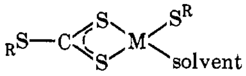
NO] $\leqslant 10^{-3}[CS_2]$ will deviations from first-order kinetics appear.

The stoichiometry for the overall reaction suggests that the rate of loss of monomer is the same as the rate of appearance of dimer product. The pmr and visible spectra establish this to within the limits of sensitivity of the techniques. From reaction 4, assuming steady-state conditions for [B], we see that the kinetic expressions reduce to (IV), as required by the stoichiometry of the system.

$$-\frac{d[\mathrm{MONO}]}{dt} = \frac{2k_r[\mathrm{MONO}]^2}{[\mathrm{MONO}] + \frac{k_{-r}}{k_d}[CS_2]} \qquad \text{(IV)}$$

It is reasonable to assume that B in reaction 4 is a partially or completely solvated monomeric mercaptide species such as indicated in V. As such, it would be expected to react with CS_2 to form the starting material or with another molecule of starting material to form the dimeric product. The rate increase observed for the reaction of $Ni(S_2CSCH_2C_6H_5)_2$ in THF compared with the reaction in $CHCl_3$ or CS_2 is consistent with the formation of such a species. However, no attempt has been made to isolate such a complex with more strongly coordinating solvents such as amines or phosphines.


V

The formation of a solvated intermediate such as V requires the breaking of a C–S bond and the formation of a metal–sulfur atom bond to the mercaptide ligand. While several possibilities exist, the rather low activation energy of ~25 kcal/mol must be consistent with the process. Three reasonable pathways are sketched in Figure 5.

Heterolytic C–S bond cleavage, k_{r1} in Figure 5, leads to the formation of a positively charged complex fragment and the mercaptide ion. The solvent dependence indicated in Tables I and II is consistent with the formation of a solvated charged species.[29] Also the relative insensitivity of the activation energy to solvent charges and the negative $\Delta S^{\ddagger}$, which becomes more negative with low solvent polarity, are trends consistent[30] with this reaction pathway.

A homolytic scission of the C–S bond, k_{r2} in Figure 5, is not as likely as the previous pathway for several reasons. No electron spin resonance signal is detected nor is disulfide product observed, two expected consequences of radical SR formation. Furthermore, the activation parameters are not typical of radical formation. Mislow and coworkers[31,32] have suggested that homolytic carbon–sulfur atom bond cleavage generally requires $\Delta H^{\ddagger} \approx 40$ kcal/mol and $\Delta S^{\ddagger} \approx 25$ eu. In a situation wherein $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ more closely approximated the present data,[32] a readily detectable epr signal was obtained.

The third reaction pathway suggested by Figure 5, the concerted pathway k_{r3}, seems about equally reasonable with the heterolytic cleavage, k_{r1}. It is perhaps only a modification of the postulate that a rearrangement to a CS_2-coordinated species may occur with the CS_2 rapidly displaced by solvent. The activation parameters and solvent relationships observed are of little help in commenting on this pathway.

Acknowledgment.—The support of the National Science Foundation, GP-11701, and the National Institutes of Health, AM-1358, is recognized in this study. We also thank Professor S. J. Lippard for numerous discussions of data obtained at Columbia University.

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Kinetics of the Reactions of 2,2'-Bipyridyl with Potassium Tetrachloropalladate(II) and Potassium Tetrachloroplatinate(II)

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The reaction between bipyridyl (bipy) and K_2MCl_4 (M = Pd, Pt) produces $M(bipy)Cl_2$ by a second-order process. Reactions are carried out in water with 10^{-3} *M* concentrations of ligand and metal complex at 5° for Pd and at 55° for Pt. In acidic solutions, bipyridyl reacts with MCl_4^{2-} ($k_2 = 1.2\ M^{-1}\ \sec^{-1}$ for Pd; $k_2 = 0.0027\ M^{-1}\ \sec^{-1}$ for Pt) and also with $M(H_2O)Cl_3^-$ ($k_2 = 37\ M^{-1}\ \sec^{-1}$ for Pd; $k_2 = 0.029\ M^{-1}\ \sec^{-1}$ for Pt). The reaction of bipyridyl is so much slower than aquation under the conditions employed that the equilibrium between the tetrachloro and the trichloroaquo complexes is maintained. As the pH is increased, the two metal complexes behave differently. Platinum reacts with bipy and $bipyH^+$ at different rates, preferring the protonated ligand. Palladium does not discriminate between bipy and $bipyH^+$, and the rate is pH independent until the aquo ligands begin to be deprotonated; then there is a marked increase in rate. Although bipyridyl reacts very slowly, some nucleophiles (notably ammonia) are almost as slow, and one, *trans*-crotylammonium ion, is even slower. No evidence seemsto exist that any reaction of MCl_4^{2-} complexes follows the usual two-term rate law (eq 1).

