# Articles

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Self-Assembling Trimolecular Redox Chains at Zeolite Y Modified Electrodes

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SnO$_2$ electrodes modified with a 2–4 monolayer thick coating of I bind a single dense layer of zeolite Y particles, presumably via siloxane linkages. The cationic silane and zeolite particles provide ion binding sites for multiply charged anions such as
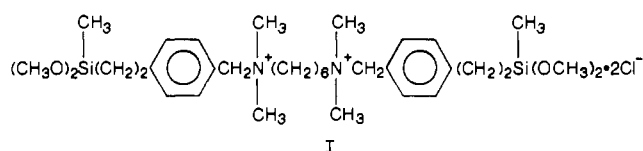

Fe(CN)$_6^{4-}$, large cations such as tris(2,2'-bipyridyl)osmium(II) and tris(1,10-phenanthroline)iron(II), and small cations such as trimethyl(ferrocenylmethyl)ammonium. Cyclic voltammetric data are consistent with occupation of sites within the zeolite framework by the small cations, occupation of zeolite outer surface sites by the large cations, and occupation of sites in the silane film by Fe(CN)$_6^{4-}$. The large cations situated on the zeolite outer surface are found to mediate all electron transfers to and from the smaller cations contained in the bulk.

Introduction

Synthetic molecular microstructures containing several redox-active components are interesting as mimics for natural photosynthetic systems. Covalently linked molecular triads containing carotenoid–porphyrin–quinone,[1] phenothiazine–ruthenium polypyridyl–viologen,[2] and amine–porphyrin–quinone[3] subunits have been shown to undergo efficient photochemical charge separation. The lifetimes of the charge-separated states in these triads are significantly longer than those found in the corresponding two-component systems (porphyrin–quinone[4] or ruthenium polypyridyl–viologen[5] molecules) because of greater spatial separation of the electron donor and acceptor components in the case of the triads.

While these molecules are interesting and potentially useful in artificial photosynthetic systems,[6] their synthesis is quite challenging. An alternative strategy for bringing together three redox-active molecular subunits in an ordered way that requires less synthetic effort is clearly desirable. In this paper we explore the use of zeolites to organize a chain of three redox-active molecules at an electrode surface. We show that molecular-level organization can be accomplished by self-assembly of three appropriate ions that differ in size and/or charge. The basic strategy for this synthesis is shown in Scheme I. An electrode with a reactive oxide surface (in this case SnO$_2$) is allowed to react with the cationic silane I. The functionalized electrode surface then
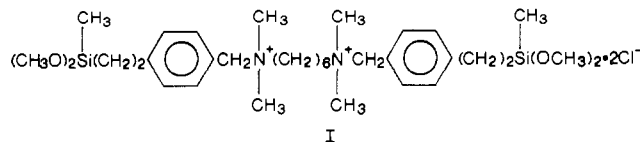
has free silanol groups that can bind a zeolite Y particle, presumably via siloxane linkages. The electrode-zeolite assembly is then immersed in a solution containing a multiply charged anion (such as Fe(CN)$_6^{4-}$), a large cation that is size-excluded from the anionic zeolite framework (a substitution-inert metal polypyridyl complex), and a small cation that can enter the framework (a

Scheme I
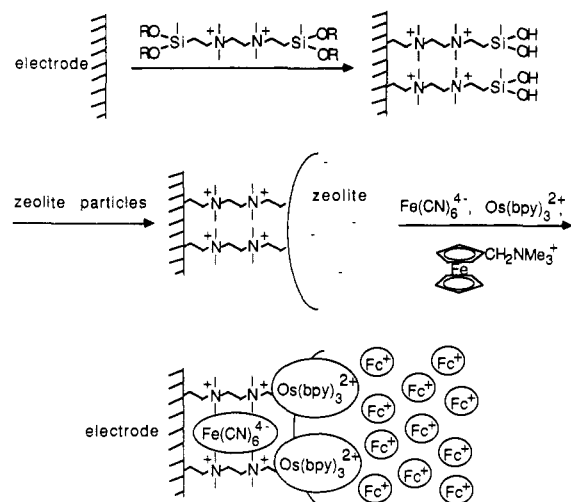
cationic metallocene). Electrochemical experiments show that the ions are spatially distributed as shown in Scheme I, with the

(1) (a) Gust, D.; Mathis, P.; Moore, A. L.; Liddel, P. A.; Nemeth, G. A.; Lehman, W. R.; Moore, T. A.; Bensasson, R. V.; Land, E. J.; Chachaty, C. *Photochem. Photobiol.* **1983**, *37S*, S46. (b) Moore, T. A.; Bust, D.; Mathis, P.; Mialocq, J. C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Diozi, D.; Liddell, P. A.; Nemeth, G. A.; Moore, A. L. *Nature (London)* **1984**, *307*, 630. (c) Gust, D.; Moore, T. A.; Bensasson, R. V.; Mathis, P.; Land, E. J.; Chachaty, C.; Moore, A. L.; Liddell, P. A.; Nemeth, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 3631. (d) Gust, D.; Moore, T. A. *J. Photochem.* **1985**, *29*, 173. (e) Gust, D.; Moore, T. A.; Liddell, P. A.; Nemeth, G. A.; Makings, L. R.; Moore, A. L.; Barrett, D.; Pessiki, P. J.; Bensasson, R. V.; Rougee, M.; Chachaty, C.; De Schryver, F. C.; Van der Auweraer, M.; Holzwarth, A. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 846.

