallic systems. In terms of thermodynamic effects, the lower ion-pairing abilities of WCAs and their good solubility in a broad range of solvents, including those of lower polarity, permitted a systematic study that yielded an integrated model of how to use solvent−electrolyte combinations to manipulate the $E_{1/2}$ differences of compounds undergoing multiple electron-transfer reactions.

Although the efficacy of WCA-based electrolytes in organometallic anodic chemistry is now established, WCAs might further expand applications of organic redox chemistry. Other WCAs, including those derived from carboranes and fluorinated alkoxyaluminates, merit additional studies.

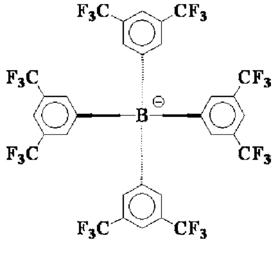
10.1021/ar1000023

Introduction

Weakly coordinating anions (WCAs) have proven to play a crucial role in reactions involving cationic organometallic compounds.[1−6] Among the most important properties of a WCA are its low nucleophilicity and the generally increased solubility of its salts in lower polarity solvents. These characteristics make WCA-based salts attractive as supporting electrolytes for oxidative electrochemical (i.e., anodic) processes, which produce cationic products that may be subject to nucleophilic attack[7] by one of the electrolyte anions traditionally employed[8] for nonaqueous electrochemistry (e.g., $[ClO_4]^-$, $[BF_4]^-$, $[PF_6]^-$). Although a number of WCAs have been employed for anodic electrochemistry (*vide infra*), to date systematic work has emphasized either the anion tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$, **1**, $[TFAB]^-$, or the aryl CF_3-substituted derivative tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, **2**, $[BArF_{24}]^-$. The body of this work, which includes the observation of long-sought or unexpected organometallic cation radicals, is now sufficient to allow for evaluation of the benefits of WCAs to the study of molecular anodic reactions.



(1)



(2)

First WCA-Based Electrochemistry. Electrochemistry in a WCA-based medium was first reported in the seminal paper of Hill et al.[9] Growing out of a collaboration between Kent Mann at the University of Minnesota and William Lamanna at 3 M Central Research, this work employed the tetrabutylammonium salt of **2**. Among the important findings was the fact that the oxidation of ruthenocene, $RuCp_2$ ($Cp = \eta^5\text{-}C_5H_5$), is a reversible one-electron process under these conditions, in contrast to the irreversible two-electron process observed previously in other electrolytes. The authors also showed that a tricationic dirhodium complex was stabilized with respect to disproportionation by up to 10^{11} in K_{disp} when the counterion $[BArF_{24}]^-$ replaced a traditional anion. Thus were underlined two important influences of electrolyte anions on the stabilities of electron-deficient metal complexes: one of kinetic and the other of thermodynamic origin. Regarding the former, traditional anions were confirmed as having nucleophilic activity toward organometallic radical cations, a notion[7] that had been proposed earlier to account for the incomplete chemical reversibility observed in the anodic electrochemistry of $Cr(\eta^6\text{-}C_6H_6)(CO)_3$.[10] Regarding the thermodynamic factor, ion-pairing strengths of traditional anions were shown to impart a significant lowering of the $E_{1/2}$ potentials for redox processes involving multiply positively charged compounds. Despite the importance of these findings, only a few papers utilizing $[BArF_{24}]^-$ salts for electrochemistry appeared in the 1990s.[11]

TABLE 1. Comparison of Electrochemically-Relevant Properties of Some Electrolyte Anions[a]

more positive electrolyte window	$TA > TFAB > BArF_{24}$
solubility of salts in lower polarity solvents	$BArF_{24} > TFAB \gg TA$
solubility of cationic electrode products	$BArF_{24} > TFAB \gg TA$
dissociation of salts in lower polarity solvents	$TFAB \approx BArF_{24} \gg TA$
reduced ion-pairing with cationic electrode products	$TFAB \approx BArF_{24} \gg TA$
lower nucleophilicity toward organometallic radical cations	$TFAB > BArF_{24} \gg TA$

[a] TA = traditional anion; $TFAB = [B(C_6F_5)_4]^-$; $BArF_{24} = [BArF_{24}]^-$.

Advantages of TFAB Anion. Our entry into this area was framed around the TFAB anion, primarily with the desire to provide a more positive electrochemical window than possible with $[BArF_{24}]^-$. It was also expected that $[TFAB]^-$ would be a weaker nucleophile than $[BArF_{24}]^-$ owing to the greater strength of aromatic vs aliphatic C−F bonds. This anion was commercially available owing to its use by Dow Chemical Co. in the single-site catalytic production of olefin-derived polymers.[12] The initial systematic work on TFAB-based electrochemistry was done by Robert LeSuer and appeared in 2000,[13] almost a decade after the report[9] on $[BArF_{24}]^-$. The oxidation of $[TFAB]^-$ is, indeed, more positive than that of $[BArF_{24}]^-$, providing an extension of the anodic electrochemical window ($E_{pa} = 1.84$ V vs ferrocene for **1** compared with 1.55 V for **2** in CH_2Cl_2; the oxidation of $[BPh_4]^-$ occurs at 0.41 V).[14] Based on published reports and on our personal experience, six relevant categories for the electrochemical effects of anions **1** and **2** are listed in Table 1, wherein $[TFAB]^-$ and $[BArF_{24}]^-$ are ranked with respect to each other and to the traditional anions. These qualitative comparisons will be referred to during our subsequent treatment.

The differences between fluoroaryl borates and traditional anions may be thought of as originating from the sharing of negative charge in the former (by 20 fluorine atoms in **1** or 8 CF_3 groups in **2**). The attendant weaker interactions with cations lead to increases in both their solubility and dissociation (and thus conductivity) in lower polarity solvents.[15]

Enhanced solubility may also be advantageous if the redox product itself is positively charged. When neutral compounds are anodically oxidized in a lower polarity solvent containing a traditional anion electrolyte, electrode surfaces often undergo passivation owing to product precipitation.[16] WCA-based electrolytes usually alleviate this adsorption effect (*vide infra*). The weaker ion-pairing interactions between WCAs and positively charged electrode products may also prove to be useful, especially in multielectron transfer reactions, as will be detailed below. Finally, WCAs may increase the longevity of the anodic product if it is susceptible to nucleophilic attack. Thus are highlighted the three aspects of the electrolyte anions around which this Account is organized: (1) fundamental properties that affect the practical aspects of electrochemical methodology, (2) thermodynamic factors, chiefly relating to how these anions affect the $\Delta E_{1/2}$ values of multielectron transfer processes, and (3) kinetic factors, emphasizing the often dramatic increase in kinetic stability of an electrogenerated cation radical.

