

Application of the Rotating Photoelectrode to the Detection of an Organotransition-Metal Intermediate.

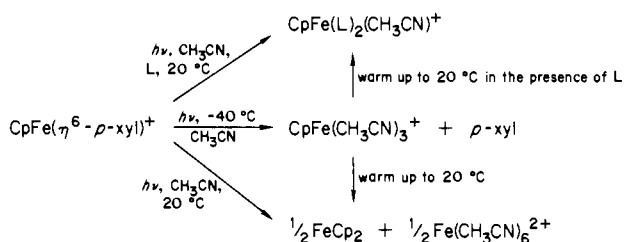
Photoelectrochemical Detection of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3\text{CN})_3^+$

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Abstract: Photolysis of $\text{CpFe}(\eta^6\text{-}p\text{-xyl})^+$ ($p\text{-xyl} = p\text{-xylene}$) in acetonitrile at -40°C results in an intensely purple solution that contains the $\text{CpFe}(\text{CH}_3\text{CN})_3^+$ ion. Allowing this purple solution to warm to room temperature results in the formation of the previously reported photoproducts: ferrocene and $\text{Fe}(\text{CH}_3\text{CN})_6^{2+}$. The cyclic voltammogram of $\text{CpFe}(\text{CH}_3\text{CN})_3^+$ exhibits one irreversible oxidation $E_{pa} = +0.64\text{ V vs. Ag/AgCl}$ which is cyclopentadienyl ligand centered. Anodic photocurrents due to the $\text{CpFe}(\text{CH}_3\text{CN})_3^+$ cation were detected at room temperature via the photolysis of acetonitrile solutions of $\text{CpFe}(\eta^6\text{-arene})^+$ (arene = $p\text{-xylene}$, 9-cinnamylidene-fluorene) through a rotating photoelectrode (RPE). A decrease in the photocurrent with increased rate of RPE rotation is observed for arene = 9-cinnamylidene-fluorene, but for arene = $p\text{-xylene}$, the photocurrent was independent of rotation rate. These observations are explained in terms of the differences in the molar absorptivity of the two compounds.

In recent work,¹ we have found that the visible light photolysis of $\text{CpFe}(\eta^6\text{-}p\text{-xyl})^+$ ($\text{Cp}^- = \eta^5\text{-C}_5\text{H}_5^-$; $\text{xyl} = \text{xylene}$) provides a high yield, versatile synthetic route to a variety of (cyclopentadienyl)iron phosphine, phosphite, and isocyanide complexes. These results and those in other laboratories² were based on the previous observation³ that photolysis of $\text{CpFe}(\eta^6\text{-arene})^+$ cations in neat CH_3CN yields equimolar amounts of ferrocene and solvated iron(II).⁴ $^1\text{H NMR}$ and UV-vis spectroscopic measurements conducted on the intensely purple solutions generated via the photolysis of $\text{CpFe}(\eta^6\text{-}p\text{-xyl})^+$ in CH_3CN at -40°C disclosed the intermediacy of $\text{CpFe}(\text{CH}_3\text{CN})_3^+$ in these reactions and suggested the following reaction scheme:



Toward furthering our understanding of the kinetic behavior of $\text{CpFe}(\text{CH}_3\text{CN})_3^+$, we sought analytical techniques more appropriate for studying the reaction kinetics of photochemically generated $\text{CpFe}(\text{CH}_3\text{CN})_3^+$. During the course of our search, we were directed to a novel photoelectrochemical technique utilizing a rotating photoelectrode (RPE) developed in the early

1970's by Prof. Dennis Johnson and his co-workers.⁵ A RPE consists of an optically transparent disk and a concentric Pt ring electrode.⁶

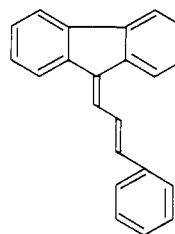
When, simultaneously, the electrode is rotated and an intense, collimated light beam is directed into the solution through the backside of the optically transparent disk, a significant concentration of photochemically generated intermediate(s) is produced and convectively transported to the surface of the Pt ring electrode for detection by linear sweep voltammetry (LSV).

