than anticipated for normal substitution. The empirical factor can be calculated from the ratio of rate constants as $k_1(\alpha\text{-Abu})/k_1(\alpha\text{-Ala}) = 2.5/6 = 0.42$ and $k_1(\alpha\text{-Abu})/k_1$ (Gly) = 0.54 (Gly = glycine). The average value is, again, approximately $^1/_2$. This result compares favorably with the procedure adopted for the Ni^{2+} complexes. Thus, this relatively small difference in the value of k_1 can be explained, and the substitution classified as normal.

For β-aminobutyric acid, values of $k_1 = 2 \times 10^4$ and $k_2 = 7 \times 10^4\ M^{-1}\ sec^{-1}$ were found. Although k_2 is larger than k_1, the effect is not nearly as pronounced as for α-aminobutyric acid. Moreover, the value of k_1 is significantly lower than the corresponding value for α-aminobutyric acid or glycine, being reduced, primarily, by the factor $(1 + k_{-0}/k_0')^{-1}$. Here, a steric effect due to the difficulty of closing the six-membered ring in the chelate complex can be postulated, as in the case of β-alanine,[6] where it was also indicated that the limiting case ($k_{-0} \gg k_0'$) was not reached. It is thus possible to predict the value of k_1 for the β complex by a semiempirical calculation as follows.

Let us assume that the steric effect appearing in Co^{2+}–β-alanine reactions is roughly equal to the steric effect with β-aminobutyric acid. Then the rate constant for Co^{2+} + β-aminobutyrate is $k_1(\beta\text{-Abu}) = k_1(\alpha\text{-Abu})\cdot[k_1(\beta\text{-Ala})/k_1(\alpha\text{-Ala})] = 2.5 \times 10^5(7.5/60) = 3.1 \times 10^4\ M^{-1}\ sec^{-1}$. The same calculation can be performed in an alternate way. Suppose that the ratio (7.5/60) expresses the steric control contribution to the closing of the six-membered ring with respect to the five-membered ring. Then, the β rate constant can be calculated from k_1(Gly) by the introduction of the statistical collision factor $P = {}^1/_2$, to adjust for the decreased active "surface of reaction." Therefore, $k_1(\beta\text{-Abu}) = Pk_1(\text{Gly})[k_1(\beta\text{-Ala})/k_1(\alpha\text{-Ala})] = {}^1/_2(4.6 \times 10^5)(7.5/60) = 2.9 \times 10^4\ M^{-1}\ sec^{-1}$, while the experimental value is $k_1 = 2.0 \times 10^4\ M^{-1}\ sec^{-1}$.

Nucleophilic Reactivity in Substitution Reactions of Square-Planar Metal Complexes. II. A Comparison of the Kinetic Behavior of Platinum(II) and Gold(III) Complexes

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Abstract: The kinetics of the displacement of chloride from the $[AuCl_4]^-$ anion by pyridine, NO_2^-, N_3^-, Br^-, I^-, and SCN^- in methanol have been studied over a range of temperature and reagent concentration. The usual two-term rate law is observed, and the rate constants and Arrhenius parameters are reported and compared with the data for the analogous $[PtCl_4]^{2-}$ anion. The discriminating power of the Au(III) reaction center is found to be very much greater than that of Pt(II) in a similar ligand environment, and an explanation is offered in terms of the extent to which the mechanism moves from an associative toward a synchronous bimolecular process.

Although kinetic studies of nucleophilic displacement of ligands from square complexes of d^8 transition metal ions have, in the past, been limited mainly to those of platinum(II),[1] sufficient information about the behavior of corresponding gold(III) complexes has now become available for it to be possible to attempt to make a preliminary general comparison of the kinetic behavior of Pt(II) and Au(III) substrates.

