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Mechanism of *cis*-Directed Four-Electron Oxidation by a *trans*-Dioxo Complex of Ruthenium(VI)

Angelos Dovletoglou[†] and Thomas J. Meyer*

Contribution from the Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

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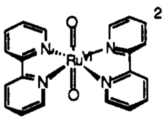
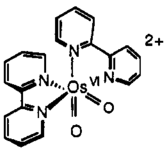
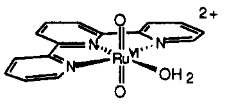
Abstract: The reductions of *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ or *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ (tpy is 2,2′:6′,2″-terpyridine) by PPh_3, $Ph_2PCH_2CH_2PPh_2$ (dppe), or $Ph_2PCH_2PPh_2$ (dppm) occur by successive Ru(VI) → Ru(IV) and Ru(IV) → Ru(II) oxygen atom transfer steps. The products appear to be five-coordinated diphosphine oxide complexes of Ru(II). They subsequently undergo stepwise solvolysis to give the free diphosphine dioxides and $[Ru^{II}(tpy)(CH_3CN)_3]^{2+}$. The kinetics of the individual redox steps were studied by stopped-flow/rapid-scan spectrophotometry. For PPh_3 as reductant, $k_{VI/IV}(20\ °C, CH_3CN) = (2.28 \pm 0.08) \times 10^6\ M^{-1}\ s^{-1}$ ($\Delta H^* = 4.2 \pm 0.8$ kcal mol^{-1}; $\Delta S^* = -19 \pm 4$ eu) and $k_{IV/II}(20°, CH_3CN) = (1.04 \pm 0.03) \times 10^4\ M^{-1}\ s^{-1}$ ($\Delta H^* = 5.9 \pm 0.5$ kcal mol^{-1}; $\Delta S^* = -20 \pm 3$ eu). With dppe or dppm, Ru(VI) acts as a *cis*-directed four-electron oxidant. The first step, {Ru(VI) → Ru(IV)}, is first order in both oxidant and diphosphine with $k_{VI/IV}(20\ °C, CH_3CN) \sim 4 \times 10^8\ M^{-1}\ s^{-1}$ (dppe) to give *trans*-$[Ru^{IV}(tpy)(O)(O{=}P(PPh_2)CH_2CH_2PPh_2)(CH_3CN)]^{2+}$. In acetonitrile with no added water, the subsequent reduction of Ru(IV) to Ru(II) follows first-order kinetics with $k_{IV/II}(20\ °C, CH_3CN) = 5 \times 10^1\ s^{-1}$ for either dppe or dppm. By inference, the rate-limiting step is intramolecular isomerization of the remaining oxo group followed by rapid O-atom transfer. In acetonitrile 1.75 M in H_2O the initial Ru(IV) product is *trans*-$[Ru^{IV}(tpy)(O)(O{=}P(PPh_2)CH_2CH_2PPh_2)(H_2O)]^{2+}$. The subsequent Ru(IV) → Ru(II) step is considerably slower, $k_{IV/II}(20\ °C) = (6.20 \pm 0.12) \times 10^{-2}\ s^{-1}$. This reaction exhibits a substantial *inverse* solvent isotope effect, $k_{H_2O}/k_{D_2O} = 0.18 \pm 0.02$, which arises from the transfer of a single proton on the basis of a mole fraction study. Isomerization is also rate limiting in this case, but the rate-determining step is intramolecular proton transfer.

Introduction

The higher oxidation states of Ru and Os are accessible from aqua complexes of Ru(II) or Os(II) by loss of electrons and protons, resulting in metal oxo formation.[1–5] With two or more aqua ligands, dioxo complexes of Ru(VI) or Os(VI) are accessible and polypyridyl complexes of Ru and Os having *cis*- or *trans*-dioxo geometries are known.[6,7] The oxo complexes tend to be reactive oxidants and are useful electrocatalysts.[8]



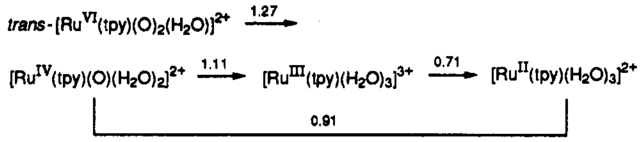




As oxidants, *cis*-dioxo complexes of M(VI) are potentially of more interest than *trans* because of the possibility of achieving *cis*-directed four-electron oxidations with the transfer of two oxygen atoms to the same reductant. However, the *cis* isomers are unstable toward ligand loss and *trans*-dioxo formation. The driving force is the electronic stabilization of the *trans*-dioxo structure by electronic donation from the oxo ligands.[6,7,9]

$$cis\text{-}[Ru(bpy)_2(O)_2]^{2+} + 2H_2O \rightarrow trans\text{-}, cis\text{-}[Ru(bpy)(O)_2(OH)_2]^{2+} + bpyH^+ + H^+$$

Recently, we elucidated the properties of the oxidant *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$.[10] The average Ru=O bond length is 1.661 Å, compared to 2.128 Å for the Ru–O bond of the aqua group, and the O=Ru=O angle is 171.3°, with the bending occurring away from the tpy ligand. Electrochemical measurements showed that the *trans*-dioxo complex is a powerful oxidant with a potential four-electron capability based on sequential Ru(VI/IV) and Ru(IV/II) couples.



[†] Present address: Analytical Research, Merck & Co., Inc., P.O. Box 2000, R80Y-120, Rahway, NJ 07065.

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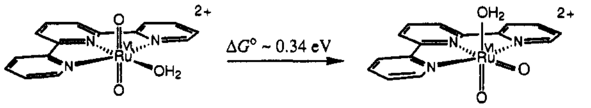
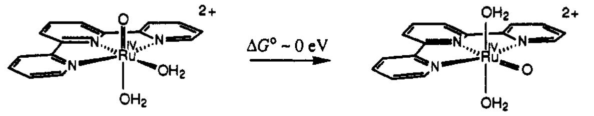
From the electrochemical data, it was concluded that there is an electronic preference of ~0.34 eV for *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ compared to *cis*, 1a. The stereochemical preferential is lost upon reduction to Ru(IV) with $\Delta G° \sim 0$ eV for the equilibrium in 1b. It was also noted that there is a possible mechanism for interconverting the isomers in 1b by intramolecular proton transfer, which requires neither ligand substitution nor molecular rearrangement.



(1a)



(1b)

By combining the Ru(VI) → Ru(IV) and Ru(IV) → Ru(II) couples and a pathway for interconversion of oxo–aqua isomers at Ru(IV), a mechanistic basis exists for *cis*-directed four-electron oxidations by *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$. It is based on the following sequence: (1) two-electron oxidation and binding via Ru(VI) → Ru(IV) oxygen atom transfer, (2) intramolecular isomerization of the remaining oxo group, and (3) a second two-electron oxidation via the Ru(IV) → Ru(II) couple. It is known that oxo complexes of Ru(IV) can undergo oxygen atom transfer to olefins,[11] phosphines,[12] sulfides,[13] and phenols,[14] and that these reactions can be rapid, e.g.,

$$cis\text{-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + PPh_3 \rightarrow cis\text{-}[Ru^{II}(bpy)_2(py)(O{=}PPh_3)]^{2+} \quad (2)$$

$$k(26.6\ °C, CH_3CN) = 1.75 \times 10^5\ M^{-1}\ s^{-1}$$

With *cis*-$[Os^{VI}(bpy)_2(O)_2]^{2+}$ as the oxidant, reactions with $Ph_2PCH_2PPh_2$ or *cis*-$Ph_2PCH{=}CHPPh_2$ are known to give chelating diphosphine dioxide complexes as products.[15]

In this work, we have investigated the reactions between *trans*-$(Ru^{VI}(bpy)(O)_2(S)]^{2+}$ (S = H_2O, CH_3CN) and PPh_3, and between the same oxidant and the diphosphines $Ph_2P(CH_2)_nPPh_2$, (n = 1, 2). The intent was to use the reactions with PPh_3 to establish the four-electron capability of the oxidant and with the diphosphines to test the possibility of achieving *cis*-directed four-electron oxidations. Part of this work has appeared in a preliminary communication.[10]

Experimental Section

Materials. Triphenylphosphine was purchased from Aldrich Chemical Co., recrystallized two times from hexane, and dried in vacuum (mp 80 °C). 1,2-Bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm) were purchased from Aldrich Chemical Co. and recrystallized from argon-degassed absolute ethanol ($^{31}P\{^1H\}$ NMR,[16] dppe, $\delta = -12.9$; dppm, $\delta = -23.5$ ppm; mp dppe, 143 °C; mp dppm, 122 °C). Infrared analysis and ^{31}P NMR confirmed the absence of the corresponding arylphosphine oxides or dioxides.

