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Supplementary Material Available: Tables of crystallographic data (Table S1), anisotropic temperature parameters (Table S2), and hydrogen atom coordinates (Table S3) and complete listings of bond lengths (Table S4) and bond angles (Table S5) for *cis(Cl)*,*trans(P)*-[$TcCl_2(PMe_2Ph)_2(phen)$] and *trans(P)*-[$TcBr(PMe_2Ph)_2(terpy)$]SO_3CF_3 (13 pages); a listing of observed and calculated structure factors (Table S6) for both compounds (24 pages). Ordering information is given on any current masthead page.

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Notes

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1,2-Difluorobenzene: A Relatively Inert and Noncoordinating Solvent for Electrochemical Studies on Transition-Metal Complexes

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The criteria required of a good solvent for electrochemical studies on metal complexes or organometallic compounds include that it should (1) be relatively easy to purify, (2) have good solvating properties for both electrolyte and metal complexes or compounds, and (3) have an extended potential "window".[1] Although these criteria are largely met by acetonitrile and other organic solvents such as DMF or DMSO, they have the ability to coordinate and often play a role as ligands in electrochemically induced substitution processes.[2] The solvents CH_2Cl_2, THF, 1,2-dimethoxyethane, and propylene carbonate have a lower tendency to coordinate, but all have limitations arising from restricted potential windows, poor solvating properties, or unwanted chemical reactivity. There have also been recent advances in the use of nonpolar solvents such as benzene for electrochemical studies.[3-5] Although useful in some studies, these solvents are often not conducive to large scale electrolyses, require specialized apparatus such microelectrodes,[3,4] or utilize molten salt electrolytes above ambient temperature.[5]

We report here that 1,2-difluorobenzene (DFB) has some significant advantages as a solvent for electrochemical studies. It has a dielectric constant that is sufficiently high to dissolve many electrolyte and metal complex salts, it is noncoordinating, it is relatively inert chemically, it has a wide potential window, and it can be used in routine, small-scale, or large-scale electrochemical studies. We report here some illustrative examples from our own work where the utilization of DFB as an electrochemical solvent has been of value.

Experimental Section

Purification of 1,2-difluorobenzene (DFB) and electrochemical studies were carried out in a drybox (Vacuum/Atmospheres). The drybox was kept under a constant flow of N_2, which acted as an atmospheric purge to prevent the contamination of DFB by other solvent vapors.

Materials. The liquid 1,2-difluorobenzene (Aldrich, 98% or Lancaster, 98+%) was purified by passing it through a column of activated alumina. DFB is expensive, and it was collected and recycled by distillation (bp = 92 °C) for reuse. To date, three recycling steps have not resulted in any noticeable degradation in the electrochemical properties of the solvent. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared and purified as reported previously.[6]

Electrochemistry. Platinum- and glassy-carbon-button electrodes of area ~0.1 cm^2 were seated in Teflon shrouds and cleaned by polishing with 1-μm diamond paste (Buehler). Cuvette-sized optically transparent electrodes (In-doped SnO_2 on glass) were purchased from Delta Technologies. Electrochemical measurements were performed by using a PAR Model 173 potentiostat in conjunction with a PAR Model 175 universal programmer. Electrochemical data were recorded on a Hewlett-Packard Model 5017B X-Y recorder, and all potentials are referenced to a saturated sodium chloride calomel reference electrode (SSCE). Three-compartment cells were employed, where the reference and auxiliary (Pt mesh) electrodes were separated from the working compartment with fine- and medium-porosity frits, respectively. For controlled-potential electrolysis experiments, a Pt mesh served as the working electrode.

