*Coordination Chemistry Reviews*, 100 (1990) 47–66
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# RETROSPECTIVE ON STUDIES OF LIGAND SUBSTITUTION REACTIONS OF METAL COMPLEXES

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(Received 30 March 1989)

CONTENTS

## A. INTRODUCTION

My interest in coordination chemistry stems from the delightful years (1940–1943) spent doing my thesis research under the able tutelage of Professor John C. Bailar, Jr. I then went to work on a classified research project (this was during World War II) in industry, and it was during these 3 years that I became interested in starting a research program on ligand substitution reactions of metal complexes. During those 3 years, I read several review papers and even books on physical organic chemistry. It appeared that the Hughes–Ingold $S_N1$ and $S_N2$ mechanisms [1], applied to

0010-8545/90/$7.00

tetrahedral substitution, should also apply to octahedral and to square-planar substitution reactions of metal complexes.

When I arrived at Northwestern University as a novice instructor in September 1946, there were no inorganic graduate students, there was no funding, and our equipment was largely limited to a Beckman DU spectrophotometer, a conductivity bridge and a Rudolph polarimeter. Fortunately, there was another instructor on our faculty, Ralph G. Pearson, who was doing research on physical organic chemistry. My initial mention to him of a possible collaboration doing much the same research he was doing but on metal complexes at first fell on deaf ears. After all, what was inorganic chemistry in those days; the action was largely in organic chemistry. However, the record shows that Ralph was finally seduced by inorganic chemistry, and the two of us had a most productive several years which resulted in 55 joint publications culminating with our book *Mechanisms of Inorganic Reactions* [2]. This article is a retrospective on those years of our research on the ligand substitution reactions of metal complexes.

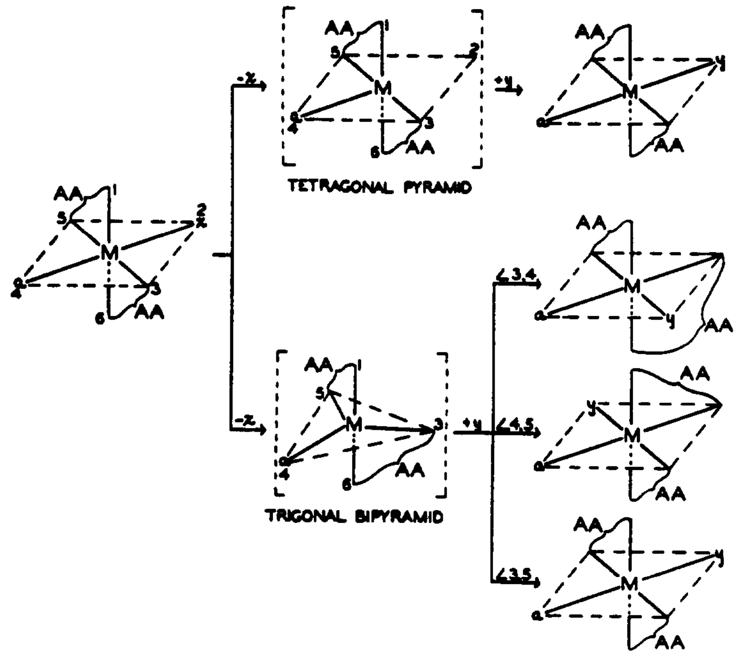
## B. OCTAHEDRAL SUBSTITUTION

### *(i) Cobalt(III) complexes*

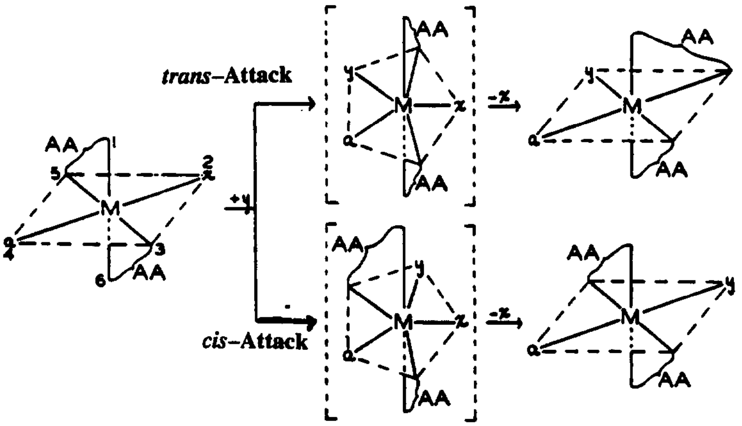
Werner [3], the "father" of coordination chemistry, arrived at his coordination theory on the basis of the large amount of research that had been done on cobalt(III) complexes. It was still true when we initiated our investigations of the mechanisms of octahedral substitution, that the place to start was with complexes of cobalt(III). Much was in the literature on stereochemical changes that take place during ligand substitution of cobalt(III) complexes, and also it was known that reactions take place at rates conveniently followed by conventional techniques (at the beginning of our studies, methods were not available for following fast reactions).

### *(a) Stereochemical changes*

Before the stereochemical changes that take place during ligand substitution reactions can be understood, it is necessary to know the molecularity of the reaction. This is clearly illustrated by tetrahedral substitution reactions at carbon, for which the bimolecular reaction takes place with inversion of configuration at carbon (Walden inversion) [4]. Even without the knowledge of the molecularity of octahedral substitution, it was possible to speculate [5] as to what rearrangements may accompany a dissociative and an associative pathway (Fig. 1). Using molecular models and considering only simple geometric isomers (*cis* and *trans*), it appeared that a dissociative pathway via a tetragonal pyramid would proceed with retention but via a trigonal bipyramid with rearrangement. For an associative pathway involving a



*Dissociation process* ($S_N1$) *for trans*-$[M(AA)_2ax]$



*Displacement* ($S_N2$) *process for trans*-$[M(AA)_2ax]$

Fig. 1. Plausible stereochemical changes during associative ($S_N1$) and dissociative ($S_N2$) octahedral substitution.

pentagonal bipyramid, *cis* attack at the metal proceeds with retention but *trans* attack goes with rearrangement.

Considerable work had been done on the stereochemistry of octahedral substitution by the pioneers [3] of metal complex chemistry. However, with the availability of UV–visible spectrophotometers, it became possible to extend and even sometimes quantify these studies. Stone [6] applied this technique to the quantitative estimation of the relative amounts of *cis* and *trans* isomer produced in situ by ligand substitution reactions of several cobalt(III) complexes. The results obtained were discussed in terms of the four mechanisms proposed (Fig. 1), but unfortunately no definite conclusion was reached other than "that no one of these mechanisms is operative in all substitution reactions".

