SUBSTITUTION REACTIONS OF METAL COMPLEXES

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INTRODUCTION

Dating back to the time of the coordination theory, there has been a continued interest in the mechanisms of reactions of metal complexes. For example, Werner[1] called attention to the fact that some reactions of cobalt(III) complexes take place with rearrangement of configuration. In an attempt to explain these observations he suggested that stereochemical change during reaction was determined by the orientation of the entering group in the second coordination sphere relative to the leaving group in the first sphere. He envisioned these two groups trading places between the first and second coordination spheres, a picture which we will see is much the same as the current view of an interchange mechanism for substitution.

The degree of sophistication of the experiments designed, and of the interpretations given to the results obtained in investigations of mechanisms of reactions of metal complexes has been most impressive during the past decade. Details of these advances can be found in several books[2–5] that have been written on the subject. This paper will attempt only to summarize some of the general aspects of substitution reactions of metal complexes and will not give an exhaustive coverage of the literature. The discussion will be limited to reactions of inert metal complexes, because the reactions of labile systems were covered by Eigen[6] at the VII International Conference on Coordination Chemistry. This would appear to be an appropriate time for a plenary lecture on substitution reactions of metal complexes for there is wide-spread agreement on the gross aspects of the mechanisms involved. It is these aspects that will be discussed. Further investigations and deliberations will be necessary to attain a better understanding of the intimate details of the reaction processes.

OCTAHEDRAL SUBSTITUTION

The most common coordination number of metals being six, it follows that much of the work on substitution reactions of metal complexes has been done on these systems. Furthermore, most of these complexes have a nearly octahedral structure and one is dealing with octahedral substitution reactions. It will be of interest to await the results of investigations on substitution reactions of trigonal prismatic complexes[7]. The discussion that follows deals primarily with reactions of cobalt(III) complexes.

Aquation and anation reactions

Extensive studies have been made of the rates of aquation (or acid hydrolysis) of acidoamminecobalt(III) complexes and some studies have been made of the reverse anation reaction (Eq. 1).

$$[Co(NH_3)_5X]^{2+} + H_2O \underset{\text{anation}}{\overset{\text{aquation}}{\rightleftharpoons}} [Co(NH_3)_5H_2O]^{3+} + X^- \qquad (1)$$

The evidence that has accumulated suggests that these reactions proceed by a dissociation process in which bond-breaking between the leaving group and cobalt(III) is much more important than its bond-making with the entering group. In support of this for the aquation reaction, Langford[8] calls attention to the free energy relationship between the rates of aquation and equilibrium constants with changes in X^- for equation (1) (*Figure 1*). Since the slope of this line is 1·0, he suggests this indicates that the nature of the leaving group in the transition state is the same as that in the product, namely a solvated anion.

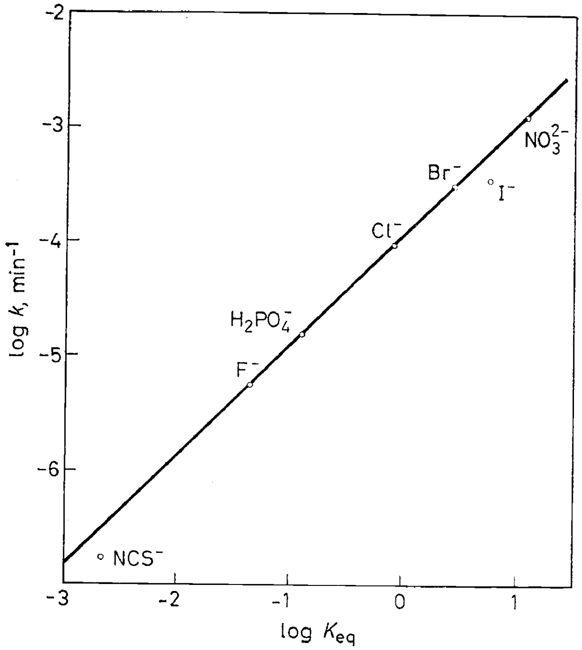


Figure 1. Linear free energy plot of the rate versus equilibrium for the aquation of $[Co(NH_3)_5X]^{2+}$. (From ref. 8)

This does not require that a five-coordinated reactive intermediate, which can survive several molecular collisions and discriminate between entering nucleophiles, be formed. Nor does it exclude the possibility of some attachment to the entering water in the transition state. It has been shown[9] that no intermediate is formed along the reaction pathway of sufficient stability to be selective in its reactions. This was done by allowing a water solution of $[Co(NH_3)_5X]^{2+}$ ($X = Br^-$ or NO_3^-) to react in the presence of added SCN^- and finding that this does not lead to the direct production of the thiocyanato complex. The experiment is conclusive because sufficient kinetic and equilibrium data are available to predict[10] the rate of capture of the intermediate $[Co(NH_3)_5]^+$, if the reaction were going by such a mechanism.

The anation reaction appears to take place by the rapid equilibration to an ion-pair (2) followed by a slow rearrangement of the ion-pair to yield the final acido product (Eq. 3).

$$[Co(NH_3)_5H_2O]^{3+} + X^- \xrightleftharpoons{K_{IP}} [Co(NH_3)_5H_2O]^{3+}\,X^- \tag{2}$$

$$[Co(NH_3)_5H_2O]^{3+}\,X^- \xrightarrow{K_{int}} [Co(NH_3)_5X]^{2+}\,OH_2 \tag{3}$$

Because of the interchange of positions between the inner and outer coordination spheres of the groups involved, reaction (3) is referred to as a *ligand interchange mechanism*[4]. The overall process may be called an *ion-pair ligand interchange mechanism.* There is ample evidence for the formation of ion-pairs in these systems and according to this mechanism the pseudo-first-order rate constant, k_{obs}, with X^- in excess is given by equation (4)

$$k_{obs} = \frac{k_{int}\,K_{IP}[X^-]}{1 + K_{IP}[X^-]} \tag{4}$$

Estimates have been reported[11] for values of k_{int} and compared with the rate of water exchange (*Table 1*).

