A significant feature of both MoO_2(**1**-NO_2)(Me_2SO) and MoO_2(**3**-NS_2) is the projection of structure of the *gem*-diphenyl groups on the Mo=O bonds. This steric protruberance in the direction of potential Mo-O-Mo bond formation is sufficient to eliminate reaction 2. Reaction of ~0.1 mM MoO_2(**3**-NS_2) and 3.0 equiv of Ph_3P in DMF gave clean isosbestic points at 473 and 386 nm and a final spectrum consistent with the MoO(**3**-NS_2)(ligand) chromophore. ^{31}P NMR signals at 43.5 (1.0, MoO(**3**-NS_2)($OPPh_3$)), 25.9 (6.8, Ph_3PO), and -4.6 (7.1, Ph_3P) ppm[21] were observed after completion of reaction (20 h) in a system initially containing 10 mM MoO_2(**3**-NS_2)/1.88 equiv Ph_3P. The observed intensity ratio (6.8 + 1.0)/7.1 = 1.10 agrees closely with the expected value of 1.14 for reaction 1 and is completely inconsistent with the ratio 0.5/1.38 = 0.36 for formation of a Mo_2O_3 species. Thus, MoO_2(**3**-NS_2) is cleanly converted to MoO(**3**-NS_2)L (L = DMF, Ph_3PO) without interference from reaction 2. The reaction is second order with k = 7 (1) × 10^{-3} M^{-1} s^{-1} (23 °C). In contrast, MoO_2(**1**-NO_2)(DMF) does *not* react with Ph_3P, a result ascribed to the large negative shift in $E_{p,c}$ values (-0.89 to -1.82 V vs. SCE) upon oxygen-for-sulfur atom substitution.

The system MoO(**3**-NS_2)(DMF)/Me_2SO affords MoO_2(**3**-NS_2) and Me_2S, with no intervention by reaction 2, and exhibits substrate saturation kinetics at sufficient Me_2SO concentrations. These observations, the last of which parallels frequent enzymatic behavior, are interpreted in terms of reactions 3 and 4. A

$$\text{MoO(3-NS}_2\text{)(DMF)} + \text{Me}_2\text{SO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{MoO(3-NS}_2\text{)(Me}_2\text{SO)} + \text{DMF} \quad (3)$$

$$\text{MoO(3-NS}_2\text{)(Me}_2\text{SO)} \xrightarrow{k_2} \text{MoO}_2\text{(3-NS}_2\text{)} + \text{Me}_2\text{S} \quad (4)$$

double-reciprocal plot[22] gives V_{max} (=k_2) = 1.5 (1) × 10^{-3} s^{-1} and an apparent K_m (≈k_{-1}[DMF]/k_1) = 3 (1) × 10^{-3} M at 23 °C in DMF. Coupling of reactions 1 (X = Ph_3P) and 3 + 4 yields a catalytic cycle capable of reducing Me_2SO with concomitant Ph_3P oxidation. The ^{31}P NMR spectrum of the system MoO_2(**3**-NS_2)/25 equiv Ph_3P in neat Me_2SO after 18 h revealed formation of ≳20 equiv of Ph_3PO. In a parallel experiment, the Me_2S product was isolated as $(Me_2S)_2(HgCl_2)_3$[23] in 97% yield based on phosphine. No reaction occurs between Ph_3P and Me_2SO at 189 °C for at least 1 h.[23]

Reduction of sulfoxides by an oxomolybdenum complex is especially noteworthy in light of the finding that *d*-biotin-*d*-sulfoxide reductase is a Mo cofactor-dependent enzyme.[24] Significantly, *d*-biotin *d*-sulfoxide[25] is reduced to *d*-biotin by MoO(**3**-NS_2)(DMF); saturation kinetics are observed and kinetic parameters are comparable to those with Me_2SO. Saturation behavior will permit a direct comparison of synthetic system and enzymatic reaction rates. MoO_2(**3**-NS_2) and MoO(**3**-NS_2)(ligand) satisfy requirements ii and iii, including catalytic transformation of a biological substrate. Although the structure of MoO_2(**3**-NS_2) is related to the Mo site of one Mo cofactor-dependent enzyme, requirement i for the sulfoxide reductase cannot be examined without further enzyme characterization. No reaction in the system MoO_2(**3**-NO_2)(DMF)/Ph_3P implies a ncessity for thiolate ligation in, at least, oxygen atom transfer from catalyst to substrate. Work directed toward the development of reaction systems based on biologically relevant reductants and on the characterization of intermediate oxidation level Mo(V) species is in progress.