(2) Danielson, E.; Elliot, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519.

(3) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562.

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large cation between the anion and the small cation; the latter do not communicate directly with the electrode. As in previously described zeolite-based systems that contain only two redox-active components,[7,8] we find that the large zeolite surface-bound cations mediate electron transfers to and from the smaller encapsulated cations.
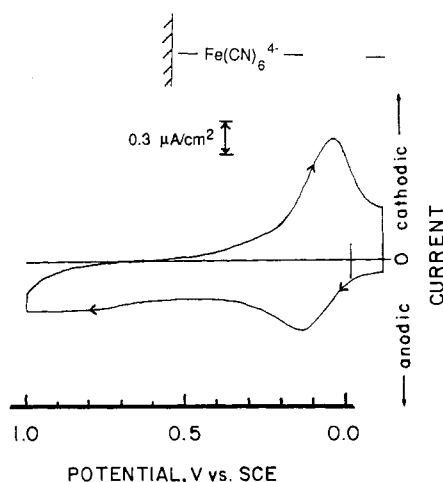
Experimental Section

Materials. Zeolite Y powder (LZ-Y-72) was obtained from Union Carbide, Linde Division. Trimethyl(ferrocenylmethyl)ammonium iodide ($FcCH_2NMe_3^+I^-$) was obtained from Strem Chemicals and used without purification. Tris(2,2′-bipyridine)osmium(II) perchlorate and tris(1,10-phenanthroline)iron(II) perchlorate were synthesized and purified according to literature procedures.[9] Acetonitrile (Fisher, HPLC grade) was distilled from P_2O_5 immediately before use. All other chemicals were of reagent grade quality and were obtained from commercial sources.

Synthesis of I. 1-(Methyldimethyloxysilyl)-2-(4-(chloromethyl)-phenyl)ethane was prepared by refluxing 1-(methyldichlorosilyl)-2-(4-(chloromethyl)phenyl)ethane (Petrarch Systems, 20 g) in 100 mL of trimethyl orthoformate (Aldrich) for 16 h. The product was purified by vacuum distillation; 14.0 g (54 mmol) was then refluxed under nitrogen in 150 mL of dry acetonitrile with 4.6 g (27 mmol) of N,N,N',N'-tetramethyl-1,6-hexanediamine (Aldrich) for 4 days. I was precipitated by addition of 100 mL of dry diethyl ether to the cooled solution. The product was filtered under nitrogen, washed with ether, and dried in vacuo. Proton NMR spectra confirmed that the precipitate was I. Elemental analysis for C, H, and N was performed by Atlantic Microlabs, Atlanta, GA. Anal. Calcd (found) for $C_{34}H_{62}N_2Si_2O_4Cl_2$: C, 59.20 (55.40); H, 9.00 (9.23); N, 4.06 (4.55).

Electrode Preparation, Functionalization, and Ion Exchange. SnO_2-coated glass ("Nesa" glass, PPG Industries) was cut into squares, cleaned, and made into electrodes as previously described.[7,8] Functionalization with I was accomplished by immersing the electrodes for 24 h in a 1 mM solution of I in dry acetonitrile at 23 °C. The electrodes were then transferred to a stirred suspension of ca. 1 μm diameter zeolite Y particles (0.1 g in 20 mL of acetonitrile), and the mixture was heated to 40 °C for 2 days. The electrodes were then removed from the suspension, dipped once in acetonitrile, and dried with a hot-air gun. SEM photographs show that a single dense layer of zeolite particles then covers 50–70% of the electrode surface. Ion exchange was carried out by immersing the electrode for several hours in 1–10 mM aqueous solutions of compounds containing the appropriate ions ($K_4Fe(CN)_6 \cdot 3H_2O$, Os-$(bpy)_3(ClO_4)_2$, $Fe(phen)_3(ClO_4)_2$, and/or $FcCH_2NMe_3^+I^-$). Under these conditions approximately (1–2) × 10^{-5} mol of $FcCH_2NMe_3^+$/g of zeolite is exchanged into the framework in bulk samples and (2–3) × 10^{-6} mol/g of $Os(bpy)_3^{2+}$ or $Fe(phen)_3^{2+}$ is exchanged onto the outer surface.[7]

Apparatus. UV–visible spectra of modified tin oxide–glass electrodes were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Electrochemical procedures used are described in ref 7. Cyclic voltammetry was carried out in aqueous 1 mM KH_2PO_4 solutions using a standard three-electrode configuration. This dilute electrolyte was used in order to prevent loss of electroactive ions from the electrode film during the electrochemical experiments. At the low current densities used in these experiments, iR drop was not a significant problem and was not compensated. All potentials are referred to the saturated calomel electrode (SCE). The electrode geometrical area was 0.20 cm^2 unless otherwise noted.

