surprising since the inorganic functionality [ZrO₂CH] can be related to an ester, which is very easily reduced by complex I[5b,20,21] in a related reaction. Step d is proven by having carried out the reaction between I and formaldehyde leading to [cp₂Zr(Cl)-(OMe)], while addition of a C=N multiple bond to the Zr–H bond in complex I was recently reported.[22] The oxophilicity of zirconium and the formation of a very stable complex II are the real driving force of the reduction of CO₂ in the reactions outlined above.

The present study suggests that reduction of CO₂ by a M–H bond could be an interesting process provided two fundamental research lines are pursued. The first one is a study on the reduction of the metalloformate functionality, while the second one, which is the most crucial problem in the activation of oxygen containing molecules, is how to react the M—O—M, M—O—R, and M=O inorganic functionalities.

(20) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340.
(21) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 413–417.
(22) Erker, G.; Fromberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 68–69; *J. Organomet. Chem.* **1984**, *280*, 343–354, 355–363.

Axial Ligand Anation and Aquation Reactions in Diplatinum(III) Complexes. Comparison of Aquation Rates between PtCl₆²⁻ and Diplatinum(III) Chloro Complexes Having μ-Phosphato or μ-Pyrophosphito Ligands

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Abstract: The diplatinum(III) complex [Pt₂(μ-PO₄H)₄(H₂O)₂]²⁻ reacts with halide ions X⁻ (X = Cl, Br) to give first [Pt₂(μ-PO₄H)₄X(H₂O)]³⁻ and then [Pt₂(μ-PO₄H)₄X₂]⁴⁻. The reaction establishes an equilibrium situation between the three complexes:

$$Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2{}^{2-} + X^- \underset{k_2}{\overset{(K_1)k_1}{\rightleftharpoons}} Pt_2(\mu\text{-}PO_4H)_4X(H_2O)^{3-} + X^- \underset{k_4}{\overset{(K_2)k_3}{\rightleftharpoons}} Pt_2(\mu\text{-}PO_4H)_4X_2{}^{4-}$$
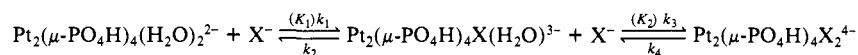
Using pseudo-first-order conditions in halide ion at 25 °C, we have used a biphasic analysis to evaluate the rate constants. The values are $k_1 = 0.9$ (2) M⁻¹ s⁻¹, $k_2 = 5$ (1) × 10⁻² s⁻¹, $k_3 = 0.8$ (2) M⁻¹ s⁻¹, $k_4 = 8$ (2) × 10⁻² s⁻¹ (X = Cl) and $k_1 = 0.3$ (1) M⁻¹ s⁻¹, $k_2 = 1.5$ (3) × 10⁻² s⁻¹, $k_3 = 0.4$ (1) M⁻¹ s⁻¹, $k_4 = 1.9$ (3) × 10⁻² s⁻¹ (X = Br). Under comparable conditions of temperature (25 °C), pH (3.0), and ionic strength (0.1 M), we have measured the equilibrium constants as $K_1 = 19$ (2) M⁻¹, $K_2 = 11$ (1) M⁻¹ (X = Cl) and $K_2 = 21$ (2) M⁻¹, $K_2 = 22$ (2) M⁻¹ (X = Br). In all cases, $k_1 > k_2$ and $k_3 > k_4$, and $k_1 \approx k_3$ and $k_2 \approx k_4$. The axially coordinated halide ligands at 6-coordinate platinum are substituted some 4 orders of magnitude faster than axial halides in the μ-pyrophosphito complexes [Pt₂(μ-P₂O₅H₂)₄X₂]⁴⁻ or chloride in PtCl₆²⁻. This axial halide labilization in [Pt₂(μ-PO₄H)₄X₂]⁴⁻ (X = Cl, Br) as compared to PtCl₆²⁻ is believed to be a consequence of a strong intermetallic bond between platinums.

The chemistry of metal–metal bonded complexes continues to be a subject of active interest.[1] A large body of work now exists describing the synthesis of numerous transition-metal complexes having a wide variety of bridging ligands and terminal end groups. Many of these complexes have been structurally characterized, but only a relatively small amount of work has been published correlating differences in substitution patterns and rates with variations in intermetallic bonding between sets of complexes. Such studies are valuable if major changes in reactivity or selectivity are to be identified because they confirm that an intermetallic bond is a variable quantity that can be changed to induce desired differences in reaction chemistry.

Recently three series of diplatinum(III) complexes have been prepared that allow us to test this premise. One set of complexes has a bridging pyridinato-*N,O* ligand,[2] and a second set has a pyrophosphito-*P,P* group as a bridge.[3] A third group, which we classify as a single set, has either a bridging sulfato-*O,O* or hy-

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley-Interscience: New York, 1982.

(2) Hollis, L. S.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 3637–3644 and references therein.
(3) Che, C.-M.; Schaefer, W. P.; Gray, H. B.; Dickson, M. K.; Stein, P.; Roundhill, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 4253–4255. Bryan, S. A.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 1882–1883. Che, C.-M.; Herbstein, F. H.; Schaefer, W. P.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4604–4607. Stein, P.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3489–3494. Hedden, D.; Walkinshaw, M. D.; Roundhill, D. M. *Inorg. Chem.*, in press. Alexander, K. A.; Bryan, S. A.; Fronczek, F. R.; Fultz, W. C.; Rheingold, A. R.; Roundhill, D. M.; Stein, P.; Watkins, S. F. *Inorg. Chem.*, in press. Che, C.-M.; Mak, T. C. W.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 4386–4388.

