

off, washed with *n*-hexane, and vacuum dried. Yield: 60–70%. Anal. Calcd for the unsolvated cluster  $C_{35}H_9CuN_3O_{19}Rh_9$ : C, 18.25; H, 0.55; N, 2.55. Found: C, 18.13; H, 0.64; N, 2.85. These analytical data indicate that, with the exception of the few larger crystals used for the X-ray analysis, the bulk of the product does not contain solvated thf, but possibly does contain some acetonitrile.

### X-ray Analysis

The crystal data are summarized in Table II. A crystal sample of  $0.10 \times 0.21 \times 0.30$  mm, on a glass fiber in the air, was mounted on an Enraf-Nonius CAD4 automated diffractometer. Cell parameters and the orientation matrix were obtained on the basis of 25 random intense reflections ( $16 < 2\theta < 25^\circ$ ). The intensity data were collected by using graphite-monochromatized Mo  $K\alpha$  radiation, by the  $\omega$ -scan method, within the limits  $3 < \theta < 24^\circ$ . A variable scan speed (from 2 to  $20^\circ/\text{min}$ ) and a variable scan range of  $(1.1 + 0.35 \tan \theta)^\circ$  were used, with a 25% extension at each end of the scan range for background determination. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the intensities, based on  $\psi$  scans ( $\psi = 0\text{--}360^\circ$  every  $10^\circ$ ) of suitable reflections with  $\chi$  values close to  $90^\circ$ ; the relative transmission factors had values in the range 0.71–1.00.

The structure was solved by direct methods and Fourier techniques, and refined by full-matrix least-squares techniques, on the basis of 4587 independent significant [ $I > 3\sigma(I)$ ] reflections. All atoms but those of the solvated tetrahydrofuran molecules were refined anisotropically. The hydrogen atoms were neglected. The final conventional agreement indices  $R$  and  $R_w$  were 0.026 and 0.034, respectively. The final difference Fourier map was rather flat, showing residual peaks not exceeding ca.  $1.2 \text{ e}/\text{\AA}^3$ . All computations were performed by using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants therein tabulated.

**Registry No.** [1]Cs<sub>3</sub>, 84179-28-2; 2, 119787-09-6; 2-C<sub>4</sub>H<sub>8</sub>O, 119793-83-8; [Cu(NCMe)<sub>4</sub>](BF<sub>4</sub>), 15418-29-8; Cu, 7440-50-8; Rh, 7440-16-6.

**Supplementary Material Available:** Listings of atomic coordinates (Table 1S), thermal parameters (Table 2S), and bond angles (Table 3S) and a summary of the crystal data (Table 4S) (8 pages); a listing of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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### Four-Electron Oxidations by Dioxo Complexes of Osmium(VI)

John C. Dobson and Thomas J. Meyer\*

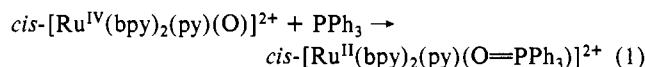
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Among a growing body of examples of higher oxidation state oxo and dioxo complexes of osmium and ruthenium<sup>1</sup> are the complexes *cis*- and *trans*-[Os<sup>VI</sup>(bpy)<sub>2</sub>(O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (bpy is 2,2'-bipyridine).<sup>1a,b</sup> From the results of a series of experiments in water, it is known that the Os(VI) complexes undergo reversible electron-proton additions via the intermediate oxidation states Os(V), Os(IV), and Os(III) to give, ultimately, [Os<sup>II</sup>(bpy)<sub>2</sub>(OH)<sub>2</sub>]<sup>2+</sup>.

Oxidation state VI for the *cis* isomer in acetonitrile is unstable with regard to isomerization to the *trans* isomer. In aqueous solution, a more rapid process than isomerism occurs in which a bpy ligand is lost, giving *trans*-Os<sup>VI</sup>(bpy)(O)<sub>2</sub>(OH)<sub>2</sub>. In oxidation state II, *trans*-[Os(bpy)<sub>2</sub>(OH)<sub>2</sub>]<sup>2+</sup> is unstable with regard to isomerization to *cis*-[Os(bpy)<sub>2</sub>(OH)<sub>2</sub>]<sup>2+</sup>.<sup>1a</sup>