Deuterium oxide (99.9% D, Aldrich Gold Label) and acetonitrile-d_3 (99.6% D, Aldrich Chemical Co.) were used as received. $[N(n\text{-}Bu)_4](PF_6)$ was recrystallized once from 1:1 (v/v) ethanol/water and twice from absolute ethanol and dried under vacuum for 10 h at 80 °C. Spectrograde acetonitrile (Burdick & Jackson) was used as received. High-purity deionized water was obtained by passing distilled water through a Nanopure (Barnstead) water purification system. The preparation of *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ was described previously.[7b] Dilute solutions of *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ were prepared *in-situ* by dissolving the aqua complex in acetonitrile. Numerous attempts were made to grow crystals of the final Ru(II) products from the reactions between Ru(VI) dioxo and the diphosphines. However, these products undergo solvolysis in acetonitrile to give $[Ru^{II}(tpy)(CH_3CN)_3]^{2+}$, which was isolated and characterized (see below). We were unable to use noncoordinating solvents such as CH_2Cl_2 becaus they undergo relatively rapid reactions with Ru(VI). The solvolysis chemistry in CH_3CN or in a 3:1 (v/v) mixture of CH_3CN and H_2O at 4 °C is greatly slowed, but we were unable to grow crystals from these solutions.

Instrumentation and Measurements. UV–visible spectra were recorded using a Hewlett-Packard Model 8452A diode array and CARY 14 spectrophotometers with 1-cm quartz cells. Infrared spectra were obtained in CH_3CN solution using NaCl plates on a Nicolet Model 20DX FTIR spectrophotometer. For the infrared measurements the concentration of the complex was 2.0 mM, that of PPh_3, 2.0–4.0 mM, and that of dppe, 2.0 mM. ^1H NMR spectra were recorded on a Bruker 200AC-MHz FT-NMR spectrometer using CD_3CN (reference vs TMS) as solvent. All ^{31}P NMR (80.015 MHz) spectra were recorded in CD_3CN under conditions of complete decoupling ($^{31}P\{^1H\}$). 85% H_3PO_4 was used as an external reference, with resonances deshielded from H_3PO_4 being reported as positive values. In these experiments the concentration of the complex was 5.0–22.5 mM, that of PPh_3, 10.0–45.0 mM, that of dppe, 5.0–25.0 mM, and that of dppm, 16.0 mM. Blank experiments showed that no air oxidation of the arylphosphines occurred in CH_3CN or CD_3CN over the time scale of the experiments.

Electrochemical measurements were conducted with a Princeton Applied Research Model 173 potentiostat/galvanostat connected to a Princeton Applied Research Model 175 universal programmer as a sweep generator for voltammetry experiments. Cyclic voltammetric experiments were carried out in single one-compartment cells using an "activated" teflon-sheathed 0.07-cm² glassy-carbon disk working electrode,[17] a platinum wire as the auxiliary electrode, and a sodium-saturated calomel reference electrode (SSCE). The concentration of the complex for the cyclic voltammetric measurements was 1.0–2.0 mM, that of PPh_3, 1.0–2.0 mM, and that of dppe, 2.0 mM. All solutions were protected from the atmosphere under a blanket of N_2. The $E_{1/2}$ values reported in this work were calculated from cyclic voltammetric measurements as an average of the oxidative and reductive peak potentials, $(E_{pa} + E_{pc})/2$.

Kinetic measurements were carried out on a Hi-Tech Scientific SF-51 stopped-flow apparatus with fiber-optic coupling to either a Beckman DU or a Harrick rapid-scan monochromator. The system was interfaced with a Zenith 158 microcomputer by use of On Line Instrument System (OLIS) data acquisition hardware and software. The temperature of the reactant solutions was controlled to within ±0.2 °C by using a Brinkman Lauda K-2/RD water bath circulator. Each rate constant is the average of 8–15 separate experimental determinations performed under constant reaction conditions. The concentration of the complex for the kinetics measurements was 5.0×10^{-6} to 1.0×10^{-4} M, that of PPh_3, 5.0×10^{-6} to 7.5×10^{-4} M, and that of dppe and dppm, 5.0×10^{-6} to 1.0×10^{-4} M.

Kinetic Analysis. Nonlinear least squares fits of the absorbance-time kinetic traces were performed by using a Microsoft QuickBASIC implementation of the Levenberg–Marquardt algorithm.[18] Two complementary computational methods were used to derive second-order rate constants from the kinetic data. For first-order and pseudo-first-order reaction conditions it was possible to fit the data according to eq 3, where A_0 is the initial absorbance, A_∞ the final absorbance after mixing, A_t the absorbance at time t, and k_{obs} the first-order or pseudo-first-order rate constant.

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$$A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{\mathrm{obs}}t) \qquad (3)$$

In the case of pseudo-first-order conditions the second-order rate constant was obtained by dividing k_{obs} by the midpoint concentration of the reactant in excess. The latter was estimated from the initial concentration, the measured change in absorbance, the cell path length (l, cm), and the known value of $\Delta\epsilon$ (M^{-1} cm^{-1}) at the wavelength of observation. Under the conditions of our experiments the majority of the kinetic runs were conducted under non-pseudo-first-order conditions. The data for equal and unequal concentrations were fit according to eqs 4a and 4b, respectively.

$$A_t = \frac{(A_0 - A_\infty)}{1 + \dfrac{(A_0 - A_\infty)}{\Delta\epsilon l}kt} + A_\infty \qquad (4a)$$

$$A_t = A_0 - \Delta\epsilon l\left[C_A - C_B + \frac{(A_0 - A_\infty)}{\Delta\epsilon l}\right]\left[\frac{\exp[(C_A - C_B)kt] - 1}{\exp[(C_A - C_B)kt] - \dfrac{C_A}{C_B}}\right] \qquad (4b)$$

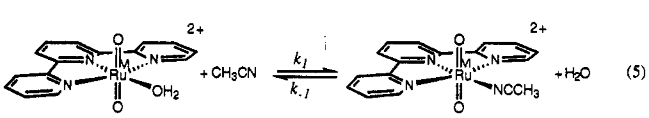
$$c_B = \frac{(A_0 - A_\infty)}{\Delta\epsilon l}, \quad c_A = C_A - C_B + c_B, \quad C_A > C_B$$

In eq 4b, C_A and C_B are the analytical values of the initial concentrations of reactants A and B at the time of mixing, c_A and c_B are the calculated concentrations observed at time = t past the instrumental t_{zero}, and the other terms remain as defined above. The form of eq 4b provides an automatic correction for instrumental dead time on the basis of explicit knowledge of the $\Delta\epsilon$ value. The values of the second-order rate constants obtained from the pseudo-first-order fits to eq 3 are within 1% of those calculated by fitting the data to the full second-order equation in 4b.

The reduction of *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ by the phosphines was studied at 20 °C in neat CH_3CN and in CH_3CN, 1.75 M in added H_2O after mixing. In the case of dppe the study was extended to include measurements in solutions 1.75 M in D_2O and in H_2O–D_2O mixtures. In a typical stopped-flow experiment a 1.0×10^{-6} M solution of the complex in acetonitrile with 3.5 M H_2O was mixed with an acetonitrile solution 2.0×10^{-6} M in PPh_3 or 1.0×10^{-6} M in one of the diphosphines. The reduction of Ru(VI), which was monitored at 416 nm, was >100 times faster than the subsequent reduction of Ru(IV) to Ru(II). The reduction of Ru(IV) was monitored at 510 nm in the reaction with PPh_3 and at 495 nm in the reaction with the diphosphines. Additional wavelengths were monitored routinely to assure that the results were independent of the monitoring wavelength.

Results

Oxidation of PPh_3. In acetonitrile the equilibrium in 5 has been established with $k_{-1} = 35.3 \pm 0.1$ M^{-1} s^{-1}, $k_1 = 4.9 \pm 0.2$ s^{-1}, and K (k_1/k_{-1}) = 0.15 ± 0.01 M at 19.5 °C. A spectrophotometric titration in acetonitrile showed that addition of 2 molar equiv of PPh_3 to *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ (λ_{max} = 416 nm, ϵ = 3500 M^{-1} cm^{-1}) caused its quantitative conversion to a new product (λ_{max} = 510 nm, ϵ = 3600 M^{-1} cm^{-1}) via a discrete intermediate which forms upon addition of 1 molar equiv of PPh_3 (Figure 1).



