(supplemental Figure S1) yielded $K_{II} = 20\ (\pm 1)\ M^{-1}$, in very good agreement with the four-parameter fit above. (3) An electrochemical experiment with the model complex, $Ru(NH_3)_5(py)^{3+/2+}$ (essentially half of the mixed-valence system), yielded a negative shift in formal potential (E_f) with crown addition and a maximum shift of −44 to −67 mV (replicate experiments) in a saturated crown solution (ca. 0.15 M). Insertion of these data into the Lingane equation

$$E_f = E^\circ - (RT/F) \ln (1 + K_{II}C) \qquad (6)$$

yields a K_{II} estimate of 30–80 M^{-1}, in fair agreement with the spectroscopic measurements. Taken together, these three observations strongly support the proposed model of crown encapsulation and energetic interaction.

With the preceding analysis in hand, we turn our attention to the original inquiry: the effect of crown encapsulation upon χ_s. From the four-parameter fit we derive an E_{op} value of 7640 ± 250 cm^{-1} for the doubly encapsulated complex. This differs significantly from the initial value of E_{op} (8500 ± 150 cm^{-1}), suggesting that χ_s is at least moderately decreased by crown binding. Some caution is called for, however. Note that the smallest *measured* value of E_{op} is 8400 cm^{-1} (see Figure 1). Clearly, extraction of the limiting "final" value from the four-parameter fit entails a lengthy extrapolation. We suggest, therefore, that E_{op}(final) may possibly be less reliable than implied by the fitting statistics.

A more definitive measure of E_{op}(final) (albeit for a slightly different system) can be obtained from the inset in Figure 1. Shown there are data for dibenzo-30-crown-10 ($n = 1$; see above), a species which binds much more strongly than dibenzo-24-crown-8. For DB-30-crown-10, E_{op}(final) (double encapsulation) is directly measured as 8250 cm^{-1}, i.e. only slightly less than the initial (crown free) value. In retrospect, this latter result is perhaps not too surprising. The crown species might, for example, provide only partial shielding from solvent.[17] Perhaps more importantly, the crown itself may serve as a polar medium (or pseudosolvent) requiring reorganization. For moderate to high polarity solvents, χ_s is known to vary approximately with n^{-2}, where n is the refractive index.[2,18] For nitromethane, n^{-2} is 0.524.[19] For molten[20] dibenzo-24-crown-8 at 119 °C (melting point = 103 °C; data were not obtained for DB-30-crown-10), we find $n^{-2} = 0.432$. Admittedly, one must exercise some caution on account of both temperature[21] and possible "molecularity"[22] effects; however, the refractive index measurements do suggest that significant reorganizational demands may exist for the crown as "solvent".

Returning to the crown asymmetry effects, there are some significant implications for charge-transfer kinetics. The observation that the optical barrier height is increased upon addition of small amounts of crown implies a corresponding increase in the thermal electron-transfer barrier height (see Figure 2). This, in turn, implies the existence of rate attenuation effects for the overall *thermal* electron-transfer process (eq 7). The magnitude

$$\text{crown}\cdot(H_3N)_5Ru^{III}\text{–}4,4'\text{-bpy–}Ru^{II}(NH_3)_5{}^{5+} \rightleftharpoons (H_3N)_5Ru^{II}\text{–}4,4'\text{-bpy–}Ru^{III}(NH_3)_5{}^{5+}\cdot\text{crown} \qquad (7)$$

of the expected rate effect is difficult to predict, as it surely must depend on the detailed reaction pathway chosen. (For example, does crown migration occur synchronously with electron transfer or does it precede or follow? What role is played by binding dynamics? Etc.)[23] Nevertheless, given the size of the optical effects, a factor of 5 or 10 in rate attenuation would not be an unreasonable prediction. Presumably the issue could be investigated experimentally by resorting to bimolecular, pseudo-self-exchange rate measurements[3] (e.g. $(H_3N)_5Ru(py)^{2+}$/$(H_3N)_5Ru(\text{methylpyridine})^{3+}$, etc.).

The focus of continuing work, however, is not self-exchange measurements. Instead we are attempting to understand in greater detail the nature of the binding effect—especially the roles played by crown size and by various solvent properties. Preliminary studies indicate stronger binding for larger crowns (see Figure 1) but weaker binding in solvents of higher basicity. Other work emphasizes encapsulation in more rigid supramolecular environments.

