the two chlorides *cis* to ethylene in solutions of Zeise's salt, $K[Pt(C_2H_4)Cl_3]$. In this case the chloride *trans* to C_2H_4 is virtually labile. This exchange[10] required one term in the rate expression to be $k[Pt(C_2H_4)Cl_3^-] \cdot [trans\text{-}Pt(C_2H_4)Cl_2(H_2O)]$. At 25° k was 8.6×10^{-3} M^{-1} sec^{-1}, only 4% as large as $k_{3\text{-ex}}$ in the present system. The $\Delta H^{\ddagger}$ was much higher for this chloride system, amounting to 19 kcal, and as expected from the charges of the reacting species the $\Delta S^{\ddagger}$ was much greater as well, amounting to −2 eu. The two *cis* chlorides of Zeise's salt anion are characterized by an exceedingly slow aquation replacement, and this feature may account for the observation of the second-order process, which has not been observed for any other chloride exchange.

Also Grinberg and Shagisultanova[11] reported that *cis*- and *trans*-$[PtBr_2(NH_3)_2]$ each traded Br ligands with $PtBr_4^{2-}$. These were examples of second-order processes that involved two species which were not related by the aquation process. Second-order rate constants which can be inferred from their results were similar in magnitude to $k_{3\text{-ex}}$ of the present study.

There are several instances now in which second-order processes are clearly demonstrated. It appears that the exchange reactions of platinum(II), and possibly substitution reactions as well, may exhibit a complexity which has not been recognized and which will require careful characterization over rather wide concentration ranges.

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[11] A. A. Grinberg and G. A. Shagisultanova, *Radiokhimiya*, **2**, 592 (1960).

CONTRIBUTION FROM CENTRO DEI COMPOSTI DI COORDINAZIONE DEL C.N.R., ISTITUTO DI CHIMICA GENERALE, PADUA, ITALY, AND THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON W.C.1, ENGLAND

The *cis* Effect of the Cyanide Group in Substitution Reactions of Square-Planar Gold(III) Complexes

BY L. CATTALINI, A. ORIO, AND M. L. TOBE

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The kinetics of the displacement of the heterocyclic amine "am" from a series of complexes of the type *trans*-$[Au(CN)_2Cl(am)]^0$ by the reagents Br^-, N_3^-, and NO_2^- in methanol at 25° have been studied and the usual two-term rate law, rate = $(k_1 + k_2[Y])$[complex], has been observed. The dependence of k_2 upon the nature of the entering group indicates that, although Au(III) has a reasonable discrimination ability in these complexes, it is marginally poorer than in the analogous $[AuCl_3am]^0$ series. The nucleophilic power and even the sequence of reactivity depends upon the nature of the leaving group. The changes in behavior that follow the replacement of the two chlorines *cis* to the leaving group by two cyanides are not very large but they indicate that the cyanide group is able to displace more negative charge toward the central gold atom than can chloride. The displacement of "am" from $[AuCl_3am]^0$ by bromide is also reported.

Introduction

In a previous paper[1] we discussed the kinetic behavior of a series of four-coordinate planar gold(III) complexes of the general type $[AuCl_3am]^0$ (am = a heterocyclic amine) when the neutral ligand "am" was replaced by the anionic nucleophiles Cl^-, NO_2^-, and N_3^- in methanol at 25.0°. A linear relationship was observed between the basicity of the leaving group and the reactivity (expressed as the logarithm of the second-order rate constant) with respect to chloride substitution, where the entering group acts essentially as a σ-bonding nucleophile. However, in the reactions with the biphilic reagents N_3^- and NO_2^- the relationship was much more complicated and was explained in terms of π bonding and polarization in the transition state.

A number of investigations of the *cis* effect in planar platinum(II) complexes have been reported. In the nucleophilic displacement of chloride from neutral complexes of the type *trans*-$[PtL_2Cl_2]^0$, where the ligands *cis* to the leaving group are able to withdraw charge from the metal into π orbitals (*e.g.*, L = $P(C_2H_5)_3$ and $As(C_2H_5)_3$), the nucleophilic discrimination power of the substrate is relatively large.[2] In order to obtain some information about the *cis* effect in nonelectrolyte gold(III) complexes, we have prepared a series of compounds of the type *trans*-$[Au(CN)_2Cl(am)]^0$, and have studied the kinetics of their reactions with Br^-, N_3^-, and NO_2^- in methanol at 25.0°. This series of complexes differs from that previously studied in that two cyanides are *cis* to the leaving amine instead of two chlorines. It was not possible to study the displacement of the amine by chloride and so, in order to obtain suitable data for comparison, it was necessary to study the reactions of the complexes of the type $[AuCl_3am]^0$ with bromide. It has also been possible to extend the range of basicity over which the leaving group effect could be studied.