Anation and Aquation in Diplatinum(III) Complexes

J. Am. Chem. Soc., Vol. 107, No. 22, 1985 6283

drogen phosphato-*O*,*O* ligand.[4] The two sets of complexes with either μ-pyrophosphito-*P*,*P* (μ-$P_2O_5H_2^{2-}$) or μ-hydrogen phosphato-*O*,*O* (μ-PO_4H^{2-}) ligands bridging platinum(III) centers (Pt_2^{6+}) make a useful pair to compare variations in equatorial ligands and intermetallic bonding with differences in chemical reactivity. Each group of complexes is soluble in water, thereby making the ionic strength and the pH of the solutions easy to control. Furthermore each bridging ligand is symmetrical and dianionic, and the well-characterized complexes of each type have the "lantern" structure with four bridging ligands in equatorial positions. Finally the two groups of complexes are attractive for a comparative kinetic study because the Pt–Pt distances in the two groups of complexes are quite different. The Pt–Pt distances in the μ-pyrophosphito complexes are in the 2.695 (1)–2.782 (1)-Å range, and those for the μ-hydrogen phosphato complexes are between 2.486 (2) and 2.592 (1) Å. The difference in these Pt(III)–Pt(III) distances is large, and if this variation reflects differences in intermetallic bonding, we can expect to see changes induced in the axial ligand reactivity.

This paper reports our kinetic study on axial ligand replacement reactions of diplatinum(III) complexes with bridging hydrogen phosphato ligands. The aquation rates of these complexes are compared with those found for $PtCl_6^{2-}$ and the corresponding μ-pyrophosphito diplatinum(III) complexes.

Experimental Section

Synthesis of Complexes. The complex $Na_2[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]$ was prepared by the literature procedure[4] from phosphoric acid and Pt(N-$O_2)_2(NH_3)_2$. A mixture of *cis*- or *trans*-Pt(NO$_2$)$_2$(NH$_3$)$_2$ (0.2 g) with phosphoric acid (2 mL) was heated at 110 °C until the brown fumes of nitrogen dioxide ceased to be liberated. The resulting solution was allowed to cool, and NaH$_2$PO$_4$ (0.1 g), dissolved in water (6 mL), was added. After stirring for 20 min the solution was filtered, and the complex precipitated as a solid by addition of ethanol. The solid was washed several times with ethanol, and after a final washing with diethyl ether the complex was air-dried. The product was characterized by UV–vis (λ_{max} = 224 and 396 nm) and ^{31}P NMR spectroscopy (δ_P = 18.4; ^2J(PtP) = 72 Hz (1:8:18:8:1 pseudoquintet)).[5] The complexes $Na_4[Pt_2(\mu\text{-}PO_4H)_4X_2]$ (X = Cl, Br) were prepared by the addition of excess of an aqueous solution of potassium halide to $K_2[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]$ (δ_P = 18.4, pseudoquintet; ^2J(PtP) = 72 Hz). The halide ions selectively substituted the axial water molecules in the complex, and the ^{31}P NMR spectra of the dihalo complexes showed the expected pseudoquintet splittings (X = Cl, δ_P = 23.4 (^2J(PtP) = 73 Hz); X = Br, δ_P = 26.8 (^2J(PtP) = 65 Hz)). The electronic spectra of aqueous solutions of $[Pt_2(\mu\text{-}PO_4H)(H_2O)_2]^{2-}$ and $[Pt_2(\mu\text{-}PO_4)_4X_2]^{4-}$ show the respective values 224 and 396 nm (H$_2$O)$_2$,[4] 296 and 408 nm (X = Cl), and 342 and 410 nm (X = Br). The literature reports different values for λ_{max} and ϵ_{max} for this group of complexes,[4] and prior to making kinetic or equilibrium measurements we needed reliable extinction coefficients. For $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ we find ϵ_{max} (224) = 16 160 M^{-1} cm^{-1}, and for $Pt_2(\mu\text{-}PO_4H)_4X_2^{4-}$ in the presence of a large amount of added X$^-$ we find ϵ_{max} (296) = 21 480 M^{-1} cm^{-1} (X = Cl), and ϵ_{max} (342) = 22 470 M^{-1} cm^{-1} (X = Br). Aqueous solutions of pure $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$ in the absence of X$^-$ gave a mixture of $[Pt_2(\mu\text{-}PO_4H)_4X(H_2O)]^{3-}$, $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ and $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$. Aqueous solutions of these complexes obey Beers law.

(4) Muraveiskaya, G. S.; Orlova, V. S.; Evstaf'eva, O. N. *Russ. J. Inorg. Chem.* (*Engl. Trans.*) **1974**, *19*, 561–565. Orlova, V. S.; Muraveiskaya, G. S.; Evstaf'eva, O. N. *Russ. J. Inorg. Chem.* (*Engl. Trans.*) **1975**, *20*, 753–758. Muraveiskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstaf'eva, O. N.; Porai-Koshits, M. A. *Dokl. Akad. Nauk SSSR.* **1976**, *226*, 596–599. Muraveiskaya, G. S.; Abashkin, V. E.; Evstaf'eva, O. N.; Golovaneva, I. F.; Shchelokov, R. N. *Sov. J. Coord. Chem.* (*Engl. Trans.*) **1981**, *6*, 218–225. Orlova, V. S.; Muraveiskaya, G. S.; Golovaneva, I. F.; Shchelokov, R. N. *Russ. J. Inorg. Chem.* (*Engl. Trans.*) **1980**, *25*, 112–116. Muraveiskaya, G. S.; Orlova, V. S.; Golovaneva, I. F.; Shchelokov, R. N. *Russ. J. Inorg. Chem.* (*Engl. Trans.*) **1981**, *26*, 994–996. Muraveiskaya, G. S.; Orlova, V. S.; Golovaneva, I. F.; Shchelokov, R. N. *Russ. J. Inorg. Chem.* (*Engl. Trans.*) **1981**, *26*, 1770–1774. Abashkin, V. E.; Muraveiskaya, G. S.; Golovaneva, I. F.; Smirnov, A. N.; Tsivadze, A. Yu.; Shchelokov, R. N. *Russ. J. Inorg. Chem.* (*Engl. Trans.*) **1983**, *28*, 1626–1631. Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 2889–2891 and 1709–1710. Conder, H. L.; Cotton, F. A.; Falvello, L. R.; Han, S.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 1887–1891. Cotton, F. A.; Han, S.; Conder, H. L.; Walton, R. A. *Inorg. Chim. Acta* **1983**, *72*, 191–193.

