Inorg. Chem. **1990**, *29*, 3636-3641

Articles

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Redox and Reaction Chemistry of Ru(OEP)-Phenyl Complexes

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Received May 3, 1990

Cyclic voltammetry of Ru(OEP)(C_6H_5)$_2$ and Ru(OEP)(C_6H_5) (OEP = octaethylporphyrin dianion) reveals diverse redox and accompanying chemical reactions. Chemical oxidations and reductions of the neutral complexes yield several isolable products, including the N-arylated [Ru(OEP-*N*-C_6H_5)(C_6H_5)]$^+$ complex. The [Ru(OEP)(C_6H_5)$_n$]$^{+/0/-}$ complexes have been characterized by electrochemical and spectroscopic methods (^{1}H and ^{2}H NMR and UV-vis). The diamagnetic Ru(OEP)(C_6H_5)$_2$ complex can be reduced to the paramagnetic [Ru(OEP)(C_6H_5)$_2$]$^-$ complex; the reduction appears to be porphyrin-localized. Further reduction to [Ru(OEP)(C_6H_5)$_2$]$^{2-}$ results in the rapid ($t_{1/2} \sim 3$ s) loss of $C_6H_5^-$ to form the diamagnetic [Ru(OEP)(C_6H_5)]$^-$ complex. Oxidation of Ru(OEP)(C_6H_5)$_2$ results in rapid (<10 μs) Ru-to-N migration of a C_6H_5 group to form the paramagnetic [Ru(OEP-*N*-C_6H_5)(C_6H_5)]$^+$ complex; N-arylation is reversed upon reduction. The paramagnetic Ru(OEP)(C_6H_5) complex is reduced to [Ru(OEP)(C_6H_5)]$^-$. Unlike with the corresponding Fe complexes, oxidation of Ru(OEP)(C_6H_5) does not result in N-arylation; a stable, paramagnetic cation is produced. Electron-self-exchange reactions for [Ru(OEP)(C_6H_5)]$^{0/+}$, [Ru(OEP)(C_6H_5)]$^{0/-}$, and [Ru(OEP)(C_6H_5)$_2$]$^{0/-}$ are rapid ($k_{ex} \sim 10^8$, 10^7, and 10^4 M^{-1} s^{-1}, respectively), as revealed by ^{1}H NMR spectroscopy. A reaction scheme based on these observations and a comparison to analogous metalloporphyrin complexes are presented.

Introduction

Organometallic porphyrin complexes[1] comprise an interesting class of bioinorganic complexes. Although the presence of a metal-carbon bond in vitamin B_{12} has been recognized[2] for years, related organometallic complexes until recently have comprised a disproportionately low fraction of metalloporphyrin complexes. The implication of metal-carbon- and N-carbon-bonded species[3] in reactions of cytochrome P-450 (cyt P-450) has prompted recent studies of the synthesis,[4-6] redox chemistry,[7-10] and reaction chemistry[11,12] of various alkyl and aryl metalloporphyrin complexes. The early work[1,13] with Fe and Co complexes has been extended to iron, ruthenium, osmium, rhodium, iridium, and related metals.[1,7-12] Although the synthetic routes to these complexes differ according to the metal and the number of metal-carbon bonds, the use of electrophilic and nucleophilic metal centers predominates. The organometallic complexes, particularly bis(alkyl),[5c,11] bis(aryl),[5c] and sterically unencumbered carbenes,[4,5c] can be quite reactive.

This wealth of synthetic and reaction chemistry is accompanied by interesting redox chemistry. The extensive studies by Kadish,[7] Lexa and Saveant,[8] and others[9,10] of the coupled redox and reaction properties of organometallic porphyrins have revealed a remarkable diversity of chemistry. These complexes can be reduced and oxidized to complexes with interesting spectroscopic and electronic properties. Often the oxidations are accompanied by metal-to-N migration of the alkyl or aryl group. The structure and reactivity of the N-alkylated (or N-arylated) porphyrin species are of interest because of their importance in cyt P-450 reactions.[3] Absent from the redox studies have been those of the Ru congeners, primarily due to the lack of versatile and convenient synthetic routes. The recent, independent reports by Collman[4] and James and Dolphin[5] on the synthesis of Ru alkyl and aryl complexes provide a new class of organometallic porphyrins. Although reports[4,5c,11] of reaction chemistry have appeared, the redox chemistry remains largely unexplored.

Our recent, preliminary report[9] of the redox pathways of Ru(OEP)(C_6H_5) and Ru(OEP)(C_6H_5)$_2$ demonstrated that the ruthenium organometallic porphyrins offer a wealth of chemistry. We report herein a detailed study of the redox and associated chemical reactions of the Ru(OEP)(C_6H_5)$_n$ complexes. Electrochemical and chemical studies of these complexes reveal that a variety of redox and reaction pathways are available. We have isolated and characterized spectroscopically (^{1}H and ^{2}H NMR and UV-vis) several of these species, including the [Ru(OEP-*N*-

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(1) Collman, J. P.; Brothers, P. J. *Acc. Chem. Res.* **1986**, *19*, 209 and references therein.

(2) Halpern, J. *Science* **1985**, *227*, 869.

(3) Lavallee, D. K. *The Chemistry and Biochemistry of N-substituted Porphyrins*; VCH: New York, 1987.

(4) (a) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570. (b) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E. *J. Am. Chem. Soc.* **1985**, *107*, 6110.

(5) (a) Sishta, C.; Ke, M.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 787. (b) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1137. (c) Ke, M.; Rettig, S. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1110.

(6) (a) Reed, C. A.; Mashiko, T.; Bently, S. P.; Kestner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948. (b) Baltioni, J.-P.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1982**, 638. (c) Clarke, D. A.; Dolphin, D.; Grigg, R.; Johnson, A. W.; Pinnock, H. A. *J. Chem. Soc.* **1968**, 881. (d) Battioni, J.-P.; Lexa, D.; Mansuy, D.; Saveant, J.-M. *J. Am. Chem. Soc.* **1983**, *105*, 207. (e) Cocolios, P.; Lagrange, G.; Guilard, R. *J. Organomet. Chem.* **1983**, *253*, 65.

(7) (a) Guilard, R.; Lecomte, C.; Kadish, K. M. *Struct. Bonding* **1987**, *64*, 205 and references therein. (b) Lancon, D.; Cocolios, P.; Guilard, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 4472. (c) Kadish, K. M.; Yao, C.; Anderson, J. E.; Cocolios, P. *Inorg. Chem.* **1985**, *24*, 4515. (d) Kadish, K. M.; Cornillon, J.-L.; Mitaine, P.; Deng, Y. J.; Korp, J. D. *Inorg. Chem.* **1989**, *28*, 2534.

