Inorg. Chem. **1992**, *31*, 4300–4307

Reactivity of $Ru(OEP)(aryl)_2$ Complexes in Extreme Oxidation States

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Received May 4, 1992

Cyclic voltammetry has been employed to study the reactivity of $Ru(OEP)(p\text{-}XC_6H_4)_2$ (OEP = octaethylporphyrin dianion; X = H, CH_3, OCH_3, Cl, F) complexes in extreme oxidation states. As previously demonstrated for $Ru(OEP)(C_6H_5)_2$, the $[Ru(OEP)(aryl)_2]^+$ complexes undergo Ru-to-N migration of an aryl group, while the $[Ru(OEP)(aryl)_2]^{2-}$ complexes lose aryl$^-$ to form $[Ru(OEP)(aryl)]^-$. The rates of these reactions (i.e., the stability of the highly oxidized or reduced complexes) depend on the nature of the aryl group. The stability of the $[Ru(OEP)(p\text{-}XC_6H_4)_2]^{2-}$ complexes lies in the order $Cl \gg F > OCH_3 > H > CH_3$ and is very sensitive to the ionic strength of the solution. This order results in a curved Hammett plot when the combined σ_p parameter is employed but in a roughly linear plot when inductive effects alone (σ_I) are considered. The stability of the $[Ru(OEP)(p\text{-}XC_6H_4)_2]^+$ complexes lies in the order $Cl > F > OCH_3 \gtrsim CH_3 \gtrsim H$ at room temperature. The enthalpies of activation for the $[Ru(OEP)(p\text{-}XC_6H_4)_2]^+$ reactions follow the trend $F > H \gtrsim Cl > CH_3 \sim OCH_3$, with $\Delta H^{\ddagger}$ values in the range 9–14 kcal/mol. The entropies of activation follow the same trend, with $\Delta S^{\ddagger}$ values in the range −9 to +4.5 cal/(mol·K). Closer inspection of these data reveals that the major difference exists for X = F ($\Delta H^{\ddagger}$ = 14 kcal/mol, $\Delta S^{\ddagger}$ = 4.5 cal/(mol·K); the remaining four complexes show similar activation parameters ($\Delta H^{\ddagger}$ = 9.3–10.8 kcal/mol, $\Delta S^{\ddagger}$ = −4 to −9 cal/(mol·K)). A discussion of the mechanisms of these and related redox-induced reactions is provided.

Introduction

The relevance of organometallic porphyrin complexes[1–6] to the suicide inactivation of cytochrome P-450[7] and to the reactivity of vitamin B_{12}[8] has led to numerous chemical studies with synthetic porphyrins. These chemical studies often also seek interesting organometallic chemistry which should result[1a] from the steric bulk and stability of the porphyrin ring. Indeed, $M(Por)R_n$ chemistry has proven to be interesting and varied:[1–6] C–C bond formation, M–C bond homolysis, C–C and C–N bond scission within the porphyrin ring, M-to-N migration of aryl/alkyl ligands, α-C–C bond scission of alkenes and alkynes, C–H bond activation, and a CH_3-to-CO transformation.

Many of these chemical reactions are influenced by or initiated by redox reactions of the complexes. Accordingly, electrochemical investigations of organometallic metalloporphyrin complexes are common.[1b,6] A broad picture of the redox and associated reaction chemistry of metalloporphyrin complexes is emerging from these studies. Although in selected cases stable anions and cations are produced, redox-induced M-to-N migration and loss of aryl/alkyl ligands are recurring themes in the redox chemistry of these complexes.

The present understanding of the migration and ligand loss reactions derives primarily from electrochemical studies of Fe, Ru, Co, Rh, and Ir complexes. With $[Fe(Por)(aryl)]^+$ complexes, migration occurs on the voltammetric time scale (seconds) for C_6H_5, $m\text{-}CH_3C_6H_4$, and $p\text{-}CH_3C_6H_4$ groups but not with the electron-withdrawing C_6F_5 and C_6F_4H groups or the CH_3 analogue.[1b] No comparative kinetic study has been reported for the Fe complexes. Unlike with the Fe congeners, migration does not occur with $[Ru(OEP)(C_6H_5)]^+$[3a] or $[Ru(OEP)(CH_3)]^+$.[4] Facile migration is observed with $[Ru(OEP)(C_6H_5)_2]^+$ and $[Ru(OEP)(CH_3)_2]^+$ to form the corresponding $[Ru(OEP\text{-}N\text{-}R)(R)]^+$ complexes.[3c,4] With the $[Co(Por)R]^+$ complexes migration occurs for most alkyl and aryl groups on the voltammetric time scale (seconds). Since the initial oxidation forms a $[Co^{III}(Por^{\bullet+})R]^+$ complex in one case and a $[Fe^{IV}(Por)R]^+$ complex in the other, direct comparison between Fe and Co is complicated. One particular Co study[6i] revealed that the difference in measured rate constant was due to the oxidation step, rather than the migration step. Comparatively less is known about those factors affecting the migrations of the other metal complexes due to the lack of systematic studies.

Ligand loss from reduced organometallic complexes has been observed[1,3,4] with Fe, Ru, Co, Rh, and Ir complexes. $[Fe(OEP)(C_6H_5)]^-$ is stable, but aryl$^-$ loss is observed for the C_6F_4H and C_6F_5 analogues.[1b] $[Ru(OEP)(C_6H_5)]^-$ and $[Ru(OEP)(CH_3)]^-$ are both stable, while $C_6H_5^-$ loss[3a] from $[Ru(OEP)(C_6H_5)_2]^{2-}$

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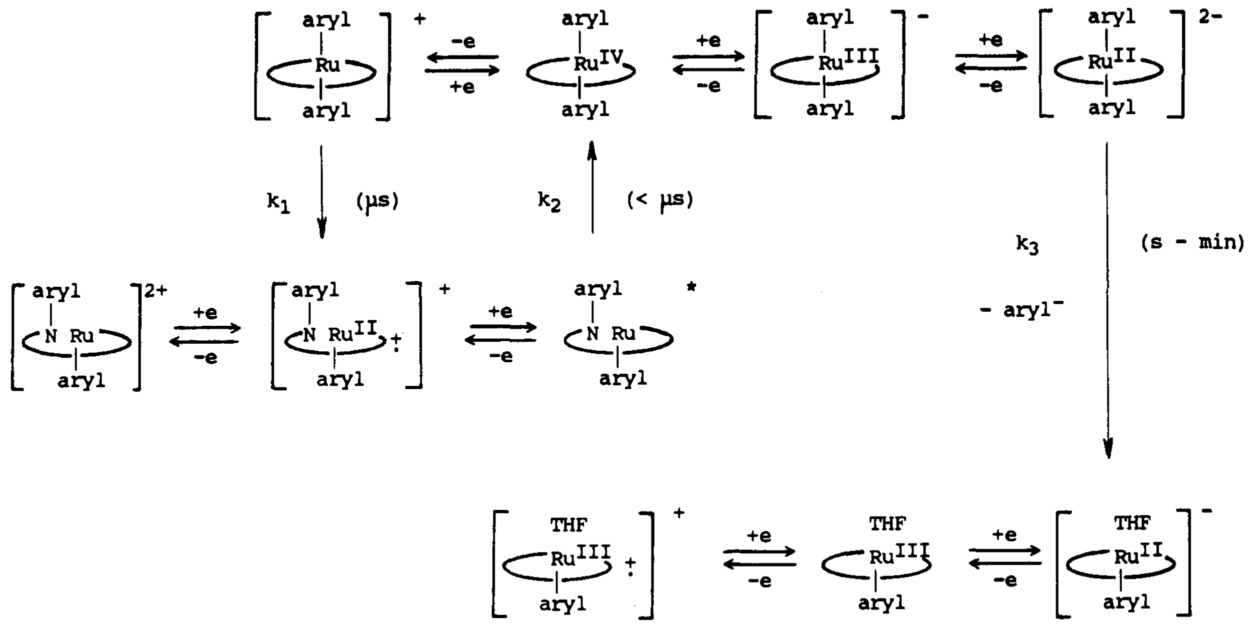
Scheme I