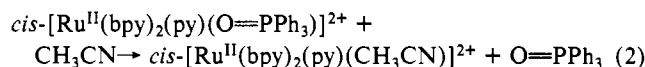
One of the reasons for our interest in dioxo complexes of Os(VI) and Ru(VI) is their implied reactivity as four-electron oxidants. Given the implied multiple electron character and the shared *cis*-dioxo structures, the *cis* complexes could conceivably mimic such oxidants as OsO<sub>4</sub> or RuO<sub>4</sub> in their reactivity.<sup>2</sup> They are also potential electrocatalysts given the known capabilities of Ru(IV/II) couples are electrocatalysts.<sup>3–5</sup> An additional question arises concerning the role of stereochemistry at the metal in determining oxidative reactivity. Electrochemical studies show that the *cis* complexes of Os(VI) or Ru(VI) are stronger oxidants thermodynamically than are the *trans* complexes. The major factor is the special electronic stabilization associated with the d<sup>2</sup> *trans*-dioxo structure for oxidation state VI. Electronic stabilization effects also affect the pattern of stable oxidation states. In acidic solution, oxidation states Os(IV) and Os(V) are actually stronger oxidants than Os(VI), and only the three-electron, three-proton couple *trans*-[Os<sup>VI</sup>(bpy)<sub>2</sub>(O)<sub>2</sub>]<sup>2+</sup>/*trans*-[Os<sup>III</sup>(bpy)<sub>2</sub>(OH)<sub>2</sub>(OH)]<sup>2+</sup> is observed.<sup>1a,6</sup>

The osmium(VI) dioxo complexes are not especially strong oxidizing agents. Compared to analogous complexes of ruthenium, which are more strongly oxidizing, the rates of oxidation of organic substrates like benzyl alcohol are quite slow. Earlier work with *cis*-[Ru<sup>IV</sup>(bpy)<sub>2</sub>(py)(O)]<sup>2+</sup> showed that the rate of oxidation of PPh<sub>3</sub> is rapid.<sup>7</sup>

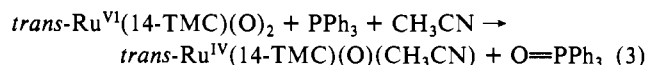


$$k(25^\circ \text{C in CH}_3\text{CN}) = 1.75 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

The coordinated OPPh<sub>3</sub> complex which is formed is unstable toward loss of phosphine oxide in a slower step.



Che and co-workers have shown that the reduction of a dioxo-osmium(VI) porphyrin complex by PPh<sub>3</sub> gives the four-electron reduction product Os<sup>II</sup>(OEP)(OPPh<sub>3</sub>)<sub>2</sub> (H<sub>2</sub>OEP = octaethylporphyrin).<sup>8</sup> Related work has shown that *trans*-dioxo complexes of Ru(VI) containing macrocyclic tertiary amines such as 14-TMC (14-TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) react with PPh<sub>3</sub> to give stable monooxo complexes of Ru(IV)<sup>9</sup>



Groves and Ahn have shown that *trans*-Ru<sup>VI</sup>(TMP)(O)<sub>2</sub> (TMP = tetramesitylporphyrin) is reduced in the presence of PPh<sub>3</sub> to give Ru<sup>II</sup>(TMP)(PPh<sub>3</sub>) and OPPh<sub>3</sub> via a Ru<sup>IV</sup>=O intermediate.<sup>10</sup> In order to probe the implied four-electron oxidative character of the *cis* and *trans* dioxo complexes of Os(VI), we have inves-

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(7) Moyer, B. A.; Sipe, B. K.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 1475.  
(8) Che, C. M.; Lai, T. F.; Chung, W. C.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 3907.  
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tigated their reactions with triphenylphosphine and two bis(phosphine) analogues.

### Experimental Section

**Materials.** Burdick and Jackson spectrograde acetonitrile was distilled under argon over  $P_2O_5$  on a Vigreux column. Triphenylphosphine (Aldrich Chemical Co.) was recrystallized from  $CH_2Cl_2$ /hexane prior to use. Bis(diphenylphosphino)methane (dppm) (97%, Aldrich Chemical Co.) and *cis*-1,2-bis(diphenylphosphino)ethylene (dppene) (Strem Chemical Co.) were recrystallized from argon-degassed absolute ethanol prior to use. Elemental analyses were conducted by Galbraith Laboratories, Knoxville, TN.

**Preparations.** The preparations of *cis*- and *trans*- $[Os^{VI}(bpy)_2(O)_2](ClO_4)_2$  have been described previously.<sup>18</sup> Dilute solutions of the latter complex ( $<10^{-3}$  M) in  $CD_3CN$  were prepared by the room-temperature isomerization of the *cis* complex,  $k(20^\circ C) = 4.3 \times 10^{-5} s^{-1}$  and monitored by  $^1H$  NMR. For the sparingly soluble *trans*- $[Os^{VI}(bpy)_2(O)_2]^{2+}$  ion in  $CD_3CN$ , resonances appear at 8.81 (d), 8.48 (d), 8.40 (t), and 7.86 ppm (t) vs TMS.<sup>11</sup>