These results show that the interchange rate constants k_{int} are almost insensitive to the nature of X^-. This result is the same as that found for many different systems for the rates of formation of metal complexes from the hydrated metal ions[6, 12]. Thus X^- does not make much of a contribution to the energetics of the interchange process, which then must be primarily one of dissociation. Since the majority of outer-sphere sites are occupied by water molecules in a 1:1 ion-pair, the most probable fate of the activated complex is recombination with an outer-sphere water molecule. Water exchange experiments show that it takes place about five times faster than substitution, which seems like a reasonable factor. The symbols used to designate this mechanism are either S_N1IP[2] or I_D[4]. Whatever symbolism or terminology is used makes little difference; the important point is that these

Table 1[a]. Interchange rate constants, k_{int}, compared with rates of water exchange, k_{H_2O}, for $[Co(NH_3)_5H_2O]^{3+}\,X^-$ at 45°C

X	k_{int}, sec^{-1}	k_{int}/k_{H_2O}
SO_4^{2-}	$2{\cdot}4 \times 10^{-5}$	0·24
Cl^-	$2{\cdot}1 \times 10^{-5}$	0·21
SCN^-	$1{\cdot}6 \times 10^{-5}$	0·16
$H_2PO_4^-$	$0{\cdot}77 \times 10^{-6}$ [b]	0·13
H_2O	$1{\cdot}0 \times 10^{-4}$	
	$5{\cdot}8 \times 10^{-6}$ [b]	

[a] From reference 11.
[b] At 25°C.

reactions appear to proceed by way of an ion-pair in which metal–ligand bond-breaking is of primary importance. Recent studies (F. Monacelli and A. J. Pöe, private communication show that the anation reactions of $[Rh(NH_3)_5HO_2]^{3+}$ may be faster than water exchange, suggesting an S_N2IP or I_a mechanism.

Two examples are known where reactions of cobalt(III) complexes take place by an S_N1(lim) rate. Wilmarth and his coworkers[13] have investigated reactions of the anionic complex $[Co(CN)_5H_2O]^{2-}$ in order to have a system free of complications due to ion-pair formation. The results obtained are in accord with the formation of a five-coordinated intermediate of sufficient stability to discriminate between the water molecules of the solvent and X^-. The reaction mechanism is represented by equations (5) and (6).

$$[Co(CN)_5H_2O]^{2-} \underset{k_w}{\overset{k_e}{\rightleftharpoons}} [Co(CN)_5]^{2-} + H_2O \qquad (5)$$

$$[Co(CN)_5]^{2-} + X^- \underset{k_a}{\overset{k_x}{\rightleftharpoons}} [Co(CN)_5X]^{3-} \qquad (6)$$

Data were collected which permit an estimate of the competition ratio $(k_x k_w)$ between X^- and water for the intermediate $[Co(CN)_5]^{2-}$. The results show the following order of decreasing nucleophilic reactivity of X^-: $OH^- > I_3^- > HN_3 > N_3^- > SCN^- >$ thiourea $> I^- > NH_3 > Br^- > S_2O_3^{2-} > NCO^- > H_2O$. The sequence is a little puzzling in that $[Co(CN)_5]^{2-}$ is expected to be a soft acid substrate. The high reactivity of the polarizable bases is expected, but the low reactivity of $S_2O_3^{2-}$ and the high reactivity of OH^- are unexpected.

This same type of S_N1(lim) mechanism was observed[14] for reactions of $[Co(NH_3)_5SO_3]^+$ and *trans*-$[Co(NH_3)_4XSO_3]$. The kinetic data obtained are in accord with the formation of the five-coordinated intermediate $[Co(NH_3)_4SO_3]^+$, assuming that SO_3^{2-} is present as a unidentate ligand. The nucleophilic order of reagents towards this substrate is similar to that found for $[Co(CN)_5]^{2-}$. The structures of these five-coordinated intermediates are not known.

Recent cleverly designed p.m.r. experiments[15] show that if the intermediate $[Co(NH_3)_5]^{3+}$ is generated by induced aquation reactions[10] (Eq. 7), it has a tetragonal pyramidal structure.

$$\left.\begin{array}{l}[Co(NH_3)_5X]^{2+} \xrightarrow{Hg^{2+}} \\ [Co(NH_3)_5N_3]^{2+} \xrightarrow{NO^+} \\ [Co(NH_3)_5OCONH_2]^{2+} \xrightarrow{NO^+}\end{array}\right| \longrightarrow [Co(NH_3)_5]^{3+} \xrightarrow{H_2O} [Co(NH_3)_5H_2O]^{3+} \qquad (7)$$

This was accomplished by using *trans*-$[Co(NH_3)_4ND_3X]^{2+}$ and observing that in all cases the reaction product was *trans*-$[Co(NH_3)_4ND_3H_2O]^{3+}$. The possible structures of $[Co(NH_3)_4ND_3]^{3+}$ are shown in *Figure 2*, and it is clear that only the tetragonal pyramid structure (a) will lead to the exclusive formation of the *trans* aquo product. The spontaneous reaction of *trans*-$[Co(NH_3)_4ND_3Br]^{2+}$ also yields the *trans* aquo product. This agrees with the observations that aquation reactions of *cis* and *trans*-$[Co(en)_2LX]^{n+}$ proceed with retention of configuration, except in the case of *trans* isomers where L is capable of π-bonding to the metal[16]. In such cases it is believed that rearrangement to a trigonal bipyramidal structure takes place to permit more efficient π-bonding[17].