In part I,[2] the factors which determine the reactivity of nucleophiles toward Pt(II) complexes were discussed. It was shown that, apart from biphilic reagents, such as NO_2^-, $SeCN^-$ and thiourea, the sequence of relative reactivity followed a linear free-energy relationship with the index, n_{Pt},[3] defined by $n_{Pt} = \log (k_2/k_s)$, where k_2 and k_s are the second-order rate constant for the entry of the nucleophile in question and the first-order rate constant for the solvolysis by methanol, respectively, of the reference substrate *trans*-$[Pt(py)_2Cl_2]$. This was taken to be a measure of the "softness" or micropolarizability of the entering nucleophile since its basicity appeared to have only a minor effect upon its reactivity.

In order to make the comparison between Pt(II) and Au(III) complexes, it was necessary to augment the available data relative to nucleophilic displacement reactions of the gold(III) derivatives. Apart from the isotopic exchange[4] of chloride ion with $[AuCl_4]^-$ and from the reactions[5] of some nucleophiles on the cationic complex $[Au(\text{dien-H})Cl]^+$, the processes studied until now were mainly limited to the use of pyridine derivatives, either as entering[6,7] or leaving[8,9] groups. We have therefore studied the reactions of $[AuCl_4]^-$ with

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pyridine and with the anionic nucleophiles NO_2^-, N_3^-, Br^-, I^-, and SCN^- in methanol. This has not only provided a new set of data and a sequence of nucleophilicity toward an anionic Au(III) substrate, but it has also made it possible to make a direct comparison of the behavior of the isoelectronic and isostructural $[AuCl_4]^-$ and $[PtCl_4]^{2-}$. This second point is quite important, since the kinetic behavior of both Pt(II) and Au(III) substrates appears to depend as much upon the nature of the ligands coordinated to the metal as it does upon the total charge of the complex. For example, it has been shown[2] that, in Pt(II) derivatives, the nucleophilic discrimination factor,[3] s, given by eq 1, changes from 0.8 to 1.6 in a series of

$$\log k_2 = s(n_{\mathrm{Pt}}) + \log k_s \qquad (1)$$

neutral complexes, whereas it is 0.312 for $[PtCl_4]^{2-}$. Similarly, the Brønsted coefficient, α, in eq 2, which

$$\log k_2 = \alpha(\mathrm{p}K_\mathrm{a}) + \text{constant} \qquad (2)$$

attempts to relate the basicity of the substituted pyridines with the free energy of activation of their reaction with gold(III) substrates, changes from 0.21 to 0.89 in a series of monopositive complex cations,[7] whereas it is 0.15 for $[AuCl_4]^-$ as substrate.

Experimental Section

Materials. Chloroauric acid was recrystallized and its purity established by analysis and comparison of its ultraviolet spectrum with published values.[10,11] The other chemicals used were all recrystallized reagent grade materials. The methanol was dried by refluxing over $Mg(CH_3O)_2$, and the distilled product was stored under anhydrous conditions. There was no indication that rigorous purification of the materials was necessary in order to obtain reproducibility.[12]

Kinetics. The reactions were studied spectrophotometrically by the procedure described in part I[2] in which the changes of optical density at a selected wavelength in the ultraviolet region were followed over a period of time by means of an Optical-CF4 double-beam recording spectrophotometer, with the appropriate attachments to maintain the cells at constant temperature (±0.1°). The reactions were started by mixing known volumes of standard solutions of the reagents in the spectrophotometer cell which also served as the reaction vessel. Constant ionic strength was maintained by the addition of lithium perchlorate solution. Freshly prepared solutions of $HAuCl_4$ were used for each experiment in order to avoid the formation of significant quantities of the solvento complex. The entering reagent was always present in sufficient excess to provide pseudo-first-order conditions and to avoid complications from the reverse reactions. The pseudo-first-order rate constants, k_{obsd}, were calculated from the slope of the plot of log $(D_\infty - D_t)$ against time, where D_t and D_∞ are the optical densities of the reaction mixture at time t and at the end of the reaction, respectively.

