the free base and not with a protonated species such as the anilinium ion. A similar difference would probably be found for ligands which are anions, *i.e.*, benzoate ion. Here the comparison required would be that between the benzoate ion (not benzoic acid) and the coördinated benzoate.

A final point which emerged from this work was an indication of a considerable degree of variation of the inertness of the inert complexes used. Thus the pyridine complex was very stable, the aniline complex less so, and the bromoaniline complexes even less stable. Thus for inert complexes, the degree of inertness of the complex may sometimes depend on the base strength of the ligand. The reactivity of the trichlorotripyridinechromium(III) and the trichlorotrianilinechromium(III) toward methanol was also quite unexpected as methanol frequently is used as a solvent in studying the reactions of such complexes. The conductivity data indicate unambiguously that a rapid reaction occurs with methanol to produce conducting species. Measurements taken even a few minutes after the solutions were prepared indicated essentially complete reaction. The reaction which occurs is presumably one in which a chloride ion in the coördination sphere is replaced by a methyl alcohol molecule. In view of the great tendency of chromium(III) to coördinate to oxygen, this is the most reasonable explanation of the conductivity data. Herwig and Zeiss[17] found anhydrous chromium (III) chloride to react with tetrahydrofuran to give $[CrCl_3(C_4H_8O)_3]$, a compound which indicates the avidity with which Cr(III) coördinates even to ethereal oxygen. The tetrahydrofuran molecules are not lost when the compound is heated to 100° at 20 mm.

Summary

1. Preparative methods which give good yields of trichlorotripyridinechromium(III) and trichlorotrianilinechromium(III) were developed.
2. The reactivities of pyridine or aniline coordinated to a metal do not differ greatly from those of the free ligands insofar as typical electrophilic reactions are considered.
3. Pauling's principle of electroneutrality provides a satisfactory qualitative theoretical explanation for the effect of coördination on the reactivity of simple neutral monodentate aromatic ligands.
4. Both of the chromium complexes examined reacted very readily with methanol to give conducting species.

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[17] W. Herwig and H. H. Zeiss, *J. Org. Chem.*, **23**, 1404 (1958).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

Mechanism of Substitution Reactions of Complex Ions. XVII.[1] Rates of Reaction of Some Platinum(II) and Palladium(II) Complexes with Pyridine[2]

BY FRED BASOLO, HARRY B. GRAY[3] AND RALPH G. PEARSON

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The relative reactivities of replaceable ligands in planar complexes of platinum(II) follow the order: $NO_3^- > Cl^- > Br^- > I^- > SCN^- > NO_2^-$. This is the same order as for octahedral complexes of cobalt(III) except for an inversion in the reactivities of the halides. In both systems labilities parallel instabilities. Analogous palladium(II) complexes of the type $Pd(dien)X^+$ react 10^5 to 10^6 times faster than corresponding platinum(II) complexes.[4] Nickel complexes are again somewhat more reactive than palladium complexes.

Although there have been several kinetic studies[5] on substitution reactions of square complexes, there is as yet little quantitative comparison of the reactivities of analogous platinum(II) and palladium (II) complexes. There is also very little information on the relative rates of displacement of different ligands from similar complexes of the same metal.

This paper reports a kinetic study of the replacement of a ligand X in platinum(II) and palladium (II) complexes of the types $M(dien)X^+$ and $M(tripy)X^+$ by pyridine in aqueous solution.