(4) (a) Bergkamp, M. A.; Dalton, J.; Netzel, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 253. (b) Netzel, T. L.; Bergkamp, A.; Chang, C.-K.; Dalton, J. *J. Photochem.* **1981**, *17*, 451. (c) Tabushi, I.; Koga, N.; Yanagita, M. *Tetrahedron Lett.* **1979**, 257. (d) Migita, M.; Okada, T.; Mataga, N. *Chem. Phys. Lett.* **1981**, *84*, 263. (d) Ho, T.-F.; McIntosh, A. R.; Bolton, J. R. *Nature (London)* **1980**, *286*, 254. (e) McIntosh, A. R.; Siemiarczuk, A.; Bolton, J. R.; Stillman, M. J.; Ho, T.-F.; Weedon, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 7215. (f) Siemiarczuk, A.; McIntosh, A. R.; Ho, T.-F.; Stillman, J. R.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 7224. (g) Joran, A. D.; Leland, B. A.; Beller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090. (h) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1082.

(5) (a) Elliott, C. M.; Freitag, R. A.; Blaney, D. D. *J. Am. Chem. Soc.* **1985**, *107*, 4647. (b) Elliott, C. M.; Freitag, R. A. *J. Chem. Soc., Chem. Commun.* **1985**, 156.

(6) Seta, P.; Bienvenue, E.; Moore, A. L.; Mathis, P. J.; Bensasson, R. V.; Liddell, P.; Pessiki, P. J.; Joy, A.; Moore, T. A.; Gust, D. *Nature (London)* **1985**, *316*, 653.

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(8) Li, Z.; Wang, C. M.; Persaud, L.; Mallouk, T. E. *J. Phys. Chem.* **1988**, *92*, 2592.

(9) Gaudiello, J. G.; Bradley, P. G.; Norton, K. A.; Woodruff, W. H.; Bard, A. J. *Inorg. Chem.* **1984**, *23*, 3.

Figure 1. Cyclic voltammetry in 1 mM aqueous KH_2PO_4 of an electrode functionalized with I and then zeolite Y and ion-exchanged overnight with 10 mM aqueous $K_4Fe(CN)_6$ (scan rate 10 mV/s).
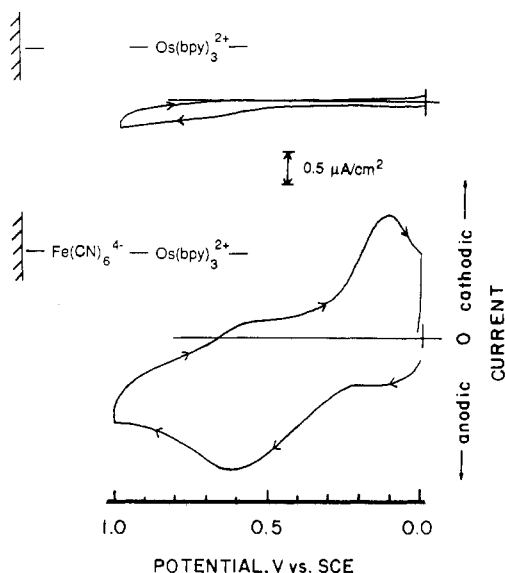
Results and Discussion

Attachment of Zeolite Y Particles to the Electrode Surface. The silane I binds to the SnO_2 surface to produce a coating (vide infra) a few monolayers thick. Most of the $SiOCH_3$ groups within the film are likely to be hydrolyzed and condensed to siloxane linkages in the derivatization step, but some free silanol groups presumably remain within the coating and are available to bind zeolite particles as shown in Scheme I. Since the outer surface of the silica-rich zeolite Y is also terminated by –SiOH groups, it is possible to form Si–O–Si linkages between the zeolite and the silane coating. The SnO_2 electrode is not likely to be smooth on the scale of the dimensions of I; however, the zeolite particle is very large on the scale of molecular dimensions and can have many points of attachment even on a microscopically rough surface. SEM photographs of electrodes modified according to Scheme I show a relatively dense single layer of zeolite particles on the electrode surface. The layer is sensitive to mechanical abrasion but is stable when subjected to manipulations required for ion exchange and electrochemistry, i.e. swirling in ion-exchange solutions or rinsing with a stream of water. No stable coatings of this type are formed if the silane derivatization step is omitted.