The remainder of this paper describes the successful application of low-temperature CV and the RPE technique to a photoelectrochemical study of the $\text{CpFe}(\text{CH}_3\text{CN})_3^+$ intermediate.

Experimental Section

The compounds $\text{CpFe}(\eta^6\text{-}p\text{-xyl})\text{BF}_4$ and $\text{CpFe}(\eta^6\text{-CF})\text{PF}_6$ (CF = 9-cinnamylidene-fluorene; CF is depicted below; the CpFe^+ unit is bound to the fluorene portion of the arene) were available from a previous study⁷ and as a gift from Dr. M. C. Palazzotto of the 3M Co., respectively.

All electrochemical measurements were performed in the dark with a Bioanalytical Systems (BAS) Model 100 electrochemical analyzer. A



three-electrode configuration consisting of working, platinum spiral auxiliary, and aqueous Ag/AgCl reference electrodes containing 1.0 M KCl was utilized in all electrochemical experiments. Working electrodes consisted of either a highly polished glassy carbon electrode (BAS) with an area of 0.07 cm^2 or a rotating photoelectrode (Pine Instruments Inc.)

(1) (a) Gili, T. P.; Mann, K. R. *Inorg. Chem.* **1980**, *19*, 3007. (b) Gill, T. P.; Mann, K. R. *J. Organomet. Chem.* **1981**, *216*, 65. (c) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1983**, *22*, 1986.

(2) (a) Catheline, D.; and Astruc, D. *J. Organomet. Chem.* **1984**, *272*, 417. (b) Swann, R. T.; Boekelheide, V. *J. Organomet. Chem.* **1982**, *231*, 143. (c) Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2657.

(3) Nesmeyanov, A. N.; Vil'Kenau, N. A.; Shiloutseva, L. S. *Dokl. Akad. Nauk SSSR*, **1970**, *190*, 857.

(4) Throughout the remainder of this paper, the solvated Fe(II) species present in acetonitrile solution will be written as $\text{Fe}(\text{CH}_3\text{CN})_6^{2+}$. This species has been previously characterized in the solid state as the BF_4^- salt: Hathway, B. J.; Holah, D. G.; Underhill, A. E. *J. Chem. Soc.* **1962**, 2444.

(5) (a) Johnson, D. C.; Resnick, E. W. *Anal. Chem.* **1972**, *44*, 637. (b) Lubbers, J. R.; Resnick, E. W.; Gaines, P. R.; Johnson, D. C. *Anal. Chem.* **1974**, *46*, 865. (c) Gains, P. R.; Peacock, V. E.; and Johnson, D. C., *Anal. Chem.* **1975**, *47*, 1373.

(6) Reference 5a contains a more complete description and diagram of a typical RPE.

(7) McNair, A. M.; Schrenk, J. L.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 2633.

with a Pt ring electrode of area 0.38 cm². 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 80–200 mesh activated alumina (Fisher Scientific, Inc.). Potentials are reported vs. aqueous Ag/AgCl and are not corrected for the junction potential. No *iR* compensation was used in any of the electrochemical studies.⁸ The E° of the ferrocenium/ferrocene couple was observed at +0.40 V at the glassy carbon electrode and +0.39 V at the RPE.⁹

Low-temperature experiments were performed through the immersion of the electrochemical cell in a CO₂(g)/acetonitrile bath. The reference electrode compartment remained outside the cold bath and was at or near room temperature (20 ± 2 °C). The observed potential for the FeCp₂⁺/FeCp₂ couple shifts only slightly from its 20 °C position to E° = +0.39 V at -40 °C.

