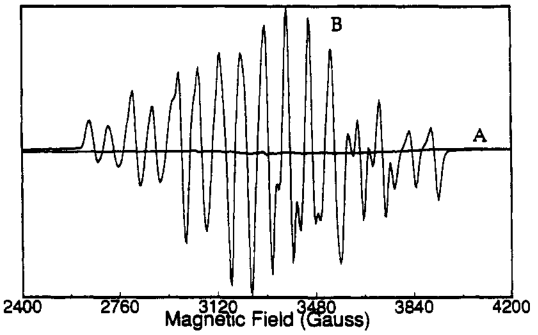

Figure 2. X-Band EPR spectrum at 9 K of (A) **1** (1 mM) in 0.1 M H_3PO_4 (pH 3) and of (B) solution A after addition of 0.05 M bpy (pH 4.5): microwave frequency, 9.05 GHz; modulation frequency, 100 kHz; modulation amplitude, 2 G; microwave power, 5 μW.

valent Mn, bpy, and PO_4 and having a considerably higher equivalent weight, has been isolated but is not yet fully characterized. These data can be summarized in eq 1 where the Mn(III)

$$2\,\mathbf{1} + H_3PO_4 \rightarrow [Mn^{IV}_2(\mu\text{-}O)_2(\mu_2\text{-}HPO_4)(bpy)_2(H_2PO_4)_2] + 4\,bpyH^+ + \text{“}[Mn^{III}_2(\mu\text{-}O)(\mu_2\text{-}H_2PO_4)_2(bpy)_2(H_2PO_4)_2]\text{”} \quad (1)$$

product cannot be fully defined. Proton-coupled disproportionation (eq 1) can be invoked for stabilizing the Mn(III) product; we have postulated[1] earlier that the disproportionation of **1** is made thermodynamically more favorable in acidic solution by protonation of a μ-oxo group in the (III,III) dimer. The presence of the strongly binding bridging phosphate must also play a significant part in stabilizing the (III,III) dimer since, in aqueous nitric acid at the same pH, the only low-valent product seen when **1** disproportionates to **2** is Mn^{2+}.

Further evidence for a disproportionation pathway is obtained by EPR spectroscopy. The green solutions prepared by the addition of **1** to an H_3PO_4 solution are EPR-silent (Figure 2A) having lost the characteristic 16-line spectrum of the III,IV dimer **1**. Adjusting the pH of this EPR-silent H_3PO_4 solution to 4.5 by the addition of 0.05 M pH 4.5 bpy buffer quantitatively regenerates **1** (Figure 2B), as determined by EPR and visible spectroscopy. Unlike the reaction of **1** in pH 2 HNO_3 where EPR demonstrates the presence of Mn^{2+} in addition to **2**, here the lack of any EPR signals for **1** dissolved in the H_3PO_4 medium rules out Mn^{2+} as the low-valent Mn species generated in the disproportionation reaction. Neither the (III,III) nor the (IV,IV) dimer would be expected to give an EPR spectrum.

The possible role of phosphate in stabilizing high-valent Mn clusters of biochemical interest is intriguing from a number of standpoints. First, the ubiquitous nature of phosphate makes it a possible ligand for high-valent Mn in biological systems. Second, it is clear that inorganic phosphate is a an excellent ligand for stabilizing Mn(IV). Acetate-bridged structures analogous to **3** have only been prepared in the (III,IV) but not the (IV,IV) oxidation state.[11,15,17] Christou has recently reported the formation of acetate-bridged Mn(III)–bpy dimers and tetramers in aqueous solution.[18] Thus, the additional stabilization provided by inorganic phosphate appears critical in achieving the (IV,IV) oxidation level. Finally, while the Mn_2 PAP remains incompletely characterized,[10] the interactions of inorganic phosphate with the metal centers may well be analogous to those for the Fe_2 PAP enzyme. With both terminal and bridging interactions being of potential importance in the PAP oxo cluster,[7] **3** provides an interesting system for comparison.

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Supplementary Material Available: Complete ORTEP diagrams, text describing the solution of the structures, and tables of crystallographic data, atomic coordinates and isotropic thermal parameters, bond distances and angles, torsion angles, and anisotropic temperature factors for **3** and **4** (38 pages); tables of structure factors for **3** and **4** (37 pages). Ordering information is given on any current masthead page.

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Preparation of Phosphoraniminato Complexes Containing Polypyridyl Ligands. Nitrogen Atom Transfer from $[Os^{VI}(tpy)(Cl)_2(N)]^+$

A characteristic reaction of oxo complexes of the transition metals in high oxidation states is oxo transfer to such reductants as phosphines, sulfides, or olefins.[1-3] A parallel, nitrogen atom transfer chemistry has been established for complexes of Fe(V),[4] Mo(VI),[5] and Os(VI).[6] We recently described the preparation and crystal structure of the salt *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]Cl$ (**1**) (tpy is 2,2′:6′,2″-terpyridine). It was shown that this d^2 complex of Os(VI) could be reduced reversibly in aqueous solution to give the corresponding ammine complex of Os^{II}, $[Os^{II}(tpy)(Cl)_2(NH_3)]$, via the intermediate oxidation states, Os(V), Os(IV), and Os(III).[7] We report here that the redox chemistry of this complex extends to nitrogen atom transfer to PPh_3 and other phosphines. The product with PPh_3 is a paramagnetic phosphoraniminato complex of Os^{IV}. This complex, in turn, has an extensive redox chemistry of its own.