Although the tetrachlorometalate(II) ions of palladium and platinum have been known for a long time and used extensively as synthetic starting materials, only recently have their kinetics begun to be widely studied. Early work on $PtCl_4^{2-}$ aquation and chloride exchange reactions was done by Martin and cowork-

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ers.[2,3] Cattalini[4] found that its reactions with a series of nucleophiles, NO_2^-, Br^-, I^-, SCN^-, $SeCN^-$, $(NH_2)_2CS$, and $S_2O_3^{2-}$, exhibited a wide range of rates. Some more recent kinetic studies have appeared for ammonia,[5] diethylenetriamine,[6] trichlorostannate(II),[7] 1,10-phenanthroline,[8-10] and a series of olefins.[11,12] The corresponding palladium ion, $PdCl_4^{2-}$, has received much less attention, possibly because its rates are at the upper limit of conventional sampling techniques but rather slow for methods such as stopped flow. Nucleophiles that have been examined are ammonia,[13] 1,10-phenanthroline,[14] and allyl alcohol.[15] The reactions of both metals have been carried out in water solutions. In many cases, contributions to the rates by ions in equilibrium with MCl_4^{2-} and various aquo- and hydroxochloro complexes were investigated. Some nucleophiles, such as diethylenetriamine,[5] are hard bases, and the effect of protonation has been examined.

In this paper, we present a kinetic study of reactions of bipyridyl with $PdCl_4^{2-}$ and $PtCl_4^{2-}$. In our earlier work, we concluded that reactions of phenanthroline with these two ions were unusually slow because the approach of the ligand to the metal was sterically hindered. Bipyridyl has coordinating nitrogens that are very similar to those in phenanthroline, and in models of their complexes the two chelates exhibit very similar geometries and effective sizes. As a nucleophile, however, bipyridyl enjoys an extra degree of freedom (rotation around the central carbon–carbon bond) which could facilitate its approach to the MCl_4^{2-} ion. The reaction mechanism we have favored[14] features dissociative activation. Unless there is a change in mechanism in going from phenanthroline to bipyridyl, the increased freedom should have little effect on the rate.

Unlike most square-planar substitution reactions, those of phenanthroline are so slow that solvation reactions of the complexes are at equilibrium, resulting in a second-order solvent route[16] to the product. In light of further studies of $PtCl_4^{2-}$ appearing in the literature and examination of the bipyridyl reaction in the present paper, it seems necessary to revise our conclusions about the uniqueness of phenanthroline reactions. Some nucleophiles have been examined which react with $PtCl_4^{2-}$ nearly as slowly as phenanthroline. In one case the reaction is slower. Although most of the unreactive nucleophiles seem to be sterically hindered, at least one, ammonia, is not.

Experimental Section

Chemicals.—Syntheses and analyses have already been reported for potassium tetrachloropalladate(II)[14] and potassium tetrachloroplatinate(II).[8] 2,2′-Bipyridyl was purchased from Distillation Products Industries. The reaction products, $Pd(bipy)Cl_2$ and $Pt(bipy)Cl_2$, precipitated as yellow solids during kinetic runs. They were collected by filtration, washed with water, and dried at 100°. *Anal.* Calcd for $PdC_{10}H_8N_2Cl_2$: C, 36.10; H, 2.40; Cl, 21.70. Found: C, 35.86; H, 2.60; Cl, 21.24. Calcd for $PtC_{10}H_8N_2Cl_2$: C, 28.50; H, 1.90; Cl, 16.69. Found: C, 28.53; H, 2.09; Cl, 16.85.

