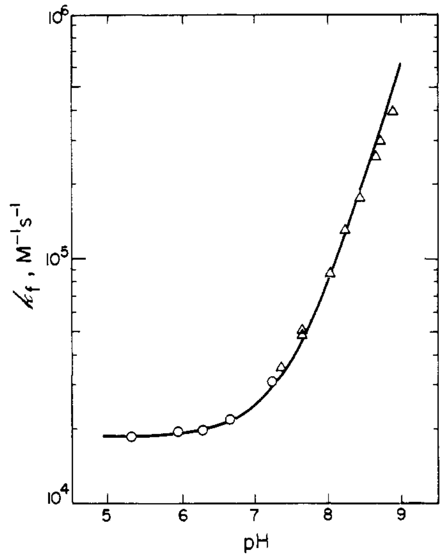

Figure 2. Semilog plot of k_f of dye **2** with Ni(terpy)$^{2+}$ as a function of pH at 25 °C and I = 0.04 M. The buffers were MES (○) and HEPES (△). The continuous curve was calculated with eq 4, the experimental pK_{a2}, and the values of k_{LH} and k_{L^-} from Table I.

Table II. Pseudo-First-Order Rate Constants for the Complexation of Dye **2** with Ni(terpy)$^{2+}$ as a Function of MES Buffer Concentration[a]

$[B^-]$, mM	k_{obsd}, s^{-1} pH 5.95	k_{obsd}, s^{-1} pH 6.28	$[B^-]$, mM	k_{obsd}, s^{-1} pH 5.95	k_{obsd}, s^{-1} pH 6.28
2.5	2.00	2.00	15.0	1.97	
5.0	2.07	2.03	20.0	1.91	1.92
10.0	1.95	2.01			

[a] 25 °C; $[\text{dye}]_0 = 1.0 \times 10^5$ M; $[\text{Ni(terpy)}^{2+}]_0 = 1.0 \times 10^{-4}$ M; I = 0.04 M.

L^- form of **1** with Ni(terpy)$^{2+}$ is enhanced by a factor of 7.5 × 10^2 compared to a modest factor of 10 for the LH species. Apparently, the combined effect of ligand stacking and Coulombic interaction of the metal ion with the ionized ligand group is more beneficial than when the Coulombic reinforcement is absent. The tendency of some anionic azo dyes to stack is very strong and cooperative when their charges are neutralized by polyions or micelles of opposite charge.[10,11]

Complexation with Dye 2. The value of pK_{a2} is 10.86 at an ionic strength of 0.04 M.[6] Rates of complexation with Ni(terpy)$^{2+}$ were measured in MES and Tris buffers in the pH range 5.3–8.9. The pyridinium species (LH_2^+) and the ionized species (L^-) made negligible contributions to $[L]_T$ in this pH range.[6] Complexation in excess Ni(terpy)$^{2+}$ followed first-order kinetics through at least 3 half-lives, and values of k_f (M^{-1} s^{-1}) were obtained from k_{obsd} (s^{-1}) in the usual way.

The effect of pH on k_f is shown in Figure 2. The continuous line was calculated with eq 4 by neglecting the K_{a1} and K_{a2} terms in the denominator. The values of k_{LH} and k_{L^-} required for the fit are listed in Table I. The calculated curve was computed by assuming that Ni(terpy)$(H_2O)_3^{2+}$ is the only Ni(terpy) species present. The slight lack of fit above pH 8.5 is probably the result of hydrolysis of Ni(terpy)$(H_2O)_3^{2+}$ to Ni(terpy)$(H_2O)_2OH^+$.

Table II gives the rate constants for complexation at pH 5.95 and 6.28 at different concentrations of MES buffer. The absence of any catalysis by the buffer contrasts with the general base catalysis observed in the chelation of Ni^{2+} with this ligand.

Since base-assisted proton transfer and ring closure appear to be rate limiting in the chelation of Ni^{2+} by the LH species of 2, the water-exchange rate is not a factor. In assessing rate enhancements, we compare the formation rate constants directly. The value of k_{LH}(Ni(terpy)) is 70 times larger than $k_{LH}(Ni^{2+})$; inclusion of the statistical factor gives a rate enhancement of 140. The system in which the rds in the reaction with Ni^{2+} is further removed from outer-sphere association appears to give the greater rate enhancement with Ni(terpy)$^{2+}$. In addition, the absence of general base catalysis in the reaction of LH with Ni(terpy)$^{2+}$ suggests that the ligand proton in the intermediate with Ni(terpy)$^{2+}$ is more acidic than in the corresponding intermediate with Ni^{2+}, so that its transfer rate to solvent is accelerated. There is no obvious rationale for this fact. Finally, the value of k_{LH}(Ni(terpy)) is larger than predicted for an unenhanced outer-sphere association constant (K_{OS}) and k_{ex}(Ni(terpy)). The magnitude of k_{LH}(terpy)) and the absence of general base catalysis suggest that ring closure may have been sufficiently accelerated in the complexation with Ni(terpy)$^{2+}$ that the rds has been shifted from ring closure with Ni^{2+} to initial ligation with Ni(terpy)$^{2+}$. This initial ligation may be enhanced by a modest increase in K_{OS} through stacking comparable to that for the LH species of **1**.