Electrochemistry. Functionalization of electrodes with I and then with zeolite Y yields a surface that persistently binds both electroactive anions and cations. Three specific ion binding sites exist: (1) an anion binding site, presumably associated with the cationic silane that forms a bridge between the electrode surface and the zeolite layer, (2) sites on the zeolite outer surface that bind size-excluded cations, and (3) sites within the zeolite framework that bind smaller cations. Figure 1 shows the cyclic voltammetry in 1 mM aqueous KH_2PO_4 of an electrode that was ion-exchanged with $Fe(CN)_6^{4-}$. A reversible wave corresponding to the surface-confined $Fe(CN)_6^{3-/4-}$ interconversion is observed. In this medium loss of $Fe(CN)_6^{3-/4-}$ via exchange with solution-phase $H_2PO_4^-$ ions is slow, and cycling for several hours has little effect on the height of the wave. Integration of charge passed in the anodic or cathodic wave at slow scan rates gives a surface coverage of (1–2) × 10^{-10} mol of $Fe(CN)_6^{4-}$/cm^2. Electroneutrality requires that each $Fe(CN)_6^{4-}$ be compensated by two silane molecules, and the surface coverage of the latter is therefore (2–4) × 10^{-10} mol/cm^2. The charge associated with this process is the same in 1 and 10 mM electrolyte solutions, so we assume that $Fe(CN)_6^{4-}$ ions have not exchanged significantly with electrolyte anions in the course of the experiment and occupy all the available anion exchange sites in the film. The silane coating is thus about 2–4 monolayers thick.[10] In this experiment the exchangeable cation sites associated with the zeolite are occupied by nonelectroactive cations from the electrolyte.

(10) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, p 191.

Figure 2. Cyclic voltammetry for (upper trace) an electrode ion-exchanged with 10 mM $Os(bpy)_3(ClO_4)_2$ and (lower trace) the same electrode after soaking 16 h in 1 mM $K_4Fe(CN)_6$ solution (scan rate 10 mV/s).
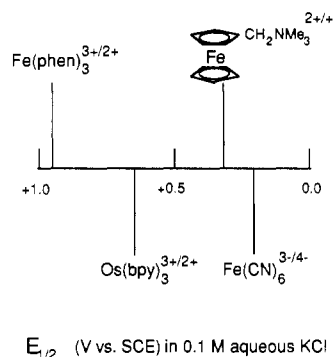
Chart I

$E_{1/2}$ (V vs. SCE) in 0.1 M aqueous KCl

Figure 2 shows cyclic voltammetry from an electrode equilibrated with $Os(bpy)_3^{2+}$ ions. In the upper trace (an electrode exchanged only with $Os(bpy)_3^{2+}$) no oxidation or reduction waves are observed in the vicinity of the $Os(bpy)_3^{3+/2+}$ potential. The $Os(bpy)_3^{2+}$ ions which are bound to the zeolite surface are sufficiently remote from the electrode surface that rapid electron transfer does not occur. The cationic silane bridge contains only nonelectroactive $H_2PO_4^-$ ions, which cannot mediate electron transfer between the electrode surface and $Os(bpy)_3^{2+}$.

When this electrode is immersed in 1 mM $K_4Fe(CN)_6$ solution and then reexamined in a blank electrolyte solution, waves corresponding to both the $Os(bpy)_3^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$ interconversions are seen (lower trace in Figure 2). The formal potentials of the $Os(bpy)_3^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$ couples are sufficiently far apart (Chart I) to prevent rapid mediated oxidation of $Os(bpy)_3^{2+}$ by $Fe(CN)_6^{3-}$. Therefore, the anodic wave peaked at +0.60 V vs SCE arises from direct oxidation of $Os(bpy)_3^{2+}$ at the electrode surface; likewise, the corresponding cathodic wave must come from direct electrode reduction of $Os(bpy)_3^{3+}$. We postulate that $Os(bpy)_3^{2+}$ is ion-paired with $Fe(CN)_6^{3-/4-}$ in the silane bridge and so is directly accessible to the electrode surface. Interestingly, the anodic wave at +0.60 V is much larger than the corresponding cathodic wave, while the cathodic wave at +0.15 V is much larger than its anodic partner. Similar effects were observed by Buttry et al., who examined pairs of electroactive cations incorporated in Nafion films.[11] Following their analysis, we attribute the large cathodic wave at +0.15 V to $Fe(CN)_6^{3-}$

(11) Buttry, D. A.; Saveant, J. M.; Anson, F. C. *J. Phys. Chem.* **1984**, *88*, 3086.
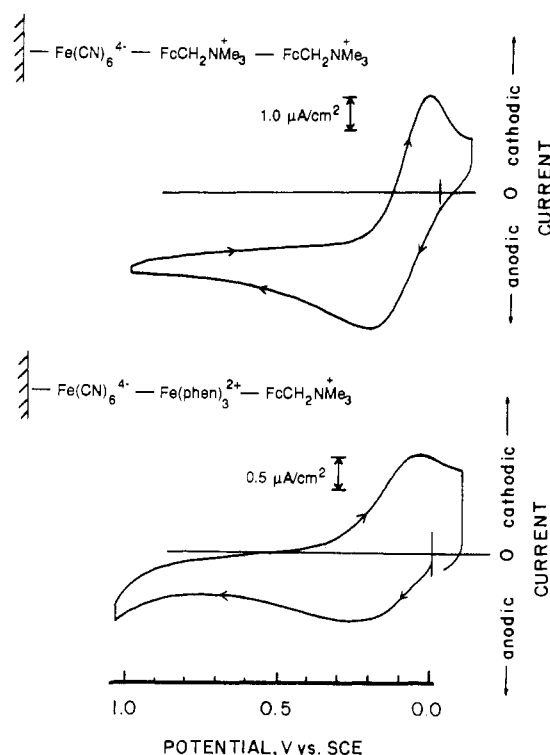
Figure 3. Cyclic voltammetry for an electrode soaked in 10 mM $FcCH_2NMe_3^+I^-$, 10 mM $K_4Fe(CN)_6$ solution: (upper trace) electrode in 1 mM aqueous K_2HPO_4 (scan rate 10 mV/s); (lower trace) the same electrode examined under identical conditions after soaking overnight in 1 mM $Fe(phen)_3(ClO_4)_2$.