Results and Discussion

Solvating Properties. The molecule 1,2-difluorobenzene is polar ($\mu = 2.59$)[7] and as a solvent has a higher dielectric constant ($D_s = 13.8$ at 28 °C)[8] than either CH_2Cl_2 ($D_s = 8.9$)[1a] or THF ($D_s = 7.4$).[1a] The electrolyte TBAH is very soluble in DFB with a saturation limit at room temperature of ~1.5 M. Alkali-metal-based electrolytes such as $Li(CF_3SO_3)$ are *not* soluble in DFB. The solvating ability of DFB toward transition-metal complexes is similar to that of CH_3CN. Many neutral complexes—$M_2(CO)_{10}$ (M = Mn and Re), ferrocene, *fac*-[$Re(bpy)(CO)_3X$] (X = Cl, Br; bpy = 2,2′-bipyridine)—monocationic salts—*fac*-[$Re(bpy)(CO)_3(CH_3CN)$](PF_6), *cis*-[$Os(bpy)_2$(4-vinylpyridine)Cl](PF_6)—and dicationic salts—[$M(bpy)_3$](PF_6)$_2$ (M = Fe, Ru, Os), *cis*-[$Ru^{IV}(bpy)_2$(4-*tert*-butylpyridine)(O)](PF_6)$_2$—have solubilities that are similar in CH_3CN and 1,2-difluorobenzene. The neutral compounds [$Ru(bpy)_2Cl_2$] and [$Re(bpy)(CO)_3$]$_2$ are only sparingly soluble in either solvent.

There are some solubility advantages to 1,2-difluorobenzene as a solvent. It will dissolve in reasonable concentrations some porphyrin and phthalocyanine complexes that are nearly or totally insoluble in acetonitrile. Ferrocene, although very soluble in DFB, leads to adsorptive behavior when oxidized to the ferrocenium ion.

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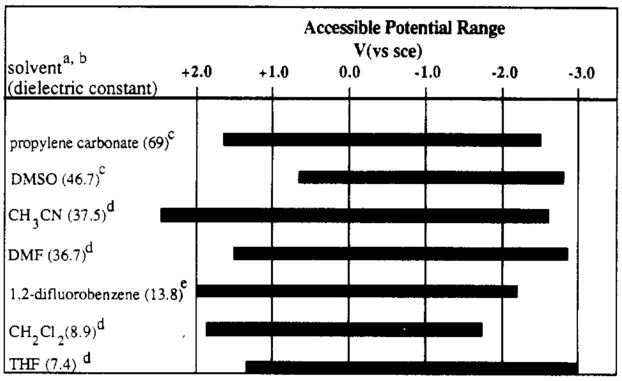
Chart I. Comparison of the Accessible Potential Ranges for Common Electrochemical Solvents



[a] The definition of a solvent limit is somewhat dependent upon the details of the experiment. The limits shown above are illustrative for a Pt electrode in solutions containing 0.1 M concentrations of tetraalkylammonium salts of the anions ClO_4^-,BF_4^-, and PF_6^-. [b] DMSO = dimethyl sulfoxide; DMF = *N,N'*-dimethylformamide; THF = tetrahydrofuran. [c] Reference 1a. [d] Reference 18. [e] This work.

Properties as an Electrochemical Solvent. A background cyclic voltammogram for a DFB solution 0.1 M in TBAH is shown in Figure 1A. The useful potential window for DFB is approximately +2.0 to −2.2 V vs SSCE when the solvent is prepurified by passing it through alumina. For comparison, the electrochemical limits for a number of commonly used solvents are shown in Chart I. If the concentration of the electroactive compound is low, $<\sim$0.1 mM, the background shown in Figure 1A is not insignificant and the working solvent limits are narrowed to +1.8 to −2.0 V. At the anodic limit a small but discernible oxidation wave appears at $E_{p,a}$ = +1.9 V. It arises from an impurity ($<\sim$0.05 mM estimated from the peak height) that is not removed by passing the solvent through an alumina column. Removal of the impurity by fractional distillation leads to an extension of the oxidative limit to between +2.0 and +2.1 V. The cathodic limit is probably due to the direct reduction of DFB. The current continues to climb rapidly beyond −2.2 V. We could find no previously published information concerning the redox properties of 1,2-difluorobenzene.