A few years later, when it appeared that reactions of cobalt(III) take place by dissociation and that ligand-to-metal $\pi$ bonding is important, somewhat greater success was reported [7] to explain the stereochemical change accompanying these reactions. In a gross general way, what seemed to evolve is that the acid hydrolyses of $[Co(en)_2LCl]^{n+}$ take place with retention for *cis* isomers and for *trans* isomers with $L = NH_3$, $NO_2^-$, but with rearrangement for *trans* isomers where $L = Cl^-$, $Br^-$, $OH^-$, $NCS^-$. Base hydrolyses of geometric isomers of $[Co(en)_2LCl]^{n+}$ proceed largely with rearrangement. These experimental observations were explained on the basis of an $S_N1$ mechanism for acid hydrolysis (see Section B(i)(b)) and an $S_N1CB$ mechanism (see Section B(i) (c)) for base hydrolysis, along with the concept that a $\pi$-bonding ligand *trans* to the leaving group will stabilize a trigonal bipyramid intermediate. Complexes with *trans* ligands containing non-bonding *p*-orbital electron pairs ($Cl^-$, $Br^-$, $OH^-$ and $NCS^-$) in acid hydrolysis and $NH_2^-$ *trans* to the leaving group in base hydrolysis drive the five-coordinate intermediate towards a trigonal bipyramid structure. A tetragonal pyramid structure, because of orbital symmetry, does not allow $\pi$ bonding (ligand → metal) of the non-bonding *p*-orbital electrons.

Independent of our investigations, similar studies on the stereochemistry of octahedral substitution were being made concurrently at University College London [8]. There the stereochemical changes were discussed in terms of an edge-displacement mechanism, based on associative substitution ($S_N2$) reactions (later shown to be incorrect) of cobalt(III) complexes. Years later, I was told [9] how Sir Christopher Ingold would often ask to see "that Fred, Bob, and Ralph paper" [6], perhaps to indicate how Americans sometimes have trivial first names.

### *(b) Acid hydrolysis*

The first paper from our laboratory on the kinetics and mechanisms of substitution reactions of metal complexes was based on the work of Bergmann and coworkers [10]. Kinetic studies on the aquation of metal complexes had been reported [11] previously, but since the solvent water was also the reactant, its role as a possible nucleophile was not determined. The approach Bergmann used was similar to one used successfully by organic chemists for substitutions at tetrahedral carbon, i.e. the determination of the effect on rates of reaction made by systematic changes in steric size of spectator ligands on the central atom. Because the compounds used were readily prepared, this was first tried for $[(NH_3)_5CoO_2CR]^{2+}$ ($R = CH_3$, $C_2H_5$, $(CH_3)_2CH$, $(CH_3)_3C$). Since the rates of aquation were all about the same, it was concluded that if water was required in a nucleophilic attack on cobalt it must react by *trans* attack because *cis* attack is expected to show rate decreases with increasing size of R.

Boston [12] prepared a series of *trans*-$[Co(AA)_2Cl_2]^+$ complexes (AA = ethylenediamine and C–$CH_3$-substituted ethylenediamines, with the final one being $NH_2C(CH_3)_2C(CH_3)_2NH_2$) and investigated their kinetics of acid hydrolysis. The rates of aquation were found to increase dramatically (more than $10^3$ times) with increasing bulkiness of the diamine. This result argues against nucleophilic attack by water, because a rate-determining increase in coordination number from six to seven is expected to be retarded by an increase in the size of AA. Instead, the steric acceleration observed is consistent with a decrease in coordination number (six to five) or a dissociative mechanism. One more experiment had to be done in order to make certain that the rate increase is due to steric factors and not to an inductive effect of the slightly more basic substituted ethylenediamines which would put a greater electron density on the metal and make it easier to break the weaker Co–Cl bond. Bergmann and Meeker [13] tested the contribution of inductive effects on the rates of reaction by investigating the acid hydrolysis of $[Co(en)_2(Rpy)Cl]^{2+}$ (Rpy = pyridine, 4-$CH_3$py, 4-$CH_3O$py) and found that the rates increase with increasing basicity of Rpy, but only by a factor of less than 1.5. This is a very small rate increase compared with the greater than $10^3$-fold increase found with *trans*-$[Co(AA)_2Cl_2]^+$, where the basicities of AA are only slightly different compared with the greater than one order of magnitude difference in basicity of the Rpy ligands. The small inductive effect supports the view that the steric acceleration observed for *trans*-$[Co(AA)_2Cl_2]^+$ indicates a dissociative aquation reaction.

Two other observations related to acid hydrolysis reactions of $[Co(NH_3)_5X]^{2+}$ were made. Matoush [13(b)] observed that the rate of aquation of $[Co(NH_3)_5F]^{2+}$ increases with increase in acidity of the solution. This was attributed to a rapid equilibrium giving the complex $[Co(NH_3)_5FH]^{3+}$ which weakens the Co–F bond and results in an increase in rate of aquation. Moore [13(c)] showed that the acid hydrolysis of $[Co(NH_3)_5X]^{2+}$ in water solution does not give the intermediate $[Co(NH_3)_5]^{3+}$. Should this happen, then the addition of $Y^-$ to an aqueous solution of $[Co(NH_3)_5X]^{2+}$ would afford substantial amounts of $[Co(NH_3)_5Y]^{2+}$. What was found is that the immediate product is $[Co(NH_3)_5H_2O]^{3+}$, followed by its slow reaction with $Y^-$ to give $[Co(NH_3)_5Y]^{2+}$. This suggests that aquation involves a solvent-assisted dissociation pathway.