reduction plus $Fe(CN)_6^{4-}$-mediated $Os(bpy)_3^{3+}$ reduction. Because the equilibrium constant for reaction 1 is approximately 10^8,

$$Fe(CN)_6^{4-} + Os(bpy)_3^{3+} \rightarrow Fe(CN)_6^{3-} + Os(bpy)_3^{2+} \quad (1)$$
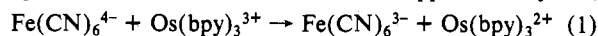
$Fe(CN)_6^{4-}$ generated at the electrode surface is efficiently consumed by $Os(bpy)_3^{3+}$. The cathodic wave at +0.15 V is enhanced because there is a fairly large reservoir of $Os(bpy)_3^{3+}$ ions on the zeolite surface and in the silane film. The corresponding anodic wave is smaller because it corresponds to oxidation of only $Fe(CN)_6^{4-}$. The unequal heights of the waves near the $Os(bpy)_3^{3+/2+}$ formal potential (+0.60 V) must have a different origin, since it is unlikely that $Os(bpy)_3^{3+}$ is mediating the oxidation of $Fe(CN)_6^{4-}$, the latter being confined to the thin silane film. It seems more reasonable that $Os(bpy)_3^{3+}$ formed on the anodic sweep binds strongly to the zeolite surface and so is not available for direct reduction. The bulk of these ions are reduced at the $Fe(CN)_6^{3-/4-}$ potential via reaction 1.

Figure 3 shows cyclic voltammetry for electrodes that have been exchanged with $FcCH_2NMe_3^+$ and $Fe(CN)_6^{4-}$. The $FcCH_2NMe_3^+$ ion is small enough to enter the zeolite Y framework and has a formal potential near that of the $Fe(CN)_6^{3-/4-}$ couple. When only these two ions are exchanged onto the electrode surface (upper trace in Figure 3), a broad anodic wave attributed to oxidation of bulk $FcCH_2NMe_3^+$ is seen. We postulate that the $FcCH_2NMe_3^+$ ions must be present not only in the bulk of the zeolite particles but also on their outer surface and that the oxidation is mediated by the $Fe(CN)_6^{3-/4-}$ couple according to reaction 2. When $Fe(phen)_3^{2+}$, which is not electroactive in the