Experimental and Results

Preparation of Compounds.—The known compounds were prepared by essentially the same methods as those described in the literature. This was the case for the halogen complexes of the types [Pt(dien)X]X,[6] [Pt(tripy)X]X[7] and [Pd(tripy)X]X.[8] The Pd(dien)X]X compounds were prepared by almost the same procedure as that used for the corresponding platinum compounds. A reaction mixture containing 5 g. of $PdCl_2$, 6 g. of dien·3HCl, 5 g. of dien and 100 cc. of H_2O was allowed to reflux for 8 hr. During this time an orange solution is formed and some metallic palladium deposits. The solution was passed through a filter and the filtrate was concentrated to 30 cc. on a steam-bath. To a 10 cc. portion of this solution was added 2 g. of solid NH_4Cl and a yellow crystalline precipitate slowly separated. The yellow product was collected and washed with a small amount of cold water. It was recrystallized from a small amount of water, air dried at 50° and found to weigh 1.7 g. (65% yield). Addition of 1 g. of NaBr to a second portion of the original filtrate yielded [Pd(dien)Br]Br and the addition of 1 g. of NaI to the third portion gave [Pd(dien)I]I.

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[1] Previous paper in this series, R. G. Pearson, H. B. Gray and F. Basolo, THIS JOURNAL, **82**, 787 (1960).

[2] This investigation was partly supported by a grant from the U. S. Atomic Energy Commission under contract AT(11-1)-89-project No. 2.

[3] Dow Chemical Company Fellow, 1958–1959.

[4] Symbols used: dien = diethylenetriamine, tripy = 2,2′,2″-tripyridyl, py = pyridine.

[5] (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 172–212; (b) O. E. Zvyagintsev and E. F. Shubochkina, *Zhur. Neorg. Khim.*, **3**, 1139–1148 (1958); (c) D. Banerjea and K. K. Tripathi, *J. Inorg. & Nuclear Chem.*, **7**, 78 (1958); (d) T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., THIS JOURNAL, **81**, 10 (1959); (e) A. A. Grinberg and Y. N. Kukushkin, *Russian J. Inorg. Chem.*, **4**, 2, 139 (1959).

[6] F. G. Mann, *J. Chem. Soc.*, 466 (1934).

[7] G. T. Morgan and F. H. Burstall, *ibid.*, 1498 (1934).

[8] G. T. Morgan and F. H. Burstall, *ibid.*, 1649 (1937).

TABLE I

ANALYSES OF Pt(II) AND Pd(II) COMPOUNDS

Compound	Pt, calcd.	Pt, found	Compound	Pd, calcd.	Pd, found
$[Pt(dien)Cl]Cl$	52.9	52.4	$[Pd(dien)Cl]Cl$	C, 17.1; H, 4.63	C, 17.1; H, 4.44
$[Pt(dien)Br]Br^{a}$	42.9	42.9	$[Pd(dien)Br]Br$	C, 13.0; H, 3.52	C, 13.1; H, 3.48
$[Pt(dien)I]I$	35.4	35.6	$[Pd(dien)I]I$	C, 10.4; H, 2.80	C, 10.5; H, 2.72
$[Pt(dien)SCN]NO_3{}^{b}$	46.6	46.0	$[Pd(dien)NO_2]NO_3$	N, 22.0	N, 21.6
$[Pt(dien)NO_2]NO_3{}^{b}$	48.0	47.2	$[Pd(dien)SCN]CNS$	N, 21.2	N, 20.7
$[Pt(dien)NO_3]NO_3{}^{b}$	46.3	45.0	$[Pd(dien)(py)][B(C_6H_5)_4]_2$	N, 6.12	N, 6.42
$[Pt(dien)CN]NO_3{}^{b}$	50.5	49.2	$[Pd(tripy)Cl]Cl\cdot H_2O$	C, 41.6; H, 3.00	C, 41.4; H, 3.45
$[Pt(dien)N_3]NO_3{}^{b}$	48.6	48.0	$[Pd(tripy)Br]Br$	C, 36.0; H, 2.20	C, 35.6; H, 2.35
$[Pt(dien)py]Br_2$	36.7	36.4	$[Pd(tripy)I]I$	C, 30.4; H, 1.86	C, 31.2; H, 2.18
$[Pt(tripy)Cl]Cl\cdot 3H_2O$	35.4	35.6	$[Pd(tripy)NO_2]NO_2\cdot H_2O$	C, 40.0; H, 2.89	C, 39.4; H, 2.77
$[Pt(tripy)Br]Br\cdot 2H_2O$	31.3	31.7	$[Pd(tripy)SCN]CNS$	C, 44.7; H, 2.41	C, 44.2; H, 2.35
$[Pt(tripy)I]I\cdot 2H_2O$	27.2	27.5	$[Pd(tripy)(py)][B(C_6H_5)_4]_2$	N, 5.34	N, 5.68
$[Pt(tripy)NO_2]NO_2\cdot 3H_2O$	34.1	34.0	$[Pt(tripy)(py)][B(C_6H_5)_4]_2$	N, 4.94	N, 5.26
$[Pt(tripy)SCN]CNS$	35.9	36.3			