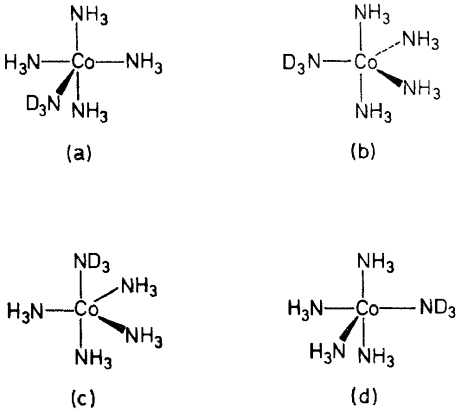


Figure 2. Possible structure for the intermediate $[Co(NH_3)_4ND_3X]^{3+}$ in the induced equation of *trans*-$[Co(NH_3)_4ND_3X]^{2+}$ by equation (7). (From ref. 15)

Base hydrolysis

The only reagent that has a large effect on substitution reactions of cobalt(III) ammines in aqueous solution is hydroxide ion. Rates of base hydrolysis reactions in one molar alkali solution exceed rates of acid hydrolysis by as much as eight orders of magnitude. The rate of base hydrolysis of reactions such as the one given in equation (8)

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Cl^- \qquad (8)$$

are second-order which may imply that these are simply S_N2 displacement reactions. However, this seems most unlikely because in such a case one would also expect other reagents to be effective, contrary to what is found. Also in accord with the second-order rate law is the S_N1CB (conjugate-base-dissociation) mechanism proposed by Garrick[18] and represented by equations (9), (10) and (11).

$$[Co(NH_3)_5Cl]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2Cl]^+ + H_2O \qquad (9)$$

$$[Co(NH_3)_4NH_2Cl]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4NH_2]^{2+} + Cl^- \qquad (10)$$

$$[Co(NH_3)_4NH_2{}^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+} \qquad (11)$$

For $[Co(NH_3)_5Cl]^{2+}$, it was reported[19a] that the rate of base hydrolysis shows less than a first-order dependance on hydroxide ion concentration at high base concentrations. However, recent rate studies[19b] show no deviation from first-order dependence on $[OH^-]$ even at $OH^- = 1{\cdot}0$ M.

There is considerable evidence in support of this mechanism which is discussed elsewhere[2-5]. Only those experiments designed to show the presence of an active intermediate will be mentioned here. Such experiments are definitive in that an S_N2 mechanism does not permit the formation of a five-coordinated intermediate. Two types of experiments have been used successfully. One is to carry out the base hydrolysis reaction in the presence of added reagents that compete as scavengers for any intermediate that is produced. The other is to determine the stereochemistry of products obtained from different substrates that may be reacting through a common intermediate.

The first example of a competition experiment was done with reaction (12) in dimethylsulphoxide solution[20].

$$[Co(en)_2NO_2Cl]^+ + Y^- \xrightarrow{OH^-} [Co(en)_2NO_2Y]^+ + Cl^- \qquad (12)$$

In the absence of base, the reaction is very slow, but it is extremely fast in the presence of added bases. Since $[Co(en)_2NO_2OH]^+$ does not react with Y^-, the role of OH^- is not one of direct attack on cobalt but rather one of producing some active intermediate. Presumably this is the five-coordinate conjugate base $[Co(en)(en\text{-}H)NO_2]^+$, which readily reacts with Y^-, picks up a proton to give the final product and regenerates the catalyst base. Identical results were recently obtained[21] for the base catalyzed reactions of *cis*-$[Rh(en)_2NO_2Cl]^+$ and of *trans*-$[Rh(en)_2NH_2CH_3Cl]^{2+}$.

Equivalent experiments have been carried out in water solution and the results also support the formation of an active intermediate and an S_N1CB mechanism. The first of these was done[22] using ^{18}O-labled water and determining the isotope fractionation factor during the base hydrolysis of $[Co(NH_3)_5X]^{2+}$. For $X = Cl^-$, Br^- and NO_3^-, this factor had a value of 1·0056 in accord with water attack rather than OH^-, and in agreement with X no longer being present in the active intermediate. Competition experiments have also been done between water and various reagents towards $[Co(NH_3)_5X]^{2+}$ in the presence of hydroxide ions[23]. Some of the data collected are shown in *Table 2*. The competition ratio $[Co(NH_3)_5Y]^{2+}/[Co(NH_3)_5OH]^{2+}$ does not depend on the leaving group X^- nor on the concentration of OH^-, but it does depend on Y^-. This requires that the role of OH^- be that of generating a common intermediate which in turn reacts either with water or Y^-, presumably as shown by the equation (13).

$$\begin{tikzcd}[row sep=small] & {[Co(NH_3)_5OH]^{2+}} \\ {[Co(NH_3)_4NH_2]^{2+}} \arrow[ur, "H_2O"] \arrow[dr, "Y^-"'] & \\ & {[Co(NH_3)_4NH_2Y]^+} \end{tikzcd} \qquad (13)$$

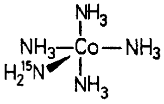
Table 2[a]. Formation of $[Co(NH_3)_5Y]^{2+}$ in the base hydrolysis ($[OH^-] = 0{\cdot}125$ M) of $[Co(NH_3)_5X]^{2+}$ in the presence of Y^- at 25°C.

	% $[Co(NH_3)_5Y]^{2+}$			
X =	I^-	Br^-	Cl^-	NO_3^-
$Y = NO_2^-$, 1·0 M	4·5	5·0	4·2	5·1
0·5 M	2·6	3·1	2·4	3·2
$Y = N_3^-$, 1·0 M	9·9[b]	8·7	8·5	10·2
0·5 M	5·9	5·3	4·9	6·3

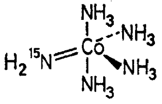
[a] From reference 23.
[b] At 1·0 M OH^-, 9·1; At 0·025 M OH^-, 8·6.

The acido amido species would then readily take on a proton from the solvent to give the pentaammine product. Similar results have been obtained for some rhodium(III) complexes[21].