In Figure 2a is shown a cyclic voltammogram of the solution at time t = 3 min after *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ (1.0 mM) had been mixed with 2 molar equiv of PPh_3 (2.0 mM) in acetonitrile. A reversible wave (ΔE_p = 70 mV) appeared at $E_{1/2}$ = 0.89 V vs SSCE for the Ru(III/II) couple of the initial product. In the $^{31}P\{^1H\}$ NMR spectrum a singlet resonance appeared at δ = 50.5 ppm (vs 85% H_3PO_4), and in the infrared spectrum a single P=O stretch appeared at ν = 1155 cm^{-1}. The ^{31}P chemical shift is deshielded compared to free $OPPh_3$ (δ = −5.8 ppm),[19] consistent with disruption of the O=P π interaction by Ru–O bonding. From these observations it can be inferred that the initial product is *trans*-$[Ru(tpy)(OPPh_3)_2(CH_3CN)]^{2+}$, formed by stepwise reduction of Ru^{VI}.[20]

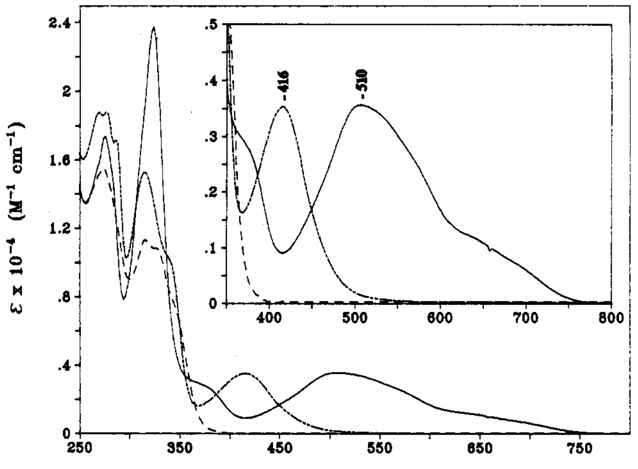


Figure 1. Electronic absorption spectra of *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ (- - — - -), $[Ru^{IV}(tpy(O)(OPPh_3)(CH_3CN)]^{2+}$ (- - -) formed by the addition of 1 molar equiv of PPh_3 in acetonitrile, and *trans*-$[Ru^{II}(tpy)(OPPh_3)_2(CH_3CN)]^{2+}$ (—) formed by the addition of 2 molar equiv of PPh_3 in acetonitrile.

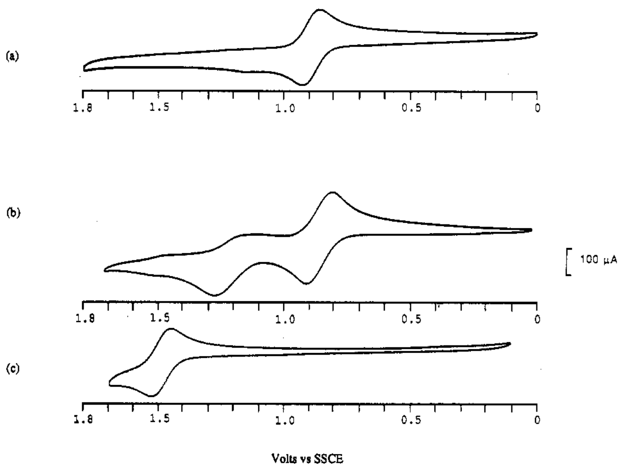


Figure 2. Cyclic voltammograms recorded (a) 3 min after preparing a solution that was initially 1.0 mM in *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ and 2.0 mM in PPh_3 in acetonitrile. The reversible wave at $E_{1/2}$ = 0.89 V is the Ru(III/II) couple *trans*-$[Ru(tpy)(OPPh_3)_2(CH_3CN)]^{3+/2+}$; (b) 30 min after mixing, showing waves for the Ru(III/II) couples $[Ru(tpy)(CH_3CN)_3]^{3+/2+}$ at $E_{1/2}$ = 1.49 V and $[Ru(tpy)(OPPh_3)(CH_3CN)_2]^{3+/2+}$ at $E_{1/2}$ = 1.25 V; and (c) 24 h after mixing with only the $[Ru(tpy)(CH_3CN)_3]^{3+/2+}$ couple remaining in solution. The voltammograms were recorded at a 0.07-cm^2 glassy-carbon disk electrode, scan rate 100 mV s^{-1}, 0.1 M TBAH, vs SSCE.

$$trans\text{-}[Ru^{VI}(typ)(O)_2(CH_3CN)]^{2+} + PPh_3 \rightarrow [Ru^{IV}(tpy)(O)(OPPh_3)(CH_3CN)]^{2+} \qquad (6a)$$

$$[Ru^{IV}(tpy)(O)(OPPh_3)(CH_3CN)]^{2+} + PPh_3 \rightarrow trans\text{-}[Ru^{II}(tpy)(OPPh_3)_2(CH_3CN)]^{2+} \qquad (6b)$$

Attempts to isolate the Ru(IV) intermediates $[Ru^{IV}(tpy)(O)(OPPh_3)(CH_3CN)]^{2+}$ or $[Ru^{IV}(tpy)(O)(OPPh_3)(H_2O)]^{2+}$ were

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[19] (a) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* **1975**, *40*, 3437. (b) Deacon, G. B.; Green, J. H. S. *Spectrochim. Acta* **1968**, *24A*, 845.

[20] Burford, N., et al. *J. Chem. Soc., Dalton Trans.* **1990**, 1521.

unsuccessful. They are unstable in acetonitrile or in the latter case in acetonitrile containing 1.75 M H_2O toward the appearance of Ru(II) ($t_{1/2} \sim 20$ min). Both *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ are also unstable in acetonitrile toward reduction to Ru(II), apparently by oxidation of the solvent.[8a]

Slower changes occurred following the Ru(VI) → Ru(II) redox step. An intermediate appeared having a single $^{31}P\{^1H\}$ resonance at 46.5 ppm, $\nu(P{=}O) = 1163$ cm^{-1}, and $E_{1/2} = 1.25$ V. After 30 min, free $OPPh_3$ (^{31}P, $\delta = 31.0$ ppm; $\nu(P{=}O) = 1195$ cm^{-1})[16,19] and $[Ru^{II}(tpy)(CH_3CN)_3]^{2+}$ ($E_{1/2} = 1.49$ V, $\lambda_{max} = 434$ nm)[21] had also appeared in the solution (Figure 2b). After 24 h, quantitative release of $OPPh_3$ had occurred (by ^{31}P NMR and $\nu(P{=}O)$ FTIR), and $[Ru^{II}(tpy)(CH_3CN)_3]^{2+}$ was the only Ru complex that remained. After separation of $OPPh_3$ from the reaction mixture,[22] $[Ru^{II}(tpy)(CH_3CN)_3]^{2+}$ was isolated as the PF_6^- salt and identified by cyclic voltammetry and UV–visible spectroscopy.[21] The observations made after the redox step are consistent with stepwise loss of $OPPh_3$. The overall reaction

$$[Ru^{II}(tpy)(OPPh_3)_2(CH_3CN)]^{2+} + CH_3CN \rightarrow [Ru^{II}(tpy)(OPPh_3)(CH_3CN)_2]^{2+} + OPPh_3 \quad (7)$$

$$[Ru^{II}(tpy)(OPPh_3)(CH_3CN)_2]^{2+} + CH_3CN \rightarrow [Ru^{II}(tpy)(CH_3CN)_3]^{2+} + OPPh_3 \quad (8)$$

between *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ and 2 molar equiv of PPh_3 is

$$trans\text{-}[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+} + 2PPh_3 + 2CH_3CN \rightarrow [Ru^{II}(tpy)(CH_3CN)_3]^{2+} + 2OPPh_3$$

The reduction of *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ by PPh_3 was followed by stopped-flow kinetics at 1:1, 1:2, and pseudo-first-order excesses of PPh_3. Absorption-time traces were analyzed at 416 nm {Ru(VI) → Ru(IV)} and 510 nm {Ru(IV) → Ru(II)}. Because of the difference in the magnitude of the rate constants for the two steps, they were separable. Their rate laws were found to be

$$-d[Ru^{VI}]/dt = k_{VI/IV}[Ru^{VI}][PPh_3] \quad (9)$$

$$-d[Ru^{IV}]/dt = k_{IV/II}[Ru^{IV}][PPh_3] \quad (10)$$

In Figure 3 are shown stopped-flow kinetic traces and nonlinear least squares fits of the data to eq 4b for both steps. Kinetics data including activation parameters obtained over the range 5.0–45.0 °C are listed in Table I.