Impact of Electrolyte Changes

Improving Electrochemical Methodologies. Enhanced Conductance. The electrochemistry of transition metal complexes is often carried out in halocarbons (e.g., CH_2Cl_2, halobenzenes) for oxidations or ethers (e.g., THF, glyme) for reductions. The fact that the dielectric constants (ε) of these solvents are less than 10 causes their electrolyte solutions to be more resistive than those historically favored for studies of organic systems (e.g., CH_3CN, DMF, DMSO, for which $\varepsilon \geq 35$). The increased dissociation of WCAs improves the conductivity of lower polarity solvents, thereby decreasing ohmic effects[17] and facilitating electrochemical experiments such as bulk electrolysis for synthesis and quantitative voltammetry for diagnosis of electrode mechanisms. For example, the resistivity of 0.1 M $[NBu_4][TFAB]$ in THF is about six times less than that of $[NBu_4][PF_6]$,[18] allowing a significant improvement in the accuracy of cyclic voltammetry data.[19] Applications in unconventional electrochemical solvents[20] such as diethyl ether ($\varepsilon = 4.3$)[21] and chloroform ($\varepsilon = 4.8$) are also facilitated, in many cases obviating the need to employ ultramicroelectrodes.[22,23] The enhanced performance of WCA salts in lower-polarity solvents also provides for better experimental conditions at reduced temperatures.[24]

Enhanced Product Solubility. Positively charged electrode products are much less likely to undergo adsorption onto the working electrode if the counterion is a WCA. Although severe adsorption may be desirable in certain applications,[25] it tends to impede the study of molecular electron-transfer processes by restricting the use of diffusion-controlled diagnostics, and it may retard the progress of bulk electrolyses owing to electrode passivation. The benefits of enhanced solubilities for tripositively charged oxidation products were shown for the triferrocenyl compounds **3**[26] and **4**.[13] The solubility of all three ferrocenyl-based oxidation products of **4** is indicated by the smooth, diffusion-controlled shape of each redox process in the CV scan shown in Figure 1. In contrast, the third anodic wave in a $[PF_6]^-$ electrolyte has a wave shape indicative of deposition of **4**$[PF_6]_3$ onto the electrode, followed by cathodic stripping on the return scan. Salts of the $[BArF_{24}]^-$ anion tend to be even more soluble than those of the [TFAB] anion.[21,27]

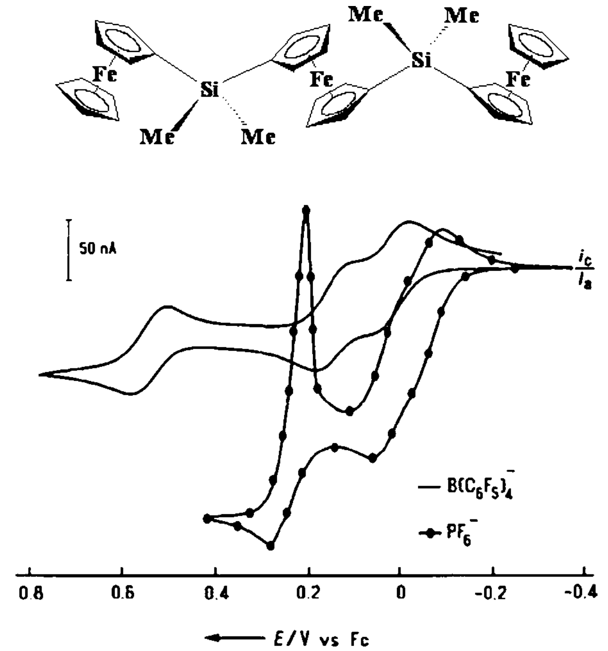
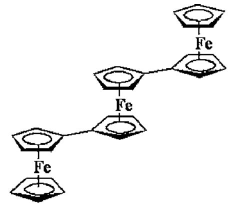
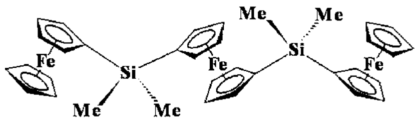


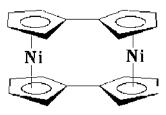
FIGURE 1. Comparison of CV scans for triferrocenyl compound **4** in CH_2Cl_2 containing 0.1 M of either $[NBu_4][PF_6]$ (–●–) or $[NBu_4][TFAB]$ (—). Adapted with permission from ref 13.



(3)



(4)



(5)

Figure 2 shows the striking improvement observed for the anodic reaction of $WCp(\eta^3\text{-}C_9H_7)(CO)_2$, which was beneficial in the study of a series of tungsten compounds.[28] A remarkable demonstration of enhanced solubility of oxidized species was noted[29] when the one-electron oxidation of bis(fulvalene)dinickel, **5**, was carried out in diethyl ether/0.1 M $[NBu_4][BArF_{24}]$.

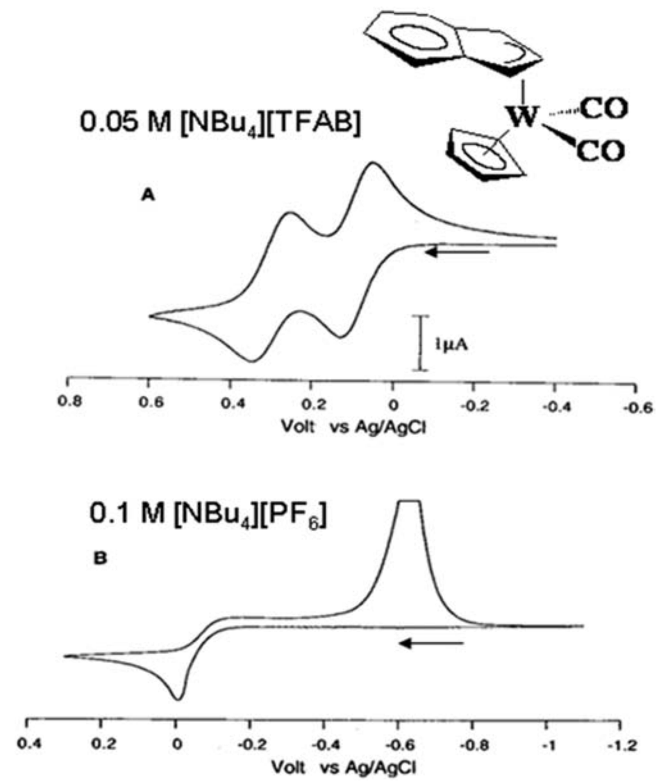


FIGURE 2. CV scans for ca. 0.7 mM $WCp(\eta^3\text{-}C_9H_7)(CO)_2$ in CH_2Cl_2 containing (A) 0.05 M $[NBu_4][TFAB]$ or (B) 0.1 M $[NBu_4][PF_6]$ at a Pt electrode. Taken from Ph.D. dissertation of Michael Stoll, University of Vermont, 2000.

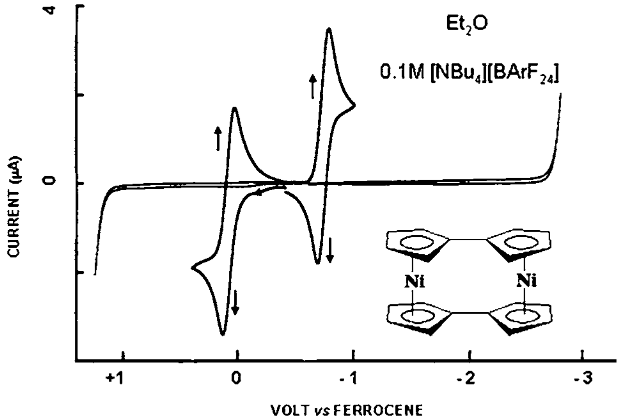


FIGURE 3. CV scans of bis(fulvalene)dinickel, **5**, before and after anodic oxidation to $\mathbf{5}^+$. "Background" curve was recorded on saturated solution of **5** in diethylether/0.1 M $[NBu_4][BArF_{24}]$. Lines with directional arrows recorded after bulk electrolysis at $E_{appl} = -0.4$ V.

The *neutral* compound **5** dissolved so poorly that its presence was virtually undetected in CV scans (line close to zero current in Figure 3). Application of −0.4 V to a large Pt electrode produced only a small current, but the solution gradually darkened as the monocation $\mathbf{5}^+$ was formed from the small amount of neutral complex available for oxidation. Over about 1 h, the coulometry reached the level expected for a one-electron oxidation of the quantity of **5** originally placed in the cell. The resulting CV scan (arrowed lines in Figure 3) gave testimony to the greatly increased solubility of the monocation $\mathbf{5}^+$.