The light source employed for the RPE studies was the Pyrex-filtered output of an Oriol Model 6281 100-W mercury lamp. The collimated light beam from the lamp was reflected through 90° with a mirror, an electronic shutter, a Pyrex filter, the photoelectrode, and into the solution. The optical train was adjusted by eye in order to maximize the light intensity delivered to the electrochemical cell. The light intensity passing through this optical train ranged from 2.9 × 10⁻⁷ to 1.4 × 10⁻⁶ einstein/min.¹⁰ In this paper photocurrents ($i_{hv}(E)$) are defined at a given potential as the difference between the currents measured in linear sweep voltammetric (LSV) experiments performed with and without photolysis of the solution through the RPE:

$$i_{hv}(E) = i(E)_{\text{light on}} - i(E)_{\text{light off}}$$

The general procedure was to collect and store in memory a LSV scan with the light off scanning from 0.00 to +1.00 or +1.50 V. The RPE was then removed from the solution and cleaned, and a LSV scan with the light passing through the RPE was taken. The point-by-point subtraction was handled by the available BAS-100 software. No smoothing or other data adulteration was used in this study.

Results and Discussion

Low-Temperature CV Studies of CpFe(CH₃CN)₃⁺. Figure 1a shows the 20 °C cyclic voltammogram exhibited by a 5.0 mM solution of CpFe(η⁶-*p*-xyl)BF₄ in CH₃CN/TBAH at a glassy carbon disk electrode. One irreversible reduction is observed ($E_{p,a} = -1.52$ V) that is coupled to several return oxidations. After the solution is cooled to -40 °C, the CV (Figure 1b) again exhibits the reduction at negative potentials, but it is quasireversible (at 100 mV/s, $E^{\circ} = 1.51$ V; $E_{p,a} - E_{p,c} = 103$ mV; $i_{p,c}/i_{p,a} = 1.0$) and the return oxidations ($E_{p,a} = +0.44, -0.07, \text{ and } -0.82$ V) present at 20 °C disappear. The lower temperature significantly increases the lifetime of the neutral 19 e⁻ CpFe(η⁶-*p*-xyl) species. Related electrochemical processes have been studied for other CpFe(η⁶-arene)⁺ cations in detail by other groups.¹¹

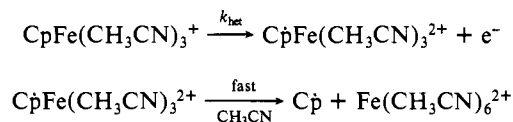
(8) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(9) E° for the FeCp₂⁺/FeCp₂ couple is +0.400 vs. NHE in H₂O solutions (see: Koopp, H. M.; Wendt, H.; Strehlow, H. Z. *Z. Electrochem.* **1960**, *64*, 483.

(10) Actinometry was accomplished by passing light into the solution for a known period of time through the RPE followed by measurement of the current due to FeCp₂ formed. Prior knowledge of the quantum yield, ϕ (ref 7), for arene release from CpFe(η⁶-*p*-xyl)⁺ and the reaction stoichiometry allows calculation of the light intensity.

(11) (a) Nesmeyanov, A. N.; Denisovich, L. I.; Gubin, S. P.; Vol'Kenau, N. A.; Sirotkina, E. I.; Boleseva, I. N. *J. Organomet. Chem.* **1969**, *20*, 169. (b) Nesmeyanov, A. N.; Vol'Kenau, N. A.; Shilovtseva, L. S.; Petrakova, V. A. *J. Organomet. Chem.* **61**, 1973, 3329. (c) Astruc, D.; Hamon, J. R.; Althoff, G.; Roman, E. *J. Am. Chem. Soc.* **1974**, *96*, 3603. (d) Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N., *Inorg. Chem.* **1975**, *14*, 500. (e) Astruc, D.; Hamon, J. R.; Althoff, G.; Roman, E. *J. Am. Chem. Soc.* **1979**, *101*, 5445. (f) Hamon, J. R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758. (g) El Murr, N. *J. Chem. Soc., Chem. Commun.* **1981**, 251. (h) Nesmeyanov, A. N.; Vol'Kenau, N. A.; Petrovskii, P. V.; Kotova, L. S.; Petrakova, V. A.; Denisovich, L. T. *J. Organomet. Chem.* **1981**, *210*, 103. (i) Moinet, C.; Roman, E.; Astruc, D. *J. Electroanal. Chem.* **1981**, *121*, 241. (j) Darchen, A. *J. Chem. Soc., Chem. Commun.* **1983**, 768. (k) Bowyer, W. J.; Geiger, W. E.; Boekelheide, V. *Organometallics* **1984**, *3*, 1079.

