Table II. Electrochemical and Spectroscopic Characteristics of the Os–Co Dimer and of Os and Co Monomers Containing Bipyridyl Ligands

complex	EPR[a] *g* value	$E_{1/2}$,[b] V vs. SCE	electronic abs[c] λ_{max}, nm (log ϵ)
I	1.998	0.617 0.314	648 (3.56), 551 (3.63), 481 (4.07), 442 (4.04), 384 (3.99), 363 (4.02), 303 (3.99), 291 (4.98), 252 sh, 243 (4.81)
IIa	silent[d]	0.597	648 (3.50), 551 (3.61), 481 (4.00), 442 (4.01), 384 (4.00), 363 (4.02), 291 (4.73)
IIIa	1.998	0.304	303 (3.99), 291 (4.80), 252 sh, 241 (5.00)
IIIb	silent	0.300	423 (1.26), 319 (4.47), 306 (4.51), 222 (5.00[e])
$Co(bpy)_3^{2+}$	4.35[f]	0.241[f]	300 (4.62)[e–g]
$Co(bpy)_3^{3+}$	silent	0.241[f]	454 (1.82), 345 (3.14), 307 (4.48), 244 (4.80)[e,f]
$Os(bpy)_3^{2+}$		0.81[h]	
2,2′-bipyridine			282 (4.08), 236 (3.95)[e]

[a] EPR spectra were recorded in the solid state at room temperature as well as in frozen dimethyl sulfoxide (−77 K) at 9.018 GHz. 2,2-Diphenyl-1-picrylhydrazyl hydrate was used as a standard. [b] Electrochemical system used: Pt-disk working electrode, Pt-wire auxiliary electrode, and saturated calomel reference electrode. Experiments were performed under nitrogen at 25 °C in acetonitrile in the presence of 0.1 M tetra-*n*-butylammonium perchlorate. [c] Spectra were recorded (Cary 210 spectrophotometer) at 25 °C in 0.10 M HCl unless otherwise noted. [d] "Silent" refers to the observation that no EPR signal was observed in the solid state nor at −77 K in dimethyl sulfoxide. [e] Aqueous solution. [f] Similar properties were observed in this work under the same experimental conditions as noted. EPR: (i) Schrauzer, G. N.; Lee, L.-P. *J. Am. Chem. Soc.* **1968**, *90*, 6541. (ii) Mizuno, K.; Imamura, S.; Lunsford, J. H. *Inorg. Chem.* **1984**, *23*, 5310. Electrochemistry: (i) Tanaka, N.; Sato, Y. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2059. (ii) Margel, S.; Smith, W.; Anson, F. C. *J. Electrochem. Soc.* **1978**, *125*, 241. [g] Simic, M. G.; Hoffman, M. Z.; Cheney, R. P.; Mulazzani, Q. G. *J. Phys. Chem.* **1979**, *83*, 439. [h] Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383.

erates the Os(III)–Co(II) dimer, which, in a slow intramolecular electron transfer step ($k_{intra} = 7.2 \times 10^{-5}\ s^{-1}$), produces the more thermodynamically stable Os(II)–Co(III) dimer.[13] The overall reaction sequence is

$$Os^{II}–Co^{II} \xrightarrow{Ce(IV)} Os^{III}–Co^{II} \xrightarrow{k_{intra}} Os^{II}–Co^{III}$$

The second reaction in this process is clearly shown to be *intra*molecular on the basis of (a) the lack of concentration dependence of the electron transfer rate[13] and (b) the determination of the rate of *inter*molecular electron transfer between the appropriate mononuclear complexes (IIb, IIIa).[6,15]