We have measured the peak-to-peak splitting, ΔE_p, for the couple $[Fe(\eta^5\text{-}Me_5C_5)_2]^{+/0}$ (η^5-Me_5C_5 is the pentamethylcyclopentadienyl anion) as a function of scan rate and electrolyte concentration. There is no sign of adsorptive behavior for this couple. With the concentration of TBAH at 0.2 M and at a sweep rate of 100 mV/s, a ΔE_p of 215 mV is observed for the $[Fe(\eta^5\text{-}Me_5C_5)_2]^{+/0}$ couple ($E_{1/2}$ = −0.059 V) *without* the use of *IR* compensation. This is considerably larger than the ideal value of 60 mV. A splitting of 190 mV occurs for the $[Fe(bpy)_3]^{3+/2+}$ couple ($E_{1/2}$ = +0.98 V) under the same conditions. With the use of *IR* compensation, ΔE_p could be reduced to $\sim$100 mV for both couples under these conditions. By comparison, with CH_3CN as the electrochemical solvent under the same cell conditions, ΔE_p is 70 mV without *IR* compensation. It is known that heterogeneous electron-transfer rates can have a considerable solvent dependence,[9] but we presume that the major contributor to the large ΔE_p is the high internal resistance of the solution arising from incomplete ionic dissociation of the electrolyte.

Electrogeneration of Reactive Intermediates. One of the most appealing features of 1,2-difluorobenzene as a solvent is its lack of a significant coordinating ability. In our work, examples of the value of this property have come from a series of electrochemical studies on the reduction of the complexes, *fac*-$[Re^I(bpy)(CO)_3L]^{n+}$ (L = Cl^-, Br^-, $CF_3SO_3^-$, *n* = 0; L = CH_3CN, *n* = 1) and the oxidation of the Re–Re-bonded compounds, $[(CO)_5Re\text{–}Re(bpy)(CO)_3]$ and $[(CO)_3(bpy)Re\text{–}Re(bpy)(CO)_3]$. The electrochemistry of the Re(I) complexes has been studied extensively.[10] Following a one-electron bipyridine-based reduction