Kinetics.—Bipyridyl (15.6 mg, 0.10 mmol), sodium chloride, and sufficient ammonium tetrafluoroborate to give the desired ionic strength were dissolved in 100 ml of water. When the solution was at the thermostat temperature, the pH was adjusted by addition of HNO_3 or NaOH. A 5-ml aliquot was removed as a spectrophotometic reference. Reaction was initiated by adding potassium tetrachlorometalate(II) (31.0 mg of K_2PdCl_4 or 39.4 mg of K_2PtCl_4, 0.095 mmol). At intervals, a 5-ml aliquot of the reaction mixture was removed and pipetted into a slightly acidified solution of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.4 g/l.) and NaCl (12 g/l). A red color rapidly developed as the unreacted bipyridyl was picked up by the iron(II) to give $Fe(bipy)_3^{2+}$. After filtration to remove $M(bipy)Cl_2$ the unreacted bipyridyl concentration was determined by comparison of the filtrate absorption at 522 nm (Beckman Model DU spectrophotometer) with that of the reference solution which had been similarly treated.

The reactions were all second order, and observed rate constants, k_{obsd}, were obtained from the slopes of graphs of $[bipy]^{-1}$ *vs.* time.

Results

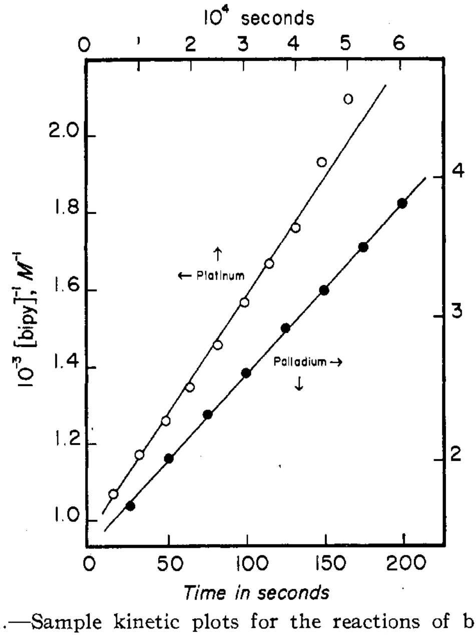

Figure 1.—Sample kinetic plots for the reactions of bipyridyl with K_2PdCl_4 (lower line) and K_2PtCl_4 (upper line).

Bipyridyl reacts with $PdCl_4^{2-}$ and $PtCl_4^{2-}$ to give $Pd(bipy)Cl_2$ and $Pt(bipy)Cl_2$. For a given set of conditions, reactions are kinetically second order. Figure 1 shows kinetic plots for two sample reactions. These second-order reactions are almost certainly first order in bipyridyl and first order in metal complex, for that is the rate law of the similar reactions of phenanthroline with $PdCl_4^{2-}$ [14] and $PtCl_4^{2-}$.[8] Substitution reactions of square-planar complexes ordinarily have first- and second-order terms in their rate laws

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{entering ligand}] \qquad (1)$$

The first-order term arises from a route to the product with a rate-determining attack on the complex by a

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molecule of solvent followed by a fast displacement of the solvent ligand by the other nucleophile.[16] The bipyridyl reactions were carried out with a low concentration of ligand, which is the optimum condition for the solvent-dependent route to the product. The failure to observe a first-order term does not indicate that solvolysis does not occur. Instead, an equilibrium is established between the tetrachloro complex and the solvated species, and attack by bipyridyl is rate determining for all routes to the product. If the only significant species in equilibrium with MCl_4^{2-} is $M(H_2O)Cl_3^-$, then the dependence of the observed rate constant on the chloride concentration if given by

$$k_{obsd} = \frac{k_{H_2O}K + k_{Cl}[Cl^-]}{K + [Cl^-]} \quad (2)$$

where the symbols are identified in reactions 3–5.

