cobaltous perchlorate (1.8 g) in water (5 ml) to a solution of the ligand (1.0 g) in water (20 ml) in the manner previously described, and the crystals were isolated and treated in the way described; yield 2.0 g. *Anal.* Calcd for $C_{20}H_{62}N_8O_{20}Cl_4Co_2$: C, 24.4; H, 5.3; N, 11.4; Cl, 14.4. Found: C, 25.4; H, 5.67; N, 11.5; Cl, 14.2.

trans-Azido(1,4,8,11-tetraazacyclotetradecane)cobalt(III)-*μ*-peroxo-*trans*-azido(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate.—A saturated solution of sodium azide (40 ml) was added to a solution of [$H_2OCo(cyclam)O_2(cyclam)CoH_2O$]-($ClO_4$)$_4$ (2.5 g) in water (200 ml), and the mixture was stirred for 1 hr. Saturated sodium perchlorate solution (5 ml) was then slowly added and brown crystals separated. The mixture was allowed to stand for 30 min in the refrigerator, and the crystals were filtered off, washed with dry ethanol and ether, and recrystallized by adding concentrated sodium perchlorate solution to a saturated aqueous solution; yield 0.8 g. *Anal.* Calcd for $C_{20}H_{48}N_{14}O_{10}Cl_2Co_2$: C, 28.8; H, 5.8; N, 23.5; Cl, 8.5. Found: C, 28.7; H, 5.8; N, 23.4; Cl, 8.5.

trans-Chloronitro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate.—Purified [$O_2NCo(cyclam)O_2(cyclam)CoNO_2$]-($ClO_4$)$_2$ (0.2 g) was added little by little to stirred concentrated hydrochloric acid (30 ml), and the mixture was allowed to stand with further stirring for 1.5 hr. The pinkish red solution was filtered and concentrated perchloric acid (20 ml) was added.

Pinkish red crystals started to separate, and the mixture was placed in the refrigerator for 1 hr. The solid was filtered off, washed with water, anhydrous ethanol, and ether, and recrystallized as rapidly as possible from hot water. The complex aquates rapidly under these conditions and may be lost if sufficient care is not taken. *Anal.* Calcd for $C_{10}H_{24}N_8O_6Cl_2Co$: C, 27.3; H, 5.5; N, 15.9; Cl, 16.1. Found: C, 27.3; H, 5.4; N, 15.8; Cl, 16.3.

trans-Bromonitro(1,4,8,11-tetraazacyclotetradecane)cobalt-(III) perchlorate trihydrate was prepared in an analogous way by adding the nitro–peroxo complex (0.8 g) to bromine-free, 48% hydrobromic acid (300 ml), which was then stirred for 1.5 hr. The pinkish brown product was recrystallized rapidly from hot water. *Anal.* Calcd for $C_{10}H_{30}N_5O_9ClBrCo$: C, 22.4; H, 5.5; N, 13.0; Br, 14.8; Cl, 6.7. Found: C, 24.5; H, 4.9; N, 12.8; Br, 14.6; Cl, 6.5.

The diffuse reflectance spectra of $MgCO_3$ mulls of the solids were measured with a Unicam SP 500 spectrophotometer. The infrared absorption spectra of Nujol and hexachlorobutadiene mulls between KBr plates were measured with a Perkin-Elmer 337 spectrophotometer. Conductivities were measured with a Wayne-Kerr Universal bridge.

# Reactivity of Amines toward a Neutral Platinum(II) Complex

BY L. CATTALINI, A. ORIO, AND A. DONI

The displacement by amines of one chloride in [Pt(bipy)Cl$_2$] has been studied in methanol at 25°. A linear relationship is observed between the logarithm of rate constants and the basicity of the entering groups. Three groups of amines have different reactivity owing to the different steric hindrance effects, and the results show that the steric influence of methyl groups in the α position to the nitrogen in the entering amine is additive. However, apart from the marked steric hindrance effect, variations of the structure, size, and basicity of the amine molecule have little effect on the rate of these reactions.