Results

The problems of following the kinetics of nucleophilic ligand displacements from $[AuCl_4]^-$ are, in principle, similar to those encountered in the study of the reactions of $[PtCl_4]^{2-}$ since, in both the substrates, there are four replaceable groups. However, the greater reactivity of the gold(III) substrate and the possibility of complication by redox processes can cause extra difficulty. Owing to the relatively high reactivity of $[AuCl_4]^-$, we have had to limit our study to the nucleophiles pyridine, NO_2^-, N_3^-, Br^-, I^-, SCN^-, and CH_3OH. Fortunately, as was previously reported for the nucleophilic substitutions of neutral complexes of the type [AuCl$_3$am],[8] the reduction of Au(III) to Au(I), or even to metallic gold, either did not occur or else was relatively slow in comparison to the ligand displacement reaction. No evidence was found for any irreproducible redox-catalyzed substitution of the type observed by Rich and Taube[12] in their studies of the chloride exchange.

All the reaction rates reported in this paper are concerned with the replacement of the first of the four chloride ligands bonded to the gold. As far as the reagents NO_2^-, N_3^-, and Br^- are concerned, the identification of the reaction steps and the products is based upon the same arguments that were previously used for the reactions of [AuCl$_3$am].[8] In each case, two reaction steps can be observed, and the isosbiestic points for the second step occur at least at one wavelength where there is a large enough change in optical density corresponding to the first step. These isosbiestic points are identical with those observed in the appropriate stages of the analogous reactions with the [AuCl$_3$am] substrate,[8,9] and the kinetics of the first stage were studied at these wavelengths. In these cases it is also found that the general kinetic behavior, after the first stage of the reaction, also corresponds to that observed for the substrates of the type [AuCl$_3$am], and the final spectra are also in agreement with those previously observed. Consequently, the reactions can be described as

$$[AuCl_4]^- + Y^- \xrightarrow{\text{slow}} [AuCl_3Y]^- + Cl^-$$

$$[AuCl_3Y]^- + Y^- \xrightarrow{\text{fast}} [AuCl_2Y_2]^- + Cl^-$$

followed by the second identifiable step

$$[AuCl_2Y_2]^- + Y^- \xrightarrow{\text{slow}} [AuClY_3]^- + Cl^-$$

$$[AuClY_3]^- + Y^- \xrightarrow{\text{fast}} [AuY_4]^- + Cl^-$$

The rates of the second reaction step are not reported here.

The reactions with NO_2^- were carried out in the presence of a small quantity of CH_3O^- in order to avoid the formation of HNO_2. Some preliminary experiments showed that this species can exert a catalytic effect similar to that observed for the reactions of some platinum(II) complexes.[13] It should be pointed out that a similar effect was not observed in the reactions of [AuCl$_3$am], and further studies of this phenomenon are now in progress.

With pyridine and methanol as entering groups, the reaction appears to stop when only one chloride is replaced. The reaction with pyridine at 25° has been reported previously.[6] The rate constant for the reaction with the solvent methanol is the k_1 value from the two-term rate law.

The reactions with I^- and SCN^- appear to occur in a single stage. The initial spectrum corresponds to that of the $[AuCl_4]^-$ starting material, and so the rate-determining step is the replacement of the first chloride. The final spectrum for the reaction with I^- corresponds exactly to that of $[AuI_4]^-$.[10] An attempt was made to follow the reaction with thiourea at 6°. The reaction

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Table I. Pseudo-First-Order Rate Constants, k_{obsd}, for the Displacement of the First Chloride in $[AuCl_4]^-$ in Methanol[a]