(5) Appleton, T. G.; Hall, J. R.; Neale, D. W.; Ralph, S. F. *Inorg. Chim. Acta* **1983**, *77*, L149–L151.
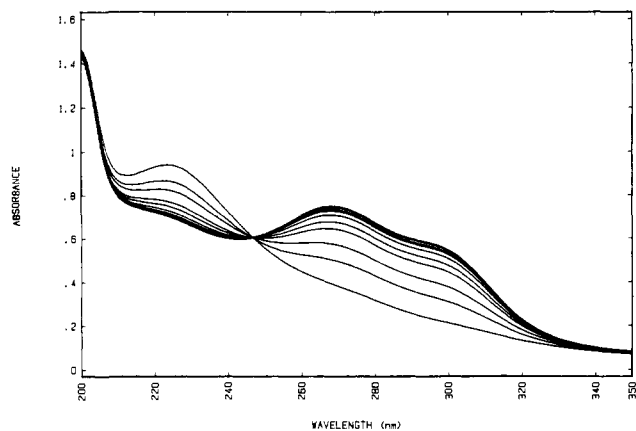
Figure 1. Spectral changes in the UV–vis region for the reaction of $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ with excess Cl$^-$ ion at temperature 25 °C, pH 3.0, 0.1 M ionic strength phosphate buffer. λ_{max} = 224, 266, and 296 nm for $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$, $[Pt_2(\mu\text{-}PO_4H)_4Cl(H_2O)]^{3-}$, and $[Pt_2(\mu\text{-}PO_4H)_2Cl_2]^{4-}$, respectively.
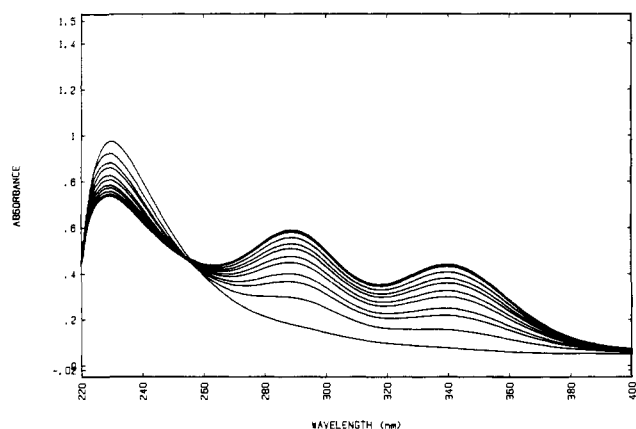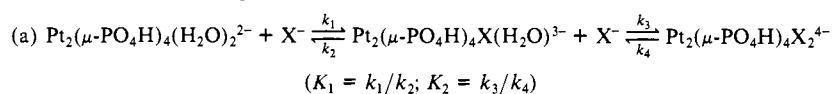

Figure 2. Spectral cahnges in the UV–vis region for the reaction of $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ with excess Br$^-$ ion. Conditions as for Figure 1. λ_{max} = 292 and 342 nm for $[Pt_2(\mu\text{-}PO_4H)_4Br(H_2O]^{3-}$ and $[Pt_2(\mu\text{-}PO_4H)_4Br_2]^{4-}$.
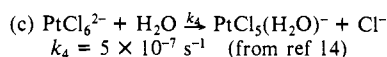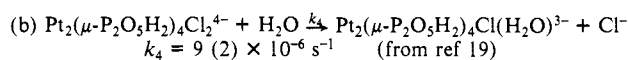
Kinetic Measurements. All concentration measurements were made by following changes in electronic absorption maxima of solutions of the complexes. All data were collected at a constant temperature of 25 ± 0.2 °C. Samples were contained in 1-cm path length quartz cells in a thermostated cell holder that was connected to a Lauda RC3 recirculating fluid bath. The pH and ionic strength of all solutions were kept constant at the respective values of pH 3 and μ = 0.1 (μ = $^1/_2\sum(\mu(Z^+)^2 + \mu(Z^-)^2)$). A phosphate buffer ($\mu$ = 0.1 M) consisting of KH$_2$PO$_4$ and H$_3$PO$_4$ was used throughout. Aliquots of the required solutions were measured and transferred into the quartz cells with a Pipetman.

Intensity and time measurements were made on a Hewlett-Packard Model 8451A diode array spectrometer. The spectrometer is equipped with a kinetics software package, and the data were collected as a numerical printout of intensity against time. Data were collected at 5-s intervals, and the instrument was programmed to collect changing intensity values at chosen constant wavelengths. Wavelengths were selected such that intensity measurements were collected against time intervals at λ_{max} for $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$, $[Pt_2(\mu\text{-}PO_4H)_4X(H_2O)]^{3-}$, and $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$ (X = Cl, Br). Rate data were collected under pseudo-first-order conditions in added halide ion. For the case of added NaCl, the concentration of $Na_2[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]$ was 130.8 μM, and rate data were collected for separate cases where the concentration of chloride ion was 13, 39, 78, and 104 mM. For the bromide measurements, the same concentration of platinum complex was used, and now the separate concentrations of bromide ion were 13, 26, 52, and 104 mM. Infinity values were taken when the final concentrations remained constant after equilibrium had been reached.