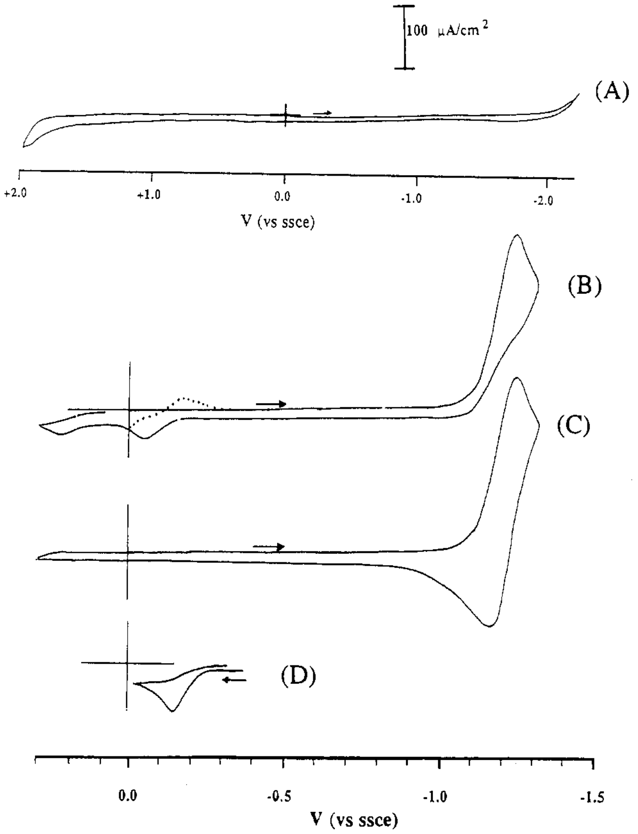


Figure 1. Background cyclic voltammogram for 0.1 M TBAH/DFB using a 0.1 cm² Pt electrode at a sweep rate of 200 mV/s. (B) Cyclic voltammogram of a solution 0.4 mM in $[Re(bpy)(CO)_3(CH_3CN)]^+$ in 0.1 M TBAH/DFB at a sweep rate of 200 mV/s. The dotted line is the voltammogram obtained upon scan reversal at 0.0 V following a reductive scan. The waves at $E_{1/2}$ = −0.12 V and $E_{p,a}$ = +0.25 V correspond to the first and second oxidations of $[Re(bpy)(CO)_3]_2$, which is formed during the reduction. (C) Cyclic voltammogram of a solution 0.4 mM in $[Re(bpy)(CO)_3(CH_3CN)]^+$ in 0.1 M TBAH/CH_3CN at a sweep rate of 200 mV/s. Very little dimer is formed at this concentration in this solvent. (D) Cyclic voltammogram illustrating the irreversible oxidation ($E_{p,a}$ = −0.12 V) of $[Re(bpy)(CO)_3]_2$ formed by a reductive scan at 200 mV/s in a solution $\sim$1mM in $[Re(bpy)(CO)_3(CH_3CN)]^+$ in 0.1 M TBAH/CH_3CN. The reductive portion of the scan is not shown for clarity.

at −1.20 V, dissociative loss of L occurs to give highly reactive metal-based radicals, reactions 1 and 2. In noncoordinating halocarbon solvents, the metal radicals undergo rapid reactions with the solvent by initial halogen atom abstraction.

$$[Re(bpy)(CO)_3(CH_3CN)]^+ \xrightleftharpoons[-e^-]{+e^-} [Re(bpy)(CO)_3(CH_3CN)]^0 \tag{1}$$

$$[Re(bpy)(CO)_3(CH_3CN)]^0 \xrightleftharpoons[k_{-1}]{k_1} [Re(bpy)(CO)_3]^0 + CH_3CN \tag{2}$$

Cyclic voltammograms of $[Re(bpy)(CO)_3(CH_3CN)]^+$ in DFB and CH_3CN are shown in Figure 1B–D. In DFB (Figure 1B) at 200 mV/s, the first reduction of $[Re(bpy)(CO)_3(CH_3CN)]^+$ is irreversible because of rapid loss of the acetonitrile ligand, reaction 2, and coupling to give the dimer, $[Re(bpy)(CO)_3]_2$, reaction 3.[10] In CH_3CN (Figure 2B) the first reduction of

$$[Re(bpy)(CO)_3(CH_3CN)]^0 \rightarrow [Re(bpy)(CO)_3]_2 + 2CH_3CN \tag{3}$$

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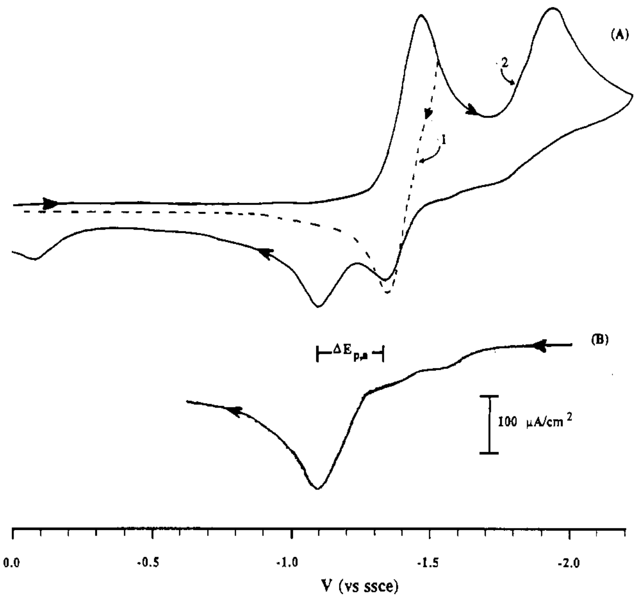


Figure 2. (A) Cyclic voltammograms of a solution 0.5 mM in [Re(bpy)(CO)$_3$Cl] in 0.2 M TBAH/DFB at 200 mV/s cycled between 0.0 and −1.5 V (1, ---) and between 0.0 and −2.2 V (2, —). (B) Oxidative sweep starting at −2.0 V following the controlled-potential electrolysis of [Re(bpy)(CO)$_3$Cl] at −1.7 V (n = 2).