Entering group, Y	[Y], *M*	Temp, °C	k_{obsd}, sec^{-1}
Pyridine[b]	0.195	6.0	0.086
	0.0975		0.043
	0.0487		0.021
	0.0650	15.0	0.055
	0.0487		0.040
	0.0284		0.024
	0.00975		0.0078
NO_2^-[c]	0.100	15.0	0.00175
	0.0800		0.00150
	0.0400		0.00088
	0.0200		0.00048
	0.100	25.0	0.0031
	0.0750		0.0025
	0.0400		0.0017
	0.0200		0.0010
	0.100	35.0	0.0058
	0.0800		0.0050
	0.0400		0.0031
	0.0200		0.0019
	0.0100		0.0015
N_3^-	0.100	6.0	0.0152
	0.0750		0.0112
	0.0500		0.0074
	0.0250		0.0030
	0.100	15.0	0.0215
	0.0750		0.0164
	0.0500		0.0118
	0.0250		0.0055
	0.100	25.0	0.039
	0.0750		0.031
	0.0500		0.022
	0.0250		0.0126
Br^-	0.100	6.0	0.0036
	0.0750		0.0026
	0.0500		0.00156
	0.0250		0.00077
	0.100	15.0	0.0068
Br^-	0.0500	15.0	0.0032
	0.0250		0.0014
	0.100	25.0	0.0164
	0.0750		0.0132
	0.0500		0.0084
	0.0250		0.0054
	0.0100		0.0035
I^-	0.0015	6.0	0.031
	0.0010		0.023
	0.0010		0.021
	0.00050		0.0111
	0.00050		0.0102
	0.00025		0.0053
	0.0010	15.0	0.045
	0.00075		0.033
	0.00050		0.021
	0.00030		0.013
	0.00075	25.0	0.061
	0.00060		0.046
	0.00050		0.042
	0.00040		0.032
	0.00025		0.021
	0.00010		0.0088
SCN^-	0.0100	6.0	0.0186
	0.0075		0.0145
	0.0050		0.0080
	0.0025		0.0044
	0.0075	15.0	0.026
	0.0050		0.0176
	0.0025		0.0088
	0.0010		0.0038
	0.0100	25.0	0.070
	0.0075		0.056
	0.0050		0.042
	0.0025		0.0182
	0.0010		0.0072
Thiourea	0.0001	6.0	0.038
	0.0001		0.038

[a] With the anionic entering groups the ionic strength was held constant at 0.10 by adding the appropriate amount of lithium perchlorate. [b] The data for pyridine at 25.0° are reported in ref 6. [c] In reactions involving the nitrite ion, the solutions also contain 0.0002 *M* $NaOCH_3$.

Table II. Specific Rate Constants for the Displacement of One Chloride from $[AuCl_4]^-$ in Methanol Solution (Ionic Strength = 0.1)

Entering group	Temp, °C	Rate constant	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, cal deg^{-1} mole^{-1}	Rate constant[a] for $[PtCl_4]^{2-}$
		10^4k^c			10^4k^c
CH_3OH	15	2			
	25	5			0.4
	35	10			
		k^d			$k_2{}^d$
NO_2^-	15	0.0155			
	25	0.028	8.3	−33	0.0009
	35	0.042			
N_3^-	6	0.16			
	15	0.21	6.5	−39	
	25	0.35			
Br^-	6	0.034			
	15	0.065	12.3	−22	
	25	0.140			0.0018
I^-	6	21.5			
	15	44	12.0	−9	
	25	84			0.0065
SCN^-	6	1.85			
	15	3.6	12.0	−14	
	25	7.4			0.0021
Pyridine	6	0.45			
	15	0.84	10.6	−22	
	25	1.6[b]			

[a] Data for aqueous solution from ref 2. [b] Data from ref 6. [c] In sec^{-1}. [d] M^{-1} sec.$^{-1}$

was very fast, even at low concentrations of this reagent, and it is possible only to say that the second-order rate constant k_2 is approximately 400 l. mole^{-1} sec^{-1}.