$$MCl_4^{2-} + H_2O \overset{K}{\rightleftharpoons} M(H_2O)Cl_3^- + Cl^- \quad (3)$$

$$MCl_4^{2-} + \text{bipy} \xrightarrow{k_{Cl}} M(\text{bipy})Cl_2 + 2Cl^- \quad (4)$$

$$M(H_2O)Cl_3^- + \text{bipy} \xrightarrow{k_{H_2O}} M(\text{bipy})Cl_2 + Cl^- + H_2O \quad (5)$$

Such conditions occur at acidities high enough to suppress the deprotonation of the trichloroaquo complex. Data for palladium(II) and platinum(II) are listed in Table I. Using these data in conjunction with eq 2 to calculate K, k_{H_2O}, and k_{Cl}, we obtain $K = 3.2 \times 10^{-3}$ M, $k_{H_2O} = 37$ M^{-1} sec^{-1}, $k_{Cl} = 1.2$ M^{-1} sec^{-1} for palladium and $K = 1.5 \times 10^{-2}$ M, $k_{H_2O} = 2.9 \times 10^{-2}$ M^{-1} sec^{-1}, $k_{Cl} = 2.7 \times 10^{-3}$ M^{-1} sec^{-1} for platinum. To check the consistency of data and theory, these constants were substituted into eq 2 to calculate the expected values of the rate constants (k_{calcd} in Table I). Other important equilibria that occur in these solutions are

TABLE I

OBSERVED SECOND-ORDER RATE CONSTANTS FOR REACTIONS

$MCl_4^{2-} + \text{bipy} \longrightarrow M(\text{bipy})Cl_2 + 2Cl^-$

AS FUNCTIONS OF CHLORIDE CONCENTRATION

$[Cl^-]$, M	k_{obsd}, M^{-1} sec^{-1}	k_{calcd}, M^{-1} sec^{-1}
	M = Pd[a]	
2.75×10^{-1}	5.1 ± 0.2	4.9
2.08×10^{-1}	6.2 ± 0.3	6.0
1.38×10^{-1}	7.6 ± 0.4	7.9
6.94×10^{-2}	13 ± 2	11
3.52×10^{-2}	18 ± 3	18
1.81×10^{-2}	21 ± 4	24
1.01×10^{-2}	29 ± 5	28
5.97×10^{-3}	32 ± 5	32
	M = Pt[b]	
2.74×10^{-1}	4.5 ± 0.6	4.1
2.07×10^{-1}	4.7 ± 1.5	4.5
1.36×10^{-1}	5.1 ± 0.7	5.3
6.83×10^{-2}	7.1 ± 0.7	7.5
3.42×10^{-2}	12 ± 2	11
1.71×10^{-2}	15 ± 1	15
9.09×10^{-3}	20 ± 1	19
4.80×10^{-3}	23 ± 1	23

[a] $[PdCl_4^{2-}] = [\text{bipy}] = 1.0 \times 10^{-3}$ F, pH 3.3, $\mu = 0.275$ M, $T = 5°$. [b] $[PtCl_4^{2-}] = [\text{bipy}] = 1.0 \times 10^{-3}$ F, pH 2.9, $\mu = 0.276$ M, $T = 55°$. k_{obsd} and k_{calcd} are $\times 10^3$.

$$\text{bipyH}^+ \rightleftharpoons \text{bipy} + H^+ \quad (6)$$

$$M(H_2O)Cl_3^- \rightleftharpoons M(OH)Cl_3^{2-} + H^+ \quad (7)$$

$$M(H_2O)Cl_3^- + H_2O \rightleftharpoons M(H_2O)_2Cl_2 + Cl^- \quad (8)$$

Equilibrium constants for reactions 6 and 7 have been measured, and at the acidities used in collecting the data in Table I, the positions of both equilibria lie far to the left. The reaction might still go through a deprotonated species, but the rate would have to be highly sensitive to pH changes, which is not the case (see below). Reaction 8 cannot be ruled out by the data in Table I, but the reasonably good correspondence between k_{calcd} and k_{obsd} does not warrant an attempt of improving the fit by introducing other equilibria.