Results

Preliminary experiments indicated that the displacement of the coordinated amine in *trans*-$[Au(CN)_2$-

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[2] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

TABLE I

SECOND-ORDER RATE CONSTANTS (M^{-1} SEC^{-1}) FOR THE DISPLACEMENT OF HETEROCYCLIC AMINES FROM *trans*-$[Au(CN)_2Cl(am)]^0$ AND (IN PARENTHESES) FROM $[AuCl_3am]^0$ IN METHANOL AT 25.0°

		Entering reagent				
am	pK_a[a]	CH_3OH (10^3k_1)[b]	Cl^-	Br^-	NO_2^-	N_3^-
Quinoline	4.95	3.0 (0.30)	(0.245)	25 (8.8)	14.5 (1.47)	17 (29.1)
Isoquinoline	5.14	3.0 (0.58)	(0.245)	23 ...	20 (6.82)	25 (72)
Pyridine	5.17	4.0 (0.75)	(0.417)	37 (13.4)	35 (6.75)	36 (108)
3-Methylpyridine	5.68	1.3 (0.70)	(0.195)	7.2 (7.2)	21 (41.4)	29 (78)
4-Methylpyridine	6.02	... (0.61)	(0.096)	... (5.7)	... (43.0)	... ...
2-Methylpyridine	6.1	... (0.096)	(0.095)	... ...	... ...	... ...
3,5-Dimethylpyridine	6.34	1.5 (0.70)	(0.090)	6.5 ...	32 (34.5)	54 (51)
2,6-Dimethylpyridine	6.75	1.5 (0.62)	(0.039)	5.4 (3.5)	39 (26.1)	62 (24.7)
2,4-Dimethylpyridine	6.99	1.5 (0.56)	(0.023)	3.9 (2.4)	37 (11.0)	57 (6.5)
2,4,6-Trimethylpyridine	7.48	5.0 ...	...	11 ...	115 ...	48 ...

[a] pK_a of the conjugate acid of the amine in water at 25°. [b] The solvolytic data are expressed as first-order rate constants (sec^{-1}).

$Cl(am)]^0$ by chloride was reversible and that the reaction reached an equilibrium. The evaluation of the rate constants for the forward reaction was therefore complicated and this study was deferred to a later stage of the investigation. The displacement of the amine by bromide could be studied readily spectrophotometrically although the evaluation of the kinetics was complicated by the fact that the displacement of the coordinated chloride, as well as the displacement of the amine, would lead to a change of spectrum. Since the concentrations of complex employed in the investigation were far too low to allow direct chemical identification of the reaction products, it was necessary to deduce the nature of the leaving group from spectrophotometric evidence alone. The reactions between $[AuCl_3am]^0$ and bromide did not appear to be as fast as was previously thought from the preliminary measurements[1] and, since it was not possible to make comparisons between the two types of complexes as far as their reactions with chloride were concerned, the rate constants for the reactions between $[AuCl_3am]^0$ and bromide were measured. By scanning the spectrum in the near-ultraviolet region from time to time during the course of the reaction, it could be seen that there was more than one stage of spectrophotometric change and, in all cases, the rate of the first stage depended upon the amine in the substrate. The rates of the second and subsequent stages were independent of the nature of the amine originally present and depended only upon whether the complex belonged to the trichloro or the *trans*-dicyanomonochloro series; in this latter group only two stages of reaction were observed. When the complexes of the $[AuCl_3am]^0$ series were studied a common isosbestic point developed after the first stage was complete as would be expected if the amine were lost in the first step, and, by making measurements at this wavelength, the subsequent stages of the reaction could be ignored. No isosbestic points were observed in the reactions of the *trans*-$[Au(CN)_2Cl(am)]^0$ complexes but fortunately the rate of the first stage was sufficiently faster than that of the second for it to be possible to use the optical density after 6 half-lives of the first stage as the value for D_∞ in the calculations.