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Supplementary Material Available: Atom coordinates and anisotropic temperature factors for MoO_2(**1**-NO_2)(Me_2SO) and MoO_2(**3**-NS_2) (8 pages). Ordering information is given on any current masthead page.

Free Radical Route to Formation of the Metal Hydride Complex Hydridoaquobis(2,2′-bipyridine)cobalt(III)[1]

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In recent years the thermodynamics and kinetics of formation of d^6 metal hydrides via proton addition to the d^8 conjugate base have been characterized in a number of systems.[2-6] As a result it is now recognized that "metal acids" (hydride complexes) generally undergo proton-transfer reactions much more slowly than nitrogen or oxygen acids of comparable strength owing to the substantial changes in metal coordination that accompany the reaction.[4,5] Here we report our observations on the formation of $Co(bpy)_2(H_2O)H^{2+}$ (bpy = 2,2′-bipyridine) from high-spin d^8 Co(I) bipyridine complexes in aqueous solutions: in this system no pathway attributable to a proton transfer is detected. The hydride is formed entirely through reactions of Co(II) complexes and (bpy)H· radicals.

The Co(I) species were produced[7-9] by pulse radiolysis of aqueous $CoSO_4$-2,2′-bipyridine mixtures (2-MeV electrons produced by a Van de Graaff accelerator;[10] formate, 2-propanol, or ethanol as OH scavenger). The cobalt(I) complexes initially present are determined by the distribution of $Co(bpy)_n^{2+}$ species as all are reduced rapidly by e_{aq}^-,[7] but equilibrium is rapidly attained through sequences of electron-transfer reactions between the Co(I) (~10^{-6} M) and Co(II) (>10^{-4} M) species, e.g.,

$$Co(bpy)_2^+ + Co(bpy)_3^{2+} \rightleftharpoons Co(bpy)_2^{2+} + Co(bpy)_3^+ \quad (1)$$

K_1 = 200, k_1 = 2 × 10^9 M^{-1} s^{-1}.[8] (Coordinated water molecules are omitted.) In the experiments considered here $Co(bpy)_3^+$ is the dominant form (>75%) of Co(I) present after the equilibration (<0.1 ms).

The equilibration of $Co(bpy)_3^+$ with acid to form the hydride complex occurs on the 0.1-0.001-s time scale and was followed by monitoring the bleaching of the 610-nm $Co(bpy)_3^+$ absorption. The net equilibration reaction is given by eq 2 and analysis of the

$$Co(bpy)_3^+ + H_3O^+ \rightleftharpoons Co(bpy)_2(H_2O)H^{2+} + bpy \quad (2)$$

equilibrium absorbance values that are presented in Figure 1 gives K_2 = 1.0.[11] The rate of approach to equilibrium is first order in [Co(I)] and increases with [H^+]. Plots of k_{obsd} vs [H^+] at different [bpy] levels are also presented in Figure 1. Consistent with the stoichiometry (eq 2), intercepts increase with the con-

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(11) The equilibrium constant for the following reaction is 0.8 × 10^7 M^{-1} (the pK_a of $Co(bpy)_2(H_2O)H^{2+}$ is 6.9).