To summarize, encapsulation of donor and acceptor charge-transfer sites in a mixed-valence complex can be achieved with dibenzo-24-crown-8 at modest crown concentrations. Incomplete encapsulation (acceptor site only) leads to significant optical intervalence energy effects which may be significant also for thermal ET kinetics. Complete encapsulation leads to only modest changes in E_{op} or reorganization energy.

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Registry No. $[(H_3N)_5Ru\text{-}4,4'\text{-bpy-}Ru(NH_3)_5]^{5+}$, 54065-65-5; dibenzo-24-crown-8, 14174-09-5.

Supplementary Material Available: A figure (Figure S1) showing the dependence of MLCT energy on crown concentration (1 page). Ordering information is given on any current masthead page.

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[19] *CRC Handbook of Chemistry and Physics*, 64th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1983; p C-373.

[20] Because relative refractive index values for any given substance as a function of temperature, pressure, phase or state of matter, etc. largely reflect relative densities, we reasoned that a molten (liquid) crown sample would provide a better model for the crown in liquid solution (nitromethane) than would a (presumably) higher volume, crystalline (room-temperature) sample.

[21] Refractive index measurements at three liquid temperatures (135, 129, and 119 °C), followed by a lengthy extrapolation, led to $n^{-2} = 0.416$ at 25 °C.

[22] Our previous work[4] with mixed solvents suggests that "molecularity" effects may not be significant. In the earlier work we found, somewhat surprisingly, that a single molecular layer of DMSO solvent in contact with the mixed-valence ion behaved very similarly to bulk DMSO.

[23] Some sense of the relative time scales involved is available, in principle, from dynamic electrochemical experiments. For example, in cyclic voltammetric studies with DB-36-crown-12 we observe *distinct* waves for oxidation of $Ru(NH_3)_5(\text{pyridine})^{2+}$ (504 mV vs SSCE) and $Ru(NH_3)_5(py)\cdot\text{crown}^{2+}$ (178 mV vs SSCE), indicating that crown exchange between metal complexes is occurring on a time scale longer than 1 s. (The dimer itself has not yet been examined.)

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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)

The interpretation of electrochemical data is often complicated by interactions between electrochemically generated species and the surrounding ionic medium.[1] For example, our group recently

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Table I. Electrochemical Data for 0.5 mM Solutions of Cp_2M (M = Fe, Ru, Os) in 0.1 M TBA^+TFPB^- in CH_2Cl_2

Cp_2M	$E°'_{+/0}$,[a] V	10^5D,[c] cm²/s	$E_{p,a} - E_{p,c}$,[d] V	$i_{p,c}/i_{p,a}$
Fe	+0.47[b]	2.7	0.085	1.0 ± 0.05
Ru	+1.03	2.5	0.095	1.0 ± 0.10
Os	+0.83	2.9	0.089	1.0 ± 0.05

[a] Potentials vs aqueous AgCl/Ag in 1.0 M KCl. [b] $E°'_{+/0}$ = +0.48 V in 0.1 M $TBA^+PF_6^-$ in CH_2Cl_2 under identical conditions. [c] Determined by double-potential step chronocoulommetry. [d] Scan rate = 100 mV/s.

showed that the various products observed during the oxidation of $[CpFe(CO)]_2$ in different electrochemical media result from secondary reactions of a common radical intermediate, $[CpFe(CO)_2]_2^+$. This cation is highly sensitive to nucleophilic attack by the solvent and/or electrolyte.[2] In an attempt to circumvent such secondary processes, we became interested in developing noncoordinating solvent/electrolyte systems. Here we wish to report our initial results with tetrabutylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate,[3,4] TBA^+TFPB^-, in CH_2Cl_2. In this medium, we have observed the quasi-reversible, 1e⁻ oxidation couples for ferrocene, ruthenocene, and osmocene. Additionally, by measuring the disproportionation constant of $Rh_2(TM4)_4^{3+}$ (TM4 = 2,5-diisocyano-2,5-dimethylhexane) in the presence of $TFPB^-$ and other common anions, we have been able to quantify the degree of association of these anions with a tetravalent metal center, $Rh_2(TM4)_4^{4+}$.