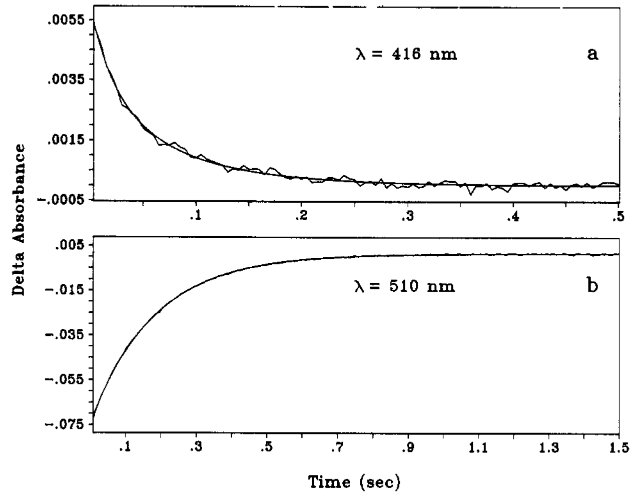

Figure 3. Stopped-flow kinetics traces (a) monitoring at 416 nm for the Ru(VI) → Ru(IV) step in the reduction of *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ (5.45×10^{-6} M) by PPh_3 (1.25×10^{-5} M) in acetonitrile at $T = 20$ °C and (b) monitoring at 510 nm for the reduction of *trans*-$[Ru^{IV}(tpy)(O)(OPPh_3)(CH_3CN)]^{2+}$ (7.05×10^{-5} M) by PPh_3 (7.48×10^{-4} M). Fits of the data to eq 4b are shown in the plots.

Table I. Rate Constants and Activation Parameters for the Reduction of *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ by PPh_3 in Acetonitrile at 20 °C

[Ru(VI)], M	$[PPh_3]$, M	$k_{VI/IV}$ ($\times 10^{-6}$, M^{-1} s^{-1})[a]	$k_{IV/II}$ ($\times 10^{-4}$, M^{-1} s^{-1})[b]
7.05×10^{-5}	7.48×10^{-4}	*c*	1.05 ± 0.01
7.00×10^{-5}	2.50×10^{-4}	*c*	1.05 ± 0.02
5.45×10^{-6}	1.09×10^{-5}	2.28 ± 0.07	1.04 ± 0.03
3.20×10^{-6}	6.40×10^{-6}	2.26 ± 0.10	1.02 ± 0.04
5.45×10^{-6}	5.45×10^{-6}	2.31 ± 0.08	
		av 2.28 ± 0.08	av 1.04 ± 0.03
$\Delta H^\ddagger$ (kcal mol^{-1})		4.2 ± 0.8	5.9 ± 0.5
$\Delta S^\ddagger$ (eu)		−19 ± 4	−20 ± 3

[a] Monitored at 416 nm. [b] Monitored at 510 nm. Each rate constant is the average of 8–15 independent experimental determinations. [c] The reaction was too rapid to be followed under these conditions.

$Ph_2PCH_2CH_2PPh_2$ (dppe) and $Ph_2PCH_2PPh_2$ (dppm) as Reductants. Addition of 1 molar equiv of dppe or dppm to an acetonitrile solution containing $[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ resulted in the rapid reduction of Ru(VI) to Ru(II) through an intermediate stage. The same stoichiometry was found for the reaction between *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ and $Ph_2PCH_2CH_2PPh_2$ in CH_3CN with 1.75 M added H_2O. In the solution containing the final redox product, a single $^{31}P\{^1H\}$ NMR resonance was observed at $\delta = 61.5$ ppm and a reversible wave at $E_{1/2} = 0.94$ V vs SSCE for the Ru(III/II) couple. With dppm a single $^{31}P\{^1H\}$ NMR resonance appeared at $\delta = 55.8$ ppm for the Ru(II) product. Attempts to isolate and grow crystals of either intermediate were unsuccessful. We were also unable to isolate analytically pure solids by precipitation probably due to the lability of the diphosphine dioxide intermediates toward substitution.[12,23]

The appearance of a single ^{31}P resonance is consistent with a five-coordinate product containing a chelating diphosphine dioxide ligand (structure 1, reaction 11a),[24,25] a *trans*-oligomeric product containing bridging diphosphine dioxide ligands (reaction 11b),[15] or a six-coordinate product for which the ^{31}P resonances of the inequivalent P atoms are accidentally degenerate (structure 2) or the molecule is fluxional on the NMR time scale. The formation of oligomers is inconsistent with first-order kinetics for the Ru(IV) → Ru(II) step under 1:1 conditions (see below), and the degree of oligomerization would have to be extensive for there to be only a single observable ^{31}P resonance, which makes oligomerization unlikely. The fact that a single resonance is observed for *both* of the diphosphine dioxide products means that accidental degeneracy is unlikely.

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(21) (a) Suen, H.-F.; Wilson, S. W.; Pomerantz, M.; Walsh, J. L. *Inorg. Chem.* **1989**, *28*, 786. (b) Dovletoglou, A. Unpublished results.

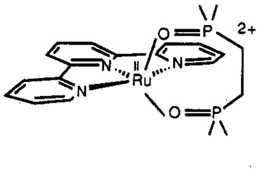
(22) After loss of $OPPh_3$ was complete, the reaction solution was added to toluene with stirring to precipitate the complex, which was filtered off and recrystallized from EtOH/H_2O.

(23) (a) Araneo, A.; Trovati, A. *Inorg. Chim. Acta* **1969**, *3*, 471. (b) Tanke, R. S.; Holt, E. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 1714.

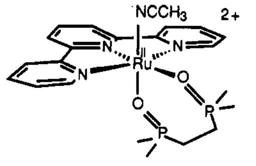
(24) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(25) (a) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. (b) Isaacs, E. E.; Graham, W. A. G. *J. Organomet. Chem.* **1976**, *120*, 407. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080. (d) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439. (e) Hietkamp, S.; Stufkken, D. J.; Vrieze, K. *J. Organomet. Chem.* **1979**, *169*, 107.

Five-coordinate structures for Ru(II) have been proposed on the basis of ^{31}P NMR spectra[25] and established for a number of phosphine complexes by X-ray crystallography.[26,27]



(1)

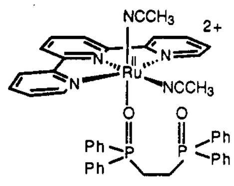


(2)

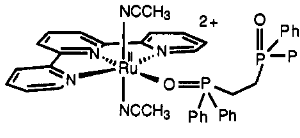
$$trans\text{-}[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+} + PPh_2CH_2CH_2PPh_2 \rightarrow [Ru^{II}(tpy)(O{=}P(Ph_2)CH_2CH_2(Ph_2)P{=}O)]^{2+} + CH_3CN \qquad (11a)$$

$$x\,trans\text{-}[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+} + xP(Ph_2)CH_2CH_2PPh_2 \rightarrow [Ru^{II}(tpy)(O{=}P(Ph_2)CH_2CH_2(Ph_2)P{=}O)(CH_3CN)]_x^{2+} \qquad (11b)$$

Solvolysis of the diphosphine dioxide intermediate of dppe occurred on a slower time scale than for $OPPh_3$. The initial Ru(II) product (λ_{max} = 495 nm; ν(P=O) = 1155 cm^{-1}; $^{31}P\{^1H\}$, δ = 61.5 ppm) underwent solvolysis to give $[Ru^{II}(tpy)(CH_3CN)_3]^{2+}$ via two intermediates, each of which contained one bound P=O and one free P=O. These are presumably the *cis* and *trans* isomers in structures **3** and **4**.



cis(**3**)



trans(**4**)

For one of the isomers $E_{1/2}$ = 1.35 V vs SSCE; ^{31}P, δ = 63.3 ppm (bound), 33.7 ppm (free); and J_{P-P} = 8 Hz. For the second isomer $E_{1/2}$ = 1.12 V; ^{31}P, δ = 62.9 ppm (bound), 33.1 ppm (free); and J_{P-P} = 8 Hz. After 1 h, free diphosphine dioxide (ν(P=O) = 1225 cm^{-1}; ^{31}P, δ = 40.5 ppm) had appeared in the solution.[28] For dppe the overall reaction with Ru(VI) is

$$trans\text{-}[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+} + Ph_2PCH_2CH_2PPh_2 + 2CH_3CN \rightarrow [Ru^{II}(tpy)(CH_3CN)_3]^{2+} + Ph_2P(O)CH_2CH_2P(O)Ph_2 \qquad (12)$$

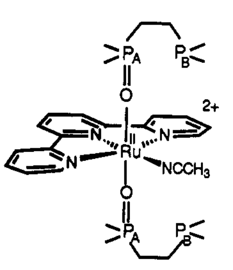
The reductions of *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ or *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ by $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2PPh_2$ were followed by stopped-flow spectrophotometry with the diphosphines present in stoichiometric or pseudo-first-order excesses. Solutions containing the aqua complex were 3.5 M in H_2O before mixing. The reactions occur in a stepwise manner through Ru(VI) → Ru(IV) and Ru(IV) → Ru(II) stages. Absorption-time traces were analyzed at 416 nm {Ru(VI) → Ru(IV)} and 495 nm {Ru(IV) → Ru(II)} and found to be consistent with the rate laws in eqs 13 and 14, where dppe is used as the example.