Reactions 6, 7, and 9 have pH-dependent equilibria

$$M(H_2O)_2Cl_2 \rightleftharpoons M(H_2O)(OH)Cl_2^- + H^+ \quad (9)$$

that cause changes in reaction rates. Table II gives the rate constants as functions of pH. Figures 2 and 3 compare the bipyridyl reactions with the corresponding reactions of phenanthroline. The effect on the Pd–bipy, Pd–phen, and Pt–phen reactions is generally similar. The rate is insensitive to pH from high acidities through the region of deprotonation of the ligand and increases in the region where the aquo ligand bound to the metal is being deprotonated. In the case of the

TABLE II

RATE CONSTANTS FOR REACTIONS

$MCl_4^{2-} + \text{bipy} \longrightarrow M(\text{bipy})Cl_2 + 2Cl^-$

AS FUNCTION OF pH

pH	k_{obsd} (for K_2PdCl_4),[a] M^{-1} sec^{-1}	10^3k_{obsd} (for K_2PtCl_4),[b] M^{-1} sec^{-1}	pH	k_{obsd} (for K_2PdCl_4),[a] M^{-1} sec^{-1}	10^3k_{obsd} (for K_2PtCl_4),[b] M^{-1} sec^{-1}
2.9	7.2 ± 1.4	4.7 ± 1.5	4.7	6.1 ± 0.6	2.2 ± 0.6
3.1	6.0 ± 0.3	...	5.0	6.4 ± 0.2	2.2 ± 0.6
3.3	6.2 ± 0.3	4.7 ± 0.9	6.0	11.5 ± 0.4	2.3 ± 0.1
3.9	...	5.1 ± 0.2	6.5	...	1.9 ± 0.1
4.2	5.7 ± 0.6	...	7.0	23.5 ± 9	...
4.3	...	4.6 ± 0.2			

[a] $[PdCl_4^{2-}] = [\text{bipy}] = 1.0 \times 10^{-3}$ F, $\mu = 0.275$ M, $T = 5°$, $[Cl^-] = 0.208$ M. [b] $[PtCl_4^{2-}] = [\text{bipy}] = 1.0 \times 10^{-3}$ F, $\mu = 0.275$ M, $T = 55°$, $[Cl] = 0.207$ M.

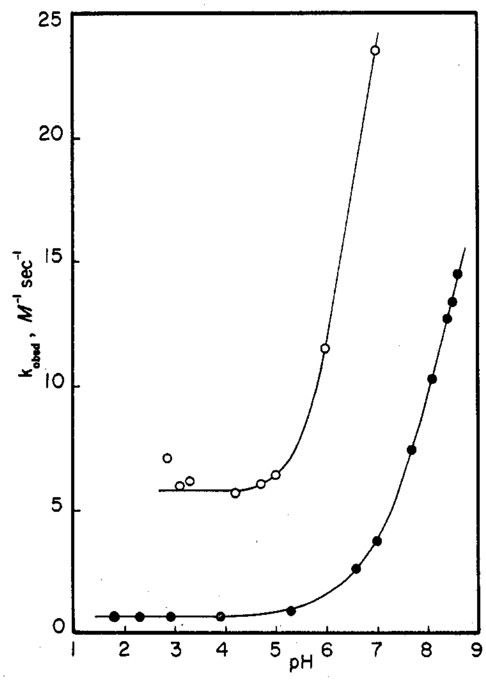

Figure 2.—Second order rate constants for the reaction of bipyridyl (upper line) and phenanthroline (lower line) with K_2PdCl_4 as a function of pH. Data for phenanthroline from reference 14.

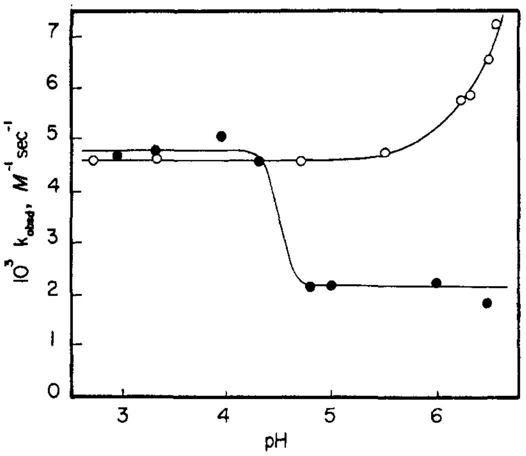

Figure 3.—Second order rate constants for the reaction of bipyridyl (●) and phenanthroline (○) with K_2PtCl_4 as a function of pH. Data for phenanthroline from reference 10.

