reaction. The sublimed white solid was identified as $[SN]^+[AsF_6]^-$ (1.88 g, 8.00 mmol; 75% yield based on $S_3N_3Cl_3$ and eq 2), from its infrared and Raman spectra.[5] Anal. Calcd for $[SN]^+[AsF_6]^-$: S, 13.64; N, 5.96; As, 31.88; F, 48.5. Found: S, 13.52; N, 6.03; As, 31.68; F, 48.70. A negligible amount of $[SN]^+[AsF_6]^-$ was carried into the volatile trap with the solvent.

Lower yields were obtained from reactions in which greater amounts of SO_2 or lesser amounts of $AgAsF_6$ were used and in reactions done in a one-tube vessel followed by sublimation of $[SN]^+[AsF_6]^-$ from a mixture of $[SN]^+[AsF_6]^-$, $AgAsF_6$, and AgCl. Attempts at subliming the $[SN]^+[AsF_6]^-$ at lower temperatures under a dynamic vacuum led to substantial (10–20%) amounts of $[SN]^+[AsF_6]^-$ condensing out into the U-tube trap, cooled at −196 °C.

Preparation of $[S_2N]^+[AsF_6]^-$. In a typical reaction, a large excess of S_8 (1.18 g, 36.91 mmol), relative to eq 3, and $[SN]^+[AsF_6]^-$ (2.24 g, 9.51 mmol) was loaded into a reaction vessel as described above. Sulfur dioxide (4.19 g, 65.4 mmol) was condensed onto this mixture. At room temperature, a reaction occurred, giving an opaque, deep red solution over a yellow insoluble solid. The soluble products were washed through the frit with several washings of the solvent. The solvent was slowly condensed from the bulb containing the soluble materials by cooling the bulb with flowing cold water (12 °C), until a minimal amount of solvent remained. This small amount of solvent was then washed back through the frit leaving behind large yellow crystals, which were similarly recrystallized several times. The solvent was then removed and the yellow, crystalline $[S_2N]^+[AsF_6]^-$ recovered (1.26 g, 4.74 mmol; 50% yield based on $[SN]^+[AsF_6]^-$ and eq 3) and identified by its infrared and Raman spectra.[10] Anal. Calcd for $[S_2N]^+[AsF_6]^-$: S, 24.01; N, 5.24. Found: S, 24.67 N, 5.26. The brown residue (0.96 g), produced by solvent removal from the material washed into the second bulb, was shown by infrared spectroscopy to be almost entirely $[S_2N]^+[AsF_6]^-$.

Small-Scale Preparation of NSF. In a typical reaction, a right-angled, closed tube (o.d. $^1/_4$ in., length approximately 25 cm) was coupled via a Teflon Swagelock compression fitting and Whitey valve, to a stainless-steel gas infrared cell, fitted with AgCl windows (volume 125 cm^3). A ground mixture of $[SN]^+[AsF_6]^-$ (0.123 g, 0.52 mmol) and CsF (0.237 g, 1.56 mmol) was loaded into the side arm. The cell was evacuated and the side arm heated to 65 °C at a rate of 14 °C min^{-1}. The steady evolution of NSF between 40 and 50 °C ceased after approximately 3 min, monitored by observing the 655-cm^{-1} S–F peak in the gas-phase infrared spectrum.[21] The infrared spectrum showed only the presence of NSF (40 Torr) and OSF_2 (2 Torr), pressures estimated by comparison with published spectra.[21,22] Thus 0.027 ± 0.002 g of NSF was produced, ca. 80% yield based on $[SN]^+[AsF_6]^-$ and eq 4.

Larger Scale Preparation of NSF. Cesium fluoride (7.0 g, 46.1 mmol) and $[SN]^+[AsF_6]^-$ (3.6 g, 15.3 mmol) was intimately ground and added to a Monel vessel equipped with a removable lid (volume 34.5 cm^3). A further charge of CsF (2.94 g, 19.35 mmol) was packed onto the top of the mixture. The vessel was evacuated and heated to 110 °C (1.5 °C min^{-1}) at which point a rapid evolution of gas was observed by an increase in pressure. The volatile products contained NSF (0.54 ± 0.07 g; 80 ± 10% yield based on $[SN]^+[AsF_6]^-$ and eq 3, OSF_2 (0.07 ± 0.03 g; 10 ± 5% yield), SF_4 (0.07 ± 0.03 g; 10 ± 5% yield), and N_2; relative amounts were estimated from published infrared spectra.[21-23] The N_2 was removed and the volatiles reacted with an excess of AsF_5 in a separate Monel vessel. The Raman spectra of the solid produced showed only the presence of $[SN]^+[AsF_6]^-$ (1.76 g) and corresponds to an initial yield of NSF of 49% if the solid produced was 100% $[SN]^+[AsF_6]^-$ (N.B. it is likely that the product contains some undetected $[SF_3]^+[AsF_6]^-$).[24]