[a] Calcd.: C, 10.5; H, 2.84. Found: C, 10.6; H, 2.77. [b] Analysis of Pt is low because of loss due to tendency of nitrate complexes to explode on ignition.

Compounds of the type $[M(dien)Y]NO_3$ were all prepared by the reaction of the halogen compound $[M(dien)X]X$ with two equivalents of $AgNO_3$. After removal of AgX, the resulting aqueous solution, presumably $[M(dien)(H_2O)](NO_3)_2$, was allowed to react with one equivalent of NaY. For example, a reaction mixture containing 2 g. of $[Pt(dien)Br]Br$, 1.5 g. of $AgNO_3$ and 30 cc. of water was heated on a steam-bath and occasionally stirred for a period of 30 min. The AgBr was removed on a filter and washed with a small amount of water. The filtrate plus washings was divided into four equal portions. To one of these was added 0.07 g. of NaN_3 and the solution was concentrated to 5 cc. on a steam-bath. The white crystalline product then separated upon cooling the solution in an ice-salt bath. The crystals were collected on a filter, washed with a minimum amount of ice-water followed by acetone. After air drying at 50°, the salt, $[Pt(dien)N_3]NO_3$, weighed 0.3 g. (87% yield).

Compounds of the type $[M(tripy)Y]Y$ were prepared by the reaction between the halogen compound and an excess of NaY. For example, 0.2 g. of $[Pd(tripy)Cl]Cl\cdot H_2O$ was dissolved in 5 cc. of hot water and 0.7 g. of $NaNO_2$ was added. An immediate precipitate separated and was collected on a filter. After water and acetone washes, the solid was dried at 50° and found to weigh 0.2 g. (95% yield of $[Pd(tripy)NO_2]NO_2\cdot H_2O$).

The pyridine derivatives, $[M(dien)py]X_2$ and $[M(tripy)py]X_2$, were prepared by the reaction of the corresponding halogen compound with an excess of pyridine. The compound $[Pt(dien)py]Br_2$ was isolated by evaporating an aqueous reaction mixture of $[Pt(dien)Br]Br$ and excess pyridine to dryness at 50°. Under similar conditions the other compounds yielded only starting material. They were prepared by allowing the parent compound to react with excess pyridine at room temperature for 30 min. Then the desired complex was precipitated by the addition of excess $NaB(C_6H_5)_4$.

Analyses for all of the compounds are reported in Table I. The platinum analysis was performed by ignition of the compound and weighing the residue. This method usually gave low results for the nitrate salts which tend to explode on ignition. The infrared spectra of all of the compounds were determined by the KBr wafer technique. All of the $M(dien)X^+$ spectra are very similar as are also all of the $M(tripy)X^+$ spectra. Conductivity measurements on aqueous solutions of these compounds showed them to be univalent electrolytes.

