1. The low- and high-spin Ni(II) forms of F430 span a Ni–N range of 1.9–2.1 Å. On the basis of a series of model hydroporphyrins, corphins, and tetraaza complexes,[3,17,18] these distances reflect changes from puckered to planar macrocycle conformations, i.e., the F430 skeleton is quite flexible.
2. The Ni(II)–N distances of 1.9 and 2.1 Å found for low- and high-spin F430, respectively, match almost exactly the *strain-free* Ni(II)–N distances of 1.91 and 2.10 Å calculated for low- and high-spin Ni(II) polyamines by molecular mechanics.[22]
3. The Ni(II)–N distances of LS F430 and its 12,13-diepimer[9] are the same within experimental error. The observed different affinities for axial ligands of the two compounds[3,9] are, therefore, not due to significant differences in the equatorial nitrogens and may reflect steric constraints due to the different conformation of the diepimer,[3d] instead.
4. Since the F430 skeleton is flexible enough to accommodate changes of 0.2 Å around Ni(II), it can equally accommodate the distortion concomitant with reduction to Ni(I).

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Supplementary Material Available: Optical, EPR, and EXAFS spectra of Ni(II) and Ni(I) F430 M (3 pages). Ordering information is given on any current masthead page.

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Novel Cis-Directed, Four-Electron Dioxo Oxidant

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The higher oxidation states of Ru and Os are accessible by loss of electrons and protons and metal oxo formation.[1] In complexes where there are two or more aqua ligands, oxidation state VI is attainable and several complexes having the *trans*-dioxo structure are known.[2] These complexes tend to be reactive oxidants. In this context, a *cis*-dioxo structure would be of more interest than the corresponding trans structure because of the possibility of achieving cis-directed, four-electron oxidations with the transfer of two O atoms to the same reductant. Normally, the *cis*-dioxo structure leads to an instability toward ligand loss and formation of *trans*-dioxo products. The driving force for the instability is the electronic stabilization associated with the *trans*-dioxo, d^2 electronic configuration.[2,3] We report here the preparation and characterization of *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ (**1**) (tpy is 2,2′:6′,2″-terpyridine), which overcomes this limitation. The complex is coordinatively stable yet has the desired reactivity as a cis-directed, four-electron oxidant, but in a novel and indirect way.

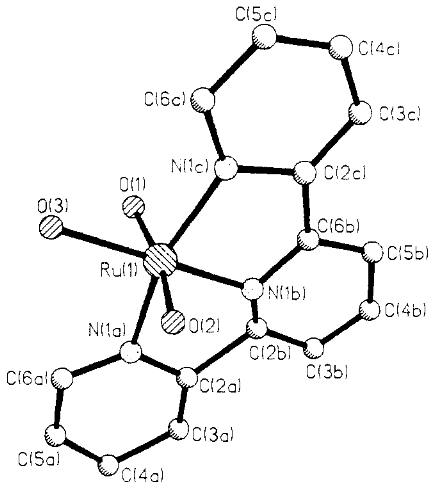

Figure 1. Crystal structure of the *trans*-$[Ru(tpy)(O)_2(H_2O)]^{2+}$ cation.

Complex **1** was prepared from $[Ru^{II}(tpy)(C_2O_4)(H_2O)]$ in 2 M $HClO_4$ by the addition of excess $(NH_4)_2Ce^{IV}(NO_3)_6$.[4] This led to a color change from red-brown to yellow and precipitation of $[Ru^{VI}(tpy)(O)_2(H_2O)](ClO_4)_2$.[5] The structure of **1** has been determined by X-ray crystallography and is illustrated in Figure 1.[6] Four important features emerge from the structure: (a) the coordination geometry is approximately octahedral; (b) the disposition of the oxo groups is trans; (c) the average Ru=O bond length is 1.661 Å, compared to 2.128 Å for the Ru—O bond of the aqua group, 1.765–1.862 Å for oxo groups bound to Ru(IV), or 1.705–1.732 Å for oxo groups bound to Ru(VI);[7] and (d) the

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(4) The complex $[Ru(tpy)(C_2O_4)(H_2O)]$ was prepared by heating $Ru(tpy)Cl_3$ and $Na_2C_2O_4$ is CH_3OH/H_2O under N_2. The complex was isolated as the monohydrate. Adeyemi, S. A.; Guadalupe, A.; Meyer, T. J., manuscript in preparation.

(5) Anal. Calcd for $C_{15}H_{15}N_3O_{12}Cl_2Ru$: C, 29.95; H, 2.49; N, 6.99; Cl, 11.80. Found: C, 29.87; H, 2.58; N, 6.87; Cl, 12.24.