The value of k_{L^-}(Ni(terpy)) is larger than predicted from k_{ex}(Ni(terpy)) and an unenhanced value of K_{OS} by a factor of ~600. Again, the dissociated ligand shows greater rate enhancement than the LH species. Part of the increased rate could result from stacking and part from the operation of an internal conjugate base (ICB) mechanism.[12,13] The value of $k_{L^-}(Ni^{2+})$ is also larger than expected (Table I), and we have ascribed the enhancement to an ICB effect.

Conclusions. Our results show that the rate enhancements provided by an attached aromatic ligand are greater with the ionized form of the entering ligand than with the protonated form. They also indicate that the attached ligand can alter the rates of ring closure steps in addition to altering outer-sphere association. It seems clear that our understanding of the effect of attached ligands on the mechanism of complexation of entering ligands is still incomplete.

Acknowledgment. Helpful discussion of this work with Professor D. W. Margerum is gratefully acknowledged.

Registry No. **1**, 10335-31-6; **2**, 85-85-8; Ni(terpy)$^{2+}$, 18308-19-5.

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Quenching of Excited-State Reactivity of (Oxalato)bis(triethylphosphine)platinum(II) by Water

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Coordinatively unsaturated, low-valent platinum phosphine complexes are important in homogeneous catalytic systems for hydration of nitriles[1,2] and olefins,[3] hydrosilation,[4,5] H–D exchange with organic substrates,[1] decomposition of formic acid,[6] and the

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Table I. Relative Disappearance Quantum Yields for Irradiation of $Pt(C_2O_4)(PEt_3)_2$ with Various Concentrations of H_2O and D_2O

concn, M	rate (ΔC), min^{-1}	rel quantum yield
	H_2O	
0	3.40×10^{-5}	1.00
0.55	2.17×10^{-5}	0.63
1.67	1.32×10^{-5}	0.38
2.80	9.61×10^{-6}	0.28
	D_2O	
1.40	2.15×10^{-5}	0.63
2.70	1.48×10^{-5}	0.43
4.10	1.17×10^{-5}	0.34
5.50	9.22×10^{-6}	0.27

water gas shift reaction.[7] The dicoordinatively unsaturated 14-electron complexes PtL_2 (L = tertiary phosphine) are stable only if L is so large that approach to the metal center is hindered. As the phosphine ligands become smaller the reactivity of PtL_2 increases.[8,9] One route to generating PtL_2 intermediates that contain small basic phosphines is by ultraviolet irradiation of $Pt(C_2O_4)L_2$, which results in the reductive elimination of the oxalato ligand as CO_2.[10] Because of our interest in the catalytic activation of water,[2,3,6] we attempted to photogenerate the reactive PtL_2 species in water–acetonitrile solutions. We now report that water quenches photoreductive elimination of oxalate from $Pt(C_2O_4)(PEt_3)_2$.

Experimental Section

Materials. High purity acetonitrile was obtained from Burdick and Jackson. Distilled water and D_2O (100 atom %, Aldrich) were degassed by three freeze–pump–thaw cycles and maintained under nitrogen before use. The complex $Pt(C_2O_4)(PEt_3)_2$ was prepared as described previously.[10]

Spectra. IR spectra were recorded on a IBM IR/32 FTIR instrument. Solution spectral samples were contained in matched 0.1-mm path length CaF_2 cells. Fourier transform NMR spectra were recorded with use of a GE-300 instrument. Optical spectra were obtained with use of a IBM 9420 UV–vis spectrophotometer. Irradiations were performed by using the output of a 200-W Hg–Xe Kratos arc lamp system with quartz optics.

Relative Quantum Yields. A 9.44×10^{-3} M solution of $Pt(C_2O_4)(PEt_3)_2$ in a quartz-walled Schlenk tube sealed with a septum stopper was irradiated with the arc lamp output filtered through a 10-cm path length distilled water filter and Corning 7-54 broad-band filter. The high light intensity of the broad-band UV filter was needed to obtain appreciable conversions with added water. Because the UV absorption spectrum of the complex does not change appreciably on water addition, the relative quantum yields for broad-band irradiation are meaningful. Oxalate loss was followed by a decrease in the IR absorbance at 1704 cm^{-1}. Aliquots of the irradiated solution were removed periodically by syringe. Conversions were determined over the first 10–15% of photolysis. The rate of oxalate loss for the quantum yield determination was also monitored by FTIR spectroscopy. A 9.34×10^{-3} M solution of $Pt(C_2O_4)(PEt_3)_2$ in acetonitrile was irradiated in a quartz cuvette with use of an Oriel 313-nm interference filter. Light intensity was measured with the ferrioxalate actinometer.[11]