TBA^+TFPB^- is readily prepared in gram quantities via the method of Kobayashi et al.[3] A background cyclic voltammogram shows that the effective electrochemical window of 0.1 M TBA^+TFPB^- in CH_2Cl_2 extends from ca. +1.6 to −1.8 V vs aqueous AgCl/Ag. The trifluoromethyl groups significantly extend the anodic limit of $TFPB^-$ over that of unsubstituted tetraphenylborate.[5] A potential drawback of this system is that solutions left unprotected from room light for extended periods of time (several weeks) slowly turn yellow.[6] These can be conveniently purified, however, by flash chromatography down a short column of alumina immediately prior to use.

Electrochemistry of Metallocenes. Despite the extensive use of ferrocene as a model redox system for nonaqueous studies, the electrochemistries of ruthenocene and osmocene have been far less studied and remain less well understood.[7] In common solvent/electrolyte systems the oxidation of Cp_2Ru is reported to proceed by an irreversible, 2e⁻ process;[8-13] under similar conditions, Cp_2Os shows an irreversible 1e⁻ oxidation followed by an ill-defined anodic process at more positive potentials.[8-12,14] The isolation of "osmocenium" as a highly reactive $[Cp_2Os]_2^{2+}$ dimer formed by the oxidation of Cp_2Os with Ce(IV) in CH_3CN[15] strongly suggests that the irreversible electrochemical response of Cp_2Os results from the generation, and subsequent reactions of this metal-metal-bonded dimer. While no analogous $[Cp_2Ru]_2^{2+}$ species has been characterized, it is possible that the observed net 2e⁻ electrochemical oxidation of ruthenocene arises from rapid dimerization of Cp_2Ru^+ followed by disproportionation. Alternatively, Cp_2Ru^+ may directly disproportionate in the presence of even weakly coordinating ligands.

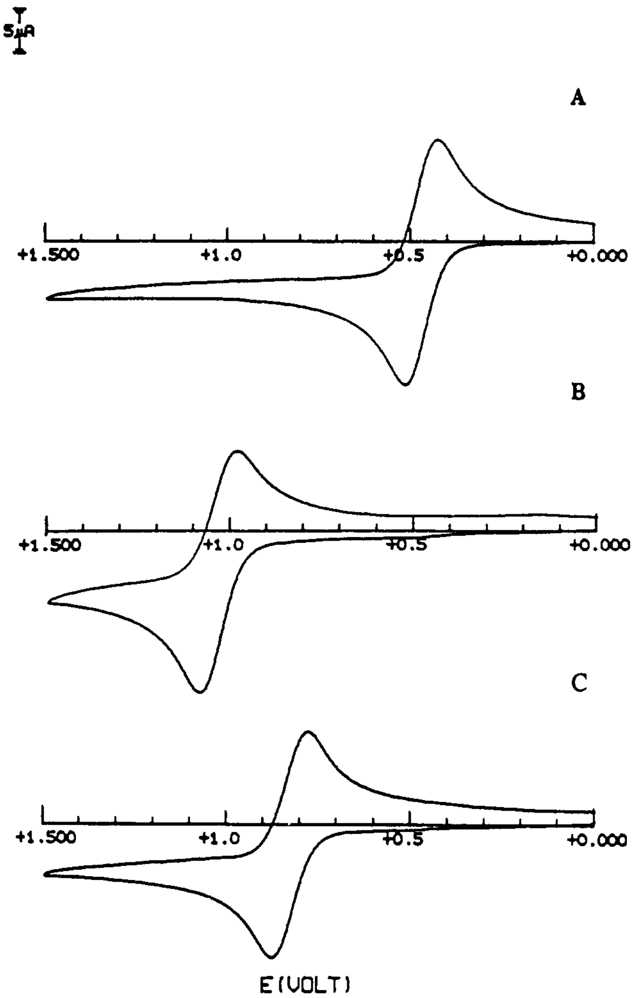

Figure 1. Cyclic voltammograms of ferrocene (A), ruthenocene (B), and osmocene (C) in 0.1 M TBA^+TFPB^- in CH_2Cl_2. All metallocene concentrations are 0.5 mM. Scan rate = 100 mV/s.