The pseudo-first-order rate constants (k_{obsd}) obtained in these studies are listed in Table I. All the reactions follow the usual two-term rate law, *viz.*, rate = (k_1 + $k_2[Y^-]$)[complex], where Y is the entering nucleophile. The values of k_1 and k_2 were obtained as the intercepts and slopes, respectively, of linear plots of k_{obsd} against [Y]. The values of k_1 and k_2 are collected in Table II together with the derived activation parameters.

Discussion

On comparing the rate constants for the entry of the various nucleophiles into the $[AuCl_4]^-$ anion with those for the analogous reactions of $[PtCl_4]^{2-}$, which are also given in Table II, it is apparent that, in all cases, the Au(III) complex reacts considerably faster than does that of Pt(II).[14] This cannot be explained simply by

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(14) The data for $[PtCl_4]^{2-}$ in Table II have been corrected for ionic strength effects and therefore refer to a standard state of pure water. No attempt has been made to treat the data for $[AuCl_4]^-$ in a similar fashion because of the unreliability of an extrapolation from an ionic strength of 0.1 when methanol (with its smaller dielectric constant) is

saying that the Pt(II) data refer to aqueous solution or that the lower charge of the $[AuCl_4]^-$ anion causes less electrostatic repulsion between the approaching reagents because this observation is more general. For example, the exchange of isotopically labeled chloride with $[AuCl_4]^-$ has a k_2 value of 0.147 M^{-1} sec^{-1} in water at 20°,[4] whereas with $[PtCl_4]^{2-}$ the bimolecular exchange of chloride is not experimentally detectable and the reaction occurs entirely by way of the solvolytic (k_1) path.[15] The rate of hydrolysis increases by a factor of 375 on going from $[PtCl_4]^{2-}$ to $[AuCl_4]^-$.[11,15] The values of k_2 for the replacement of the coordinated chloride by bromide in $[Au(dien)Cl]^{2+}$ and $[Pt(dien)Cl]^+$ are 380 and 5.3×10^{-3} M^{-1} sec^{-1}, respectively, in water at 25°[5,15,16] and 190 M^{-1} sec^{-1} in the monocationic $[Au(dien\text{-}H)Cl]^+$ [5] (dien-H = di(2-aminoethyl)-amine that has lost one proton). Furthermore, the reactions of $[Au(bipy)Cl_2]^+$ with amines are faster than those of $[Pt(bipy)Cl_2]$,[7,17] even though a strict comparison cannot be made because the reactions have not been studied in the same solvent.

If one considers the factors that determine the nucleophilicity of the reagents toward the planar substrates (*e.g.*, micropolarizability, π interactions, and basicity), one can observe, from the data in Table II, that all of these factors become more important on going from the Pt(II) to the Au(III) substrate. As far as Br^- and I^- are concerned, the micropolarizability has probably the overwhelming influence upon the nucleophilicity since I^- is some 600 times more reactive than Br^- toward $[AuCl_4]^{2-}$, whereas the ratio of $k_2(I^-) : k_2(Br^-)$ is only 3.6 in the reactions with $[PtCl_4]^{2-}$. Thus, not only does Au(III) act as a "soft" reaction center (*i.e.*, I^- is a better reagent than Br^-), but it has a greater discriminating ability than Pt(II). The same is true when we compare thiocyanate and bromide since $k_2(SCN^-)/k_2(Br^-)$ is 53 and 1.18, respectively, for reactions with $[AuCl_4]^-$ and $[PtCl_4]^{2-}$, although in this case it is not possible to know whether the thiocyanate is bound by the same end in both the transition states.

As far as π interactions are concerned, it should be pointed out that the azide ion has no biphilic properties when it reacts with a Pt(II) substrate,[2] whereas its biphilic properties are quite important in its reactions with Au(III) substrates.[8,9] It also appears that the biphilic reagents, N_3^- and NO_2^-, are characterized, in the reactions listed in Table II, by a low value of $\Delta H^{\neq}$ and a large negative $\Delta S^{\neq}$. This may be due to the more stringent stereochemical requirements of the transition states.