Discussion

$[SN]^+[AsF_6]^-$ of high purity can be prepared in 75% yield according to eq 2. $S_3N_3Cl_3$ is easily prepared from S_2Cl_2 and NH_4Cl via $S_3N_3Cl_2$ and chlorine in a well-described, published procedure.[20] $AgAsF_6$ is commercially available or can be easily prepared from silver and AsF_5.

The utility of $[SN]^+[AsF_6]^-$ is illustrated by its reaction with elemental sulfur to give crystalline $[S_2N]^+[AsF_6]^-$ in 50% recovered yield. The advantages of this synthesis of $[S_2N]^+[AsF_6]^-$ are that the starting materials, $S_3N_3Cl_3$, $AgAsF_6$, $[SN]^+[AsF_6]^-$, and S_8 are easy to handle and nonexplosive. The previously described synthesis of $[S_2N]^+[AsF_6]^-$ [10] uses potentially explosive S_4N_4[25] and toxic, corrosive AsF_5.[26] The disadvantages are that the overall yield of crystalline product is lower (50% based on $S_3N_3Cl_3$ and 78% based on S_4N_4) and the synthesis involves more steps.

The utility of $[SN]^+[AsF_6]^-$ is further demonstrated by its reaction with CsF in a solid/solid reaction leading to the versatile reagent, NSF, according to eq 4. The small-scale reaction gave NSF directly in reasonable purity (ca. 95%) in 80% yield, the impurity detected in the infrared spectrum being OSF_2 formed by the hydrolysis of SF_4. A reaction carried out on a gram quantity scale led to about 50% yield of NSF. The larger scale preparation likely involved less efficient heat transfer to reactants and therefore a higher heating temperature. This led to greater decomposition of NSF according to eq 5.

$$4NSF \xrightarrow{\Delta} 2N_2 + SF_4 + {}^3/_8S_8 \qquad (5)$$

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(21) Richert, H.; Glemser, O. *Z. Anorg. Allg. Chem.* **1961**, *307*, 328.

(22) O'Loan, J. K.; Wilson, M. K. *J. Chem. Phys.* **1955**, *23*, 1313.

(23) Seel, F.; Budenz, R. *Chem. Ber.* **1965**, *98*, 251.

(24) Gibler, D. D.; Adams, C. J.; Fischer, A. Z.; Bartlett, N. *Inorg. Chem.* **1972**, *10*, 2325.

(25) Banister, A. J. *Inorg. Synth.* **1977**, *17*, 197.

(26) Braker, W.; Mossman, A. L.; Siegel, D. *Effects of Exposure to Toxic Gases—First Aid and Medical Treatment*, 2nd ed.; Matheson: Lyndhurst, NJ, 1977.

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Kinetic Study of Ternary Complex Formation between (Terpyridine)nickel and Isomeric (Pyridylazo)naphthol Dyes: Acceleration of a Ring-Closure Step

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It is established that rates of ternary complex formation of some planar aromatic ligands with 1:1 nickel chelates that already contain such a ligand can be unexpectedly high.[1-4] The accelerations are greater than can be accounted for by inner-sphere water exchange rates and have been ascribed to enhanced outer-sphere association of the chelate and entering ligand.[1] Margerum and his co-workers have attributed the increased association to favorable stacking interactions of the planar aromatic ligands.[2-4] We have invoked the same interpretation to explain unusually high rates of formation of bis dye–nickel complexes from the 1:1 complexes.[5-6]

Most examples of accelerated formation of ternary complexes have involved cases where the initial ligation step is rate limiting.[4] It was anticipated that the advantages of enhanced outer-sphere association would diminish if the rate-determining step (rds) came later in the chelation reaction. To our knowledge there have been no studies of the effect of outer-sphere stacking on rates of complexation where ring closure is rate limiting. We have recently found a case where ring closure appears to be rate limiting in the formation of a 1:1 chelate of Ni^{2+} with a β-PAN dye ligand (**2**), yet formation of the bis complex from the 1:1 complex is unusually

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(1) Holyer, R. H.; Hubbard, C. D.; Kettle, S. F. A.; Wilkins, R. G. *Inorg. Chem.* **1966**, *5*, 622.