It is likely that the enhanced susceptibility of Cp_2Ru^+ and Cp_2Os^+ toward nucleophilic attack and/or dimerization is due in part to the larger ring–ring separation expected for these complexes relative to that of Cp_2Fe^+.[16] The additional steric hindrance afforded the metal by the permethylated derivatives $Cp^*{}_2Ru$ and $Cp^*{}_2Os$ is sufficient to block the metal centers, as evidenced by reports of the quasi-reversible 1e⁻ electrochemical oxidations of these compounds.[20,21]

In CH_2Cl_2 solutions of TBA^+TFPB^-, ruthenocene and osmocene each exhibit a single, quasi-reversible 1e⁻ oxidation.[22,23] Figure

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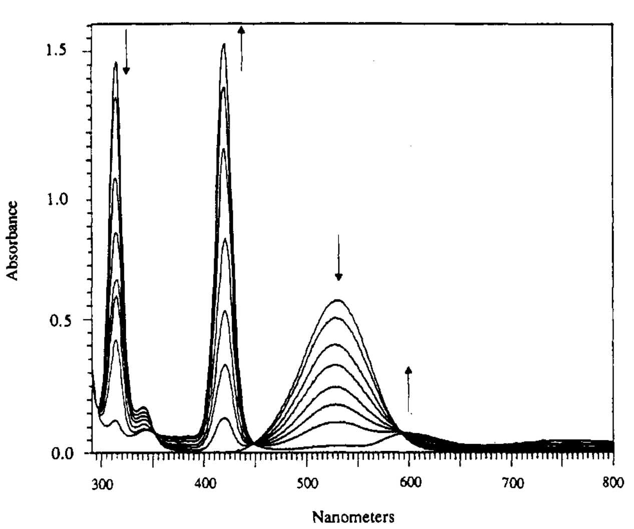

Figure 2. UV–vis spectroelectrochemical oxidation of 1.5 mM $[Rh_2(TM4)_4][TFPB]_2$ in 0.1 M TBA^+TFPB^- in CH_2Cl_2. Spectra were recorded at ca. 10-s intervals. Arrows indicate the directions of absorbance change.

1 shows the cyclic voltammograms of 0.5 mM Cp_2M, where M = Fe, Ru, and Os; $E^{\circ\prime}{}_{+/0}$'s, peak current ratios, and diffusion constants are summarized for all three compounds in Table I. The relative ordering of redox potentials, $Cp_2Ru > Cp_2Os > Cp_2Fe$, follows that reported for the decamethyl derivatives ($E^{\circ\prime}{}_{+/0}$ = −0.11,[7] +0.46,[21] and +0.55 V[20] vs SCE for $Cp^*{}_2M$ where M = Fe, Os, and Ru, respectively). It is significant that reversible oxidations of $Cp^*{}_2Ru$ and $Cp^*{}_2Os$ were achieved by steric blocking of the electrophilic metal centers, while the more accessible unsubstituted metallocenes exhibit reversible electrochemical responses only when the extremely weakly coordinating $TFPB^-$ is used as the supporting anion. All other anions used in this study give irreversible CV's for Cp_2Ru and Cp_2Os. In contrast, Cp_2Fe^+, which is significantly less accessible to anion interactions, yields reversible electrochemistry with all of these anions.

Electrochemistry of $Rh_2(TM4)_4{}^{2+}$. To quantitate the noncoordinating nature of $TFPB^-$, we investigated the electrochemistry and UV–vis–IR spectroelectrochemistry of $[Rh_2(TM4)_4][TFPB]_2$.[26] Like the closely related $Rh_2(dimen)_4{}^{2+}$ complex (dimen = 1,8-diisocyanomenthane)[27], $Rh_2(TM4)_4{}^{2+}$ exhibits a quasi-reversible $2e^-$ oxidation in CH_2Cl_2 solutions containing 0.1 M $TBA^+ClO_4^-$ according to eq 1.

$$Rh_2(TM4)_4{}^{2+} + 2ClO_4^- \rightleftharpoons Rh_2(TM4)_4(ClO_4)_2{}^{2+} + 2e^- \quad (1)$$

In a recent study,[28] we measured the temperature-dependent equilibrium constant for the disproportionation of $Rh_2(TM4)_4{}^{3+}$ in the presence of ClO_4^-, according to Scheme I. (Note that the binding constant of ClO_4^- to the $Rh_2(TM4)_4{}^{4+}$ core is expressed in the apparent disproportionation constant, K_{disp}'.)