Thermodynamics: Effect of WCAs on $E_{1/2}$ and $\Delta E_{1/2}$ Potentials. The effect of ion pairing on $E_{1/2}$ potentials is naturally magnified in lower-polarity solvents with more strongly coordinating anions. In eq 1, we assume the *idealized absence* of ion-pairing for a redox couple with a formal potential $E_{1/2}^{\mathrm{Red/Ox+}}$. If Red is a neutral compound and Ox^+ is a monocation, the ion-pairing equilibrium of Ox^+ with the anion of the electrolyte, A^-, eq 2, comes into play and the $E_{1/2}$ of the system is lowered by an amount dependent on the association constant K_{11}, eq 3, where C_A is the concentration of the electrolyte anion.

$$\mathrm{Red} \rightleftharpoons \mathrm{Ox}^+ + \mathrm{e}^- \qquad E_{1/2}^{\mathrm{Red/Ox^+}} \tag{1}$$

$$\mathrm{Ox}^+ + \mathrm{A}^- \rightleftharpoons [\mathrm{Ox}^+(\mathrm{A}^-)] \qquad K_{11} \tag{2}$$

$$E_{1/2}^{(0/+)} = E_{1/2}^{\mathrm{Red/Ox^+}} - RT/F \ln(1 + K_{11}C_A) \tag{3}$$

Expanding the redox series, we include a second one-electron process in which the *monocation* Ox^+ is further oxidized to a *dication* Ox^{2+} at the idealized potential $E_{1/2}^{\mathrm{Ox^+/Ox^{2+}}}$, eq 4. The experimental potential for the Ox^+/Ox^{2+} couple, $E_{1/2}^{(+/2+)}$, again reflects ion pairing, this time also of Ox^{2+} with either one or two anions, eqs 2 and 5−7.

$$\mathrm{Ox}^+ \rightleftharpoons \mathrm{Ox}^{2+} + \mathrm{e}^- \qquad E_{1/2}^{\mathrm{Ox^+/Ox^{2+}}} \tag{4}$$

$$\mathrm{Ox}^{2+} + \mathrm{A}^- \rightleftharpoons [\mathrm{Ox}^{2+}(\mathrm{A}^-)]^+ \qquad K_{21} \tag{5}$$

$$\mathrm{Ox}^{2+} + 2\mathrm{A}^- \rightleftharpoons [\mathrm{Ox}^{2+}(\mathrm{A}^-)_2] \qquad K_{22} \tag{6}$$

$$E_{1/2}^{(+/2+)} = E_{1/2}{}^{\mathrm{Ox^+/Ox^{2+}}} - RT/F \ln\{(1 + K_{21}C_A + K_{21}K_{22}(C_A)^2)/(1 + K_{11}C_A)\} \tag{7}$$

The difference between the two *experimental* potentials, $\Delta E_{1/2} = E_{1/2}^{(+/2+)} - E_{1/2}^{(0/+)}$, is a convenient measure[30] of the relative ion-pairing abilities of different anions. Beyond that, however, the magnitude of $\Delta E_{1/2}$ is of inherent significance owing to its relationship to the comproportionation reaction (eq 8), which helps to determine the fundamental behavior of the $Red/Ox^+/Ox^{2+}$ series.[31]

$$\mathrm{Red} + \mathrm{Ox}^{2+} \rightleftharpoons 2\mathrm{Ox}^+ \qquad K_{comp} = [\mathrm{Ox}^+]^2/[\mathrm{Red}][\mathrm{Ox}^{2+}] \tag{8}$$

In contrast to the considerable literature on ion-pairing interactions for negatively charged products (often involving alkali metal vs tetraalkylammonium electrolyte ions),[32] corresponding studies of positively charged products were severely lacking. Blount and co-workers showed that the $\Delta E_{1/2}$ values of polyaromatic cations generally increased in the order $[ClO_4]^- < [BF_4]^- < [PF_6]^-$, with the counterion effect being "leveled" in more polar solvents such as acetonitrile.[33] Even in dichloromethane, however, the spreads in $\Delta E_{1/2}$ values caused by changes in the traditional anions were less than 200 mV. In contrast, inclusion of a WCA into the set of anions used to probe oxidation of the dirhodium complex mentioned[9] in the Introduction resulted in a much larger increase of the spread in potentials. Based on the comproportionation constants reported by Hill et al., a difference of over 500 mV is calculated when going from $[PF_6]^-$ to the WCA **2**. Based on data in dichloromethane, the relative order of ion-pairing strength was given by those authors as $[Cl]^- \gg [ClO_4]^- > [BF_4]^- > [PF_6]^- > [SbF_6]^- \gg$ **2**.[9]

The leveling effect in acetonitrile observed by Blount and co-workers[33] brings up the question of the interplay between solvent and electrolyte in influencing $\Delta E_{1/2}$ values. Although there is considerable literature on the effect of solvent on $\Delta E_{1/2}$ values, a broad study of the blended effects of solvent and electrolyte changes on anodic processes had not appeared. Noting that the favorable properties of electrolytes based on **1** and **2** greatly widened the family of solvents and electrolytes that could be employed for anodic reactions, we expanded the scope of earlier studies to include a more comprehensive array of media with the goal of developing an integrated medium approach to the tuning of $\Delta E_{1/2}$ values.[34,35] The differential pulse voltammograms shown in Figure 4 are representative of the large changes in $\Delta E_{1/2}$ observed for **5** in different media, and Figure 5 is a diagrammatic summary of data collected in 45 different media. For a given set of electrolyte anions, the alterations in $\Delta E_{1/2}$ are largest when the solvent is a poor donor and of low polarity [e.g., dichloromethane, donor number (DN) = 0], moderated when the solvent has significant donor character (THF, DN = 20), and almost nonexistent in a highly polar, strong donor solvent (DMSO, $\varepsilon = 47.2$, DN = 29.8).

A qualitative overview of these results portrays media as having "mirror image" effects on $\Delta E_{1/2}$ for redox products that are either cations or anions. As shown graphically in Figure 5, the spread in the $|\Delta E_{1/2}|$ value increases for solvents of lower polarity with maximum changes being seen in going from halide ions to WCAs for positively charged products and alkali metal ions to longer-chain tetraalkyammonium ions for negatively charged products. In this sense, the behavior of a WCA toward cations is analogous to that of the tetra*butyl*ammonium ion toward anions, with the behavior of traditional anions being charge-analogous to that of the tetra*methyl*ammonium ion.

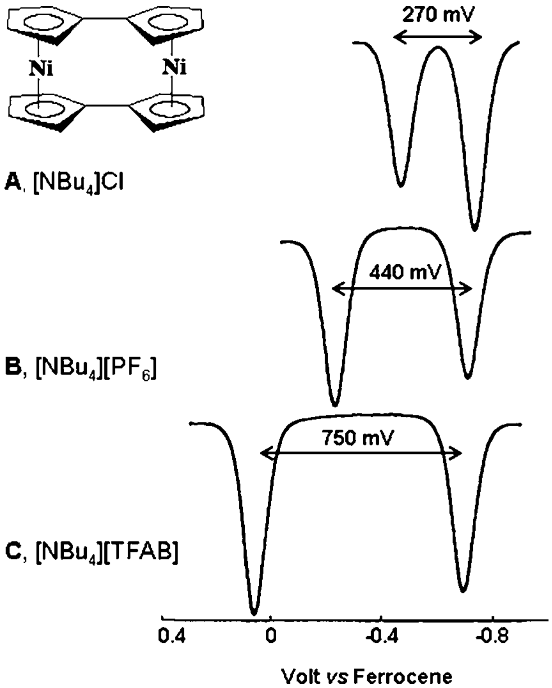


FIGURE 4. Differential pulse voltammograms (pulse height 25 mV) for 1 mM **5** in CH_2Cl_2 containing 0.1 M [NBu$_4$][An], where An = Cl^- (A), PF_6^- (B), or TFAB (C).