### *(c) Base hydrolysis*

The rates of base hydrolysis (at a pH of about 9) can be as much as $10^6$ times faster than the corresponding rates of acid hydrolysis (at a pH of about 1–3) of cobalt(III) ammine complexes. Second-order rate laws, first-order in complex and in $OH^-$ concentrations, are observed for these base hydrolysis reactions (eqn. (1)):

$$[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + Cl^- \tag{1}$$

Since $OH^-$ is the strongest base possible in water and since it is a good nucleophile towards organic halides, it was stated [8] that for the cobalt complex reaction (eqn. (1)) "the mechanism is well established and is certainly a bimolecular nucleophilic substitution $S_N2$". One troubling feature at the time was that it appeared that only $OH^-$ was a particularly good reagent and other nucleophiles (when properly buffered) had little effect on the rates of release of the leaving ligand. This made very attractive a mechanism involving a rapid acid–base pre-equilibrium (eqn. (2)), followed by a rate-determining dissociative step (eqn. (3)) and a rapid uptake of water (eqn. (4)):

$$[Co(NH_3)_5Cl]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4(NH_2)Cl]^{+} + H_2O \tag{2}$$

$$[Co(NH_3)_4(NH_2)Cl]^{+} \xrightarrow{\text{slow}} [Co(NH_3)_4(NH_2)]^{2+} + Cl^- \tag{3}$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+} \tag{4}$$

This mechanism, consistent with the second-order rate law, is given the symbol $S_N1CB$ because the rapid dissociation of the conjugate base (eqn. (3)) is rate determining. The acid–base pre-equilibrium (eqn. (2)) had been proposed [14] to account for H/D exchange in metal ammine complexes.

The late Sir Christopher Ingold and Sir Ronald Nyholm [8] insisted on a simple $S_N2$ mechanism for the base hydrolyses of cobalt(III) ammine complexes, rather than the $S_N1CB$ mechanism we championed. It then was necessary for Pearson and me to take on these two giants of chemistry. We are eternally grateful to Ingold and Nyholm for their help, and we thank our lucky stars we were not wrong.

A mechanism, like a scientific theory, can never be proven correct but it can be proven wrong. One can test a mechanism in various ways and if it always holds up to the test, then one believes that the mechanism may be correct. For example, the $S_N1CB$ mechanism for base hydrolysis requires that: (1) the cobalt(III) ammines contain protonic N–H hydrogen atoms; (2) the acid strength of the complex be weak in order to form only low equilibrium concentrations of the conjugate base; and (3) the H/D exchange be sufficiently fast to permit a sufficiently rapid acid–base pre-equilibrium required by the rate of base hydrolysis. All these conditions were met, when tested, rendering the $\mathrm{S_N1CB}$ mechanism attractive.

Meeker [15] prepared the complexes *trans*-$[\mathrm{Co(Rpy)_4Cl_2}]^+$ (Rpy = pyridine, 2-$\mathrm{CH_3}$py, 4-$\mathrm{CH_3}$py) and found the rates of solvolysis in water solution to be the same at pH 2 and at pH 9. This established that protonic N–H hydrogen atoms were needed for $\mathrm{OH^-}$ to be an effective reagent.

During the academic year 1954–1955, Professor Arthur Adamson and I enjoyed a delightful year at the Technical University of Denmark, with Professor Jannik Bjerrum as our gracious host. There we shared the laboratory that had been used by Professor S.M. Jørgensen, the real pioneer in the synthesis of metal complexes. Using the gradient-tube technique [16] for deuterium analyses in the laboratory of the late Professor Linderstrøm-Lang at the Carlsberg laboratory, we [17] measured the rate of H/D exchange of $[\mathrm{Co(NH_3)_5Cl}]^{2+}$. The exchange rate was found to be sufficiently fast to allow for an $\mathrm{S_N1CB}$ mechanism of the reaction (eqn. (1)).

In spite of the $\mathrm{S_N1CB}$ mechanism withstanding all the tests put to it, there came a time when it was necessary to prove that the $\mathrm{S_N2}$ mechanism was wrong. Schmidtke [18] was able to do this with the following observations (eqns. (5)–(8)):

$$[\mathrm{Co(en)_2NO_2Cl}]^+\ (10^{-3}\ \mathrm{M}) + \mathrm{NO_2^-}\ (10^{-1}\ \mathrm{M}) \xrightarrow{t_{1/2}=5\ \mathrm{h}} [\mathrm{Co(en)_2(NO_2)_2}]^+ + \mathrm{Cl^-} \tag{5}$$

$$[\mathrm{Co(en)_2NO_2Cl}]^+\ (10^{-3}\ \mathrm{M}) + \mathrm{OH^-}\ (10^{-3}\ \mathrm{M}) \xrightarrow{\text{complete, 2 min}} [\mathrm{Co(en)_2NO_2OH}]^+ + \mathrm{Cl^-} \tag{6}$$

$$[\mathrm{Co(en)_2NO_2Cl}]^+\ (10^{-3}\ \mathrm{M}) + \mathrm{NO_2^-}\ (10^{-1}\ \mathrm{M}) + \mathrm{OH^-}\ (10^{-3}\ \mathrm{M}) \xrightarrow{\text{complete, 2 min}} [\mathrm{Co(en)_2(NO_2)_2}]^+ + \mathrm{Cl^-} + \mathrm{OH^-} \tag{7}$$

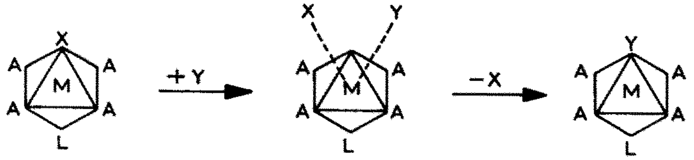
$$[\mathrm{Co(en)_2NO_2OH}]^+\ (10^{-3}\ \mathrm{M}) + \mathrm{NO_2^-}\ (10^{-1}\ \mathrm{M}) \longrightarrow \text{no reaction in hours} \tag{8}$$

The rates of base hydrolysis (eqn. (6)) and of the reaction with $\mathrm{NO_2^-}$ in the presence of $\mathrm{OH^-}$ are both very fast. If base hydrolysis (eqn. (6)) involves an $\mathrm{S_N2}$ pathway, then $\mathrm{OH^-}$ would attack cobalt and initially form $[\mathrm{Co(en)_2NO_2OH}]^+$. This hydroxo intermediate would then have to react rapidly to form the dinitro product (eqn. (7)), which is shown not to happen (eqn. (8)). Therefore the $\mathrm{S_N2}$ mechanism for the base hydrolysis of cobalt ammines was unequivocally proven wrong. Similar, more detailed, competition experiments were later reported [19] to support the $\mathrm{S_N1CB}$ mechanism.