The effect of the basicity of the reagent upon its nucleophilicity can be shown to be greater for the Au(III) complexes by applying eq 2 to corresponding Pt(II) and Au(III) derivatives.[6,7] The Brønsted coefficient, α, which is very small when the coordinated chloride in $[Pt(bipy)Cl_2]$ is displaced (0.06),[17] becomes greater for $[AuCl_4]^-$ (0.15)[6] and even greater for cationic gold(III) complexes of the type $[Au(phen)Cl_2]^+$ (0.21), $[Au(bipy)Cl_2]^+$ (0.46), and $[Au(5\text{-}NO_2\text{-}phen)Cl_2]^+$ (0.89).[7] It should also be noted that, on going from $[AuCl_3am]$ to *trans*-$[Au(CN)_2Cl(am)]$, the *cis* effect of the cyanide ligands is ascribed to a positive inductive effect that increases the amount of negative charge at the reaction center.[9] The anomalously high reactivity of pyridine and even CH_3OH toward $[AuCl_4]^-$ might also be ascribed to this effect and to the greater importance of electrostatic effects in general.

All of these results agree well with the original proposal of Baddley and Basolo[5] that the extent to which bond formation develops in the rate-determining transition state is more important in the case of Au(III) than it is in Pt(II). However, it is also clear, mainly from the studies of heterocyclic amines as leaving groups,[8,9] that the extent of bond breaking is also more important for Au(III) than it is for Pt(II). It has now been observed in a number of studies that, although the nature of the leaving group affects the rate of reaction of a Pt(II) complex, it has no effect upon the nucleophilic discrimination factor. For example, it has been shown that, in a series of complexes of the types $[Pt(dien)X]^+$ [18a] (X = Cl, Br, I, or N_3) *trans*-$[Pt(C_5H_{11}N)_2NO_2X]$[18b] and $[Pt(bipy)NO_2X]$[19] (X = Cl, Br, I, NO_2, or N_3), when ligand X is replaced by a series of nucleophiles, a change of X does not lead to any change in the nucleophilic discrimination factor as measured by s in eq 1 but only affects the intrinsic reactivity (log k_s in eq 1). In other words, plots of log k_2 against n_{Pt} produce a series of parallel straight lines for the different leaving groups in any one series of complexes. This behavior has been interpreted as evidence for a relative independence of the bond-making and the bond-breaking aspects of the substitution. In so far as data are available, it is clear that no such simple relationship exists in the case of the Au(III) complexes, and it has already been pointed out, in the reactions of $[AuCl_3am]$, where the heterocyclic amine (am) is the leaving group, that not only is the nucleophilic discrimination power of the Au(III) dependent upon the nature of the leaving group but the order of relative nucleophilicity can also be changed.[8] This indicates a much closer interdependence of the bond-making and bond-breaking aspects of substitution. The observation that the reaction rates of the Au(III) complexes appear to be more sensitive than those of Pt(II) to both the nature of the entering group and that of the leaving group is in no way a paradox. The fact that bond making is more important does not, in any way, require that bond breaking is less important, or *vice versa*. It might be possible to approach such a situation, but certainly not reach it, in an associative mechanism when the stability of the five-coordinate intermediate increases sufficiently. In Figure 1 there is a collection of diagrammatic free-energy profiles for a bimolecular reaction showing how the truly synchronous process, with no intermediate, which represents one extreme (A), can develop into one where an intermediate of higher coordination number can form (B) and live long enough to come to thermal equilibrium with its environment. The increasing stability of this intermediate is represented by a deepening of the trough (C), and a situation can be envisaged

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the solvent. The errors introduced by not comparing the data under identical conditions of ionic strength are small compared to those introduced by not comparing them in the same solvent, and even these are negligible when compared to the magnitudes of the differences we are discussing.

