VEX C1. Variation of R_{77} with R_{67} fixed leads to a minimum energy for both configurations in the region of R_{77} = 1.98 Å (2.00 Å for ec2 and 1.99 Å for ec3). Fixing R_{77} to this value and allowing R_{67} to vary give a minimum at 1.87 Å for ec2 and 1.85 Å for ec3. Thus the two potential surfaces have minima in the same region of coordinate space, close to the grid point at R_{67} = 1.84 Å, R_{77} = 1.98 Å.

In the region of the minima the $(T_{1g})^6$ configuration is predicted to lie below $(T_{1u})^6$ by ~0.5 eV. The separation is probably quite sensitive to improvements in basis set, but such a small energy difference also suggests that interaction between the two configurations may be important. Until a CI calculation in a large basis set becomes possible for this system a definite assignment of configuration will remain elusive.

It is interesting that the predicted ground-state configuration disagrees with the simplest qualitative model of borane bonding—the tensor surface harmonic (TSH) theory of Stone.[14] In TSH theory a closo borane is treated as a spherical cluster and predicted to have $(n + 1)$ skeletal bonding MOs, of which one is totally symmetric and the others span the symmetries of the even vector spherical harmonics. Descent in symmetry gives a T_{1u} HOMO and a T_{1g} LUMO, i.e. configuration ec3 rather than the ec2 found in the ab initio calculations. However, more detailed qualitative calculations based on EH[15] or "structural"[16] extensions of TSH agree with the minimal-basis SCF result. The structural TSH theory[16] predicts that at high cluster nuclearity the even and odd vector spherical harmonics cross over in energy, with even (π) orbitals becoming antibonding and odd ($\bar{\pi}$) orbitals becoming bonding. In $B_{32}H_{32}^{2-}$ the T_{1u} HOMO has a $\bar{\pi}$ spherical parentage[5] so that our SCF results verify that such a crossover can indeed occur.

The bond lengths R_{67} = 1.87 Å and R_{77} = 2.00 Å represent a near-optimal geometry within icosahedral symmetry for this molecule, with boron atoms lying on or inside a sphere of radius ~3.0 Å. The whole molecule including H atoms has a radius of ~4.2 Å. Calculations in the STO-3G basis can give useful estimates of boron–boron distances. For example, the STO-3G-optimized geometry[17,18] for $B_6H_6^{2-}$ has R_{BB} = 1.68 Å compared with the experimental bond length of 1.69 ± 0.01 Å for the ion in its tetramethylammonium salt.[19] Results for larger borane cages, which have more atoms to share the "excess" negative charge, may be even better, but in any case our estimated R_{67} and R_{77} are probably accurate to ±0.03 Å.

Stability

Lipscomb and coworkers[4,12] proposed that the absolute value of the energy per BH unit, $\bar{E} = |E_{SCF}|/n$, should be used as a criterion of relative stability for closo boranes $B_nH_n^{2-}$. At the grid point nearest the optimal geometry the STO-3G basis give $\bar{E}(B_{32}H_{32}^{2-}) = 24.934\ E_h$. This may be compared with the value for $B_6H_6^{2-}$ at the fully optimized geometry for the same basis:[17,18] $\bar{E}(B_6H_6^{2-}) = 24.898\ E_h$. $\bar{E}$ for $B_{12}H_{12}^{2-}$ at the experimental geometry (R_{BB} = 1.77 Å, R_{BH} = 1.07 Å) and in the same basis[13] is $\bar{E}(B_{12}H_{12}^{2-}) = 24.954\ E_h$. On this criterion, therefore, a $B_{32}H_{32}^{2-}$ anion would be intermediate in stability between these two known species, a hopeful sign for its possible synthesis.

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Registry No. $B_{32}H_{32}^{2-}$, 113249-16-4.