*species not observed due to short lifetime.

and $CH_3^\bullet$ loss[4a] from $[Ru(OEP)(CH_3)_2]^-$ have been reported. Saveant has suggested $R^\bullet$ loss from $[Fe(Por)R]^{2-}$ complexes on the basis of the relative stabilities of the *n*-Bu, *sec*-Bu, and *t*-Bu complexes.[6g] The π anion radicals formed from the electrochemical reduction of M(OEP)(alkyl) complexes (M = Co,[1b] Rh,[2g] Ir[1b]) lose R^- to form M(OEP), which reacts further depending upon the metal and the ligand.

Our contributions to this area have entailed the electrochemical, chemical, and spectroscopic studies[3] of the coupled redox and reaction chemistry of phenyl,[3] methyl,[4] and mixed phenyl–methyl[5] Ru(OEP) complexes. We have recently turned our attention to the chemistry of related Ru(OEP)(aryl)$_2$ complexes. The results presented herein pertain to the redox-induced chemical reactions of the Ru(OEP)(p-XC_6H_4)$_2$ complexes, where X = H, CH_3, OCH_3, Cl, and F. Cyclic voltammetry has been used to determine the rates of reaction of the $[Ru(OEP)(p\text{-}XC_6H_4)_2]^+$ and $[Ru(OEP)(p\text{-}XC_6H_4)_2]^{2-}$ complexes. These kinetic results are viewed from the perspective of the stability of the complexes in extreme oxidation states. Comparisons with related metalloporphyrin complexes are presented.

Experimental Section

All synthetic manipulations were performed in a Vacuum Atmospheres inert-atmosphere drybox with an oxygen level less than 2 ppm (Model AO-316-C oxygen analyzer) or on a Schlenk line, unless otherwise noted. All glassware was oven-dried.

Reagents and Solvents. All materials used in this study were dried and degassed before use in the drybox. Solvents were dried by distillation from Na/benzophenone or P_2O_5. THF for electrochemical experiments was distilled and used within 8 h. C_6H_5Br (Aldrich) was dried by passage through an Al_2O_3 column and collected by vapor-phase transfer on a Schlenk line. C_6H_5Li and p-$(CH_3O)C_6H_4Li$ were prepared by metathesis of the aryl bromide with *n*-BuLi (Alfa). For the other aryls commercially available (Aldrich), Grignard solutions were employed. Bu_4NClO_4 was prepared and purified by literature methods.[9] Sodium naphthalenide (NaNaph) was prepared by stirring a THF solution of naphthalene (sublimed) over sodium. $AgBF_4$ (Aldrich) was used as received.

Ru Porphyrin Complexes. Ru(OEP)(aryl)$_2$ complexes were prepared in ca. 30% yield by the method of James and Dolphin.[2f] In a typical preparation, 0.285 mmol of p-ClC_6H_4MgBr (1 M in ether) was added to a C_6H_6 solution of Ru(OEP)Cl_2 (40 mg; 0.057 mmol). After 20 min, the solution was washed with 3 × 50 mL of H_2O and then filtered through Al_2O_3. C_6H_6 elution yielded crude Ru(OEP)(p-ClC_6H_4)$_2$, while 3% THF/C_6H_6 elution yielded crude Ru(OEP)(p-ClC_6H_4)(THF). Final purification of these complexes was achieved with column chromatography inside the drybox.

Ru(OEP)(aryl)(THF) complexes were obtained from filtrates of the above Ru(OEP)(aryl)$_2$ syntheses. Removal of the solvent yielded a red solid that was purified Al_2O_3 on a column using C_6H_6 and then 3% THF/C_6H_6. Prolonged pumping of the solid removed the axially-bound THF. Typical yield: 50%.

Na[Ru(OEP)(aryl)$_2$] solutions were prepared by addition of 0.6–0.7 equiv of NaNaph/THF to a well-stirred C_6H_6 solution of Ru(OEP)(aryl)$_2$. This mixture of 40–60% $[Ru(OEP)(aryl)_2]^-$, 30–40% Ru(OEP)(aryl)$_2$, and 10–20% $[Ru(OEP)(aryl)]^-$ was used for spectroscopic experiments. EPR measurements were not impeded by the presence of the diamagnetic Ru(OEP)(aryl)$_2$ or $[Ru(OEP)(aryl)]^-$ species. However, ^1H NMR spectra displayed broadening and changes in chemical shift indicative of electron exchange;[3a] for this reason, NMR spectroscopic parameters are not reported for the $[Ru(OEP)(aryl)_2]^-$ species. Reductions performed with 0.9–1.0 equiv of NaNaph yielded significant (20–50% depending on X) $[Ru(OEP)(aryl)]^-$ contamination resulting from decomposition of $[Ru(OEP)(aryl)]^{2-}$ (see Scheme I). As discussed in the text, reduction of the p-ClC_6H_4 complex yielded a drastically different composition and an unidentified paramagnetic intermediate.

$Na_2[Ru(OEP)(p\text{-}(CH_3O)C_6H_4)_2]$ and $Na_2[Ru(OEP)(p\text{-}FC_6H_4)_2]$ samples containing ca. 25% Na[Ru(OEP)(aryl)(THF)] were isolated following the addition of excess NaNaph/THF to a C_6H_6 solution of Ru(OEP)(aryl)$_2$, solvent removal, and C_6H_6 wash. With X = H and Cl, aryl$^-$ loss was so extensive that minimal $[Ru(OEP)(aryl)_2]^{2-}$ was observed.

Na[Ru(OEP)(aryl)(THF)] complexes were prepared by addition of excess NaNaph/THF to a C_6H_6 solution of Ru(OEP)(aryl)(THF) (ca. 5 mg). Alternatively, $[Ru(OEP)(C_6H_5)]^-$ was prepared by addition of excess NaNaph/THF to a benzene solution of Ru(OEP)(C_6H_5)$_2$ (ca. 5 mg). Removal of the solvents yielded a red-black precipitate that was separated from the solid NaNaph with C_6H_6; no colored (porphyrinic) material remained with the solid. Removal of the solvent afforded the final product in a quantitative yield (^1H NMR).

[Ru(OEP-*N*-aryl)(aryl)](BF_4) complexes were prepared by the addition of excess $AgBF_4$/toluene to a toluene solution of Ru(OEP)(aryl)$_2$. After 30 min, the dark precipitate was filtered off and reprecipitated with CH_2Cl_2/hexanes. Typical isolated yields: 80%.

[Ru(OEP)(aryl)](BF_4) complexes were prepared by the addition of excess $AgBF_4$/toluene to a toluene solution of Ru(OEP)(aryl). After 30 min, the dark precipitate was filtered off and reprecipitated with CH_2Cl_2/hexanes. Typical isolated yields: 80%.