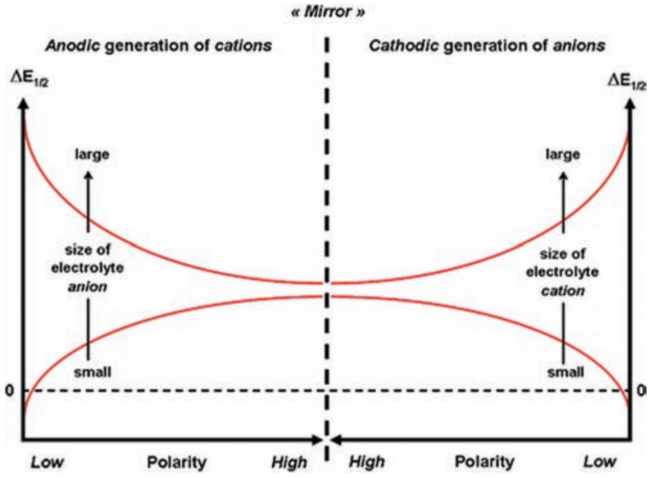


FIGURE 5. Mirror image model of solvent and supporting electrolyte effects on $\Delta E_{1/2}$ values. The abscissa is meant to correspond only roughly to dielectric constant. The solvent donor/acceptor strength also plays a role, as described in the text. Adapted with permission from ref 34.

The fact that medium effects may give rise to such large changes in $|\Delta E_{1/2}|$ raises a cautionary note[35–37] on the common usage of these values in estimating the degree of electronic interaction between different redox sites in a molecule. The general rules for maximizing and minimizing $|\Delta E_{1/2}|$ values given for both anodic and cathodic multielectron reactions were applied to control the one-electron vs

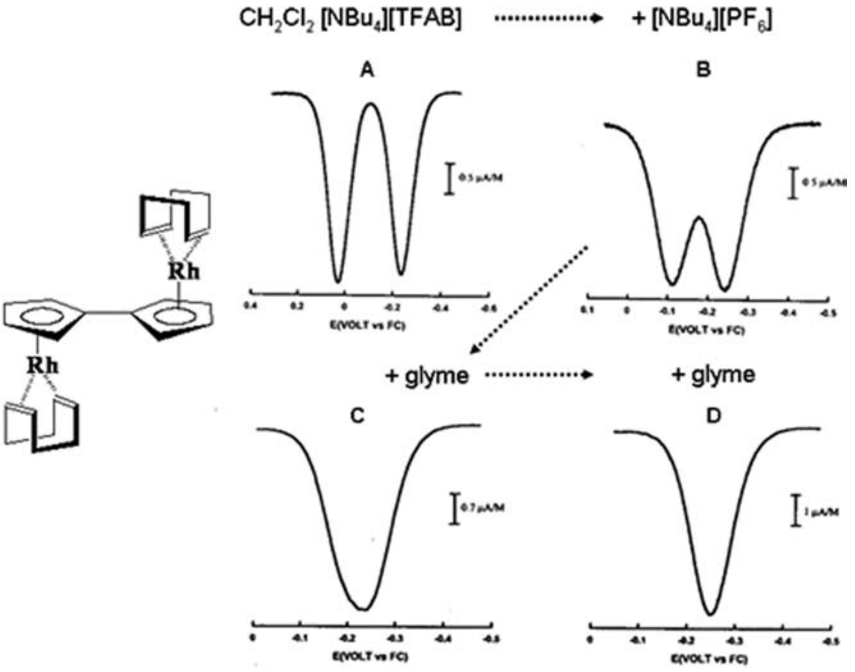
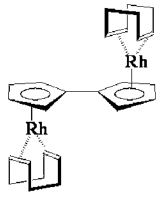
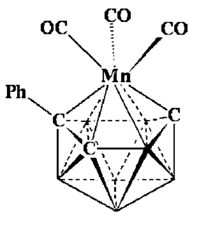


FIGURE 6. Square wave voltammograms (10 Hz) of 0.6 mM $Rh_2Fv(COD)_2$ (**6**) in different media: (A) CH_2Cl_2/0.1 M $[NBu_4][TFAB]$; (B) CH_2Cl_2/0.1 M $[NBu_4][TFAB]$ + 250 equiv of $[NBu_4][PF_6]$; (C) $6CH_2Cl_2$/4glyme/0.1 M $[NBu_4][TFAB]$ + 250 equiv $[NBu_4][PF_6]$; (D) $1CH_2Cl_2$/1 glyme/0.1 M $[NBu_4][TFAB]$ + 250 equiv $[NBu_4][PF_6]$. Ordinate is current-normalized for better viewing. Adapted with permission from ref 38.

two-electron stoichiometries of representative organometallic compounds.[38,39] For example, oxidation of the dirhodium complex $Rh_2Fv(COD)_2$ (**6**, Fv = fulvalendiyl, COD = cyclooctadiene) proceeds by two well-resolved one-electron processes ($\mathbf{6}^{0/+}$ and $\mathbf{6}^{+/2+}$) in CH_2Cl_2/0.1 M $[NBu_4][TFAB]$ but by a single two-electron wave upon addition of a donor solvent and a traditional anion. As partially reproduced in Figure 6, the $\Delta E_{1/2}$ value can be readily manipulated within an overall spread of about 330 mV, thereby varying the comproportionation equilibrium constant (eq 8) by more than 10^5.[38] The important phenomenon[31] of "potential crossover" (in this case, $E_{1/2}(\mathbf{6}^{+/2+}) < E_{1/2}(\mathbf{6}^{0/+})$) was achieved with the combination of a strong donor solvent and a traditional electrolyte anion.



(**6**)



(**7**)

Mirror-image manipulation of the medium also allowed stoichiometric traversal between single two-electron and separate one-electron *reduction* processes for the tricarbadecaboranyl complex $Mn(CO)_3(\eta^6\text{-}C_3B_7H_9Ph)$, **7**, Figure 7.[39] In this case, owing to the anionic nature of the electrode products, the combination of strong donor solvent and a tetrabutylammonium-based electrolyte stretched the potential difference and separated the two waves. Potential-crossover-based two-electron conditions were reached by changing to a nondonor solvent and a smaller tetraalkylammonium ion electrolyte.

Taken together, refs 38 and 39 demonstrated the efficacy of the general electrolyte rules previously outlined.[34] Applications of this approach to the separation of ferrocenyl redox couples in dendrimers[40] and in hexa(ferrocenylethynyl)benzene derivatives[41] have been reported.