Bulk photolysis at -40 °C of the Figure 1b, CpFe(η⁶-*p*-xyl)⁺ solution was monitored by CV and continued until the starting material could no longer be detected. The intensely purple solution of CpFe(CH₃CN)₃⁺ so generated exhibits the CV illustrated in Figure 1c. An irreversible oxidation ($E_{p,a} = +0.64$ V) and an irreversible reduction ($E_{p,c} = -1.50$ V) are observed. The nature of the reduction process has not been studied. The oxidation of CpFe(CH₃CN)₃⁺ exhibits no coupled return reduction peaks within the range of scan rates studied (10–1000 mV/s). Application of double-potential-step chronocoulometry¹² ($\tau = 10$ ms – 1000 ms) also demonstrates the chemically irreversible nature of this oxidation process. The quantity $(Q_{\tau} - Q_{2\tau})/(Q_{\tau})$ failed to approach the theoretical value of 0.586 obtained in reversible systems. We assign this irreversible oxidation process observed at +0.64 V to the oxidation of bound Cp⁻ to Cp with concomitant decomplexation:



This assignment of the oxidation process as *ligand centered* is somewhat surprising in view of the facile oxidation of the Fe(II) in ferrocene ($E^{\circ} = +0.40$) but is supported by previous work¹³ that indicates oxidation of transition-metal-bound Cp⁻ is an observable process¹⁴ when the transition metal is not oxidizable. Results obtained from a bulk electrolysis of the CpFe(CH₃CN)₃⁺ species conducted at -40 °C are also consistent with the oxidation of bound Cp⁻. Bulk electrolysis of CpFe(CH₃CN)₃⁺ at +1.0 V results in the removal of slightly less than 1 e⁻/cation. The CV of the resulting solution exhibits the cyclic voltammogram¹⁵ expected for Fe(CH₃CN)₆²⁺ (vide infra), *not* an Fe(III) complex.

When the solution of CpFe(CH₃CN)₃⁺ (Figure 1c) is allowed to warm up slowly, the peak present at +0.64 V gradually decreases and peaks due to the final products ferrocene and Fe(CH₃CN)₆²⁺ gradually increase in intensity (Figure 1d). No process corresponding to the oxidation of Fe(CH₃CN)₆²⁺ to Fe(CH₃CN)₆³⁺ is observed at potentials less than +1.5 V. Of passing interest is the derivatization of the electrode that occurs after the electrode potential is scanned into the region of the bulk, multielectron reduction of Fe(CH₃CN)₆²⁺ ($E_{p,c} = -1.17$ V). Upon reversal of the scanning direction, hysteresis is observed at the foot of the reduction process, and two new anodic peaks are observed at $E_{p,a} = +0.13$ and +0.36. We believe that this behavior is indicative of the production and subsequent removal of a surface layer of metallic iron. Further study of this phenomenon is needed to more accurately define the nature of these processes.