(6) Data were collected on a Nicolet R3m/V diffractometer at 173 K by using Mo Kα radiation. The space group was $P2_1/n$ with a = 7.950 (13) Å, b = 18.940 (20) Å, c = 14.000 (16) Å, β = 102.08 (11)°, V = 2061 (4) Å^3, Z = 4, and FW = 599.21. For 1020 observed reflections and variables, the current discrepancy indices are R = 10.9% and R_w = 10.7%. We are currently attempting to grow crystals of higher quality in order to refine the structure further.

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O=Ru=O angle is 171.3° with the bending occurring away from the tpy ligand.

From Raman and FT-IR studies, the symmetrical $\bar{\nu}$(Ru=O) stretch occurs at 834 cm^{-1} and the asymmetrical stretch at 841 cm^{-1} in the solid state. In the electronic spectrum in H_2O at pH = 1, an absorption band appears at 410 nm (ϵ = 3700 M^{-1} cm^{-1}) along with tpy-based $\pi^* \leftarrow \pi$ transitions at 315, 285 (sh), 275 (sh), and 265 (sh) nm. In CH_3CN, the low-energy absorption band appears at 416 nm (ϵ = 3500 M^{-1} cm^{-1}). Complex **1** is stable in acidic aqueous solution and is stable in CH_3CN for at least 1 week.

The ^{1}H NMR spectrum of **1** is consistent with a diamagnetic complex with a series of tpy resonances appearing in the range 9.50–7.50 ppm.[8] Addition of **1** to CD_3CN led to *trans*-$[Ru^{VI}(tpy)(O)_2(CD_3CN)]^{2+}$ with k_1 = 5 M^{-1} s^{-1} (k_{-1} = 35 M^{-1} s^{-1}). An isolated doublet that appears at 9.17 ppm is sensitive to the ligand trans to tpy. For the corresponding acetonitrile complex *trans*-$[Ru^{VI}(tpy)(O)_2(CD_3CN)]^{2+}$, the chemical shift is 9.45 ppm. On the basis of the relative integrated areas of the resonances at 9.17 and 9.45 ppm in CD_3CN/D_2O mixtures, K = 0.15 M for the equilibrium in eq 1.

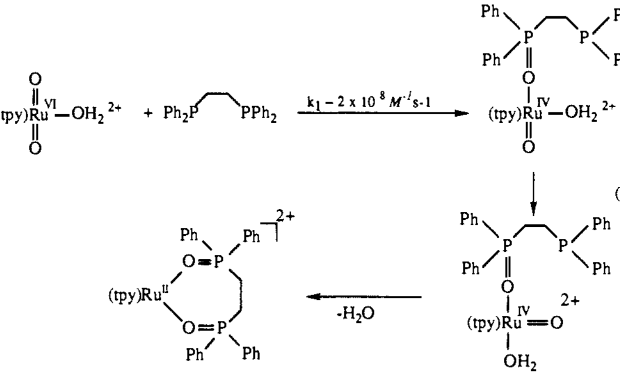
$$[Ru^{VI}(tpy)(O)_2(D_2O)]^{2+} + CD_3CN \xrightleftharpoons{K} [Ru^{VI}(tpy)(O)_2(CD_3CN)]^{2+} + D_2O \quad (1)$$

The results of electrochemical studies on aqueous solutions containing **1** reveal a pH-dependent behavior as well as a pattern of redox couples that is analogous to those found for *trans*-$[Ru^{IV}(bpy)_2(O)_2]^{2+}$.[2c] In cyclic voltammograms at pH = 1, waves appear for the $[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}/[Ru^{IV}(tpy)(O)(H_2O)_2]^{2+}$ couple at $E_{1/2}$ = 1.03 V, for the $[Ru^{IV}(tpy)(O)(H_2O)_2]^{2+}/[Ru^{III}(tpy)(OH)(H_2O)_2]^{2+}$ couple at $E_{1/2}$ = 0.87 V, and for the $[Ru^{III}(tpy)(OH)(H_2O)_2]^{2+}/[Ru^{II}(tpy)(OH_2)_3]^{2+}$ couple at $E_{1/2}$ = 0.47 V (vs SSCE, at 25 °C, I = 0.1 M). Chemical, Zn(Hg), or electrochemical reduction gave $[Ru^{II}(tpy)(H_2O)_3]^{2+}$, quantitatively.