$$Fe(CN)_6^{3-} + FcCH_2NMe_3^+ \rightleftharpoons Fe(CN)_6^{4-} + FcCH_2NMe_3^{2+} \quad (2)$$
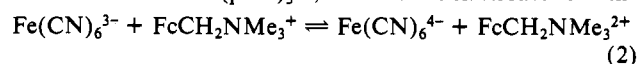
region of the $Fe(CN)_6^{3-/4-}$ interconversion, is added to occupy the zeolite surface sites, reaction 2 is blocked and only the surface $Fe(CN)_6^{3-/4-}$ waves are seen (lower trace in Figure 3). Ion exchange with $Fe(phen)_3^{2+}$ removes $FcCH_2NMe_3^+$ from the zeolite surface cation exchange sites. $FcCH_2NMe_3^+$ is then confined to the bulk of the zeolite and is not accessible for rapid electron exchange with either the electrode surface or with $Fe(CN)_6^{3-}$ ions in the silane bridge.
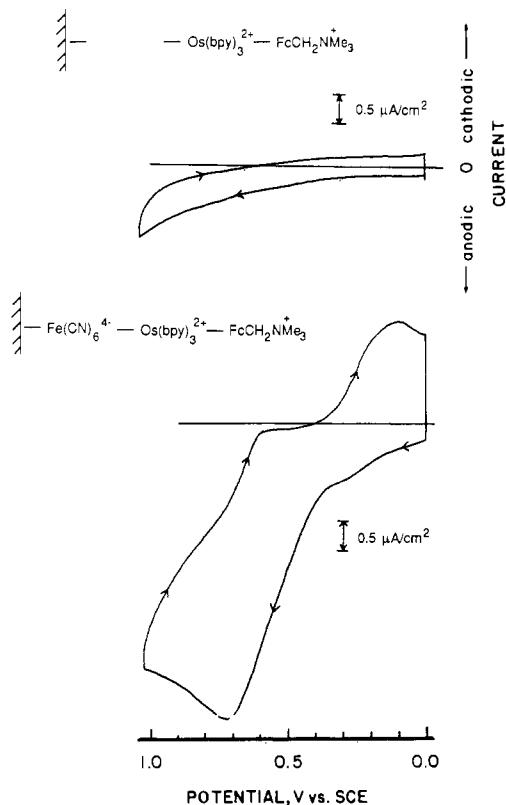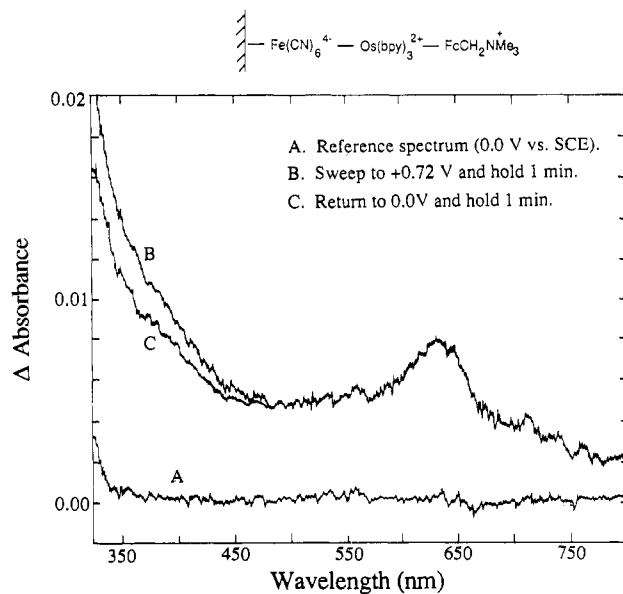
Figure 4. Cyclic voltammetry for (upper trace) an electrode ion-exchanged with 10 mM $FcCH_2NMe_3^+I^-$, 10 mM $Os(bpy)_3(ClO_4)_2$ and (lower trace) the same electrode soaked 16 h in 1 mM $K_4Fe(CN)_6$ (scan rate 10 mV/s).

Additional evidence that the zeolite surface cations mediate the oxidation of $FcCH_2NMe_3^+$ ions contained within the zeolite comes from cyclic voltammetry shown in Figure 4 and associated UV–visible spectra in Figure 5. In the upper trace of Figure 4, an electrode exchanged with $FcCH_2NMe_3^+$ and $Os(bpy)_3^{2+}$ shows no electrochemistry in the range 0–1 V. Neither cation is accessible for oxidation at the electrode surface. When the same electrode is equilibrated with $Fe(CN)_6^{4-}$ ions and then reexamined (lower trace), two sets of anodic and cathodic waves are seen. The situation is comparable to that shown in Figure 2, where zeolite surface bound $Os(bpy)_3^{2+}$ became accessible to the electrode through ion pairing with $Fe(CN)_6^{3-/4-}$. In Figure 4 we note, however, that the anodic wave near the $Os(bpy)_3^{3+/2+}$ potential is greatly enhanced. The $Os(bpy)_3^{3+}$ ions produced at the electrode surface are oxidizing $FcCH_2NMe_3^+$ ions via reaction 3. This
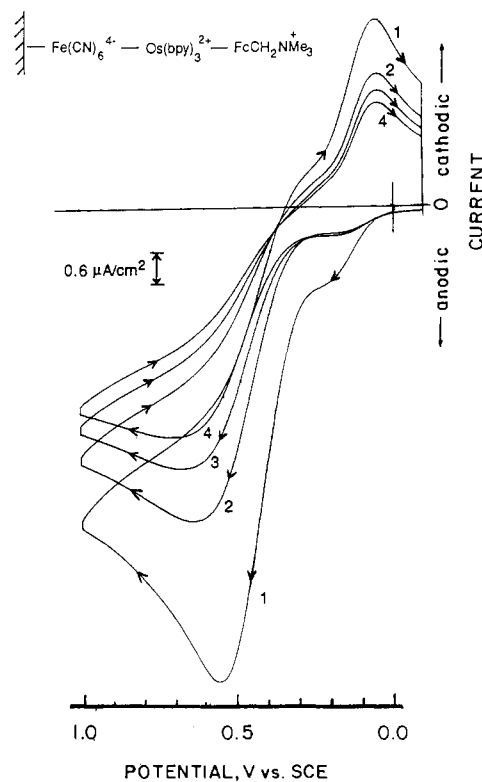
$$Os(bpy)_3^{3+} + FcCH_2NMe_3^+ \rightarrow Os(bpy)_3^{2+} + FcCH_2NMe_3^{2+}$$

$$(3)$$

reaction is irreversible because of the ca. 300-mV separation of the $Os(bpy)_3^{3+/2+}$ and $FcCH_2NMe_3^{2+/+}$ formal potentials, so there is little reduction current on the return sweep near the $Os(bpy)_3^{3+/2+}$ potential.