Equilibrium Measurements. The equilibrium constants K_1 and K_2 were measured both at the same temperature and under the same pH and ionic strength conditions as the solutions used in the kinetic measurements. Values for K_1 were experimentally obtained with small added quantities of halide ion to solutions of $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$. Under these experimental conditions the mixture of $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ and

Table I. Rate and Equilibrium Constant Data for Aquation and Anation Reactions

$$\text{(a)} \quad Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2{}^{2-} + X^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Pt_2(\mu\text{-}PO_4H)_4X(H_2O)^{3-} + X^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Pt_2(\mu\text{-}PO_4H)_4X_2{}^{4-}$$

$$(K_1 = k_1/k_2;\ K_2 = k_3/k_4)$$

X	k_1, M^{-1}	k_2, s^{-1}	k_3, M^{-1} s^{-1}	k_4, s^{-1}	K_1 M^{-1}	K_2 M^{-1}
Cl	0.9 (2)	5 (1) × 10^{-2}	0.8 (2)	8 (2) × 10^{-2}	19 (2)	11 (1)
Br	0.3 (1)	1.5 (3) × 10^{-2}	0.4 (1)	1.9 (3) × 10^{-2}	21 (2)	22 (2)

$$\text{(b)} \quad Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2{}^{4-} + H_2O \overset{k_4}{\rightleftharpoons} Pt_2(\mu\text{-}P_2O_5H_2)_4Cl(H_2O)^{3-} + Cl^-$$
$$k_4 = 9\ (2) \times 10^{-6}\ s^{-1} \quad \text{(from ref 19)}$$

$$\text{(c)} \quad PtCl_6{}^{2-} + H_2O \overset{k_4}{\rightleftharpoons} PtCl_5(H_2O)^- + Cl^-$$
$$k_4 = 5 \times 10^{-7}\ s^{-1} \quad \text{(from ref 14)}$$

$[Pt_2(\mu\text{-}PO_4H)_4X(H_2O)]^{3-}$ contained only very small amounts of $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$. To obtain K_2 we used experimental conditions with halide ion X$^-$ added to $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$, where $[Pt_2(\mu\text{-}PO_4H)_4X(H_2O)]^{3-}$ was a significant solution component but the concentration of $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]$ was negligible. Using our measured extinction coefficients for these complexes, along with the known added halide ion concentrations, we calculated the equilibrium constants K_1 and K_2 from the measured absorption maxima.

Data Fitting. Our experimental data shown in Figures 1 and 2 are for the changes in absorption spectra with time of solutions of $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ in the presence of added halide ion (X = Cl, Br). These spectra confirm that all three ions $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$, $[Pt_2(\mu\text{-}PO_4H)_4X(H_2O)]^{3-}$, and $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$ coexist in solution. The halo aquo complexes $[Pt_2(\mu\text{-}PO_4H)_4X(H_2O)]^{4-}$ cannot be obtained quantitatively in solution; hence we cannot *directly* measure the extinction coefficients σ_{max} for the absorption bands at $\lambda_{max} = 266$ (X = Cl) and 292 nm (X = Br). These ϵ_{max} values have been calculated from eq 1 where ϵ_B is the only unknown quantity. The cell path length used was

$$C_{total} = C_A + C_B + C_C = A_A/\epsilon_A + A_B/\epsilon_B + A_C/\epsilon_C \quad (1)$$

1 cm, and we use the abbreviations A for $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$, B for $[Pt_2(\mu\text{-}PO_4H)_4X(H_2O)]^{3-}$, and C for $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$. In order to test for constancy of $\epsilon_B{}^6$ we have applied eq 1 to intensity data measured at both the early and later stages of reactions. As a further check we have made this test for solutions having all concentration ratios of platinum complex to added halide ion. Using this method we obtain ϵ values of 20 000 and 21 000 M^{-1} cm^{-1} for $[Pt_2(\mu\text{-}PO_4H)_4X(H_2O)]^{3-}$ with X = Cl and Br, respectively. Evaluation of these extinction coefficients allowed us to determine the concentrations of all the platinum complexes in the solutions and to thereby evaluate the rate and equilibrium constants.

From the spectral data presented in Figures 1 and 2 it is apparent that we cannot obtain useful values of the species concentrations C_A, C_B, and C_C without correcting for the effects of overlapped peaks at each of the positions of λ_{max} for the three species A, B, and C. We have measured the individual ϵ values of A, B, and C at the λ_{max} positions of the other pairs in the trio and have used these values to set up eq 2-7. These

$$C_A = (A_A - (\epsilon_A{}^\alpha A_B + \epsilon_A{}^\beta A_C))/\epsilon_A \quad (2)$$

$$C_B + (A_B - (\epsilon_B{}^\alpha A_A + \epsilon_B{}^\beta A_C))/\epsilon_B \quad (3)$$

$$C_C = (A_C - (\epsilon_C{}^\alpha A_B))/\epsilon_C \quad (4)$$

$$C_A = (A_A - (\epsilon_A{}^\gamma A_B + \epsilon_A{}^\delta A_C))/\epsilon_A \quad (5)$$

$$C_B = (A_B - (\epsilon_B{}^\gamma A_A + \epsilon_B{}^\delta A_C))/\epsilon_B \quad (6)$$