The rate reported herein for a system of known electrochemical driving force ($\Delta E_{1/2}$ = 300 mV) is within the same order of magnitude as the intramolecular electron transfer rates estimated by Anderes and Lavallee[3] in a dicyanobicyclo[2.2.2]octane-bridged Co(III)–Ru(II) dimer ($k_{intra} < 3 \times 10^{-6}\ s^{-1}$) and measured by Isied and Vassilian[4] in a proline-bridged Co(III)–Ru(II) dimer ($k_{intra} = 10.4 \times 10^{-5}\ s^{-1}$). In contrast to the rather slow rates of intramolecular electron transfer observed in these three dinuclear metal systems, Miller, Calcaterra, and Closs[16] have observed extremely rapid (10^5–$10^9\ s^{-1}$) intramolecular rates involving strongly reducing organic free radicals. As recently discussed by Sandrini et al.,[14] numerous factors contribute to the slow rates of electron transfer of Co complexes as in the dinuclear metal systems. Nonetheless, it is clear that more work with both metal- and free-radical-containing systems will be necessary to determine the effect of distance on the rates of intramolecular electron transfer. For studying such reactions between metals, the approach outlined here has the distinct advantage that it can easily be extended to completely rigid bridging dioxime ligands having variable Os–Co separations. In addition, the reduction potentials of both metals and therefore the driving force can be readily varied by addition of substituents on the bipyridyl ligands. A systematic study of the rate of thermal *intra*molecular electron transfer between metals across a nonconjugated barrier as a function of the distance of separation and of the electrochemical driving force is now possible.

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Registry No. I, 96041-27-9; I(Os^{II}–Co^{III},Os^{III}–Co^{II}), 96041-33-7; IIa, 96041-30-4; IIb, 96041-32-6; IIIa, 96041-28-0; IIIb, 96041-31-5; [*cis*-$(bpy)_2OsCl(H_2O)]^+$, 96041-29-1; [*cis*-$(bpy)_2CoI_2]I$, 96148-96-8.

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(13) Kinetics experiments were performed in 0.2 M HCl at 25 °C. Absorbance measurements were begun 1 min after addition of 1 equiv of Ce(IV) to I in solution. Rate constants were determined from the slope of the linear least-squares fit of log $(A_\infty - A_t)_{442nm}$ vs. time. The reaction was followed in a concentration range of 1.00×10^{-5} to 7.41×10^{-5} M in I and was found to be first order with respect to [I]. The rate constants obtained from duplicate experiments at each of six concentrations of I ranged from 6.99×10^{-5} to $7.31 \times 10^{-5}\ s^{-1}$. The reactions were followed for at least 3 half-lives.

(14) Sandrini, D.; Gandolfi, M. T.; Maestri, M. Bolletta, F.; Balzani, V. *Inorg. Chem.* **1984**, *23*, 3017 and references therein.

(15) For the *inter*molecular experiments, the Os(III) complex (IIb) was generated in 0.20 M HCl by addition of 1 equiv of Ce(IV). The reaction between IIb and IIIa followed second-order kinetics where rate = k_{inter}[Os(III)–dioxime][Co(II)–dioxime] (25 °C, μ = 0.10 M (LiCl)). The rate constant determined was $5.09 \times 10^{-4}\ M^{-1}\ s^{-1}$. From the values of k_{intra} and k_{inter}, it is possible to calculate that at the concentration of I used in our experiments[13] (<10^{-4} M), intermolecular electron transfer contributes less than 2% to the observed rate.

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Hydroxide-Induced Reduction of (Tetraphenylporphinato)iron(III) in Pyridine

Sir:

In a recent investigation of the effects of axial ligands and solvents upon the electrochemistry for iron(III) porphyrins, we were surprised to find that the addition of hydroxide ion to a pyridine solution caused the iron(III) center to be reduced to iron(II).[1] Although our initial inclination was to attribute this base-induced reduction to impurities in the pyridine, the phenomenon has been confirmed after careful purification of reagents and has been observed in other workers' laboratories.[2,3] This has prompted a systematic study of the essential elements for the redox process.