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Spectroelectrochemical Studies of High-Valent Nitridomanganese Porphyrins

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The reactivity of synthetic high-valent metalloporphyrins that model the active site of cytochrome P-450 has received considerable interest.[1-6] High-valent oxomanganese and oxoiron porphyrins have been described as intermediates in the catalytic transfer of oxygen from iodosylbenzene, peroxybenzoic acids, or amine *N*-oxides to numerous substrates including hydrocarbons. Recently, nitridochromium and nitridomanganese porphyrins have been prepared by Buchler,[7] Hill,[8] and Groves.[9] Remarkably, the nitrido metalloporphyrins are thermally and chemically stable. This is especially interesting since the N≡Mn core is isoelectronic with O=Fe, the reactive moiety involved in the oxygen atom transfer chemistry of the native enzyme and synthetic models.

The impetus for this study was twofold. First, we sought to place nitridomanganese porphyrins within the general framework of manganese porphyrin electrochemistry as established by Kadish.[10] Second, we hoped to electrochemically activate the $N{\equiv}Mn^V$ moiety and exploit its chemistry. The spectroelectrochemical results presented herein show that although we were unable to activate the $N{\equiv}Mn^V$ moiety electrochemically, the redox reactivity of nitridomanganese porphyrins is unique when compared with that of other manganese porphyrins.

Experimental Section

Several high-valent manganese porphyrins[13] were synthesized from the corresponding manganese (III) porphyrins (previously prepared accord-

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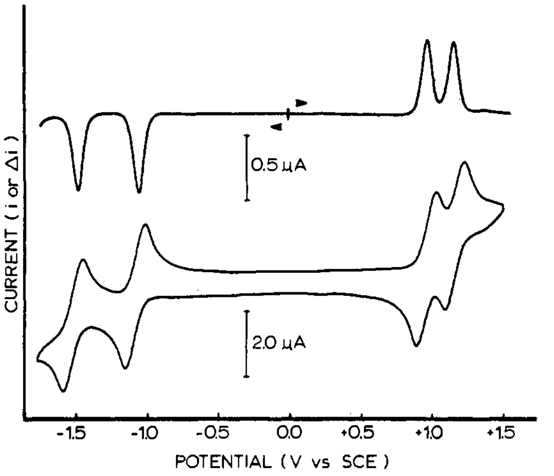

Figure 1. Voltammetric data obtained on a 0.204 mM solution of (4-Me-TPP)Mn(N) in 0.1 M TBAP/PhCN. The upper trace is a differential pulse voltammogram taken at a potential sweep rate of 10 mV/s, a pulse amplitude of 25 mV, and a pulse frequency of 0.1 s. The lower trace is a steady-state cyclic voltammogram taken at a potential sweep rate of 200 mV/s.

Table I. $E_{1/2}$ Values[a] (V) for (4-Me-TPP)Mn(N) in Selected Solvents

charge on complex[b]	CH_2Cl_2	$EtCl_2$	PhCN	pyridine
+2/+1	1.15	1.17	1.15	*c*
+1/0	0.95	0.97	0.96	*c*
0/-1	-1.14	-1.10	-1.08	-1.09
-1/-2	-1.50	-1.45	-1.53	-1.54

[a] Potentials were measured in 0.1 M tetrabutylammonium perchlorate, referenced against the SCE, and are uncorrected for liquid-junction potentials. [b] Defined in eq 1–4 in the text. [c] Beyond accessible solvent potential range.

ing to the procedure of Adler[11]) by the method of either Buchler[7] or Takahashi.[12] Product purity was verified by UV-Vis, NMR, and mass spectral measurements. All reagents were obtained from Aldrich Chemical Co. and purified in the manner previously described.[14] The spectroelectrochemical instrumentation and techniques were identical with those previously reported.[14] The EPR experiments were performed on a Varian E3 spectrometer. All experiments were carried out at ambient temperature (21 ± 1 °C). Unless otherwise noted, all solutions were deoxygenated with solvent-saturated nitrogen and blanketed with nitrogen during all experiments. All potentials are referenced to the SCE.[13].

Results and Discussion

Figure 1 depicts cyclic and differential pulse voltammograms typical of a nitridomanganese porphyrin in PhCN.[13] Analysis of data from variable-scan-rate experiments (over the range 20–10 000 mV/s) and variable-pulse-amplitude differential pulse experiments (over the range 5–100 mV) revealed that all four electrode reactions are electrochemically reversible one-electron transfers. Voltammograms observed for (4-Me-TPP)Mn(N) dissolved in CH_2Cl_2, $EtCl_2$, and pyridine were similar in appearance and gave comparable trends as a function of potential sweep rate and pulse amplitude.[15] Potential data for (4-Me-TPP)Mn(N) as a function of solvent are given in Table I. Similar experiments were carried out on the 10 other nitridomanganese porphyrins with comparable results. Table II lists the potentials observed (in $EtCl_2$ only) for electrode reactions of the nitridomanganese porphyrin complexes investigated.