Results and Discussion

While examining the photochemistry of $Pt(C_2O_4)L_2$ (L = $P(CH_3)_3$ or $P(C_2H_5)_3$), we found that irradiation of solutions containing water showed poor conversion to products. In the same time period in which we saw nearly complete conversion of the oxalate ligand to CO_2 in aprotic solvents, such as CH_2Cl_2 and CH_3CN, we saw little photoreductive elimination of the oxalate ligand when a large amount of water was added to an acetonitrile solution. This was apparent from the decrease in the rate of catalytic hydration of acetonitrile[2] and from direct examination of the irradiated solution by ^{31}P NMR spectroscopy.

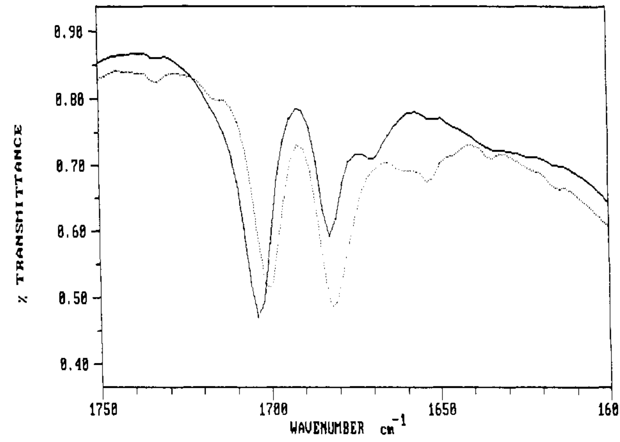

Figure 1. FTIR spectra of 9.44×10^{-3} M $Pt(C_2O_4)(PEt_3)_2$ in CH_3CN solvent. Solid line = dry solvent; dashed line = $[D_2O]$ = 5.5 M.

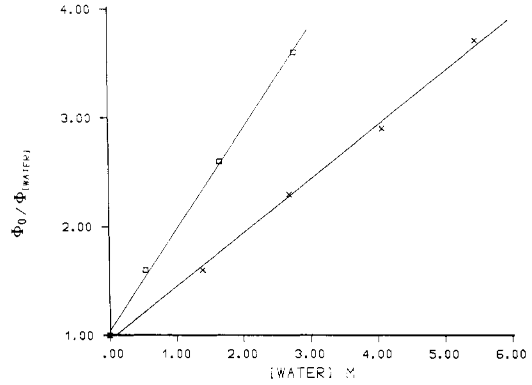

Figure 2. Stern–Volmer plots of relative quantum yields for loss of oxalate as CO_2 from $Pt(C_2O_4)(PEt_3)_2$: (×) with D_2O; (□) with H_2O.

These observations may be understood either in the context of weak hydrogen bonding of water to oxygen atoms of the oxalate ligand or weak binding of water in the axial coordination sites. As a test of this hypothesis we added D_2O and H_2O to a solution of $Pt(C_2O_4)(PEt_3)_2$ in acetonitrile. An increase in the water concentration causes a decrease in the relative quantum efficiency (Table I) for oxalate fragmentation on ultraviolet irradiation. This decrease in quantum yield is accompanied by a change in the solution IR spectrum of the platinum oxalate compound. In dry solvent the carbonyl region of the IR spectrum consists of a strong absorption at 1704 cm^{-1}, attributed to the antisymmetric[10a] C=O stretch of the oxalate ligand, and a less intense absorption at 1680 cm^{-1}, attributed to the symmetric C=O stretch. As water or D_2O is added to the solution the antisymmetric stretch decreases in intensity from 2650 to 2150 M^{-1} cm^{-1}, while for the symmetric stretches it increases from 1500 to 2300 M^{-1} cm^{-1}. Accompanying this change in intensity was a slight shift in absolute positions of the absorptions. The higher energy feature moved 8 cm^{-1} to lower energy; the lower energy feature moved about 3 cm^{-1} to lower energy (Figure 1). Weak hydrogen bonding results[10b] in red shifts of 10–15 cm^{-1} for organic carbonyls. An alternative explanation for these observations is water binds to Pt above or below the square plane of the complex to form 5- and 6-coordinate adducts that have perturbed IR spectra.