Detection of CpFe(CH₃CN)₃⁺ at 20 °C with the RPE. With the low-temperature photochemical generation and CV detection of CpFe(CH₃CN)₃⁺ as a guide, we were able to proceed to the RPE experiments with some confidence. For the RPE studies, ca. 10 mM solutions of CpFe(η⁶-*p*-xyl)⁺ were utilized to minimize the depth of light penetration into the solution (ϵ_{max} at 388 nm for CpFe(η⁶-*p*-xyl)⁺ is only about 86 M⁻¹ cm⁻¹). The photocurrents (see Experimental Section) were measured by linear

(12) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; pp 199–206.

(13) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

(14) The $E_{1/2}$ for the oxidation of LiCp in 90:10 THF-HMPA at -30 °C is reported (ref 13) at -0.44 V. By making the assumptions that the LiCp potential and the +0.64 measured at -40 °C for the oxidation of bound Cp⁻ in CpFe(CH₃CN)₃⁺ are near their thermodynamic values and that solvent/ion pairing effects are minimal, a ΔG value of -25 kcal is calculated for the process 3CH₃CN + CpFe(CH₃CN)₃⁺ → Cp⁻ + Fe(CH₃CN)₆²⁺ at -40 °C.

(15) The CV of Fe(ClO₄)₂·6H₂O in CH₃CN/TBAH exhibits a reduction peak and a coupled oxidation peak that are nearly identical with those we attribute to Fe(CH₃CN)₆²⁺. The oxidation of Fe(II) to Fe(III) under these conditions occurs at $E_{p,a} = +1.8$ V. This process was studied previously with polarographic techniques: Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 1852.

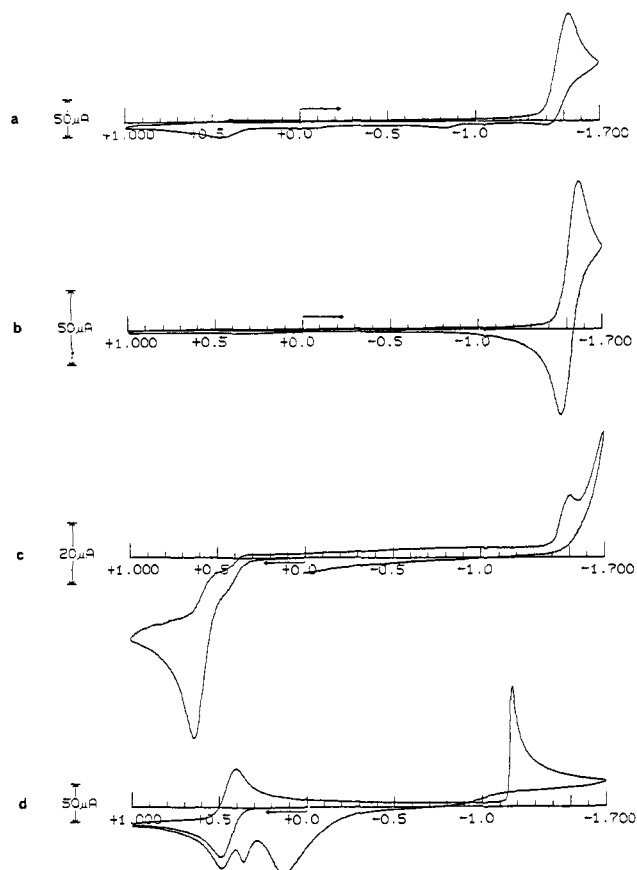


Figure 1. (a) Cyclic voltammogram of 5.0 mM $[\text{CpFe}(\eta^6\text{-}p\text{-xyl})\text{BF}_4]$ recorded in 0.1 M $\text{CH}_3\text{CN}/\text{TBAH}$ at 100 mV/s (glassy carbon electrode of area 0.07 cm^2) at 20 °C. (b) At -40 °C. (c) After 70 min of photolysis at -40 °C. (d) CV observed upon return of (c) solution to room temperature (see text for details).

sweep voltammetry (LSV). Figure 2a shows the photocurrent scan exhibited upon photolysis of $\text{CpFe}(\eta^6\text{-}p\text{-xyl})^+$ at 20 °C with $\omega = 262$ rad/s. The wave observed yields $E_{1/2} = +0.53$ V and $i_d \approx 8.5$ μA .