(8) (a) Lexa, D.; Mispelter, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6806. (b) Lexa, D.; Saveant, J.-M. *J. Am. Chem. Soc.* **1982**, *104*, 3503. (c) Gueutin, C.; Lexa, D.; Momenteau, M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 1874. (d) Lexa, D.; Saveant, J.-M.; Battioni, J.-P.; Lange, M.; Mansuy, D. *Angew. Chem.* **1981**, *93*, 585.

(9) Seyler, J. W.; Leidner, C. R. *J. Chem. Soc., Chem. Commun.* **1989**, 794.

(10) (a) Perree-Fauvet, M.; Gaudemer, A.; Boudy, P.; Devynck, J. *J. Organomet. Chem.* **1976**, *120*, 439. (b) Kuila, D.; Kopelove, A. B.; Lavallee, D. K. *Inorg. Chem.* **1985**, *24*, 1443.

(11) Collman, J. P.; McElwee-White, L.; Brothers, P. J.; Rose, E. *J. Am. Chem. Soc.* **1986**, *108*, 1332.

(12) (a) Cocolios, P.; Lagrange, G.; Guilard, R. *J. Organomet. Chem.* **1982**, *228*, C39. (b) Battioni, J.-P.; Mahy, J. P.; Gillet, G.; Mansuy, D. *J. Am. Chem. Soc.* **1983**, *105*, 1399. (c) Arasasingham, R. D.; Balch, A. L.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **1987**, *109*, 5846. (d) Arasasingham, R. D.; Balch, A. L.; Cornman, C. R.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **1989**, *111*, 4357.

(13) (a) Dolphin, D.; Johnson, A. W. *J. Chem. Soc., Chem. Commun.* **1965**, 494. (b) Clarke, D. A.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Chem. Commun.* **1966**, 208. (c) Clarke, D. A.; Dolphin, D.; Grigg, R.; Johnson, A. W.; Pinnock, H. A. *J. Chem. Soc. C* **1968**, 881.

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Table I. Spectroscopic Data for $[Ru(OEP)(C_6H_5)_n]^{+/0/-}$ Complexes

	NMR[a] δ, ppm				
Ru(OEP) complex	CH_3	CH_2	H (meso)	$(Ru)C_6H_5$	UV–vis[b] λ_{max}, nm (ϵ_{rel})
$(C_6H_5)_2$	1.73	3.68	9.92	5.02, 4.82, 1.17	346 (0.71), 380 (1.00), 516 (0.32)
$[(C_6H_5)_2]^-$		(8.5, 5.5)[c]			
$[(C_6H_5)(N\text{-}C_6H_5)]^+$	−0.91, −0.43, 2.28, 3.39	−1.25, 1.34,[d] 4.91, 7.47, 12.01, 13.96, 28.9	−12.30, −1.00	48.88, 45.0, 10.47, 8.48, −106.8, −130.8	406 (1.00), 518 (0.16), 594 (0.11)
$(C_6H_5)(THF)$[e]	−1.23	13.44, 5.80	0.35	49.9, −47.5, −81.8	361 (0.65), 391 (1.00), 510 (0.22)
$[C_6H_5]^-$	1.83	3.70	8.96	4.98, 4.76, 2.61	307 (0.40), 390 (1.00), 460 sh, 485 sh, 516 (0.34), 602 (0.05)
$[(C_6H_5)(THF)]^+$[f]	7.61	85.9, 56.8	28.1	72.8, −186.4, −208.7	388 (1.00), 498 (0.12), 513 (0.12), ~780 (0.01)

[a] NMR spectra obtained in C_6D_6, except for those of cationic species in CD_2Cl_2. [b] Absorbance maxima and relative extinction coefficients. [c] Extremely broad (ca. 300 Hz) resonances; no assignments possible. [d] 4 H. [e] Coordinated THF observed at 4.41 and 11.42 ppm. [f] Coordinated THF observed at 19.6 and −5.9 ppm.

$C_6H_5)(C_6H_5)]^+$ complex.[14] The ^1H NMR spectra of mixtures of $[Ru(OEP)(C_6H_5)]^{0/+}$, $[Ru(OEP)(C_6H_5)]^{0/-}$, and $[Ru(OEP)(C_6H_5)_2]^{0/-}$ reveal facile electron exchange. A reaction scheme based on these observations and a comparison to analogous metalloporphyrin complexes are presented.

Experimental Section

All manipulations were performed in a Vacuum Atmospheres inert-atmosphere box with an oxygen level less than 2 ppm (Model AO-316-C oxygen analyzer) or on a Schlenk line. 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. Bu_4NClO_4 was prepared and purified by literature methods.[15] Sodium naphthalenide was prepared by stirring a THF solution of naphthalene (sublimed) over sodium. C_6H_5Li was prepared by metathesis of C_6H_5Br with *n*-BuLi (Alfa). $AgBF_4$ (Aldrich) was used as received.

Ru Porphyrin Complexes. $Ru(OEP)(C_6H_5)_2$ and $Ru(OEP)(C_6D_5)_2$ were prepared in ca. 30% yield by the method of James and Dolphin.[5a]

$Ru(OEP)(C_6H_5)(THF)$ was collected from filtrates of $Ru(OEP)(C_6H_5)_2$ syntheses. Removal of the solvent yielded a red solid that was purified on an Al_2O_3 column using 3:1 C_6H_6/hexanes and then 3:1 C_6H_6/hexanes with 2% THF. Typical yield was 50%. $Ru(OEP)(C_6H_5)(THF)$ was also prepared by addition of excess C_6H_5Li/THF to a well-stirred suspension of $[Ru_2(OEP)_2](BF_4)_2$[11] in C_6H_6. Yield based on the ^1H NMR spectrum was 40%; $Ru_2(OEP)_2$, formed from reduction of the dication, comprised the remainder of the reaction mixture.

$[Ru(OEP)(C_6H_5)(THF)](BF_4)$ was prepared by addition of 8.0 mg (0.040 mmol) of $AgBF_4$ (solid or in THF) to a benzene solution of $Ru(OEP)(C_6H_5)(THF)$ (20 mg; 0.025 mmol). After 1 h, the brown precipitate was collected by filtration and then reprecipitated with CH_2Cl_2/hexanes. Typical yield was 80%.