Figure 1 illustrates the cyclic voltammograms for (*meso*-tetraphenylporphinato)iron(III) ($Fe^{III}TPP^+$) in dimethyl sulfoxide (Me_2SO) and in pyridine (Figure 1A,C). For solutions of $Fe^{III}TPP^+$ in Me_2SO the addition of OH^- results in axial binding

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(1) Jones, S. E.; Srivatsa, G. S.; Sawyer, D. T.; Traylor, T. G.; Mincey, T. C. *Inorg. Chem.* **1983**, *22*, 3903.

(2) Caughey, W. S., private communication, Department of Biochemistry, Colorado State University, 1983.

(3) Kadish, K. M., private communication, Department of Chemistry, University of Houston, 1984.

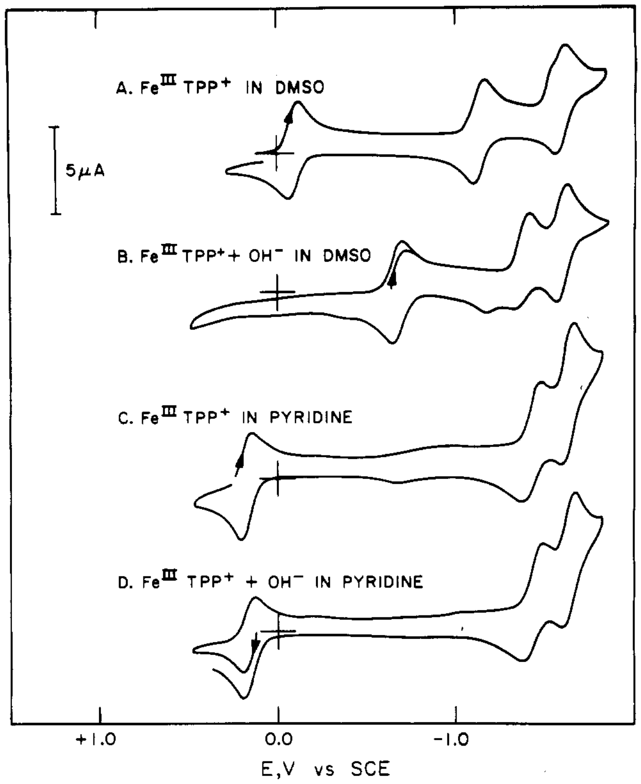


Figure 1. Cyclic voltammograms for 1 mM solutions of $Fe^{III}TPP(Cl)$ (A) in dimethyl sulfoxide (Me_2SO) and (C) in pyridine. Curves B and D are for solutions that also contain 1 mM tetraethylammonium hydroxide (25% in MeOH, Eastman). Each solution contained 0.1 M tetraethylammonium perchlorate as supporting electrolyte. Conditions: platinum electrode, area 0.033 cm^2; scan rate 0.1 V s^{-1}.

to the metal center. This causes the reduction peak potential ($E_{p,c}$) for the Fe^{III}/Fe^{II} couple to shift from −0.21 to −0.70 V vs. SCE (Figure 1B). The increase in electron density due to the axial OH^- group also causes the subsequent reduction to occur at more negative potentials.[1] In contrast, the addition of OH^- to $Fe^{III}TPP(py)_2^+$ in pyridine results in the immediate reduction of the metal center (Figure 1D). This solution, which exhibits an optical spectrum that is identical with that for $Fe^{II}TPP(py)_2$, is ESR silent and is resistant to air oxidation. The order of addition of reagents does not affect the results, and there is no evidence for the formation of the $(\mu\text{-O})(Fe^{III}TPP)_2$ species.[4] If *N*-methylimidazole is used as the solvent, analogous OH^--induced reduction of $Fe^{III}TPP(Me\text{-}im)_2^+$ occurs.

The voltammetric peak current for the oxidation of 1 mM $Fe^{II}TPP$ in pyridine is 3.4 μA (Figure 1). The addition of sufficient tetraethylammonium hydroxide to give a concentration of 1 mM OH^- causes the $Fe^{II}TPP(py)_2$ peak current to increase to 3.9 μA; 4 mM OH^- gives an irreversible 4.8-μA peak and 7 mM OH^- an irreversible 8.4-μA peak. Such an enhancement of anodic current (accompanied by irreversibility) indicates that the $Fe^{II}TPP(py)_2/Fe^{III}TPP(py)_2^+$ electron-transfer process catalyzes the oxidation of axially bound pyridine.