Introduction

Polarizability rather than basicity seems to have the most important role in determining the nucleophilic reactivity toward square-planar platinum(II) complexes.[1] For example, olefins and phosphines are good nucleophiles in reactions with complexes of platinum-(II), whereas hydroxide and ethoxide ions are very poor nucleophiles[2] and the reactivity order of halide ions is $I^- > Br^- > Cl^-$.[3]

The dependence of reactivity on the basicity of the leaving group has been studied in reactions of gold-(III) complexes[4]

$$[Au(am)Cl_3]^0 + Y^- \longrightarrow [AuCl_3Y]^- + am$$
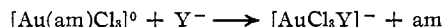
(am = heterocyclic nitrogen base), and a linear free energy relationship was found in the case in which Y^-

was essentially a pure nucleophile, *e.g.*, Cl^-, whereas this simple behavior was not followed by "biphylic" reagents such as azide and nitrito ions. At the present time, there is no information about the influence of the basicity of a series of entering groups with the same donor atom upon the reactivity of planar complexes with d^8 electronic configuration. On the other hand, a considerable amount of information is available about the relation between basicity and reactivity in organic reactions. Hudson and Withey[5] have shown that the rate constants for the reaction between substituted pyridines and ethyl methanesulfonate follow a linear free energy dependence upon basicity when steric effects are similar. Thus, α and α,α' substitutions decrease the magnitude of the rate constant considerably, but the slopes of the linear log k *vs.* pK_a relationships are the same if only molecules with similar steric properties are compared. Similar retardation effects by α substitution in heterocyclic

(1) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962); R. G. Pearson, *ibid.*, **85**, 3533 (1963).

(2) D. Banerjea, F. Basolo, and R. G. Pearson, *ibid.*, **79**, 4055 (1957).

(3) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

(4) L. Cattalini and M. L. Tobe, *Inorg. Chem.*, **5**, 1145 (1966).

(5) R. F. Hudson and R. J. Withey, *J. Chem. Soc.*, 3513 (1964).

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amines have been observed in other reactions.[6,7] The influence of steric hindrance always appears to be quite important.

In this paper we report the kinetics of the replacement of one chloride in [Pt(bipy)Cl$_2$] by a series of amines in methanol solution and relate the rate constants to the basicity of the reagent. In the absence of comprehensive pK_a values for these bases in methanol, we have been forced to use pK_a values determined in aqueous solution. However, the work of Hall[8] on the potentiometric determination of the base strength of amines in nonprotolytic solvents shows that the base strength in water is a reliable index of the base strength in organic solvents. We assume that this is true for methanol which has a greater similarity to water than aprotic solvents.

Results

Examination of the changing spectrum of a methanolic solution originally containing [Pt(bipy)Cl$_2$] and an excess of amine shows, through the development of well-defined isosbestic points, that a single-stage process is involved. The final product of the reaction with NH$_3$ has been isolated, and the analysis indicates that it is [Pt(bipy)(NH$_3$)Cl]Cl. The spectrum of a pure sample corresponds exactly to that of the reaction mixture at the end of the reaction, while it is quite different from the spectrum of [Pt(bipy)(NH$_3$)$_2$]Cl$_2$. Since the initial spectrum is that of the dichloro neutral complex, it is clear that the experimentally determined first-order rate constants are those of the replacement of the first chloride

$$[Pt(bipy)Cl_2] + NH_3 \longrightarrow [Pt(bipy)(NH_3)Cl]^+ + Cl^-$$
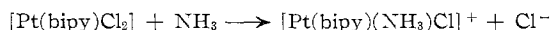
Although this is the only case where the reaction product has actually been isolated and examined, it has been possible to follow the conductivity changes resulting from the addition of these amines to solutions of the complex. The initial conductivity, which is very small, as one would expect from a nonionic system, increases with time in a first-order fashion, and the final molar conductivity is very nearly the same irrespective of the nature of the amine for a particular initial concentration of nonelectrolyte complex and corresponds to 89 ohm^{-1} cm^{-1}, which is very close to that of a 1:1 electrolyte under these conditions (5×10^{-4} M) and indicates quite clearly that the products of the reaction are always the monosubstituted [Pt(bipy)(am)-Cl]$^+$ complexes.