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Table I. ^1H NMR and UV–Vis Spectroscopic Parameters for $Ru(OEP)(p\text{-}XC_6H_4)_2$ and $Ru(OEP)(p\text{-}XC_6H_4)$ Complexes

	δ, ppm[a]						
				$p\text{-}XC_6H_4$			
X	meso	CH_2	CH_3	*p*	*m*	*o*	λ_{max}, nm[b] (log ε, $M^{-1}\ cm^{-1}$)
				$Ru(OEP)(p\text{-}XC_6H_4)_2$			
H	9.92 (s) 4 H	3.68 (q) 16 H	1.73 (t) 24 H	5.02 (t) 1 H	4.82 (t) 2 H	1.17 (d-d) 2 H	345 (4.66) 379 (4.81) 516 (4.33)
CH_3	9.93 (s) 4 H	3.70 (q) 16 H	1.75 (t) 24 H	0.70 (s) 3 H	4.62 (t) 2 H	1.12 (d-d) 2 H	343 (4.70) 382 (4.85) 516 (4.36)
OCH_3	9.95 (s) 4 H	3.72 (q) 16 H	1.76 (t) 24 H	2.06 (s) 3 H	4.48 (t) 2 H	1.30 (d-d) 2 H	345 (4.74) 388 (4.81) 514 (4.44)
F	9.91 (s) 4 H	3.65 (q) 16 H	1.70 (t) 24 H		4.54 (d-d) 2 H J_{HF} = 3–5 Hz	1.14 (d-d) 2 H J_{HF} = 6–10 Hz	344 sh (4.70) 379 (4.85) 518 (4.39)
Cl	9.94 (s) 4 H	3.65 (q) 16 H	1.70 (t) 24 H		4.75 (d) 2 H	1.01 (d) 2 H	348 sh (4.65) 377 (4.77) 518 (4.30) 636 (3.80)
				$Ru(OEP)(p\text{-}XC_6H_4)$[c]			
H	0.53 (br s) 4 H	14.02, 5.63 (br s) 8 H	−1.21 (br s) 24 H	49.97 (br s) 1 H	−49.24 (br s) 2 H	−84.1 (br s) 2 H	360 (4.62) 395 (4.83) 510 (4.16)
CH_3	1.34 (br s) 4 H	13.92, 5.61 (br s) 8 H	−1.09 (br s) 24 H	111.1 (br s) 3 H	50.42 (br s) 2 H	−97.5 (br s) 2 H	362 (4.64) 395 (4.84) 516 (4.16)
OCH_3	3.58 (br s) 4 H	14.41, 5.93 (br s) 8 H	−0.65 (br s) 24 H	25.13 (br s) 3 H	44.56 (br s) 2 H	−116.1 (br s) 2 H	362 sh (4.73) 396 (4.96) 512 (4.27)
F	1.36 (br s) 4 H	14.38, 6.17 (br s) 8 H	−1.06 (br s) 24 H		48.06 (br s) 2 H	−93.2 (br s) 2 H	360 sh (4.62) 395 (4.86) 512 (4.14)
Cl	0.89 (br s) 4 H	14.57, 6.30 (br s) 8 H	−1.10 (br s) 24 H		50.21 (br s) 2 H	−83.3 (br s) 2 H	361 (4.68) 395 (4.86) 508 (4.17)

[a] NMR spectra obtained in C_6D_6. [b] UV–vis spectra obtained in THF. [c] NMR samples did not contain THF as the sixth ligand; coordination of THF causes slight changes in chemical shift.[2c,3a]

Spectroscopic Measurements. UV–vis spectra were obtained on a Hewlett-Packard 8450 diode array spectrophotometer using 0.1-cm cells. ^1H NMR spectra were obtained on a Varian 200-MHz or GE 300-MHz spectrometer. Samples for long-term NMR spectroscopy experiments were prepared in evacuated and sealed tubes. EPR measurements were performed on a Varian E-line Century Series Q-band spectrometer.

Electrochemical Experiments. Cyclic voltammetry was performed in Ar- or N_2-saturated 0.2 M Bu_4NClO_4/THF solutions containing ca. 2–4 mM metalloporphyrin complex. The standard three-electrode configuration contained either a Pt disk electrode (A = 0.08 cm^2) for scan rates of 20–500 mV/s or a Pt microdisk electrode (diameter = 10 μm) for scan rates of 1–20 000 V/s. The slow-scan experiments were performed on a Bioanalytical Systems CV-1 potentiostat with a Soltec VP-6423S X-Y recorder. The fast-scan experiments were performed on a locally-constructed potentiostat,[10] a Hewlett-Packard 3314A function generator, and a Tektronix 4230A digital storage oscilloscope. Data from this system were transferred to a Zenith 80386 personal computer over a GPIB (IEEE-488) interface bus. Data software for acquisition was written in Microsoft Quickbasic 4.5 with the aid of Tektronix EZ-Test PC Test Development Software. All potentials are relative to a Ag/AgCl pseudoreference electrode; the ferrocene/ferrocenium couple is observed at +0.43 V under these experimental conditions. Fast-scan cyclic voltammetric experiments were performed with a locally-constructed[12] ferrocene–ferrocenium reference electrode which provided stable reference potentials within 10 mV. Potentials were corrected to the Ag/AgCl pseudoreference using a known analyte (e.g., ferrocene) or using peak potentials of equivalent scan rate voltammograms obtained with the Ag/AgCl system. Uncertainties in the potential values are ~ 10 mV for the fast-scan measurements and ≤5 mV for the slow-scan experiments. The redox couples were assigned as reductions or oxidations on the basis of the rest potential of the solution. The reversible redox couples were assigned as one-electron processes on the basis of similar magnitudes of current functions[11] and mass balance of the NaNaph reduction of $Ru(OEP)(C_6H_5)_2$.

Rate constants for the follow-up chemical reactions (EC mechanism) were calculated from the relative peak currents as a function of scan rate using a working curve[12] analogous to that previously published.[11] Scan rates were selected such that the current ratios were 0.4–0.9 in order to minimize errors in background estimation that would bias the results.[13] Under such conditions, the measured rate constants typically varied by a factor of 2 over a range of 4–5 in scan rate. Typically four to six scan rates were employed; all values within the range are reported (cf. Figure 4 and supplementary material) and were used in Eyring plots. Average values were used in Hammett plots.

Results and Discussion

The $Ru(OEP)(aryl)_2$ complexes are readily prepared from $Ru(OEP)Cl_2$ using the procedure of James and Dolphin.[2f] These diamagnetic, air-stable complexes display the expected ^1H NMR and UV–vis spectroscopic parameters, listed in Table I. The Ru(OEP)(aryl) complexes are obtained from the same preparations as described above; spectroscopic parameters are provided in Table I. The spectroscopic parameters for the corresponding $[Ru(OEP)(aryl)]^{-/+}$ complexes are provided in the supplementary material; these are used in identification of chemical reactions coupled to redox reactions of the $[Ru(OEP)(aryl)_2]^{2-}$ complexes. The properties of the $Ru(OEP)(p\text{-}XC_6H_4)_2$ and $Ru(OEP)(p\text{-}XC_6H_4)$ complexes are consistent with the assignments by James and Dolphin[2c,f] of a diamagnetic d^4 $Ru^{IV}(OEP)(C_6H_5)_2$ complex and a paramagnetic d^5 $Ru^{III}(OEP)(C_6H_5)$ complex. Quite often, particularly for the $[Ru(OEP)(aryl)]^+$ complexes and for electrochemical experiments in THF, the sixth coordination site of