$$d[Ru^{VI}]/dt = k_{VI/IV}[Ru^{VI}][dppe] \qquad (13)$$

$$-d[Ru^{IV}]/dt = k_{IV/II}[Ru^{IV}] + k'_{IV/II}[dppe][Ru^{IV}] \qquad (14)$$

With a 1:1 ratio of *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ and dppe the rate law for the first step is consistent with eq 13, with $k_{VI/IV}$(20 °C) ~ 4 × 10^8 M^{-1} s^{-1}. The subsequent reduction of Ru(IV) to Ru(II) follows simple first-order kinetics under these conditions, eq 14, [dppe] = 0, with $k_{IV/II}$(20 °C, CH_3CN) = (4.42 ± 0.02) × 10^1 s^{-1}. In this equation $[Ru^{IV}]$ is the concentration of the Ru(IV) intermediate containing the once-oxidized diphosphines, *trans*-$[Ru^{IV}(tpy)(O)(O{=}P(Ph_2)CH_2CH_2PPh_2)(CH_3CN)]^{2+}$ or *trans*-$[Ru^{IV}(tpy)(O)(O{=}P(Ph_2)CH_2PPh_2)(H_2O)]^{2+}$. With dppm as the reductant and monitoring at 495 nm, Ru(II) appeared with $k_{IV/II}$(20 °C, CH_3CN) = (4.59 ± 0.04) × 10^1 s^{-1}. The kinetics of the Ru(IV) → Ru(II) step were independent of [dppe] or [dppm] and of $[Ru^{VI}]$ under equal concentration conditions over the range 1.0 × 10^{-4} to 5.0 × 10^{-6} M. With the diphosphine in excess (5:1) the parallel bimolecular term in the rate law in eq 14 dominates the rate law.

The reactions with the diphosphines in excess were monitored by rapid-scan/stopped-flow and $^{31}P\{^1H\}$ NMR measurements. Rate constants are listed in Table II. With dppe in excess, ^{31}P resonances appeared at $\delta(^{31}P_A)$ = 60.9 ppm (bound O=P) and $\delta(^{31}P_B)$ = −6.3 ppm (free P), J_{P-P} = 36 Hz, consistent with formation of *trans*-$[Ru^{II}(tpy)(O{=}P_A(Ph_2)CH_2CH_2P_BPh_2)_2(CD_3CN)]^{2+}$ (structure **5**) containing the half-oxidized ligand diphenyl[2-(diphenylphosphinyl)ethyl]phosphine oxide.



(**5**)

The kinetics of the Ru(IV) → Ru(II) step were also investigated with 3.5 M H_2O added to the acetonitrile solution containing *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$. Under these conditions (1.75 M in H_2O after mixing) the distribution between *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ and *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ is 96:4, with $t_{1/2}$ = 141 ms for their interconversion (reaction 5). With added water the reduction of Ru(VI) to Ru(IV) by dppe in a 1:1 ratio was relatively unaffected with $k_{VI/IV}$(20 °C) ~ 2 × 10^8 M^{-1} s^{-1}. The subsequent reduction of Ru(IV) to Ru(II) was far slower. It occurred with an isosbestic point at 365 nm, and $k_{IV/II}$(20 °C) = (6.20 ± 0.12) × 10^{-2} s^{-1}. In Figure 4 is shown a typical multiple scan spectrum obtained by rapid-scan spectrophotometry at 6-s intervals.

The kinetics were also investigated in acetonitrile containing varying ratios of H_2O and D_2O, with $[H_2O] + [D_2O]$ = 1.75 M after mixing. Rate constant data with added H_2O or D_2O are listed in Table II. A plot of k_X/k_D vs mole fraction D_2O (X_D) for the oxidation of $Ph_2PCH_2CH_2PPh_2$ by Ru(VI) is shown in Figure 5. The quantity k_D is the rate constant with 99.9% D_2O added and k_X the rate constant at mole fraction X_D. From these data there is an inverse isotope effect of 0.18 ± 0.02.

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(26) (a) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945. (b) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221. (c) Armit, P. W.; Boyd, S. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1663. (d) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511. (e) Briggs, J. C.; McAuliffe, C. A.; Dyer, G. *J. Chem. Soc., Dalton Trans.* **1984**, 423. (f) Thorburn, I. S.; Rettig, S. J.; James, B. R. *J. Organomet. Chem.* **1985**, *296*, 103. (g) Pierpont, C. D.; Pucci, A.; Eisenberg, R. *J. Am. Chem. Soc.* **1971**, *93*, 3050. (h) Pierpont, C. D.; Eisenberg, R. *Inorg. Chem.* **1972**, *12*, 199. (i) Hoffman, P. R.; Miller, J. S.; Ungermann, C. B.; Caulton, K. G. *J. Am. Chem. Soc.* **1973**, *95*, 7902.

(27) Pregosin, P. S.; Kunz, R. W. In *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979.

(28) An authentic sample of 1,2-bis(diphenylphosphinyl)ethane was prepared by oxidation of dppe by hydrogen peroxide (3%) in acetone and showed a single resonance at 40.6 ppm. Purity was checked by ^1H NMR: Aguiar, A. M.; Beisler, J. *J. Org. Chem.* **1964**, *29*, 1660.

Table II. Rate Constants for the Reduction of *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ and *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ by dppe or dppm in Acetonitrile at 20 °C[a]

oxidant	reductant	$k_{VI/IV}$ (M^{-1} s^{-1}	$k_{IV/II}$ (s^{-1})
trans-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$	dppe[a]	~4 × 10^8	(4.42 ± 0.02) × 10^1
trans-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$	dppm		(4.59 ± 0.04) × 10^1
trans-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$	dppe	~2 × 10^8	(6.20 ± 0.12) × 10^{-2} [b]
trans-$[Ru^{VI}(tpy)(O)_2(D_2O)]^{2+}$	dppe	~2 × 10^8	(3.63 ± 0.05) × 10^{-1} [b]
oxidant	**reductant**	**$k_{VI/IV}$ (M^{-1} s^{-1})**	**$k_{IV/II}$ (M^{-1} s^{-1})**
$[Ru^{IV}(tpy)(O)(O{=}PP)(CH_3CN)]^{2+}$	dppe[c]		(6.62 ± 0.02) × 10^4
$[Ru^{IV}(tpy)(O)(O{=}PP)(H_2O)]^{2+}$	dppe[c]		(1.49 ± 0.01) × 10^4

[a] dppe is $PPh_2PCH_2CH_2PPh_2$ and dppm is $PPh_2PCH_2PPH_2$. [b] 1.75 M in H_2O or D_2O after mixing. [c] O=PP is ($O{=}P(Ph_2)CH_2CH_2PPh_2$); the dppe was added in 5-fold excess.

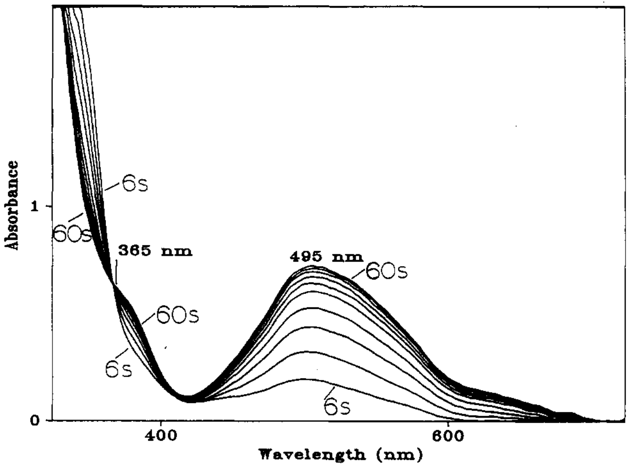


Figure 4. UV-visible spectral changes at 6-s intervals for the Ru(IV) → Ru(II) step in the reaction between *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ (7.00 × 10^{-4} M) and dppe (7.00 × 10^{-4} M) in acetonitrile 1.75 M in H_2O at T = 20 °C.

