Ru(OEP)(PPh$_3$) (4). This complex was made from **3** by the method described for **2** (2 h at 200 °C, 1×10^{-5} Torr, 1 mol equiv of PPh$_3$ being removed by sublimation). Anal. Calcd for $C_{54}H_{59}N_4PRu$: C, 72.40; H, 6.59; N, 6.26. Found: C, 72.49; H, 6.70; N, 6.13. ^{1}H NMR: δ 9.56 s (4 H, meso H), 6.50 t (3 H, *p*-H), 6.29 m (6 H, *m*-H), 4.21 m (6 H, *o*-H), 3.78 m (16 H, CH$_2$), 1.85 t (24 H, CH$_3$). These data agreed with those noted earlier for an impure sample[8] (see below). ^{31}P NMR: δ 58.59 s. The UV/visible spectrum is the same as that recorded for the species formed in situ.[7,8]

Results and Discussion

The synthesis of the five-coordinate complexes **2** and **4** demonstrates again the utility of the pyrolysis procedure in metalloporphyrin chemistry.[3] An earlier synthesis of **4** via amalgam reduction of RuBr(OEP)(PPh$_3$) gave a product contaminated with inorganics.[8] The lack of a porphyrin plane of symmetry in the five-coordinated species leads to ^{1}H NMR inequivalent *o*-CH$_3$ groups and meta protons within **2**[3] and inequivalent $-CH_2-$ protons of the ethyl groups within **4**.[8]

Both **2** and **4** can be stored under N$_2$ for months without decomposition, and in benzene at $\sim 10^{-3}$ M the species are unreactive toward 1 atm of N$_2$, H$_2$, and even dry (P$_2$O$_5$-treated) O$_2$. Solid samples of **2** and **4** are stable in air over days, but in solution, oxidation by air or undried O$_2$ occurs in minutes. ^{1}H NMR spectral changes show that **4** generates the Ru^{IV} μ-oxo species [Ru(OEP)OH]$_2$O,[11] a process clearly requiring the presence of trace moisture. The product from **2** has not been identified, but it is not Ru(TMP)(O)$_2$.[3,12] Earlier studies[8] showed that impure **4** in toluene reacted with O$_2$ (undried) to give [Ru(OEP)(OH)]$_2$O, which decomposed at 50 °C with trace water into RuO$_2$ and free-base porphyrin. The formation of the μ-oxo species during the O$_2$ oxidation of [Ru(OEP)]$_2$ has been similarly attributed to trace moisture.[13] These data highlight the trace water problem in this area. A stoichiometric O$_2$ oxidation of Ru(OEP)(PPh$_3$)$_2$ had been considered[8] to proceed via either (a) replacement of the O$_2$ of undetectable Ru(OEP)(PPh$_3$)O$_2$ as peroxide by attack of free PPh$_3$ or (b) a pathway that involves reaction of Ru(OEP)(PPh$_3$)O$_2$ with Ru(OEP)(PPh$_3$). The present findings rule out (b) but remain consistent with (a). An alternative outer-sphere O$_2$ oxidation of the bis(phosphine) species, assisted by protons (from water), that involved superoxide and then peroxide formation ($HO_2 \rightarrow {}^1/_2H_2O_2 + {}^1/_2O_2$) was ruled out on kinetic grounds,[8] but the rate data were preliminary, and more detailed studies using a controlled water content should be carried out to test for possible contribution from an outer-sphere process.

Both five-coordinate complexes react rapidly in benzene (10^{-3} M) with CO to give Ru(porp)(PR$_3$)CO[14] and with 1 equiv of the appropriate phosphine to give the precursor bis(phosphine) species. Of interest in a catalytic context, neither **2** or **4** in benzene show reactivity toward benzaldehyde even at 100 °C in sealed tubes. Solutions of Ru(TPP)(PPh$_3$)$_2$ containing added *n*-Bu$_3$P are extremely effective for catalytic decarbonylation of aldehydes;[9] a radical mechanism, although poorly defined, has been established,[9] and loss of CO (from Ru(porp)(PR$_3$)CO formed via aldehyde decarbonylation) according to demonstrated equilibria[7] such as eq 1 was considered as a possible step in all the overall catalysis.

$$\mathrm{Ru(porp)(PR_3)CO + PR_3 \rightleftharpoons Ru(porp)(PR_3)_2 + CO} \quad (1)$$