$$C_C = (A_C - (\epsilon_C{}^\gamma A_B))/\epsilon_C \quad (7)$$

equations have then been used to obtain concentration against time data from kinetic runs. The data for X = Br are fitted according to eq 2-4 and those for X = Cl to eq 5-7. Values of $\epsilon_X{}^\alpha$ and $\epsilon_X{}^\beta$ (X = A, B, C) are the extinction coefficients at the wavelength X of species that do not have ϵ_{max} at this position. The ϵ_X values are the ϵ_{max} values for the individual complexes A, B, and C. The measured values of $\epsilon_X{}^\alpha$ we have used are $\epsilon_A{}^\alpha = 0.25\epsilon_B$, $\epsilon_B{}^\alpha = 0.20\epsilon_A$, $\epsilon_C{}^\alpha = 0.30\epsilon_B$, $\epsilon_A{}^\beta = 0.25\epsilon_C$, $\epsilon_B{}^\alpha = 0.15\epsilon_C$, $\epsilon_A{}^\gamma = 0.38\epsilon_B$, $\epsilon_B{}^\gamma = 0.23\epsilon_A$, $\epsilon_C{}^\gamma = 0.23\epsilon_B$, $\epsilon_A{}^\delta = 0.50\epsilon_C$, $\epsilon_B{}^\delta = 0.10\epsilon_C$. For the case of added bromide ion a second correction was necessary because a solution of KBr in the buffer solution has significant absorption at 224 nm. This absorption was corrected by using a null procedure with a solution of KBr in buffer as a reference sample.

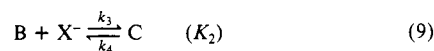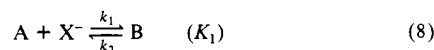(6) Shimura, M.; Espenson, J. H. *Inorg. Chem.* **1984,** *23,* 4069–4071.
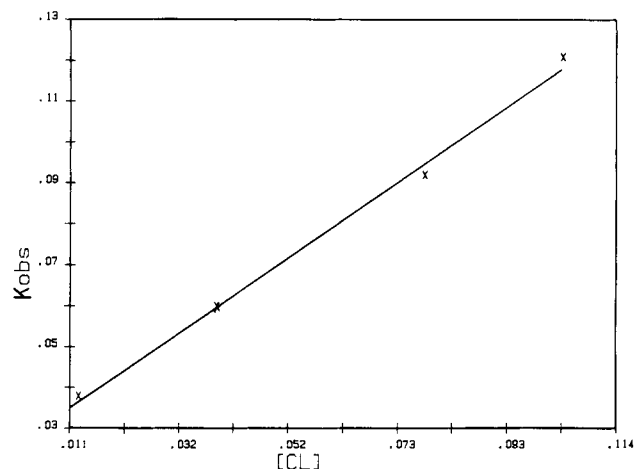
Figure 3. Plot of k_{obsd} against [Cl$^-$] for the first step (k_1/k_2) in the reaction of $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ with excess Cl$^-$.
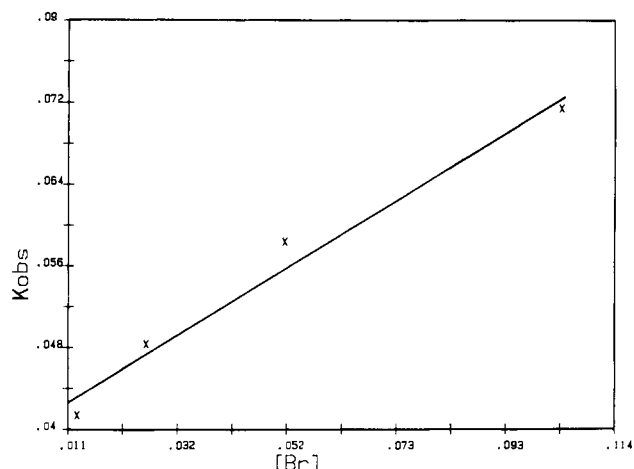
Figure 4. Plot of k_{obsd} against [Br$^-$] for the first step (k_1/k_2) in the reaction of $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ with excess Br$^-$.

In each case (X = Cl, Br), the data have been analyzed on the basis of a pathway involving two reversible pseudo-first-order reactions (eq 8 and 9).[7] A full analysis of such a kinetic system is complex; however,

$$A + X^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \quad (K_1) \quad (8)$$

$$B + X^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C \quad (K_2) \quad (9)$$

a simpler analysis can be applied when K_1 and K_2 are separately evaluated. The first equilibrium (k_1, k_2, K_1) was analyzed by plotting ln (C_A − C_∞) against time t, where C_∞ is the equilibrium concentration of C_A.
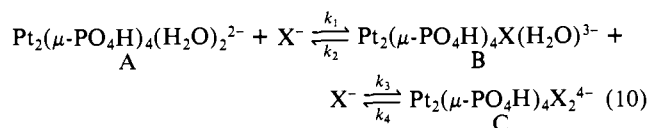
(7) Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981. Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974. Capellos, C.; Bielski, B. H. J. "Kinetic Systems"; Wiley-Interscience: New York, 1972.

This plot has a slope of $-(k_1[X^-] + k_2)$, or k_{obsd}. Plotting k_{obsd} against $[X^-]$ for the data collected at different halide ion concentrations gave k_1. From the measured K_1 values, k_2 was obtained. In principle k_2 can be evaluated from the intercept of the k_{obsd} against $[X^-]$ plot; however, this extrapolation leads to inaccurate k_2 values. The second equilibrium (k_3, k_4, K_2) was analyzed by plotting ln ($C_\infty - C_C$) against time t, where C_∞ is the equilibrium concentration of C_C. This plot has a slope of $-(k_3[X^-] + k_4)$, or k_{obsd}. Plotting k_{obsd} against $[X^-]$ gave k_3, and division by K_2 gave k_2. The plots used to obtain these rate constants are shown in Figures 3 and 4, and the rate constant values for X = Cl and Br are collected in Table I.