Pt–phen system, this increase has been quantitatively accounted for[10] on the basis of reaction 7 by assuming a fairly rapid reaction

$$Pt(OH)Cl_3^- + phen \longrightarrow Pt(phen)Cl_2 + Cl^- + H_2O \quad (10)$$

The Pd–bipy and Pd–phen systems seem to be complicated by other equilibria such as (8) and (9), but a lower limit can be placed on the rate constants for reactions of the chelates with the hydroxo complex (see Table IV).

The effect of ionic strength is shown in Table III.

TABLE III

RATE CONSTANTS FOR THE REACTIONS

$MCl_4^{2-} + bipy \longrightarrow M(bipy)Cl_2 + 2Cl^-$

AS FUNCTIONS OF IONIC STRENGTH

μ, M	k_{obsd} (for K_2PdCl_4),[a] M^{-1} sec^{-1}	10^3k_{obsd} (for K_2PtCl_4),[b] M^{-1} sec^{-1}	μ, M	k_{obsd} (for K_2PdCl_4),[a] M^{-1} sec^{-1}	10^3k_{obsd} (for K_2PtCl_4),[b] M^{-1} sec^{-1}
0.0387	27.2 ± 0.9	14.4 ± 1.5	0.150	18.7 ± 1.6	14.3 ± 0.5
0.100	23.4 ± 1.3	19.0 ± 0.4	0.274	17.8 ± 2.7	11.9 ± 1.9

[a] $[PdCl_4^{2-}] = [bipy] = 1.3 \times 10^{-3}$ F, pH 3.3, $T = 5°$, $[Cl^-] = 0.0352$ M. [b] $[PtCl_4^{2-}] = [bipy] = 1.0 \times 10^{-3}$ F, pH 2.9, $T = 55°$, $[Cl^-] = 0.0342$ M.

Rates increase with decreasing ionic strength, which is as expected for reactions between species of opposite charge.

Discussion

Reactions of bipyridyl and K_2PdCl_4 and K_2PtCl_4 are similar in most respects to reactions of phenanthroline. The ligands attack both the MCl_4^{2-} ions and the hydrolyzed ions $M(H_2O)Cl_3^-$ as demonstrated by the dependence of rate on chloride concentration. That these are the two reacting species, rather than some other aquochloro pair, is corroborated by the agreement between the directly measured equilibrium constant (K in reaction 3) and the one calculated from the data in Table I. Table IV gives various constants for the reactions of bipyridyl and phenanthroline. For palladium, both the measured[17] and calculated values of K, when corrected for ionic strength differences, are 0.0037 M at 25°. Reactions of palladium with bipyridyl were too fast to measure at 25°. The K values for phenanthroline and bipyridyl reactions at 5°, however, are in reasonable agreement, considering the indirectness of the method and the difficulty in obtaining bipyridyl rates at low chloride concentrations. For platinum, the directly measured K value[8] of 0.025 M at 55° is probably within the experimental error of the kinetically determined value of 0.015 M for the bipyridyl reaction.

TABLE IV

RATE OR EQUILIBRIUM CONSTANTS FOR REACTIONS 3, 4, 5, 7 AND 10 FOR K_2PdCl_4 AND K_2PtCl_4 WITH BIPYRIDYL AND PHENANTHROLINE

Constant (reaction no.)	Pd + bipy[a]	Pd + phen[b]	Pt + bipy[c]	Pt + phen[d]
k_{Cl}, M^{-1} sec^{-1} (4)	1.2	0.34	0.0027	0.0037
k_{H_2O}, M^{-1} sec^{-1} (5)	37	6.7	0.029	0.012
K, M (3)	0.03	0.0094	0.015	0.025
k_{OH}, M^{-1} sec^{-1} (10)	24	17	...	0.021[e]
K_a, M (7)	10^{-7} [f]	10^{-7} [f]	10^{-7} [g]	10^{-7} [g]

[a] $T = 5°$, $\mu = 0.275$ M. [b] Reference 13; $T = 5°$, $\mu = 0.279$ M. [c] $T = 55°$, $\mu = 0.275$ M. [d] Reference 7; $T = 55°$, $\mu = 0.103$ M. [e] $T = 45°$. [f] Reference 13. [g] Reference 1.