When *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]Cl$ (**1**) (λ_{max} = 525 nm)[7] was allowed to react with PPh_3 in acetonitrile, a rapid reaction occurred to give a new product with λ_{max} = 488 nm. On the basis of the results of a spectrophotometric titration with PPh_3 in acetonitrile, the stoichiometry of the reaction was shown to be 1:1. The reaction was first order in both PPh_3 and Os(VI) with $k(CH_3CN, 25\ ^\circ C) = 1.36\ (\pm 0.08) \times 10^4\ M^{-1}\ s^{-1}$ as shown by stopped-flow kinetics.

The product of the reaction was isolated and characterized as its hexafluorophosphate salt, *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]PF_6$

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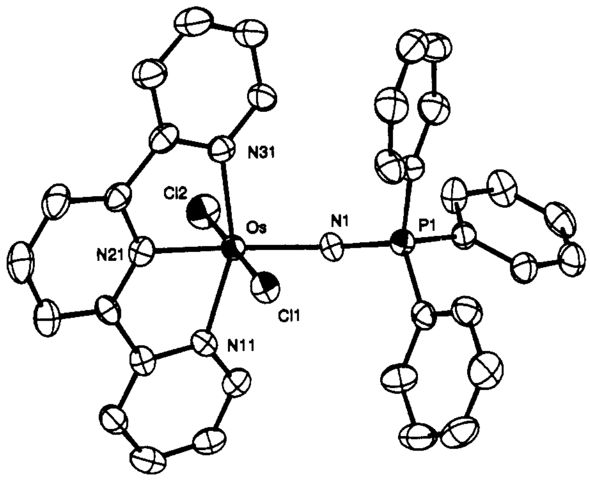

Figure 1. ORTEP[15] view of the cation *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]^+$. Relevant bond distances (Å) and angles (deg): Os–N(1), 2.093 (5); Os–Cl(1), 2.3717 (18); Os–Cl(2), 2.3626 (19); Os–N(11), 2.081 (5); Os–N(21), 1.988 (5); Os–N(31), 2.075 (5); N(1)–P(1), 1.618 (5); Os–N(1)–P(1), 132.5 (3); Cl(1)–Os–Cl(2), 178.65 (6); Cl(1)–Os–N(1), 92.46 (15); Cl(2)–Os–N(1), 87.41; N(11)–Os–N(1), 100.8 (2); N-(12)–Os–N(1), 176.4 (2); N(31)–Os–N(1), 102.1 (2); N(11)–Os–N(21), 78.6 (2); N(11)–Os–N(31), 156.6 (2); N(21)–Os–N(31), 78.9 (3).

(**2**).[8] In a typical reaction, **1** (200 mg, 0.37 mmol) and PPh_3 (140 mg, 0.53 mmol) were dissolved in CH_2Cl_2 (200 mL) and the mixture was stirred at room temperature for 2 h. Following filtration and column chromatography on alumina, elution with CH_2Cl_2/CH_3CN and finally with methanol gave a brown fraction. Reduction of the volume to 30 mL and addition of KPF_6 (200 mg) gave a brown precipitate, which was filtered off, washed with methanol, hexanes, and diethyl ether, and dried in vacuo to give 180 mg (53%) of **2**. By using the same or closely related procedures, it was possible to isolate the series of salts $[Os(tpy)(Cl)_2(NPPh_{3-n}R_n)]PF_6$ (n = 1–3; R = Me, Et).[9] Crystals of **2** were grown by redissolving the salt (20 mg) in CH_3CN (ca. 2 mL) and layering the solution with diethyl ether. The structure of the salt was determined by X-ray crystallography;[10] the cation is illustrated in Figure 1. This is one of nine structurally characterized examples of transition-metal complexes that contain a phosphoraniminato ligand.[5] The structure is distinctive in having the longest M–N bond distance (2.093 (5) Å) and smallest MNP bond angle (132.5 (3)°) of the examples that have been characterized structurally. The N–P bond distance was 1.618 (5) Å.

We formulate the cation as a paramagnetic, d^4 phosphoraniminato complex of Os(IV). This formulation is consistent with its room-temperature magnetic moment of 1.8 μ_B[13] and its temperature-dependent, strongly paramagnetically shifted ^1H NMR spectrum.[14]

It appears that *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]^+$ can act as a chemical oxidant with transfer of the phosphoraniminato group. When **2** was heated at reflux in CH_3CN, with excess PPh_3, for an extended period, $Ph_3PNPPh_3^+$ appeared in the solution, as shown by the appearance of its characteristic ^{31}P resonance at 21.67 ppm vs 85% H_3PO_4.