Table II. Potential Data[a] for the Redox Reactions of Nitridomanganese Porphyrins in $EtCl_2$

porphyrin	redox reacn reacn 1	reacn 2	reacn 3	reacn 4
(2,4,6-$(MeO)_3$-TPP)Mn(N)	1.10	0.83	-1.30	-1.77
(2,6-$(MeO)_2$-TPP)Mn(N)	1.14	0.87	-1.25	-1.73
(2,4-$(MeO)_2$-TPP)Mn(N)	1.06	0.89	-1.18	-1.59
(2-MeO-TPP)Mn(N)	1.11	0.94	-1.14	-1.56
(4-MeO-TPP)Mn(N)	1.12	0.93	-1.13	-1.49
(2,4,6-Me_3-TPP)Mn(N)	1.21	0.96	-1.25	-1.67
(4-Me-TPP)Mn(N)	1.17	0.97	-1.11	-1.45
(TPP)Mn(N)	1.20	1.00	-1.09	-1.46
(4-Cl-TPP)Mn(N)	1.24	1.05	-1.02	-1.38
(2,6-Cl_2-TPP)Mn(N)	1.40	1.17	-0.99	-1.44
(OEP)Mn(N)	1.19	0.80	-1.30	-1.68

[a] Potentials were measured in 0.1 M tetrabutylammonium perchlorate, referenced against the SCE, and are uncorrected for liquid-junction potentials.

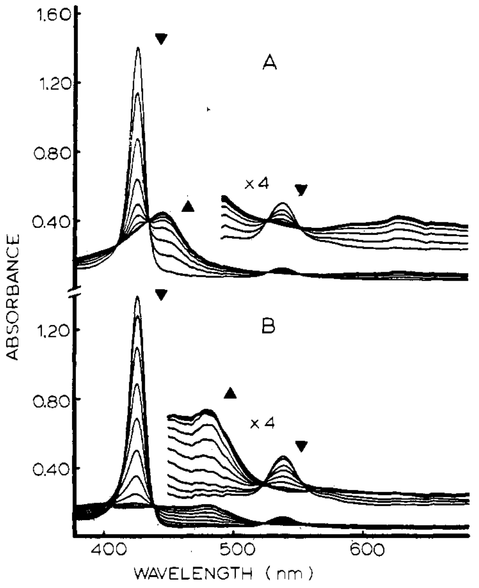

Figure 2. Visible spectra obtained during the electrolysis of a 0.204 mM solution of (4-Me-TPP)Mn(N) in 0.1 M TBAP/PhCN at the OTTLE. In part A the potential was stepped from -0.80 to -1.35 V, and in part B it was stepped from +0.80 to +1.06 V.

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(13) Abbreviations used: saturated calomel electrode = SCE; OTTLE = optically transparent thin-layer electrode; 1,2-dichloroethane = $EtCl_2$; benzonitrile = PhCN; porphyrin dianion = POR; nitrido(*meso*-tetrakis(2,4,6-trimethoxyphenyl)porphinato)manganese(V) = (2,4,6-$(MeO)_3$-TPP)Mn(N); nitrido(*meso*-tetrakis(2,6-dimethoxyphenyl)porphinato)manganese(V) = (2,6-$(MeO)_2$-TPP)Mn(N); nitrido(*meso*-tetrakis(2,4-dimethoxyphenyl)porphinato)manganese(V) = (2,4-$(MeO)_2$-TPP)Mn(N); nitrido(*meso*-tetrakis(2-methoxyphenyl)porphinato)manganese(V) = (2-MeO-TPP)Mn(N); nitrido(*meso*-tetrakis(4-methoxyphenyl)porphinato)manganese(V) = (4-MeO-TPP)Mn(N); nitrido(*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato)manganese(V) = (2,4,6-Me_3-TPP)Mn(N); nitrido(*meso*-tetrakis(4-methylphenyl)porphinato)manganese(V) = (4-Me-TPP)Mn(N); nitrido(tetraphenylporphinato)manganese(V) = (TPP)Mn(N); nitrido(*meso*-tetrakis(4-chlorophenyl)porphinato)manganese(V) = (4-Cl-TPP)Mn(N); nitrido(*meso*-tetrakis(2,6-dichlorophenyl)porphinato)manganese(V) = (2,6-Cl_2-TPP)Mn(N); nitrido(octaethylporphinato)manganese(V) = (OEP)Mn(N).