The present data show that any such carbonyl complex is unlikely to be formed by a purely thermal (or laboratory-light-induced) reaction of the aldehyde with a (porphinato)(phosphine)ruthenium(II) species. Attempts to synthesize Ru(TPP)(PPh$_3$) by vacuum pyrolysis of Ru(TPP)(PPh$_3$)$_2$ simply led to sublimation of the bis(phosphine) complex; this behavior was unexpected, in that the degree of dissociation of PPh$_3$ from the Ru(porp)(PPh$_3$)$_2$ complexes in toluene was greater for the TPP than for the OEP systems.[7]

Treatment of solutions of **2** or **4** with HBr(g) or 48% aqueous HBr under aerobic conditions gives high yields of RuBr(TMP)(*n*-Bu$_3$P)[15] or RuBr(OEP)(PPh$_3$),[16] respectively. Aerobic treatment of Ru(porp)(PR$_3$)$_2$ complexes with HX has proved useful previously for the synthesis of Ru^{III} porphyrin halide species, but the oxidation process concomitantly generates phosphine oxide, which has to be removed by chromatography.[8,16] Use of the five-coordinate precursors obviates the necessity of the separation procedure.

Finally, ^{1}H NMR and ^{31}P NMR studies show (a) that there is no tendency of **2** or **4** in solution to dissociate a phosphine to give Ru(TMP)[3] or [Ru(OEP)]$_2$,[1] respectively, and (b) that 1:1 mixtures of the mono- and bis(phosphine) species **3** and **4** undergo fast exchange of phosphine, while mixtures of **1** and **2** do not.

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Contribution from the Department of Chemistry,
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Synthesis, Reactivity, and Electrochemical Characterization of $[(\eta^5\text{-}C_5H_5)Ru(\eta^7\text{-}C_7H_7)](PF_6)_2$ and $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_7H_8)](PF_6)$

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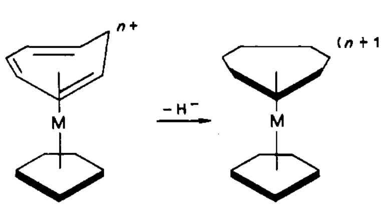
During the last few years, we have been interested in the syntheses and properties of new [CpM(L)$_3$]$^+$ complexes (Cp = η^5-cyclopentadienyl; M = Fe, Ru; L$_3$ = 6-electron-donor ligand) via the photolytically generated [CpM(S)$_3$]$^+$ solvato complexes (M = Fe, S = CH$_2$Cl$_2$; M = Ru, S = CH$_3$CN).[1,2] One new complex that we synthesized in high yields via the photochemical route is [CpFe(CHT)](PF$_6$) (CHT = η^6-cycloheptatriene).[3] The relative ease of obtaining this material and its favorable chemical properties suggested that it would be a good candidate for hydride abstraction studies designed to convert the coordinated CHT ligand to the coordinated tropylium (trop$^+$) ligand:



As we pursued our chemical investigations, we also became in-

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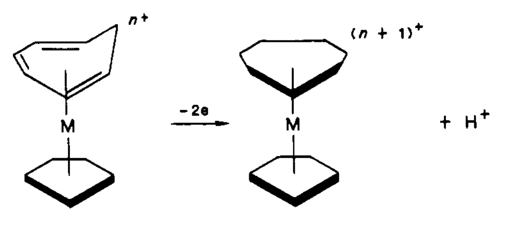
terested in studying the electrochemical equivalent of the hydride abstraction



and related processes with the hope of obtaining thermodynamic information that would be useful for the prediction of the chemical reactivity of this system. Herein is the initial report of these studies and the more successful studies of the $[CpRu(CHT)]^+$ and $[CpRu(trop)]^{2+}$ analogues.

Experimental Section

General Considerations. All synthetic procedures were carried out under an inert N_2 atmosphere unless otherwise noted. Solvents used were of spectroscopic grade and were used without further purification. Cycloheptatriene and $(Ph_3C)PF_6$ were purchased from Aldrich Chemical Co. $[C_7H_7][PF_6]$,[4] $[CpFe(CHT)](PF_6)$,[3] $[CpFe(C_6H_6)](PF_6)$,[5] $[CpRu(C_6H_6)](PF_6)$,[6,7] and $[CpRu(CH_3CN)_3](PF_6)$[2] were prepared by literature procedures. ^1H NMR spectra were recorded on a Varian Associates CFT 20 NMR spectrometer equipped with a 79.5-MHz proton accessory. Chemical shifts, δ, are relative to Me_4Si. High-field ^1H NMR spectra were recorded on a Nicolet NT 300-MHz instrument. Elemental analyses were performed by MHW laboratories, Phoenix, AZ.