$Na[Ru(OEP)(C_6H_5)_2]$ solutions were prepared by addition of sodium naphthalenide/THF to a well-stirred C_6H_6 solution of $Ru(OEP)(C_6H_5)_2$. The reaction mixture contained $Ru(OEP)(C_6H_5)_2$, $Na[Ru(OEP)(C_6H_5)_2]$, and $Na[Ru(OEP)(C_6H_5)(THF)]$, as evidenced by the ^1H NMR spectrum in C_6D_6. The samples used for ^1H NMR spectra described in the text (Figure 2) were prepared in the corresponding deuterated solvents.

$Na[Ru(OEP)(C_6H_5)(THF)]$ was prepared by addition of excess sodium naphthalenide in THF to a toluene solution of $Ru(OEP)(C_6H_5)(THF)$ (ca. 5 mg) or excess sodium naphthalenide in 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 sodium naphthalenide with C_6H_6. Removal of the solvent afforded the final product in a quantitative yield (^1H NMR).

$[Ru(OEP\text{-}N\text{-}C_6H_5)(C_6H_5)](BF_4)$ was prepared by the addition of excess $AgBF_4$/THF to a toluene solution of $Ru(OEP)(C_6H_5)_2$. After 1 h, the dark precipitate was filtered out and then reprecipitated with CH_2Cl_2/hexanes. The C_6D_5 analogue was prepared and purified in a similar manner. Typical yields were 80%.

Physical 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, GE 300-MHz, Varian 500-MHz, or Varian 600-MHz spectrometer. 2-D COSY experiments were performed on a Varian 600-MHz spectrometer using a standard[16] (τ_1–$\pi/2$–τ_2–$2\pi/3$–acquire) pulse sequence. ^2H NMR experiments were performed on a Varian XR500 spectrometer (76.8 MHz for ^2H) using the lock transmitter and receiver coils.

Electrochemical experiments were performed in 0.2 M Bu_4NClO_4/THF with a Bioanalytical Systems CV1 potentiostat using standard cells and a three-electrode configuration comprising a Teflon-shrouded Pt-disk (A = 0.08 cm^2) working, Pt-wire auxiliary, and Ag/AgCl pseudoreference electrodes. The ferrocene/ferrocenium couple was observed at +0.43 V vs Ag/AgCl under these experimental conditions. 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[17] and mass balance of the sodium naphthalenide reduction of $Ru(OEP)(C_6H_5)_2$.

Results and Discussion

$Ru(OEP)(C_6H_5)_2$ and $Ru(OEP)(C_6H_5)$ Complexes. Synthetic routes to the neutral $Ru(OEP)(C_6H_5)_n$ complexes have been reported by James and Dolphin.[5a,c] $Ru(OEP)(C_6H_5)_2$ is prepared conveniently by reaction[5a] of $Ru(OEP)Cl_2$ with C_6H_5Li/THF; following crystallization and column chromatography, $Ru(OEP)(C_6H_5)_2$ is obtained in ca. 30% yield. We have found that the mother liquor of the crystallization contains a substantial amount of $Ru(OEP)(C_6H_5)$, so the $Ru(OEP)(C_6H_5)_2$ synthesis reaction also provides 50% yield of the monophenyl complex. This route is simpler and cleaner than thermolysis of $Ru(OEP)(C_6H_5)_2$[5c] or reaction of C_6H_5Li/THF with $[Ru_2(OEP)_2](BF_4)_2$.[11] The ^1H NMR spectral data (Table I) of $Ru(OEP)(C_6H_5)$ reveal that THF (used to deliver C_6H_5Li or used in chromatography) is present as an axial ligand. Crystallization of $Ru(OEP)(C_6H_5)(THF)$ from C_6H_6 yields a low-quality single crystal that lacks the axial THF ligand; the crystal structure[18] is identical with that obtained by Dolphin[5c] for $Ru(OEP)(C_6H_5)$. Apparently, in the solid state the axial THF ligand is unnecessary. Although for simplicity we omit the THF ligand in the formula, we expect[5c] the coordinatively unsaturated complex to bind any available ligand in solution. The presence of the THF ligand is ensured in the electrochemical and electron-transfer reactions described below.

The oxidation-state formalism presented by James and Dolphin[5] affords $Ru(OEP)(C_6H_5)_2$, possessing a Ru^{IV} center (d_{xz}^2, d_{yz}^2), and $Ru(OEP)(C_6H_5)$, possessing a Ru^{III} center (low-spin d^5). These assignments account for the observed magnetic properties (see chemical shift data in Table I) of the $Ru(OEP)(C_6H_5)_n$ complexes, so we adopt this formalism for our discussion of redox states.

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(14) Seyler, J. W.; Fanwick, P. E.; Leidner, C. R. *Inorg. Chem.* **1990**, *29*, 2021.

(15) Sawyer, D. T.; Roberts, J. L. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1974.

(16) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: Oxford, 1987.

(17) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(18) Seyler, J. W.; Fanwick, P. E.; Leidner, C. R. Unpublished results.

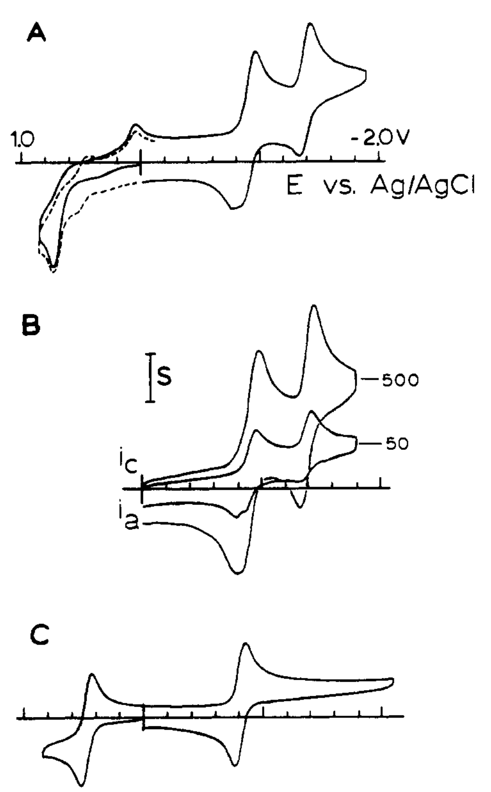


Figure 1. Cyclic voltammetric responses of the $Ru(OEP)(C_6H_5)_n$ complexes in 0.2 M Bu_4ClO_4/THF at a Pt-disk electrode (0.08 cm^2): (A) $Ru(OEP)(C_6H_5)_2$, scan initiated in positive direction from 0 V, S = 5 μA/cm^2, v = 200 mV/s; (B) $Ru(OEP)(C_6H_5)_2$, scan initiated in negative direction from 0 V at 50 and 500 mV/s, as indicated; (C) Ru(OEP)(C_6H_5), scan initiated in positive direction from 0 V, S = 10 μA/cm^2, v = 200 mV/s. (All potentials are vs Ag/AgCl.)