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(15) This conclusion is based on the following observed trends. For all reactions of the various compounds investigated, $E_{1/2}$ values were invariant with potential scan rate. Forward peak currents were proportional to the square root of the potential sweep rate, and current ratios were equal to unity at all scan rates. At 20 mV/s, each process gave a peak potential separation of 60 ± 2 mV, which increased slightly at higher scan rates. $E_{1/2} - E_p$ and $E_{1/2} - E_{p/2}$ values were 31 ± 2 and 29 ± 2 mV, respectively, at a potential sweep rate of 20 mV/s and increased slightly at higher sweep rates. The trends observed for the variable-pulse-amplitude differential pulse data were also those expected for reversible charge transfers. Solvent discharge in pyridine prevented the observation of the oxidation processes.

Constant-potential chronoabsorptometric experiments[16] were performed at an optically transparent electrode to evaluate the stability of each of the redox products. The results depicted in Figure 2 are typical of the results obtained for all other nitridomanganese porphyrins. Over the potential range +0.80 to −0.95 V, the typical spectrum of (4-Me-TPP)Mn(N) was observed.[17] Stepping the potential to −1.35 V produced the rapid spectral changes depicted in Figure 2A. The final spectrum was stable for at least 3 h under the applied potential.[18] Application of the potential at −0.80 V quantitatively regenerated the initial spectrum. A multiple-potential-step (in 10-mV increments) experiment was performed over the potential region of the first oxidation process. Analysis of the change in absorbance as a function of applied potential yielded an $E^{\circ\prime}$ value of −1.08 V and confirmed the passage of one electron. The electrogeneration of the first reduction product was also carried out in the cavity of an EPR spectrometer at ambient temperature. A single resonance devoid of Mn hyperfine was observed at $g = 2.017$ (in CH_2Cl_2) or $g = 2.008$ (in PhCN), confirming the retention of the low-spin, d^2 configuration of the Mn center upon electroreduction.

Applying a potential of 1.06 V to a fresh solution of (4-Me-TPP)Mn(N) in the OTTLE produced the spectral transition depicted in Figure 2B. The spectral transition was complete within 40 s after application of the oxidizing potential. Stepping the potential back to 0.80 V 5 min after completion of the electrooxidation regenerated a Soret band at 424 nm. At longer times, the electrooxidation produced mixtures[19] of $\{(4\text{-Me-TPP})Mn^{III}\}^+$ or $\{(4\text{-Me-TPP})Mn^{III}\}^{2+}$ (depending upon the applied potential) and $\{(4\text{-Me-TPP})Mn^{V}(N)\}^+$. When the electrogeneration of the first oxidation product was carried out in the cavity of an EPR spectrometer, a singlet was observed at $g = 2.011$ (in CH_2Cl_2). In PhCN, superimposed on the singlet resonance at $g = 1.965$ was a low-intensity sextuplet. Takahashi has also observed this phenomenon upon chemical oxidation of (4-Me-TPP)Mn(N) by ferric perchlorate. He attributes the spectral overlap to an equilibrium between the Mn(V) cation radical and a Mn(VI) cationic species facilitated by solvent coordination.[12] The sextuplet results from the formal Mn(VI) d^1 center with spin $^5/_2$. Under our conditions, the cation radical species predominated.