The ligands also react with one or more hydroxo complexes, which, in the case of the Pt–phen reaction, was found to be $Pt(OH)Cl_3^-$. Palladium reactions are more complicated, for there appear to be two or more hydrolyzed complexes. The Pt–bipy reaction is so slow at higher pH's that erratic results were obtained in the region of deprotonation of $Pt(H_2O)Cl_3^-$. In general, hydroxo complexes seem to be more reactive than their aquo or chloro analogs. The conclusion is unexpected, since hydroxide is generally thought to be a poor leaving or trans-directing group, although diethylenetriamine reacts with $Pt(OH)Cl_3^{2-}$ at about the same rate as with $PtCl_4^{2-}$.[6] In no case is it certain that OH^- is the leaving group of the rate-determining step.

In an earlier paper,[8] we asserted that reactions of $PtCl_4^{2-}$ with bipyridyl and phenanthroline were unusually slow. Table V shows the second-order rate constants of a number of nucleophiles. For convenience, rate constants have all been adjusted to 55° using reported thermal parameters, when these were available. Otherwise the constants have been estimated by doubling the measured values for each 10°

TABLE V

SECOND-ORDER RATE CONSTANTS ADJUSTED TO 55° FOR REACTIONS OF $PtCl_4^{2-}$ WITH VARIOUS NUCLEOPHILES

Nucleophile	k_2, M^{-1} sec^{-1}	Ref
trans-Crotylammonium ion	0.0019[a]	11
2,2'-Bipyridyl	0.0027[b]	
1,10-Phenanthroline	0.0037[b]	7
Ammonia	0.0045[a]	4
Nitrite	0.007[c]	3
Allylsulfonate ion	0.0071,[a] 0.0079[a]	10, 11
Allyltriethylarsonium ion	0.0085[a]	11
Allyl alcohol	0.010[a]	10, 11
Bromide	0.015[c]	3
Thiocyanate	0.015[c]	3
Allylammonium ion	0.016[a]	10
Diethylenetriamine	0.04[c]	5
Iodide	0.05[c]	3
Thiosulfate	0.2[c]	3
Thiourea	2[c]	3
Selenocyanate	4[c]	3
Trichlorostannate(II) ion	70[c]	6

[a] Adjusted to 55° using published thermal parameters. [b] Measured at 55°. [c] Estimated: no thermal data available.

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(17) H. A. Droll, B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, **61**, 1000 (1957).

increase in temperature. No attempt has been made to correct for effects of ionic strength, which generally were in the range 0.2-2 *M*. Although in many cases the constants for $PtCl_4^{2-}$ have not been distinguished from those of its hydrolysis products, conditions were usually chosen to suppress the concentrations of the latter species. Rate constants reported in ref 4 are for zero ionic strength and very low chloride concentrations and may be somewhat too large in comparison with the others.

Table V shows that bipyridyl and phenanthroline are among the poorest nucleophiles for $PtCl_4^{2-}$, even though their reaction products are very stable. Their reactivities exceed only that of the sterically hindered olefin *trans*-crotylammonium chloride. The unexpected feature of the series is that ammonia, for which steric hindrance is presumably unimportant, is nearly as slow. This parallels the only results[18] available for $PdCl_4^{2-}$. It has a second-order rate constant of 1.7 M^{-1} sec^{-1} (adjusted to 5° using published thermal parameters) compared with 1.2 M^{-1} sec^{-1} for bipyridyl and 0.34 M^{-1} sec^{-1} for phenanthroline.