When sodium azide or sodium nitrate was added to a methanolic solution of *trans*-$[Au(CN)_2Cl(am)]^0$, the sequence of changes observed was very similar to that found when the substrate was $[AuCl_3am]^0$. In all of their substitution reactions, therefore, the two series of complexes resemble one another very closely and so the evidence and reasoning used to prove that the leaving group in the first stage of the reaction of $[AuCl_3am]^0$ was the neutral amine[1] applies equally well to the *trans*-dicyano analogs.

All of the reactions were carried out in the presence of a large excess of the entering reagent so that, in any single kinetic run, the kinetics were of first-order form. The rate constants were obtained from the slope of the plot of log ($D_\infty - D_t$) against time, where D_t and D_∞ were the optical densities of the solution at time t and at the end of the first stage of the reaction, respectively. The pseudo-first-order rate constant varied with nucleophile concentration in the way that is usual for square-planar substitution, *i.e.*, $k_{obsd} = k_1 + k_2[Y]$, and the values of k_1 and k_2, obtained from the intercept and the slope of the linear plot of k_{obsd} against [Y], are collected in Table I, together with some of the data obtained in the previous work[1] for the purposes of comparison.

Change of ionic strength does not affect the rate constants to any appreciable extent, as might be expected for substitution reactions involving an uncharged substrate. Preliminary studies of the spectra of the complexes in methanol in the absence of added nucleophile showed that Beer's law was obeyed and indicated that the complexes were stable toward solvolysis (in an equilibrium rather than a kinetic sense).

Discussion

Although the purpose of this work was to study the reactions of the complexes in the series *trans*-$[Au(CN)_2Cl(am)]^0$, it was necessary, for reasons which have already been stated, to study the kinetics of the reactions between the complexes of the type $[AuCl_3am]^0$ and bromide ions. Consequently it is now possible to examine the difference between the nucleophilic properties of chloride and bromide in their reaction with $[AuCl_3am]^0$ as the basicity of the leaving group, "am," changes. When log (k_2/k_1) is plotted against the basicity of the leaving amine (expressed as the pK_a of its conjugate acid in water), the data lie on a straight line. This linear free energy relationship between the free energy of activation for bromide substitution and the basicity of the leaving group indicates that, as in the case of chloride substitution,[1] there is no significant development of π interaction in forming the transition state. A similar absence of π interaction has also been proposed in the reactions of certain Pt(II) complexes when a halide ion is the entering group,[3] the leaving group, and the *trans* partner.[4] There it was suggested that the difference in reactivity and *trans* effect of the halogens arose mainly from the difference in polarizability: the same conclusions can be reached for these gold(III) complexes. The reactivity of bromide is some 30–100 times greater than that of chloride within the range of complexes studied which is considerably greater than the reactivity ratios $(k_2^{\text{Br}^-}/k_2^{\text{Cl}^-})$ for the nonelectrolyte platinum(II) complexes of the type *trans*-$[\text{PtL}_2\text{Cl}_2]^0$, even when these complexes have high discriminating power.[2] As the basicity of the leaving group decreases, the reactivity ratio $(k_2^{\text{Br}^-}/k_2^{\text{Cl}^-})$ for the reactions of the $[\text{AuCl}_3\text{am}]^0$ complexes also decreases and the Au(III) complexes take on a behavior reminiscent of that of Pt(II). This similarity is also seen in the reactions with the biphilic ions NO_2^- and N_3^-, where, for the displacement of the weakly basic amines, there is a reactivity sequence of the form $\text{N}_3^- \approx \text{Br}^- > \text{Cl}^- \approx \text{NO}_2^-$.

The slopes of the linear relationship between log (k_2/k_1) and the pK_a of the leaving group for the reactions of $[\text{AuCl}_3\text{am}]^0$ are -0.35 and -0.61, respectively, for the reactions with bromide and chloride. This would suggest that the importance of bond breaking in the substitution process is less with bromide than it is when chloride is the entering reagent, which is in accordance with the known ability of bromide to form a stronger bond with the "soft" gold(III) central atom. Thus, while it is likely that bond breaking is still rate controlling, the presence of bromide in the complex requires less extension of the Au–N bond in the appropriate transition state than does the presence of chloride. It has not yet been possible to measure the rates of the reactions with iodide because, in addition to them being rather fast, the reaction appears to have some redox character from preliminary studies.