Table II. Electrochemical Data for $Ru(OEP)(C_6H_5)_n$ Complexes[a]

complex	$E°'$, V vs Ag/AgCl
$[Ru(OEP)(C_6H_5)]^{+/0}$	0.48
$[Ru(OEP)(C_6H_5)]^{0/-}$	-0.80
$[Ru(OEP)(C_6H_5)_2]^{+/0}$	0.73 ($E_{p,a}$)
$[Ru(OEP\text{-}N\text{-}C_6H_5)]^{+/0}$	0.04 ($E_{p,c}$)
$[Ru(OEP)(C_6H_5)_2]^{0/-}$	-0.91
$[Ru(OEP)(C_6H_5)_2]^{-/2-}$	-1.38

[a] Electrochemical experiments were performed in 0.2 M Bu_4NClO_4/THF.

Reduction of $Ru(OEP)(C_6H_5)_n$ Complexes. We anticipated rich redox chemistry for the $Ru(OEP)(C_6H_5)_n$ complexes, on the basis of the studies[7,8,10] of related metalloporphyrins. The cyclic voltammetric response of $Ru(OEP)(C_6H_5)_2$ in 0.2 M Bu_4NClO_4/THF at a Pt-disk electrode is shown in Figure 1. A reversible, one-electron reduction ($E°'$ = -0.91 V vs Ag/AgCl) yields $[Ru(OEP)(C_6H_5)_2]^-$. The second reduction ($E°'$ = -1.38 V) is accompanied by decomposition of $[Ru(OEP)(C_6H_5)_2]^{2-}$. The decomposition product is observed at -0.80 and 0.48 V in Figure 1A. Lowering the scan rate (Figure 1B) or holding the potential at -1.8 V before initiating the reverse, positive scan enhances the decomposition. On the basis of an analysis of the scan rate dependence[17] of the anodic and cathodic peak currents, we calculate a rate constant for the decomposition of $[Ru(OEP)(C_6H_5)_2]^{2-}$ of 0.23 s^{-1}. Pertinent electrochemical information is listed in Table II for these and other redox processes.

The reductions observed with cyclic voltammetry can be achieved chemically by using sodium naphthalenide. Addition of excess sodium naphthalenide yields $[Ru(OEP)(C_6H_5)_2]^{2-}$, which rapidly decomposes, as observed in Figure 1. The ^1H NMR spectrum of the isolated decomposition product reveals that it is a diamagnetic monophenyl complex. The results described below indicate that this species is $[Ru(OEP)(C_6H_5)]^-$, resulting from the loss of $C_6H_5^-$ from $[Ru(OEP)(C_6H_5)_2]^{2-}$. These observations are incorporated into Scheme I. Delivering a precise, stoichiometric amount of sodium naphthalenide to a small amount (ca. 10 mg) of $Ru(OEP)(C_6H_5)_2$ in order to achieve complete (single) reduction is not trivial; a small amount of $[Ru(OEP)(C_6H_5)_2]^{2-}$ usually forms and decomposes to $[Ru(OEP)(C_6H_5)]^-$. We have yet to prepare a pure sample of $[Ru(OEP)(C_6H_5)_2]^-$ due to this decomposition. Substoichiometric addition of reductant results in a mixture of $Ru(OEP)(C_6H_5)_2$, $[Ru(OEP)(C_6H_5)_2]^-$, and $[Ru(OEP)(C_6H_5)_2]^-$ that exhibits a ^1H NMR spectrum (Figure 2) containing broadened $Ru(OEP)(C_6H_5)_2$ resonances, sharp $[Ru(OEP)(C_6H_5)]^-$ resonances, and extremely broad resonances

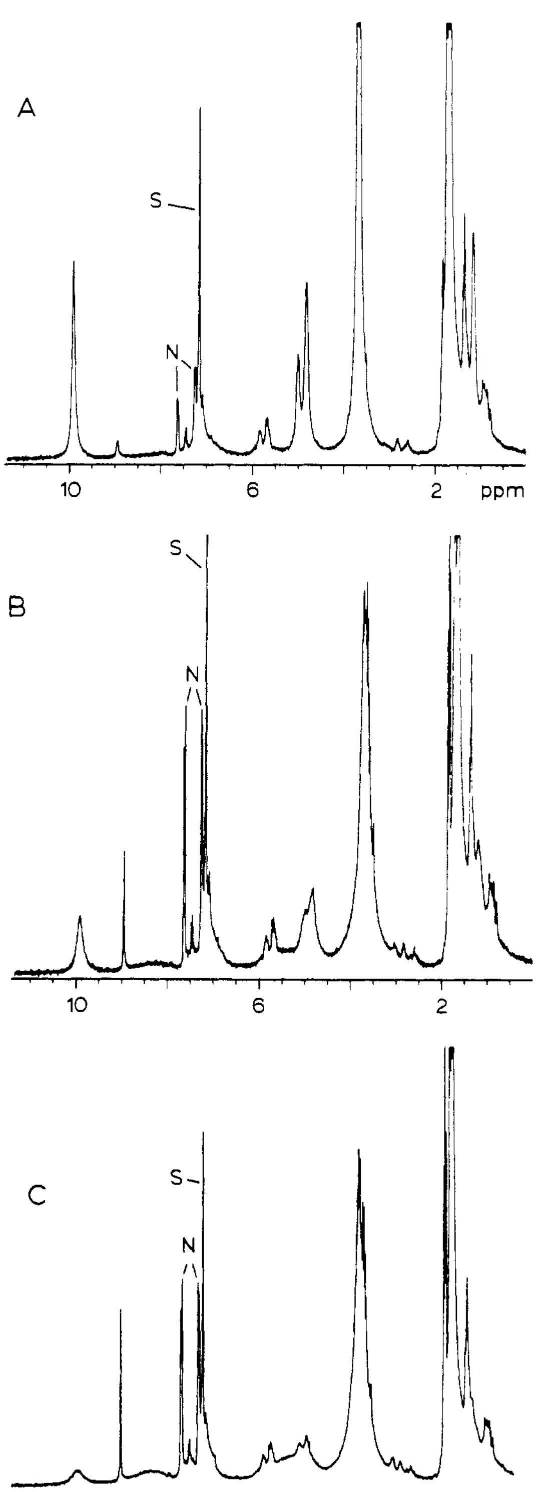


Figure 2. 300-MHz ^1H NMR spectra in C_6D_6 of reduction products of $Ru(OEP)(C_6H_5)_2$ (N signifies naphthalene, and S signifies solvent): (A) 0.25 equiv; (B) 0.6 equiv; (C) 1.0 equiv.