Kinetic Stabilization of Radical Cations. Long-Lived Radicals from Family Parents. A long sought-after class of organometallic radical cations is that derived from readily available unsubstituted half-sandwich carbonyls such as $Cr(\eta^6\text{-}C_6H_6)(CO)_3$ (**8**), $MnCp(CO)_3$ (**9**) (cymantrene), and $CoCp(CO)_2$ (**10**). The one-electron anodic processes of the Cr and Mn complexes had been shown to be at least partially chemically reversible on the CV time scale, and the anodic fate of the Co compound was ambiguous.[42] However, prior to investigations of their oxidations in WCA-based electrolytes, the radical cations $\mathbf{8}^+$–$\mathbf{10}^+$ had been neither isolated nor spectroscopically characterized. Instead, more stable radicals were generated from analogues altered either through replacement of the π-hydrocarbon by a more donating ligand (e.g., C_5H_5 by C_5Me_5), through substitution of a carbonyl group by a donor ligand, or both.[42] In setting out to test the possibility that WCA electrolytes provide a beneficial medium for the enhanced kinetic stabilities of the parent systems, we probed **8**–**10** as well as $ReCp(CO)_3$ (**11**), the third-row congener of **9**. Not only

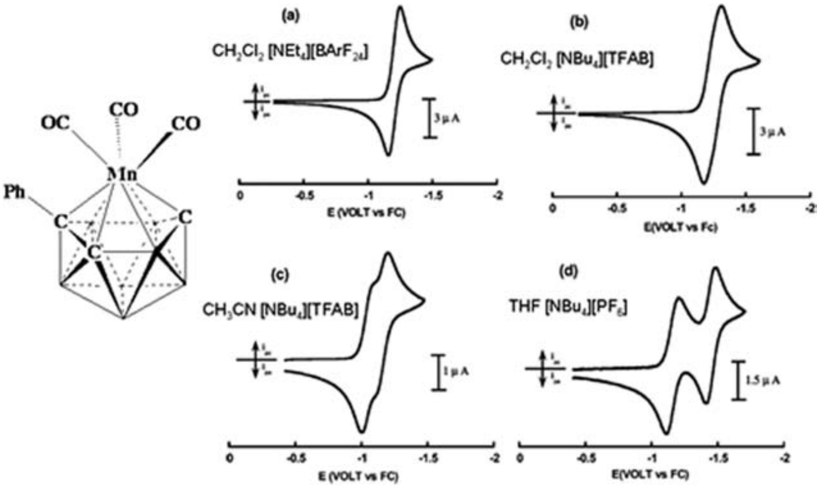
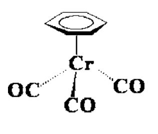


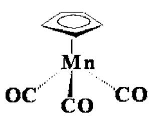
FIGURE 7. CV scans of 1,1,1-$(CO)_3$-2-Ph-*closo*-1,2,3,4-$MnC_3B_7H_9$ (**7**) in different media. Adapted with permission from ref 39.

did 8^+-11^+ prove to be long-lived in WCA-based electrolytes, but in some cases, they were also shown to undergo novel reactions that make possible new applications for organometallic radical cations.

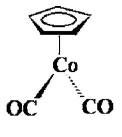
The quasi-Nernstian one-electron oxidations of the Cr system **8**[43] and the Mn system **9**[44] permitted the facile spectral characterization of the corresponding radical cations by IR and ESR (8^+ and 9^+) and by optical, near-IR, and NMR methods (9^+). The especially rich spectral responses of the $[MnCp(CO)_3]^+$ radical allowed mapping of the spin and charge localization in 8^+ (ca. 50% Mn character, most of the remaining charge in the carbonyl groups) and measurement of the small energy separation between the ground and first excited states (4840 cm^{-1}) responsible for the rapid electronic relaxation, which renders 8^+ NMR-active. These findings encouraged extension of the redox study to the Cp-substituted complexes $Mn(C_5H_4NH_2)(CO)_3$ (**12**) and $Mn(C_5Me_5)(CO)_3$ (**13**), which culminated in X-ray diffraction characterization of TFAB salts of 12^+ and 13^+. The fact that oxidation of $Mn(C_5H_4R)(CO)_3$ is generally reversible under controlled medium conditions prompted the suggestion that this moiety might find use as a "redox tag" analogous to the widely employed ferrocenyl group.[44]



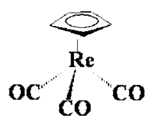
(8)



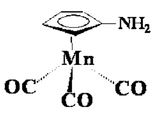
(9)



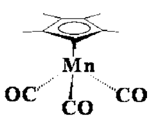
(10)



(11)



(12)



(13)

The longevity of the radicals 8^+ and 9^+ makes possible their participation in a switching process wherein substitution of CO by a donor ligand, L, can be carried out at a synthetic level. As described in eqs 9−11, the applied potential, E_{appl}, is first set at a value that is sufficiently positive to exhaustively oxidize the tricarbonyl complex represented as $M(CO)_3$ (i.e., $E_{appl} > E_{1/2}^{(CO)_3}$). In the presence of L, or after its addition to the oxidized solution, rapid CO substitution occurs[45] to give $[M(CO)_2L]^+$. Resetting the potential sufficiently negative (i.e., $E_{appl} < E_{1/2}^{(CO)_2 \cdot L}$) gives the substitution product in its desired 18-electron form, which can be readily extracted from the electrolysis solution. Switching schemes such as these provide a synthetic alternative to the photochemically initiated methods usually employed for carbonyl substitution of half-sandwich complexes.

$$M(CO)_3 \rightleftharpoons [M(CO)_3]^+ + e^- \qquad E_{1/2}^{(CO)_3} \tag{9}$$

$$[M(CO)_3]^+ + L \rightarrow [M(CO)_2L]^+ + CO \tag{10}$$

$$[M(CO)_2L]^+ + e^- \rightleftharpoons [M(CO)_2L] \qquad E_{1/2}^{(CO)_2L} \tag{11}$$

Fragile Cationic Dimers: Formation and Reactions. The anodic behavior of the formally five-coordinate cobalt compound **10** was far more complex than its pseudo-octahedral counterparts **8** and **9**, showing a concentration dependence in which a single, almost Nernstian-shaped wave at very low concentrations yielded to a double wave of overall one-electron height at high concentrations (Figure 8). Ultimately,[46] this unusual behavior was shown to arise from the reaction of the electrogenerated radical 10^+ with another mole of starting material **10**, thereby forming the unique dimer radical $[Co_2Cp_2(CO)_4]^+$ (14^+, Scheme 1), the oxidation of which was responsible for the second anodic feature (feature B in Figure 8).

This unusual "radical−substrate" reaction occurs owing to rehybridization of the metal orbital in electron-deficient 10^+, which makes possible its acceptance of the strongly basic metal center of neutral **10**. The computed long cobalt−cobalt

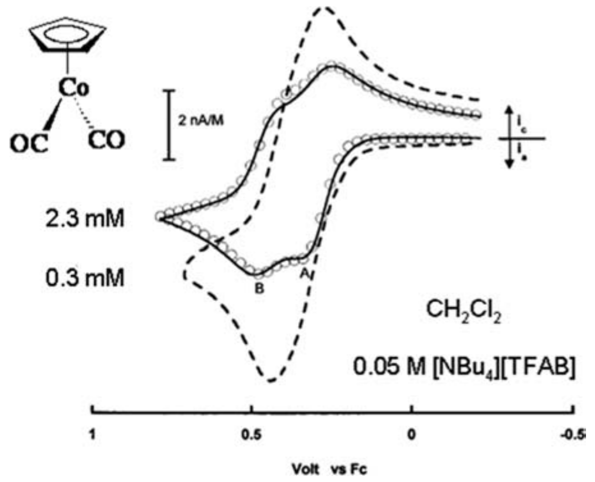
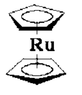


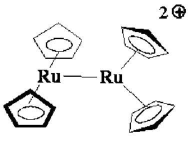
FIGURE 8. CV scans of $CoCp(CO)_2$, **10**, in CH_2Cl_2/0.05 M $[NBu_4][TFAB]$ at two different concentrations: 0.3 mM for dashed line; 2.3 mM for solid line. Digital simulation results are shown as circles; the ordinate gives concentration-normalized current. Adapted with permission from ref 46.