In contrast to acid hydrolysis, base hydrolysis reactions of cobalt(III) ammines take place with extensive rearrangement[16]. This has been attributed to the stabilization of the five-coordinate conjugate base by π-bonding of the amido group to cobalt[17]. The most efficient π-bonding can be obtained with a trigonal bipyramidal structure and the amido group in the trigonal plane. With this working hypothesis, it is possible to account for the stereochemical changes that accompany the base hydrolysis of some $[Co(en)_2LX]^{n+}$ complexes[24]. This approach has recently received support from the observation[25] that the base hydrolysis of *trans*-$[Co(NH_3)_4{}^{15}NH_3X]^{2+}$ gives a product ratio of 50 per cent *cis* and 50 per cent *trans*-$[Co(NH_3)_4{}^{15}NH_3OH]^{2+}$. If the amido group is formed by the ammonia group *trans* to the leaving group, then it follows that $p\pi$–$d\pi$ bonding is not available to structure (I) but readily occurs in (II).



(I)



(II)

Structure (I) would lead to retention of configuration, whereas (II) can give rise to rearrangement in accord with experiment. That a common intermediate is formed is shown by the observation that the *cis*/*trans* product ratio is the same for $X = Cl^-, Br^-, NO_3^-$. This observation is the same as that made previously[26] that the isomeric products of base hydrolysis of *cis* and *trans*-$[Co(en)_2LX]^{n+}$ do not depend on the leaving group X^-.

Recently, it was suggested[27] that the active intermediate generated in the base hydrolysis of cobalt(III) ammines is not a five-coordinated conjugate base, but is instead a cobalt(II) species. For $[Co(NH_3)_5Cl]^{2+}$, the species formed from the 1:1 ion-pair is represented as $[Co^{II}(NH_3)_5Cl]^+, \cdot OH$. Since cobalt(II) complexes are substitution labile, such a system may provide a low energy path for reaction. However, this explanation does not account for the fact that hydroxide ion is as much as a million-fold more effective than other anions which are even better reducing agents. The ion-pair formation constant for the complex with hydroxide ion would not be much more than ten-fold greater than that for other mononegative anions.

Reactions in non-aqueous solvents

Tobe and his coworkers[28] have investigated the reactions of several cobalt(III) complexes in various solvents such as methanol, dimethylsulphoxide, sulpholane, dimethylformamide and dimethylacetamide. Keeping in mind that ion-pair formation constants are greater in these solvents than in water, it appears that the mechanism of ligand interchange in the ion-pair, as described for reactions in water, also applies to these non-aqueous solvents. Generally the rate of reaction increases with increasing concentration of the entering ligand and reaches a limiting rate when ion-pair formation is complete. Further complications are introduced by the formation of ion-pairs containing more than one anion per cation. As in water, the ligand interchange process is generally insensitive to the entering group and is best described in terms of bond-breaking or dissociation.

SQUARE PLANAR SUBSTITUTION

The chemistry of square planar complexes is almost synonymous with platinum(II) chemistry. Therefore, most of the work done on substitution reactions in these systems relates to investigations of platinum(II) complexes, but other low-spin d^8 systems have been studied and all appear to have the same general behaviour. Exhaustive reviews[2–5] have been written on the subject and only a brief summary will be given here along with some recent observations.

In contrast to octahedral substitution, the rates of reaction of square planar complexes show a pronounced dependance on the nature of the entering ligand. For a reaction of the type (14) a two-term rate law (15) is observed.

$$[MA_3X] + Y \longrightarrow [MA_3Y] + X \qquad (14)$$

$$\text{Rate} = \{k_1 + k_2[Y^-]\}\,[MA_3X] \qquad (15)$$

The reaction path represented by k_1 involves the solvent and that by k_2 is the direct displacement path by the entering nucleophile. Both paths are considered to take place by an S_N2 mechanism with an expansion of co-ordination number. The five-coordinated species in most systems is perhaps best designated as an active intermediate (see *Figure 3*) because many stable five-coordinated complexes are known[29].

Since the rates of reaction of square planar complexes respond to the nature of the entering reagent, it has been of interest to collect as much data as possible on a variety of different nucleophiles. Hopefully, this would permit an assessment of the factors that contribute to the nucleophilic strength of different reagents. The reactivities of several nucleophiles towards *trans*-$[Pt(py)_2Cl_2]$ in methanol solution relative to the solvolysis rate were reported[30] as values of n_{Pt} given by equation (16).

$$n_{Pt} = \log(k_Y/k_S) \qquad (16)$$

These values have been recalculated by first dividing the solvolysis constant by 26 moles/litre (the molar concentration of CH_3OH) and additional values have been determined[31] (*Table 3*). Edwards[32] suggested that a large amount of kinetic and thermodynamic data for organic and inorganic systems can be correlated by equation (17),

$$\log(k_Y/k_S) = \alpha P + \beta H \qquad (17)$$

where P is polarizability and H is proton basicity. On this basis the results in *Table 3* clearly show that the more important parameter in the Edwards equation is the polarizability term. Thus platinum(II) is a class (b) or soft metal and interacts best with soft nucleophiles[33].

It would be most helpful if one were able to apply the n_{Pt} values to predict the rates of reaction of other complexes containing class (b) metals which

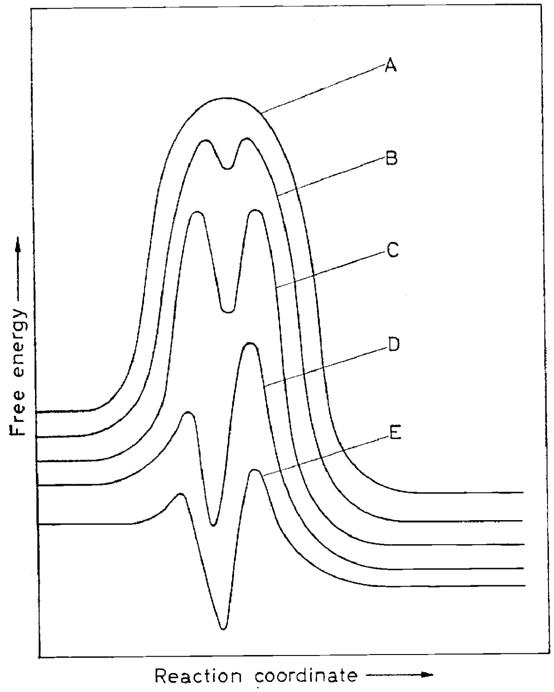


Figure 3. Free-energy profiles for a series of bimolecular substitution reactions where the stability of active intermediate progressively increases from A to E. (From ref. 35)