***cis*- $[Os^{II}(bpy)_2(OPPh_3)_2](ClO_4)_2$ .** To 50 mL of  $CH_3CN$  under an inert argon atmosphere were added 100 mg (0.126 mmol) of *cis*- $[Os^{VI}(bpy)_2(O)_2](ClO_4)_2$  and 72 mg (0.273 mmol) of  $PPh_3$ . The solution was stirred for 10 min, after which time the volume was reduced to  $\sim 10$  mL on a rotary evaporator. The remaining 10 mL was pipetted into 150 mL of anhydrous diethyl ether to precipitate the complex as the  $ClO_4^-$  salt. The red-brown precipitate was collected on a medium glass frit and dried in vacuo. Yield: 135 mg, 85%. Anal. Calcd for  $OsC_{36}H_{46}P_2N_4O_{10}Cl_2$ : C, 53.45; H, 3.66; N, 4.45; P, 4.93. Found: C, 53.93; H, 4.05; N, 4.28; P, 4.72.

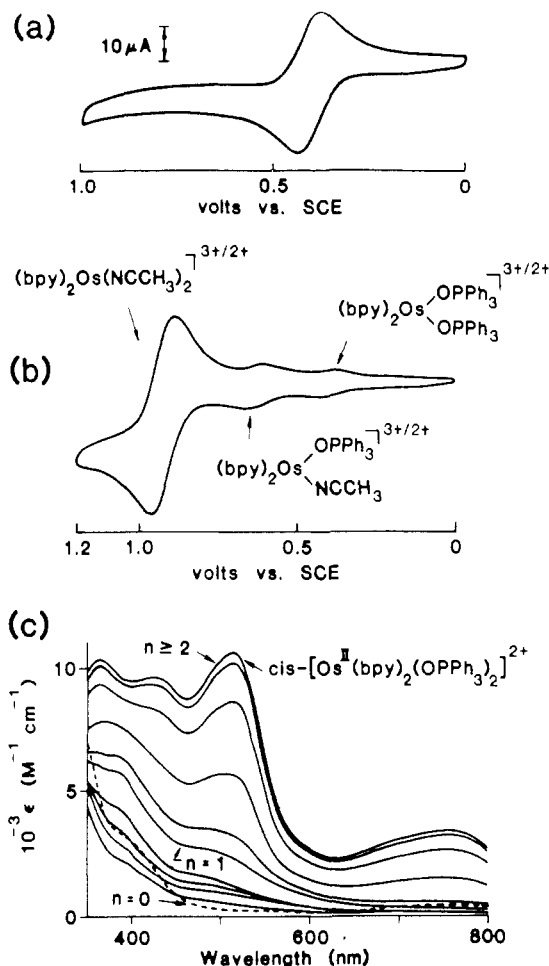
***trans*- $[Os^{II}(bpy)_2(OPPh_3)_2](ClO_4)_2$ , *cis*- $[Os^{II}(bpy)_2(O=PPh_2CH_2Ph_2P=O)](ClO_4)_2$  and *cis*- $[Os^{II}(bpy)_2(O=PPh_2CH=CHPh_2P=O)](ClO_4)_2$ .** These complexes were prepared in a manner similar to that described for *cis*- $[Os^{II}(bpy)_2(OPPh_3)_2](ClO_4)_2$  above but by using the indicated ligand and appropriate stoichiometries.

**Spectroscopy.** UV-vis spectra were recorded in 1 cm quartz cells at room temperature on a Hewlett-Packard Model 8450A diode-array spectrophotometer.  $^{31}P$  NMR spectra were recorded on a Bruker 250-MHz Fourier transform spectrometer.

**Electrochemistry.** Electrochemical measurements were made by using a PAR Model 173 potentiostat with a Model 276 interface and a PAR Model 175 universal programmer as a sweep generator for voltammetric experiments. Measurements were made vs the saturated calomel electrode (SCE) at  $22 \pm 2^\circ C$  and are uncorrected for junction potential effects. Cyclic voltammetric experiments were performed in a 10-mL beaker using a  $\sim 0.07$  cm<sup>2</sup> glassy-carbon disk electrode (Tokai Carbon, Inc.) as the working electrode and a platinum wire as the auxiliary electrode.