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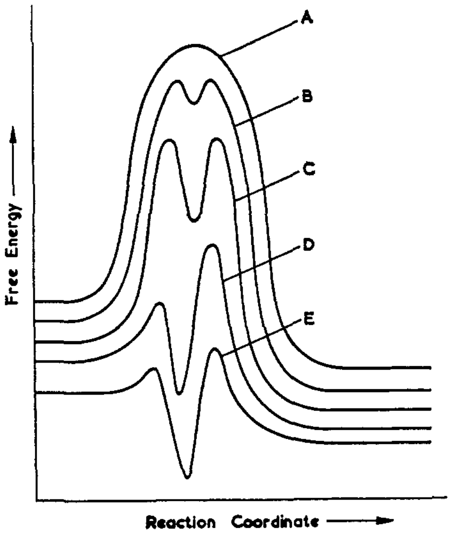

Figure 1. Diagrammatic representation of the free-energy profiles for a series of bimolecular substitutions where the stability of the trigonal bipyramidal intermediate increases with respect to the rate-determining transition state from A (no intermediate) to E (stable intermediate).

where the intermediate is more stable than the mixture of the reagents but less stable than the products (D). Finally a situation can be reached where the five-coordinate intermediate is more stable than either form of the four-coordinate system (E) and is not realistically referred to as a substitution reaction. Case A is typical of an SN2 process involving substitution at a tetrahedral carbon atom. Case D represents a situation recently reported[20] where the addition of amines to [$C_8H_{10}RhClSb(p\text{-tolyl})_3$] results in the rapid formation of a five-coordinate intermediate which then slowly loses the stibine ligand in the rate-determining step to give planar [$C_8H_{10}RhCl(am)$]. The behavior of Pt(II) and Au(III) complexes is represented by a situation between A and D.

We would like to suggest that the progressive stabilization of the five-coordinate intermediate on going from A to E in Figure 1 (provided that this is trigonal bipyramidal in form) represents the increasing covalency of all five metal–ligand bonds which, in valence-bond terms, could be expressed as the increasing utilization of the fifth orbital in the $d + s + p^3$ set of the metal. As this intermediate becomes more stable, the process of bond making becomes more and more divorced from that of bond breaking. In the limit, the addition of the incoming group to the complex is affected by the leaving group only in so far as this is one of the four ligands already present in the complex. The process of bond breaking would be affected in the same way by the now entered fifth ligand. In this way both must have some effect upon the reaction rates. However, if the rate-determining transition state is developed before the intermediate,[21] it would be reasonable to expect that the factors leading to the formation of the bond with the incoming group would have a much greater effect upon the rate of reaction than those leading to the subsequent breaking of the bond with the leaving group. If this transition state developed after the intermediate was formed, the reverse situation would obtain. As the intermediate becomes less stable and the mechanism approaches a synchronous process, it no longer becomes possible to divorce bond making from bond breaking and, in the rate-determining transition state, the bond with the incoming group is not fully developed and that with the leaving group is partly broken. It is therefore possible to explain the gross differences between Pt(II) and Au(III) reaction centers by saying that the five-coordinate intermediate developed in the reaction of a gold(III) substrate is less stable, with respect to the rate-determining transition state, than that appearing in the reactions of platinum(II). Both of these are less stable than the intermediate formed in the substitution reactions of planar Rh(I) where, in one case at least, the species can be observed without difficulty. This is in accord with the concept that the utilization of all five orbitals for covalent bonding becomes progressively more difficult as the effective nuclear charge of the central atom increases, *i.e.*, Rh(I) > Pt(II) > Au(III).[22]

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(20) L. Cattalini, A. Orio, R. Ugo, and F. Bonati, *Chem. Commun.*, 48 (1967).

(21) Reference 1, p 47.

(22) R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961); R. S. Nyholm and M. L. Tobe, *Experimentia Suppl.*, 9, 112 (1965).