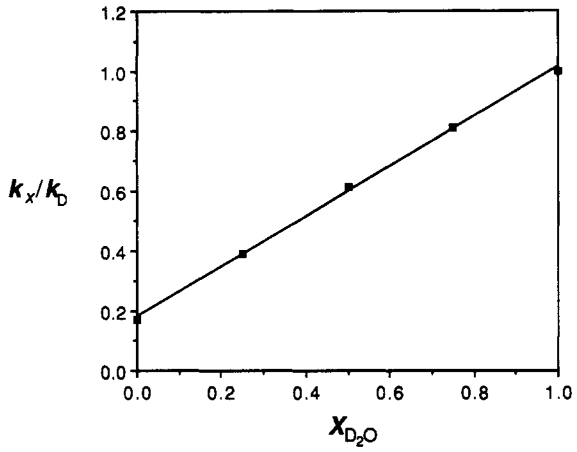
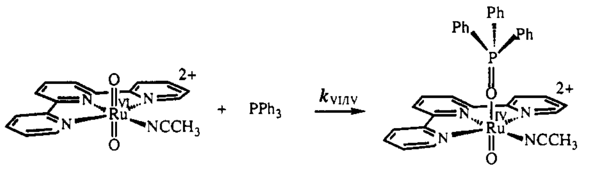


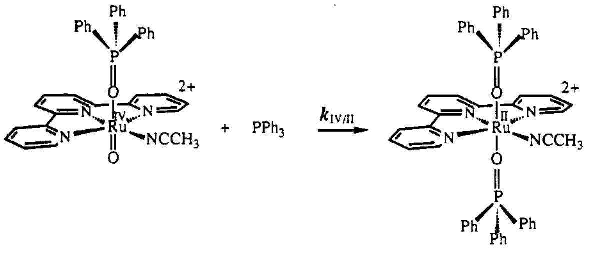
Figure 5. Plot of k_X/k_D vs mole fraction D_2O (X_D) for the Ru(IV) → Ru(II) step in the oxidation of $PPh_2CH_2CH_2PPh_2$ by *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ in CH_3CN at T = 20 °C. The quantity k_D is the rate constant with added D_2O and k_X the rate constant at the composition X_D; $[H_2O]$ + $[D_2O]$ = 1.75 M after mixing.

Discussion

Oxidation of PPh_3. The oxidation of PPh_3 by *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ in acetonitrile was studied to provide a comparison with the reactions between dppe or dppm and the same oxidant. Oxidation of PPh_3 is rapid and occurs by consecutive oxygen atom transfers (reactions 15, 16) to give the *trans*-bis(triphenylphosphine oxide) complex, which is observed as an intermediate. The first step is faster than the second by a factor of ~100 and occurs through Ru(IV) as a discrete intermediate.



(15)



(16)

The final products, $OPPh_3$ and $[Ru^{II}(tpy)(CH_3CN)_3]^{2+}$, are formed quantitatively in the presence of 2 or more equiv of PPh_3 by the sequential solvolysis of the bound phosphine oxides (reactions 7, 8). The first solvolysis step is faster than the second.

The appearance of the *trans*-bis(triphenylphospine oxide) product points to the *trans* isomer of the oxidant as the active form rather than *cis* (reaction 1a). The *trans* isomer of Ru(IV) is further reduced to Ru(II) without *trans* → *cis* isomerization (reaction 1b) occurring. Although a more powerful two-electron oxidant than *trans* (by ~0.34 eV), *cis* is highly disfavored thermodynamically (K_{isom} ~ 10^{-7} for reaction 1a) and present in small amount in solution.

Extensive reviews of metal-centered oxygen atom transfer and metal oxo complexes by Holm[29a] and by Nugent and Mayer[29b] have appeared. In Table III are listed relevant rate constants and activation parameters for O-atom-transfer reactions involving oxo complexes of Ru(VI) and Ru(IV). The oxidations of PPh_3, dppe, and dppm by *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ are among the most rapid O-atom-transfer reactions yet measured. The rate constants for the diphosphines are within a factor of ~10^2 of the diffusion-controlled limit in acetonitrile.

There are some notable trends in the data in Table III. Where the temperature dependence has been examined, the nearly constant values of $\Delta S^{\ddagger}$ for O-atom transfer to phosphines by Ru(VI) or Ru(IV) point to a common mechanism. For these reactions, the factor that dictates the relative rates is the energy of activation (or $\Delta H^{\ddagger}$). Comparisons with SMe_2, $OSMe_2$, and C_6H_5OH, where there are differences in $\Delta S^{\ddagger}$, suggest that $\Delta S^{\ddagger}$ may be symptomatic of mechanistic differences between O-atom transfers to different reductants. More data will have to be acquired to explore this point further.

An important factor influencing the rate constant for these and related reactions is the driving force. In Figure 6 is shown

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(29) (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401; *Coord. Chem. Rev.* **1990**, *100*, 183. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(30) (a) Muller, J. G.; Acquaye, J. H.; Takeuchi, K. J. *Inorg. Chem.* **1992**, *31*, 4552. (b) Acquaye, J. H.; Muller, J. G.; Takeuchi, K. J. *Inorg. Chem.* **1993**, *32*, 160.

Table III. Rate Constants and Activation Parameters for Some Oxygen Atom Transfer Reactions in Acetonitrile

oxidant	reductant	T (°C)	k ($M^{-1}\ s^{-1}$)	ΔH^{*} (kcal mol^{-1})	ΔS^{*} (eu)	reference
trans-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$	dppe[a]	20	$\sim 4 \times 10^8$			this work
trans-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$	PPh_3	20	2.28×10^6	4.2 ± 0.8	−19 ± 4	this work
$[Ru^{IV}(typ)(bpy)(O)]^{2+}$	PPh_3	20	1.25×10^6			12d
cis-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$	PPh_3	19	1.33×10^5	4.7 ± 0.5	−19 ± 3	12a
trans-$[Ru^{IV}(tpy)(O)(OPPh_3)(CH_3CN)]^{2+}$	PPh_3	20	1.05×10^4	5.9 ± 0.5	−20 ± 3	this work
trans-$[Ru^{IV}(tpy)(O)(O{=}PP)(CH_3CN)]^{2+}$	dppe	20	6.62×10^4			this work
trans-$[Ru^{IV}(tpy)(O)(O{=}PP)(H_2O)]^{2+}$[b]	dppe	20	1.49×10^4			this work
cis-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$	PhOH	25	1.9×10^2	10.3 ± 0.6	−14 ± 2	14b
trans-$[Ru^{VI}(14\text{-}TMC)(O)_2]^{2+}$[c]	PPh_3	20	8.36×10^1	8.7 ± 0.8	−20 ± 2	12c
cis-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$	$S(CH_3)_2$	20	1.71×10^1	8.0 ± 0.9	−26 ± 3	13
cis-$[Ru^{IV}(bpy)_2(PPh_3)(O)]^{2+}$	$S(C_4H_9)_2$	20	4.30	9.8 ± 2.7	−20 ± 7	3b
cis-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$	$OS(CH_3)_2$	25	1.34×10^{-1}	6.8 ± 0.2	−39 ± 3	13
cis-$[Ru^{IV}(bpy)_2(PPh_3)(O)]^{2+}$	$OS(C_4H_9)_2$	25	5.3×10^{-2}			3b
cis-$[Os^{VI}(bpy)_2(O)_2]^{2+}$	PPh_3	25	8.5×10^1			15

[a] dppe is $PPh_2PCH_2CH_2PPh_2$. [b] O=PP is diphenyl[2-(diphenylphosphinyl)ethyl]phosphine, $(O{=}P(Ph_2)CH_2CH_2PPh_2)$. [c] 14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

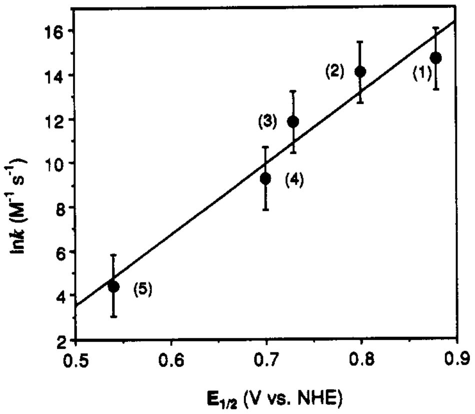


Figure 6. A plot of ln k (k in $M^{-1}\ s^{-1}$) for the oxidation of PPh_3 to the coordinated phosphine oxide in acetonitrile at 20 °C vs $E_{1/2}$ for the analogous Ru(VI/IV) or Ru(IV/II) couples at $T = 22$ °C, e.g., eq 17. The potentials are vs NHE at pH = 7.0 in H_2O. The oxidants are (1) *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$, (2) $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$, (3) *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$, (4) *trans*-$[Ru^{IV}(tpy)(O)(OPPh_3)(CH_3CN)]^{2+}$, and (5) *trans*-$[Ru^{VI}(14\text{-}TMC)O_2]^{2+}$, 14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. The linear correlation is to the equation $\ln k = -11.7 + 30.5E_{1/2}$.