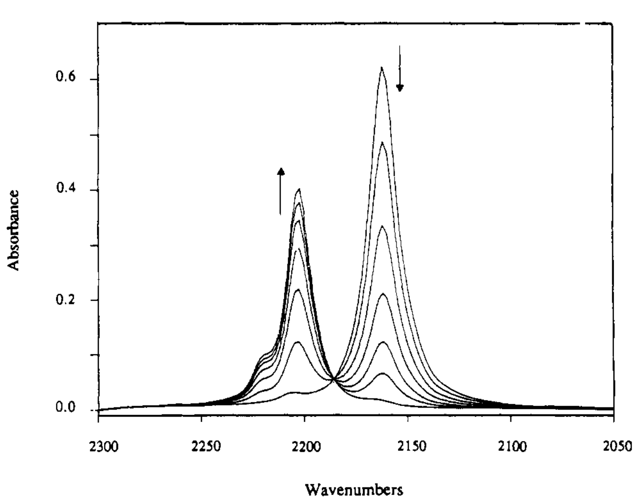

Figure 3. IR spectroelectrochemical oxidation of 1.5 mM $[Rh_2(TM4)_4][TFPB]_2$ in 0.1 M TBA^+TFPB^- in CH_2Cl_2. Spectra were recorded at ca. 15-s intervals.

Table II. Disproportionation Constants, K_{disp}', for $Rh_2(TM4)_4{}^{3+}$ in 0.1 M TBA^+X^-

X^-	$K_{disp}'{}^{a,b}$	$\Delta G_{disp}'$, cal/mol
Cl^-	$>10^6$	<−8200
ClO_4^-	18 (2)	−1700
BF_4^-	4 (3)	−800
PF_6^-	8.7 (15) × 10^{-2}	+1450
SbF_6^-	8 (3) × 10^{-3}	+2800
$TFPB^-$	$<10^{-10}$	>+13600

[a] Measured at 25 °C. [b] Standard deviations in the last significant digits are listed in parentheses.

Scheme I

$$2Rh_2(TM4)_4{}^{3+} \rightleftharpoons Rh_2(TM4)_4{}^{2+} + Rh_2(TM4)_4{}^{4+}$$

$$Rh_2(TM4)_4{}^{4+} + 2ClO_4^- \rightleftharpoons Rh_2(TM4)_4(ClO_4)_2{}^{2+}$$

$$K_{disp}' = \frac{[Rh_2(TM4)_4{}^{2+}][Rh_2(TM4)_4(ClO_4)_2{}^{2+}]}{[Rh_2(TM4)_4{}^{3+}]^2}$$

At 25 °C, we found that K_{disp}' is equal to 18 ± 2, which corresponds to a $\Delta G_{disp}'$ of −1700 cal/mol. Moreover, we found that the thermodynamic driving force for the disproportionation of $Rh_2(TM4)_4{}^{3+}$, $Rh_2(dimen)_4{}^{3+}$, and other related d^7–d^8 radicals arises primarily from the energetically favorable complexation of ligands (in the above case, ClO_4^-) to the resulting $2e^-$ oxidized d^7–d^7 species.[28,29] As a result, these compounds constitute sensitive probes for the coordinating ability of potential anions. Comparison of the disproportionation constants of $Rh_2(TM4)_4{}^{3+}$ in the presence of various ligands, L, provides a relative measure of the thermodynamic stabilities of the $Rh_2(TM4)_4L_2{}^{4+}$ complexes, and hence a relative measure of the ability of L to stabilize electrophilic centers.