The onset of the photocurrent coincides closely with the onset of the oxidation process observed for $\text{CpFe}(\text{CH}_3\text{CN})_3^+$ in the low-temperature experiments. To eliminate the possibility that the observed photocurrent might be due to oxidation of a final product (i.e., ferrocene, $E^\circ \approx +0.40$ V), the difference LSV obtained before and after 2 min of bulk photolysis was obtained (Figure 2b). This LSV exhibits a wave with $E_{1/2} = 0.40$ V due to the infusion of ferrocene into the bulk, indicating conclusively that at least the major portion of the photocurrent displayed in Figure 2a is due to oxidation of $\text{CpFe}(\text{CH}_3\text{CN})_3^+$ and not ferrocene. As expected, no photocurrent was measurable for $\omega = 0$ (stationary electrode) because diffusive transport of the unstable intermediate from the region of the quartz disk to the surface of the Pt ring during its lifetime was not possible.

Qualitatively, increasing the concentration of $\text{CpFe}(\eta^6\text{-}p\text{-xyl})^+$ increased the photocurrent because more of the intermediate species is generated near enough to the RPE surface to be subjected to convective transport to the ring electrode. Somewhat surprisingly, at a given concentration, the photocurrents observed are independent of electrode rotation rate from 42 to 513 rad/s. These results indicate a constant collection efficiency obtains for the intermediate under these conditions. The quantitative theoretical analysis of the similar problem of the semitransparent rotating photoelectrode¹⁶ with weakly absorbing species suggested that modification of the precursor species to be a strong absorber would result in an increase in the magnitude of the photocurrents

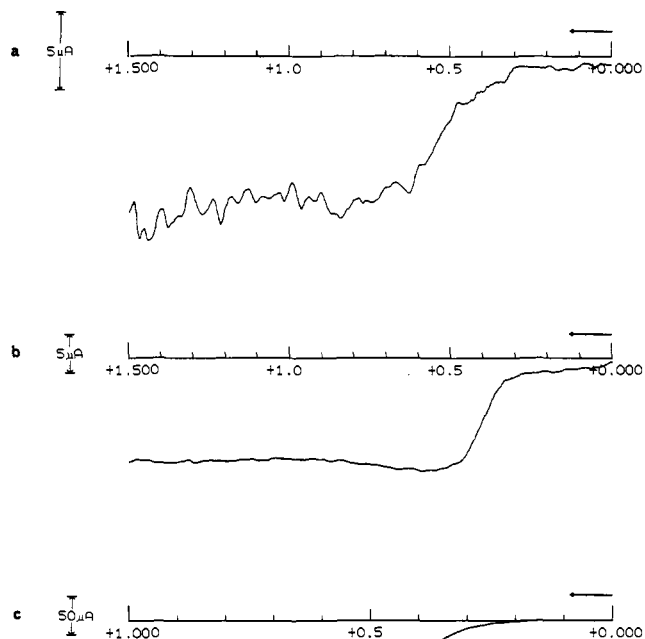


Figure 2. (a) Photocurrent LSV of 10.2 mM $[\text{CpFe}(\eta^6\text{-}p\text{-xyl})\text{BF}_4]$ in $\text{CH}_3\text{CN}/\text{TBAH}$ at RPE ($\omega = 267$ rad/s). (b) Difference LSV after the photochemical infusion of ferrocene into (a) solution. (c) Photocurrent LSV of 5.3 mM $[\text{CpFe}(\eta^6\text{-CF})\text{PF}_6]$ in $\text{CH}_3\text{CN}/\text{TBAH}$ at RPE ($\omega = 10.5$ rad/s).