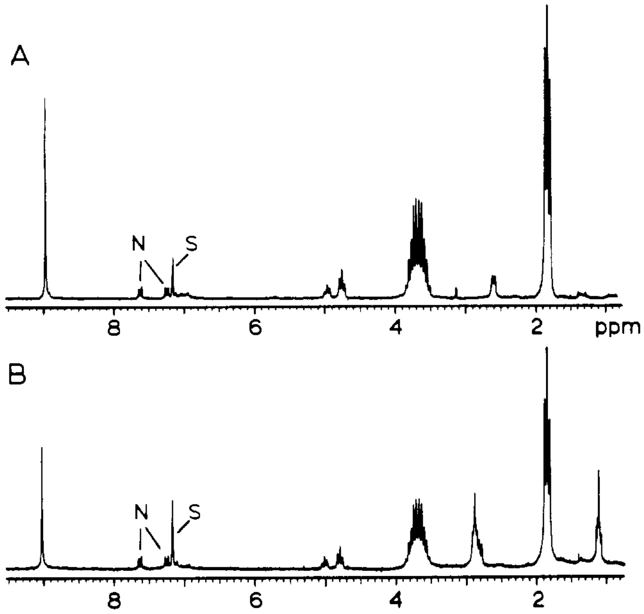
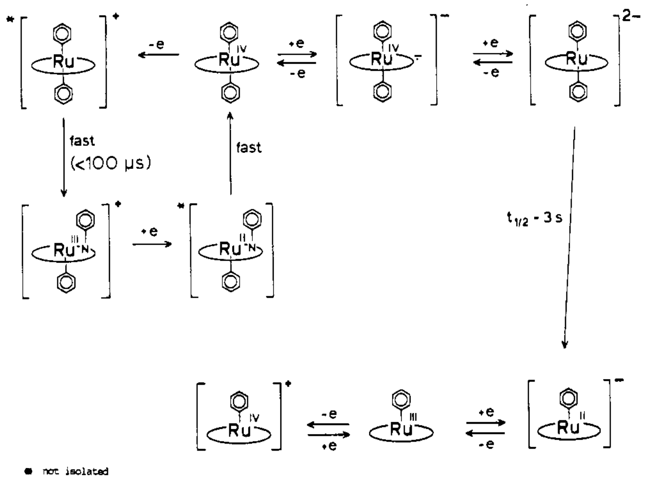


Figure 3. ^{1}H NMR spectra of (A) $[Ru(OEP)(C_6H_5)]^-$ and (B) $[Ru(OEP)(C_6H_5)(THF)]^-$ in C_6D_6 (N signifies remaining naphthalene, and S signifies solvent).

Scheme I



(ca. 300 Hz) barely perceptible beneath the manifold of the other resonances. The extremely broad resonances are due to the paramagnetic $[Ru(OEP)(C_6H_5)]^-$ complex. We are unable to locate accurately or assign unambiguously these resonances; however, their extreme broadness suggests that the reduction is porphyrin-localized. Porphyrin radicals are rarely observed in NMR spectroscopy, due to the extremely rapid spin–spin relaxation from substantial dipole–dipole coupling.[19] The broadening of the remaining $Ru(OEP)(C_6H_5)_2$ resonances, which are not significantly shifted from their normal chemical shifts, indicates a slow electron-transfer exchange between $Ru(OEP)(C_6H_5)_2$ and $[Ru(OEP)(C_6H_5)_2]^-$. This and related electron-exchange reactions are discussed below.

The electrochemistry of $Ru(OEP)(C_6H_5)$ is comparatively simple. The cyclic voltammetric response of $Ru(OEP)(C_6H_5)$, shown in Figure 1C, reveals a one-electron (reduction) couple at −0.8 V and a one-electron (oxidation) couple at +0.48 V that precisely match those of the decomposition product of $[Ru(OEP)(C_6H_5)_2]^{2-}$. The reduction of $Ru(OEP)(C_6H_5)$ by excess sodium naphthalenide yields the diamagnetic $[Ru(OEP)(C_6H_5)]^-$ species. The ^{1}H NMR spectrum in Figure 3B (Table I) and cyclic voltammetric response of this species are identical with those of the decomposition product of $[Ru(OEP)(C_6H_5)_2]^{2-}$. Samples of $[Ru(OEP)(C_6H_5)]^-$, obtained after prolonged pumping of the solid, fail to exhibit a bound THF ligand (Figure 3A); when present, THF (or presumably other ligands[5c]) occupies the sixth coordination site. Since this complex is diamagnetic, we assign it as a Ru^{II} species; the reduction of $Ru(OEP)(C_6H_5)$ is thus metal-centered. As discussed below, mixtures of $Ru(OEP)(C_6H_5)$ and $[Ru(OEP)(C_6H_5)]^-$ exhibit electron-exchange broadening in the ^{1}H NMR spectra.