When it finally became apparent that these base hydrolysis reactions in aqueous solution are specific to hydroxide ion, this brought into question the earlier report [8] of dual mechanisms for ligand displacements of cobalt complexes in alcoholic solutions. It was claimed that good nucleophiles ($OCH_3^-$, $N_3^-$ and $NO_2^-$) react with $[Co(en)_2Cl_2]^+$ by an $S_N2$ mechanism, while poor nucleophiles ($NCS^-$, $Br^-$, $Cl^-$ and $NO_3^-$) react by an $S_N1$ mechanism. Henry [20] was able to show that the large rates with good nucleophiles (basic anions) are almost completely repressed (except for ion-pair formation) by strong buffering, indicating that $OCH_3^-$ alone produces an increased rate. The rates with $OCH_3^-$ in methanol correlate with the rates with $OH^-$ in water (base hydrolysis), and the rates with other anions in methanol correlate with the rates of acid hydrolysis in water. Dissociation mechanisms are indicated in all cases.

### *(ii) Rhodium(III) and iridium(III) complexes*

In order to extend systematically our investigations on cobalt(III) complexes, it logically followed that analogous studies should be done on the other two members of the cobalt triad. Unfortunately, very little had been reported on the syntheses and reactions of rhodium(III) and iridium(III) complexes, so it was necessary first for Johnson [21] and Bauer [22] to prepare and resolve complexes of the type *cis*-D,L- and *trans*-$[M(en)_2XY]^+$ (M = Rh, Ir; X and Y = $Cl^-$, $Br^-$, $I^-$, $NO_2^-$, $NCS^-$). Johnson et al. [23] then studied the kinetics and mechanisms of hydrolysis reactions of rhodium(III) complexes that corresponded to our earlier studies on the analogous cobalt(III) complexes. The rates of reaction of rhodium(III) complexes are slower than those of cobalt(III) complexes, which is as expected for the more stable rhodium(III) complexes. Similarities and differences were found in the behavior of rhodium(III) compared with cobalt(III) complexes. Steric rate acceleration also occurs for rhodium(III) complexes, but it is less pronounced than for cobalt(III), and the suggestion was that the larger size of rhodium(III) reduces steric strain in the ground state. Furthermore, the rates of reaction of rhodium(III) complexes, like those of cobalt(III), except with $OH^-$, were found to be independent of the nature and concentration of nucleophile. One clear difference is that the charge on a rhodium(III) complex has little affect on its rate of reaction, while $[Co(NH_3)_4Cl_2]^+$ reacts $10^3$ times faster than does $[Co(NH_3)_5Cl]^{2+}$. This is believed to be due to the $S_N1$ reaction of cobalt(III) making it more difficult to break $Cl^-$ away from the larger cationic charge. This then argues for a greater degree of an association reaction for rhodium(III), with the higher cationic charge on its complex having opposing effects on bond breaking and bond making in the transition state. Also extremely important was the observation that rhodium(III) complexes, unlike cobalt(III) complexes, react with retention of configuration. In present terminology, the reaction mechanism may be described as dissociative ligand interchange ($I_d$) [24]. Substitution without stereochemical change can be described as *cis* attack (Fig. 1) or perhaps better as attack at a trigonal face of the octahedron with movement of the leaving group in the opposite triagonal face (eqn. (9)):

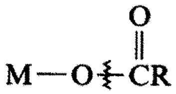


(9)

*trans* 100% *trans*

One other observation of a difference is that *trans*-$[Rh(en)_2Cl_2]^+$ solvolysis rates are the same at pH 1 and 13, but *cis*-$[Rh(en)_2Cl_2]^+$ and $[Rh(NH_3)_5Cl]^{2+}$ react more rapidly at the higher pH. It may be that in the latter two complexes the N–H protons *trans* to Cl may be sufficiently acidic to permit an $S_N1CB$ mechanism. Such a mechanism is supported by the results of competition experiments reported by Panunzi [25].

Bauer [22] studied the kinetics of substitution reactions of *trans*-$[Ir(en)_2X_2]^+$ ($X = Cl, Br, I$) and of *trans*-$[Ir(en)_2LCl]^+$ ($L = NCS, NO_2, Br, I$). The results obtained were similar to those for rhodium(III) complexes, but the rates were slower. The rates of reaction for this triad of complexes thus decrease in the order cobalt(III) > rhodium(III) > iridium(III). As with rhodium(III) complexes, it does appear that for iridium(III) complexes, bond breaking is also important in the transition state; therefore the mechanism can be designated as $I_d$. Furthermore, a kinetic *trans* effect was found to increase with change in L of *trans*-$[Ir(en)_2LCl]^+$ in the order $Cl^- < Br^- < NO_2^- < I^-$. The large *trans* effect of $I^-$ had previously been reported for rhodium(III) complexes by Bounsall and Poë [26]. Also of interest are the observations of Monacelli [27] that the rates of acid-catalyzed reactions of $[M(NH_3)_5(O_2CR)]^{2+}$ ($M = Co, Rh, Ir$; $R = CH_3, (CH_3)_3C, CF_3$) are all about the same. These results suggest acyl–oxygen bond fission



$$M{-}O \nmid \overset{\overset{\displaystyle O}{\|}}{C}R$$

a pathway where the metal has only a secondary effect on the rate-determining process.

Many of the early syntheses of rhodium(III) complexes reported [28] indicated that alcohol facilitates reaction. Rund [29] investigated the role of alcohol, and found that it is to reduce rhodium(III) and to generate catalytic amounts of rhodium(I). Catalysis then appears to occur by a two-electron inner-sphere transfer mechanism analogous to that described below (eqns. (11) and (12)) for platinum(II) catalysis of the substitution reactions of platinum(IV) complexes.