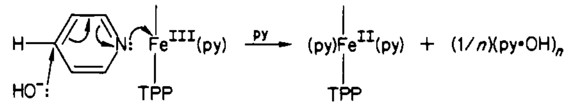
Addition of OH^- to $Fe^{III}TPP^+$ in mixtures of pyridine and dimethylformamide (DMF) produces mixtures of $Fe^{III}TPP(OH^-)$ and $Fe^{II}TPP$ (on the basis of their cyclic voltammetry and UV-vis spectra). The product composition ranges from 100% $Fe^{III}TPP(OH^-)$ in pure DMF to 100% $Fe^{II}TPP(py)_2$ in pure pyridine. The addition of OH^- to higher concentrations of $Fe^{III}TPP(Cl)$ (10 mM) in pyridine results in the partial formation of $Fe^{III}TPP(OH^-)$ (confirmed by electrochemistry, UV-vis spectra, and ESR). With $Fe^{III}TPP^+ClO_4^-$ in pyridine the addition of OH^- gives a quantitative yield of $Fe^{II}TPP(py)_2$ (due to the facile displacement of ClO_4^- by pyridine, which facilitates electron transfer from OH^- to the iron(III) center). The reaction rate for the latter system is fast and appears to be limited by the mixing time (on the basis of rotated ring-disk voltammetry). The reaction rate is unaffected by the exclusion of light and/or oxygen.

Within an ESR cavity, the OH^-–$(py)_2Fe^{III}TPP^+$ reaction does not produce a meaningful signal for an organic radical. (This is not surprising because pyridine radicals are short lived and yield oligomers.) Direct analysis of the product solution by mass spectrometry (EI) gives numerous low-mass ions plus significant *m/z* peaks that are consistent with three- and four-unit oligomers (or polymer fragments with $n \geq 6$) for the py·OH adduct. When the immobile spot from a TLC separation of the product solution is analyzed by GC–MS (EI), a significant peak at *m/z* 97 is observed for a late-eluting peak. Such an ion is consistent with the two-proton adduct of the py·OH dimer.

When OH^- is added to acetonitrile solutions of tris(phenanthroline)iron(III) perchlorate and tris(bipyridyl)iron(III) perchlorate, both complexes are reduced to their iron(II) states. Again, this appears to be a OH^--induced reduction of the Fe(III) center via a bound pyridine-like ligand.

Although reduction of iron(III) porphyrins by piperidine,[5] cyanide,[6] *n*-hexanethiol,[7] and tributylphosphine[7] has been observed previously, each of these systems requires direct electron transfer from the ligand. Several other examples of iron(III)–porphyrin reductions in pyridine have been described[7-10] but have not invoked OH^- as the reducing agent. The extent of the reduction by pyridine is minimal (as shown by Mössbauer[8] and electrochemical data), but the addition of equimolar OH^- results in the stoichiometric production of Fe(II)–porphyrin.

The direct transfer of an electron from OH^- to $Fe^{III}TPP^+$ is not possible on thermodynamic grounds[1] (stable solutions of $Fe^{III}TPP(OH^-)$ are formed in Me_2SO, DMF, CH_2Cl_2, and 2,6-dimethylpyridine). However, the present results provide compelling evidence that iron(III), via a bound pyridine as a transfer agent, is reduced by electron transfer from a hydroxide ion. A reasonable reaction scheme that is consistent with the results and previous ligand-induced reductions[6,7] involves nucleophilic attack by OH^- on the C-4 carbon of a bound pyridine