(2) Cayley, G. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, 1002.

(3) Pagenkopf, G. K.; Margerum, D. W. *Inorg. Chem.* **1968**, *7*, 2514.

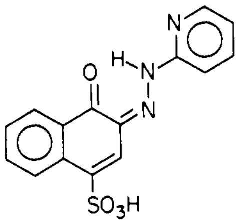
(4) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenhopf, G. K. In *Coordination Chemistry, Vol. 2*; Martell, A. E., Ed.; ACS Monograph No. 174, American Chemical Society: Washington, DC, 1978; p 140.

(5) Reeves, R. L.; Calabrese, G. S.; Harkaway, S. A. *Inorg. Chem.* **1983**, *22*, 3076.

(6) Reeves, R. L. *Inorg. Chem.* **1986**, *25*, 1473.

0020-1669/86/1325-4452$01.50/0 © 1986 American Chemical Society

rapid.[6] Here we report the kinetics of ternary complex formation between nickel 2,2′:6′,2″-terpyridine (Ni(terpy)$^{2+}$) and isomeric α-PAN (**1**) and β-PAN (**2**) dyes.[7] Earlier work on the chelation of Ni^{2+} with these dyes[5,6] showed that the rates of the undissociated (LH) and dissociated (L$^-$) forms of **1** were close to those predicted from the water exchange rate of Ni^{2+} (k_{ex}). This dye should serve as a benchmark for assessing the advantage of any outer-sphere stacking when the initial ligation is rate limiting. The chelation rate of the LH form of **2** was considerably less than predicted from k_{ex} and was subject to general base catalysis. This indicated that a ring-closure step requiring proton removal from a weakly acidic intermediate was rate limiting.[6] The two dyes provide structurally similar ligands with different rds's for assessing the relative advantages of favorable outer-sphere effects. We also report a simplified preparation of 1:1 Ni(terpy)$^{2+}$ as the diacetate monohydrate.



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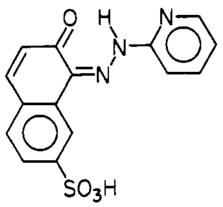

2

Experimental Section

2,2′:6′,2″-Terpyridine (10.0 g in 200 mL of tetrahydrofuran) was added slowly to a solution of nickel acetate hexahydrate in a mixture of 50 mL of water, 50 mL of methanol, and 25 mL of acetic acid. The solution was stirred for 1 h at room temperature and was then evaporated to dryness. Acetonitrile (100 mL) was added and evaporated to dry the solid. Trituration with acetonitrile and filtration gave a 67% yield of the 1:1 product. The 1:2 product was retained in the filtrate. Calcd for $C_{19}H_{19}N_3O_5Ni$: C, 53.3; H, 4.5; N, 9.8. Found: C, 54.0; H, 4.5; N, 9.9.

The preparation and purification procedures for the dyes have been described.[5,6] The *N*-morpholinoethanesulfonic acid (MES) and *N*-(2-hydroxyethyl)piperazine-*N*′-ethanesulfonic acid (HEPES) were Fluka puriss. grade and were used as received. The purification of tris(hydroxymethyl)aminomethane (Tris) has been described.[5] The chloroacetic acid (Kodak reagent grade) was used as received.