Table 3[a]. Properties of some nucleophiles Y

Y	pK_a	n_{Pt}	Y	pK_a	n_{Pt}
CH_3OH	−1·7	0·00	$S(CH_2)_4$	−4·8	5·14
CH_3COO^-	4·75	<2·0	$SnCl_3^-$	—	5·44
CO	—	<2·0	I^-	−10·7	5·46
CH_3O^-	15·7	<2·4	$Se(CH_2C_6H_5)_2$	—	5·53
F^-	3·45	<2·2	$Se(CH_3)_2$	—	5·70
Cl^-	−5·7	3·04	SCN^-	−0·7	5·75
NH_3	9·25	3·07	SO_3^{2-}	7·26	5·79
Imidazole	7·10	3·08	CNC_6H_{11}	—	6·34
Piperidine	11·21	3·13	$Sb(C_6H_5)_3$	—	6·79
Aniline	4·58	4·16	$As(C_6H_5)_3$	—	6·89
Pyridine	5·23	3·19	$SeCN^-$	—	7·11
NO_2^-	3·37	3·22	CN^-	9·3	7·14
$S(CH_2C_6H_5)_2$	—	3·43	$^-SC_6H_5$	6·52	7·17
N_3^-	4·74	3·58	$SC(NH_2)_2$	−0·96	7·17
NH_2OH	5·82	3·85	$P(OCH_3)_3$	—	7·23
N_2H_4	7·93	3·86	$S_2O_3^{2-}$	1·9	7·34
C_6H_5SH	—	4·15	$As(C_2H_5)_3$	<2·6	7·68
Br^-	−7·7	4·18	$P(C_6H_5)_3$	2·73	8·93
$S(C_2H_5)_2$	—	4·52	$P(n\text{-}C_4H_9)_3$	8·43	8·96
$P(N(C_2H_5)_2)_3$	—	4·54	$P(C_2H_5)_3$	8·69	8·99
$S(CH_3)_2$	−5·3	4·87			
$^-OP(OCH_3)_2$	—	5·01			
$S(CH_2)_5$	—	5·02			

[a] From reference 31

react by a displacement mechanism. However, nature is not this cooperative and at best only qualitative estimates or trends in rates can be assigned on the basis of these values. Even by restricting the consideration to platinum(II) complexes, substantial deviations can occur between calculated and experimental rate constants[34]. For π-bonding nucleophiles, such as $SeCN^-$, thiourea and NO_2^-, there is a positive deviation from the calculated rate for a complex of low charge such as $PtCl_4^{2-}$ and a negative deviation for a cationic complex such as $[Pt(dien)Cl]^+$.

The discriminating power of Au(III) in $AuCl_4^-$ was found[35] to be very much greater than that of Pt(II) in $PtCl_4^{2-}$. It is suggested that this can be explained in terms of the relative stabilities of the five-coordinated intermediates. The larger the stability of the intermediate, the more important becomes bond-breaking relative to bond-making, and consequently the entering group would have a smaller effect on the overall energetics of the process. Referring to *Figure 3,* the Au(III) system would be represented by B and Pt(II) by C. An example of D has been found[36] for the reaction of a Rh(I) complex in which the five-coordinated intermediate is readily formed followed by its slow dissociation to product. These results are in accord with the concept[37] that the utilization of all five orbitals for covalent bonding becomes progressively more difficult as the effective nuclear charge of the central atom increases in the order Rh(I) > Pt(II) > Au(III). Case E is one where the five-coordinated complex is more stable than either of the four-coordinated systems.

Several examples have been found of electrophilic catalysis in substitution reactions of some platinum(II) complexes[38]. It seems reasonable that a low-spin d^8 system with its d orbitals filled with electrons may behave as a Lewis base and be susceptible to attack by electrophilic reagents. Examples are known where metals in complexes donate electrons to H^+ or BF_3 to form stable addition compounds[39]. Kinetic studies have recently been reported[40] on the electrophilic reaction (18).

$$\begin{gathered} trans\text{-}[Pt(PEt_3)_2(CH_3)Cl] + (H^+, Cl^-) \rightarrow \\ trans\text{-}[Pt(PEt_3)_2Cl_2] + CH_4 \end{gathered} \tag{18}$$

The pseudo-first order rate constants, k_{obs}, depend on the concentration of acid and of chloride ion (19).

$$k_{obs} = \{k_2 + k_3[Cl^-]\}\ [H^+] \tag{19}$$

The reaction mechanism proposed is shown in *Figure 4.* This shows the formation of Pt(IV) active intermediates (A) and (B) followed by the loss of methane involving the activated complex (C). The importance of such reactions has achieved new dimensions with the fascinating chemistry of homogeneous catalysis, which often involves such reversible redox processes in low-spin d^8–d^6 systems[41].

PSEUDO-OCTAHEDRAL COMPLEXES

Steric factors are known to have a pronounced effect on the rates of substitution reactions. The presence of bulky ligands in an octahedral complex, other factors being similar generally accelerates its rate of reaction because of the driving force towards the formation of a less strained five-coordinated species. The reverse is true for reactions of square planar complexes where steric retardation occurs, in accord with a process that involves an expansion of coordination number. For example, the rate of aquation of $[Pd(dien)Cl]^+$ is approximately 10^4 times faster than that of the sterically hindered complex $[Pd(Et_4dien)Cl]^+$. Furthermore, it was also observed[42] that in the latter system the rate response to entering nucleophiles more closely resembled octahedral substitution than square planar substitution. Because of this behaviour the complex was designated a pseudo-octahedral complex.

