Table II. Redox Potentials of Osmium Complexes[a]

complex	redox potentials, V					
	Os^{III}/Os^{II}	D^+/D^0 [b]	$PQ^{2+}/PQ^{\bullet+}$	$PQ^{\bullet+}/PQ^0$	Os^{II}/Os^I [c]	Os^I/Os^0 [c]
$Os(Me\text{-}phterpy)_2^{2+}$	+0.90				−1.20	−1.45
$Os(Me\text{-}phterpy)(PTZ\text{-}phterpy)^{2+}$	+0.90	+0.75			−1.20	−1.45
$Os(Me\text{-}phterpy)(Diaa\text{-}phterpy)^{2+}$	+0.94	+0.76			−1.20	−1.48
$Os(Me\text{-}phterpy)(PQ^{2+}\text{-}phterpy)^{4+}$	+0.90		−0.35	−0.75	−1.20	−1.45

[a] Cyclic voltammetry measurements on glassy-carbon electrode in CH_3CN, vs SCE; Bu_4NClO_4 (0.1 M) as supporting electrolyte; scan rate = 100 mV s^{-1}. [b] D^+/D^0 are the oxidized and reduced parts of PTZ-phterpy (line 2) and Diaa-phterpy (line 3). [c] The osmium oxidation states I and 0 are only formal.

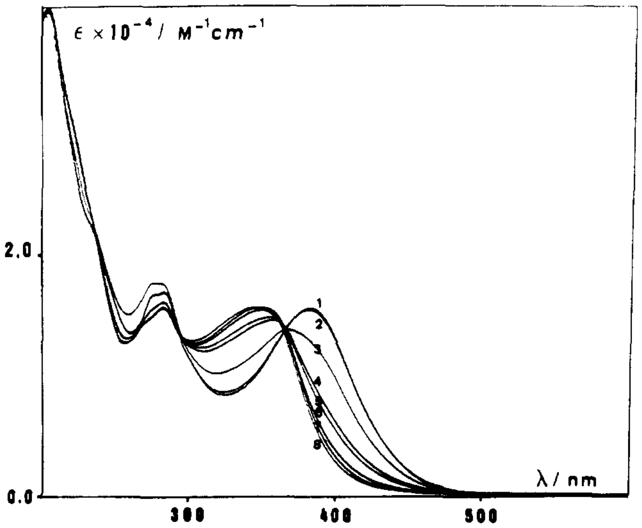

Figure 1. Electronic spectra of $[Os(Me\text{-}phterpy)(O)_2(OH)^+][NO_3^-]$ (7.0×10^{-5} M) in aqueous solution at pH = (1) 1.65, (2) 1.79, (3) 2.45, (4) 2.98, (5) 3.13, (6) 3.60, (7) 3.89, and (8) 5.47.

Preparation of $Os(Me\text{-}phterpy)(terpy\text{-}Y)(PF_6)_2$. Method A. A typical preparation is as follows. $[Os(Me\text{-}phterpy)(O_2)(OH)^+][NO_3^-]$ and a given functionalized terpy (in a stoichiometric amount) were dissolved in a H_2O/THF (1:1) mixture. A few drops of hydrazine were added while stirring, and the mixture was heated to 40 °C for 10 min. After evaporation of THF, the complex was precipitated out by addition of NH_4PF_6. It was further purified by column chromatography on silica (CH_3CN–aqueous KNO_3 as eluent).

Method B. With H_2/Pt(O), the experimental procedure was slightly different. The solvent used was methanol/H_2O (9:1) at pH = 3.0 (acid used: HNO_3). A solution of $[Os(Me\text{-}phterpy)(O)_2(OH)^+][NO_3^-]$ was added dropwise to a refluxing solution of the ligand under a hydrogen atmosphere and in presence of small amounts of platinum black (Ventron). This procedure minimizes oxidative degradation of the electron donor groups attached to the terpy chelate by the osmium(VI) starting complex.

Results

In order to avoid the presence of coordinating chlorine atoms, potassium osmate ($K_2Os(O)_2(OH)_4$) was used in the first step, leading to a monoterpy Os(VI) complex, by using a procedure analogous to that recently developed by Meyer et al.[11] $K_2Os(O)_2(OH)_4$ was added at room temperature to an aqueous solution of Me-phterpy at pH = 3. $[Os(Me\text{-}phterpy)(O)_2(OH)^+][NO_3^-]$ was obtained as a pale green solid in 92% yield.