All electrochemical experiments were performed in the dark at 20 ± 2 °C with a BAS Model 100 electrochemical analyzer. A three-electrode configuration consisting of a highly polished glassy-carbon disk working electrode ($A = 0.07$ cm^2), a platinum-spiral auxiliary electrode, and a AgCl/Ag reference electrode, which contained 1.0 M KCl, was utilized. The working compartment of the electrochemical cell was separated from the auxiliary compartment by a fritted-glass salt bridge and from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of supporting electrolyte. Acetonitrile (Burdick and Jackson Laboratories, Inc.) and tetra-n-butylammonium hexafluorophosphate (TBAH) (Southwestern Analytical Chemicals, Inc.) were used without further purification. Working solutions were deoxygenated with purified, solvent-saturated argon. Solutions of complex were prepared from solvent/supporting electrolyte stored over 3 Å activated sieves and 80–200-mesh activated alumina (Fisher Scientific, Inc.). Potentials are reported vs. aqueous AgCl/Ag and are not corrected for the junction potential.[8] No *iR* compensation was used in any of the electrochemical studies. The $E^{\circ\prime}$ of the ferrocenium/ferrocene couple under these experimental conditions was +0.41 V.[9]

$[CpRu(CHT)](PF_6)$.[7] A 0.1-mL (0.96-mmol) aliquot of cycloheptatriene was added to a degassed solution of 0.040 g of $[CpRu(CH_3CN)_3]PF_6$ (0.09 mmol) in 10 mL of acetonitrile. After the solvent was removed by rotary evaporation at 50 °C, the product was washed with diethyl ether to remove unreacted cycloheptatriene. A total of 0.032 g (0.078 mmol) of yellow, crystalline $[CpRu(CHT)](PF_6)$ (85% yield) was recovered. Mp: 160 °C dec. Anal. Calcd for $C_{12}H_{13}F_6PRu$: C, 35.74; H, 3.25. Found: C, 35.94; H, 3.36. ^1H NMR (acetone-d_6, 300 MHz): δ 6.82 (m, $H^{3,4}$, 2 H), 5.69 (m, $H^{2,5}$, 2 H), 5.60 (s, C_5H_5, 5 H), 4.09 (m, $H^{1,6}$, 2 H), 3.06 (m, $H^7{}_{endo}$, 1 H), 1.32 (d of t, $H^7{}_{exo}$, 1 H; J = 13.6 Hz, J_{vic} = 4.38 Hz).

$[CpRu(trop)](PF_6)_2$.[10] A solution of 0.062 g (0.26 mmol) of $(C_7H_7)PF_6$ in 20 mL of 1,2-dichloroethane was degassed with vigorous nitrogen bubbling for 15 min. To this solution was added 0.081 g (0.19 mmol) of $[CpRu(CH_3CN)_3](PF_6)$ with an additional 10 min of N_2 bubbling. As the reaction mixture was heated for 1.5 h, a white precipitate formed. After the solution volume was reduced by rotary evaporation, the white product was collected by filtration and washed repeatedly with cold dichloromethane and diethyl ether. The solid was further purified by dissolution in acetonitrile followed by precipitation with dichloromethane. A total of 0.073 g (0.13 mmol) of white $[CpRu(trop)](PF_6)_2$ (71% yield) was collected by filtration. Anal. Calcd for $C_{12}H_{12}RuP_2F_{12}$: C, 26.34; H, 2.21. Found: C, 26.59; H, 2.29. ^1H NMR (acetonitrile-d_3): δ 7.57 (s, C_7H_7, 7 H), 6.13 (s, Cp, 5 H). ^{13}C NMR (acetonitrile-d_3): δ 92.5 (s, C_7H_7), 84.3 (s, Cp).