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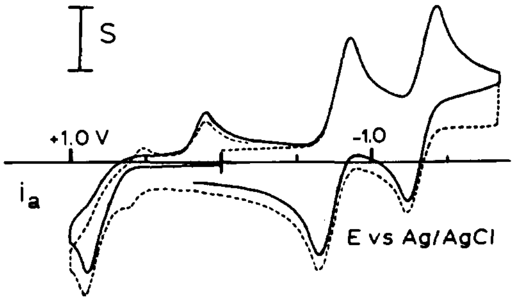

Figure 1. Cyclic voltammetric response of Ru(OEP)(p-FC_6H_4)$_2$ in 0.2 M Bu_4NClO_4/THF at 23 °C. v = 200 mV/s; S = 50 μA/cm^2. The voltammetric scan was initiated in the positive direction from 0 V for the solid trace and in the negative direction from 0 V for the dashed trace. For the dashed trace, the potential scan was held at −1.8 V for 30 s before initiating the reverse positive scan. The waves at 0.5–0.6 V are for the [Ru(OEP)(p-FC_6H_4)(THF)]$^{0/+}$ couple.

the mono(aryl) complexes is occupied by THF. The five-coordinate complex can be isolated for the neutral and anionic forms by extensive pumping of the solid. For simplicity the THF ligand is not included in the formula.

The typical cyclic voltammetric response of the Ru(OEP)(aryl)$_2$ complexes in THF is illustrated in Figure 1 for Ru(OEP)(p-FC_6H_4)$_2$. The irreversible anodic peak at 0.91 V coupled to the irreversible cathodic peak at 0.12 V is associated with the reversible Ru-to-N migration of one of the aryl groups (Scheme I). The Ru-to-N migration (k_1 step) occurs in the microsecond time scale, so the ephemeral electrochemically-generated [Ru(OEP)(p-FC_6H_4)$_2$]$^+$ species can be observed using fast-scan cyclic voltammetry. We describe in the next section the use of variable-temperature, fast-scan voltammetry with microdisk electrodes to study the stability of various [Ru(OEP)(aryl)$_2$]$^+$ complexes. The return N-to-Ru migration (k_2 step) occurs too rapidly even for observation at 20 000 V/s, indicating a lifetime of <1 μs for the Ru(OEP-N-aryl)(aryl) species. This extremely short lifetime precluded any further study of the [Ru(OEP-N-aryl)(aryl)]$^{0/+}$ couples. For certain complexes a second oxidation peak is observed nearly in the solvent limit. The scan rate dependence of the magnitude of this wave (cf. Figure 3) verifies that it is the [Ru(OEP-N-aryl)(aryl)]$^{+/2+}$ couple. Kadish[1b] has reported related [Fe(Por-N-aryl)]$^{+/2+}$ couples for several Fe complexes. Since this couple is so near the solvent limit and the electrogenerated [Ru(OEP-N-aryl)(aryl)]$^{2+}$ species precipitates onto the electrode (particularly at low temperatures), we have not studied this species in any detail.

The voltammetric waves at −0.72 and −1.31 V correspond to the [Ru(OEP)(p-FC_6H_4)$_2$]$^{0/-}$ and [Ru(OEP)(p-FC_6H_4)$_2$]$^{-/2-}$ couples. The first reduction, as with all of the Ru(OEP)(aryl)$_2$ complexes, is chemically and electrochemically reversible. However, the second reduction is coupled to aryl$^-$ loss from the dianion (Scheme I). The lifetime of the [Ru(OEP)(p-XC_6H_4)$_2$]$^{2-}$ species depends on the nature of X, as discussed below. Since these lifetimes are miliseconds–seconds, "normal" scan rates (20–500 mV/s) are adequate to study the decomposition reaction.

Nature of the Redox Couples. A natural question arises for each of the various Ru(OEP)(p-XC_6H_4)$_2$ and Ru(OEP)(p-XC_6H_4) redox couples: Is the redox process (essentially) metal- or porphyrin-localized? Often[1b,14] this questions is straightforward to answer; sometimes it is necessary to invoke a mixture of the two, and in one case[15] a reaction from one to the other was reported. Numerous experimental probes have developed to address this question; UV–vis spectroscopy, magnetic properties, and electrochemical measurements are three common approaches.

Table II. Electrochemical Parameters for Ru(OEP)(p-XC_6H_4)$_2$ and Ru(OEP)(p-XC_6H_4) Complexes and for Ru(OEP)(C_6F_5)$_2$ and Ru(OEP)(C_6F_5)

	$E_{1/2}$, V vs Ag/AgCl		
complex	0/+	0/−	1−/2−
Ru(OEP)(p-XC_6H_4)$_2$			
X = H	0.81	−0.90	−1.38
X = CH_3	0.67	−0.94	−1.42
X = OCH_3	0.68	−0.96	−1.43
X = F	0.88	−0.75	−1.35
X = Cl	0.87	−0.72	−1.31
Ru(OEP)(C_6F_5)$_2$	(1.20)[a]	0.12	(−1.50)[a]
Ru(OEP)(p-XC_6H_4)			
X = H	0.48	−0.80	
X = CH_3	0.46	−0.83	
X = OCH_3	0.43	−0.85	
X = F	0.54	−0.78	
X = Cl	0.55	−0.77	
Ru(OEP)(C_6F_5)	0.75	−0.67	

[a] E_p for irreversible process at 100 mV/s.

The results of these physical measurements on various neutral and ionic Ru(OEP)(aryl)$_n$ complexes, listed in Tables I and II and the supplementary material, are discussed below. It should be stressed that, purely from the perspective of the kinetic results discussed below, the precise site of electron transfer is not crucial, providing that it does not vary throughout a particular p-XC_6H_4 series.

The magnitude of the dependence of formal potentials on the nature of axially-bound ligands has been used[1b] to infer the site of electron transfer. For complexes with porphyrin-localized redox reactions $E_{1/2}$ changes very little through a p-XC_6H_4 series (typically, X = OCH_3, H, CH_3, and Cl or F) with no consistent trend with σ_p. For example, with Rh(TPP)(p-XC_6H_4), there is less than a 10-mV change for four redox couples.[1b] With Co(TPP)(p-XC_6H_4) an equilibrium between metal- and ligand-centered processes is sometimes invoked;[1b] the $E_{1/2}$ changes are 50–100 mV[1b] in these cases. Likewise, in the comparison of C_6F_4H or C_6F_5 with C_6H_5, there is only a 20-mV change for the porphyrin-localized [In(OEP)(aryl)]$^{0/-}$ and [In(TPP)(aryl)]$^{0/-}$ couples.[1b] For metal-centered redox couples, the change is more dramatic. For example, with Fe(TPP)(aryl) complexes the Fe$^{II/III}$ and Fe$^{III/IV}$ couples exhibit 280- and 330-mV shifts, respectively, upon going from C_6H_5 to C_6F_5.[1b] Another convenient means of identifying porphyrin-localized couples is the constancy in the difference in half-wave potentials ($E_{1/2}$) for porphyrin-localized couples. Differences of 2.25 ± 0.15 V between a reduction and an oxidation, 0.29 (±0.05) V for two successive oxidations, and 0.44 (±0.04) V for two successive reductions all accompany porphyrin-localized processes.[14]