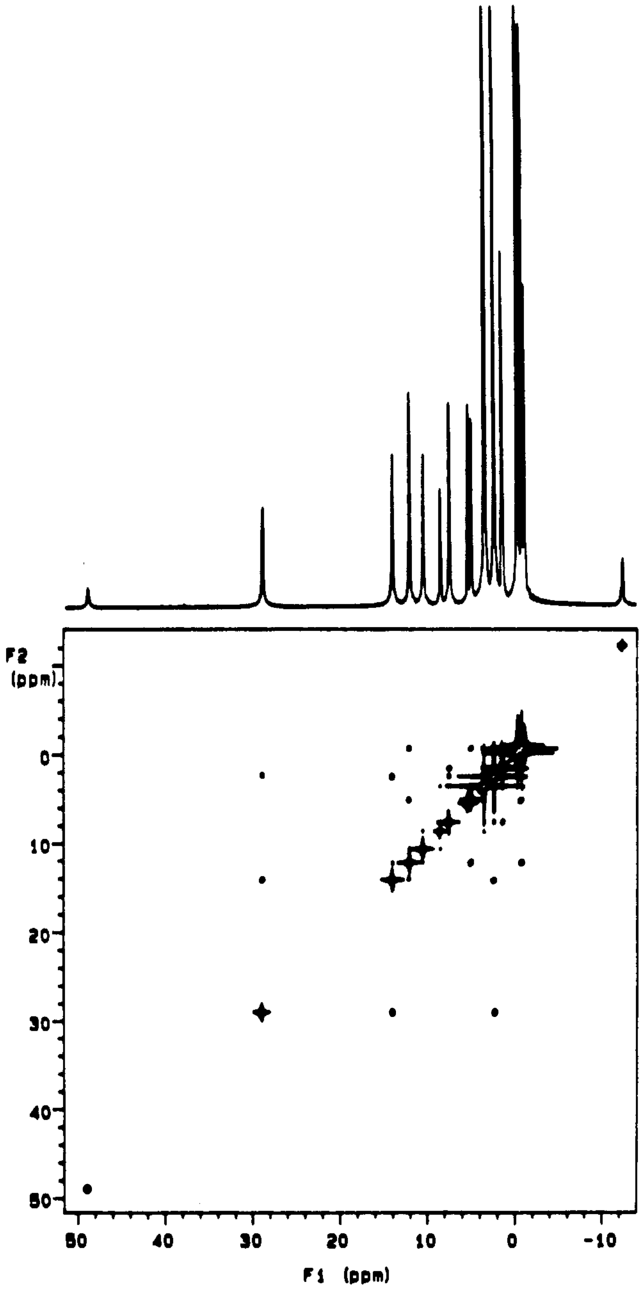


Figure 4. ^{1}H 2-D COSY NMR spectrum of $[Ru(OEP\text{-}N\text{-}C_6H_5)(C_6H_5)](BF_4)$ in CD_2Cl_2. The broad peak at 45.0 ppm is not visible due to the threshold setting in the data-processing method.

Oxidation of $Ru(OEP)(C_6H_5)_n$ Complexes. The cyclic voltammetric response of $Ru(OEP)(C_6H_5)_2$ shown in Figure 1A also reveals an irreversible oxidation ($E_{p,a}$ = +0.73 V and $E_{p,c}$ = +0.04 V). The anodic peak lacks a corresponding return wave at scan rates up to 1000 V/s,[20] indicating that $[Ru(OEP)(C_6H_5)_2]^+$ has a lifetime of less than 10 μs.[17] The cathodic peak at +0.04 V is for the reduction of the reaction product of $[Ru(OEP)(C_6H_5)_2]^+$. Such voltammetric response has been observed for Fe(Por)(R) complexes and has been assigned to a reversible metal-to-N migration of the R ligand.[7] Oxidation of a toluene solution of

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[19] LaMar, G. N.; Horrocks, W. DeW., Jr.; Holm, R. H. *NMR of Paramagnetic Molecules*; Academic: New York, 1973.

[20] Safford, L. K.; Seyler, J. W.; Leidner, C. R. Unpublished results.

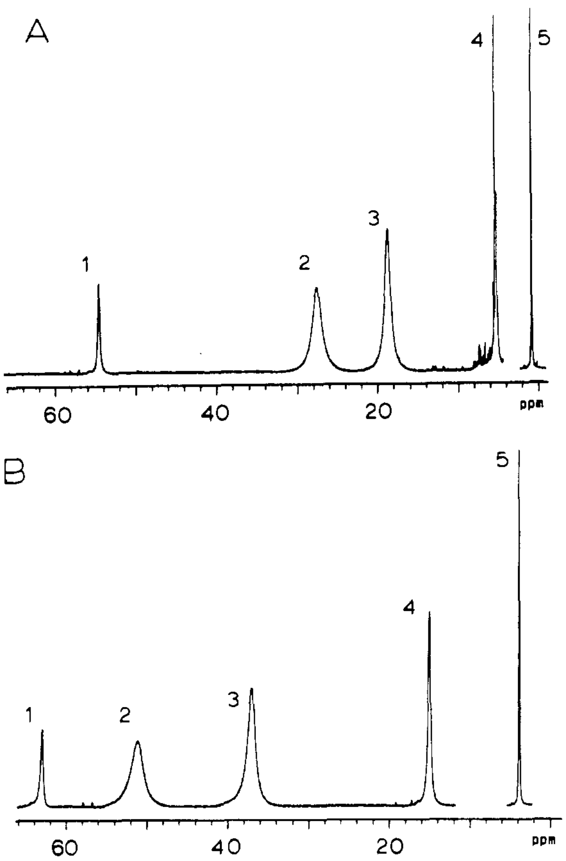

Figure 5. 500-MHz ^1H NMR spectra of solutions (5 mM total concentration) of $Ru(OEP)(C_6H_5)/[Ru(OEP)(C_6H_5)]^+$ in CD_2Cl_2 with 1% THF-d_8: (A) 76% $Ru(OEP)(C_6H_5)$; (B) 39% $Ru(OEP)(C_6H_5)$. Peaks 1–5 are H (meta), CH_2 (β), CH_2 (α), H(meso), and CH_3 peaks, respectively. Isolated solvent (CD_2Cl_2 and THF) peaks are removed for clarity.

$Ru(OEP)(C_6H_5)_2$ with $AgBF_4$ yields a pure solid whose existence as an N-arylated species, $[Ru(OEP\text{-}N\text{-}C_6H_5)(C_6H_5)]^+$, is documented by the recently reported[14] crystal structure. The ^1H NMR spectrum (Figure 4) of this paramagnetic complex indicates that the original 4-fold symmetry of the porphyrin ring has been broken. The paramagnetism of this complex (consistent with Ru^{III}) and the greatly increased number of ^1H NMR peaks make the definitive assignment of this spectrum difficult, so we employed 2-D correlated spectroscopy (2-D COSY). For practical reasons[16] 2-D COSY must be performed with a limited spectral window, so the 2-D COSY spectrum in Figure 4 reveals only the resonances between −10 and 50 ppm. Even with the limited spectral window and the considerable broadening due to paramagnetism, the 2-D COSY spectrum reveals the CH_2CH_3 couplings. The ^1H and ^2H spectra of the C_6D_5 analogue, $[Ru(OEP\text{-}N\text{-}C_6D_5)(C_6D_5)]^+$, locate the aryl proton resonances. With these and the information from the 2-D COSY experiment, we can assign with reasonable confidence the peaks in Figure 4. These assignments are listed in Table I. The cyclic voltammetric response of $[Ru(OEP\text{-}N\text{-}C_6H_5)(C_6H_5)]^+$ reveals couples that match those of $Ru(OEP)(C_6H_5)_2$; the rest potential for the cation solution is far more positive. These data indicate that the N-arylation step is reversed upon generating $Ru(OEP\text{-}N\text{-}C_6H_5)(C_6H_5)$ at +0.040 V. This reversible C_6H_5 migration, shown in Scheme I, is similar to that reported by Kadish[7] for other organometallic porphyrins.