(1)

where the iron(III) center induces an enhanced degree of electrophilicity at the C-4 carbon center. The addition of OH^- to the C-4 carbon promotes electron transfer from the pyridine nitrogen to iron(III). The resultant oxidized hydroxy-pyridine (py·OH) appears to be equivalent to the addition product from the reaction of hydroxyl radical (·OH) with pyridine[11,12]

$$\cdot OH + py \xrightarrow{k = 3 \times 10^9\ M^{-1}\ s^{-1}} (1/n)(py\cdot OH)_n \qquad (2)$$

which produces a brown-bronze diamagnetic polymer that is inert and is without significant UV–visible spectra.[12] Other possible products from the oxidized pyridine–hydroxide adduct include 4-pyridone, 2-pyridone, 2,2′- and 4,4′-bipyridine, and pyridine *N*-oxide. However, none of these compounds are detected in the product solutions (TLC, HPLC, and GC–MS). The MS results

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(4) $Fe^{II}TPP$ in the presence of OH^- is stable in Me_2SO, DMF, and pyridine. In DMF, $Fe^{II}TPP$ is oxidized to $(\mu\text{-O})(Fe^{III}TPP)_2$ if O_2 is leaked into the system before the addition of OH^-. In the absence of O_2 the only product from the addition of OH^- to $Fe^{II}TPP$ in DMF is $Fe^{II}TPP(OH^-)$.

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indicate the presence of (py·OH) oligomers in the product solutions.

The present results indicate that the iron(III) center must have a pyridine-like ligand for a hydroxide-induced electron transfer to occur (eq 1). This is confirmed by the failure of OH^- to induce the reduction of $Fe^{III}TPP^+$ in a 2,6-dimethylpyridine solution. Although a pyridine-like solvent, it is unable to bind to the iron(III) center because of steric hindrance.[13]

The reduction of Fe(III)–porphyrins by piperidine[5] or *n*-hexanethiol[7] is not feasible on thermodynamic grounds[14] and requires activation by deprotonation, either by base or by displacement of the protons by a good Lewis acid such as ferric ion. The hydroxide-induced reduction via pyridine, on the other hand, occurs by nucleophilic addition of OH^- to the aromatic ring. Although the net reaction (eq 1) is similar to that for other ligand-induced reductions of Fe(III)–porphyrins,[6,7] the activation of bound pyridine by OH^- to produce a strong reducing agent is unique.

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Registry No. $Fe^{III}TPP^+Cl^-$, 14187-12-3; $Fe^{III}TPP(py)_2{}^+$, 60542-64-5; $Fe^{II}TPP(py)_2$, 16999-25-0; $Fe^{III}TPP(Me\text{-}im)_2{}^+$, 52155-25-6; $Fe^{III}TPP(OH^-)$, 25482-26-2; $Fe^{II}TPP$, 16591-56-3; $Fe^{III}TPP^+ClO_4{}^-$, 59370-87-5; OH^-, 14280-30-9; (phenanthroline)iron(III) perchlorate, 14634-90-3; tris(bipyridyl)iron(III) perchlorate, 15388-50-8.

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(14) Unpublished electrochemical data.

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Synthesis of the Dinuclear Manganese(I) Species $[Mn_2(CO)_6(SPh)_3]^-$ and Its Oxidation to a Mixed-Valent Dimanganese(I,II) Complex

Sir:

Recently we described[1] the reactions of $Mo(CO)_6$ with alkane- and arenethiolates to yield the dinuclear Mo(0) species $[Mo_2(CO)_8(SR)_2]^{2-}$. These compounds were remarkable in that, although relatively simple in nature and in method of preparation, they had not been previously reported and also because they displayed a reversible two-electron oxidation in a single step. This latter behavior was attributed to metal–metal bond formation accompanied by structural rearrangement in the Mo(I) product $Mo_2(CO)_8(SR)_2$ to maintain an 18-electron configuration about each Mo. In an attempt to extend this type of chemistry to other metal systems, we have begun a study of the reactivity of dimanganese decacarbonyl with thiolate ions and herein describe some of our initial results.