It was characterized by ^1H NMR spectroscopy, FAB-MS, and elemental analysis. Its redox properties[12] and its electronic spectrum are strongly dependent on pH similar to its parent complex $[Os(terpy)(O)_2(OH)^+][NO_3^-]$,[11,12] as represented in Figure 1.

In the pH range 1–6, two redox couples can clearly be observed, one corresponding to a three-electron process (+0.36 V vs. SCE at pH = 2.5) and the other being a one-electron reaction (−0.06 V at pH = 2.5). As usual, the redox reactions are accompanied by protonation–deprotonation reactions.[12,13] At pH < 6, the four-electron reduction product is probably $Os(Me\text{-}phterpy)(OH_2)_3^{2+}$, which looks promising for substituting further the coordination sphere of the metal. Indeed, we found that the chemical reduction of $Os(Me\text{-}phterpy)(O)_2(OH)^+$ in the presence of a second terpy leads to the desired bis(2,2′:6′,2″-terpyridine)osmium(II) complex in a reproducible fashion with appreciable yields. Among the various reducing agents tested, hydrogen (in the presence of platinum(O)) and hydrazine in neutral medium gave the best results.

The various results obtained by using either of the two methods are collected in Table I.

Each complex was isolated pure (TLC control on silica) and characterized by ^1H NMR and FAB-MS. For example, ^1H NMR and elemental analysis are given for $Os(Me\text{-}phterpy)(PTZ\text{-}phterpy)^{2+}$. δH (CD_3CN): 9.01 (2 H, s); 9.00 (2 H, s); 8.61 (4 H, d, J = 8.4 Hz); 8.13 (2 H, d, J = 8.3 Hz); 8.07 (2 H, d, J = 8.3 Hz); 7.83–7.74 (6 H, m); 7.58 (2 H, d, J = 8.3 Hz); 7.31–6.92 (16 H, m); 5.37 (2 H, s); 2.57 (3 H, s). Anal. Calcd for $C_{56}H_{41}N_7SP_2F_{12}Os$: C, 50.79; H, 3.12; N, 7.40. Found: C, 50.97; C, 3.41; N, 7.15. Cyclic voltammetry confirmed in a convenient way the presence of the electroactive groups linked to the osmium complexes. Redox potentials of four osmium complexes are reported in Table II.

Discussion

From the results of Table I, it is clear that the best yields were obtained by using Pt/H_2 as a reductant, especially if one of the terpy ligands contains an oxidizable group (Diaa = di-*p*-anisylamino or PTZ = phenothiazine–CH_2–). In any case, the presence of these electrophores anchored to the complex seems to lower the yield significantly.

A possible limitation of the method resides in the high reactivity of the postulated intermediate complex $Os(Me\text{-}phterpy)(OH_2)_3^{2+}$. Clearly, reactions other than coordination to the second terpy may occur: deprotonation, formation of bridged polynuclear complexes (μ-hydroxo and μ-oxo), etc.[14]

The method described in the present report for preparing molecular diades built on osmium(II) complexes should allow the synthesis of electron-donor-osmium(II)–electron-acceptor complexes (triades) in a more preparative way than the use of classical thermal methods.

Acknowledgment. We thank the CNRS for financial support.

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The Ferrocene Assumption in Redox Thermodynamics: Implications from Optical Intervalence Studies of Ion Pairing to Ferrocenium

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The "ferrocene assumption" forms the basis of a popular approach to the ubiquitous problem of relating redox potentials

Table I. Estimated Nernstian Potential Shifts Due to Ion Pairing to Ferrocenium

solvent	electrolyte	ϵ	β,[a] M^{-1}	$E - E°$, mV ($[X^-] = 0.100$ M)[b]	$E - E°$, mV ($[X^-] = 0.100$ M)[b]
acetonitrile	$(TBA)BF_4$	37.5	38	−30	−0.8
acetonitrile	$NaClO_4$	37.5	66	−40	−1.5
nitromethane	$(TBA)PF_6$	38.6	70	−36	−1.6
acetone	$(TBA)BF_4$	20.7	180	−52	−3
acetone	$(TBA)PF_6$	20.7	370[c]	−69[c]	−7[c]
dichloromethane	$(TBA)PF_6$	9.1	720000[d,e]	−229[f]	−61[f]