All of the reactions were carried out in the presence of a large excess of amine, so that, in any particular run, the kinetics were of a first-order form. The rate constants were obtained from the slope of a semilogarithmic plot of log ($D_t - D_\infty$) vs. time, where D_t and D_∞ are the optical densities of the solution at the wavelength of the maximum change (307 mμ) at times t and at the end of the reaction, respectively. Measurements carried out at other wavelengths, where there is an adequate change of optical density, give the same values for the rate constants.

The dependence of the observed rate constant upon the concentration of the nucleophile, X, in square-planar substitutions is usually

$$k_{obsd} = k_1 + k_2[X]$$

but in this case a simpler relationship arises from the fact that k_1 is negligible so that $k_{obsd} = k_2[X]$. Preliminary studies of the spectra of the complexes show that they obey Beer's law and indicate that the complexes are stable toward solvolysis. Addition of 0.1 M NaClO$_4$ did not significantly alter the observed rate constants indicating that, as might be expected in processes involving neutral compounds, there is no primary salt effect. The results are summarized in Table I.

Discussion

The various amines are divided into three groups, depending upon the nature of the amine. For amines having the same form of hindrance, a linear free energy relationship is obtained. The first group contains amines that do not give rise to hindrance; the second group contains pyridine derivatives which have a methyl group in α position. The third group contains the pyridines having two methyl groups in α position, of which only two examples have been studied. The linear relationship for the three groups of amines can be expressed by

$$\log k_2 = 0.057 \text{p}K_a - 2.56 \text{ (group I)}$$
$$\log k_2 = 0.061 \text{p}K_a - 3.57 \text{ (group II)}$$
$$\log k_2 = 0.060 \text{p}K_a - 4.48 \text{ (group III)}$$

bearing in mind that the last line is represented by only two points. Diethylamine appears to behave as though it were a member of the second group and has therefore been placed there in Table I. It is possible that the steric hindrance, equivalent to a single α substituent, arises from the free rotation of the ethyl groups because piperidine, which has a similar basicity and structure, except that rotation of the aliphatic chains is impossible, fits cleanly into the first group. There are other pairs of amines that differ mainly in their steric effect, e.g., 4-methylpyridine and 2-methylpyridine, 3,5- and 2,6-dimethylpyridine.

Looking at the separation between the three straight lines, it can be concluded that the steric effects of methyl groups in the α position are additive. The separations between the three straight lines are equal within experimental error. Similar results have been reported for the additivity of steric hindrance effects of amines in the reactions with ethyl methanesulfonate.[5] A comparison of the platinum(II) complex with the organic compound shows that the influence of steric effects in decreasing the reactivity is of the same order of magnitude for both substrates, with a somewhat greater effect in the case of the platinum-(II) complex.

The slope observed for the lines (0.06) is small compared to that obtained in organic reactions. In

(6) A. J. Kirby and W. P. Jenks, *J. Am. Chem. Soc.*, **87**, 3209 (1965).
(7) V. Gold and E. G. Jefferson, *J. Chem. Soc.*, 358 (1960).
(8) H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 63 (1956).