distance of 3.14 Å (and implied weak metal–metal bond) was consistent with the fact that $\mathbf{14}^+$ partially dissociates in solution to give equilibrium amounts of **10** and $\mathbf{10}^+$.[46]

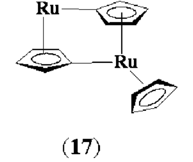
A weakly bonded metal–metal dimer was also shown to be responsible for the concentration-dependent anodic behavior of ruthenocene **15** in WCA-based electrolytes.[47] Low-temperature electrolysis of $RuCp_2$ permitted isolation of the dimer $[Ru_2Cp_4][TFAB]_2$, which is likely to have a structure (see **16**) analogous to that of the previously isolated osmium analogue.[48] A more detailed mechanistic and spectral *in situ* study of this system by Swarts et al.[49] revealed that the monomer/dimer equilibrium of eq 12 was a key factor in the hydrogen-atom shuttling process responsible for the subsequent formation of the dimetalated complex $[Ru_2Cp_2(\sigma{:}\eta^5\text{-}C_5H_4)_2]^{2+}$ (**17**).



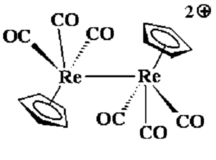
(**15**)



(**16**)



(**17**)

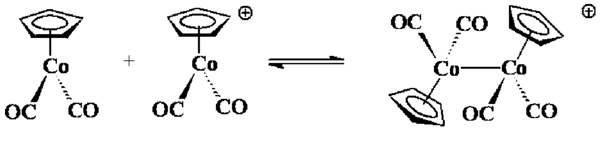


(**18**)

$$2[RuCp_2]^+ \rightleftharpoons [Ru_2Cp_4]^{2+} \qquad (12)$$

Fundamental to the differences in reactions of the ferrocenium and ruthenocenium ions is the ability of the heavier transition metal to expand its coordination sphere beyond that of pseudo-octahedral. With this possibility of coordination expansion in mind, we investigated the oxidation of the third-row metal complex $ReCp(CO)_3$ (**11**), permitting isolation of the bis-TFAB salt of the dimer **18**, $[Re_2Cp_2(CO)_6]^{2+}$.[50] The weak metal–metal bond implied by the computed[50] Re–Re bond length of 3.229 Å explained the observation that solutions of **18** provide modest proportions of the monomer-radical $\mathbf{11}^+$ (close to 10% under typical conditions). An important property of this rhenium system is the very positive potential of the $\mathbf{11}^{0/+}$ couple (1.16 V vs ferrocene), which makes $\mathbf{11}^+$ a very strong one-electron oxidant.[51,52] The isolated dimer $\mathbf{18}[TFAB]_2$ is a convenient source of the oxidant, which can be used to synthesize TFAB salts of oxidized organic and organometallic compounds such as the X-ray characterized $[Re_2(\eta^5\text{-}C_5H_4NH_2)_2(CO)_6][TFAB]_2$ (Figure 9).[53]

SCHEME 1



(**10**) (**10**$^+$) (**14**)

Summary and Recommendations

Electrochemistry, in its various guises, is arguably the most powerful and widely used approach to the study of oxidative electron-transfer reactions. The benefits inherent to the use of WCA-based electrolytes in molecular electrochemistry are sufficient to rightly classify them as the third-generation of supporting electrolyte anions (halide → "traditional", for example, $[BF_4]^-$ → WCA). In terms of physical and physicochemical effects, the improved conductivities of their electrolyte salts and increased solubilities of their reaction products facilitate use of the lower-polarity solvents that are often desirable for electrochemical applications. The more dramatic chemical effects of WCAs, however, which originate in their intrinsically low ion-pairing strengths and nucleophilicities, are in how they influence the thermodynamic and kinetic properties of redox reactions involving cationic products.

Weakly coordinating anions have already been shown to be a valuable addition to the electrochemical toolbox for manipulating the medium in order to control the thermodynamics of multielectron processes, even to the point of allowing changes between a one-electron and two-electron stoichiometry. A conceptually simple "mirror image" model is now available,[34] which integrates the medium effects of electrolyte ions and solvent on the $\Delta E_{1/2}$ values of multielectron processes involving *either* cations or anions. In this model, the traditional anions, such as $[BF_4]^-$ and $[PF_6]^-$, are seen to have

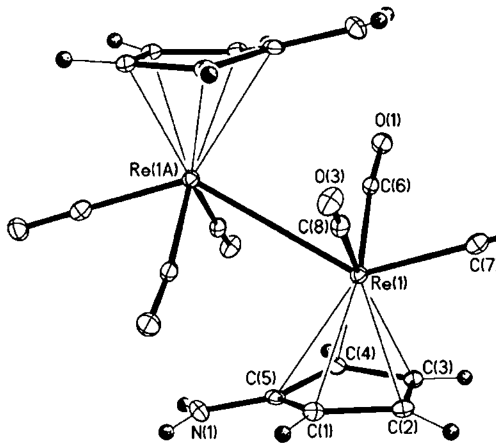


FIGURE 9. X-ray of cationic structure for $[Re_2(\eta^5\text{-}C_5H_4NH_2)_2(CO)_6][TFAB]_2$. Reprinted with permission from ref 53.

an effect on anodic $\Delta E_{1/2}$ values that is intermediate between those of halides and WCAs, much as the cation $[NMe_4]^+$ is seen[32] as ranking intermediate between alkali metal ions and the tetrabutylammonium ion in its effect on cathodic $\Delta E_{1/2}$ values.

The fact that new possibilities for the generation and reactions of kinetically stable organometallic radical cations emerged so readily from the study of prototypical metal sandwich[9,47,49] and half-sandwich complexes[43,44,46,53] has established the value of fluoroarylborate electrolyte anions in organometallic applications. WCAs other than **1** and **2** also hold promise. Voltammetry has been carried out in benzene with the aide of $Li[CB_{11}Me_{12}]$ as the supporting electrolyte.[54] The rather facile oxidation of this carborane anion (ca. 0.7 V vs FcH) limits its anodic utility, but the potential range of the hexachloro-substituted analogue $[CB_{11}Cl_6Me_6]^-$ extends more positive by about 1 V, giving it promise as a functional electrolyte anion.[55] Fluorinated alkoxyaluminates[56] are also promising,[57] and one member of the traditional family, namely, hexafluoroarsenate anion, has proven useful.[55] An analogue of **2**, in which the CF_3 groups are replaced by C_6F_{13}, allows voltammetry to be carried out in very low polarity fluorous solvents.[58]

Less well-developed is the scope of how WCAs might be used to deal with problems of nucleophilic attack by the electrolyte anion on organic radical cations.[59,60] This is an area in which systematic comparisons between traditional anions and various weakly coordinating anions would be welcome, inquiries that are facilitated by the now modest costs of some commercially available[61] fluoroarylborates.

W.E.G. is grateful to the National Science Foundation for support (Grant CHE-0808909) and thanks Kent Mann for personal correspondence. We gratefully acknowledge the partial donation of electrolytes by Boulder Scientific Co.

BIOGRAPHICAL INFORMATION

William Geiger is Pomeroy Professor of Chemistry at the University of Vermont, where he has spent the greater part of his academic career studying the electrochemical behavior of transition metal compounds.

Frédéric Barrière is Associate Professor at the University of Rennes 1. He is interested in all aspects of electron transfer at the molecular, enzymatic, and cellular levels.