### Results

When acetonitrile solutions containing either *cis*- or *trans*- $[Os^{VI}(bpy)_2(O)_2]^{2+}$  are allowed to react with  $PPh_3$  in excess, rapid reactions occur. For the *cis* complex the product of the reaction was isolated and found to be *cis*- $[Os^{II}(bpy)_2(OPPh_3)_2]^{2+}$  by elemental analyses. In Figure 1a is shown a cyclic voltammogram of the reaction solution at time  $t = 2$  min after *cis*- $[Os^{VI}(bpy)_2(O)_2]^{2+}$  was mixed with 2 equiv of  $PPh_3$  in acetonitrile. A reversible ( $\Delta E_p = 60$  mV) wave appears at  $E_{1/2} = 0.41$  V vs SCE for the Os(III/II) couple *cis*- $[Os^{II}(bpy)_2(OPPh_3)_2]^{3+/2+}$ . On a longer time scale the  $(OPPh_3)_2$  complex is unstable with regard to solvolysis. The cyclic voltammogram in Figure 1b after 24 h provides clear evidence for the initial complex, the known bis(acetonitrile) complex whose Os(III/II) couple appears at  $E_{1/2} = 0.90$  V vs SCE,<sup>12</sup> and an intermediate with  $E_{1/2} = 0.65$  V. After 24 h  $OPPh_3$  was also present in the solution as evidenced by TLC and  $^{31}P$  NMR in  $CD_3CN$ . In accord with the expected enhanced inertia toward substitution of Os(II) compared to Ru(II), the half-life for  $OPPh_3$  loss in  $CH_3CN$  is many hours longer for *cis*- $[Os^{II}(bpy)_2(OPPh_3)_2]^{2+}$  than for *cis*- $[Ru^{II}(bpy)_2(py)(OPPh_3)]^{2+}$  (reaction 2). The intermediate observed during the solvolysis was not isolated, but the appearance of the Os(III/II) wave at an average value of the potentials for the  $(OPPh_3)_2$  and  $(CH_3CN)_2$  complexes is consistent with its formulation as *cis*-



**Figure 1.** (a) Cyclic voltammogram (100 mV/s) of a solution containing 1 mM *cis*- $[Os^{II}(bpy)_2(OPPh_3)_2]^{2+}$  in  $CH_3CN/0.1$  M  $[N(C_4H_9)_4](PF_6)$  vs SCE. (b) Cyclic voltammogram (100 mV/s) of a solution containing *cis*- $[Os^{II}(bpy)_2(OPPh_3)_2]^{2+}$  in  $CH_3CN$  after 24 h ( $\mu = 0.1$  M (TBAH); vs SCE). (c) UV-vis spectra obtained in the titration of *cis*- $[Os^{VI}(bpy)_2(O)_2]^{2+}$  by  $PPh_3$  in  $CH_3CN$ . Spectra were recorded for individual solutions containing  $2.16 \times 10^{-4}$  M *cis*- $[Os^{VI}(bpy)_2(O)_2]^{2+}$  ( $ClO_4^-$ ) and  $n$  equiv ( $n = 0, 0.2, 0.4, 0.6, \dots, 2.0$ ) of  $PPh_3$  in  $CH_3CN$ .

**Table I.** Visible Spectral Data for Complexes of the Type *cis*- $[Os^{II}(bpy)_2(L)_2]^{2+}$

complex	$\lambda_{max}$ , nm ( $\epsilon$ , $M^{-1} cm^{-1}$ )
<i>cis</i> - $[Os^{II}(bpy)_2(OH_2)_2]^{2+ a}$	350 (7200), 419 (6900), 500 (8000), 718 (2800)
<i>cis</i> - $[Os^{III}(bpy)_2(OH_2)(OH)]^{2+ a}$	372 (4200)
<i>cis</i> - $[Os^{II}(bpy)_2(OPPh_3)_2]^{2+ b}$	361 (9600), 431 (8700), 516 (10200), 747 (3900)
<i>cis</i> - $[Os^{II}(bpy)_2(O=PPh_2CH_2Ph_2P=O)]^{2+ b}$	368 (6500), 520 (6500), 746 (2300)

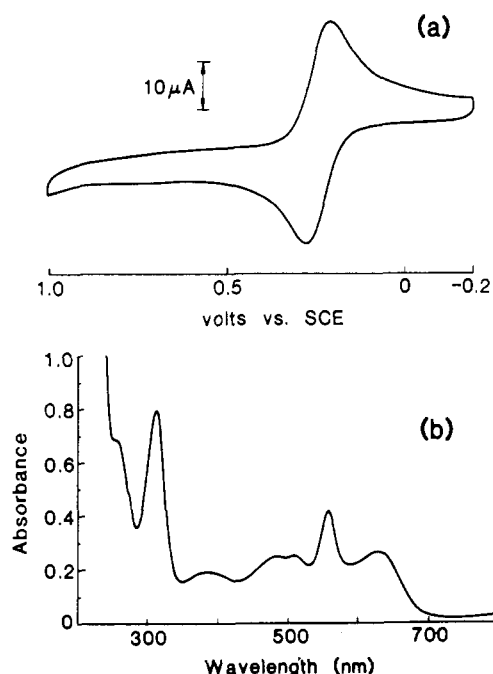
<sup>a</sup>Spectra recorded in 0.1 N  $H_2SO_4(aq)$ . <sup>b</sup>Spectra recorded in  $CH_3CN$ .