TABLE I

RATE CONSTANTS FOR THE DISPLACEMENT OF ONE CHLORIDE
FROM THE COMPLEX [Pt(bipy)Cl$_2$] IN METHANOL AT 25°

Entering amine	$pK_a{}^a$	[am], M	$10^4 k_{obsd}$, sec^{-1}	$10^3 k_2$, M^{-1} sec^{-1}
Group I				
4-Cyanopyridine	1.9	0.125	5.00	4.0
		0.084	3.45	4.10
		0.032	1.31	4.10
Pyridine	5.17	0.122	7.2	5.9
		0.061	3.45	5.7
		0.030	1.75	5.8
3-Methylpyridine	5.68	0.287	18.0	6.36
		0.140	8.3	5.84
		0.072	4.6	6.37
4-Methylpyridine	6.02	0.406	26.0	6.40
		0.203	12.6	6.21
		0.1015	6.85	6.80
3,5-Dimethylpyridine	6.34	0.40	27.0	6.75
		0.20	12.8	6.40
		0.10	6.3	6.30
Morpholine	8.4	0.432	37.5	8.64
		0.216	20.1	9.30
		0.108	9.7	9.0
		0.087	8.4	9.6
Ammonia	9.24	0.71	77.0	10.8
		0.365	37.0	10.1
		0.182	16.2	8.9
n-Butylamine	10.6	0.52	63.2	12.1
		0.34	42.0	12.3
		0.0975	11.38	11.6
Cyclohexylamine	10.64	0.161	17.20	10.7
		0.0805	10.7	13.2
		0.0402	5.35	13.4
Piperidine	11.12	0.775	90.0	11.6
		0.265	24.6	9.3
		0.177	17.8	10.1
		0.066	6.5	9.8
Group II				
Quinoline	4.95	0.273	1.21	0.443
		0.1365	0.71	0.52
		0.0682	0.37	0.54
2-Methylpyridine	6.1	0.582	3.35	0.575
		0.296	1.70	0.575
		0.231	1.40	0.605
2,4-Dimethylpyridine	6.99	0.4015	3.25	0.809
		0.238	1.88	0.794
		0.120	0.94	0.784
Diethylamine	11.0	0.248	3.25	1.31
		0.124	1.44	1.16
		0.062	0.72	1.16
Group III				
2,6-Dimethylpyridine	6.75	0.78	0.65	0.0835
		0.39	0.325	0.0832
		0.195	0.162	0.0830
2,4,6-Trimethylpyridine	7.48	0.292	0.276	0.0945
		0.146	0.131	0.0898
		0.075	0.065	0.0866

^{a} pK_a of the conjugate acid in water.

the reactions of amines with ethyl methanesulfonate[5] the slope is 0.11, and greater values are common for other alkylating agents, *e.g.*, 0.2 for chloroacetate ion,[9] 0.32 for ethylene oxide,[10] and 0.22 for 3-bromopropanol.

The small slope found for the platinum(II) complex

(9) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1062 (1962).
(10) R. F. Hudson and G. Loveday, *ibid.*, 1068 (1962).

might indicate that bond making in the transition state is not very important, as was assumed by Hudson in organic reactions,[5] suggesting that the transition state has "a greater SN1 character." We do not believe that this explanation applies to the present case because the platinum(II) complexes, in general, discriminate in favor of the polarizability of the entering reagent rather than its basicity.[1] The small slope does not necessarily mean that bond breaking rather than bond making supplies the driving force for the reaction. It simply means that basicity of the entering group plays a minor role in the formation of the transition state.

The results in Table I show that amines as different from one another as pyridine, ammonia, piperidine, and n-butylamine give points that lie on the same straight line. Therefore, there is very little fundamental difference between the behavior of aromatic and aliphatic amines and so there cannot be any significant contribution from a π interaction between the metal and the incoming amine in the transition state. The absence of π interactions between aromatic amines and platinum has also been observed when the amines are *cis* to the leaving group,[11] and it is supported by the fact that the quantitative *trans* effects of amines in general are much the same.[12]

The different sizes of the molecules and the presence of mesomeric systems do not influence the reactivity except for the small effect arising from the change in basicity. From these results one can conclude that, as far as the same type of donor atom is concerned, the molar polarizability of the entering reagent is not important in square-planar nucleophilic substitutions.

Experimental Section

[Pt(bipy)Cl$_2$], [Pt(bipy)(NH$_3$)Cl]Cl, and [Pt(bipy)(NH$_3$)$_2$]Cl$_2$ were obtained following the method of Morgan and Burstall.[13] Commercial aliphatic amines and substituted pyridines were distilled over potassium hydroxide pellets. Anhydrous methanol was prepared by distillation over (CH$_3$O)$_2$Mg, but small traces of water did not appear to have any appreciable effect upon the reactions.

Conductivity measurements were carried out by means of an LKB 3216B conductivity bridge.

Kinetics.—Methanolic solutions of the complex [Pt(bipy)-Cl$_2$] (in the range 10^{-5} to 10^{-4} M) and of the amine were thermostated and mixed in the spectrophotometer cell which was placed in the thermostated compartment of the spectrophotometer. The measurements were made with a Beckman DK2A recording spectrophotometer, scanning the near-ultraviolet spectrum from time to time in the course of the reaction. Some kinetic runs were made several times under the same conditions, and the rate constants were generally reproducible to better than 5%.

(11) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).
(12) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 385 (1962).
(13) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 965 (1934).