Reaction of $[CpRu(CHT)](PF_6)$ with Ph_3CPF_6. A 0.044-g (0.11-mmol) sample of $[CpRu(CHT)](PF_6)$ under a nitrogen atmosphere was treated with 0.052 g of Ph_3CPF_6 (0.14 mmol) in 5 mL of CH_2Cl_2. The solution was stirred for 24 h. After reduction of the solvent volume, the CH_2Cl_2-insoluble material was collected. A ^1H NMR spectrum of this material revealed a mixture of undiscernible decomposition products.

Reaction of $[CpRu(trop)](PF_6)_2$ with CH_3Li. A sample of 0.049 g of $[CpRu(Trop)](PF_6)_2$ (0.089 mmol) was suspended in 15 mL of dry, degassed THF, and 0.1 mL of 1 M CH_3Li (0.1 mmol) was added. The metal complex instantly dissolved to give a colorless solution, but the solution turned brown within a minute. After rotary evaporation, the solid was washed with diethyl ether. An ^1H NMR spectrum of the CH_3CN-soluble fraction exhibited no resonance ascribable to products.

Reaction of $[CpRu(trop)](PF_6)_2$ with Zn. A mixture of 0.039 g (0.072 mmol) $[CpRu(trop)](PF_6)_2$ and 1 g of Zn dust in a degassed solution of CH_3CN/ethanol (solvent ratio 1:2) was stirred under N_2 for 3 days. After filtration to remove the remaining Zn dust, the solvent was removed by rotary evaporation. The resulting light tan solid was washed with diethyl ether to remove any organic impurities. Characterization by NMR led to the assignment of the product as $[CpRu(CHT)](PF_6)$ (0.026 g, 0.064 mmol, 89% yield).

Photolysis of $[CpRu(trop)](PF_6)_2$ in CD_3CN. A sample of $[CpRu(trop)](PF_6)_2$ was dissolved in CD_3CN in an NMR tube. This solution was degassed in a Pyrex NMR tube and irradiated for 35 min. A ^1H NMR spectrum of the photolyzed solution indicated that, in addition to the resonances due to unreacted $[CpRu(trop)]^{2+}$ (45%), new peaks assignable to the free tropylium cation at 9.30 ppm and a singlet at 4.29 ppm were present. The position of the peak at 4.29 ppm is in excellent agreement with the position of the Cp resonance of $[CpRu(CD_3CN)_3](PF_6)$. Continued photolysis (70 min) of the solution converted the remainder of the starting material cleanly to $[CpRu(CD_3CN)_3](PF_6)$ with no apparent side reactions or decomposition.

Attempted Preparations of $[CpFe(trop)](PF_6)_2$ from Reactions of $[CpFe(CHT)](PF_6)$ with Oxidants.[3] $[CpFe(CHT)](PF_6)$ was reacted with a variety of oxidants[11] ($SbCl_5$,[12] $NOBF_4$,[13] PCl_5,[14] Ph_3CPF_6[15]) in CH_2Cl_2, CH_3CN, SO_2,[16] and propylene carbonate at temperatures ranging from −80 to +95 °C in an attempt to prepare $[CpFe(trop)]^{2+}$. Small amounts of the desired product were detected in several of these reactions. Taking into account these preliminary results suggested that the combination of Ph_3CPF_6/CH_3CN at 20 °C with $[CpFe(CHT)](PF_6)$ for an extended time period might be successful. The reaction of $[CpFe(CHT)](PF_6)$ with Ph_3CPF_6 in CH_3CN at room temperature for 11 days resulted in a red material that was a 50:50 mixture of $[CpFe(trop)](PF_6)_2$ and $[CpFe(CHT)](PF_6)$. The compound could not be purified, but the ^1H NMR spectrum obtained in CD_3CN for the mixture is consistent with the presence of the $[CpFe(trop)]^{2+}$ cation (δ 8.00 (s, C_7H_7, 4 H), 5.30 (s, C_5H_5, 5 H)).