Results and Discussion

The binuclear platinum(III) complex $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ has been prepared by the method of Muraveiskaya.[4] The complex is bimetallic both in the solid state and in aqueous solution. The water molecules are coordinated in the axial positions at equivalent platinum centers. The water molecules are successively replaced by chloride or bromide ion in a reversible reaction. There is no evidence for anation by fluoride ion, but addition of excess iodide ion causes some substitution of the μ-phosphato ligand.[8]

Kinetics of Axial Ligand Replacement in $[Pt_2(\mu\text{-}PO_4H)_4$-$(H_2O)_2]^{2-}$. The complex $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ has an intense band at 224 nm that is primarily due to the Pt(III)–Pt(III) ($\sigma \rightarrow \sigma^*$) transition. This chromophore is sensitive to the nature of the axial ligand and is observed in $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$ at 296 nm (X = Cl) and 342 nm (X = Br). The reaction between $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ and halide ion X^- gives first $[Pt_2(\mu\text{-}PO_4H)_4X$-$(H_2O)]^{3-}$ and then $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$. The reaction establishes an equilibrium eq 10). The intermediate $[Pt_2(\mu\text{-}PO_4H)_4X$-

$$Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2{}^{2-} + X^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Pt_2(\mu\text{-}PO_4H)_4X(H_2O)^{3-} +$$
$$\text{A} \qquad\qquad\qquad\qquad\qquad \text{B}$$

$$X^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Pt_2(\mu\text{-}PO_4H)_4X_2{}^{4-} \quad (10)$$
$$\text{C}$$

$(H_2O)]^{3-}$ cannot be formed quantitatively in solution, and complete reaction to $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$ occurs only in the presence of a large excess of X^- (X = Cl, Br).

We have measured the rate constants k_1, k_2, k_3, and k_4 for both added Cl^- and Br^-, along with the equilibrium constants K_1 and K_2. All measurements have been made in phosphate buffer at constant ionic strength of 0.1 M and pH of 3.0. The equilibrium constants K_1 (k_1/k_2) and K_2 (k_3/k_4) are 19 (2) and 11 (1) M^{-1} for X = Cl and 21 (2) and 22 (2) M^{-1} for X = Br. The rate data have been collected by following changes in λ_{max} of A, B, and C with time. The separate rate constants have been evaluated with a biphasic treatment of the data. Addition of halide ion to complex A causes a rapid conversion of the compound into B, and a plot of ln ($C_A - C_\infty$) against time, in conjunction with the measured K_1 value, gives k_1 and k_2. As equilibrium is approached, the reaction consists primarily of C being formed from B, and plotting ln ($C_\infty - C_C$) against time gives, with K_2, the rate constants k_3 and k_4. This method of analysis gives the following values for the rate constants: X = Cl, $k_1 = 0.9$ (2) $M^{-1} s^{-1}$, $k_2 = 5$ (1) $\times$ $10^{-2} s^{-1}$, $k_3 = 0.8$ (2) $M^{-1} s^{-1}$, $k_4 = 8$ (2) $\times 10^{-2} s^{-1}$; X = Br, k_1 = 0.3 (1) $M^{-1} s^{-1}$, $k_2 = 1.5$ (3) $\times 10^{-2} s^{-1}$, $k_3 = 0.4$ (1) $M^{-1} s^{-1}$, $k_4 = 1.9$ (3) $\times 10^{-2} s^{-1}$.

These rate constant values show that the forward rate constants (k_1 and k_3) are larger than the reverse rate constants (k_2 and k_4). Second, the rate data show that chloride ion reacts with $[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ faster than does bromide ion. Third, it is apparent for both X = Cl and Br that the values for k_1 and k_3 and those for k_2 and k_4 are closely similar. This last result shows that there is no significant trans effect difference between H_2O and X^- being transmitted through the Pt(III)–Pt(III) bond for either the hydration or the anation reaction. On statistical grounds we may expect that $k_1 = 2k_3$ and $k_4 = 2k_2$. Application of this ratio to the measured rate constants leads to the conclusion that the halide ligand exerts a greater trans effect than the complexed water

in the forward reaction, although in the back-reaction the opposite conclusion is reached. We therefore observe no statistically significant trans effect across the Pt(III)–Pt(III) bond. This conclusion agrees with kinetic studies previously made on axial ligand substitution reactions of Re(III)–Re(III) in $Re_2(\mu\text{-}OCOC_2H_5)_4Cl_2$[9] and of Pt(I)–Pt(I) in $Pt_2(\mu\text{-}dppm)_2Cl_2$[6]. For the ground-state trans influence, however, bond lengthening effects have been observed orthogonal to the dimolybdenum quadruple bond,[10] and also an enhanced trans influence lengthening of the axial ligand to metal bond distance due to a Au–Au bond has been observed.[11]

Chemical Influence of the Pt(III)–Pt(III) Bond. This study was initiated to investigate whether the presence of a platinum–platinum bond could have a significant effect on the substitution chemistry of hexacoordinate platinum complexes and also to discover whether differences in intermetallic bond strengths in bimetallic complexes can affect axial ligand reactivity.