Reaction of $Mn_2(CO)_{10}$ with 3 equiv of $[Et_4N][SPh]$ in MeCN for 18 h at 50 °C gave a yellow reaction mixture which, after concentration and addition of *i*-PrOH, deposited a yellow-orange crystalline solid.[2] Elemental analysis[3] and CO evolution data[4] were consistent with the formulation $[Et_4N][Mn_2(CO)_6(SPh)_3]$ (**1**), and plots of equivalent conductivity in MeCN vs. the square root of concentration were linear with slopes of ca. −200 units. This value is consistent with that for 1:1 electrolytes[1,5,6] and indicates that the above formulation (and not an oligomer of it) is correct for the product. The IR spectrum of **1** contains bands at 2000 (m), 1950 (sh), 1935 (s), and 1915 (s) cm^{-1}, consistent with the presence of terminal CO groups, but none below 1900 cm^{-1}, indicating the absence of bridging carbonyl. The combined spectral and analytical data suggest that the most reasonable formulation for the product consists of two $Mn(CO)_3$ fragments bridged by three μ-SPh groups, a structural arrangement that satisfies the 18-electron rule for both metals without invoking metal–metal bonding.

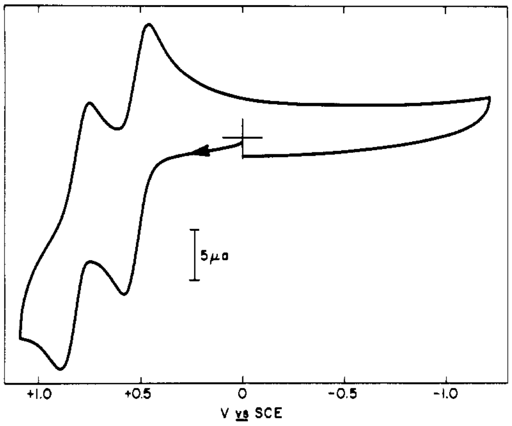
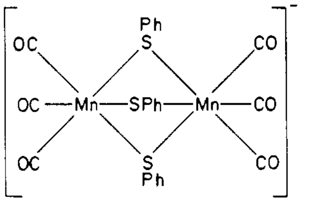


Figure 1. Cyclic voltammogram of a 1.41 mM solution of **1** in DMF at 200 mV/s scan rate and −45 °C.



The product is formally a Mn(I) dimer, and its synthesis was not anticipated from a Mn(0) starting material under anaerobic conditions. Although the mechanism of this reaction is unknown, it is pertinent to note that the halide analogues of **1**, $[Mn_2(CO)_6X_3]^-$, were prepared[7] by photolysis of $Mn_2(CO)_{10}$ in the presence of $[Et_4N]X$. Like the aforementioned molybdenum systems, it is remarkable that these simple dinuclear thiolate complexes have apparently not been reported previously. Other known[8,9] manganese–carbonyl–thiolate complexes include $[Mn_4(CO)_{12}(SR)_4]$ and $[Mn_2(CO)_8(SR)_2]$.

The electrochemistry of **1** is strikingly different from that of $[Mo_2(CO)_8(SPh)_2]^{2-}$. The cyclic voltammogram[10] of the man-

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(2) All reactions were carried out under an inert atmosphere by using degassed solvents and Schlenk tube techniques. On the basis of the proposed formulation, the yield was 45%. The synthetic method used here is virtually identical with that employed for $[Et_4N]_2[Mo_2(CO)_8(SR)_2]$ described in ref 1.
(3) Anal. Calcd. for $[Et_4N][Mn_2(CO)_6(SPh)_3]$ ($C_{32}H_{35}NO_6Mn_2S_3$): C, 52.24; H, 4.76; N, 1.90. Found: C, 52.24; H, 4.92; N, 1.97.
(4) The CO evolved on oxidation of the complex with excess Cl_2 was transferred by Toepler pumping to a calibrated manometric system and quantitated. The amount of CO collected was 97% of that predicted on the basis of this formulation.
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