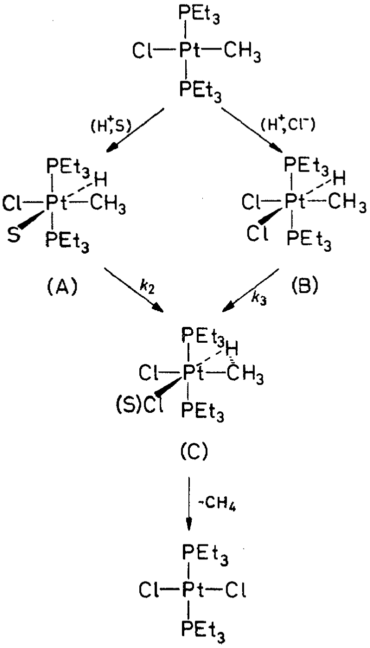


Figure 4. The mechanism proposed for the reaction of *trans*-$[Pt(PEt_3)_2Cl(CH_3)]$ with HCl. (From ref. 40)

For most of the nucleophiles used, the rate of reaction (20) is independent of Y^- (*Figure 5*).

$$[Pd(Et_4dien)X]^+ + Y^- \rightarrow [Pd(Et_4dien)Y]^+ + X^- \quad (20)$$

(dien $= NH_2C_2H_4NHC_2H_4NH_2$, Et₄dien $= (C_2H_5)_2NC_2H_4NHC_2H_4N(C_2H_5)_2$, MeEt₄dien $= (C_2H_5)_2NC_2H_4N(CH_3)C_2H_4N(C_2H_5)_2$)

Two exceptions to this are OH^- and $S_2O_3^{2-}$ which react both by a first (k_1) and a second (k_2) order path, in accordance with rate law (15). It was suggested[42] that the reactivity of OH^- is due to an S_N1CB mechanism, since it is not effective when the N—H hydrogen in the substrate is replaced by a methyl group. This cannot be the explanation for the reaction of $S_2O_3^{2-}$ which is a good reagent towards both substrates[43].

The reactivity of $S_2O_3^{2-}$ is probably due to its double negative charge, enhancing ion-pair formation, and its large nucleophilic strength (see $n_{\mathrm{Pt}} = 7{\cdot}34$ in *Table 3*). That both factors contribute to its reactivity is supported by the fact that neither SO_4^{2-} nor thiourea, respectively of low and high nucleophilic strength, are good reagents. Also in accord with a direct displacement by $S_2O_3^{2-}$ is the observation that the reaction of [Pd(MeEt$_4$dien)Cl]$^+$ with $OH^- + S_2O_3^{2-}$ yields the thiosulphato complex at a rate predicted by k_2. Had an aquo intermediate been produced, it would have instantly reacted with base to form the hydroxo complex, retarding the formation of the thiosulphato complex.

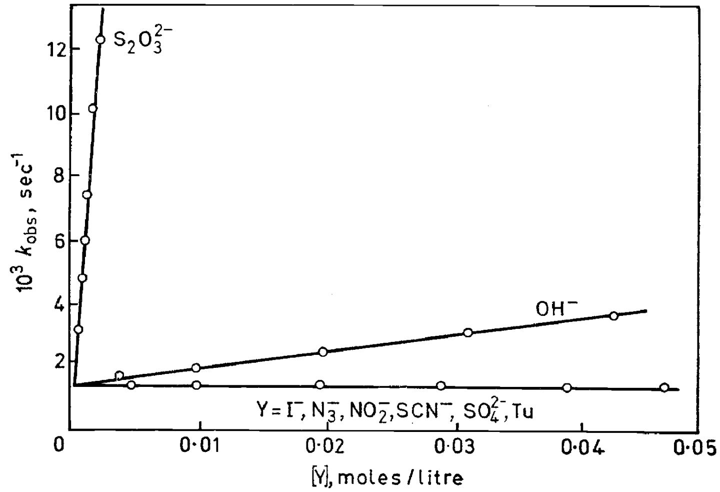


Figure 5. Rates of reaction of [Pd(Et$_4$dien)Br]$^+$ with various reagents in water at 25°C. (From ref. 43)

In further agreement with an S$_N$2IP mechanism are the data collected in *Table 4* for reaction (21).

$$[\mathrm{Pd(Et_4dien)H_2O}]^{2+} + \mathrm{Y}^- \rightarrow [\mathrm{Pd(Et_4dien)Y}]^+ + \mathrm{H_2O} \qquad (21)$$

Table 4[a]. Rates of reaction of [Pd(Et$_4$dien)H$_2$O]$^{2+}$ with Y at 25°C, $\mu = 0{\cdot}02$ and n_{Pt} values of Y

Y	n_{Pt}	k, M^{-1} sec^{-1}
$S_2O_3^{2-}$	7·34	1775
HSO_3^-	5·79	505
SCN^-	5·65	75
NO_2^-	3.22	13
Cl^-	3·04	7·4
Br^-	4·18	6·0
I^-	5·42	4·5
CH_3COO^-	<2·0	2.2
$SC(NH_2)_2$	7·17	1·4

[a] From reference 43.

Ion-pair formation constants have not been measured because the rate of water replacement is fast. However, theoretical estimates[44] suggest constants of the order of unity for Y^- and ten for Y^{2-} at the experimental ionic strength of $\mu = 0{\cdot}02$. Also it is seen that the reactivity of the halide ions decrease in the order $Cl^- > Br^- > I^-$, which is the same as the order of ion-pair formation. The nucleophilic strength towards a class (b) metal increases in the order $Cl^- < Br^- < I^-$ and for comparison the values of n_{Pt} are included in *Table 4*. Since the difference in the ion-pair formation constants of the complex with Cl^- and with I^- is expected to be less than one order of magnitude and their values of n_{Pt} differ by more than two orders of magnitude, it is surprising to find that Cl^- is the better reagent. This may be due to the smaller discriminating power of Pd(II) relative to Pt(II). Also the bulky Et$_4$dien ligand may sterically retard attack by the larger I^- and reduce its relative nucleophilic strength in this system.