Results and Discussion

Synthetic Chemistry. In general, hydride abstraction from CHT complexes has been the method of choice for the preparation of tropylium complexes.[17-23] We attempted to apply this methodology to the synthesis of $[(CpFe(trop)]^{2+}$ ($trop^+ = \eta^7\text{-}C_7H_7$, tropylium) because the starting material, $[CpFe(CHT)]^+$ ($CHT = \eta^6\text{-}C_7H_8$, cycloheptatriene), was readily available from a previous photochemical investigation of metal arene compounds.[3] However,

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treatment of [CpFe(CHT)](PF$_6$) with oxidants known to oxidize C-H bonds (PCl$_5$,[14] SbCl$_5$,[12] Ph$_3$C$^+$,[15] NO$^+$ [13]) via hydride abstraction resulted in either little or no [CpFe(trop)]$^{2+}$ formation (PCl$_5$, NO$^+$) or products contaminated with paramagnetic impurities (SbCl$_5$). When suitable reaction conditions were discovered (Ph$_3$C$^+$, CH$_3$CN, 20 °C), only a 50% conversion of [CpFe(CHT)]$^+$ to [CpFe(trop)]$^{2+}$ could be effected. The [CpFe(trop)]$^{2+}$ formed could not be separated from the starting material due to its high degree of water sensitivity. Given the generally higher stability of second-row metal complexes relative to analogous first-row compounds, we synthesized [CpRu(CHT)]$^+$ in order to prepare and isolate the Ru analogue [CpRu(trop)]$^{2+}$. Once again, hydride abstraction failed to yield the desired [CpRu(trop)]$^{2+}$ complex, but in this case we were able to prepare [CpRu(trop)]$^{2+}$ via direct reaction of trop$^+$ with the labile [CpRu(CH$_3$CN)$_3$]$^+$ complex:

$$[\mathrm{CpRu(CH_3CN)_3}]^+ + \mathrm{trop}^+ \xrightarrow{\mathrm{DCE}} [\mathrm{CpRu(trop)}]^{2+} + 3\mathrm{CH_3CN}$$

Treatment of [CpRu(CH$_3$CN)$_3$](PF$_6$) with an excess of the tropylium cation ((trop)PF$_6$) in dichloroethane (DCE) results in the replacement of the three acetonitrile ligands by the trop$^+$ unit. The PF$_6^-$ salt of the dication precipitates from solution as a white solid as the reaction mixture is heated. The dication is somewhat thermally unstable as evidenced by its decomposition when the reaction mixture is heated beyond the 1–2 h necessary for complete displacement of the acetonitrile ligands. The white solid exhibited an elemental analysis consistent with the formulation [CpRu(trop)](PF$_6$)$_2$. The proton NMR spectrum of a CD$_3$CN solution of the complex consists of two singlets in the ratio of 5:7 at 6.13 and 7.57 ppm. The ^{1}H NMR spectral data are consistent with the presence of η^5- and η^7-binding for Cp and trop, respectively. Cooling solutions of the complex to −80 °C gave no broadening or other significant changes to indicate fluxional behavior of any type for either ring. The 6.13 ppm resonance assigned to the η^5-cyclopentadienyl ring is shifted considerably downfield relative to resonances of known [CpRu(η^6-arene)]$^+$ complexes.[24-26] An upfield shift of approximately 1.7 ppm is observed for the coordinated η^7-tropilium resonance at 7.57 ppm relative to the resonance for the tropylium cation. The direction and magnitude of the shift are similar to those observed for aromatic rings upon complexation to the CpRu$^+$ moiety. The proton-decoupled ^{13}C NMR spectrum obtained at room temperature for acetonitrile solutions exhibits two resonances at 84.3 and 92.5 ppm vs. Me$_4$Si that are assigned to the Cp and trop$^+$ rings, respectively. these values can be compared with those obtained for the isoelectronic Cr (75.4, 86.9) and Mo (83.8, 80) compounds.[20]

Two thermal patterns and one photochemical pattern of chemical reactivity were explored for [CpRu(trop)](PF$_6$)$_2$. Nucleophilic attack on coordinated tropylium has been observed previously.[27-29] Reactions of CH$_3$Li or C$_6$H$_5$Li with [CpCr(trop)]$^+$ leads to addition to the 7-membered ring to give the corresponding substituted cycloheptatriene complex.[28] Treatment of [CpRu(trop)](PF$_6$)$_2$ with LiCH$_3$ results in a chemical reaction evidenced by immediate dissolution of the dication in THF upon addition of LiCH$_3$. Within a minute, however, the solution turns brown and no characterizable Ru-containing products are found. Perhaps the desired addition product, [CpRu(η^6-C$_7$H$_7$CH$_3$)]$^+$, is initially formed but is unstable under the reaction conditions. The reductive coupling of two bound C$_7$H$_7^+$ moieties to form [(CpRu)$_2$(ditropyl)](PF$_6$)$_2$ was another reaction of potential interest in the Ru system. Previously, the reductive coupling of free tropylium cation was achieved with Zn dust in aqueous solutions.[30] Similarly, metal complexes of the general form [(CO)$_3$M(C$_7$H$_7$)]$_2$ (M = Cr,[31] Fe[32], have been synthesized. The reaction of [CpRu(trop)](PF$_6$)$_2$ with Zn dust in a mixture of ethanol and acetonitrile afforded not the expected binuclear coupling product, but [CpRu(CHT)](PF$_6$), identified by ^{1}H NMR spectroscopy.