Determination of Rates of Reaction.—The reactions with pyridine were followed by measuring changes in electrical conductivity of the solution under investigation. The concentration of the complex was in the range between 0.0004 and 0.001*M* and the pyridine concentration was varied as shown in the Tables. Before adding pyridine, the conductances of the solutions of the complexes corresponded to one to one electrolytes and did not change with time. Thus no hydrolysis occurred. The change in conductance on adding pyridine corresponded to the reaction, *e.g.*

$$Pt(dien)X^+ + py \longrightarrow Pt(dien)py^{+2} + X^- \quad (1)$$

TABLE II

RATES OF THE REACTION OF SOME PLATINUM(II) COMPLEXES WITH PYRIDINE IN WATER AT 25.1°

$$Pt(dien)X^+ + py \rightarrow Pt(dien)(py)^{+2} + X^-$$

Complex	Pyridine, *M*	$k_{obsd.} \times min.^{-}$
$[Pt(dien)NO_3]NO_3$	.....	Aquates, fast
$[Pt(dien)Cl]Cl$	0.00090	$4.23 \times 10^{-4\,a}$
	.00592	2.09×10^{-3}
	.0096	3.17×10^{-3}
$[Pt(dien)Br]Br$	.0006–	2.4×10^{-4}
	.00090	$3.03 \times 10^{-4\,b}$
	.00090[c]	2.94×10^{-4}
	.00372-	1.03×10^{-3}
	.00592	1.38×10^{-3}
	.0096–	2.10×10^{-3}
	.0124–	2.56×10^{-3}
	.0372–	7.95×10^{-3}
	.062–	1.29×10^{-2}
$[Pt(dien)I]I$	.00090	1.47×10^{-4}
	.00592	6.02×10^{-4}
	.0096	9.3×10^{-4}
$[Pt(dien)N_3]NO_3$	.00090	1.2×10^{-5}
	.00592	5.0×10^{-5}
$[Pt(dien)SCN]NO_3$	.00090	$3.7 \times 10^{-6\,d}$
	.00592	$1.82 \times 10^{-5\,e}$
$[Pt(dien)NO_2]NO_3$	.00090	Slow
	.00592	3.0×10^{-6}
	.0592	1.5×10^{-5}
$[Pt(dien)CN]NO_3$	.00090	Slow
	.00592	1.0×10^{-6}

[a] *k* is 9.13×10^{-4} at 33.3° and 3.33×10^{-3} at 50°. [b] *k* is 6.16×10^{-4} at 33.3° and 2.39×10^{-3} at 50°. [c] Added substance, 0.00080 *M* NaBr. [d] *k* is 1.02×10^{-5} at 33.3° and 5.36×10^{-5} at 50°. [e] *k* is 3.73×10^{-4} at 50°.

Standard aqueous solutions of the complex and of pyridine were placed in separate compartments of a Y-shaped conductance cell and thermostated. After reaction temperature was reached, the reactants were mixed by tipping the cell. In this way it was possible to take a resistance reading within about 10 seconds after mixing. The conductance data were analyzed as described earlier[9] and the observed first order rate constants calculated are given in Tables II, III and IV. Figure 1 shows that good first order plots were obtained through one half-life although in some cases the pyridine concentration was not very much greater

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(9) D. Banerjea, F. Basolo and R. G. Pearson, THIS JOURNAL, **79**, 4055 (1957).

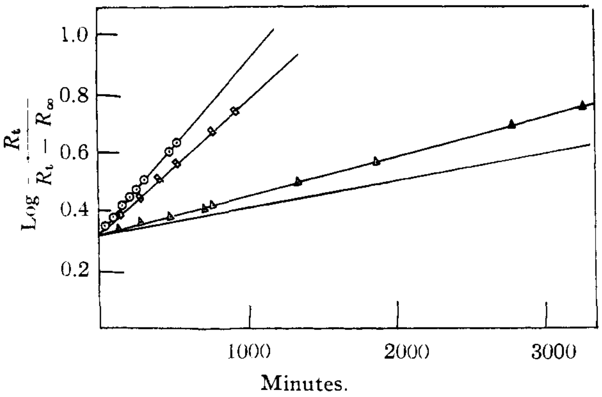

Fig. 1.—First order rate analysis at different pyridine concentrations at 25°: concn. [Pt(dien)Br]Br, 0.0004 *M*; concn. py: △, 0.0009 *M*; □, 0.00372 *M*; ⊙, 0.00592 *M*; ——, calculated limiting slope (k_1).

than the complex concentration. The reason for this is discussed later. Reactions in which the calculated infinity resistance was reached at the first reading (10 sec.) are labelled "Fast" in the Tables. Duplicate runs were made in many cases with reproducibility being about 5%.