The formal potentials for the five observable redox couples in Scheme I depend on the nature of the aryl group, as illustrated by the data in Table II. As expected, more electron-withdrawing groups ($\sigma_p > 0$) result in more positive $E_{1/2}$ values. This is represented graphically in Figure 2, an electrochemical analogue of a Hammett plot.[16,17] As with other electrochemical Hammett relationships,[17] the best correlation ($r > 0.94$) is found for the combined σ_p parameter; considering resonance effects alone (σ_R) leads to no correlation ($r < 0.2$), while considering inductive effects alone (σ_I) gives only moderate correlation ($r \sim 0.6$–0.8). The [Ru(OEP)(aryl)$_2$]$^{0/-}$ and [Ru(OEP)(aryl)$_2$]$^{0/+}$ couples possess similar slopes of ca. 0.5 V, while the [Ru(OEP)(aryl)]$^{0/+}$ and [Ru(OEP)(aryl)]$^{0/-}$ couples possess slopes of ca. 0.2 V. Unlike the other two bis(aryl) couples, the [Ru(OEP)(aryl)$_2$]$^{-/2-}$ couple possesses a slope of 0.23, a value more similar to that for the

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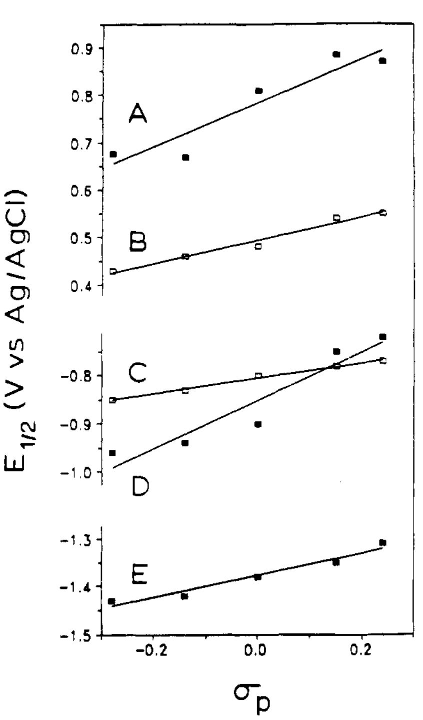

Figure 2. Plots of $E_{1/2}$ vs σ_p for the redox couples of Ru(OEP)(p-$XC_6H_4)_2$ and Ru(OEP)(p-XC_6H_4) complexes: (A) [Ru(OEP)(p-$XC_6H_4)_2]^{0/+}$; (B) [Ru(OEP)(p-XC_6H_4)]$^{0/+}$; (C) [Ru(OEP)(p-XC_6H_4)]$^{0/-}$; (D) Ru(OEP)(p-$XC_6H_4)_2]^{0/-}$; (E) [Ru(OEP)(p-$XC_6H_4)_2]^{-/2-}$. Note breaks in the y axis.

mono(aryl) series. Comparison of the C_6H_5 and C_6F_5 complexes reveals substantial differences for the [Ru(OEP)(aryl)]$^{0/+}$ and [Ru(OEP)(aryl)]$^{0/-}$ couples, 270 and 130 mV, respectively. For the [Ru(OEP)(aryl)$_2]^{0/-}$ couples this difference is even more substantial, 1.02 V. The [Ru(OEP)($C_6F_5)_2]^{-/2-}$ and [Ru(OEP)($C_6F_5)_2]^{0/+}$ couples are irreversible, so precise comparisons are not available; however, the changes appear to be quite large on the basis of E_p. Cumulatively, these electrochemical results are intermediate between those of the Co and Fe complexes, so metal-centered nature is suggested.

The [Ru(OEP)(aryl)]$^{0/+}$ and [Ru(OEP)(aryl)]$^{0/-}$ couples possess an ~1.3-V difference in $E_{1/2}$, a value inconsistent with two porphyrin-localized couples; at least one of these couples should be metal-centered. Further, neither of these couples is accompanied by a second couple 0.3–0.45 V more negative/positive, as would be expected for porphyrin-localized couples. The $E_{1/2}$ values are consistent with metal-centered reactions for the Ru(OEP)(aryl) couples. The Ru(OEP)(aryl)$_2$ couples are slightly more difficult to interpret, in part because the greater number of couples provides ample opportunity for a difference of 0.29, 0.44, or 2.15 V to be observed. The difference in $E_{1/2}$ values for the [Ru(OEP)(aryl)$_2]^{0/-}$ and [Ru(OEP)(aryl)$_2]^{-/2-}$ couples are 0.47–0.60 V, slightly higher than for a typical OEP$^{0/-}$–OEP$^{-/2-}$ pair. (Furthermore, the EPR results presented below indicate a metal-centered reaction for the [Ru(OEP)(aryl)$_2]^{0/-}$ couple.) The difference for the [Ru(OEP)(aryl)$_2]^{-/2-}$ and [Ru(OEP)(aryl)$_2]^{0/+}$ couples is 2.09–2.23 V, which is consistent with an OEP$^{0/-}$–OEP$^{0/+}$ pair. However, the data in Figure 6B,C show no couple within 0.5 V of the [Ru(OEP)(aryl)$_2]^{0/+}$ couple, as would be expected for a OEP$^{0/+}$ couple (and the EPR results suggest that the reduction is metal-localized). On the basis of these simple $E_{1/2}$ difference criteria, the data are inconsistent with all the couples being porphyrin-localized—at least one of the Ru(OEP)(aryl)$_2$ couples has to be metal-centered. The electrochemical data provide no compelling evidence for porphyrin-localized redox reactions.

Complexes like Zn(OEP) and Mg(OEP), which obviously involve porphyrin-localized redox reactions, exhibit distinctive OEP$^{•+}$ or OEP$^{•-}$ UV–vis spectral features upon oxidation or reduction.[14] Using these spectroscopic features to indicate ligand-localized reactions in other complexes must be viewed with some caution, since, in certain cases, such as with reduced Rh(Por)(R) complexes,[2g] the features are not pronounced. The [Ru(OEP)(p-$XC_6H_4)_2]^+$ species are too short-lived to observe spectroscopically, and the [Ru(OEP)(p-$XC_6H_4)_2]^{2-}$ samples are too impure to be confident of the shape and magnitude of the spectral features. Of the remaining [Ru(OEP)(p-$XC_6H_4)_n]^{+/0/-}$ complexes, only the [Ru(OEP)(p-XC_6H_4)]$^+$ species exhibit characteristic bands above 650 nm. These OEP$^{•+}$ bands occur between 760 and 850 nm with log ϵ ~ 3.3–4.

EPR spectroscopy often provides a clear distinction between porphyrin- and metal-localized radicals.[14] The diamagnetic [Ru(OEP)(C_6H_5)]$^-$ complex shows no EPR signal, while the paramagnetic [Ru(OEP)(C_6H_5)] complex shows a signal at 3.11 kG with g = 2.102 and Δ_{peak} = 150 G, characteristic of a Ru^{III} species. The spectrum of [Ru(OEP)(C_6H_5)]$^+$ reveals a very weak (<10% the expected magnitude[18]) Por$^{•+}$ signal. Either a small amount of impurity is giving rise to a signal or there is a mixed electronic character with majority Ru^{IV} and minority Por$^{•+}$; given the UV–vis results described above, the latter is more likely. The diamagnetic Ru(OEP)($C_6H_5)_2$ and [Ru(OEP)($C_6H_5)_2]^{2-}$ complexes show no EPR signals, while the [Ru(OEP)($C_6H_5)_2]^-$ complex shows a signal at 3.09 kG with g = 2.115 and Δ_{peak} = 160 G, characteristic of a Ru^{III} species. Clearly, the [Ru(OEP)($C_6H_5)_2]^{0/-}$ couple is a Ru$^{IV/III}$ couple. The EPR spectra of the p-F and p-OCH_3 analogues show similar characteristics, indicating the same electronic properties throughout the [Ru(OEP)(p-$XC_6H_4)_2]^-$ series. Although it is not part of a primary redox reaction, the [Ru(OEP-N-C_6H_5)(C_6H_5)]$^+$ complex exhibits a characteristic OEP$^{•+}$ signal at 3.24 kG with g = 2.010 and Δ_{peak} = 10 G, clearly demonstrating the existence of OEP$^{•+}$ species. As with the UV–vis spectroscopic results, the EPR spectroscopic evidence for prophyrin-localized nature exists only for the [Ru(OEP)(p-XC_6H_4)]$^{0/+}$ couple.