$[Os^{II}(bpy)_2(CH_3CN)(OPPh_3)]^{2+}$ .

In Figure 1c is shown the results of a spectrophotometric titration of *cis*- $[Os^{VI}(bpy)_2(O)_2]^{2+}$  by  $PPh_3$  in acetonitrile solution. The figure shows spectra obtained after the addition of  $n$  equiv ( $n = 0, 0.2, 0.4, 0.6, \dots, 2.0$ ) of  $PPh_3$ . The final spectrum, which was obtained after the addition of 2 or more equiv or more of  $PPh_3$ , is labeled *cis*- $[Os^{II}(bpy)_2(OPPh_3)_2]^{2+}$ . The spectrum is similar in both intensity and band shape to the spectrum of *cis*- $[Os^{II}(bpy)_2(OH_2)_2]^{2+}$  (Table I).<sup>1a,11</sup> It is an important point that as the titration proceeds to a nearly 1:1 stoichiometry, there is still essentially none of the final Os(II) product in the solution as shown by the absence of significant absorption at 747 nm. The spectral changes observed in the titration are consistent with the appearance of Os(III), and electrochemical experiments in solutions containing a 1:1 ratio of  $PPh_3$  to Os(VI) show that the *cis*- $[Os(bpy)_2(OPPh_3)_2]^{3+/2+}$  couple is present in solution. The initial reduction

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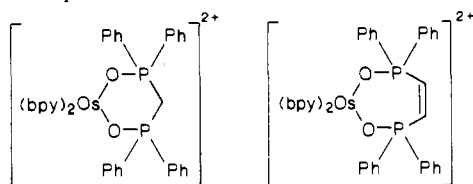


**Figure 2.** (a) Cyclic voltammogram (100 mV/s) of a solution containing 1 mM *trans*-[Os<sup>II</sup>(bpy)<sub>2</sub>(OPPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> in CH<sub>3</sub>CN/0.1 M [N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>](PF<sub>6</sub>) vs SCE. (b) UV-vis spectrum of a solution containing  $\sim 4 \times 10^{-5}$  M *trans*-[Os<sup>II</sup>(bpy)<sub>2</sub>(OPPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> in CH<sub>3</sub>CN.

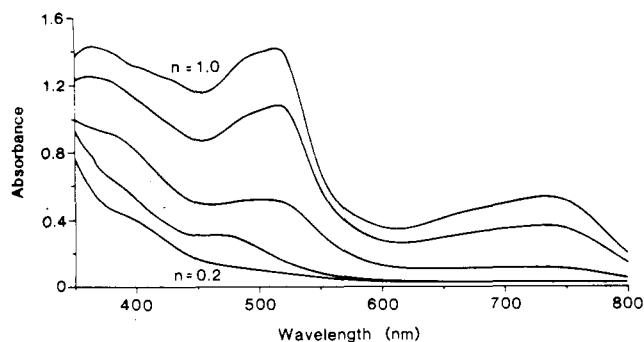
of Os(VI) by PPh<sub>3</sub> is rapid. A preliminary stopped-flow experiment monitored at 520 nm with solutions  $4.09 \times 10^{-2}$  M in PPh<sub>3</sub> and  $4.09 \times 10^{-4}$  M in *cis*-[Os<sup>VI</sup>(bpy)<sub>2</sub>(O)<sub>2</sub>]<sup>2+</sup> showed that the initial stage of the reaction occurs with a rate constant of  $\sim 85$  M<sup>-1</sup> s<sup>-1</sup>, if it is assumed that the reaction is first order in each reactant.

The reaction between *trans*-[Os<sup>VI</sup>(bpy)<sub>2</sub>(O)<sub>2</sub>]<sup>2+</sup> and PPh<sub>3</sub> proceeds via the same stoichiometry. The cyclic voltammogram in Figure 2a shows the characteristic shift of the Os(III/II) couple to lower potentials relative to the *cis* isomer with  $E_{1/2} = 0.23$  V vs SCE for the *trans*-[Os(bpy)<sub>2</sub>(OPPh<sub>3</sub>)<sub>2</sub>]<sup>3+/2+</sup> couple. As shown by the spectrum of the final product in Figure 2b, *trans*-[Os<sup>II</sup>(bpy)<sub>2</sub>(OPPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> exhibits the characteristic band pattern associated with bis(bipyridyl) complexes of Os(II) in the *trans* geometry and is similar to *trans*-[Os<sup>II</sup>(bpy)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> in that regard.<sup>1a,13</sup> The *trans*-(OPPh<sub>3</sub>)<sub>2</sub> complex is far more stable than the *cis* complex toward solvolysis, and electrochemical studies show no evidence for loss of OPPh<sub>3</sub> after a period of 24 h.