Table I. Observed Photocurrent i_{hv} for 5.3 mM $\text{CpFe}(\eta^6\text{-CF})^+$ as a Function of Rotation Speed

ω , rad/s	$i_{hv}(+1.0 \text{ V})$, μA	ω , rad/s	$i_{hv}(+1.0 \text{ V})$, μA
10	195	209	140
52	176	314	66
105	165	419	65

observed and $i_{hv}(E)$ would decrease with an increase in rotation speed.

The compound $\text{CpFe}(\eta^6\text{-CF})^+$ illustrates the observation of these expected changes in behavior of i_{hv} with an increase in extinction coefficient. $\text{CpFe}(\eta^6\text{-}p\text{-xyl})^+$ has an extinction coefficient⁷ of 86 $\text{M}^{-1} \text{cm}^{-1}$, while $\text{CpFe}(\eta^6\text{-CF})^+$ has an extinction coefficient¹⁷ of 28 600 $\text{M}^{-1} \text{cm}^{-1}$ at $\lambda_{\text{max}} = 384$ nm. Figure 2c shows the photocurrent observed for the irradiation of 5.3 mM $\text{CpFe}(\eta^6\text{-CF})^+$ at $\omega = 10$ rad/s under the otherwise similar experimental conditions for $\text{CpFe}(\eta^6\text{-}p\text{-xyl})^+$ in Figure 2a. Approximately 195 μA of photo-current are observed for 5.3 mM $(\text{CpFe}(\eta^6\text{-CF}))^+$ while 10 mM $\text{CpFe}(\eta^6\text{-}p\text{-xyl})^+$ generated only 8.5 μA of photocurrent. The $E_{1/2}$ values of i_{hv} are identical for the two different precursor complexes indicating the same photochemical intermediate is generated in each case.

In Table I, data illustrating the falloff in i_{hv} at $E = +1.0$ V are given. The large value of the extinction coefficient of $\text{CpFe}(\eta^6\text{-CF})^+$ results in absorption of the light in a very thin layer next to the quartz disk. Increasing the rotation speed ω , increasingly dilutes this high concentration of photogenerated intermediate as it is convectively transported to the Pt ring, resulting in the photocurrent falloff.

In summary we can only agree with the previous workers⁵ that the RPE technique shows great promise as a method of detecting and identifying photochemically generated reaction intermediates. We believe that the technique will prove particularly useful when

(16) Albery, W. J.; Archer, M. D.; Edgell, R. G. *J. Electroanal. Chem.* 1977, 82, 199.

(17) Palazzatto, M. C., private communication.

applied to transition-metal systems. We are presently investigating a variety of systems for which photogenerated transition-metal intermediates are hypothesized but not well characterized.

Acknowledgment. We would like to thank Dr. M. C. Palazzotto of the 3M Co. for the gift of CpFe(η^6 -CF)PF₆, and the 3M

Company and the Department of Energy for the support of this work.

Registry No. CpFe(CH₃CN)₃⁺, 85702-13-2; CpFe(η^6 -*p*-xyl)BF₄, 74176-24-2; CpFe(η^6 -*p*-CF)PF₆, 94943-93-8; Fe(CH₃CN)₆²⁺, 32982-11-9; Cp, 2143-53-5; ferrocene, 102-54-5.

Intervallence Transfer in Cyano-Bridged Bi- and Trinuclear Ruthenium Complexes

Carlo Alberto Bignozzi,^{1a} Sergio Roffia,^{1b} and Franco Scandola*^{1a}

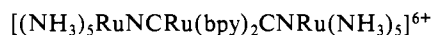
Contribution from the Istituto Chimico dell'Università, Centro di Fotochimica CNR, 44100 Ferrara, Italy, and Istituto Chimico "G. Ciamician" dell'Università, Centro di Studio di Elettrochimica Teorica e Preparativa, 40100 Bologna, Italy. Received July 2, 1984