Discussion

TABLE III

RATES OF THE REACTION OF SOME PALLADIUM(II) COMPLEXES WITH PYRIDINE IN WATER

$Pd(dien)X^+ + py \longrightarrow Pd(dien)(py)^{+2} + X^-$

Complex	Pyridine, *M*	k_{obsd} × min.$^{-1}$ 0°	25.1°
[Pd(dien)Cl]Cl	0.00124	Fast	..
[Pd(dien)Br]Br	.00124	Complete in 15	Fast
	.00124^a	sec.	Fast
[Pd(dien)I]I	.00062	1.53	Fast
	.00124	1.95	..
	.00248	3.35	..
[Pd(dien)SCN]NO_3	.00124	(1) 3.92×10^{-1}	2.52^b
	.00124	(2) 3.98×10^{-1}	2.68^c
	.00248	4.92×10^{-1}	..
	.0124	1.53	..
[Pd(dien)NO_2]NO_3	.00124	2.0×10^{-1}	1.98
	.00248	2.22×10^{-1}	..
	.0124	3.22×10^{-1}	..

[a] Added substance, 0.00080 *M* NaBr. [b] *k* is 4.36 at 33.3°. [c] *k* is 4.57 at 33.3°.

From the rate data in Table II and III it may be seen that the reactions are not of simple order with respect to pyridine. A more comprehensive study of the reaction order in these systems has been made and will be published elsewhere. These studies indicate that a general rate law for square complexes reacting with such a reagent is

$$k_{obsd} = k_1 + k_2[Y] \qquad (2)$$

where k_{obsd} is the observed first order constant. The data collected here all seem to conform to such an equation and it is possible to extract rate constants k_1, presumably involving the solvent as nucleophilic agent and k_2 with pyridine as the reagent. For example, a straight line is obtained by plotting $k_{obsd.}$ *versus* pyridine concentration for the reaction between [Pt(dien)Br]Br and pyridine (Fig. 2), with k_2 the slope and k_1 the intercept. Furthermore the second order process becomes less important at low pyridine concentrations and $k_{obsd.}$ approaches k_1 which means that $k_{obsd.}$ resembles more closely a true first order rate constant. This is supported by the observation that good first order plots are obtained (Fig. 1) at low pyridine concentrations when its concentration is only slightly greater than that of the complex. Estimates indicate that the second order process must not contribute over 20% to the total rate at 0.0009 *M* pyridine and 0.0004 *M* [Pt(dien)Br]Br.

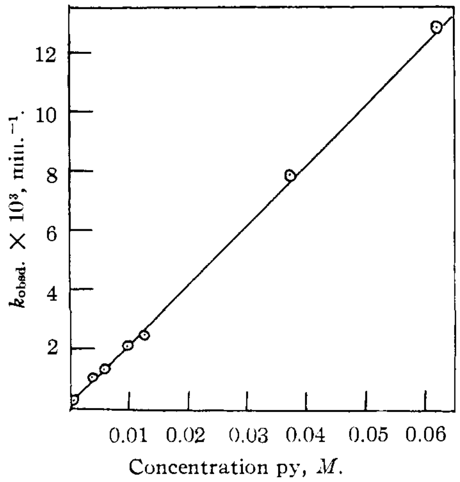

Fig. 2.—Dependence of $k_{obsd.}$ on concentration of pyridine for its reaction with [Pt(dien)Br]Br at 25°.