One must also recognize that displacement of the bidentate oxalate ligand could occur and inhibit photofragmentation. For example, addition of excess PEt_3 to a solution of $Pt(C_2O_4)(PEt_3)_2$ causes the two oxalate carbons to become inequivalent in the ^{13}C

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NMR spectrum.[6] It was shown[10] that the phosphine ligand displaces one end of the oxalate. Similarly the inhibiting effect of water could be explained if water displaced one end of the oxalate chelate. The ^{13}C NMR spectrum of a solution of $Pt(C_2O_4)(PEt_3)_2$ containing the maximum amount of water (before the complex, which is water insoluble, precipitates) showed only the sharp singlet at 166.8 ppm[10] from bidentate oxalate carbons.

To quantify the inhibiting effect of water on photoreductive elimination of bound oxalate, we followed the decrease in absorption intensity of the higher energy IR absorption at 1704 cm^{-1} vs. time at several water concentrations. We found that the rate of oxalate loss (i.e. the relative quantum yield) was inversely related to the amount of H_2O or D_2O present[12,13] (see Table I). The data obey the Stern–Volmer expression $\Phi_0/\Phi_{H_2O} = 1 + k_2\tau[H_2O]$ (τ = lifetime of the excited state in the absence of H_2O, k_2 = quenching rate constant), as seen in Figure 2. This behavior is also consistent with the proposed bimolecular preequilibrium formation of a hydrogen-bonded or water-ligated complex that has a greatly diminished quantum yield. Extrapolation of the data to pure H_2O and D_2O solvents leads to calculated quantum yields 0.019 and 0.036 times those in pure CH_3CN. If the mechanism for deactivation involves bound water, the presence of an α-hydrogen must be crucial since the potentially ligating solvent CH_3CN does not greatly quench photoreactivity.

The deuterium isotope effect on quenching (k_{2H}/k_{2D} = 1.9) was obtained from the ratio $k_{2H}\tau/k_{2D}\tau$ obtained from the Stern–Volmer plots with H_2O and D_2O. This result is expected because high-frequency vibrations are most effective at promoting nonradiative decay. Perdeuteriation is well-known[14] to yield an increase in radiative lifetimes by slowing nonradiative decay. This deuterium isotope effect suggests that hydrogen bonding to the oxalate ligand or weak binding of water to Pt provides an efficient path for the transfer of excited state energy to solvent. The magnitude of the isotope effect approaches that seen for direct isotopic substitutions in rhodium(III) ammine complexes.[15] Solvent interaction with the excited state of the molecule could also produce a solvent isotope effect on excited-state lifetimes.[16] Our work suggests that water solvent may change the quantum yields for photoreactions of metal complexes by as much as 50-fold as compared to those in aprotic solvents.

Acknowledgment. We thank Dr. C. M. Jensen for helpful discussions. This research was supported by the U.S. Army Research Office under Contract DAAG29-85-K-0263, and W. C.T. thanks the Alfred P. Sloan Foundation for a research fellowship.

Registry No. $Pt(C_2O_4)(PEt_3)_2$, 81457-59-2; H_2O, 7732-18-5; D_2O, 7789-20-0; CO_2, 124-38-9.

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(12) D_2O was used since the IR spectrum of water interferes with the oxalate absorption at 1680 cm^{-1}.

(13) The UV-vis spectra of $Pt(C_2O_4)(PEt_3)_2$ show no change in band positions or intensities on addition of H_2O or D_2O. While the absolute quantum yields could not be determined for the water inhibition studies, a quantum yield of 0.11 was measured for the disappearance of the oxalate ligand from $Pt(C_2O_4)(PEt_3)_2$ in dry acetonitrile solvent on 313-nm irradiation.

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Additions and Corrections

1986, Volume 25

Megumu Munakata,* Susumu Kitagawa, Shigeru Kosome, and Akio Asahara: Studies of Copper(I) Olefin Complexes. Formation Constants of Copper Olefin Complexes with 2,2′-Bipyridine, 1,10-Phenanthroline, and Their Derivatives.

Page 2627. In column 3 of Table IV, entries 1 (0.13), 3 (0.28), 13 (0.10), and 14 (0.18) should read 13, 28, 10, and 18, respectively.—Megumu Munakata

Phalguni Chaudhuri,* Karen Oder, Karl Wieghardt, Bernhard Nuber, and Johannes Weiss*: Magnetic Exchange Interactions in Some Novel μ-Azido-Bridged Copper(II) Dimers. Crystal Structures of $[L_2Cu_2(\mu\text{-}N_3)(N_3)_2](ClO_4)\cdot H_2O$, $LCu(N_3)_2$, $[L_2Cu_2(\mu\text{-}N_3)_2(ClO_4)_2]$, and $L'Cu(N_3)_2$ (L = *N,N′,N″*-Trimethyl-1,4,7-triazacyclononane and L′ = 1,4,7-Triazacyclononane).

Page 2819. In Table I the experimental details given for compound **2** are in fact those of compound **4**, and those given for **4** are the data for compound **2**.—Karl Wieghardt