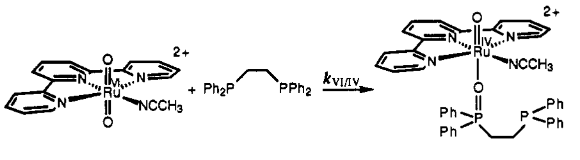
a plot of ln k for the bimolecular oxidation of PPh_3 in acetonitrile by a series of oxo complexes vs redox potentials for the analogous Ru(VI/IV) or Ru(IV/II) couples in water, e.g.,

$$\textit{trans-}[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+} + 2H^+ + 2e^- \rightarrow [Ru^{IV}(tpy)(O)(H_2O)_2]^{2+} \quad (17a)$$

$$\textit{cis-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + 2H^+ + 2e^- \rightarrow [Ru^{II}(bpy)_2(py)(H_2O)]^{2+} \quad (17b)$$

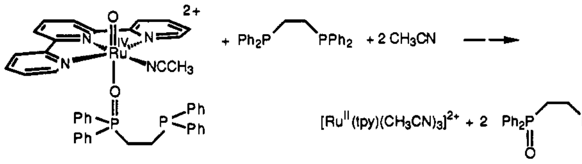
Driving forces for the actual O-atom-transfer reactions in acetonitrile are not known. The M(VI/IV) or M(IV/II) potentials, which involve the addition of two protons and two electrons to the oxidants, provide a relative measure of their thermodynamic abilities as two-electron oxidants. The unknown potential for the $OPPh_3/PPh_3$ couple in acetonitrile is a constant in the correlation. The data are too limited to draw firm conclusions, but they clearly illustrate the effect of driving force on rate constant for these reactions. There is a linear increase in k from 8.36×10^1 to $2.28 \times 10^6\ M^{-1}\ s^{-1}$ for oxidants whose driving forces increase by ~0.45 eV in H_2O. A related correlation has been found by Takeuchi et al., but between $E_{1/2}$ values for Ru(IV/II) couples for a series of triarylphosphine complexes, e.g., $[Ru(bpy)_2(PPh_3)(O)]^{2+}$, and their rate constants for oxidation of benzyl alcohol. Those authors developed a detailed analysis based on substituent effects both at the phosphine ligand and for a series of para-substituted benzyl alcohols.[30a] Linear correlations were also found between $E_{1/2}$ and rate constants for the oxidations of thioanisole and methylphenyl sulfoxide.[30b]

Oxidation of dppe and dppm. Oxidation of dppe (and dppm) also occurs sequentially, by Ru(VI) → Ru(IV) and Ru(IV) → Ru(II) steps which are separable kinetically. By inference, the first step gives a monodentate mono-phosphine oxide intermediate of Ru(IV), as was the case for PPh_3.



(18a)

Direct evidence for the once-oxidized ligands was obtained with the diphosphines present in 5- or 10-fold excess. Under these conditions Ru(IV) is reduced further by a second diphosphine. The mono-phosphine oxide ligand appears as the product, reaction 18b, following solvolysis of the intermediate shown in structure **5**.



(18b)

Under 1:1 conditions, the Ru(IV) → Ru(II) reduction takes a different course. The kinetics become first order. A chelated diphosphine dioxide complex of Ru(II) appears as an intermediate,

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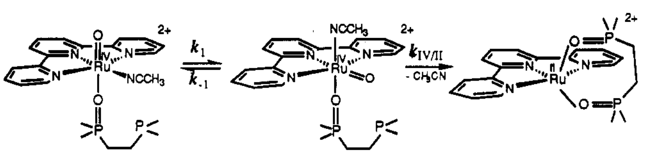
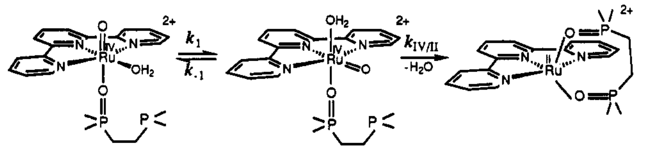
(31) (a) In the intermolecular oxidation of PPh_3 by *trans*-$[Ru^{IV}(tpy)(O)(OPPh_3)(CH_3CN)]^{2+}$ the rate constant for the redox step is $k_{IV/II} > k_{obs}/K_A$, where k_{obs} is the experimentally observed rate constant and K_A the equilibrium constant for preassociation between the reactants. This quantity can be estimated from the Eigen–Fuoss equation $K_A = 4\pi N_0(\alpha_1 + \alpha_2)^3/3000$ in which N_0 is Avogadro's number and α_1 and α_2 molecular radii of the reactants assumed to be spheres.[31b–d] By assuming close contact, $\alpha_1 = 4.5$ Å for PPh_3, $\alpha_2 = 5.6$ Å for the complex, and $K_A = 2.6\ M^{-1}$.[31e] Since $k_{obs} = 1.04 \times 10^4\ M^{-1}\ s^{-1}$, this gives $k_{IV/II} > 4.0 \times 10^3\ s^{-1}$ compared to $k_{IV/II} = 4.5 \times 10^1\ s^{-1}$ from Table II. The inequality arises from the fact that K_A provides an estimate of the equilibrium constant for bringing spherical reactants into close contact. Given the spatial and orientational demands of the oxo-transfer reaction, only a fraction of the relative orientations of the reactants can participate in O-atom transfer. Similarly, as pointed out by a reviewer, the demands imposed by formation of the large ring systems in the intramolecular O-atom-transfer step must also play a role. (b) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059. (c) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883. (d) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657. (e) The radii equivalent to the sphere of equal volume values were calculated by using the relation $\alpha = {}^1/_2(d_1d_2d_3)^{1/3}$. The d_i are the "diameters" along the three molecular axes. Values of d_i were estimated from ChemDraw 3D molecular models and corrected to agree with known crystallographic values (py–Ru–py = 13.6 Å, py–Ru–$NCCH_3$ = 12.8 Å, O=Ru–O=PPh_3 = 8.2 Å).

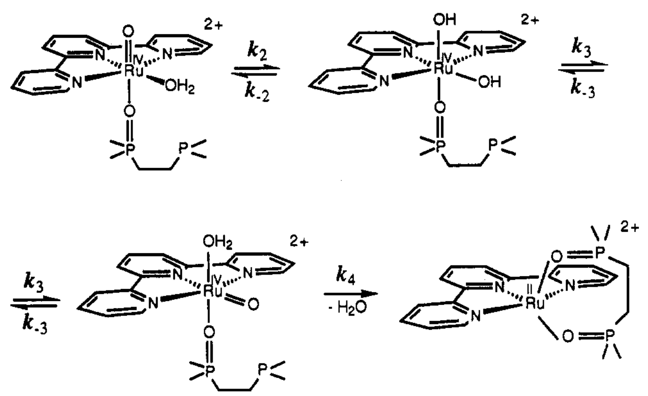
Scheme I



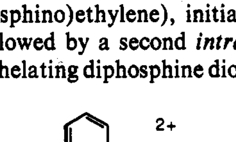
Scheme II



Scheme III

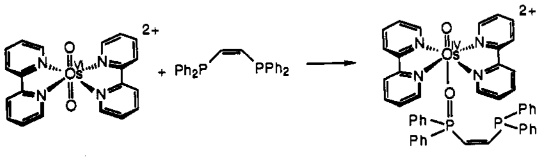


and it undergoes stepwise solvolysis to give the final diphosphine dioxide product. These observations are consistent with an intramolecular mechanism, but one in which isomerization of the remaining oxo group occurs *prior* to oxidation. For the reactions between *cis*-[Os^{VI}(bpy)$_2$(O)$_2$]$^{2+}$ and dppm or *cis*-dppene (*cis*-1,2-bis(diphenylphosphino)ethylene), initial *intermolecular* O atom transfer is followed by a second *intramolecular* O-atom transfer to give the chelating diphosphine dioxide, **6**.[15] For *trans*-



(**6**)

[Os^{VI}(bpy)$_2$(O)$_2$]$^{2+}$ the once-oxidized ligand does not span the coordination sphere to the second oxo group. A second O-atom transfer occurs, but it is intermolecular to give a diphosphine dioxide oligomer.[15]



(19)

By inference, Ru(IV) → Ru(II) reduction also involves *cis*-O-atom transfer and, therefore, prior isomerization at Ru(IV), Scheme I. Given the facile oxidation of PPh$_3$ by Ru(IV), and the fact that k_{obs} is nearly the same within experimental error for both dppe and dppm, the rate-determining step appears to be isomerization at Ru(IV) preceding O-atom transfer with $k_{IV/II} > k_{-1}$ in Scheme I.[31] With this interpretation, $k_{obs} = k_1 = 4.5 \times 10^1$ s^{-1}, and isomerization may be induced by dissociative loss of acetonitrile.