Table I. Electrochemical Data[a]

complex	peak potentials, V e$^-$ + M(II) → M(I)	 CHT → 2e$^-$ + trop$^+$ + H$^+$	 e$^-$ + trop$^+$ → trop^0
[CpFe(CHT)]$^+$	−1.10	+1.67	−0.19
[CpRu(CHT)]$^+$	−1.33	+1.85	−0.20
[CpRu(trop)]$^{2+}$	−1.32		−0.11
free CHT		+1.49	
free C$_7$H$_7^+$			−0.18
[CpFe(C$_6$H$_6$)]$^+$	−1.50		
[CpRu(C$_6$H$_6$)]$^+$	−1.85		

[a] All values are reported vs. aqueous AgCl/Ag for CH$_3$CN/TBAH solutions. The scan rate for all experiments was 100 mV/s.

A cursory examination of the photochemical reactivity of [CpRu(trop)](PF$_6$)$_2$ indicated it to have reactivity comparable to the previously studied [CpRu(C$_6$H$_6$)]$^+$ complex.[2,24] The photolysis of [CpRu(trop)](PF$_6$)$_2$ in CD$_3$CN was monitored by ^{1}H NMR. After 35 min of photolysis, 55% conversion of [CpRu(trop)]$^{2+}$ to [CpRu(CH$_3$CN)$_3$]$^+$ was observed. This product is the result of photochemical replacement of the 7-membered ring in [CpRu(trop)](PF$_6$)$_2$ by three acetonitrile ligands. A dark control reaction of [CpRu(trop)](PF$_6$)$_2$ dissolved in CD$_3$CN indicated no changes due to loss of the trop$^+$ ligand after 24 h.

Although several [LM(CHT)]^n/[LM(trop)]$^{n+1}$ complex pairs are well characterized (L = Cp, M = Mn;[22] L = (CO)$_3$, M = W,[21] M = Cr, Mo[16]), the electrochemical interconversion that involves the formal oxidation of a C–H bond has not been studied:[33]

$$[\mathrm{CpM(CHT)}]^{n+} \xrightarrow[\text{oxidation}]{\text{electrochemical}} [\mathrm{CpM(trop)}]^{(n+1)+} + 2\mathrm{e}^- + \mathrm{H}^+$$

Additionally, we expected to observe metal-centered electrochemical processes for the CHT and trop$^+$ complexes because they are common for other CpFe and CpRu complexes that have been studied.[9,11,25] Curiously, the electrochemical behavior of all three complexes ([CpFe(CHT)]$^+$, [CpRu(CHT)]$^+$ and [CpRu(trop)]$^{2+}$) is dominated by ligand-centered redox processes. Electrochemical data for these three compounds, the free ligands,[34] and for several complexes useful for comparative purposes are summarized in Table I. [CpRu(CHT)](PF$_6$) undergoes an irreversible, two-electron,[35] ligand-centered oxidation at +1.85 V while the analogous oxidations in [CpFe(CHT)](PF$_6$) and free CHT are observed at +1.67 and +1.49 V, respectively. Both metal complex oxidations produce the corresponding cyclopentadienyl metal tropylium complex as evidenced by a return reduction at approximately −0.2 V. These coupled reductions are very similar to bulk processes observed in solutions of both free tropylium and

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$[CpRu(trop)](PF_6)_2$.[36] Unfortunately, bulk electrolyses of $[CpFe(CHT)]^+$ and $[CpRu(CHT)]^+$ at +1.9 V designed to oxidize the coordinated cycloheptatriene ligand to tropylium were unsuccessful due to passivation of the electrode surface. The partial abstraction of hydride by trityl cation from $[CpFe(CHT)]^+$ and the unsuccessful abstraction from $[CpRu(CHT)]^+$ with this reagent are consistent with the observed increase in the potential at which the oxidation occurs in the Ru case. The shift to more positive potentials first on CHT coordination to Fe and then the further positive shift observed for the Ru complex are indicative of either some degree of interaction between the C–H bond and the metal center or more likely an inductive effect that removes electron density from the C–H bonding orbital.