REFERENCES

1 Strauss, S. H. The search for larger and more weakly coordinating anions. *Chem. Rev.* **1993**, *93*, 927–942.

2 Reed, C. A. Carboranes: A new class of weakly coordinating anions for strong electrophiles, oxidants, and superacids. *Acc. Chem. Res.* **1998**, *31*, 133–139.

3 Krossing, I.; Raabe, I. Noncoordinating anions-fact or fiction? A survey of likely candidates. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066–2090.

4 Jordan, R. F. Chemistry of cationic dic yclopentadienyl group 4 metal-alkyl complexes. *Adv. Organometal. Chem.* **1991**, *32*, 323–387.

5 Chen, E. Y.-K.; Marks, T. J. Cocatalysts for metal-catalyzed olefin polymerization: Activators, activation processes, and structure-activity relationships. *Chem. Rev.* **2000**, *100*, 1391–1434.

6 Reed, C. A.; Chan, K.-C.; Bolskar, R. D.; Mueller, L. J. Taming superacids: Stabilization of the fullerene cations HC_{60}^+ and C_{60}^+. *Science* **2000**, *289*, 101–104.

7 Beck, W.; Sünkel, K. Metal complexes of weakly coordinating anions. Precursors of strong cationic organometallic Lewis acids. *Chem. Rev.* **1988**, *88*, 1405–1421.

8 Fry, A. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T.; Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; pp 469−485. The term “electrolyte” technically refers to the combined solvent/supporting electrolyte system. We use it here to refer to the supporting electrolyte alone and employ “medium” to denote the combined system.

9 Hill, M. G.; Lamanna, W. M.; Mann, K. R. Tetrabutylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as a noncoordinating electrolyte: Reversible 1e$^-$ oxidations of ruthenocene, osmocene, and $Rh_2(TM4)_4^{2+}$ (TM4=2,5-diisocyano-2,5-dimethylhexane). *Inorg. Chem.* **1991**, *30*, 4687–4690.

10 Stone, N. J.; Sweigart, D. A.; Bond, A. M. Effects of temperature and supporting electrolyte on the electrochemical oxidation of (benzene)tricarbonylchromium and other π-hydrocarbon complexes. *Organometallics* **1986**, *5*, 2553–2555.

11 Gassman, P. G.; Deck, P. A. Tricarbonyl(η6-hexachlorobenzene)chromium(0). *Organometallics* **1994**, *13*, 1934–1939.

12 Stevens, J. C.; Neithamer, D. R. U.S. Patent No. 5,064,082, 1991.

13 LeSuer, R. J.; Geiger, W. E. Improved electrochemistry in low-polarity media using tetrakis(pentafluorophenyl)borate salts as supporting electrolytes. *Angew. Chem., Int. Ed.* **2000**, *39*, 248–250.

14 Pal, P. K.; Chowdhury, S.; Drew, M. G. B.; Datta, D. The electrooxidation of the tetraphenylborate ion revisited. *New J. Chem.* **2002**, *26*, 367–371.

15 Bond, A. M. *Broadening Electrochemical Horizons*; Oxford University Press: Oxford, 2002; pp 43−46.

16 Barrière, F.; Kirss, R. U.; Geiger, W. E. Anodic electrochemistry of multiferrocenyl phosphine complexes in weakly nucleophilic electrolytes. *Organometallics* **2005**, *24*, 48–52.

17 Roe, D. K. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; p 195 ff.

18 LeSuer, R. J.; Buttolph, C.; Geiger, W. E. Comparison of the conductivity properties of the tetrabutylammonium salt of tetrakis(pentafluorophenyl)borate anion with those of traditional supporting electrolyte anions in nonaqueous solvents. *Anal. Chem.* **2004**, *76*, 6395–6401. It is worth noting that lower resistivities are *not* achieved when more polar solvents such as acetonitrile or DMF are employed. In those cases, there is already a high degree of dissociation with salts of the traditional anions, and the larger size of the WCA actually results in a slight increase in resistivity owing to its lower ionic conductivity.

19 For example, CV scan rates might be ten-fold faster in THF before encountering the same ohmic errors seen with a $[PF_6]^-$-based electrolyte.

20 Abbott, A. P.; Schiffrin, D. J. Conductivity of tetra-alkylammonium salts in polyaromatic solvents. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1453–1459.

21 Chávez, I.; Alvarez-Carena, A.; Molins, E.; Roig, A.; Maniukiewicz, W.; Arancibia, A.; Arancibia, V.; Brand, H.; Manríquez, J. M. Selective oxidants for organometallic compounds containing a stabilising anion of highly reactive cations: $[(3,5(CF_3)_2C_6H_3)_4B^-]Cp_2Fe^+$ and $[(3,5(CF_3)_2C_6H_3)_4B^-]Cp^*{}_2Fe^+$. *J. Organomet. Chem.* **2000**, *601*, 126–132.

22 Drew, S. M.; Wightman, R. M. Voltammetry of ferrocene in low electrolyte solutions. *J. Electroanal. Chem.* **1991**, *317*, 117–124.

23 Bond, A. M. Past, present, and future contributions of microelectrodes to analytical studies employing voltammetric detection. A review. *Analyst* **1994**, *119*, R1–R21.

24 Evans, D. H.; Lerke, S. A. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; pp 487−509.

25 Oyama, M.; Nitta, Y.; Okazaki, S. Anion-controlled electrocrystallization of perylene cation radical salts. *J. Electroanal. Chem.* **2001**, *511*, 88–93.

26 Camire, N.; Mueller-Westerhoff, U. T.; Geiger, W. E. 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. *J. Organomet. Chem.* **2001**, *637−639*, 823–826.

27 Buschmann, W. E.; Miller, J. S.; Bowman-James, K.; Miller, C. N. Useful reagents and ligands. Synthesis of $[M^{II}(NCMe)_6]^{2+}$ (M = V, Cr, Mn, Fe, Co, Ni) salts of tetra[3,5-bis(trifluoromethyl)phenyl]borate. *Inorg. Synth.* **2002**, *33*, 83–91.

28 Stoll, M. E.; Belanzoni, P.; Calhorda, M. J.; Drew, M. G. B.; Félix, V.; Geiger, W. E.; Gamelas, C. A.; Gonçalves, I. S.; Romão, C. C.; Veiros, L. F. Stepwise hapticity changes in sequential one-electron redox reactions of indenyl-molybdenum complexes: Combined electrochemical, ESR, X-ray, and theoretical studies. *J. Am. Chem. Soc.* **2001**, *123*, 10595–10606.

29 Barrière, F. University of Vermont, April 2nd, 2001, personal observation.

30 This obviates the need to account for changes in liquid junction potentials as the medium is altered.

31 Evans, D. H. One-electron and two-electron transfers in electrochemistry and homogeneous solution reactions. *Chem. Rev.* **2008**, *108*, 2113–2144.

32 Fry, A. J. Effects of strong ion-pairing on the electrochemical reduction of cyclooctatetraene in tetrahydrofuran in the presence of lithium ion. Peak coalescence does not imply potential inversion. *Electroanalysis* **2006**, *18*, 391–398.

33 Bancroft, E. E.; Pemberton, J. E.; Blount, H. N. Reactions of cation radicals of EE systems. 10. The influence of ion association on cation radical disproportionation. *J. Phys. Chem.* **1980**, *84*, 2557–2560.

34 Barrière, F.; Geiger, W. E. Use of weakly coordinating anions to develop an integrated approach to the tuning of $\Delta E_{1/2}$ values by medium effects. *J. Am. Chem. Soc.* **2006**, *128*, 3980–3989.