TABLE IV

RATES OF REACTION OF SOME PLATINUM(II) AND PALLADIUM (II) COMPLEXES WITH PYRIDINE IN WATER

$M(tripy)X^+ + py \longrightarrow M(tripy)(py)^{+2} + X^-$

Complex	Pyridine, *M*	k_{obsd} × min.$^{-1}$ 0°	25.1°
[Pt(tripy)Cl]Cl	0.00124	..	Fast^a
	.0124	6.9×10^{-1}	4.0
[Pt(tripy)Br]Br	.00124	..	Fast^a
[Pt(tripy)I]I	.00062	5.0×10^{-1}	...
	.00124	5.5×10^{-1}	3.9
	.00258	1.4	...
	.0124	Fast	...
[Pt(tripy)SCN]CNS	.00124	..	6.15×10^{-3}
	.0124	..	2.90×10^{-2}
[Pt(tripy)NO_2]NO_2	.00090	..	3.06×10^{-3}
	.00124	..	3.50×10^{-3}
	.00592	..	5.30×10^{-3}
	.0296	..	1.01×10^{-3}
[Pd(tripy)Cl]Cl	.00124	Fast	...
[Pd(tripy)Br]Br	.00124	Fast	...
[Pd(tripy)I]I	.00124	Fast	...
[Pd(tripy)SCN]CNS	.00124	Fast	...
[Pd(tripy)NO_2]NO_2	.00124	Fast	...

[a] Reaction complicated by a slower secondary process.

A "dissociation" mechanism[5a] in which groups such as water or pyridine are added above and below the plane of the complex and which move into the metal atom to displace the group X may be used to visualize the course of the reaction. A five coördinated intermediate, probably a square pyramid, is formed which rapidly reacts with various potential ligands in the solution. An intermediate aqua complex would be reactive and rapidly convert to the pyridine complex.

Adding NaBr had no effect on the rate of reaction of [Pt(dien)Br]Br or [Pd(dien)Br]Br with pyridine. This may seem surprising since it should be possible to inhibit "dissociative" type reactions by adding other reagents which would compete for the active intermediate. However, it is likely that pyridine is much more efficient than the bromide ion in capturing the intermediate, since pyridine binds more strongly.[10] These reactions go to completion even when excess bromide ion is added.

Using either k_1 or k_2 as a measure, the order of decreasing reactivity of different X groups in the $Pt(dien)X^+$ series is

$$NO_3^- > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$$

This nicely parallels both the order of increasing bond strength[10,11] and the position of these ligands in the *trans* effect series.[5a] Thus, at least in these examples, strongly *trans* activating groups are difficult groups to dislodge.

The total separation in rate is about 2000 in going from $Pt(dien)Cl^+$ to $Pt(dien)CN^+$. This is approximately the same spread as is found for octahedral cobalt(III) complexes where the order of reactivity is[12]

$$NO_3^- > I^- > Br^- > Cl^- > SCN^- > NO_2^-$$

It is of considerable interest that the order of reactivity for halide complexes is reversed in going from cobalt(III) to platinum(II). Thus, the changes in stability parallel the changes in lability in both cases since from equilibrium data[12] cobalt(III) holds the halogens in the order $Cl^- > Br^- > I^-$. This indicates that π-bonding is more important for platinum(II) than for cobalt(III).

For $Pd(dien)X^+$ the general order of reactivity seems to be the same as for platinum but the rates are much closer together. For example, there is only a 7-fold difference in rate between $Pd(dien)I^+$ and $Pd(dien)NO_2^+$, whereas for platinum the factor is 200. This supports the view that π-bonding is less important for palladium(II) than for platinum(II) complexes.[13]