[a] Taken from ref 3b. [b] Calculated by using eq 4a (see refs 6 and 7). [c] Activity corrections and electrolyte self-association effects assumed to be identical with those for $(TBA)BF_4$ in acetone. [d] K for ion pairing is 9000 M^{-1}; K for ion tripling is 80 M^{-1} (see ref 3). [e] Activity corrections and electroyte self-association effects neglected (see text). [f] Includes contributions from ion tripling.

obtained in one solvent to those obtained in another.[1] Simply put, the assumption states that on an absolute scale the formal one-electron reduction potential of the ferrocenium ion (Fc^+; eq 1) is independent of the nature of the solvent. The assumption

$$Fc^+ + e^- \overset{E}{\rightleftharpoons} Fc \qquad (1)$$

amounts, of course, to an extrathermodynamic assertion, since the entire absolute-potential problem defies rigorous thermodynamic evaluation. Nevertheless, the assertion makes sense on intuitive grounds: the metal center within ferrocene is well isolated from solvent; the cyclopentadienyl ligands are "innocent" hydrocarbons; the overall molecular charges are one and zero. Furthermore, there is fair agreement with other extrathermodynamic approaches such as the tetraphenylarsonium–tetraphenylborate assumption and the zero ligand-junction potential assumption.[2] The purpose of this note is to outline a simple—perhaps obvious—caveat to the ferrocene assumption and to present data that prescribe experimental limits beyond which one should exercise caution in its application.

The basis of the caveat centers on the energetic consequences of ion pairing to ferrocenium. The origin of our concern is in related spectroscopic studies.[3] Specifically, we and others have been exploring the role of ionic association in intervalence charge-transfer experiments.[3-5] In such experiments an electron (or hole) is transferred optically while the various nuclear coordinates, including those of any counterions, are held constant. Although we have examined a number of systems, the most informative has been the acetylene-bridged biferrocene monocation ($Fc{-}C{\equiv}C{-}Fc^+$). Here the ferrocenium end is subject to ground-state ion pairing (and tripling) but the ferrocene end is not (at least for the range of solvents and counterion concentrations investigated). The consequence of ion pairing in the spectroscopic experiment is a shift of the intervalence charge-transfer transition (eq 2) to higher energy. The magnitude of the shift is substantial,

$$Fc{-}C{\equiv}C{-}Fc^+ \xrightarrow{h\nu} {}^+Fc{-}C{\equiv}C{-}Fc^* \qquad (2a)$$

$$Fc{-}C{\equiv}C{-}Fc^+,X^- \xrightarrow{h\nu} {}^+Fc{-}C{\equiv}C{-}Fc,X^{-*} \qquad (2b)$$

ranging (depending on solvent) from several hundred wavenumbers to a few thousand.[3] A line-shape analysis has revealed that the ion-induced energy effect is probably due to a relative displacement of initial-state/final-state zero-point energies, i.e. a change in ground-state/excited-state "thermodynamics".[3a,4b]

These observations and the obvious analogies between the optical and electrochemical processes led us to suspect the existence of related effects for the electrochemical process. Ion pairing in the electrochemical reaction (eq 3) would be manifest in a negative

$$Fc^+,X^- + e^- \rightleftharpoons Fc + X^- \qquad (3)$$

shift in the ferrocenium reduction potential. To the extent that such shifts occur and are solvent dependent, the conditions for appropriate application of the ferrocene assumption (based on the *unpaired* ferrocenium ion) would then be violated.

Assuming that ferrocene itself is not paired, and that there exists nearly complete association between ferrocenium and a counteranion, the magnitude of the potential shift can be estimated from the Lingane equation:[6]

$$E - E° = -(RT/F)\ln\beta - (RTp/F)\ln a_{X^-} \qquad (4)$$

In eq 4, β is the overall formation constant for $Fc^+(X^-)_p$, while a_{X^-} is the activity of the counteranion. $E°$ is the potential in the absence of association. To implement eq 4, estimates are needed for β. Fortunately these are available for four solvents and up to three anions (see Table I) from our previous optical studies of pairing (and higher order association) to the ferrocenium portion of $Fc{-}C{\equiv}C{-}Fc^+$.[3]

Assuming that the appended bridge and neutral ferrocene do not perturb the ionic equilibrium,[3a] the only other quantity that must be specified is the activity of X^-. If X^- is a component of the supporting electrolyte, its concentration will typically be 0.1 M. Its identity typically will be perchlorate, tetrafluoroborate, or hexafluorophosphate, with a tetraalkylammonium ion as the electrolyte cation. If the extent of electrolyte self-association is known, then the activity can be estimated from the extended Debeye–Hückel equation or related expressions.[7] We have done just this for each of the ion/solvent combinations in Table I except PF_6^- in dichloromethane; here a self-association constant is lacking. Finally, we have collected in Table I the values of $E - E°$ evaluated from eq 4 at $[X^-] = 0.1$ M. (Note that eq 4 can probably be employed even in the hexafluorophosphate/dichloromethane case without tremendous error by replacing the anion activity with the concentration, since our value for β is also derived from concentrations; i.e. the activity errors in the two quantities should largely cancel.)