[Re(bpy)(CO)$_3$(CH$_3$CN)]$^+$ is largely reversible at concentrations < 0.5 mM. Although k_1 has been determined to be 1.6 s^{-1} in CH$_3$CN solution,[11] the high concentration of solvent supresses the formation of the metal-based radical (reaction 2), which results in reversible electrochemical behavior. Since DFB is not a good ligand, there is no supression of radical formation. Electrochemical reduction in DFB results in relatively high concentrations of the metal radical and rapid dimerization.

In DFB, the [Re(bpy)(CO)$_3$]$_2$ that forms on the initial reductive sweep (Figure 1B) has a nearly reversible one-electron oxidation at $E_{1/2}$ = −0.10 V ($i_{p,a}/i_{p,c}$ = 0.75). There is another irreversible one-electron oxidation at $E_{p,a}$ = +0.25 V.[12] These data match those for an authentic sample of the dimer. The first oxidation is fully reversible with ($i_{p,a}/i_{p,c}$ = 1) at a sweep rate of 1 V/s. This allows the redox potential for the M-M-bonded [Re(bpy)(CO)$_3$]$^{+/0}$ couple to be established. In CH$_3$CN only one, irreversible dimer-based oxidation is observed at $E_{p,a}$ = −0.12 V, which gives [Re(bpy)(CO)$_3$(CH$_3$CN)]$^+$ as the product (Figure 1D). In CH$_3$CN, the one-electron Re–Re-bonded cation, [Re(bpy)(CO)$_3$]$_2$$^+$, is unstable with regard to solvolysis (reaction 4). A

$$[\mathrm{Re(bpy)(CO)_3}]_2^+ + 2\mathrm{CH_3CN} \rightarrow [\mathrm{Re(bpy)(CO)_3(CH_3CN)}]^+ + [\mathrm{Re(bpy)(CO)_3(CH_3CN)}]^0 \qquad (4)$$

major factor in the instability of the cation is the formation of the Re(I)–nitrile bond, which occurs at the expense of the relatively weak Re–Re half-bond. In DFB, which is relatively noncoordinating, the once oxidized dimer has sufficient stability to persist on the cyclic voltammetry time scale.

Another application where the use of DFB has been revealing is in the observation of the direct electrochemical reoxidation of the anion [Re(bpy)(CO)$_3$]$^-$. A cyclic voltammogram of [Re(bpy)(CO)$_3$Cl] is shown in Figure 2A. At a scan rate of 200 mV/s, this compound has a fully reversible one-electron reduction at $E_{1/2}$ = −1.37 V. It arises from the π^*(bpy)-based [Re(bpy)(CO)$_3$Cl]$^{0/-}$ couple. It is followed by a second, irreversible reduction at $E_{p,c}$ = −1.85 V. At the second reduction, Cl$^-$ is rapidly lost to give [Re(bpy)(CO)$_3$]$^-$.[10]

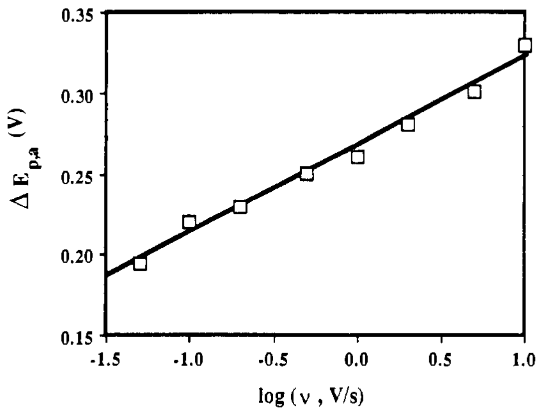


Figure 3. Plot of the shift in the oxidative peak potential for the anion [Re(bpy)(CO)$_3$]$^-$ relative to that for oxidation of [Re(bpy)(CO)$_3$Cl]$^-$ ($\Delta E_{p,a}$) versus the log of the scan rate, v. The scan rates used ranged from 0.05 to 10 V/s. The slope of the least-squares line is 0.054 V/decade.