The fate of the nitrogen moiety upon electrooxidation of (POR)Mn(N)[13] is unknown. Repeated attempts at capturing the N^0 or N^{3-} species with either cyclooctene or norbornylene were unsuccessful.[20]

On the basis of these results, the following mechanism is proposed:

$$\{(POR)Mn(N)\}^{2+} + e^- \rightleftharpoons \{(POR)Mn(N)\}^+ \qquad (1)$$

$$\{(POR)Mn(N)\}^+ + e^- \rightleftharpoons (POR)Mn(N) \qquad (2)$$

$$(POR)Mn(N) + e^- \rightleftharpoons \{(POR)Mn(N)\}^- \qquad (3)$$

$$\{(POR)Mn(N)\}^- + e^- \rightleftharpoons \{(POR)Mn(N)\}^{2-} \qquad (4)$$

At the electrode, all charge transfers involving $(POR)Mn^V(N)$ occur initially with no formal change in the valence of the central metal. Justification of these assignments follows several lines of evidence. First, electrochemical oxidation produced a species whose UV–vis spectral features are characteristic of cation radicals; the spectra possess broad Soret bands of diminished intensity, and visible spectral bands are shifted to longer wavelengths. Similar spectral changes occur following electroreduction. Second, the EPR spectra acquired on the charge-transfer products are singlet resonances with *g* values consistent only with cation radical and anion radical formation. Charge transfer involving the Mn center (i.e. transformation of the low-spin d^2 configuration to a d^1 or d^3 configuration) would be implicated by the presence of Mn hyperfine. Third, Takahashi[12] has shown that chemical oxidation of (4-Me-TPP)Mn(N) produced a green complex whose infrared spectrum exhibited a N≡Mn stretch at 1044 cm^{-1} and a strong band at 1282 cm^{-1}, indicative of porphyrin ring oxidation. We have obtained an infrared spectrum of electrochemically generated oxidized material with identical vibrations.

The potential difference between the first oxidation and first reduction of all (POR)Mn(N) complexes investigated averaged 2.11 V. The spread in this value was only 48 mV. This band gap and the potential differences between successive oxidations (the potential difference between reactions 1 and 2) or reductions (the potential difference between reactions 3 and 4) are in excellent agreement with the theoretical values as well as those previously observed for other metalloporphyrins with electroinactive metal centers.[10] Linear free energy relationships equating the half-wave potentials for the various porphyrins measured in $EtCl_2$ with the Hammett–Taft substituent constant were constructed in the usual fashion.[21] The values of ρ for reactions 1–4 were 0.043, 0.049, 0.047, and 0.060, respectively. These values are within the range obtained by other investigators for porphyrin-ring-centered reactions.[10]

Kadish[10] has found that the redox potentials of manganese porphyrins are not well correlated with solvent donor or acceptor number. Nitridomanganese porphyrins exhibit similar behavior. The half-wave potentials for all four processes remain essentially unchanged regardless of solvent. This phenomenon was common to all (POR)Mn(N) complexes investigated and indicated the absence of solvent coordination to the Mn(V) center.[22]

In summary, axial coordination of manganese porphyrins by the nitride ligand deactivates an otherwise electroactive central metal. Other examples of the modification of the site of charge transfer induced by changes in metalloporphyrin axial ligands are known. Oxidation of ruthenium(II) porphyrins has been shown to occur at the central metal except when CO or CS is the axial ligand.[23] Reduction of iron(II) phthalocyanine occurs at the metal center except when imidazole is an axial ligand.[24] The nitrido-

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(16) An excellent description of the chronoabsorptometric experiments is available in: *Laboratory Techniques in Electroanalytical Chemistry*; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1984; pp 64–78.

(17) This spectrum was characterized by an intense 424-nm Soret band and two visible bands at 537 and 572 nm (molar absorptivities of 4.57×10^5, 2.17×10^4, and 3.30×10^3, respectively).

(18) The Soret band decreased in intensity and shifted to 448 nm. The visible region became devoid of spectral features. The spectral transition was completed within 40 s and occurred with isosbestic points at 410, 434, 526, and 553 nm.

(19) To identify the products, identical experiments were performed on (4-Me-TPP)Mn(Cl). The spectrum of (4-Me-TPP)Mn(Cl) in PhCN is characterized by bands at 480, 405, 534, 588, and 624 nm with logarithms of the molar absorptivities of 5.08, 4.70, 4.17, 4.54, and 4.35, respectively. Electroreduction to a Mn(II) species at an applied potential of −0.60 V produced a final spectrum with bands at 450, 408, 540, 580, and 623 nm with logarithms of the molar absorptivities of 5.37, 4.70, 4.16, 4.34, and 4.39, respectively.