**Reactions with Chelating Diphosphines.** An attempt to demonstrate the four-electron capability of the oxo complexes as oxidants toward a single substrate was made based on their reactions with the potentially chelating diphosphines Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (dppm) and *cis*-Ph<sub>2</sub>PCH=CHPPh<sub>2</sub> (*cis*-dppene). As with PPh<sub>3</sub>, the reactions were rapid and stoichiometric, in this case with a 1:1 ratio of added ligand. The products were very similar for both ligands. For the reaction between dppm and the *cis*-dioxo complex an Os(III/II) couple appears in the final product solution with  $E_{1/2} = 0.44$  V vs SCE (CH<sub>3</sub>CN/0.1 M TBAH). For *cis*-dppene a reversible couple appears at  $E_{1/2} = 0.40$  V. The magnitudes of the redox potentials and the patterns of UV-visible bands (Table I) are consistent with the following chelating phosphine oxide complexes as products:

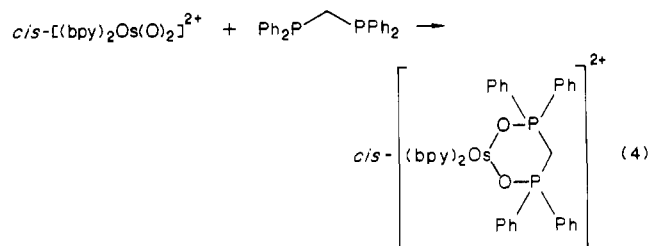


(13) Megehee, E. Ph.D. Dissertation, The University of North Carolina, Chapel Hill, NC, 1986.



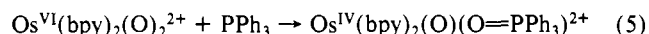
**Figure 3.** UV-vis spectra of solutions containing  $2.27 \times 10^{-4}$  M *cis*-[Os<sup>VI</sup>(bpy)<sub>2</sub>(O)<sub>2</sub>]<sup>2+</sup> and  $n$  equiv ( $n = 0.2, 0.4, 0.6, 0.8, 1.0$ ) of dppm.

The results of the spectrophotometric titration with dppm in Figure 3 verified the reaction stoichiometry in reaction 4.

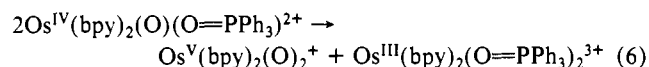


## Discussion

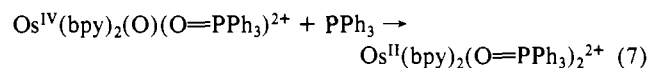
The results described here show that *cis*- and *trans*-[Os<sup>VI</sup>(bpy)<sub>2</sub>(O)<sub>2</sub>]<sup>2+</sup> undergo rapid and quantitative reactions with stoichiometric or excess amounts of PPh<sub>3</sub> to give the corresponding OPPh<sub>3</sub> complexes. Spectral and electrochemical observations at varying PPh<sub>3</sub> to dioxo ratios show that the initial product that appears is the Os(III) form of the (OPPh<sub>3</sub>)<sub>2</sub> complex. The reactions must occur in a stepwise manner. The initial step in the mechanism presumably involves reduction of Os(VI) to Os(IV) by analogy with reaction 1.



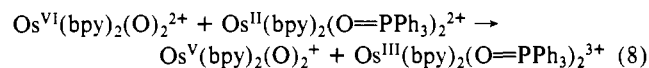
Given the appearance of the Os(III) form of the (OPPh<sub>3</sub>)<sub>2</sub> product, a second step must also occur involving either disproportionation of Os(IV)



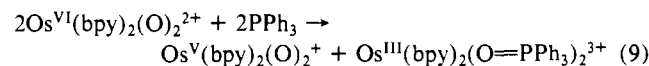
or oxidation of a second PPh<sub>3</sub> by Os(IV)



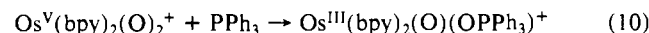
followed by outer-sphere electron transfer between Os(VI) and Os(II)



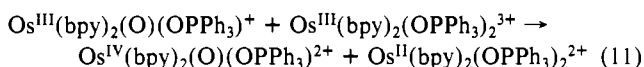
From the redox potentials for the *cis*-[Os(bpy)<sub>2</sub>(OPPh<sub>3</sub>)<sub>2</sub>]<sup>3+/2+</sup> couple at  $E_{1/2} = 0.41$  V vs SCE and the *cis*-[Os(bpy)<sub>2</sub>(O)<sub>2</sub>]<sup>2+/+</sup> couple at  $E_{1/2} = 0.80$  V, the electron transfer in reaction 8 is favorable. At PPh<sub>3</sub> to dioxo ratios less than 1, reactions 5–8 lead to the stoichiometry in reaction 9. The details of the subsequent



reduction of *cis*-[Os<sup>V</sup>(bpy)<sub>2</sub>(O)<sub>2</sub>]<sup>+</sup> by PPh<sub>3</sub> are not available from the spectral data, but given the formation of the (OPPh<sub>3</sub>)<sub>2</sub> product, Os(V) must undergo two successive O atoms transfer reactions, perhaps via