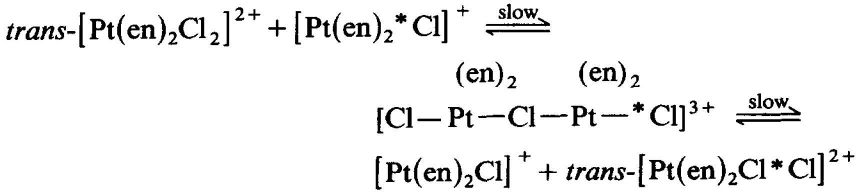
### *(iii) Platinum(IV) complexes*

Since octahedral substitution reactions of cobalt(III) complexes had been found to be dissociative, it was decided to search for an associative octahedral substitution in a system with stronger M–X bonds, thus requiring some bond-making assistance in the transition state for reaction. At that time, a logical choice seemed to be the platinum(IV) ammines. Initial experiments by Messing [30] on the reactions of *trans*-$[Pt(en)_2Cl_2]^{2+}$ with $Br^-$ to form the bromo complexes were extremely encouraging. Good kinetic data were obtained showing the reaction to be second order, with first-order dependence on concentrations of the complex and of $Br^-$. This seemed to be a clear case of an $S_N2$ octahedral substitution, but luckily just before communicating these results it was found that different preparations of platinum(IV) complexes gave good kinetic data with widely different rate constants. Catalytic amounts of some impurity had to be suspected and, because *trans*-$[Pt(en)_2Cl_2]^{2+}$ is prepared by chlorinating $[Pt(en)_2]^{2+}$, the presence of catalytic amounts of platinum(II) was a distinct possibility. Fortunately, 2 years before this, Taube [31] had discovered the one-electron inner-sphere transfer between $[Co(NH_3)_5Cl]^{2+}$ and $Cr^{2+}_{(aq)}$. A corresponding two-electron inner-sphere transfer between *trans*-$[Pt(en)_2Cl_2]^{2+}$ and $[Pt(en)_2]^{2+}$ seemed possible, and this was tested by studying the kinetics and mechanism of $^{36}Cl^-$ exchange. Wilks, Wilkins and Morris [32] found that $^{36}Cl^-$ exchange with *trans*-$[Pt(en)_2Cl]_2^{2+}$ in the presence of $[Pt(en)_2]^{2+}$ follows a third-order rate law (eqn. (10)):

$$\text{Rate} = k[\text{Pt(IV)}][\text{Pt(II)}][\text{Cl}^-] \qquad (10)$$

The mechanism proposed is that of a classical two-electron inner-sphere transfer (eqns. (11) and (12)):

$$[\text{Pt(en)}_2]^{2+} + {}^*\text{Cl}^- \xrightleftharpoons{\text{fast}} [\text{Pt(en)}_2{}^*\text{Cl}]^+ \qquad (11)$$



$$\textit{trans}\text{-}[\text{Pt(en)}_2\text{Cl}_2]^{2+} + [\text{Pt(en)}_2{}^*\text{Cl}]^+ \xrightleftharpoons{\text{slow}} [\text{Cl}-\overset{(\text{en})_2}{\text{Pt}}-\text{Cl}-\overset{(\text{en})_2}{\text{Pt}}-{}^*\text{Cl}]^{3+} \xrightleftharpoons{\text{slow}} [\text{Pt(en)}_2\text{Cl}]^+ + \textit{trans}\text{-}[\text{Pt(en)}_2\text{Cl}{}^*\text{Cl}]^{2+} \qquad (12)$$

Examples of using this mechanism for the design of syntheses of platinum(IV) complexes are given in Section D.

Uncatalyzed ligand substitution reactions of platinum(IV) complexes must be very slow, and have yet to be studied. Ellison [33] attempted this by a kinetic study of the reactions of some platinum(IV) chloroammines with $NO_2^-$ to effect $Cl^-$ replacement, but in the absence of platinum(II) the reaction has an induction period of 1–2 h. The induction period appears to produce platinum(II), and substitution then takes place by platinum(II) catalysis. Another attempt was made by Johnson et al. [34] with an investigation of the base hydrolysis of some platinum(IV) ammines. Unfortunately, because the complexes exist as different amido species in basic solution and because reduction accompanies hydrolysis, it was not possible to elucidate a reaction mechanism.

### *(iv) Ruthenium(III) complexes*

Broomhead [35] investigated the kinetics of acid and base hydrolysis of $[Ru(NH_3)_5Cl]^{2+}$ and found that base hydrolysis is about $10^6$ times faster than acid hydrolysis. This is similar to the base hydrolysis behavior of cobalt(III) complexes and different from chromium(III) and rhodium(III) complexes. The rates for the different metal ions were explained on the basis of an $S_N1CB$ mechanism. No conclusion was reached on the mechanism of acid hydrolysis.

The late Professor Allen [36] told me that the appearance of the paper by Broomhead was in part responsible for the discovery of the first $M–N_2$ complex, $[Ru(NH_3)_5N_2]^{2+}$. They were in the process of making similar kinetic studies, so when they saw the report [35] it was decided instead to study the mysterious reaction [37] of $RuCl_3$ with $N_2H_4$. The treatment of this reaction mixture with HCl is the method of synthesis of $[Ru(NH_3)_5Cl]^{2+}$. Investigations of the hydrazine reaction with $RuCl_3$, prior to HCl addition, led to the important discovery of $[Ru(NH_3)_5N_2]^{2+}$.

This discovery prompted much excitement among coordination chemists worldwide, and soon many such different compounds were prepared. In our laboratory, taking advantage of the efficient reaction between metal-azido ligands with $NO^+$ to give $N_2 + N_2O$, Kane-Maguire [38] prepared *cis*-$[Ru(en)_2(N_2)_2]^{2+}$. Later, it was further observed that $[Ru(NH_3)_5N_3]^{2+}$ reacts with strong acid to yield a mixture of $[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$ and $[Ru(NH_3)_5N_2]^{2+}$, presumably via the nitrene intermediate $[(NH_3)_5Ru–NH]^{3+}$.

### *(v) Chromium(III) complexes*

Munson [39] examined the kinetics of the acid and base hydrolysis of *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$, and found the rates of acid hydrolysis to be slightly greater than for the corresponding cobalt(III) complexes. This result was as expected [2] on the basis of the greater crystal field activation energy of $d^6$ low spin cobalt(III) vs. $d^3$ chromium(III). The remarkable result was that the rates of base hydrolysis are $10^5$ times less for chromium(III) than for cobalt(III) complexes. Such a result is not compatible with an $S_N2$ mechanism, but it was explained on the basis of an $S_N1CB$ mechanism. Since the conjugate bases are formed to about the same extent with both complexes, it was suggested that the cobalt(III) complex conjugate base is by far the more reactive towards ligand dissociation. The great reactivity of the cobalt(III) conjugate base was attributed [7] to repulsive $\pi$ interaction between filled $p$ orbitals of N in the amido group and filled $d_{xy}$ orbitals on the metal. This repulsive interaction provides a driving force for loss of the leaving group accompanied by rearrangement to a trigonal bipyramid intermediate, which then allows $\pi$ bonding between the filled $p$ orbital and the empty $d_{x^2-y^2}$ orbital. Clearly, $d^3$ chromium(III), with only half as many electrons as $d^6$ cobalt(III), does not supply as much driving force for base hydrolysis.