Stock solutions of Ni(terpy)$^{2+}$ were prepared by weight from the diacetate. Dissolution of the solid gives the 1:1 complex, which disproportionates slowly.[1] Solutions were used within 2 h of preparation to avoid disproportionation. Kinetic measurements were made at 25 °C and at $I = 0.04$ M (0.01 M buffer ion and 0.03 M sodium perchlorate) on a Durrum stopped-flow instrument interfaced with an OLIS Model 3820 data system. Three or more traces were averaged for the evaluation of each rate constant. Runs were made under pseudo-first-order conditions with an excess of Ni(terpy).$^{2+}$

Results and Discussion

Complexation with Dye 1. Spectral titration gave a pK_{a1} value of 2.90 for dissociation of the pyridinium ion ($LH_2^+ \rightleftharpoons LH + H^+$) at $I = 0.04$ M. The value of pK_{a2} ($LH \rightleftharpoons L^- + H^+$) is 8.14 at the same ionic strength.[5] Titration of 4.0×10^{-5} M dye with Ni(terpy)$^{2+}$ by the molar ratio method gave a single spectral change in the visual region with a sharp isosbestic point. Thus, there is a simple two-component system at all concentrations of Ni(terpy)$^{2+}$, consisting of the uncomplexed dye and the ternary nickel–dye–terpy complex.

Rates of formation of the ternary complex were pseudo first order through 3 half-lives in a 10–40-fold excess of Ni(terpy)$^{2+}$. Rate constants measured at 450 nm (dye disappearance) and at 560 nm (complex appearance) were the same, and there was no evidence for the accumulation of an intermediate. Complexation was complete at pH values as low as 3.2; plots of k_{obsd} (s^{-1}) vs. [Ni(terpy)$^{+2}$] were linear and passed through the origin.

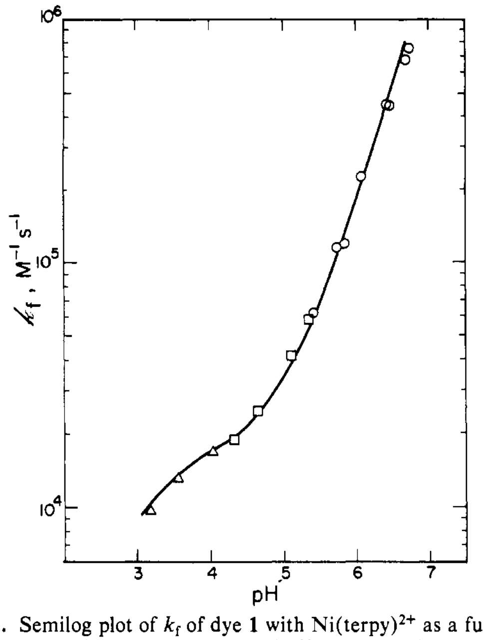

Figure 1. Semilog plot of k_f of dye **1** with Ni(terpy)$^{2+}$ as a function of pH at 25 °C and $I = 0.04$ M. The buffers were chloroacetate (△), acetate (□), and MES (○). The continuous curve was calculated with eq 4, the experimental pK_a's, and the values of k_{LH} and k_{L^-} from Table I.

Table I. Formation Rate Constants for Complexation of the Undissociated and Dissociated Dye Ligands with Ni(terpy)$^{2+}$ and Ni^{2+} [a]

	Ni(terpy)$^{2+}$ [b]		Ni^{2+}		
dye	k_{LH}, M^{-1} s^{-1}	k_{L^-}, M^{-1} s^{-1}	k_{LH}, M^{-1} s^{-1}	k_{L^-}, M^{-1} s^{-1}	ref
1	1.6×10^4	2.6×10^7	1.8×10^3	4.0×10^4	5
2	1.9×10^4	4.8×10^7	2.7×10^2	1.1×10^6	6

[a] 25 °C; $[\text{dye}]_0 = (1–2) \times 10^{-5}$ M, $I = 0.04$ M. [b] This work.

The effect of pH on the second-order formation rate constants (k_f) was measured between pH 3.2 and 6.7 in dilute chloroacetate, acetate, and MES buffers as shown in Figure 1. The data were fitted by assuming that the rate constant for complexation of the pyridinium species (LH_2^+) was negligible and that the rate law is given by eq 1 and 4. The continuous line in Figure 1 was

$$-d[L]_T/dt = v_T = [\text{Ni(terpy)}^{2+}](k_{LH}[LH] + k_{L^-}[L^-]) \quad (1)$$

$$[L]_T = [LH_2^+] + [LH] + [L^-] = [LH]\left(\frac{[H^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]}\right) \quad (2)$$

$$\frac{v_T}{[\text{Ni(terpy)}^{2+}][L]_T} = k_f = \frac{[LH]}{[LH]_T}\left(k_{LH} + \frac{k_{L^-}K_{a2}}{[H^+]}\right) \quad (3)$$

$$k_f = \left(k_{LH} + \frac{k_{L^-}K_{a2}}{[H^+]}\right) \Big/ \left(\frac{[H^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]}\right) \quad (4)$$

calculated via eq 4 with the experimental K_a's and the values of k_{LH} and k_{L^-} given in Table I. For comparison, the table also lists the corresponding rate constants for complexation of the two ligand species with Ni^{2+}.