On changing the substrate from $[\text{AuCl}_3\text{am}]^0$ to *trans*-$[\text{Au(CN)}_3\text{Cl(am)}]^0$ it is clear that there is no drastic change in the kinetic behavior. The rates of the solvolytic reaction and the bimolecular attack by bromide are somewhat greater in all cases but the reactions with nitrite and azide have no such simple relationship. Inspection of Figure 1, in which log (k_2/k_1) is plotted against the pK_a of the conjugate acid of the leaving group, shows clearly that the ability of gold to discriminate between the four anionic nucleophiles is much poorer in *trans*-$[\text{Au(CN)}_2\text{Cl(am)}]^0$ than it is in $[\text{AuCl}_3\text{am}]^0$,[1] especially when the least basic amines are being displaced. Comparison of the actual values of k_2/k_1 between the two series can be misleading because it overemphasizes the changes in k_1, but, within either of the two series, such a comparison serves as a useful measure of the relative nucleophilicities. The displacement of the amine by bromide still obeys a linear free energy relationship with the basicity of the leaving group but the slope of the line (-0.23) is considerably less steep than that found for the $[\text{AuCl}_3\text{am}]^0$ series (-0.35). This would suggest that bond breaking is less rate controlling in the *trans*-dicyano complex and this conclusion is supported by the way in which the rate of entry of azide and nitrite depends upon the basicity of the leaving group. It can be seen in Figure 1 that the region of behavior where k_2/k_1 actually increases as the basicity of the leaving group increases extends to leaving groups of higher basicity and presumably of stronger ground-state bonding. The biphilic reagents are therefore able to develop the electrophilic component of their reactivity over a wider range of basicity of the leaving group when two of the chlorines in $[\text{AuCl}_3\text{am}]^0$ are replaced by two cyanides.

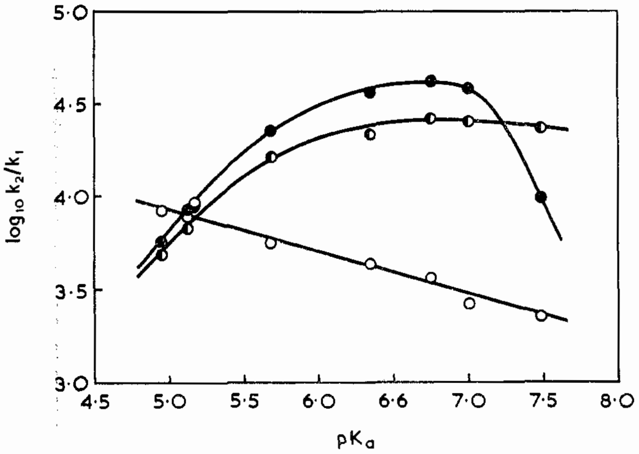

Figure 1.—Log (k_2/k_1) plotted as a function of the pK_a of the leaving group: ○, bromide; ◐, nitrite; ●, azide.

The poorer discriminating power of the *trans*-$[\text{Au(CN)}_2\text{Cl(am)}]^0$ complexes suggests that the presence of two cyanides makes the Au(III) a little more like Pt(II). This could be accounted for in terms of the greater basicity and polarizability of cyanide as compared to chloride and suggests that the cyanide functions mainly through the σ bond to displace charge inductively toward the metal, thereby decreasing its effective nuclear charge as felt by the entering and leaving groups. The similarity with platinum(II) is still only marginal even in the most extreme case because the order of nucleophilicity as well as the discrimination power of the substrate depends markedly upon the nature of the leaving group in both series of compounds, whereas it has been shown,[5] at least in the reactions of complexes of the type $[\text{Pt(dien)X}]^+$ (dien = diethylenetriamine), that the nature of the leaving group not only does not affect the order of nucleophilicity, but the linear dependence of log (k_2/k_1) upon $n_{\text{Pt}}{}^2$ remains and the slope does not change with any change in the nature of the leaving group. In fact, any effect that the nature of the leaving group has upon the rates of reaction affects all

(3) L. Cattalini, U. Belluco, R. Ettore, and M. Martelli, *Gazz. Chim. Ital.*, **94**, 356 (1964).

(4) U. Belluco, L. Cattalini, M. Martelli, and R. Ettore, *ibid.*, **94**, 733 (1964).

(5) U. Belluco, personal communication, 1966.