The anion $[Pt_2(\mu\text{-}PO_4H)_4X_2]^{4-}$ is a binuclear complex of the $Pt_2{}^{6+}$ type and the intermetallic bond between the d^7 metal centers is of type $\sigma(d_{z^2})$. This σ-bonding between platinums causes a close intermetallic spacing, resulting in each metal center having a hexacoordinate geometry. It has been known for decades that substitution rates in *monomeric* octahedral platinum complexes are slow, and the d^6 and d^8 ions are classified as substitution inert.[12] The octahedral monomeric complexes usually undergo replacement reactions either by platinum(II)-catalyzed or by reductive elimination–oxidative addition (REOA) pathways, and simple dissociative substitution reactions are rarely observed.[13] We have therefore used data from Archibald's early study of aquation of $PtCl_6{}^{2-}$ as a model reaction for halide aquation at octahedral platinum.[14] For Archibald's thermal data we calculate a rate constant (k) of $5 \times 10^{-7} s^{-1}$ for reaction 11.[15] This rate is some

$$PtCl_6{}^{2-} + H_2O \xrightarrow{k} PtCl_5(H_2O)^- + Cl^- \quad (11)$$
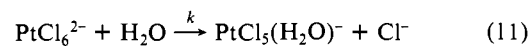
5 orders of magnitude *slower* than we observe for the aquation rate of $[Pt_2(\mu\text{-}PO_4H)_4Cl_2]^{4-}$. The lability of the axial chloride ligands to substitution in the binuclear μ-pyrophosphito complex shows that the interplatinum bond exerts a high trans effect.

Both $[PtCl_6]^{2-}$ and $[Pt_2(\mu\text{-}PO_4H)_2(\mu\text{-}PO_4H_2)_2Cl_2]^{2-}$ (a doubly protonated $[Pt_2(\mu\text{-}PO_4H)_4Cl_2]^{4-}$) have been structurally characterized. The Pt–Cl distance in K_2PtCl_6 is 2.323 (1) Å, whereas in $(Et_4N)_2[Pt_2(\mu\text{-}PO_4H)_2(\mu\text{-}PO_4H_2)_2Cl_2]$ the Pt–Cl separation is 2.448 (4) Å.[16,17] The Pt–Cl distance in the binuclear complex is therefore some 30 standard deviations longer than this same distance in K_2PtCl_6. This Pt–Cl distance in the diplatinum complex is very long and is a consequence of the strong homometallic bond causing poor bonding orbital overlap with the axial ligands.[18]

In conjunction with this study, we have also made a kinetic analysis of the substitution reactions of the P,P-bonded di-

(8) Axially substituted μ-hydrogen phosphato complexes are identified either by the pseudoquintet pattern in the ^{31}P NMR spectrum or by their quantitative conversion to $Pt_2(\mu\text{-}PO_4H)_4Cl_2{}^{4-}$ with added excess chloride ion.

(9) Webb, T. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1974**, *96*, 6289–6294.
(10) Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 2041–2042.
(11) Fackler, J. P., Jr.; Murray, H. H.; Basil, J.; Trzcinska, B.; Mazary, A.; Dudis, D.; Tocher, J. Abstracts of 40th Southwest Regional Meeting, Dec 5–7, 1984, Lubbock, TX, Abstract 312.
(12) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; Chapter 3. Taube, H. *Chem. Rev.* **1952**, *50*, 69–126.
(13) Langford, C. H.; Sastri, V. S. In *MTP Rev. Sci.: Inorg. Chem. Ser. 1* **1972**, *9*, 242.
(14) Archibald, E. H. *J. Chem. Soc., Trans.* **1920**, *117*, 1104–1120. We should note, however, that electron densities at platinum as estimated by photoelectron spectroscopy do indeed support the trivalent designation for these binuclear platinum complexes. The Pt($4f_{7/2}$) binding energy in $K_2(N$-$H_4)_2[Pt_2(PO_4H)_4(OH)_2]\cdot H_2O$ is 75.4 eV, whereas the respective energies in K_2PtCl_4 and K_2PtCl_6 are 74.4 (3) and 76.8 (2) eV (Moddeman, W. E.; Blackburn, J. R.; Kumar, G.; Morgan, K. A.; Albridge, R. G.; Jones, M. M. *Inorg. Chem.* **1972**, *11*, 1715–1717).
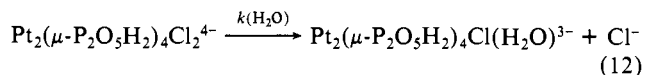(15) Calculated for up to 1.5 halflives from data in Table IV of ref 14.
(16) Williams, R. J.; Dillon, D. R.; Milligan, W. O. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1369–1372.
(17) Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Han, S.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *87*, 147–153.
(18) Reference 1, p 343.

platinum(III) complex $[Pt_2(\mu\text{-}P_2O_5H_2)_4X_2]^{4-}$. This complex is soluble in aqueous solution, but in contrast to $[Pt_2(PO_4H)_4Cl_2]^{4-}$, there is no observable halide (X = Cl, Br, I) aquation even after several days. Anation of $[Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2]^{4-}$ occurs by a combination of $[Pt_2(\mu\text{-}P_2O_5H_2)_4]^{4-}$ catalyzed and REOA pathways, as well as by a slow dissociative pathway (eq 12).[19] We have made a full kinetic analysis of this system, and the slow

$$Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2{}^{4-} \xrightarrow{k(H_2O)} Pt_2(\mu\text{-}P_2O_5H_2)_4Cl(H_2O)^{3-} + Cl^-$$
$$(12)$$