Comparing the results in Tables II and III reveals a great difference in reactivity between analogous Pt(II) and Pd(II) complexes. For example, $Pd(dien)SCN^+$ reacts 700,000 times faster than $Pt(dien)SCN^+$. This is at variance with some of the results reported by Banerjea and Tripathi.[5c] These workers found most reactions of palladium(II) complexes too fast to measure at 36°, but occasionally they report rate constants which indicate about the same reactivity for corresponding platinum and palladium complexes. As a comparison, they give data on the reaction

$$trans\text{-}Pd(NH_3)_2pyCl^+ + py \longrightarrow Pd(NH_3)_2(py)_2^{+2} + Cl^- \quad (3)$$

from which a half-life of 280 min. at 36° can be calculated. We find the very similar reaction

$$Pd(dien)Cl^+ + py \longrightarrow Pd(dien)py^{+2} + Cl^- \quad (4)$$

is complete in 10 sec. at 0°. It is unlikely that the pyridine substituent in (3) can make such a difference in rate. For example, the rates of acid hydrolysis of $Pt(bipy)Cl_2$ and $Pt(en)Cl_2$ are 0.7×10^{-3} and $3.2 \times 10^{-3} \times$ min.$^{-1}$ [14] at 25°.

The rates of reaction of analogous nickel(II) complexes are much too fast to study by our method. However, recent studies[15] on some sterically hindered systems such as $M(PEt_3)_2(o\text{-tolyl})Cl$ show relative rates of reaction with pyridine of 5,000,000:100,000:1 for Ni(II), Pd(II) and Pt(II), respectively. For comparison the relative rates of acid hydrolysis of $M(NH_3)_5Br^{2+}$ complexes are about 4,000:100:1 for Co(III), Rh(III), Ir(III), respectively.[12] This much larger spread in rates for the nickel triad may be due to the greater ease with which Ni(II) and Pd(II) are known to add a fifth and sixth group relative to Pt(II). Thus the observed results are in agreement with a "dissociation" mechanism[5a] in which groups are added above and below the plane of the complex. This process is not involved in the six-coördinated complexes of the cobalt triad and the differences in their rates of reaction are found to be much smaller.

Table IV gives the rates of the reactions of $Pt(tripy)X^+$ and $Pd(tripy)X^+$ with pyridine. The $Pt(tripy)X^+$ complexes react 1000 to 10,000 times faster than corresponding $Pt(dien)X^+$ complexes. This is probably also the case with palladium(II) but no good comparisons can be made, since the $Pd(tripy)X^+$ complexes are all too reactive to measure. This result is somewhat surprising in view of the fact that $Pt(bipy)Cl_2$ and $Pt(en)Cl_2$ do not differ appreciably in their reactivity. Since 2,2′-bipyridine shows no great *trans* labilizing effect, it is unlikely that the more rapid reactions of the 2,2′,2″-tripyridyl complexes are the result of a *trans*-effect.

The structures of some 2,2′,2″-tripyridyl complexes of bivalent metals have been determined by Corbridge and Cox.[16] They found that $Zn(tripy)Cl_2$ is five-coördinated and has a distorted trigonal bipyramid structure. The tripyridyl rings remained coplanar, but the N–Zn–N bond angles were less than 90° (72 and 79°). However, conductivity measurements in nitrobenzene made by us indicate that [Pt(tripy)X]X and [Pd(tripy)X]X complexes are 1:1 electrolytes,[17] so it is likely that they have strained planar structures. This strain could render the complexes unstable and explain their high reactivity. An attractive mechanism, consisting of a M–N bond breaking in a slow step, also has been suggested to explain these rapid reactions.[18]

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(10) S. Ahrland, J. Chatt and N. Davies, *Quart. Rev.*, Vol. XII, No. 3 (1958).

(11) J. Chatt, L. A. Duncanson, B. L. Shaw and L. M. Venanzi, *Discussions Faraday Soc.*, **26**, 131 (1958).

(12) Reference 5a, page 121–122.

(13) J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955).

(14) See reference 5a, p. 194.

(15) Detailed kinetic studies on these compounds will be published in *J. Chem. Soc.*

(16) D. E. C. Corbridge and E. G. Cox, *ibid.*, 594 (1956).

(17) Molar conductance of [Pt(tripy)I]I is 22.2 cm.^{2} mole^{-1} ohm^{-1}, of [Pd(tripy)SCN]CNS is 20.0 at 25°.

(18) L. M. Venanzi, private communication.