$$Co(bpy)_2^+ + H_3O^+ \rightleftharpoons Co(bpy)_2(H_2O)H^{2+}$$

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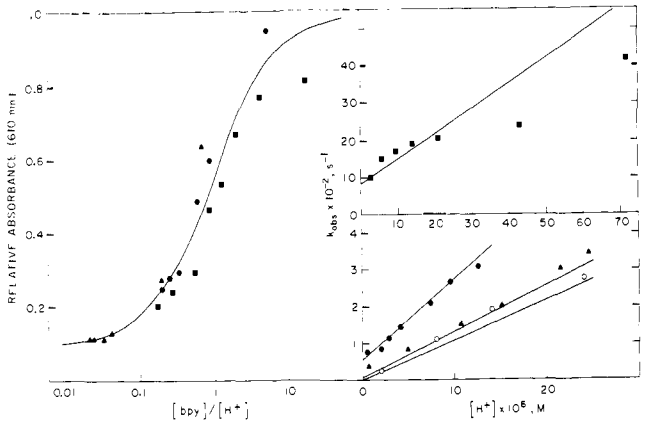

Figure 1. Dependence of equilibrium (left) and kinetics (right) of hydride formation from $Co(bpy)_3^{+}$ on H^+ and bpy concentrations. The absorbing species is $Co(bpy)_3^{+}$ (at $(0.3-1.0) \times 10^{-6}$ M). ○, 0.02 M Co(II), 0.002 M total bpy (1.2×10^{-7} M free bpy), 0.1 M ionic strength (no equilibrium data); ▲, 0.005 M Co(II), 0.0016 M total bpy (4.6×10^{-7} M free bpy), 0.04 M ionic strength; ●, 0.001 M Co(II), 0.001 M total bpy (2.5×10^{-6} M free bpy), 0.03 M ionic strength; ■, 0.001 M Co(II), 0.002 M total bpy (1.2×10^{-5} M free bpy), 0.03 M ionic strength. All solutions contained 0.02 M acetate–acetic acid and were deoxygenated with argon. The 1:1 Co(II) to bpy solution contained 0.3 M ethanol; the others contained 0.26 M 2-propanol. (Note: k_{obsd} values at high [bpy] and $[H^+]$ (upper right-hand corner) have not been corrected for the fact that under these conditions eq 1 is comparable in rate to eq 2.)

centration of free bipyridine. Remarkably, however, the slopes also increase with [bpy] and the rate law for the equilibration is given by eq 3 with $a = 1.0 \times 10^7$ M^{-1} s^{-1} and $b = 5.0 \times 10^{12}$ M^{-2}

$$k_{obsd} = (a + b[bpy])([H^+] + ([bpy]/K_2)) \quad (3)$$

s^{-1}. The reaction proceeds by parallel (a and b) paths. The two terms in $[H^+]$ are the forward components of the rate of approach to equilibrium while the two terms in $[bpy]/K_2$ are from the reverse rates.

The magnitude and concentration dependence of the b term in eq 3 suggests the sequence eq 4–7[12] in which the formation of

$$bpy + H^+ \overset{fast}{\rightleftharpoons} (bpy)H^+ \quad (4)$$

$$Co(bpy)_3^{+} + (bpy)H^+ \overset{slow}{\rightleftharpoons} Co(bpy)_3^{2+} + (bpy)H\cdot \quad (5)$$

$$(bpy)H\cdot + H^+ \overset{fast}{\rightleftharpoons} (bpy)H_2^{+}\cdot \quad (6)$$

$$(bpy)H\cdot/(bpy)H_2^{+}\cdot + Co(bpy)^{2+}/Co(bpy)_2^{2+} \xrightarrow{fast} Co(bpy)_2(H_2O)H^{2+} \quad (7)$$

(bpy)H· (eq 5) is the rate-determining step in the forward direction. In terms of this mechanism, $b = K_4k_5$ and the b values used in calculating the lines in Figure 1 were obtained from the values reported previously:[9] $K_4 = 2.6 \times 10^4$ M^{-1}, $k_5 = 1.8 \times 10^8$ M^{-1} s^{-1} ($K_6 = 1 \times 10^8$ M^{-1}).