35 Barrière, F.; Camire, N.; Geiger, W. E.; Mueller-Westerhoff, U. T.; Sanders, R. Use of medium effects to tune the $\Delta E_{1/2}$ values of bimetallic and oligometallic compounds. *J. Am. Chem. Soc.* **2002**, *124*, 7262–7263.

36 Fox, M. A.; Roberts, R. L.; Baines, T. E.; Le Guennic, B.; Halet, J.-F.; Hartl, F.; Yufit, D. S.; Albesa-Jové, D.; Howard, J. A. K.; Low, P. J. Ruthenium complexes of C,C′-Bis(ethynyl)carboranes: An investigation of electronic interactions mediated by spherical pseudo-aromatic spacers. *J. Am. Chem. Soc.* **2008**, *130*, 3566–3578.

37 D'Alessandro, D. M.; Keene, F. R. A cautionary warning on the use of electrochemical measurements to calculate comproportionation constants for mixed-valence compounds. *J. Chem. Soc., Dalton Trans.* **2004**, 3950–3954.

38 Nafady, A.; Chin, T. T.; Geiger, W. E. Manipulating the electrolyte medium to favor either one-electron or two-electron oxidation pathways for (fulvalenediyl)dirhodium complexes. *Organometallics* **2006**, *25*, 1654–1663.

39 Nafady, A.; Butterick, R., III; Calhorda, M. J.; Carroll, P. J.; Chong, D.; Geiger, W. E.; Sneddon, L. G. Hyperelectronic metal-carborane analogues of cymantrene ($MnCp(CO)_3$) anions: Electronic and structural noninnocence of the tricarbadecaboranyl ligand. *Organometallics* **2007**, *26*, 4471–4482.

40 Xu, D.; Wang, W.; Gesua, D.; Kaifer, A. E. A new series of dendrimers containing two ferrocenyl units and a Fréchet dendron around a triazine nucleus. *Org. Lett.* **2008**, *10*, 4517–4520.

41 Diallo, A. K.; Daran, J.-C.; Varret, F.; Ruiz, J.; Astruc, D. How do redox groups behave around a rigid molecular platform? *Angew. Chem., Int. Ed.* **2009**, *48*, 3141–3145.

42 Leading references to work on substituted complexes may be obtained from the full papers describing the oxidation of the unsubstituted parent compounds. For a summary of work to 1995, see: Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH Publishers: Weinheim, Germany, 1995.

43 Camire, N.; Nafady, A.; Geiger, W. E. Characterization and reactions of previously elusive 17-electron cations: Electrochemical oxidations of $(C_6H_6)Cr(CO)_3$ and $(C_5H_5)Co(CO)_2$ in the presence of $[B(C_6F_5)_4]^-$. *J. Am. Chem. Soc.* **2002**, *124*, 7260–7261.

44 Laws, D. R.; Chong, D.; Nash, K.; Rheingold, A. L.; Geiger, W. E. Cymantrene radical cation family: Spectral and structural characterization of the half-sandwich analogues of ferrocenium ion. *J. Am. Chem. Soc.* **2008**, *130*, 9859–9870.

45 For leading references, see: Geiger, W. E. Organometallic electrochemistry: Origins, development, and future. *Organometallics* **2007**, *26*, 5738–5765, esp. pp 5757−5759.

46 Nafady, A.; Costa, P. J.; Calhorda, M. J.; Geiger, W. E. Electrochemical oxidation of $CoCp(CO)_2$: Radical-substrate reaction of a 17 e^-/18 e^- pair and production of a unique dimer radical. *J. Am. Chem. Soc.* **2006**, *128*, 16587–16599.

47 Trupia, S.; Nafady, A.; Geiger, W. E. Electrochemical preparation of the bis(ruthenocenium) dication. *Inorg. Chem.* **2003**, *42*, 5480–5482.

48 Droege, M. W.; Harman, W. D.; Taube, H. Higher oxidation state chemistry of osmocene: Dimeric nature of the osmocenium ion. *Inorg. Chem.* **1987**, *26*, 1309–1315.

49 Swarts, J. C.; Nafady, A.; Roudebush, J.; Trupia, S.; Geiger, W. E. One-electron oxidation of ruthenocene: Reactions of the ruthenocenium ion in gentle electrolyte media. *Inorg. Chem.* **2009**, *48*, 2156–2165.

50 Chong, D.; Nafady, P. J.; Costa, P. J.; Calhorda, M. J.; Geiger, W. E. Anodic preparation of $[Re_2Cp_2(CO)_6]^{2+}$: A dimeric dication that provides the powerful one-electron oxidant $[ReCp(CO)_3]^+$. *J. Am. Chem. Soc.* **2005**, *127*, 15676–15677.

51 Connelly, N. G.; Geiger, W. E. Chemical redox agents for organometallic chemistry. *Chem. Rev* **1996**, *96*, 877–910.

52 Chong, D.; Stewart, M.; Geiger, W. E. Cycloaddition reactions of unactivated olefins catalyzed by an organorhenium electron-transfer mediator. *J. Am. Chem. Soc.* **2009**, *131*, 7968–7969.

53 Chong, D.; Laws, D. R.; Nafady, A.; Costa, P. J.; Rheingold, A. L.; Calhorda, M. J.; Geiger, W. E. $Re(\eta 5\text{-}C_5H_5)(CO)_3]^+$ family of 17-electron compounds: Monomer/dimer equilibria and other reactions. *J. Am. Chem. Soc.* **2008**, *130*, 2692–2703.

54 Pospíšil, L.; King, B. T.; Michl, J. Voltammetry in benzene using $LiCB_{11}Me_{12}$ as a supporting electrolyte. *Electrochim. Acta* **1998**, *44*, 103–108.

55 Bruno, C.; Marcaccio, M.; Paolucci, D.; Castellarin-Cudia, C.; Goldoni, A.; Streletskii, A. V.; Drewello, T.; Barison, S.; Venturini, A.; Zerbetto, F.; Paolucci, F. Growth of p- and n-dopable films from electrochemically generated C_{60} cations. *J. Am. Chem. Soc.* **2008**, *130*, 3788–3796.

56 Raabe, I.; Wagner, K.; Guttsche, K.; Wang, M.; Santiso-Quinones, G.; Krossing, I. Tetraalkylammonium salts of weakly coordinating anions. *Chem.—Eur. J.* **2008**, *15*, 1966–1976.

57 Stewart, M. P.; Paradee, L. M.; Raabe, I.; Trapp, N.; Slattery, J. S.; Krossing, I.; Geiger, W. E., Anodic oxidation of organometallic sandwich complexes using $[Al(OC(CF_3)_3)_4]^-$ or $[AsF_6]^-$ as the supporting electrolyte anion *J. Fluorine Chem.* **2010**, in press.

58 Olson, E. J.; Boswell, P. G.; Givot, B. L.; Yao, L. L.; Bühlmann, P. Electrochemistry in media of exceptionally low polarity: Voltammetry with a fluorous solvent. *J. Electroanal. Chem.* **2010**, *639*, 154–160.

59 He, Z.; Kispert, L. D. Effect of electrolytes and temperatures on dications and radical cations of caretenoids: Electrochemical, optical absorption, and high-performance liquid chromatography studies. *J. Phys. Chem. B* **1999**, *103*, 10524–10531.

60 Clark, D. B.; Fleischmann, M.; Pletcher, D. The partial oxidation of aliphatic hydrocarbons in aprotic solvents. *J. Electroanal. Chem.* **1973**, *42*, 133–138.

61 Quotations on K[TFAB] and $Na[BArF_{24}]$ from Boulder Scientific can be obtained at sales@bouldersci.com.