However, there seems little doubt that the entering reagents in the ligand interchange process contribute to the displacement of the leaving group. This is shown by the wide spread in the rates of reaction for different univalent anions. Likewise, $S_2O_3^{2-}$ is a much more effective reagent than would be predicted on the basis of its charge alone. That this system reacts by an S_N2IP mechanism rather than the S_N1IP found for octahedral complexes seems reasonable. The pseudo-octahedral complex can still expand its coordination number, since stable five-coordinated complexes containing Et$_4$dien are known[45]. Thus the behaviour of such a sterically hindered system is intermediate between octahedral and square planar substitution.

TETRAHEDRAL SUBSTITUTION

The well-studied prototype of tetrahedral systems is, of course, the organic compounds containing four groups bound to carbon. It is well established that both S_N1 and S_N2 type reactions occur for such compounds. In contrast, compounds of other Group IV elements react by an S_N2 mechanism[46a]. The same appears to be true for reactions of phosphorus compounds[46b]. It does not seem unreasonable that four-coordinate compounds of elements such as Si(IV) and P(V) should react by a displacement process because they are known to form stable higher coordinated species.

Investigations of the kinetics and mechanism of tetrahedral substitution for transition metal compounds is largely limited to $Ni(CO)_4$ and the pseudo-nickel carbonyl series $CoNO(CO)_3$, $Fe(NO)_2(CO)_2$ and $Mn(NO)_3CO$. The compounds in this series are isoelectronic, presumably isostructural, and the metals may be assigned the formal charges Ni(0), Co(—I), Fe(—II) and Mn(—III). In spite of this close similarity, the rates and mechanism of substitution reactions of these compounds do differ. For example, reactions of $Ni(CO)_4$ are first-order, whereas reactions of $CoNO)CO)_3$ and $Fe(NO)_2(CO)_2$ follow second-order kinetics. A first- and second-order reaction path, corresponding to rate law (15), is found for $Mn(NO)_3CO$.

This same two term rate law is found for the reaction of $CoNO(CO)_3$ with poor nucleophiles or at low reagent concentrations[47], and with $Fe(NO)_2(CO)_2$ in tetrahydrofuran solutions.

In an earlier communication[48] it was reported that the carbon monoxide exchange reaction (22)

$$\mathrm{Ni(CO)_4 + L \rightleftarrows Ni(CO)_3L + CO} \qquad (22)$$

($L = {}^{14}CO$) appeared to occur by a different mechanism from other substitution reactions ($L = PR_3$, $P(OR)_3$, CNR). In all cases a first-order rate law was observed, i.e. the reaction rate was independent of the conconcentration of nucleophile. However, the activation parameters for exchange differed from the values obtained for substitution.

Recently the exchange reaction was reinvestigated[49] using $C^{18}O$ and following the rate of exchange by means of infrared studies. The results obtained differ from the earlier results obtained by using ^{14}CO and measuring radioactivity. The present $C^{18}O$ exchange kinetic data obtained in hexane solution are experimentally identical with the data obtained for the substitution reaction with $P(C_6H_5)_3$ in the same solvent. The data are: $k = 1{\cdot}2 \times 10^{-5}$ sec^{-1} at 10°C; $\Delta H\ddagger = 24{\cdot}2 \pm 0{\cdot}2$ kcal mole^{-1}; $\Delta S\ddagger = + 13 \pm 1$ e.u. Also competition experiments show that $C^{18}O$ and $P(C_6H_5)_3$ compete for the same active intermediate. It appears that $Ni(CO)_4$ reacts by an S_N1 mechanism. The error in the original ^{14}CO-exchange experiments is believed to be the occurrence of gas-phase exchange, caused by the volatility of $Ni(CO)_4$. Caution must be taken in the use of this ^{14}CO-exchange method.

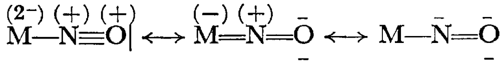
Compared with $Ni(CO)_4$, carbon monoxide exchange with $CoNO(CO)_3$ and with $Fe(NO)_2(CO)_2$ in toluene solution is extremely slow[50]. However, the nitrosyl carbonyls readily react with other reagents at rates that are first-order in substrate and first-order in reagent concentration[51a,b]. The reagent reactivity is in accord with the systems consisting of class (b) or soft metals and having a preference for soft ligand atoms in the usual order N < P > As > Sb. The relative reagent reactivity towards some different substrates are collected in *Table 5*.

Table 5. Relative rate constants for various nucleophiles towards different substrates. Values are for $k_Y/k_{P(C_6H_5)_3}$.

Substrate	C_5H_5N	$P(n\text{-}C_4H_9)_3$	$P(C_6H_5)_3$	$P(OC_6H_5)_3$	$As(C_6H_5)_3$
CH_3I (ref. 31)	0·017	50	1	0·015[a]	0·25
trans-$[Pt(py)_2Cl_2]$ (ref. 31)	2×10^{-6}	1·1	1	0·019[a]	0·009
$CoNO(CO)_3$ (ref. 51a)	0·04	90	1	0·03	0·002
$Fe(NO)_2(CO)_2$ (ref. 51b)	5·6	290	1	0·01	0·015
$MnNO(CO)_4$ (ref. 51c)	1·7	40	1	0·07	0·015
$C_5H_5Rh(CO)_2$ (ref. 51d)	Small	12	1	0·25	Small

[a] For $P(OCH_3)_3$.

Metal carbonyls often react by first-order processes, whereas corresponding metal nitrosyl carbonyls react with good reagents by second-order processes. Viewing only the M—NO portion of the nitrosyl compound, it is possible to write the canonical structures (I), (II), and (III).



$$\overset{(2-)}{M}-\overset{(+)}{N}\equiv\overset{(+)}{O}| \longleftrightarrow \overset{(-)}{M}=\overset{(+)}{N}=\underset{-}{\overset{-}{O}} \longleftrightarrow M-\overset{-}{N}=\underset{-}{\overset{-}{O}}$$

(I) (II) (III)

Although the ground state may be largely represented by (II), it is possible that (III) becomes important in the transition state. This localization of a pair of electrons on nitrogen would make available a vacant orbital of low energy on the metal which can then readily accept a pair of electrons from the entering nucleophile. Such a process in a metal carbonyl would be less likely because it would require the formation of $\overset{+}{\mathrm{M}}-\underset{-}{\overset{(-)}{\mathrm{C}}}=\underset{-}{\overset{-}{\mathrm{O}}}$, which is surely of higher energy than (III).