Figure 5 shows UV–visible spectra taken in transmission with an electrode containing $Fe(CN)_6^{4-}$, $Os(bpy)_3^{2+}$, and $FcCH_2NMe_3^+$. In this experiment the reference spectrum is recorded at 0.0 V, i.e., with all three ions in their reduced form. The electrode is stepped abruptly to +0.78 V (past the large anodic wave of Figure 4) and held 1 min, whereupon the spectrum in Figure 5B is recorded. The absorbance maximum at 640 nm corresponds[12] to conversion of $(1-2) \times 10^{-8}$ mol of $FcCH_2NMe_3^+$ to $FcCH_2NMe_3^{2+}$ per cm^2. It is clear that almost all of the current passed in this process arises from this oxidation, since there are no absorbance changes which can be attributed to $Os(bpy)_3^{2+}$

(12) In making this calculation, we assume a molar extinction coefficient for $FcCH_2NMe_3^+$ similar to that of Fc^+, 360 M^{-1} cm^{-1}, as recorded by: Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125.

Figure 5. Transmission UV–visible spectra of a zeolite Y modified SnO_2 electrode ion-exchanged with $FcCH_2NMe_3^+$, $Os(bpy)_3^{2+}$, and $Fe(CN)_6^{4-}$: (A) reference spectrum, recorded at 0.0 V vs SCE; (B) spectrum for the electrode stepped to +0.78 V and held 1 min; (C) spectrum for the electrode stepped back to 0.0 V and held 1 min.

Figure 6. Repetitive scans for an electrode ion-exchanged with $FcCH_2NMe_3^+$, $Os(bpy)_3^{2+}$, and $Fe(CN)_6^{4-}$. The initial potential was –0.10 V vs SCE, and the electrode was held for 3 min at –0.10 V between scans (scan rate 10 mV/s).

oxidation. When the electrode is returned to 0.0 V and held 1 min, the $FcCH_2NMe_3^{2+}$ absorbance is not diminished. This is consistent with the enormous difference in anodic and cathodic charges passed in Figure 4. $Os(bpy)_3^{2+}$ is not a sufficiently strong reducing agent to mediate the reduction of zeolite-encapsulated $FcCH_2NMe_3^{2+}$, so the oxidizing equivalents are trapped within the zeolite. Repetetive scans (Figure 6) recorded at 3-min intervals give progressively smaller anodic currents, because less $FcCH_2NMe_3^{2+}$ is available for mediated oxidation.

Interestingly, the large anodic wave in Figures 4 and 6 onsets near the $Os(bpy)_3^{3+/2+}$ potential, consistent with mediated oxi-

dation via reaction 3; there is no evidence for direct $FcCH_2NMe_3^+$ oxidation or for $Fe(CN)_6^{3-}$-mediated oxidation via reaction 2. The picture is therefore like that of the $Fe(CN)_6^{4-}$–$Fe(phen)_3^{2+}$–$FcCH_2NMe_3^+$ triad (Figure 3), where the large zeolite surface cations ($Fe(phen)_3^{2+}$ or $Os(bpy)_3^{2+}$) block direct communication between $Fe(CN)_6^{3-}$ ions contained in the silane bridge and $FcCH_2NMe_3^+$ ions within the zeolite framework. Electron transfer between the zeolite surface and zeolite bulk ions (reaction 3) is nevertheless fast on the time scale of the electrochemical experiment, as evidenced by the large anodic wave near the $Os(bpy)_3^{3+/2+}$ potential. A picture consistent with the data then is oxidation of bulk $FcCH_2NMe_3^+$ ions by zeolite surface $Os(bpy)_3^{3+}$ ions; the latter are reoxidized via $Os(bpy)_3^{3+}$ ions in the silane bridge. Coverage of the zeolite surface by $Os(bpy)_3^{3+/2+}$ ions must be reasonably complete in order to block mediated oxidation via reaction 2.

Conclusions

Electrochemical data provide evidence for structural organi-

zation of molecular triads that self-assemble via ion-exchange reactions at a zeolite Y modified electrode. While the situation is complicated by ion pairing of some of these multiply charged ions, the data consistently show that electrons can be exchanged with zeolite bulk cations only via the intermediacy of redox levels of the zeolite surface ions. It is particularly interesting that rapid electron exchange between ions on either side of this zeolite surface layer does not occur; such exchange represents the short-circuiting or back-electron-transfer pathway in photochemically active molecular triads.[1-3] Experiments involving zeolite surface ions that are good photosensitizers, with donor and acceptor ions exchanged into the silane bridge and zeolite bulk sites, are presently in progress.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Syntheses and Crystal Structures of Syn and Gauche Isomers of the Chloride-Bridged Face-Sharing Bioctahedral Molybdenum(III) Dimers [PHMe3][Mo2Cl7(PMe3)2]