Abstract: The binuclear and trinuclear [(NH₃)₅RuNCRu(bpy)₂CN]³⁺ [3,2] and [(NH₃)₅RuNCRu(bpy)₂CNRu(NH₃)₅]⁶⁺ [3,2,3] complexes were synthesized. The reduction at the pentaammineruthenium sites was studied chemically and electrochemically, and the visible and near-IR spectra of the [3,2] and [3,2,3] species and of their reduced forms [2,2], [3,2,2], and [2,2,2] were investigated. Several types of electronic transitions between the various low-energy redox sites of the ions were observed, including (i) Ru(II) → bpy charge transfer originating in the ruthenium atom of the Ru(bpy)₂ moiety, (ii) Ru(II) → bpy charge transfer originating in the ruthenium atoms of the pentaammine moieties, (iii) Ru(II) → Ru(III) intervalence transfer (IT) between cyano-bridged adjacent ruthenium atoms, and (iv) Ru(II) → Ru(III) IT between remote ruthenium atoms of the pentaammine units. All these transitions are present in the spectrum of the [3,2,2] ion. The various species were checked for emission or long-lived ($\tau > 50$ ns) transient absorption in laser flash photolysis. The results were negative, indicating that radiationless intramolecular electron-transfer processes are very efficient in these molecules.

In the last decade, particularly due to the work of Taube,² Meyer,³ and their associates,⁴ the chemistry and mixed-valence behavior of binuclear ruthenium complexes have been deeply and elegantly probed. When mainly Ru(NH₃)₅ⁿ⁺ ($n = 2, 3$) and Ru(bpy)₂²⁺ as building units and a variety of bridging ligands (especially diaza aromatics but also disulfides and dinitriles) were used, a large number of binuclear ruthenium complexes were synthesized and studied by these authors.⁴ Depending mainly on the type of bridging ligand, a wide range of degrees of delocalization was encountered in these complexes, going from limiting class III to class II Robin and Day⁵ behavior. In a few instances, the same authors have studied in detail^{6,7} or mentioned⁸ analogous trinuclear ruthenium species. These species are expected, and to some extent found,⁷ to exhibit a particularly rich mixed-valence behavior.

Previous work from this⁹⁻¹¹ and other^{12,13} laboratories has shown that *cis*-dicyanobis(2,2'-bipyridine)ruthenium(II), Ru(bpy)₂(CN)₂, can behave as a nitrile ligand toward a variety of aquo metal ions and metal complex moieties. We thought it worthwhile to take

advantage of this possibility to synthesize the trinuclear complex ion μ -[dicyanobis(2,2'-bipyridine)ruthenium]bis(pentaammineruthenium)(6+).



This complex may be viewed as an analogue of Taube's binuclear dinitrile complexes,¹⁴⁻¹⁶ having Ru(bpy)₂(CN)₂ as the bridging "ligand", or as an analogue of Meyer's trimeric complexes,⁶ having cyano instead of diaza aromatic bridges.

In the course of the work, we have also isolated the corresponding binuclear species



which is a cyano-bridged analogue of Meyer's unsymmetrical dimeric complexes.^{17,18}

We report here on the synthesis, the intervalence transfer behavior, and the intramolecular electron-transfer properties of these ions and of their one- and two-electron reduced forms.

Experimental Section

Materials. *cis*-Dicyanobis(2,2'-bipyridine)ruthenium(II)¹⁹ and chloropentaammineruthenium(III) chloride²⁰ were prepared by literature procedures. Ammonium hexachlororuthenate(IV) (Fluka), hexaammineruthenium(III) chloride (Johnson Matthey), europium(III) chloride (Schuchardt), chromium(III) chloride hexahydrate (Carlo Erba), ammonium hexafluorophosphate (Merck), and hydrazine hydrate (BDH) were commercial products of reagent grade. Spectrograde or-

- (1) (a) University of Ferrara. (b) University of Bologna.
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