One final set of observations is important to consider. The reduced solutions of Ru(OEP)(p-$XC_6H_4)_2$ contain Ru(OEP)(p-$XC_6H_4)_2$, [Ru(OEP)(p-$XC_6H_4)_2]^-$, [Ru(OEP)(p-$XC_6H_4)_2]^{2-}$, and [Ru(OEP)(p-XC_6H_4)]$^-$, with the proportions depending upon the relative amount of reductant and the identity of X. However, the reduction of Ru(OEP)(p-$ClC_6H_4)_2$ yields Ru(OEP)(p-$ClC_6H_4)_2$, [Ru(OEP)(p-$ClC_6H_4)_2]^-$, and an "unidentified" paramagnetic component that can account for up to 60% of the solution. If this is the [Ru(OEP)(p-$XC_6H_4)_2]^{2-}$ species, it exhibits a ^{1}H NMR spectrum distinctly different from those of the other diamagnetic dianions. Further, reduction of Ru(OEP)(p-ClC_6H_4) yields [Ru(OEP)(p-ClC_6H_4)]$^-$ as expected, but the o- and m-H ^{1}H NMR resonances are quite broad (70 and 120 Hz, respectively). Partial electron residence on the p-ClC_6H_4 ligand would result in such broad resonances via electron–proton dipolar coupling. Assignment of the site of reduction to the axially-bound ligand rather than simply the porphyrin or the metal has been made for [Co(TPP)(p-$(NO_2)C_6H_4$)]$^-$,[1b] so such an assignment with our complex is not unreasonable. (It should be noted that reduced Ar–Cl species are known[19] to lose Cl$^-$. However, if this were to occur in our case, we would make the familiar C_6H_5 species, not the unknown species observed here.) Both of these unusual observations with the reduced X = Cl species must be viewed with some concern, since they may indicate that the site of reduction for the X = Cl species is different from that of the other complexes. This could have significant effects on the reactivity of the reduced species described below.

Combining these three physical measurements, we are in the position to say that the only convincing evidence for the presence of porphyrin-localized redox processes exists for the [Ru-

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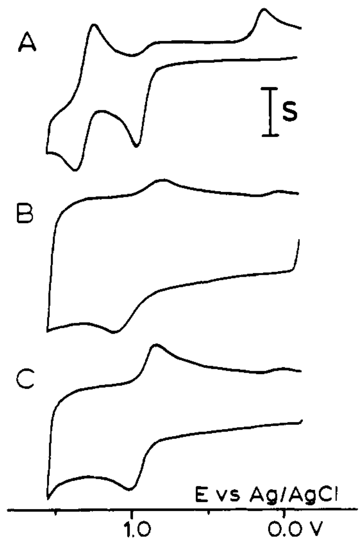


Figure 3. Cyclic voltammetric response of Ru(OEP)(p-FC$_6$H$_4$)$_2$ in 0.2 M Bu$_4$NClO$_4$/THF: (A) T = 21 °C, v = 87.5 V/s, S = 9.8 mA/cm^2; (B) T = 21 °C, v = 8750 V/s, S = 0.13 A/cm^2; (C) T = –41 °C, v = 87.5 V/s, S = 3.9 mA/cm^2.

(OEP)(p-XC$_6$H$_4$)]$^{0/+}$ couple. The [Ru(OEP)(p-XC$_6$H$_4$)$_2$]$^{0/-}$ couple is certainly a Ru$^{\text{III/IV}}$ couple on the basis of EPR measurements and ancillary measurements. A metal-centered (Ru$^{\text{II/III}}$) reaction is implicated in the [Ru(OEP)(p-XC$_6$H$_4$)$_2$]$^{-/2-}$ and [Ru(OEP)(p-XC$_6$H$_4$)]$^{0/-}$ couples on the basis of the diamagnetism of the reduced species. The nature of the [Ru(OEP)(p-XC$_6$H$_4$)$_2$]$^{0/+}$ couple is uncertain, since we have only electrochemical data involving an ephemeral species that could support either metal-centered ($E_{1/2}$ shifts in Figure 2) or porphyrin-centered reactions (2.3-V separation). (If the 2.3-V separation is used to assert porphyrin-centered reactions, then the [Ru(OEP)(p-XC$_6$H$_4$)$_2$]$^{-/2-}$ couple must also be so designated, despite the lack of an EPR signal for [Ru(OEP)(p-XC$_6$H$_4$)$_2$]$^{2-}$.) At this point, we are satisfied that, with the possible exception of the reduced X = Cl species, the nature of the electron-transfer reactions is sufficiently constant throughout the p-XC$_6$H$_4$ series that we can interpret the kinetic results without considering a dramatic change in the nature of the reactants or products.

Stability of [Ru(OEP)(p-XC$_6$H$_4$)$_2$]$^+$ Complexes. The rate constant for the Ru-to-N migration step (k_1) can be calculated from relative peak currents of the [Ru(OEP)(aryl)$_2$]$^{0/+}$ waves. Figure 3 illustrates the voltammetric response of Ru(OEP)(p-FC$_6$H$_4$)$_2$ at different scan rates (v = 87.5 and 8750 V/s). Conversion of the relative peak currents into rate constants leads to k_1 = 6000–12 000 s^{-1} over the range of scan rates from 2000 to 10 000 V/s. This factor of 2 range of rate constants over a factor of 5 in scan rate, typical of the results obtained for the [Ru(OEP)(aryl)$_2$]$^+$ species, likely[13] reflects slight inaccuracies in assessment of the scan rate dependent baseline. Assessing the baseline is difficult, particularly with the [Ru(OEP)(aryl)$_2$]$^{0/+}$ couples, since the foot of the [Ru(OEP-N-aryl)(aryl)]$^{+/2+}$ wave interferes with the tail of the [Ru(OEP)(aryl)$_2$]$^{0/+}$ wave. Nonetheless, k_1 values for the various [Ru(OEP)(aryl)$_2$]$^+$ reactions have been measured; a complete listing is available in the supplementary material.

The Ru-to-N migration step can be "frozen out" by lowering the temperature, as illustrated in Figure 3 for X = F. The measured k_1 value decreases to 48 (±20) s^{-1} at –41 °C. The variable-temperature data yield a linear Eyring plot, ln (k/T) vs $1/T$, as shown in Figure 4 for X = H. Fitting these data to the Eyring equation[19]

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (1)$$

where k_B is Boltzmann's constant and h is Planck's constant,

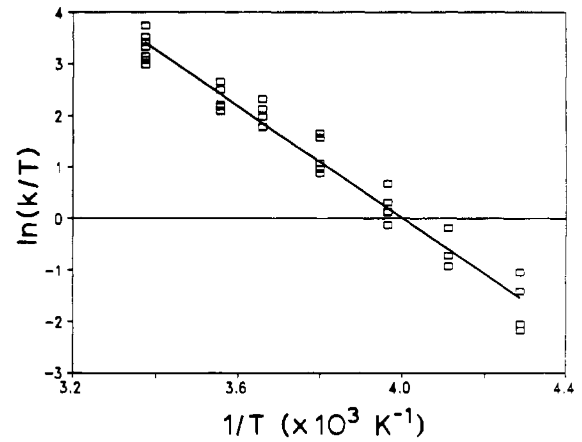


Figure 4. Eyring plot for variable scan rate determination of k_1 for Ru(OEP)(C$_6$H$_5$)$_2$ in 0.2 M Bu$_4$NClO$_4$/THF. Points at each temperature are for various scan rates. The range of scan rates for the highest temperature experiment is 2–10 kV/s, and that for the lowest temperature experiment is 50–200 V/s.