Moore [40] made the interesting observation that the large *trans* effect of $I^-$ in $[Cr(H_2O)_5I]^{2+}$ is responsible for the rapid exchange of only one water molecule with $H_2^{18}O$. It had been suggested [41] that the reaction of $[Cr(H_2O)_5I]^{2+}$ with $Cl^-$ to give a mixture of $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5Cl]^{2+}$ resulted from a competition between solvent water and $Cl^-$ for the presumed five-coordinate intermediate $[Cr(H_2O)_5]^{3+}$. Instead, this appears to involve a dissociative interchange, $I_d$, mechanism, where if a five-coordinated species exists it would be $[Cr(H_2O)_4I]^{2+}$.

## C. SQUARE-PLANAR SUBSTITUTION

### *(i) Platinum(II) complexes*

#### *(a) Associative mechanism*

At the beginning of our studies, platinum(II) complexes were to square-planar complexes what cobalt(III) complexes were to octahedral complexes. Naturally, because so much was known about the syntheses, stereochemistry and reactions of platinum(II) complexes, here was the place to commence a project on the mechanisms of square-planar substitution. In those days of valence bond theory, these $d^8$ systems were viewed as involving $dsp^2$ hybrid orbitals, leaving a vacant $p$ metal orbital of low energy which could accept a pair of electrons from an entering nucleophile. Furthermore, coordination numbers larger than four are commonplace, suggesting the possibility of an increase in coordination number and an associative ($S_N2$) mechanism for substitution. This all seemed plausible to coordination chemists, but it had yet to be adequately tested. Banerjea et al. [42] addressed the question of mechanism by investigating the kinetics of the $Cl^-$ replacement of *trans*-$[Pt(NH_3)_2Cl_2]$ with a large number of different entering ligands. The results showed two categories of entering ligands: one for which the rates of reaction were all the same, and the other with faster rates dependent on the nature and concentrations of the entering ligands. This suggested a dual pathway: one involving solvent and one proceeding directly with the entering ligand. Gray [43] demonstrated the importance of solvents by determining the rates of $^{36}Cl^-$ exchange with *trans*-$[Pt(py)_2Cl_2]$ in a variety of different solvents. A two-term rate law (eqn. (13))was established

$$\text{Rate} = k_1[\text{Pt(II)}] + k_2[\text{Pt(II)}][\text{Y}] \tag{13}$$

which was explained by a solvent pathway and a direct nucleophilic pathway:

$$\begin{tikzcd}
 & {[PtA_3(\text{solvent})X]} \arrow[r, "-X", "\text{fast}"'] & {[PtA_3(\text{solvent})]} \arrow[dd, "+Y"', "\text{fast}"] \\
{[PtA_3X]} \arrow[ur, "\text{solvent}", "k_s"'] \arrow[dr, "+Y", "k_y"'] & & \\
 & {[PtA_3XY]} \arrow[r, "-X", "\text{fast}"'] & {[PtA_3Y]}
\end{tikzcd} \tag{14}$$

*(b) Values of $\eta_{Pt}$*

Belluco, Catalini and Turco [44] quantified the nucleophilic strengths of 18 different entering ligands towards the standard substrate, *trans*-$[Pt(py)_2Cl_2]$. The nucleophilic reactivity constant, $\eta_{Pt}$, was defined as

$$\eta_{Pt} = \log\left(\frac{k_Y}{k_S}\right) \tag{15}$$

where $k_Y$ and $k_S$ are the rate constants (eqn. (14)) for the reactions of *trans*-$[Pt(py)_2Cl_2]$ in methanol. Values of $\eta_{Pt}$ vary from less than one for $CH_3O^-$ to 5.9 for $S_2O_3^{2-}$, the highest reported at the time. This million-fold difference in reactivities of nucleophiles towards platinum(II) complexes dramatically contrasts with nucleophilic reactivity towards cobalt(III) complexes, strongly supporting $S_N2$ and $S_N1$ mechanisms respectively. Furthermore, the strongest base in methanol, $CH_3O^-$, is the weakest nucleophile, supporting a special role for $OH^-$ in the base hydrolysis of cobalt(III) ammines ($S_N1CB$). The strongest nucleophiles towards platinum(II) complexes are the more polarizable, or soft, ligands, which is in keeping with the more stable soft–soft [45] interaction with the polarizable substrate.

*(c) Kinetic trans effect*

The kinetic *trans* effect (the *trans* labilizing ability of ligands *trans* to the leaving group) of platinum(II) complexes has been known for almost a century [46] and extensive use was made of the effect in the syntheses of platinum(II) complexes. Several theories of the *trans* effect were proposed [47] and gradually quantitative kinetic data were collected which showed the decreasing *trans* effect order [2] to be CO, $CN^-$, $C_2H_4 > PR_3$, $H^- > CH_3^-$, $SC(NH_2)_2 > C_6H_5^-$, $NO_2^-$, $I^-$, $SCN^- > Br^-$, $Cl^- >$ py, $NH_3$, $OH^-$, $H_2O$.

Professor Chatt and I worked out a collaboration in which we studied the kinetics of substitution reactions of the hydrido, alkyl, and aryl platinum(II) complexes prepared in his laboratory. This was done [48] by using the compounds *trans*-$[Pt(PEt_3)LCl]^+$ where $Cl^-$ was replaced, and the *trans* effect of L was found to decrease in the order $PMe_3 > PEt_3$, H > $PPr_3$ > Me > phenyl, *p*-methoxyphenyl, *p*-chlorophenyl > biphenyl > *o*-tolyl > mesityl > Cl.

Chatt [49] gave the following interesting account of why the research was so rapidly accomplished. "Shaw said 'that man Gray must be an absolute glutton for work. I did not know it was possible to do kinetics so fast; as soon as I get a compound out of the lab the result is in and he is waiting for another. I cannot keep up with him'." When I met Fred Basolo at our next conference he said "that guy Shaw's a worker. He nearly drove Harry Gray mad, the compounds came in so fast; as soon as he had done one the next compound was waiting".