The phosphoraniminato complex also has an extensive one-electron-transfer chemistry. In a cyclic voltammogram of *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]PF_6$ in 0.1 M $[N(n\text{-}Bu)_4]PF_6$·CH_3CN at 200 mV/s vs SSCE, a chemically reversible, one-electron reduction appeared at $E_{1/2}$ = −0.27 V, a further, pseudoreversible reduction at −1.70 V, and a one-electron oxidation at $E_{1/2}$ = 0.92 V. These potentials are dependent upon the phosphine in the phosphoraniminato complex. For example, for *trans*-$[Os(tpy)(Cl)_2(NPMe_3)]PF_6$, the corresponding waves for the $Os^{V/IV}$ and $Os^{IV/III}$ couples appear at $E_{1/2}$ = 0.83 and −0.37 V, respectively. Coulometric reduction of **2** past the first reduction wave at E_{app} = −0.5 V occurred reversibly with n = 1 to give $[Os^{III}(tpy)(Cl)_2(NPPh_3)]^0$, with λ_{max} = 518 nm.

Although stable on the cyclic voltammetric time scale at a scan rate of 200 mV/s, the one-electron-oxidation product, $[Os^V(tpy)(Cl)_2(NPPh_3)]^{2+}$, is unstable on longer time scales. Coulometric oxidation past the $E_{1/2}$ value occurred with n = 1 to give as products the starting nitrido complex, *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ ($E_{p,c}$ = −0.3 V),[7] and an additional product that remains to be identified but has electrochemical waves at $E_{1/2}$ = 1.42, 0.14 V and $E_{p,c}$ = −1.58 V. The chemistry that can be induced following one-electron oxidation is currently under investigation.

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Registry No. **1**, 127571-46-4; **2**, 133930-95-7; **2**·CH_3CN, 133930-96-8; $Ph_3PNPPh_3^+$, 48236-06-2; PPh_3, 603-35-0; N^{3-}, 18851-77-9; *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]^{2+}$, 133930-97-9; *trans*-$Os(tpy)(Cl)_2(NPPh_3)$, 133930-98-0; *trans*-$[Os(tpy)(Cl)_2(NPPh_2Me)](PF_6)$, 133931-00-7; *trans*-$[Os(tpy)(Cl)_2(NPPhMe_2)](PF_6)$, 133931-02-9; *trans*-$[Os(tpy)(Cl)_2(NPMe_3)](PF_6)$, 133931-04-1; *trans*-$[Os(tpy)(Cl)_2(NPPh_2Et)](PF_6)$, 133931-06-3; *trans*-$[Os(tpy)(Cl)_2(NPPhEt_2)](PF_6)$, 133931-08-5; *trans*-$[Os(tpy)(Cl)_2(NPEt_3)](PF_6)$, 133931-10-9; Ph_2PMe, 1486-28-8; $PhPMe_2$, 672-66-2; PMe_3, 594-09-2; Ph_2PEt, 607-01-2; $PhPEt_2$, 1605-53-4; PEt_3, 554-70-1; *trans*-$[Os(tpy)(Cl)_2(NPMe_3)]^{2+}$, 134054-72-1; *trans*-$[Os(tpy)(Cl)_2(NPMe_3)]$, 134054-73-2.

Supplementary Material Available: A fully labeled diagram of the cation and tables of crystal data, atomic positional and thermal parameters, bond distances, and bond angles for **2** (10 pages); a listing of observed and calculated structure factors for **2** (30 pages). Ordering information is given on any current masthead page.

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[8] Anal. Calcd for $C_{33}H_{26}Cl_2N_4P_2OsF_6$: C, 43.29; H, 2.86; Cl, 7.74; N, 6.12. Found: C, 44.52; H, 3.47; Cl, 7.76; N, 5.91.

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[10] Crystals of $[Os(tpy)(Cl)_2(NPPh_3)]PF_6$·$CH_3CN$ were monoclinic, of space group $P2_1/n$, with a = 13.384 (5) Å, b = 15.222 (7) Å, c = 17.717 (6) Å, β = 103.10 (3)°, V = 3516 (2) $Å^3$, Z = 4, d_{calc} = 1.807 Mg/m^{-3}, and μ = 3.94 mm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by using an ω–2θ scan with $2\theta_{max}$ = 50°, resulting in 6155 unique reflections of which 4454 were observed ($I > 2.5\sigma(I)$). The structure was solved by Patterson methods, and an empirical absorption correction was applied by using DIFABS.[11] Refinement by full-matrix least-squares techniques, with all non-hydrogen atoms assigned anisotropic thermal parameters, gave residuals of R = 0.034, R_w = 0.035 (0.060 and 0.039 including all reflections). H atoms were included in calculated positions with thermal parameters derived from the atom to which they were bonded. All computations were performed by using the NRCVAX suite of programs.[12]

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Organotransition-Metal Metallacarboranes. 20.[1] Fluoride-Catalyzed C–Si Bond Cleavage in $Cp^*Co(Me_3Si)_2C_2B_4H_4$. Synthesis of Parent $Cp^*CoC_2B_4H_6$ and Conversion to C-Substituted $Cp^*CoRR'C_2B_4H_4$ Derivatives

Previous papers in this series[1,2] have described pathways by which small metallacarborane complexes of the types *closo*-LM-