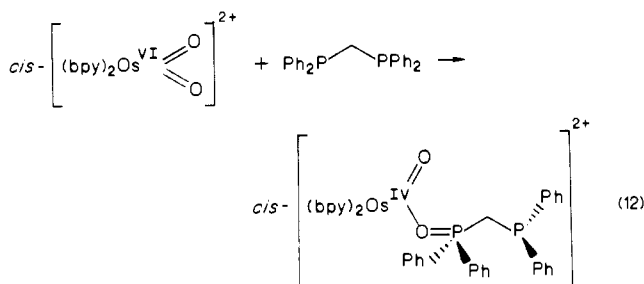


followed by

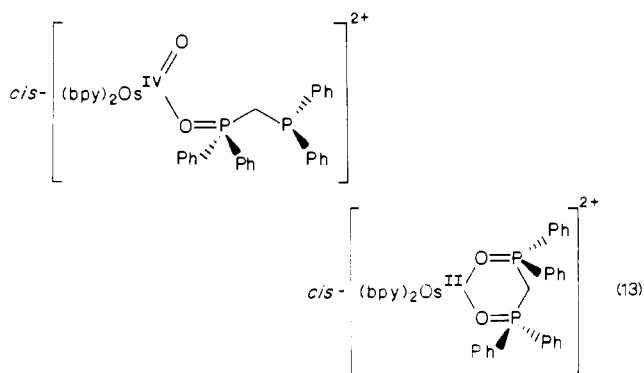


and reaction 7.

The reactions with the potentially chelating phosphine ligands *dppm* and *cis-dppene* show that the *cis*-dioxo complex has the capability of carrying out the four-electron oxidation of a single substrate. The reactions presumably occur through an intermediate  $\text{Os}(\text{IV})$  stage

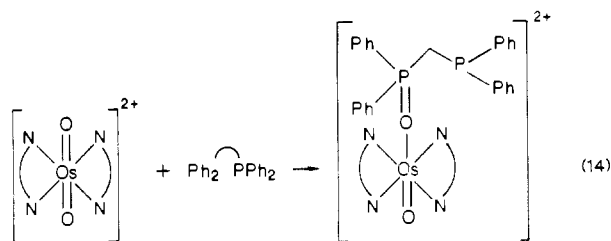


followed by rapid intramolecular oxidation of the second phosphine site

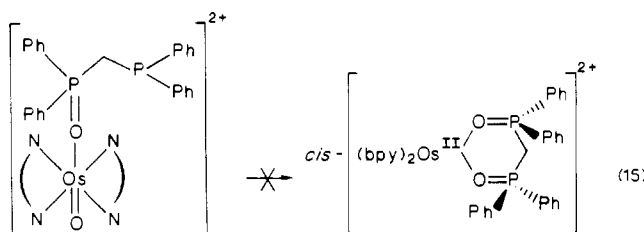


At diphosphine to dioxo ratios less than 0.5 (Figure 3),  $\text{Os}(\text{III})$  appears as the initial product by disproportionation as in reaction 6 or by outer-sphere electron transfer as in reaction 8.

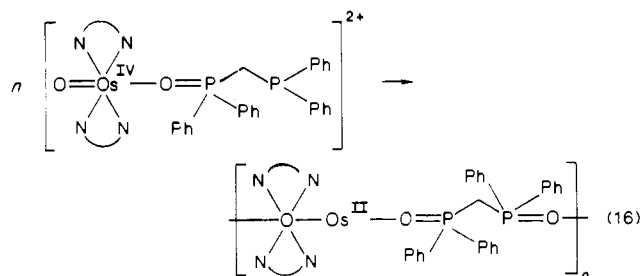
The results of cyclic voltammetry and UV-vis spectra show that the reactions between  $\text{trans-}[\text{Os}^{\text{VI}}(\text{bpy})_2(\text{O})_2]^{2+}$  and the diphosphines give *trans*  $\text{Os}(\text{II})$  products. These results rule out an initial two-electron oxidation by  $\text{Os}(\text{VI})$



followed by intramolecular oxidation and *trans*  $\rightarrow$  *cis* isomerization



The reactions must occur via initial  $\text{Os}(\text{VI}) \rightarrow \text{Os}(\text{IV})$  reduction (reaction 14) followed by further oxidation of the coordinated ligand to form coordination polymers as in



We have made no attempt to isolate and characterize the polymers.