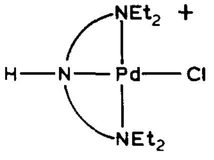
### *(ii) Nickel(II) and palladium(II) complexes*

Early investigations of the kinetics of square-planar substitutions were limited to platinum(II) complexes which react slowly enough to be followed by conventional methods. However, even before the use of techniques to study fast reactions were available, it was possible either to use complexes with poor leaving groups or to retard substitution sterically and investigate reactions of nickel(II) and palladium(II) complexes. Gray [50] reported rates of replacement of the poor leaving groups $NO_2^-$ and $SCN^-$ from $[Pd(dien)X]^+$ (dien = $H_2NC_2H_4NHC_2H_4NH_2$), which were about $10^6$ times faster than for substitution reactions of the corresponding platinum(II) complexes. Sterically hindered systems such as $[M(PEt_3)_2(o\text{-tolyl})Cl]$ show relative rates of reaction [48] with pyridine of $5 \times 10^6$, $1 \times 10^5$ and unity for nickel(II), palladium(II) and platinum (II) respectively.

This monotonic decrease in the rates of substitution is the usual behavior for triads of transition metals complexes, e.g. cobalt(III) > rhodium(III) > iridium(III) and nickel(II) > palladium(II) > platinum(II). However, some years later, Schuster-Woldan and Meier [51] observed that low valent metal complexes (transition metal organometallic complexes) undergo ligand substitution reactions with the second-row transition metal being the fastest to react, e.g. cobalt < rhodium > iridium and nickel < palladium > platinum. Advantage has been taken of this behavior in that most commercial homogeneous catalysis processes using organometallic complexes use second- row transition metals [52].

Baddley [53] prepared the extremely sterically hindered complex $[Pd(Et_4dien)_4X]^+$ ($Et_4dien$ = 1,1,7,7-tetraethyldiethylenetriamine) and found it to substitute X slowly by various nucleophiles at the same rate, with zero order in nucleophilic concentration. This suggested that the reactions are dissociative, and so the complex was called a pseudooctahedral complex.

The only reagent that enhanced the rate of X replacement was $OH^-$, with its lower $\eta_{Pt}$ value, suggesting a possible $S_N1CB$ mechanism. In fact, when the one N–H protonic hydrogen (structure I) was replaced by a methyl group (structure II), $OH^-$ was no longer an effective reagent. Later Goddard [54] observed that the reaction of $S_2O_3^{2-}$, a very strong nucleophile, with $[Pd(Et_4dien)Cl]^+$ follows a two-term rate law (see eqn. (14)). Furthermore, the solvent pathway, $k_1$, decreases in the order $H_2O > (CH_3)_2SO > CH_3OH > CH_3CN$, reflecting the ability of the solvent to coordinate with palladium(II) and to solvate the leaving group.



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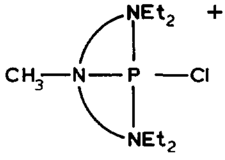


II

### *(iii) Gold complexes*

Baddley and Weick [55] investigated the kinetics of $Cl^-$ replacement in the complexes $[Au(dien)Cl]^{2+}$ and $[Au(Et_4dien)Cl]^{2+}$ and in their conjugate bases. The rates of reaction follow a two-term rate law (eqn. (13)) and presumably involve solvent ($k_1$) and direct nucleophilic ($k_2$) pathways (eqn. (14)) as do reactions of platinum(II) complexes. The relative contribution of the solvent pathway is much smaller for gold(III) complexes, which react about $10^5$ times faster than do the corresponding platinum(II) complexes. In addition, the gold(III) complexes are sufficiently acidic, so that in properly buffered solutions the species present is the conjugate base, e.g. $[Au(dien\text{-}H)Cl]^+$. The conjugate base reacts more slowly than its parent acid, in accordance with charge neutralization (bond making) being more important than charge separation (bond breaking) in the transition state for the reaction. The nucleophilic strengths of entering ligands decrease in the order $I^- > SCN^- > Br^- > N_3^- > OH^-$, showing again that $OH^-$ is a poor nucleophile towards such substrates.

## D. REACTION MECHANISMS AS A GUIDE TO SYNTHESES OF METAL COMPLEXES

In the 1940s and 1950s, inorganic chemists were preparing compounds by analogy to original recipes and with the aid of known trends in the Periodic Table. There is nothing wrong with this approach, which is still often used today. For some of us, studies of inorganic reaction mechanisms had as its goal not only a fundamental understanding of how such reactions take place, but also the possible use of this knowledge in the synthesis of known compounds by new methods or in the syntheses of new compounds. Organic chemists were making good use of their knowledge of mechanisms in syntheses, and there was no reason why inorganic chemists could not do the same. This was achieved in our laboratory [56] and by others in the late 1950s and 1960s. A few illustrative examples from our laboratory are given below.

### *(i) Linkage isomers*

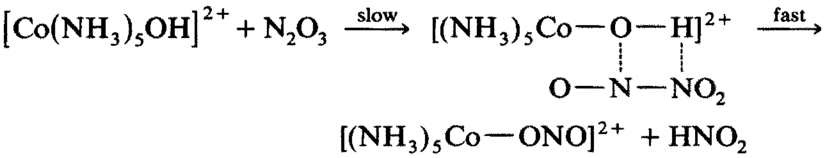
Henry and Bergmann [57] investigated the well-known synthesis of $[Co(NH_3)_5NO_2]^{2+}$ by the reaction of $[Co(NH_3)_5Cl]^{2+}$ with $NO_2^-$. They observed that aquation was the first thing to happen, and so it was decided to study the kinetics of the reaction of $[Co(NH_3)_5H_2O]^{3+}$ with buffered $NO_2^-$. The reaction was found to have a third-order rate law:

$$\text{Rate} = k[\text{Co(III)}][HNO_2]^2 \qquad (16)$$

This rate law is similar to that for the nitrosation of amines [58], and a three-step mechanism is suggested:

$$[Co(NH_3)_5H_2O]^{3+} + H_2O \xrightleftharpoons{\text{fast}} [Co(NH_3)_5OH]^{2+} + H_3O^+ \qquad (17)$$

$$2HNO_2 \xrightleftharpoons{\text{fast}} N_2O_3 + H_2O \qquad (18)$$



$$[Co(NH_3)_5OH]^{2+} + N_2O_3 \xrightarrow{\text{slow}} \begin{array}{c}[(NH_3)_5Co-O-H]^{2+}\\ \vdots\quad\vdots\\ O-N-NO_2\end{array} \xrightarrow{\text{fast}} [(NH_3)_5Co-ONO]^{2+} + HNO_2 \qquad (19)$$

The nitrito complex (Co–ONO) was then believed to rearrange intramolecularly to give the thermodynamically stable nitro ($Co-NO_2$) product. Oxygen-18 labeling experiments by Murmann and Taube [59] later supported this mechanism.