In contrast to the $2e^-$ response exhibited in $TBA^+ClO_4^-$ solutions, the electrochemistry of $[Rh_2(TM4)_4][TFPB]_2$ exhibits a single quasi-reversible $1e^-$ oxidation in TBA^+TFPB^- in CH_2Cl_2. Figures 2 and 3 show the UV–vis and IR spectroelectrochemical oxidation of $Rh_2(TM4)_4{}^{2+}$ in this medium. The isosbestic points observed during the generation of the d^7–d^8 radical (characterized by absorbances at 420 and 590 nm in the UV–vis region and 2201 cm^{-1} in the IR region) indicate that $Rh_2(TM4)_4{}^{3+}$ is thermodynamically stable with respect to disproportionation in the presence of $TFPB^-$. Addition of $TBA^+ClO_4^-$ to the above solution results in the reappearance of a quasi-reversible $2e^-$ electrochemical

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(23) It is noteworthy that under our experimental conditions osmocenium shows no evidence for dimerization.[24] This contrasts with a recent low-temperature CV study of Cp_2Os, which showed the rapid formation of $[Cp_2Os]_2{}^{2+}$ in 0.1 M $TBA^+PF_6^-$ at a platinum microelectrode.[11] While more information regarding the mechanism and thermodynamics of the dimerization reaction is needed, the stability of monomeric Cp_2Os^+ under our experimental conditions suggests that the ability of $TFPB^-$ to stabilize a more highly charged dicationic dimer in a low dielectric medium such as CH_2Cl_2 may be significantly lower than that of PF_6^-.

(24) The UV–vis spectroelectrochemical oxidation of Cp_2Os in 0.1 M TBA^+TFPB^- in CH_2Cl_2 results in the appearance of a weak band centered at 750 nm. We assign this absorption to the LMCT transition of Cp_2Os^+ by analogy to the similar transition found for Cp_2Fe^+ at ca. 650 nm.[25] No intense, high energy band attributable to the σ–σ^* transition expected for $[Cp_2Os]_2{}^{2+}$ was observed. In the presence of CH_3CN (~5 M), however, the spectroelectrochemistry reveals a strong band at 330 nm, indicative of a metal–metal-bonded species.

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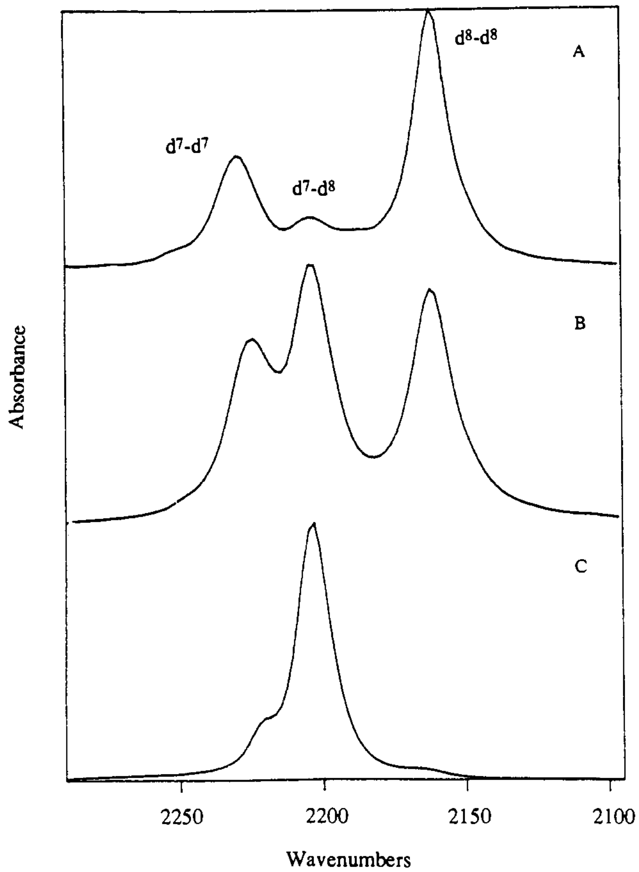

Figure 4. IR spectra of 1.5 mM solutions of $[Rh_2(TM4)_4][TFPB]_2$ in 0.1 M TBA^+X^- in CH_2Cl_2 after the removal of 1 equiv of charge: (A) X = ClO_4^-; (B) X^- = PF_6^-; (C) X = $TFPB^-$.

response, due to the increased stability of $Rh_2(TM4)_4^{4+}$ afforded by the coordination of ClO_4^-.