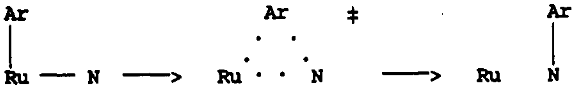
Table III. Activation Parameters for Reactions of [Ru(OEP)(p-XC$_6$H$_4$)$_2$]$^+$ Complexes

X	ΔH^*, kcal/mol	ΔS^*, cal/mol K	T range, K
H	10.8 (±0.4)	–4.0 (±1.4)	233–296
CH$_3$	9.4 (±0.6)	–8.9 (±2.2)	233–293
F	13.9 (±0.6)	4.5 (±2.4)	232–294
OCH$_3$	9.3 (±1.0)	–9.2 (±3.7)	233–294
Cl	10.1 (±0.4)	–8.1 (±1.7)	243–296

yields the activation parameters ΔH^* = 10.8 (±0.4) kcal/mol and ΔS^* = –4.0 (±1.4) cal/(mol·K) for Ru(OEP)(C$_6$H$_5$)$_2$. Voltammetric measurements of k_1 were performed for the series of Ru(OEP)(aryl)$_2$ complexes at several temperatures between –40 and +23 °C with similar degrees of success. Activation parameters thus obtained for the [Ru(OEP)(aryl)$_2$]$^+$ reactions are listed in Table III.

The initial response to these data is the recognition of the trend in ΔH^* of F > H $\gtrsim$ Cl > CH$_3$ $\sim$ OCH$_3$, with values in the range 9–14 kcal/mol. The ΔS^* values show a similar trend, F > H $\gtrsim$ Cl $\gtrsim$ CH$_3$ $\sim$ OCH$_3$, with values in the range +4.5 to –9.2 cal/(mol·K). Closer inspection of these data reveals that the main difference lies with the X = F data: F > H $\gtrsim$ Cl $\sim$ CH$_3$ $\sim$ OCH$_3$. The F data yield $\Delta H^* \simeq$ 14 kcal/mol and $\Delta S^* \simeq$ 4.5 cal/(mol·K); the remaining four complexes possess $\Delta H^* \sim$ 10 kcal/mol and $\Delta S^* \sim$ –8 cal/(mol·K). Even when the slightly different data are recognized, *it thus appears that changes in the nature of the aryl ligand have minimal effect on the reaction energetics of the Ru-to-N migration step.*

The magnitude and sign of ΔH^* and ΔS^* warrant some comment. The ΔH^* values are "typical" values for room temperature, condensed-phase reactions;[19] little insight into the reaction mechanism is available from the ΔH^* values. Except for the case where X = F, the ΔS^* values are explicable—the transition state should be slightly more ordered than the reactant (or product)



$$\overset{\text{Ar}}{\underset{\text{Ru}}{|}}\text{—N} \longrightarrow \left[\text{Ru}\cdots\overset{\text{Ar}}{\cdot\cdot}\cdots\text{N}\right]^{\ddagger} \longrightarrow \text{Ru} \quad \overset{\text{Ar}}{\underset{\text{N}}{|}} \quad (2)$$

so a small, negative ΔS^* is expected. The X = F value, +4.5 cal/(mol·K), is quite surprising, since it would imply a *dissociative* component of the transition state. Certainly from a statistical standpoint, the ΔS^* value for X = F is different from those for the others. However, whether a value of +4.5 vs –9 cal/(mol·K) has any chemical significance is questionable. Further, the situation of –10 < ΔS^* < 10 cal/(mol·K) must be interpreted with care,[19] since solvent (and ionic) effects may dominate such small, measured ΔS^* values.

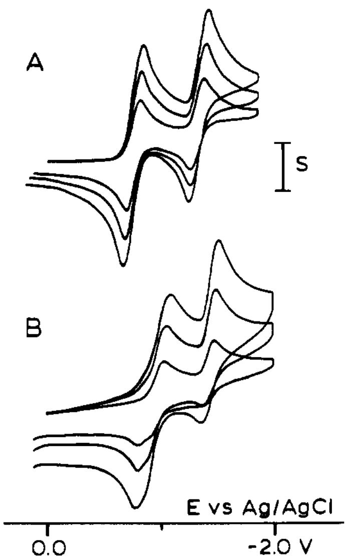


Figure 5. Cyclic voltammetric response of $\mathrm{Ru(OEP)}(p\text{-}\mathrm{FC_6H_4})_2$ (A) and $\mathrm{Ru(OEP)}(p\text{-}\mathrm{(CH_3)C_6H_4})_2$ (B) in 0.2 M $\mathrm{Bu_4NClO_4}$/THF at 23 °C. v = 100, 50, 20 mV/s in (A) and 500, 200, 50 mV/s in (B); S = 50 μA/cm^2 in (A) and 62.6 μA/cm^2 in (B).

Table IV. Rate Constants and Hammett Parameters[a] for Reactions of $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})_2]^{2-}$ Complexes

X	k, s^{-1}	σ_p	σ_I	$\sigma_R°$
H	0.22	0	0	0
$\mathrm{CH_3}$	0.43	−0.14	−0.05	−0.13
F	0.02	0.15	0.50	−0.31
$\mathrm{OCH_3}$	0.05	−0.28	0.27	−0.44
Cl	≤ 0.0001	0.24	0.46	−0.18

[a] Values obtained from ref 16.

Stability of $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})_2]^{2-}$ Complexes. The rate constant for the aryl$^-$ loss (k_3) can be calculated from relative peak currents of the $[\mathrm{Ru(OEP)(aryl)_2}]^{-/2-}$ waves. Figure 5 illustrates the voltammetric response of $\mathrm{Ru(OEP)}(p\text{-}\mathrm{FC_6H_4})_2$ and $\mathrm{Ru(OEP)}(p\text{-}\mathrm{CH_3C_6H_4})_2$ at varying scan rates. Conversion of the peak currents into rate constants for the reaction

$$[\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})_2]^{2-} \xrightarrow{k_3} [\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})]^- \qquad (3)$$

for these and other $\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})_2$ complexes yields the k_3 values listed in Table IV. Note the lack of an immediately apparent dependence of k_3 on the nature of the X group. This is reflected in the Hammett plot of these data shown in Figure 6A, which possesses an unusual curved shape.

Replotting the data as a function of σ_R, which accounts for the resonance effects of the p-$\mathrm{XC_6H_4}$ group, reveals no correlation. However, using σ_I, which accounts for the inductive effects of the p-$\mathrm{XC_6H_4}$ group, yields a linear plot for all substituents except X = Cl (Figure 6B). (We discuss below our reservations with the X = Cl data.) Even considering all the data, there is a rough correlation—*electron-withdrawing X groups stabilize the highly reduced* $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})_2]^{2-}$ *complexes.* This rough correlation is also consistent with the electrochemical and spectroscopic results discussed above, which argued against a change in the mechanism or different electron location (metal vs porphyrin) in the reduced complexes as the reason for the curved σ_p plot in Figure 6A.