**Acknowledgment** is made to the National Science Foundation under Grant No. CHE-8601604 for support of this research.

**Registry No.** *dppm*, 2071-20-7; *dppene*, 983-80-2; *cis-}[\text{Os}^{\text{VI}}(\text{bpy})\_2(\text{O})\_2](\text{ClO}\_4)\_2, 101980-20-5; *trans-}[\text{Os}^{\text{VI}}(\text{bpy})\_2(\text{O})\_2](\text{ClO}\_4)\_2, 102045-51-2; *cis-}[\text{Os}^{\text{II}}(\text{bpy})\_2(\text{OPPh}\_3)\_2](\text{ClO}\_4)\_2, 120022-10-8;  $\text{PPh}_3$ , 603-35-0;  $\text{O}^{2-}$ , 16833-27-5; *trans-}[\text{Os}^{\text{II}}(\text{bpy})\_2(\text{OPPh}\_3)\_2](\text{ClO}\_4)\_2, 120056-97-5; *cis-}[\text{Os}^{\text{II}}(\text{bpy})\_2(\text{O}=\text{PPh}\_2\text{CH}\_2\text{Ph}\_2\text{P}=\text{O})](\text{ClO}\_4)\_2, 120032-85-1; *cis-}[\text{Os}^{\text{II}}(\text{bpy})\_2(\text{O}=\text{PPh}\_2\text{CH}=\text{CHPh}\_2\text{P}=\text{O})](\text{ClO}\_4)\_2, 120022-12-0; *cis-}[\text{Os}^{\text{II}}(\text{bpy})\_2(\text{O}=\text{PPh}\_3)\_2]^{3+}, 120022-13-1; *cis-}[\text{Os}^{\text{II}}(\text{bpy})\_2(\text{MeCN})\_2]^{2+}, 116946-87-3; *cis-}[\text{Os}^{\text{II}}(\text{bpy})\_2(\text{CH}\_3\text{CN})(\text{OPPh}\_3)]^{2+}, 120022-14-2; *trans-}[\text{Os}(\text{bpy})\_2(\text{OPPh}\_3)\_2]^{3+}, 120056-98-6; *cis-}[\text{Os}(\text{bpy})\_2(\text{O})\_2]^{4+}, 101980-22-7.***********

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### Redetermination of the Crystal and Molecular Structure of Tris(bipyridine)chromium(III) Hexafluorophosphate

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Received November 2, 1988

The structure of  $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$  (where *bpy* = 2,2'-bipyridine) has been previously described in space group *R*32,<sup>1</sup> with an asymmetric unit containing two independent cations, each possessing crystallographic 32 (*D*3) symmetry, and two independent anions, each possessing crystallographic 2-fold (*C*2) symmetry. The two cations, which alternate along a 3-fold axis coincident with the *c* axis of the unit cell, were found to have "opposite chirality". Wide variations in the bonding parameters of chemically equivalent groups were observed, which included<sup>2</sup> N–Cr–N bite angles of 74.8 and 84.7°, N(1)–C(2) distances ranging from 1.33 to 1.40 Å, N(1)–C(6) distances ranging from 1.31 to 1.41 Å, C(2)–C(2a) distances of 1.39 and 1.55 Å, C–C distances within pyridine rings ranging from 1.20 to 1.53 Å, P–F distances ranging from 1.38 to 1.63 Å, and F–P–F<sub>cis</sub> angles ranging from 78.5 to 101.5°.

We became interested in the structure of  $\text{Cr}(\text{bpy})_3^{3+}$  because of our work with the related complexes  $\text{Cr}(\text{bpm})_2\text{Cl}_2^+$ ,  $\text{Cr}(\text{bpm})_3^{3+}$ , and  $\text{Cr}(\text{dpp})_3^{3+}$  (where *bpm* = 2,2'-bipyrimidine and *dpp* = 2,3-bis(2-pyridyl)pyrazine) as building blocks of polynuclear complexes. We were comparing the structures of our systems to those of  $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$  and could not rationalize the differences observed. The large distortions from idealized geometries for  $\text{Cr}(\text{bpy})_3^{3+}$  coupled with the "approximate" inversion symmetry relating the two cations led us to reinvestigate the structure of this compound.

#### Experimental Section

(i) **Preparation.**  $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$  was prepared directly from the perchlorate salt.

$[\text{Cr}(\text{bpy})_3](\text{ClO}_4)_3$  was prepared by using the procedure of Baker and Mehta<sup>3</sup> with the exception that  $\text{Cr}(\text{aq})^{2+}$  was generated by using zinc

(1) Hauser, A.; Mäder, M.; Robinson, W. T.; Murugesan, R.; Ferguson, J. *Inorg. Chem.* **1987**, *26*, 1331–1338.

(2) Atom labels refer to Figure 1 of this paper.