The cyclic voltammetric response of $Ru(OEP)(C_6H_5)$, shown in Figure 1C, is distinctly different. The (oxidation) couple at +0.48 V (Table II) is reversible, with no indication of a coupled chemical reaction. Oxidation of $Ru(OEP)(C_6H_5)$ with $AgBF_4$ yields a stable, paramagnetic cation, $[Ru(OEP)(C_6H_5)]^+$, that does not N-arylate. The observation of an NMR spectrum with reasonable peak positions and line widths rules out formation of a porphyrin cation radical, so we assign $[Ru(OEP)(C_6H_5)]^+$ as a Ru^{IV} species. The observed paramagnetism indicates a coordination environment or symmetry about the Ru^{IV} different from that in $Ru(OEP)(C_6H_5)_2$, which was diamagnetic. The pertinent ^1H NMR spectroscopic data are listed in Table I. The electron-exchange reaction of $[Ru(OEP)(C_6H_5)]^{0/+}$ is discussed below. The stability of the monophenyl cation contrasts that of the bisphenyl cation and those of the related $[Fe(Por)(R)]^+$ species.[7] Since the stability of $[M(Por)(R)]^+$ correlates with the stability of higher oxidation states,[3] the difference between the corresponding Fe and Ru complexes is attributable to the relative inertness[21] of oxidized Ru complexes.

Table III. Electron-Transfer Exchange Rate Constants for $[Ru(OEP)(C_6H_5)]^{0/+}$ (eq 3)

	$10^{-8}k_{ex}$,[a] $M^{-1}\ s^{-1}$			
X_0	H (meso)	CH_2 (α)	CH_2 (β)	CH_3
0.76	1.0	1.4	1.5	0.86
0.39	1.2	1.3	1.4	1.1

[a] Average $k_{ex} = 1.2\ (\pm 0.2) \times 10^8\ M^{-1}\ s^{-1}$.

Electron-Exchange Reactions. The broad and shifted ^1H NMR resonances observed in mixtures of $[Ru(OEP)(C_6H_5)_2]^{0/-}$, $[Ru(OEP)(C_6H_5)]^{0/-}$, and $[Ru(OEP)(C_6H_5)]^{0/+}$ reveal electron-exchange reactions. Figure 5 illustrates this phenomen for the $[Ru(OEP)(C_6H_5)]^{0/+}$ pair in CD_2Cl_2 with 1% THF-d_8. (The THF-d_8 is present to maintain an available and constant axial ligand for the $[Ru(OEP)(C_6H_5)]^{0/+}$ complexes in order to avoid potentially severe, inner-shell perturbations on the electron-transfer reaction.) The 500-MHz ^1H NMR spectra for 76 and 39 mol % $Ru(OEP)(C_6H_5)$ solutions, Figure 5, can be used to calculate a second-order rate constant for the electron-transfer reaction

$$Ru(OEP)(C_6H_5) + [Ru(OEP)(C_6H_5)]^+ \xrightleftharpoons{k_{ex}} [Ru(OEP)(C_6H_5)]^+ + Ru(OEP)(C_6H_5) \quad (1)$$

Using the standard equation[22]

$$k_{ex} = \frac{4\pi X_0 X_+ (\Delta\omega)^2}{(W_{+0} - X_+W_+ - X_0W_0)C_T} \quad (2)$$

where 0 and + signify the two reactants, X is the mole fraction, $\Delta\omega$ is the difference in chemical shifts between the two forms, W is the line width, and C_T is the total concentration, we obtain the replicate k_{ex} values listed in Table III. The CH_3 resonances experience minimal broadening, so the k_{ex} values obtained from them are slightly lower but still agree reasonably well with the remaining values. The agreement of the k_{ex} values obtained from the different resonances is reassuring, since the CH_2 and CH_3 resonances are multiplets for diamagnetic complexes and hence heterogenous broadening could contribute to the observed line widths. The consistent results in Table III rule out this and other possible complications. The average value of $k_{ex} = 1.2\ (\pm 0.2) \times 10^8\ M^{-1}\ s^{-1}$ is remarkably high, exceeding those of the classic outer-sphere reactions of $M(bpy)_3^{2+/3+}$ (M = Fe, Ru, Os; bpy = 2,2′-bipyridine) whose rate constants[22a] are (0.3–2.0) × $10^7\ M^{-1}\ s^{-1}$.

These initial results for the $[Ru(OEP)(C_6H_5)]^{0/+}$ reaction are complemented by those of the $[Ru(OEP)(C_6H_5)]^{0/-}$ and $[Ru(OEP)(C_6H_5)_2]^{0/-}$ reactions. The rate constant for the $[Ru(OEP)(C_6H_5)]^{0/-}$ reaction obtained from a cursory ^1H NMR study is similar (ca. $10^7\ M^{-1}\ s^{-1}$) to that of $[Ru(OEP)(C_6H_5)]^{0/+}$. The $[Ru(OEP)(C_6H_5)_2]^{0/-}$ reaction is complicated by the decomposition reaction mentioned above; however, our initial estimate of the rate constant is somewhat smaller (ca. $10^4\ M^{-1}\ s^{-1}$). The reason(s) for the differences in rate constants for the three reactions may lie in the strength and extent of binding of the axial THF ligand in the $[Ru(OEP)(C_6H_5)]^{+/0/-}$ series, the porphyrin-localized redox reaction in the $[Ru(OEP)(C_6H_5)_2]^{0/-}$ pair, or

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(21) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1988; p 878.