At a scan rate of 200 mV/s the reoxidation of [Re(bpy)(CO)$_3$]$^-$ occurs at $E_{p,a}$ = −1.09 V. The scan rate dependence was investigated for reoxidation of the anion relative to the oxidation of [Re(bpy)(CO)$_3$Cl]$^-$ as an internal standard. Since the [Re(bpy)(CO)$_3$Cl]$^{0/-}$ couple is kinetically facile, the difference was taken as a means of correcting for uncompensated resistance effects. As can be seen in the plot in Figure 3, the difference in peak potentials shifts by 54 mV/log v unit. This is near the theoretical value of ~60 mV for a couple that undergoes slow heterogeneous electron-transfer kinetics.

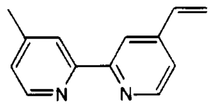
The anion [Re(bpy)(CO)$_3$]$^-$ can also be generated on the cyclic voltammetry time scale with CH$_3$CN as solvent. Its reoxidation, however, is catalyzed by the [Re(bpy)(CO)$_3$(CH$_3$CN)]$^{+/0}$ couple (reaction 5).[10c] Because of the electron-transfer catalysis, re-

$$[\mathrm{Re(bpy)(CO)_3(CH_3CN)}]^+ + [\mathrm{Re(bpy)(CO)_3}]^- \xrightarrow{\mathrm{CH_3CN}} 2[\mathrm{Re(bpy)(CO)_3(CH_3CN)}]^0 \qquad (5)$$

oxidation of the anion in CH$_3$CN is independent of scan rate and always occurs at E$_{p,a}$ = −1.15 V, which obscures the direct oxidation of the anion at the electrode.

Controlled-potential electrolysis of [Re^{I}(bpy)(CO)$_3$Cl] in DFB at E_{app} = −1.7 V, which is at the foot of the second wave in Figure 2, occurs with n = 2 to give [Re(bpy)(CO)$_3$]$^-$. The anion is dark purple (λ_{max} = 560 nm) and stable in DFB. It is not stable for extended periods (minutes) in CH$_3$CN, DMF, or THF. Following the electrolysis in DFB, a wave for reoxidation of the anion at $E_{p,a}$ = −1.09 V appears in a voltammetric trace begun at −2.0 V (Figure 2B). There is little or no sign of the [Re(bpy)(CO)$_3$Cl]-based couples in the voltammogram.

Electropolymerization. As a further application of DFB as a solvent for electrochemical studies, we investigated the reductive electropolymerization of complexes containing 4-methyl-4′-vinyl-2,2-bipyridine (vbpy) as a ligand. Acetonitrile has typically



vbpy

been the solvent of choice in such procedures.[6,13,14] We find that DFB is an excellent solvent as well.

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[11] O'Toole, T. R.; Meyer, T. J.; Sullivan, B. P. Manuscript in preparation.

[12] The anodic peak current for the first oxidation should, in theory, be approximately half that for the cathodic peak current of the nitrile complex. However, during the time between reduction of the nitrile complex and reoxidation of the dimer (~5 s), the concentration of dimer at the electrode surface is decreased significantly because of diffusion away from the electrode.