An interesting aspect of the reactions of $PtCl_4^{2-}$ is that there seems to be no evidence that they obey the two-term rate law (eq 1). Nucleophiles lying below diethylenetriamine in Table V react too rapidly to allow a solvent route to be detected. The remaining reactions from ref 3 do not fit linear plots of k_{obsd} *vs.* [nucleophile] well enough to show whether the intercept is k_1 for aquation or zero. Bipyridyl, phenanthroline, and the olefins are strictly second order, and there is no indication that ammonia is otherwise.

The effect of protonation of bipyridyl and phenanthroline is rather difficult to explain. In all systems the reaction proceeds through both the free and the protonated ligand. In the Pt-bipy system, platinum discriminates in favor of the protonated ligand, as shown by the inflection point in the k_{obsd} *vs.* pH graph (Figure 3) at the pK_a of $bipyH^+$ (4.3 at $T = 25°$, $\mu = 0$).[19] In the other three systems, however, the metal is insensitive to whether or not the ligand is protonated. The first kind of behavior may be caused by the electrostatic attraction between $bipyH^+$ and the complex anion. $bipyH^+$ still has one free nitrogen, and bond formation may occur through it. The other kind of behavior is more puzzling, for we would have believed that $phenH^+$ should be less reactive than phen. Structural studies suggest that a proton on one phenanthroline nitrogen would partly block the other nitrogen from the metal. This unusual behavior was the principal feature of the phenanthroline reaction that led us to suggest a dissociatively activated mechanism.[14] For the present, the problem remains unsolved. The only alternative explanation we can think of requires some fortuitous combination of reactivity effects causing the protonated and unprotonated chelates to react at the same rate. Since two metals and two ligands show the same behavior, the explanation relies heavily on chance.

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[18] We believe that the interpretation of the data in ref 13 is not entirely unambiguous. The rates at high chloride concentrations are directly reciprocal to $[Cl^-]$. The nucleophile might not react directly with $PdCl_4^{2-}$ but only with $Pd(H_2O)Cl_3^-$. The rate constant of the reaction would then be much larger. A similar situation was observed for the reaction of $PtCl_4^{2-}$ with Cl^-.[2]

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Cationic Organometallic Complexes with Unsaturated Systems. II. Platinum(II)-Isocyanide and -Carbene Complexes

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A variety of cationic platinum(II)-isocyanide complexes of the types *trans*-$[PtXL_2(CN-R)]Z$ and *trans*-$[Pt(CN-R)_2L_2]Z_2$ (where $L = P(CH_3)_2C_6H_5$ or $P(CH_3)(C_6H_5)_2$; $X = Cl$, I, or CH_3; $R-NC$ = alkyl or aryl isocyanide; $Z^- = PF_6^-$, BF_4^-, SbF_6^-, or $B(C_6H_5)_4^-$) have been prepared. The isocyanide is shown to be a good σ donor and very weak π acceptor, and the increase in $\nu(N{\equiv}C)$ on coordination is dependent on the positive charge at the platinum nucleus. One mole of phosphine in *cis*-$Pt(CH_3)_2L_2$ is readily displaced by *p*-methoxyphenyl isocyanide to give *cis*-$Pt(CH_3)_2L(CN-C_6H_4-OCH_3)$ which reacts with acetyl chloride to give *cis*-$PtCH_3ClL(CN-C_6H_4-OCH_3)$. The nmr spectra of the cationic methylplatinum(II) complexes show very rapid exchange of phosphines at room temperature which may be explained by delocalization of positive charge from platinum to the isocyanide. $[Pt(CN-C_2H_5)_2L_2](PF_6)_2$ reacts slowly with protic nucleophiles to give a variety of carbene complexes whose mode of formation and stereochemistry are discussed.

Introduction

Previous studies[1-5] have shown that acetylenes and olefins react with methylplatinum(II) compounds to yield a variety of products, depending on the nature of the acetylene or olefin and the reaction conditions.

We have previously reported the preparation and characterization of a wide variety of cationic methylplatinum(II)-nitrile complexes[6,7] and have found that alcohols react with coordinated perfluoroarylnitriles to give imino ether derivatives. The course of the reaction was dependent on the size of the anion as well as the nature of the alcohol.

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