dissociative step is the aquation reaction.[19] This aquation reaction has a first-order rate constant of 9 (2) × 10^{-6} s^{-1}. This rate is slightly faster than that found for $[PtCl_6]^{2-}$ but *considerably* slower than that found for the phosphato complex $[Pt_2(\mu\text{-}PO_4H)_4Cl_2]^{4-}$. In these μ-pyrophosphito-*P,P* complexes the Pt–Pt bond distance is considerably longer than that found in $[Pt_2(\mu\text{-}PO_4H)_4Cl_2]^{4-}$.[3] For example the Pt–Cl distance in $[Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2]$ is 2.407 (2) Å, which is intermediate between that of $[PtCl_6]^2$ (2.323 (1) Å) and $[Pt_2(\mu\text{-}PO_4H)_2(\mu\text{-}PO_4H_2)_2Cl_2]^{4-}$ (2.448 (4) Å). In earlier papers we and others[3,2] have proposed that the differences in Pt(III)–Pt(III) distances in $[Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2]^{4-}$ and $[Pt_2(\mu\text{-}PO_4H)_4Cl_2]^{4-}$ are primarily due to differences in preferred bridge angles in the two ligands and do not necessarily reflect changes in intermetallic bonding. We believe that this conclusion remains valid, but that a 4 orders of magnitude increase in the rate constants for aquation in $[Pt_2(\mu\text{-}PO_4H)_4Cl_2]^{4-}$ over $[Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2]^{4-}$ reflects a major difference in reactivity, which may be due to changes in equatorial ligands or intermetallic bonding.

Estimation of the strength of a metal–metal bond in a bridged bimetallic complex is not achieved simply. Variations in intermetallic separation may give a useful first approximation, but it is certainly not a definitive method.[20] Mulliken has shown that the oscillator strength in an electronic transition is approximately proportional to the square of the overlap integral.[21] We find that the oscillator strength of the 296-nm band in $[Pt_2(\mu\text{-}PO_4H)_4Cl_2]^{4-}$ is 0.46, which is actually smaller than that of 0.70 found for the 282-nm band in $[Pt_2(\mu\text{-}P_2O_5H_2)_4Cl_2]^{4-}$.[22] If these 296- and 282-nm absorptions are accurately assigned to a pure $d\sigma \rightarrow d\sigma^*$ transition between platinums, these oscillator strength values would suggest that $[Pt_2(\mu\text{-}PO_4H)_4Cl_2]^{4-}$ has the weaker intermetallic bond. This spectral assignment, however, remains speculative, and until a better assessment of the Pt–Pt bonding in these complexes becomes available we cannot draw definitive conclusions about its effect on kinetic reactivity.

Obviously much more work needs to be done before we can make strong correlations between chemical reactivity and intermetallic bonding, nevertheless these results show that large variations in kinetic reactivity can be induced by changes in equatorial ligands or by differences in intermetallic bonding.

(19) Bryan, S. A. Ph.D. Thesis, Washington State University, 1985.

(20) Reference 1, p 339–341. Meyer, T. J. *Prog. Inorg. Chem.* **1975**, *19*, 1–50. Chisholm, M. H.; Rothwell, I. P. *Prog. Inorg. Chem.* **1982**, *29*, 1–72.
(21) Mulliken, R. A. *J. Chem. Phys.* **1939**, *7*, 20–34.
(22) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968; p 124.

Coenzyme Models. 41. On the Unusual Reactivities of N(5)-Hydrogen-Bonded Flavin. An Approach to Regiospecific Flavin Activation through Hydrogen Bonding[1]

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Abstract: A new flavin with hydrogen-bonded N(5) (OHFl: sodium 1-hydroxy-7-methylnaphtho[8,7-*g*]pteridine-9,11-(7*H*,10*H*)-dione-3-sulfonate) was synthesized. The second-order rate constants (k_2) for the oxidation of NADH model compounds by OHFl ($E_{1/2}$ = −0.579 V) were similar to those for the oxidation by 3-methyllumiflavin (MeLFl, $E_{1/2}$ = −0.538 V), and the plot for OHFl was included in a linear relation between log k_2 vs. $E_{1/2}$ ($E_{1/2}$: polarographic half-wave potential of flavins). Hence, OHFl acts as a "normal" flavin in this reaction. On the other hand, the pseudo-first-order rate constants (k_1') for the oxidation of thiols by OHFl were greater by 33–645-fold than those for the oxidation by MeLFl, and log k_1' for OHFl deviated to the upper area from the linear log k_1' vs. $E_{1/2}$ relationship by more than two log units. The pseudo-first-order rate constant ($k_{obsd(1)}$) for the adduct formation of OHFl with SO$_3{}^{2-}$ was further enhanced (1830-fold relative to that of MeLFl!). The upper deviation from the linear log $k_{obsd(1)}$ vs. $E_{1/2}$ relationship corresponded to 3.61 log units. The OHFl–SO$_3{}^{2-}$ adduct (λ_{max} 458 nm) further reacted with SO$_3{}^{2-}$ and finally yielded 8-sulfonated 1,5-dihydro-OHFl. It was suggested on the basis of several experimental data that the intermediate absorbing at 458 nm is the 4a adduct. It was concluded, therefore, that OHFl is "regiospecifically" activated toward reactions involving 4a intermediates such as oxidation of thiols and adduct formation with SO$_3{}^{2-}$. This novel finding was ascribed to activation of the 4a position through hydrogen bonding with N(5). Thus, the present study is the first example to support a hypothesis proposed by Massey and Hemmerich that the relative reactivity of C(4a) to N(5) in flavin coenzymes is regulated by the position of hydrogen bonding with flavoapoproteins.

Flavin coenzymes serve as versatile redox catalysts in many biological systems, and it is now known that more than 100 proteins require flavin coenzymes as their prosthetic groups.[2–5] Recently, Massey and Hemmerich[6] suggested that a large number

(1) Preliminary communication: Shinkai, S.; Honda, N.; Ishikawa, Y.; Manabe, O. *Chem. Lett.* **1984**, 327.

(2) Hemmerich, P.; Nagelschneider, G.; Veeger, C. *FEBS Lett.* **1970**, *8*, 69.