All the complexes studied exhibit electrochemically irreversible 1-electron-reductions processes at approximately −1.32 V for Ru and −1.10 V for Fe. The absence of a corresponding reduction in either free tropylium or CHT suggests a metal-centered assignment for these processes. These one-electron reductions are analogous to those observed for $[CpFe(arene)]^+$[37] (−1.50 V) and $[CpRu(C_6H_6)]^+$ (−1.85 V). The assignments for the CHT and $trop^+$ complexes are in harmony with the 0.35-V shift to more negative potentials observed for $[CpFe(C_6H_6)]^+$ to $[CpRu(C_6H_6)]^+$.

Conclusions

Unsuccessful attempts to synthesize pure $[CpFe(trop)]^{2+}$ via hydride abstraction from $[CpFe(CHT)]^+$ suggested that the corresponding Ru complexes might be favorably investigated. $[CpRu(CHT)](PF_6)$ was readily synthesized from $[CpRu(CH_3CN)_3](PF_6)$. $[CpRu(CHT)](PF_6)$ is similar in characteristics to the previously reported Fe analogue. While an attempt to abstract hydride from $[CpRu(CHT)](PF_6)$ with Ph_3CPF_6 in CH_2Cl_2 gave no reaction, the direct reaction of $[CpRu(CH_3CN)_3](PF_6)$ with $(trop)PF_6$ afforded $[CpRu(trop)](PF_6)_2$ in high yield as the first example of a η^7-tropylium complex formed via the direct reaction of $trop^+$ with a metal complex. Reduction of $[CpRu(trop)](PF_6)_2$ by Zn in $EtOH/CH_3CN$ forms $[CpRu(CHT)](PF_6)$ in high yield. Reaction of CH_3Li with $[CpRu(trop)](PF_6)_2$ in THF gave no isolable products. Photolysis of acetonitrile solutions of $[CpRu(trop)]^{2+}$ results in the quantitative displacement of the tropylium ring with formation of $[CpRu(CH_3CN)_3](PF_6)$.

Electrochemical studies indicate that ligand-centered oxidation of bound CHT to bound $trop^+$ occurs on the cyclic voltammetric time scale, but electrode passivation precludes quantitative conversion to products. A metal-centered reduction at potentials more negative than −1.0 V is also observed for the $[CpRu(trop)]^{2+}$, $[CpRu(CHT)]^+$, and $[CpFe(CHT)]^+$ complexes.

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Iron Porphyrin and Hydroporphyrin Magnetic Anisotropies Derived from High-Field ^2H NMR Spectra

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Magnetic anisotropies have been studied by biological and porphyrin chemists to deduce the electronic structures and, hence, molecular structures of active sites of important classes of proteins and enzymes. Single-crystal susceptibility measurements,[2] analyses of dipolar contributions to isotropic shifts in NMR spectra,[3] or interpretations of *g*-value anisotropies in EPR spectra[4] have been used to calculate $\Delta\chi_{\parallel}$ $(\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy}))$ and $\Delta\chi_{\perp}$ $(\chi_{xx} - \chi_{yy})$. A recent technique has been developed by MacLean and coworkers for measurement of diamagnetic anisotropies in aromatic compounds: very large magnetic fields cause a sufficient dynamic alignment of anisotropic molecules so that measurable quadrupole splittings are observed in ^2H NMR spectra of solutions of these compounds.[5] The observed splittings, $\Delta\nu$, are directly related to $\Delta\chi_{\parallel}$ and $\Delta\chi_{\perp}$ (see below). The technique is applicable to paramagnetic metal complexes.[6] In this paper we report ^2H NMR spectra and derived magnetic anisotropies for deuteriated samples of the four-coordinate, square-planar S = 1 complexes Fe(OEP)[7] and Fe(OEC).[7] This is the first application of this new technique to the study of the magnetic properties of iron porphyrins and related hydroporphyrins,[8,9] an area in which several of us are particularly active.[10]

Experimental Section

Selective deuteriation of $H_2(OEP)$ and $H_2(OEC)$ was accomplished by the use of literature procedures.[11,12] Samples of Fe(OEP-*meso*-d_4)

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