A most pronounced difference was also observed between the reaction of Co(NO(CO)$_3$) and of Fe(NO)$_2$(CO)$_2$. The rates of reaction of the cobalt compound are only slightly changed by changes in solvent, but contrary to what was reported[15b] it does react with halide ion. In contrast, solvents have a pronounced effect on the reactivity of the iron compound, which also readily reacts with halide ions. The rates of reaction of Fe(NO)$_2$(CO)$_2$ in toluene and in dichloromethane are about the same, but the complex reacts about 10^3 times faster in tetrahydrofuran and even faster in methanol. The rates of reaction of halide ions decrease in the order $Cl^- > Br^- > I^-$[51b].

The rates of reaction of Fe(NO)$_2$(CO)$_2$ in tetrahydrofuran solution as a function of nucleophile concentration are plotted in *Figure 6*. This shows that

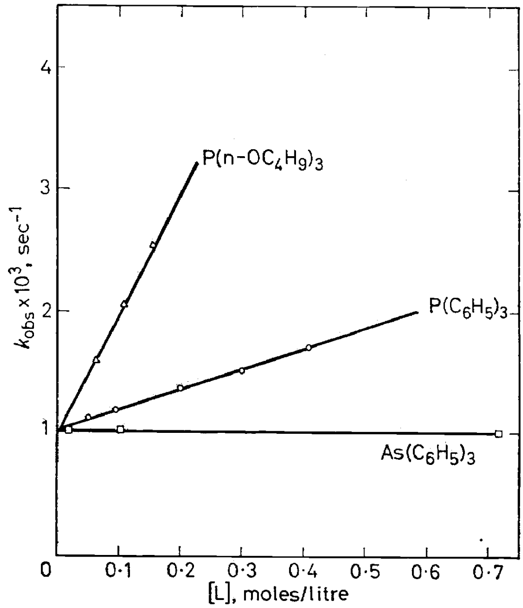
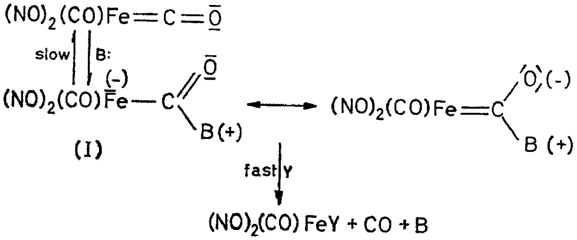


Figure 6. Rates of reaction of Fe(NO$_2$)(CO)$_2$ with various reagents in tetrahydrofuran at 25°C. (From ref. 51b)

the rates of reaction follow a two-term rate law of the type given by equation (15). For poor reagents such as As(C$_6$H$_5$)$_3$ the reaction takes place by the solvent path, whereas with good nucleophiles the k_2[Y] term contributes to the overall rate. For good reagents there is no detectable non-zero intercept for solvents such as toluene and dichloromethane and a poor reagent such as As(C$_6$H$_5$)$_3$ reacts extremely slowly. However, this reaction to form Fe(NO)$_2$COAs(C$_6$H$_5$)$_3$ in dichloromethane is catalyzed by the presence of halide ions, azide ion, methoxide ion, amines and imidizole. The catalytic effect of the halide ions decrease in the order $Cl^- > Br^- > I^-$.

There is ample evidence of nucleophilic attack on the carbonyl carbon of metal carbonyls usually involving hard bases such as amines and methoxide ion[52]. The greater reactivity of Cl^- over I^- also supports an attack at the hard carbonyl centre instead of the soft class (b) metal. Assuming that the solvent path provided by tetrahydrofuran and by methanol and the catalysis of reactions of $Fe(NO)_2(CO)_2$ proceed by carbonyl attack, then the mechanism for this path is represented by scheme (23).



(23)

Here B is the solvent or the catalyst and canonical structure (I) may be stabilized by delocalization of the electron density on iron due to the strong π-bonding NO groups.

TRIGONAL BIPYRAMIDAL SUBSTITUTION

Five-coordinated metal complexes are now commonplace and more such compounds are continuously being prepared[53]. In spite of this, kinetic and mechanism studies in these systems are as yet very limited. Heck[54] has made detailed studies on the reactions of various acylcobalt tetracarbonyls with triphenylphosphine. The rates are first-order and it is assumed that the reactions proceed by a dissociation process. Both steric and electronic factors of the acyl group have an effect on the rates of reaction.

Substitution reactions of $Fe(CO)_5$ and its derivative $Fe(CO)_4P(C_6H_5)_3$ are slow and take place by a first-order process[55]. However, the isoelectronic compound $MnNO(CO)_4$ reacts more rapidly and the rates of reaction are first-order in reagent concentrations[51c]. The nucleophilic strengths of reagents towards this substrate are in accord with its being a class (b) or soft metal (*Table 5*).

There is no information on the structure of the six-coordinated species in these reactions, nor on the four-coordinated species involved in the dissociation reactions.

CONCLUSION

The gross features of octahedral substitution and of square planar substitution reactions seem to be fairly well defined. With but a few possible exceptions, octahedral substitutions take place by primarily a dissociation process. Except in systems with excessive steric hindrance, square planar complexes react by a displacement mechanism. Reagents classified as soft bases are good nucleophiles towards these low-spin d^8 systems. Only limited studies have been made of substitution reactions of tetrahedral and of trigonal bipyramidal complexes. These systems, and metal complexes of higher and of lower coordination numbers, will have to be studied further before their mechanisms of substitution reactions are reasonably well understood

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