From the tabulation, the following can be noted: (1) The difference in $E - E°$ values covers a range of roughly 200 mV for the available solvents. (2) The calculated shift in potential is larger for the lower dielectric solvents. We have noted elsewhere

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(6) More generally, for an ion-pairing equilibrium

$$E - E° = (RT/F)\ln(1 + \beta a_{X^-}) \qquad (4a)$$

(7) Estimates for a_{X^-} were taken from ref 3b. These in turn were obtained by making use of the concentration-dependent mean activity coefficients (extended Debeye-Hückel equation) and electrolyte self-association constants listed by Borchardt and Wherland (*Inorg. Chem.* **1981**, *21*, 2537 and supplementary material). In principle, the ionic strength dependent activity coefficient for ferrocenium should also be taken into account in the analysis. (Likewise, a single-ion activity coefficient, rather than a mean coefficient, should ideally be employed for a_{X^-}.) Lacking appropriate data, however, we chose to assume equal activity coefficients for ferrocene and ferrocenium at all electrolyte concentrations; this assumption yields eq 4a. While some ambiguity and/or error is thereby introduced (unavoidably) into the calculation of β, the errors should largely cancel when the β values are subsequently used to calculate $E - E°$.

that the expected linear correlation between log β(ion pairing) and the reciprocal of the static dielectric constant (ϵ) apparently does exist for Fc^+,X^- association;[3b] this provides an approximate basis for extending the estimates to other solvents.[8] (3) For at least one solvent (methylene chloride), significant contributions to the formal potential exist from higher order ionic association.

It should be clear from the tabulation that the shifts in formal potential are large enough in some instances (i.e., the low-dielectric solvents) to introduce unacceptable errors in the application of the ferrocene assumption. One remedy would be to employ the ferrocene strategy only in very dilute electrolyte solutions. Traditionally, dilute solution experiments have been avoided in electrochemistry because of problems associated with high solution resistance. With the advent of microelectrodes, however, these problems can be overcome.[9] The last column of Table I shows the $E - E°$ values that are obtained from eq 4 when $[X^-] = 0.001$ M. They are indeed smaller; more importantly, the variations in $E - E°$ with solvent are smaller than in the corresponding series of 0.1 M electrolyte solutions.

To summarize, optical intervalence measurements provide evidence for energetically significant ion pairing and tripling interactions; these interactions can shift the formal reduction potential of ferrocenium by up to a few hundred millivolts (ca. 5 kcal) in common polar solvents (and presumably by even more in very low polarity media). To the extent that the interactions vary with the identity of the solvent, the strict applicability of the ferrocene assumption should probably be questioned. It could be argued that, in electrochemical experiments, ion pairing will affect not only the ferrocenium/ferrocene reference couple but also the redox couple of interest. Consequently, such effects should cancel when reduction potentials are compared on the ferrocene scale. Certainly this must be true to some extent when the redox couple of interest is cationic (or better yet, cationic/neutral). Indeed, this may account for the widespread success of the ferrocene assumption in correlating a range of solvent-dependent electrochemical phenomena (e.g., donor–acceptor interactions, basicity effects, etc.). On the other hand, when the redox couple of interest is anionic (or neutral/anionic), the effects should be additive and systematic errors in correlating solvent–solute interactions may become more prominent.[10]

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(8) For example, an $E - E°$ value of roughly −25 mV would be predicted for ferrocenium reduction in the presence of 0.1 M electrolyte in water. On the other hand, much more negative values (several hundred millivolts or more) would be predicted for low-polarity solvents such as toluene and heptane. Also, higher order association and self-association effects would likely be prominent. For further discussion, see: (a) Geng, L.; Ewing, A. G.; Jernigan, J. C.; Murray, R. W. *Anal. Chem.* **1986**, *58*, 852. (b) Geng, L.; Murray, R. W. *Inorg. Chem.* **1986**, *25*, 3115.

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(10) See, for example, discussions in ref 8a.