Although the a term in the rate law is of the form expected if eq 2 is an elementary reaction (i.e., $k_2 = 1.0 \times 10^7$ M^{-1} s^{-1}), the fact that (bpy)H· production is implicated for the b term suggests an analogous process for the a term, i.e., eq 4 and 6–9, in which rapid preequilibrium eq 8 is maintained by the reverse

$$Co(bpy)_3^{+} \overset{fast}{\rightleftharpoons} Co(bpy)_2^{+} + bpy \quad (8)$$

$$Co(bpy)_2^{+} + (bpy)H^+ \overset{slow}{\rightleftharpoons} Co(bpy)_2^{2+} + (bpy)H\cdot \quad (9)$$

of eq 1. In this mechanism $a = K_4K_8k_9$. The magnitude of $K_8 = 1.3 \times 10^{-7}$ M, and k_9 is estimated as 3×10^9 M^{-1} s^{-1} from the $Co(bpy)_2^{2+/+}$ and $(bpy)H^{+/0}$ $E°$ values (−1.03[8] and −0.97 V,[9] respectively) and the fact that both couples undergo very rapid electron exchange[8,9] ($\sim 1 \times 10^9$ M^{-1} s^{-1}). Thus $K_4K_8k_9$ is estimated as 1×10^7 M^{-1} s^{-1}, and this route is sufficiently rapid to account quantitatively for the a term. Thus conventional Brønsted proton-transfer paths are not detected in this system. They could, nevertheless, be relatively rapid: our observations impose a limit of $<10^7$ M^{-1} s^{-1} for reaction of either $Co(bpy)_3^{+}$ or $Co(bpy)_2^{+}$ with H_3O^+.

The above considerations suggest that the generation of (bpy)H· via reduction of $(bpy)H^+$ by $Co(bpy)_3^{+}$ or $Co(bpy)_2^{+}$ is the rate-determining step in $Co(bpy)_2(H_2O)H^{2+}$ formation. Thus actual assemblage of the hydride—presumably via reaction of $Co(bpy)^{2+}$ or $Co(bpy)_2^{2+}$ with (bpy)H· or $(bpy)H_2^{+}$· (eq 7)—must be extremely facile. The reaction could involve H atom transfer or sequential electron and proton transfer, with either possibly coupled to substitution of (bpy)H· on Co(II). Finally, the generality of the free radical route to hydrides is of some interest. Such routes likely obtain in other Co(I) polypyridine systems, being facilitated by the similarity of the reduction potentials for $CoL_n^{2+/+}$ and $LH^{+/0}$ couples,[9] the rapidity of electron transfer among these couples, and (probably) the relatively high substitutional lability of the Co(II) species.[13] Whether or not such routes prevail with other metal centers or other reducible ligands remains to be demonstrated.

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(12) Given the buffer and Co(II) concentrations used, eq 6 is probably rapid compared to eq 7. Thus reaction of either (bpy)H· or $(bpy)H_2^{+}$· with Co(II) (eq 7, $Co(bpy)^{2+}$ or $Co(bpy)_2^{2+}$) is a possibility.

(13) Hydride formation mechanisms in other Co(I) polypyridine systems are currently under study as are the routes via which the hydrides react with water to give H_2. Hydride formation via H-atom abstraction from organic radicals finds precedent in the $Co(CN)_5^{3-}$/alkyl halide systems (Chock, P. B.; Halpern, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 582).

A d(GpG)-Platinated Oligonucleotide Can Form a Duplex with a Complementary Strand

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In the cell, DNA appears to be the primary target of the active aquated forms of the antitumor drug *cis*-$[PtCl_2(NH_3)_2]$ (*cis*-DDP),[2] and the cytotoxicity of the drug could result of a particular bifunctional binding of the *cis*-$Pt^{II}(NH_3)_2$ moiety.[3] It has been shown, using enzymatic digestion methods, that platinum cross-links between adjacent guanines are formed upon reaction of DNA with *cis*-DDP[4,5] and represent more than 50% of the lesions.[5] This is in agreement with the results obtained by enzymatic restriction

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