(20) Tandem electrochemistry–mass spectrometry experiments carried out on solutions containing the products of electrooxidation verified that the nitrido moiety slowly dissociated from the Mn center but new nitrogen-containing species were undetected. In one experiment, He was continuously bubbled through the electrolysis solution during the course of a controlled-potential oxidation. The volatiles were concentrated in a cold trap (immersed in liquid nitrogen) that had been constructed at the inlet of the GC–MS. At the end of the electrolysis, the He purge was stopped and the contents of the cold trap thawed. A sample was then injected onto the column, and mass spectra were acquired as components of the mixture eluted from the column. In a second experiment, aliquots of the electrolysis solution were drawn during the course of a controlled-potential oxidation and directly injected into the inlet port of the GC–MS. Spectra were acquired as components eluted from the column.

(21) Kadish, K. M.; Morrison, M. M. *Bioelectrochem. Bioenerg.* **1977**, *3*, 480.

(22) Buchler[7] and Groves[9] have shown that the addition of a second ligand to the Mn center can occur only after the N≡Mn bond has been substantially weakened by addition of either triphenylphosphine[7] or trifluoroacetic anhydride[9] to the N atom.

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manganese porphyrins are the first example of the modification of the site of charge transfer for manganese porphyrins, and this is the first time this phenomenon has been observed for a high-valent metalloporphyrin.

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Registry No. (2,4,6-(MeO)$_3$-TPP)Mn(N), 113132-55-1; (2,6-(MeO)$_2$-TPP)Mn(N), 113132-56-2; (2,4-(MeO)$_2$-TPP)Mn(N), 113132-57-3; (2-MeO-TPP)Mn(N), 113132-58-4; (4-MeO-TPP)Mn(N), 83632-52-4; (2,4,6-Me$_3$-TPP)Mn(N), 84987-03-1; (4-Me-TPP)Mn(N), 84206-81-5; (TPP)Mn(N), 83632-54-6; (4-Cl-TPP)Mn(N), 113132-59-5; (2,6-Cl$_2$-TPP)Mn(N), 113132-60-8; (OEP)Mn(N), 84206-82-6.

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A New Synthetic Entry to Tungsten–Sulfur Cluster Chemistry: Preparation and Structure of [$W_3S_4Cl_3(dmpe)_3$]$^+$

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Although the chemistry of the trinuclear cluster compounds has developed in a similar way for both molybdenum and tungsten, that of molybdenum has always been in advance and is at present more highly developed. This is particularly true of the metal–sulfur clusters. Methods of obtaining derivatives of the $Mo_3S_4^{4+}$ cluster, as well as mixed species of the type $Mo_3O_{4-n}S_n^{4+}$, are numerous, whereas almost our entire knowledge of the analogous tungsten systems is covered by a few recent papers of Shibahara and coworkers.[1-4]

We recently developed a new type of synthetic entry to $Mo_3S_4^{4+}$ chemistry,[5] and we now wish to report that a similar type of chemistry exists for tungsten as well. Our approach, which is of an essentially nonaqueous nature, is perhaps of even greater interest for tungsten than for molybdenum because the entire body of $W_3O_{4-n}S_n^{4+}$ chemistry is still so limited.

Experimental Section

Materials. NaSH[6] and WCl$_4$[7] were prepared as described elsewhere. Dmpe was synthesized from commercially available $Cl_2PCH_2CH_2PCl_2$ (Aldrich Chemicals) according to the literature method.[8]

Physical Measurements. The electronic spectra were measured in methanol solutions with a Cary 17D spectrophotometer. Electrochemical measurements were performed with a Bioanalytical Systems, Inc., Model BAS 100 electrochemical analyzer in conjunction with a Houston Instruments Model DMP 40 digital plotter. Electrochemical data were obtained on acetone solutions of the BPh_4^- salt of the complex that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to an Ag/AgCl electrode at room temperature. A platinum disk (Model BAS MF 2032) was used as the working electrode.