TABLE II

ANALYTICAL DATA FOR THE NONELECTROLYTE GOLD(III) COMPLEXES

am	Formula	% C		% H		% N		% Au	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
		(a) Type $[AuCl_3am]^0$ Complex							
2-Methylpyridine	$C_6H_7NCl_3Au$	18.2	18.5	1.7	1.85	3.5	3.6	49.7	49.4
2,4-Dimethylpyridine	$C_7H_9NCl_3Au$	20.5	20.8	2.2	2.3	3.4	3.5	48.1	47.8
		(b) Type $[Au(CN)_2Cl_2]^0$ Complex							
Quinoline	$C_{11}H_7N_3ClAu$	31.9	31.5	1.7	1.9	10.2	10.0	47.7	46.8
Isoquinoline	$C_{11}H_7N_3ClAu$	31.9	32.1	1.7	2.0	10.2	10.3	47.7	46.7
Pyridine	$C_7H_5N_3ClAu$	23.1	23.3	1.4	1.5	11.6	11.8	54.2	53.9
3-Methylpyridine	$C_8H_7N_3ClAu$	25.4	25.7	1.9	1.9	11.1	11.5	52.2	52.0
3,5-Dimethylpyridine	$C_9H_9N_3ClAu$	27.6	27.5	2.3	2.5	10.7	11.1	50.3	50.2
2,6-Dimethylpyridine	$C_9H_9N_3ClAu$	27.6	27.7	2.3	2.5	10.7	11.1	50.3	50.0
2,4-Dimethylpyridine	$C_9H_9N_3ClAu$	27.6	28.0	2.3	2.5	10.7	10.9	50.3	50.1
2,4,6-Trimethylpyridine	$C_{10}H_{11}N_3ClAu$	29.6	30.2	2.7	2.9	10.4	10.6	48.6	48.3

of the entering nucleophiles in equal proportion. At this stage, any attempt to provide a satisfactory explanation of the difference in the behavior of Pt(II) and Au(III), whether this be in terms of effective nuclear charge differences, solvation differences, or other possible effects, is premature and more work covering a wider range of substrates and reagents is needed.

Finally, it should be pointed out that a number of the leaving groups have one or even two methyl groups in *ortho* position to the nitrogen that is bonded to the metal. There is no indication, in these reactions, that the steric restrictions imposed by these substituents have any pronounced effect upon the kinetics. This point has recently been discussed for the reverse reaction[6]

$$[AuCl_4]^- + am \longrightarrow [AuCl_3am]^0 + Cl^-$$

where the steric effects are clearly present and need not be repeated here.

Experimental Section

The complexes of the type $[AuCl_3am]^0$ were prepared and purified in the ways previously described.[1] The analytical data for the complexes not previously prepared are collected in Table II.

Potassium dicyanoaurate(I) was prepared by adding ammonia to an aqueous solution of chloroauric acid, filtering off the resultant precipitate, and, after washing it with water until the filtrate was free of chloride, dissolving it in the minimum amount of aqueous potassium cyanide solution. The required product crystallized out on evaporating the solution.

Potassium *trans*-dichlorodicyanoaurate(III) was prepared by oxidizing an aqueous solution of $K[Au(CN)_2]$ with an excess of bromine and then displacing the bromine with chlorine gas. The chlorine caused the color of the solution to change from red to yellow and, on evaporation, the required product was obtained in crystalline form. The purity of the complex was confirmed by comparing its infrared spectrum with that reported in the literature.[7]

The complexes of the type *trans*-$[Au(CN)_2Cl(am)]^0$ were obtained by treating an aqueous solution of the *trans*-$[Au(CN)_2Cl_2]^-$ salt with a small excess of the appropriate amine. The neutral complexes precipitated almost immediately and were washed with water and methanol. The products, dried under vacuum over P_2O_5 and washed again with ligroin in order to remove any remaining traces of amine, were sufficiently pure for the kinetic studies. The analytical data for these complexes are collected in Table II. In order to avoid possible photodecomposition, all the complexes were stored in the dark. The *trans* configuration has been assigned purely on the basis of the general observation that configuration is retained during the substitution reactions of planar four-coordinate d^8 complexes and is confirmed by the kinetic behavior.

The methods used to follow the kinetics were similar to those reported previously.[1] Known volumes of thermostated solutions of the complex and the reagent were mixed in the spectrophotometer cell which was placed in the thermostated compartment of an Optica CF-4 recording spectrophotometer. The spectrum changes characteristic of the reacting system were first determined by scanning the near-ultraviolet region at known intervals. Once the spectra changes were characterized and suitable wavelengths chosen to study the first stage of the reaction, the kinetics were followed by locking the wavelength at the chosen value and recording the change of optical density as a function of time.

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(6) L. Cattalini, M. Nicolini, and A. Orio, *Inorg. Chem.*, **5**, 1674 (1966).

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