The lack of a second oxidation of $Rh_2(TM4)_4^{3+}$ to $Rh_2(TM4)_4^{4+}$ in TBA^+TFPB^- precludes an accurate assessment of K_{disp}'; however, on the basis of the difference between the $E°'_{3+/2+}$ couple and the anodic limit, we can place an upper limit on the disproportionation of $Rh_2(TM4)_4^{3+}$ of 1×10^{-10}. At 25 °C, this translates into a disproportionation reaction that is endothermic by greater than 13.5 kcal/mol. Table II summarizes the disproportionation constants of $Rh_2(TM4)_4^{3+}$ in the presence of a variety of common electrolyte anions. The relative ability of these anions to stabilize the $Rh_2(TM4)_4^{4+}$ core follows the order $Cl^- \gg ClO_4^- > BF_4^- > PF_6^- > SbF_6^- \gg TFPB^-$. This series closely follows a previous ordering of the relative nucleophilicities of several common anions based on quantum yield studies of the photosubstitution of $CpFe(toluene)^+X^-$ CH_2Cl_2 solutions.[30]

By making the assumption that the difference between $\Delta G_{disp}'$ in TBA^+X^- and $\Delta G_{disp}'$ in TBA^+TFPB^- is due primarily to differences in the coordinating abilities of X^- and $TFPB^-$, it is possible to assess the relative thermodynamics of associating various anions with the $Rh_2(TM4)_4^{4+}$ core. Our data demonstrate that $TFPB^-$ interacts far less than the standard noninteractive anions.[31] For example, we find that $Rh_2(TM4)_4^{4+}$ is more than 12 kcal/mol more stable in the presence of PF_6^- than in the presence of $TFPB^-$. Figure 4 shows this pictorially by plotting the IR spectra of equimolar solutions of $Rh_2(TM4)_4^{2+}$ after the removal of 1 equiv of charge in the presence of ClO_4^-, PF_6^-, and $TFPB^-$. While both the ClO_4^- solution (top curve) and PF_6^- solution (middle curve) show substantial amounts of $Rh_2(TM4)_4^{4+}$, the $TFPB^-$ solution (bottom curve) consists only of $Rh_2(TM4)_4^{3+}$.

Conclusions. We have found that TBA^+TFPB^- is very useful as a noninteracting electrolyte for electrochemical studies that generate electrophilic species. Quantitative studies with an anion-sensitive redox couple indicate that a difference of greater than 22 kcal/mol is spanned by the series $Cl^- > ClO_4^- > BF_4^- > PF_6^- > SbF_6^- > TFPB^-$. Surprisingly, the $TFPB^-$ ion is nearly 11 kcal/mol less interactive than SbF_6^-, which is generally regarded as a very poorly interactive anion. We believe that this interaction ordering will be generally applicable but might break down for species which show a particular propensity to abstract F^- from the fluoride-containing anions in the series.[4] Future studies will further address the coordinating ability of the $TFPB^-$ ion and other potentially less coordinating anions which we are currently studying.

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Registry No. TBA^+TFPB^-, 112724-99-9; CH_2Cl_2, 75-09-2; Cp_2Ru, 1287-13-4; Cp_2Os, 1273-81-0; $Rh_2(TM4)_4^{2+}$, 73367-41-6; Cp_2Ru^+, 54538-51-1; Cp_2Os^+, 54438-61-8; Cp_2Fe, 102-54-5; Cp_2Fe^+, 12125-80-3; TBA^+Cl^-, 1112-67-0; $TBA^+ClO_4^-$, 1923-70-2; $TBA^+BF_4^-$, 429-42-5; $TBA^+PF_6^-$, 3109-63-5; $TBA^+SbF_6^-$, 22505-58-4; $Rh_2(TM4)_4^{3+}$, 137039-42-0; $[Rh_2(TM4)_4][TFPB]_2$, 137039-43-1; $[Rh_2(TM4)_4][Cl]_2$, 99327-01-2.

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Pd-H-P Bridging in a Palladium(I) Dimer

The ability of a carbon-hydrogen bond to function as a donor to a transition metal is now widely recognized.[1] Indeed, for the general case L_nM-H-E, with E = an appropriately substituted carbon, there is a continuum of bounding modes stretching from very weak to bridging.[2] In a more general vein, if one views an agostic interaction as one form of the class L_nM-H-E, where, apart from a carbon fragment, E can be a different transition metal[3] or a nitrogen[4,5] or boron[6] function, then it is interesting to note that no representative with E = P is known, although this possibility has been recently mentioned.[7]

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