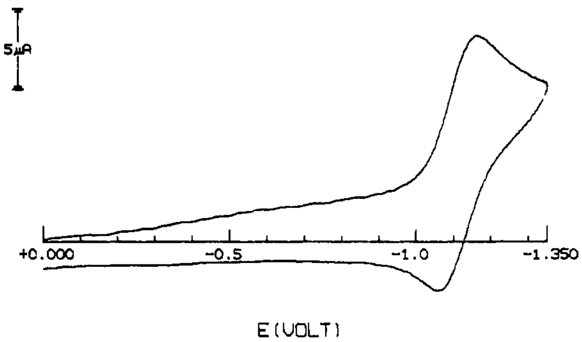

Figure 1. Cyclic voltammogram of [$W_3S_4Cl_3(dmpe)_3$]BPh_4 in acetone solution at a scan rate of 400 mV s^{-1} (reference: Ag/AgCl).

Table I. Crystal Data for [$W_3S_4Cl_3(dmpe)_3$]$PF_6 \cdot H_2O$

formula	$W_3S_4Cl_3P_7F_6OC_{18}H_{50}$
fw	1399.57
space group	$R3c$
systematic absences	$(hkil)$: $-h + k + l \neq 3n$
	$(h\bar{h}0l)$: $h + l \neq 3n$, $l \neq 2n$
	$(000l)$: $l \neq 6n$
a, Å	15.269 (2)
c, Å	30.620 (6)
V, Å^3	6182 (3)
Z	6
d_{calcd}, g/cm^3	2.25
crystal size, mm	0.3 × 0.3 × 0.4
μ(Mo Kα), cm^{-1}	92.4
data col instrument	Syntex P3
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)
orientation reflcns: no., range (2θ)	24, 20–30
temp, °C	11
scan method	ω–2θ
data col range, 2θ, deg	4–45
total no. of unique data	1031
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	907
no. of params refined	125
trans factors: max, min	0.99, 0.59
R^a	0.0324
R_w^b	0.0458
quality-of-fit indicator^c	1.228
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	1.3

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality of fit $= [\sum w(|F_o| - |F_c|)^2/N_{observns} - N_{params})]^{1/2}$.

Synthesis of [$W_3S_4Cl_3(dmpe)_3$]$PF_6 \cdot H_2O$. NaSH (86 mg, 1.54 mmol) was added to a suspension of WCl$_4$ (374 mg, 1.15 mmol) in 15 mL of THF. Addition of 10 mL of methanol (to dissolve the NaSH) produced an instantaneous color change to green. Dmpe (190 μL, 1.15 mmol) was introduced and the reaction mixture refluxed for 2 h. After the mixture was cooled to room temperature, a brown precipitate was separated from a dark blue solution by filtration under argon. This blue solution is air stable and was absorbed onto a silica gel column. After the column was washed with acetone, the blue band that remained on the top was eluted with methanol. This resulting blue solution was treated with NH_4PF_6, and the mixture was allowed to evaporate slowly in air to give black crystals suitable for X-ray diffraction studies. Yield: ca. 20%. These crystals were characterized as [$W_3S_4Cl_3(dmpe)_3$]$PF_6 \cdot H_2O$. The BPh_4^- salt could also be obtained by addition of NaBPh$_4$ to the blue eluate. The UV–vis spectrum of this compound shows two bands at 560 and 300 nm.

Electrochemistry. The cyclic voltammogram of a solution of [$W_3S_4Cl_3(dmpe)_3$]BPh_4 in 0.1 M TBAH–acetone showed the presence of a quasi-reversible couple which corresponds to a reduction ($E_{1/2}$ = 1.11 V vs. Ag/AgCl). The separation between the "coupled" anodic and cathodic peaks (ΔE_p) was 100 mV at 300 mV/s and the $i_{p,c}/i_{p,a}$ ratios were in the range 0.5–0.55 depending on the scan speed. The ratio approached 1 as the scan speed increased. This is indicative of a reversible reaction at fast scan speeds, with some chemical event that follows the electrochemical process. The voltammogram obtained at 400 mV/s is shown in Figure 1.

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