The results of simple mixing experiments show that **1** has an extensive reactivity chemistry that extends to olefins, hydrocarbons, and polyaromatic hydrocarbons. We have been able to demonstrate the existence of a *cis*-dioxo reactivity in the reactions between **1** and a series of arylphosphines. Oxo complexes of Ru are known to act as oxygen atom transfer reagents toward phosphines, sulfides, or olefins.[9] When **1** was allowed to react with PPh_3 in excess in CH_3CN, a rapid reaction occurred to give a red-violet Ru^{II} product (λ_{max} = 510 nm). On the basis of stopped-flow measurements, the reaction occurred in a stepwise manner, Ru(VI) → Ru(IV) followed by Ru(IV) → Ru(II). The Ru(IV) → Ru(II) step occurred with k(20 °C, CH_3CN) = 1.05 × 10^4 M^{-1} s^{-1}. The Ru(VI) → Ru(IV) step was faster by a factor of >100. Subsequent changes, as followed by FT-IR and $^{31}P\{^1H\}$ NMR, occurred on a far slower time scale. An intermediate appeared having a single ^{31}P resonance at 50.5 ppm (vs 85% H_3PO_4) and $\bar{\nu}$(P=O) = 1155 cm^{-1}, consistent with *trans*-$[Ru(tpy)(OPPh_3)_2(S)]^{2+}$ (S = CH_3CN, H_2O). After 30 min, free O=PPh_3 (^{31}P, δ = 31.0 ppm; $\bar{\nu}$(P=O) = 1195 cm^{-1}) had appeared in the solution, and after 12 h, nearly complete release of $OPPh_3$ had occurred. On the basis of these observations we conclude that the reaction between **1** and PPh_3 occurs in two steps to give *trans*-$[Ru(tpy)(OPPh_3)_2(S)]^{2+}$ (S = CH_3CN, H_2O), followed by its stepwise solvolysis.

In the reaction between **1** and the potentially chelating diphosphine 1,2-bis(diphenylphosphino)ethane (dppe) in a 1:1 ratio, in CH_3CN (3.5 M H_2O), it was shown, by using stopped-flow techniques, that reduction of Ru(VI) to Ru(IV) was rapid, k_1(20 °C) ~ 2 × 10^8 M^{-1} s^{-1} and the subsequent reduction of Ru(IV) to Ru(II) occurred with k_2(20 °C) = 6.2 × 10^{-2} s^{-1} via an isosbestic point at 365 nm. With the diphosphine in excess (5:1), a competition exists between the second, intramolecular oxidation and intermolecular oxidation of a second diphosphine as shown by spectrophotometric measurements. The initial Ru(II) product at a 1:1 ratio (λ_{max} = 495 nm; $\bar{\nu}$(P=O) = 1155 cm^{-1}; ^{31}P, δ = 61.5 ppm) was unstable. It was converted into an intermediate which contained both bound P=O (^{31}P, δ = 63.3, 62.9 ppm) and free P=O (^{31}P, δ = 33.7, 33.1 ppm). After 1 h, free diphosphine dioxide $\bar{\nu}$(P=O) = 1225 cm^{-1}; ^{31}P, δ = 40.5 ppm) had appeared in the solution. Similar observations have been made with $Ph_2PCH_2PPh_2$ or *cis*-Ph_2PCH=$CHPPh_2$ as the diphosphines. With $Ph_2PCH_2PPh_2$, the initial Ru(II) product was more stable. It underwent loss of the bis(phosphine oxide) ligand with $t_{1/2}$ ~ 1 h.

On the basis of our observations, it can be concluded that, in its reactions with diphosphines, *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ can function as a cis-directed, four-electron oxidant. Other examples are known in the chemistry of MO_4 (M = Ru, Os).[10] The sequence of reactions that allow the initially trans oxidant to transfer two O atoms from cis positions is shown in eq 2, in which $Ph_2PCH_2CH_2PPh_2$ is shown as the reductant. The final redox product may be five-coordinate as shown in eq 2 or contain a bound solvent molecule.



(2)

The key to the mechanism is the intramolecular rearrangement of the oxo group from an axial coordination position to one in the tpy plane following reduction of Ru(VI) to Ru(IV). The rearrangement brings the second oxo group into a position to attack the partly oxidized diphosphine. It may occur by proton transfer from bound OH_2 to the oxo group rather than by substitution, although this point remains to be proven. For the diphosphines $Ph_2PCH_2PPh_2$ and $Ph_2PCH_2CH_2PPh_2$, the rate constants for the second, intramolecular oxidation are comparable. From the relative insensitivity of the rate constants for the second step to the nature of the diphosphine, rearrangement of the oxo group may be rate limiting.

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Supplementary Material Available: Tables of atomic positional and thermal parameters, bond distances, and bond angles for **1** (4 pages); listing of observed and calculated structure factors for **1** (10 pages). Ordering information is given on any current masthead page.

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[8] At 9.17 ppm (dd, J_{56} = 5.6 Hz, J_{46} = 1.3 Hz, 2 H, H_6, $H_{6''}$), at 8.70 ppm (multiplet, 5 H, H_3, $H_{3''}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), at 8.51 ppm (ddd, J_{45} = 7.9 Hz, J_{43} = 8 Hz, J_{46} = 1.3 Hz, 2 H, H_4, $H_{4''}$), and at 8.02 ppm (ddd, J_{56} = 5.7 Hz, J_{45} = 7.9 Hz, J_{53} = 1.4 Hz, 2 H, H_5, $H_{5''}$), in D_2O.

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