The results show that the LH and L$^-$ forms of **1** react more rapidly with Ni(terpy)$^{2+}$ than with Ni^{2+}. The rate enhancement for reaction of Ni(terpy)$^{2+}$ with the *i*th species of the ligand is defined as twice the ratio of the formation rate constants [$2k_i$(Ni(terpy))/k_i(Ni^{2+})] divided by the ratio of water exchange rate constants [k_{ex}(Ni(terpy))/k_{ex}(Ni^{2+})]. The factor of 2 is a statistical factor. The values of k_{ex}(Ni(terpy)) and k_{ex}(Ni^{2+}) are 5.2×10^4 s^{-1} and 3.0×10^4 s^{-1}, respectively.[8,9] Reaction of the

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(7) All the dyes exist as azo and hydrazone tautomers in rapid equilibrium. The predominant hydrazone tautomers are shown.

(8) Rablen, D.; Gordon, G. *Inorg. Chem.* **1969**, *8*, 395.

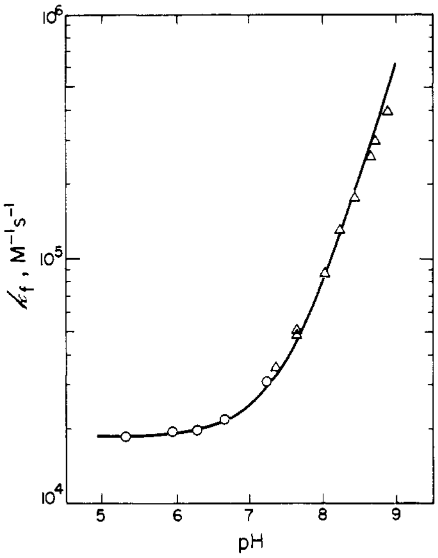

Figure 2. Semilog plot of k_f of dye **2** with Ni(terpy)$^{2+}$ as a function of pH at 25 °C and $I = 0.04$ M. The buffers were MES (○) and HEPES (△). The continuous curve was calculated with eq 4, the experimental pK_{a2}, and the values of k_{LH} and k_{L^-} from Table I.

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$^-$],	k_{obsd}, s^{-1}		[B$^-$],	k_{obsd}, s^{-1}	
mM	pH 5.95	pH 6.28	mM	pH 5.95	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; [dye]$_0$ = 1.0 × 10^5 M; [Ni(terpy)$^{2+}$]$_0$ = 1.0 × 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$_2$O)$_3^{2+}$ 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$_2$O)$_3^{2+}$ to Ni(terpy)(H$_2$O)$_2$OH$^+$.

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.

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

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(9) Connick, R. E.; Fiat, D. *J. Chem. Phys.* **1966**, *44*, 4103.

(10) Quadrifoglio, F.; Crescenzi, V. *J. Colloid Interface Sci.* **1971**, *35*, 447.

(11) Reeves, R. L.; Harkaway, S. A. In *Micellization, Solubilization, and Microemulsions*; Mittal, K. L., Ed.; Plenum: New York, 1977; Vol. 2, p 819.

(12) Rorabacher, D. B. *Inorg. Chem.* **1966**, *5*, 1891.

(13) Taylor, R. W.; Stepien, H. K.; Rorabacher, D. B. *Inorg. Chem.* **1974**, *13*, 1282.

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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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(1) (a) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750-1759. (b) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027-2038. (c) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *149*, 119-135.

(2) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723-729.

(3) Jensen, C. M.; Trogler, W. C. *Science* (*Washington, D.C.*) **1986**, *233*, 1069-1071.

(4) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407-445.

(5) Prignano, A. L.; Trogler, W. C. *Monatsh. Chem.* **1986**, *117*, 617-619.

0020-1669/86/1325-4454$01.50/0