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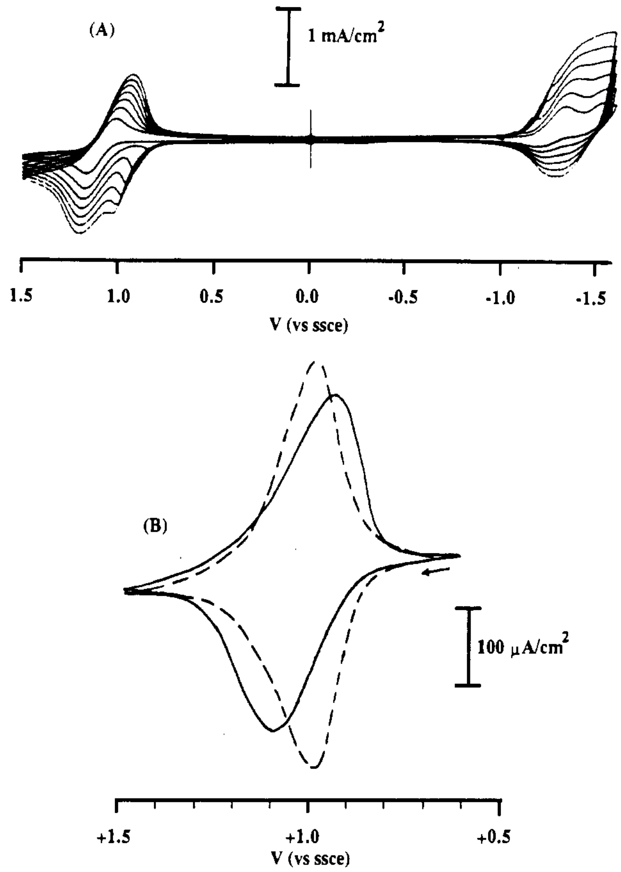
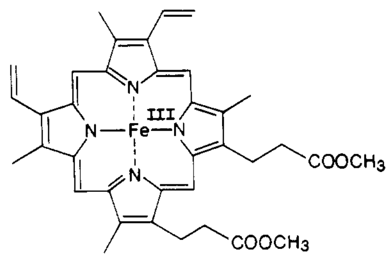


Figure 4. (A) Consecutive cyclic voltammetric traces for [Fe(vbpy)$_3$]$^{2+}$ in 0.1 M TBAH/DFB at a 0.1 cm^2 Pt electrode at a sweep rate of 100 mV/s, illustrating polymeric film growth by electropolymerization. (B) Cyclic voltammograms of the Fe(III/II) couple in the polymeric [Fe(vbpy)$_3$]$^{2+}$ film from part A at 50 mV/s when immersed in 0.1 M TBAH solutions of DFB (—) and CH$_3$CN (---).

As examples, we have studied the reductive electropolymerizations of [Fe(vbpy)$_3$]$^{2+}$ and [Re(vbpy)(CO)$_3$Cl], both of which have been studied previously in CH$_3$CN.[13,14] The rate of electropolymerization of [Fe(vbpy)$_3$]$^{2+}$ in DFB (Figure 4A) is comparable to that in CH$_3$CN as judged by the increase in peak currents for the film-based couples on sequential scanning. Cyclic voltammetric traces of a polymeric [Fe(vbpy)$_3$]$^{3+/2+}$ film in DFB and CH$_3$CN are shown in Figure 4B. At a sweep rate of 50 mV/s, the peak-to-peak splitting for the Fe(III/II) couple is 200 mV in DFB while it is only 35 mV in CH$_3$CN, showing that charge propagation through the film is considerably slower in DFB. As an electropolymerization solvent, DFB has proven to be especially valuable for the electropolymerization of [Re(vbpy)(CO)$_3$Cl], the details of which have been described in detail in CH$_3$CN elsewhere.[6,14] As a solvent, it offers the advantages that the resulting films are much more stable toward reductive cycling and that electropolymerization onto optically transparent In-doped SnO$_2$ electrodes yields much more uniform coverages at a considerably enhanced rate.[15]