In acetonitrile solutions containing 3.5 M H$_2$O (1.75 M after mixing) the distribution between *trans*-[Ru^{VI}(tpy)(O)$_2$(H$_2$O)]$^{2+}$ (96%) and *trans*-[Ru^{VI}(tpy)(O)$_2$(CH$_3$CN)]$^{2+}$ (4%) favors the aqua complex, reaction 5. The two react independently since their interconversion is slow ($t_{1/2}$ = 141 ms) on the time scales of the reactions with the diphosphines. Under these conditions 96% of the Ru(VI) → Ru(IV) events must give the Ru(IV) aqua complex initially. The subsequent intramolecular oxidation is also first order in this case *but is slower by a factor of ~10³* compared to pure acetonitrile (k(20 °C) = (6.20 ± 0.12) × 10^{-2} s^{-1}). By inference, intramolecular isomerization is far slower for the aqua complex, Scheme II.

In acetonitrile solutions containing equal amounts of the aqua and acetonitrile complexes (0.075 M in H$_2$O after mixing), the reduction of Ru(VI) follows biexponential kinetics with the rate constants from the fits $k_1(20\ ^\circ\mathrm{C}) = 5 \times 10^1$ s^{-1} and $k_2(20\ ^\circ\mathrm{C}) = 6 \times 10^{-2}$ s^{-1}. Under these conditions parallel uncoupled reactions occur for the acetonitrile and aqua complexes. From this observation, interconversion between *trans*-[Ru^{IV}(tpy)(O)(O=P(PPh$_2$)CH$_2$CH$_2$PPh$_2$)(H$_2$O)]$^{2+}$ and *trans*-[Ru^{IV}(tpy)(O)(O=P(PPh$_2$)CH$_2$CH$_2$PPh$_2$)(CH$_3$CN)]$^{2+}$ must be slow, with $k < 2 \times 10^{-2}$ s^{-1}.

Isomerization of the aqua complex is not only slow, but occurs with an inverse H$_2$O/D$_2$O kinetic isotope effect of 0.18 ± 0.02. From this it can be inferred tht there is a change in mechanism from dissociative loss of acetonitrile to one involving proton transfer. A possible mechanism is shown in Scheme III. It involves intramolecular proton transfer to give a dihydroxo isomer which is expected to be thermodynamically unstable due to loss of multiple bonding at Ru(IV).[29] This mechanism assumes that the *cis*-oxo complex (rather than the dihydroxo intermediate) is the reactive form toward O-atom transfer. There are literature precedents for intramolecular proton transfer between aqua and oxo groups in organometallic compounds, between oxo and peroxo ligands, between oxo and allyloxo ligands, between imido and amido ligands, and among oxygen and nitrogen acids and bases (e.g., in the chemistry of diamine monocations).[31,32]

Presumably, a solvent-loss isomerization pathway exists for the aqua complex as well as for the acetonitrilo complex but is too slow to compete. Given this conclusion, loss of water from Ru(IV) is considerably slower ($k < 2 \times 10^{-2}$ s^{-1}) than loss of acetonitrile ($k = 4.5 \times 10^1$ s^{-1}).

Since intramolecular O-atom transfer is expected to be rapid[31] ($k_4 \gg k_{-3}$ in Scheme III), the generalized rate constant expression for the mechanism in Scheme III is

$$k_{obs} = k_2 k_3/(k_{-2} + k_3) \tag{20}$$

The two limiting forms of eq 20 both involve rate-determining proton transfer: (1) with $k_3 \gg k_{-2}$, $k_{obs} = k_2$ and rate-limiting proton transfer occurs from aqua to oxo; (2) with $k_{-2} \gg k_3$, rate-limiting transfer occurs from hydroxo to hydroxo. Both the k_{-2} and k_3 steps involve hydroxo → hydroxo proton transfer, in one case to give the *trans* isomer and, in the other, the *cis* isomer.

Proton transfer to or from oxygen in an organic molecule is normally rapid as long as the hybridization at oxygen remains sp^3.[33] In oxo complexes there are significant electronic interactions between the dπ orbitals of the metal and pπ orbitals at oxygen, and a loss in π bonding occurs upon protonation of the oxo.[34] The

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resulting changes in bonding and structure can create a significant barrier to intramolecular proton transfer consistent with the slow process observed here being the result.[35]

Additional evidence concerning the proton-transfer step(s) is available from the data on the H_2O/D_2O kinetic isotope effect. In magnitude it is one of the smallest kinetic isotope effects ever reported.[36] The effect varies linearly with the mole fraction of D_2O in D_2O/H_2O mixtures (Figure 5). From this it can be inferred that the H/D fractionation factor for the bound H_2O molecule in *trans*-$[Ru^{IV}(tpy)(O)(O{=}P(PPh_2)CH_2CH_2PPh_2)(H_2O)]^{2+}$ is close to unity, comparable to bulk water in acetonitrile. Further, it can be concluded that, to any significant degree, *only a single proton is involved* in the step or steps responsible for the inverse isotope effect.[37] This rules out, for example, proton transfer through intervening bridging H_2O molecules.

The appearance of normal or inverse kinetic isotope effects has been used to distinguish rate-limiting and pre-equilibrium proton transfer.[37] Experimental precedent suggests that inverse isotope effects appear more commonly in reactions involving rapid pre-equilibria with unstable intermediates which possess increased zero-point energy relative to the reactants.[38,39] This could be the case here. For the exchange reaction in 21, $K = 0.19$.[40] The heavier isotope tends to concentrate in water in this equilibrium because of the gain in zero-point energy. There are three vibrational modes for water and only two for the two hydroxide ions. On the basis of zero point energy considerations and the equilibrium k_2/k_{-2} in Scheme III, deuterium would be expected to concentrate in *trans*-$[Ru^{IV}(tpy)(O)(O{=}P(PPh_2)CH_2CH_2PPh_2)(H_2O)]^{2+}$. The magnitude of K for reaction 21 is comparable to the inverse kinetic isotope effect that we measure.

$$2HO^- + D_2O \overset{K}{\rightleftharpoons} 2DO^- + H_2O \qquad (21)$$

It is not necessary to involve a pre-equilibrium. An inverse effect can exist for a single elementary step if there is proton tunneling.[41]

***trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ as a *cis*-Directed Four-Electron Oxidant.** The ion *trans*-$[Ru^{VI}(tpy)(O)_2(H_2O)]^{2+}$ circumvents the coordinative instability of *cis*-dioxo–Ru(VI) complexes by its *trans*-dioxo geometry and, at the same time, provides a pathway for isomerization at Ru(IV) by intramolecular proton transfer. In order for it to act as a *cis*-directed four-electron oxidant, the mechanism of the Ru(VI) → Ru(IV) step must involve O-atom transfer or a related pathway which "anchors" the reductant. Further, the subsequent intramolecular Ru(IV) → Ru(II) reaction must complete with *intermolecular* reduction of Ru(IV) by a second molecule of reductant. Normally, the intramolecular reaction would have a significant rate advantage because of the "anchoring" of the proximal reductant. However, with either *trans*-$[Ru^{IV}(tpy)(O)(O{=}P(PH_2)CH_2CH_2PPh_2)(CH_3CN)]^{2+}$ or *trans*-$[Ru^{IV}(tpy)(O)(O{=}P(Ph_2)CH_2CH_2PPh_2)(H_2O)]^{2+}$, intramolecular oxidation is rate limited by *trans* → *cis* isomerization and not by the second redox step. For the acetonitrilo complex, isomerization is limited by dissociative loss of acetonitrile and for the aqua complex by intramolecular proton transfer, which is even slower.

Slow intramolecular isomerization restricts the ability of Ru(IV) to complete the intramolecular four-electron oxidation. With the diphosphines in excess, product distributions are shifted toward the mono-phosphine oxides. The half-lives for intramolecular oxidation in *trans*-$[Ru^{IV}(tpy)(O)(O{=}P(Ph_2)CH_2CH_2PPh_2)(CH_3CN)]^{2+}$ and intermolecular oxidation of a second dppe are the same ($t_{1/2} = 0.017$ s) at a diphosphine concentration of 4.4×10^{-4} M. The problem of rate-limiting isomerization must be overcome in order for *cis*-directed four-electron oxidation to be successful under catalytic conditions with the reductant in excess. It will be less severe with bifunctional reductants which are less reactive and in dry acetonitrile, where isomerization of Ru(IV) is dictated by dissociative loss of acetonitrile rather than by intramolecular proton transfer.

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