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The reaction of $Mo_2Cl_4(PMe_3)_4$ and $2PhICl_2$ yields the compound $[PHMe_3][Mo_2Cl_7(PMe_3)_2]$, in which the anion is the syn conformer with respect to the arrangement of the two terminal tertiary phosphine ligands. Two crystalline forms containing this syn conformer, **1** and **2**, are reported. The equilibration of the syn and gauche conformers has been monitored by ^1H NMR spectroscopy and is found to involve phosphine dissociation. Solutions of these two forms eventually attained the statistically expected 1:2 (syn:gauche) ratio ($k_1 = 1.09 \times 10^{-4} s^{-1}$, $k_{-1} = 5.43 \times 10^{-5} s^{-1}$ in CD_2Cl_2 at 293 K), and from such solutions single crystals of the gauche isomer were obtained. Crystal data: compound **1** (syn conformer, from CH_2Cl_2), triclinic, space group $P\bar{1}$, $a = 13.271$ (2) Å, $b = 17.855$ (3) Å, $c = 11.418$ (2) Å, $\alpha = 107.18$ (1)°, $\beta = 101.13$ (2)°, $\gamma = 93.82$ (1)°, $V = 2513.8$ (8) Å^3, $Z = 4$, $R = 0.041$ ($R_w = 0.066$) for 379 parameters and 4621 unique data having $F_o^2 > 3\sigma(F_o^2)$; compound **2** (syn conformer, from CH_2Cl_2/hexane), orthorhombic, space group $Pnma$, $a = 28.098$ (6) Å, $b = 10.140$ (1) Å, $c = 9.839$ (2) Å, $V = 2803.4$ (9) Å^3, $Z = 4$, $R = 0.079$ ($R_w = 0.103$) for 115 parameters and 1091 unique data having $F_o^2 > 3\sigma(F_o^2)$; compound **3** (gauche conformer, from acetone-d_6), monoclinic, space group $P2_1/n$, $a = 10.888$ (2) Å, $b = 20.633$ (2) Å, $c = 11.375$ (1) Å, $\beta = 106.86$ (1)°, $V = 2445.4$ (7) Å^3, $Z = 4$, $R = 0.022$ ($R_w = 0.031$) for 302 parameters and 3764 unique data having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Several edge-sharing bioctahedral complexes of molybdenum having the stoichiometry $Mo_2Cl_6(PP)_2$ (PP = bidentate tertiary phosphine) are known,[1] but analogues containing monodentate tertiary phosphines ($Mo_2Cl_6(PR_3)_4$) have not been discovered up to this time. The trimethylphosphine derivative was considered to be of great interest as it would allow a comparison with the known and structurally characterized homologues $Cr_2Cl_6(PMe_3)_4$[2] and $W_2Cl_6(PMe_3)_4$.[3] This report describes the chlorination of the quadruply bonded molybdenum dimer $Mo_2Cl_4(PMe_3)_4$.[4] This was undertaken with the goal of synthesizing $Mo_2Cl_6(PMe_3)_4$, since the homologous bidentate tertiary phosphine complexes just mentioned had been synthesized in this manner. To our surprise, this reaction resulted instead in the formation of a compound containing a face-sharing bioctahedral complex, $[PHMe_3]$-$[Mo_2Cl_7(PMe_3)_2]$, with the two terminal tertiary phosphines in a syn arrangement. This result is similar to that obtained in the reaction of $Mo_2I_4(PMe_3)_4$ and I_2, where the iodide analogue $[PHMe_3][Mo_2I_7(PMe_3)_2]$ was produced.[5]

The syn complex was found to crystallize in two different forms, triclinic and orthorhombic, depending on the conditions under which the crystals grew. Further, solutions of the syn complex slowly equilibrated with the gauche conformer, finally attaining a statistical ratio of syn:gauche equal to 1:2 over a period of 2 days. Crystals of the gauche conformer suitable for single-crystal X-ray diffraction were obtained from this acetone-d_6 solution. The addition of PMe_3 was found to slow down this process, indicating a dissociative mechanism for the isomerization. The single-crystal X-ray structures of each of the compounds containing the syn geometric isomer and the first structural report of a gauche conformer are reported in this paper.

Experimental Section

General Data. All manipulations were carried out under an atmosphere of argon. Solvents apart from dichloromethane were dried over sodium/potassium alloy and distilled under nitrogen before use. Dichloromethane was dried over and distilled from phosphorus pentoxide. $Mo_2Cl_4(PMe_3)_4$ was prepared from the reaction of $Mo_2(\mu\text{-}O_2CCH_3)_4$, Me_3SiCl, and PMe_3 in refluxing benzene according to similar reported preparations,[1a] and $PhICl_2$ was prepared according to a literature method.[6] The ^1H NMR spectra were recorded by using Varian XL-200 and XL-400 spectrometers. ^{31}P NMR spectra referenced to 85% H_3PO_4 were recorded at 81 MHz by using a Varian XL-200. The microanalysis was done by Galbraith Laboratories, Inc., Knoxville, TN.

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