(22) (a) Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542. (b) Nielson, R. M.; McManis, G. M.; Safford, L. K.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 2152.

ion pairing[22b] within the low-dielectric solvent CD_2Cl_2. We are presently attempting a more extensive study of these three electron-exchange reactions in order to address these issues.

Conclusions

The redox and reaction chemistry revealed from this study complement that reported previously for other organometallic porphyrins, particularly the iron complexes. The nature of the reactions in Scheme I is similar to that reported by Kadish for various M(Por)R and $M(Por)R_2$ species; however, the details of the reactions in Scheme I are unique to Ru. First, the $[Ru(OEP)(C_6H_5)_n]^{+/0/-}$ complexes exhibit electron-transfer reactions easily studied by ^1H NMR spectroscopy. While electron exchange is likely to occur with other organometallic porphyrin complexes, the measurable differences in k_{ex} resulting from the subtle structural variations make the present systems particularly attractive. Second, $[Ru(OEP)(C_6H_5)]^+$, unlike the $[Fe(Por)(C_6H_5)]^+$ species,[7] does not N-arylate. Kadish has shown[7] that by varying the chemical nature (presumably, electron-withdrawing ability) of the Ar group, the propensity of the $[M(Por)(Ar)]^+$ to N-arylate is controllable. Presumably, $[Ru(OEP)(C_6H_5)]^+$ possesses a central Ru (Ru^{IV}, using the electron count formalism employed herein) that possesses enough electron density to support the C_6H_5 ligand.[3] We hope that, by preparing the analogous Ru(OEP)(Ar) species[5c] with Ar = $C_6H_4CH_3$, C_6F_5, or $C_6H_2F_3$, we can modulate the reactivity of the $[Ru(OEP)(AR)]^+$ species. Third, the $M(Por)(C_6H_5)_2$ species has not been reported for M = Fe, so direct comparison is not possible. However, the salient characteristics of $Ru(OEP)(C_6H_5)_2$ are the N-arylation of the cation, the porphyrin-localized first reduction, and the decomposition of the dianion linking the $Ru(OEP)(C_6H_5)_n$ redox schemes. Again, variation of the Ar group will provide additional information about the properties and reactivity of $[M(Por)(R)_n]^{+/0/-/2-}$ complexes. Combined with the extensive information gathered by others on related metals, our results with $Ru(Por)(R)_n$ complexes may permit a comprehensive and coherent picture of the properties of organometallic porphyrin complexes.

Acknowledgment. We thank the Purdue Research Foundation for financial support and Drs. Claude R. Jones and Scott Woehler for their assistance with NMR experiments. We thank Lance Safford for his assistance with the fast-scan cyclic voltammetry experiments. Professor Ian P. Rothwell provided C_6D_5Li and many useful comments. NMR experiments were performed on instruments funded by NIH Grant RR01077 and NSF Grant BBS-8714258.

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A Pentaammineruthenium Mixed-Valence Complex with 1,4-Dicyanamido-2,3,5,6-tetrachlorobenzene Dianion as Bridging Ligand: Symmetry-Attenuated Electronic Coupling between Redox Sites

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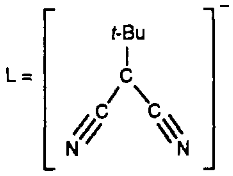
Received February 8, 1990

The dinuclear complex $[(NH_3)_5RuLRu(NH_3)_5][Cl]_4$, where L^{2-} = 1,4-dicyanamido-2,3,5,6-tetrachlorobenzene dianion, has been prepared. UV–vis–near-IR spectroscopy and electrochemical data strongly indicate that its mixed-valence derivative is a weakly coupled case, with H_{ab} estimated to be 185 cm^{-1}. It is suggested that coupling between the metal centers via the low-energy LMCT system is symmetry forbidden, while coupling via the high-energy LMCT system is energetically unfavorable.

Introduction

In coordination chemistry, mixed-valence complexes have been used to study the factors that control the extent of donor and acceptor interaction and the rates of thermal electron transfer.[1] Of primary importance to the degree of electronic coupling between donor and acceptor is the nature of the bridging ligand. For example, in the mixed-valence "Creutz–Taube" ion[2]

electronic coupling is believed to occur via ruthenium $d\pi$ and pyrazine $p\pi^*$ orbital mixing (a resonance-exchange mechanism) and is sufficiently strong to delocalize charge in the ground state, resulting in a partial oxidation state of 2.5 for each ruthenium.[3] Replacement of the bridging pyrazine with saturated 1,4-dithiane eliminates the π^* pathway for resonance exchange. This results in a trapped valence ground state in which Ru(II) is weakly coupled to Ru(III).[4] An alternative resonance-exchange mechanism for electronic coupling is that which occurs via the mixing of ruthenium $d\pi$ and the bridging ligand's highest occupied molecular orbital (HOMO). This mechanism (also called superexchange or hole transport) accounts for the delocalized mixed-valence state observed in $[(NH_3)_5Ru{-}L{-}Ru(NH_3)_5]^{4+}$,[5] where



There are only a few examples of mixed-valence complexes in which metal–metal coupling occurs via a superexchange mechanism,[5,6] and because of this, not much is known concerning the dependence of the superexchange mechanism for electronic coupling on the nature of the bridging ligand.

In this study, we have prepared a dinuclear pentaammineruthenium mixed-valence complex, using the bridging ligand 1,4-dicyanamido-2,3,5,6-tetrachlorobenzene dianion (L^{2-}). It has already been demonstrated[7,8] that anionic phenylcyanamide ligands are both σ and π donating and that the cyanamide group is coplanar with the phenyl ring even when coordinated to Ru(III), suggesting a significant degree of π coupling. Coupling between

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(1) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.
(2) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988.
(3) Best, S. P.; Clark, R. J. H.; McQueen, R. C. S.; Joss, S. *J. Am. Chem. Soc.* **1989**, *111*, 548.
(4) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1978**, *100*, 1635.
(5) Krentzien, H.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 6379.
(6) (a) Bauman, J. A.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 345. (b) Weaver, T. R.; Meyer, T. J.; Adeyemi, S. A.; Brown, G. M.; Eckberg, R.; Hatfield, W. E.; Johnson, E. C.; Murray, R. W.; Untereker, D. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
(7) Crutchley, R. J.; Naklicki, M. L. *Inorg. Chem.* **1989**, *28*, 1955.
(8) Crutchley, R. J.; McCaw, K.; Lee, F. L.; Gabe, E. J. *Inorg. Chem.* **1990**, *29*, 2576.

0020-1669/90/1329-3641$02.50/0