The kinetic results in Table IV suggest that $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{FC_6H_4})_2]^{2-}$ and $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{(OCH_3)C_6H_4})_2]^{2-}$ complexes should decompose too quickly to isolate them at any reasonable level. Surprisingly, NaNaph reduction of the $\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})_2$ complexes results in stable $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})_2]^{2-}$ complexes whose NMR, EPR, and UV–vis spectroscopic properties are described above. This apparent difference in chemical and electrochemical results is due to a pronounced salt effect. Addition of $\mathrm{Bu_4NClO_4}$ to the NMR sample leads to rapid decomposition of the $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})_2]^{2-}$ complexes. The magnitude of this salt effect is ca. 10^4 for 0.2 M $\mathrm{Bu_4NClO_4}$ with X = $\mathrm{CH_3O}$ on the basis of ^{1}H NMR spectroscopy (k_{obs} = 4.7 (±0.1) × 10^{-6} s^{-1} with no salt in THF-d_8).

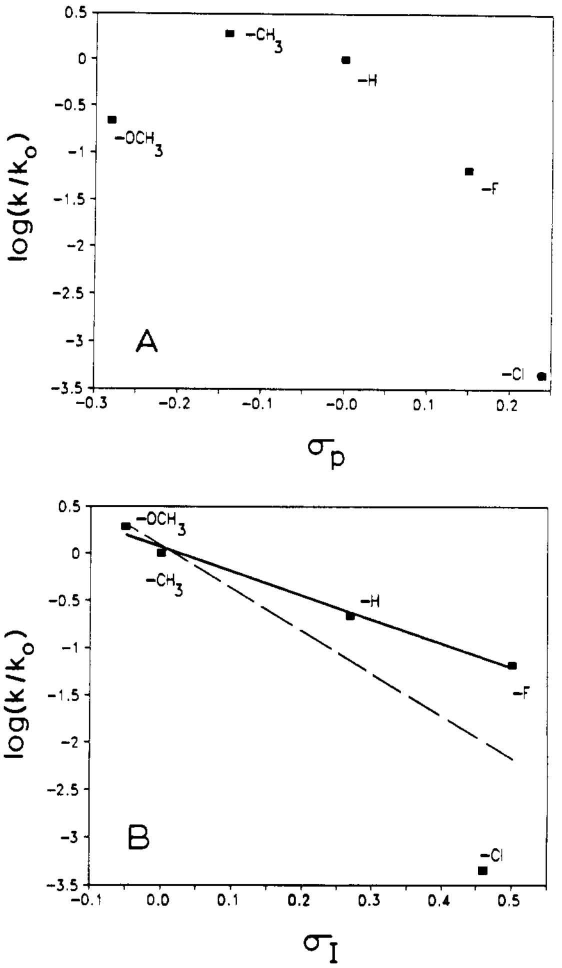


Figure 6. Hammett plots for the $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{XC_6H_4})_2]^{2-}$ reactions in 0.2 M $\mathrm{Bu_4NClO_4}$/THF at 23 °C (k_3 values determined from the relative peak currents): (A) ln (k/k_0) vs σ_p; (B) ln (k/k_0) vs σ_I (solid line is least-squares fit ignoring X = Cl; dashed line includes X = Cl).

The kinetic results also suggest that $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{ClC_6H_4})_2]^{2-}$ should be isolable in a reasonably pure form; however, NaNaph reduction of $\mathrm{Ru(OEP)}(p\text{-}\mathrm{ClC_6H_4})_2$ leads to $[\mathrm{Ru(OEP)}(p\text{-}\mathrm{ClC_6H_4})]^-$. The decomposition reaction of the chemically-reduced material proceeds rapidly both with and without added $\mathrm{Bu_4NClO_4}$. This puzzling difference between electrochemical and chemical reductions is not readily explained. Perhaps the reducing strength of NaNaph ($E°$ ≈ −2.55 V[20]) is sufficient to access a more reactive, reduced form of the $\mathrm{Ru(OEP)}(p\text{-}\mathrm{ClC_6H_4})_2$ complex, so that chemical and electrochemical reductions are not entirely analogous. An alternative source of this kinetic difference could be traced to the tendency[19] of reduced Ar–Cl species to lose Cl$^-$. We are hestitant to suggest this as an explanation, since Cl$^-$ loss subsequent to metal–ligand bond heterolysis would increase, not decrease, the observed rate. This difference in reactivity is not the only unusual feature of X = Cl compounds; recall the discussion above of the unusual spectro-

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scopic features of [Ru(OEP)(p-ClC$_6$H$_4$)]$^-$ and the purported [Ru(OEP)(p-ClC$_6$H$_4$)$_2$]$^{2-}$ species. We suspect that reduced X = Cl species differ from the other compounds, likely involving reduction of the axial ligand. In any event, we view the "anamolously low" k_3 for X = Cl in Table IV with some skepticism. As mentioned above, the trend of k_3 with σ_I is the same, in fact with much better correlation, when the X = Cl result is ignored.

Conclusions. A direct comparison between these Ru(OEP)(p-XC$_6$H$_4$)$_n$ complexes and other M(Por)(aryl)$_n$ complexes is somewhat difficult at this point, especially for the Ru(OEP)(p-XC$_6$H$_4$)$_2$ complexes. Bis(aryl) complexes have been reported only for Os and the group 14 metalloids (Si and Ge); neither of these have been studied in sufficient detail to make a meaningful comparison. A comparison with Os(OEP)(p-XC$_6$H$_4$)$_2$ complexes would be interesting, since stable [Os(OEP)(p-XC$_6$H$_4$)$_2$]$^+$ complexes, or at least slower N-arylation, might be observed. The Si and Ge complexes[1b] exhibit a reversible porphyrin-localized reduction (and a second for TPP complexes) and an irreversible porphyrin-localized oxidation, which quickly leads to M(Por)-R$^+$. The electrochemical and spectroscopic results for the Ru(OEP)(p-XC$_6$H$_4$)$_2$ complexes suggest that the redox reactions are metal-centered and yield stable monoanions and reactive cations and dianions.

The M(Por)(aryl) complexes are far more numerous, so a comparison is possible. The electrochemical and spectroscopic results for the Ru(OEP)(p-XC$_6$H$_4$) complexes suggest that the metal-centered reduction and porphyrin-centered oxidation yield stable ionic species. The oxidized complexes do not N-arylate as do the Fe and Co species.[1b] The reduced complexes do not lose the axial ligand as do Co, Ir, Rh (under certain conditions) and Fe species (for fluorinated aryls).[1b] Overall, the Ru complexes provide greater stability than other transition metal congeners.

Acknowledgment. We thank the W. R. Grace Co. for fellowship support (to J.W.S.) and Prof. M. J. Weaver for access to the microelectrode voltammetry equipment. The advice of Prof. W. E. Geiger on cyclic voltammetric data analysis and that of W. R. Scheidt on EPR data analysis were invaluable. NMR experiments were performed on instruments supported by NIH Grant RR01077 and NSF Grant BBS-8714258.

Supplementary Material Available: Tables of rate constants as a function of scan rate and temperature for the N-arylation step and spectroscopic parameters for various ionic Ru(OEP)(p-XC$_6$H$_4$) complexes (9 pages). Ordering information is given on any current masthead page.