1,2-Difluorobenzene is also a useful solvent for oxidative electropolymerizations. We have studied the oxidative electropolymerization of Fe(PPIX-dme)Cl (PPIX-dme = protoporphyrin IX dimethyl ester), which can be carried out on carbon, Pt, and In-doped SnO$_2$ electrodes. Films of polymeric [Fe(PPIX-dme)Cl] were prepared by cycling the applied potential between 0.0 and +1.3 V at a sweep rate of 100 mV/s in 0.1 M TBAH/DFB. The electropolymerization proceeds more rapidly and reproducibly in DFB than in DMF, CH$_2$Cl$_2$, or CH$_3$CN,[16,17] and it is possible to grow films that are thicker by factors of 10 or greater. This porphyrin also undergoes slow *reductive* electropolymerization in DFB by scanning between 0.0 and −1.6 V. Of the four solvents, DFB, DMF, CH$_2$Cl$_2$, or CH$_3$CN, reductive electropolymerization only occurs in DFB.[17]



Fe(PPIX-dme)$^+$

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Registry No. DFB, 367-11-3; TBAH, 3109-63-5; Pt, 7440-06-4; C, 7440-44-0; In-Sn-O, 50926-11-9; [Fe(bpy)$_3$]$^{3+}$, 18661-69-3; [Fe(bpy)$_3$]$^{2+}$, 15025-74-8; [Fe(η^5-Me$_5$C$_5$)$_2$]$^+$, 54182-41-1; [Fe(η^5-Me$_5$C$_5$)$_2$], 12126-50-0; [Re(bpy)(CO)$_3$Cl], 52064-98-9; [Re(bpy)(CO)$_3$Br], 56498-59-0; [Re(bpy)(CO)$_3$CF$_3$SO$_3$], 97170-94-0; [Re(bpy)(CO)$_3$(CH$_3$CN)]$^+$, 89708-63-4; [(CO)$_5$Re-Re(bpy)(CO)$_3$], 61993-42-8; [(CO)$_3$(bpy)Re-Re(bpy)(CO)$_3$], 107228-01-3; [Fe(vbpy)$_3$]$^{2+}$, 75675-26-2; [Re(vbpy)(CO)$_3$Cl], 100243-94-5; Fe(PPIX-dme)Cl, 15741-03-4.

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Preferential Solvation Effects Observed in a Kinetic Study of the Reaction of [(η^6-C$_6$Me$_6$)Ru(η^6-anth)][PF$_6$]$_2$ with Acetonitrile (anth = Anthracene)

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Recently our group described kinetic measurements on the reaction of a series of [CpRu(η^6-arene)]$^+$ and [Cp*Ru(η^6-arene)]$^+$ complexes (Cp = η^5-cyclopentadienyl; Cp* = η^5-pentamethylcyclopentadienyl) with acetonitrile to give free arene and the corresponding tris(acetonitrile) compound.[1] Rate data for the reaction with [Cp*Ru(anth)]$^+$ (anth = η^6-anthracene) were acquired at different temperatures and acetonitrile concentrations. As a continuation of our inquiry in this area, we have studied the analogous bis(arene) complex [(HMB)Ru(anth)]$^{2+}$ (HMB = η^6-hexamethylbenzene).

Bennett et al. reported that the bis(arene) compound [(mes)Ru(anth)]$^{2+}$ (mes = η^6-mesitylene) undergoes a facile, thermal reaction with DMSO to yield the tris-DMSO complex (reaction 1).[2] We have shown that [(HMB)Ru(anth)]$^{2+}$ reacts similarly

$$[(\text{mes})\text{Ru}(\text{anth})]^{2+} + 3\text{DMSO} \rightarrow [(\text{mes})\text{Ru}(\text{DMSO})_3]^{2+} + \text{anthracene} \quad (1)$$

with acetonitrile (reaction 2). The kinetic investigation of reaction

$$[(\text{HMB})\text{Ru}(\text{anth})]^{2+} + 3\text{CH}_3\text{CN} \rightarrow [(\text{HMB})\text{Ru}(\text{CH}_3\text{CN})_3]^{2+} + \text{anthracene} \quad (2)$$

2 was undertaken in two solvent systems, acetonitrile/methylene

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