With this mechanistic information at hand, it appeared that it should be possible to design experiments for preparing new metal nitrito isomers which, at the time, were known only for cobalt(III) complexes. Hammaker [60] accepted the challenge and was rewarded with almost immediate success in the syntheses and characterization of the new nitrito complexes $[M(NH_3)_5ONO]^{n+}$ (M = Rh(III), Ir(III), Pt(IV)). This is one publication of ours for which I always remember the reference (Inorg. Chem., 1 (1962) 1). When Hammaker did her library work on the synthesis of $[Rh(NH_3)_5H_2O]^{3+}$, she read that S.M. Jørgenson [61] (pioneer expert on syntheses of metal complexes who had prepared the cobalt(III) nitrito isomer) had tried to prepare $[Rh(NH_3)_5ONO]^{2+}$ and failed. If he could not prepare the rhodium(III) nitrito isomer, she wondered if we could not select a more promising project. Jørgenson, knowing that rhodium(III) complexes react more slowly than cobalt(III) complexes, carried out the reactions at elevated temperatures which gave only the thermodynamic product, $[Rh(NH_3)_5NO_2]^{2+}$. The nitrosyl attack step (eqn. (19)) does not require M–O bond cleavage, and so the metal plays only a minor role in determining the rate of reaction, which means that the rates of reaction for cobalt(III) and rhodium(III) were expected to be about the same. In fact, the nitrito kinetic products of rhodium(III), iridium(III) and platinum(IV) were prepared and isolated at 0 °C before there was time for rearrangement to the stable nitro isomers.

Having tasted success in making new linkage isomers for the first time since Jørgensen [61] discovered the cobalt(III) nitrito–nitro isomers in 1893, it was tempting for researchers to try to prepare such isomers using other ambidentate ligands. Thiocyanate ion was known to coordinate to metals to form either M–NCS or M–SCN complexes, but no linkage isomers had been reported. This seemed to be the place to look for new linkage isomers, and the guide to synthesis could be the recently elucidated mechanisms of reactions. An early attempt [62] at preparing such linkage isomers of chromium(III) complexes, based on an inner-sphere electron-transfer reaction between Co(III)–NCS complexes and $Cr^{2+}_{(aq)}$, had failed. Since it appeared that this reaction should have yielded as a kinetic product the S-bonded isomer $[(H_2O)_2Cr{-}SCN]$, Burmeister and Poë [63] spent considerable time using various approaches of this type, but with no success (later others [64] were able to obtain spectroscopic evidence for the formation of Cr(III)–SCN). What did finally work for Burmeister [63] was based on an observation that for palladium(II) and platinum(II), coordinated thiocyanate ion is either S or N bonded, depending on the nature of the other ligands present. Therefore it was decided to use a ligand near the cross-over point for S and N bonding of thiocyanate ion, and to use palladium(II) complexes known to undergo rapid ligand substitution. The ligand chosen was $AsPh_3$ and the conditions were 0 °C in methanol solution. The kinetic product was the Pd–SCN isomer, which at elevated temperatures rearranges into the thermodynamic product Pd–NCS:

$$[Pd(SCN)_4] \xrightarrow[-SCN^-]{+AsPh_3,\ 0\,^\circ C} [Pd(SCN)_2(AsPh_3)_2]_{(s)} \xrightarrow[30\ \text{min}]{156\,^\circ C} [Pd(NCS)_2(AsPh_3)_2]_{(s)} \qquad (20)$$

Unlike the Hammaker [60] synthesis which met with immediate success, the Burmeister synthesis met success only after many different fruitless attempts. In fact, so excited was he with success that he telephoned me from the laboratory at 1 a.m. to awake me to announce "it worked, it worked, at last we have it!" Burmeister went on to become an expert on linkage isomers of metal complexes, and his review [65] on the subject won "this week's citation classic" citation on 4 July 1988.

Burmeister, Baddley and Weidenbaum [66] were also able to demonstrate the importance of steric factors with the synthesis of linkage isomers of $[Pd(Et_4dien)(NCS)]^+$. It was further shown, unlike the intramolecular isomerization of nitrito → nitro, that in this system Pd–SCN isomerizes to Pd–NCS by an intermolecular mechanism.

### *(ii) Platinum(IV) complexes*

Finally, platinum(IV) complexes are generally prepared by the oxidation of the corresponding platinum(II) complexes, e.g. $[Pt(NH_3)_4]^{2+} + Cl_2 \rightarrow$ *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$. With the discovery [32] of the platinum(II) catalysis of substitution reactions of platinum(IV) complexes (eqns. (11) and (12)), it appeared that this route should offer a new approach to the syntheses of platinum(IV) complexes. For example, Johnson [67] made use of this mechanism to prepare for the first time the complex *trans*-$[Pt(en)_2(SCN)_2]^{2+}$. The reaction of *trans*-$[Pt(en)_2Cl_2]^{2+}$ with $NCS^-$ in the presence of catalytic amounts of $[Pt(en)_2]^2$ under mild conditions afforded the desired product in high yield. The same mechanism was able to explain [32] what had been reported [68], but it always appeared a little suspect that $[Pt(NH_3)_5Cl]^{3+}$ reacts with HCl in the presence of $[Pt(NH_3)_4]^{2+}$ to give high yields of *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$.

## ACKNOWLEDGEMENTS

I want to thank Professor A.B.P. Lever for his invitation to write this article, which I enjoyed doing because it recalled pleasant memories of the "good old days". I thank Professor R.G. Pearson for our years of productive collaboration; neither one of us could have done it alone. I am grateful to all the students and post-doctorate students who did the research and who are responsible for many of the ideas. Over the years different aspects of this research were supported by the Atomic Energy Commission, the National Science Foundation, the National Institutes of Health, the Office of Air Force Scientific Research and Northwestern University.

## REFERENCES

1 C.K. Ingold, Structure and Mechanisms in Organic Chemistry, 2nd edn., Cornell University Press, Ithaca, 1969.

2 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd edn., New York, 1967.

3 A. Werner, Z. Anorg. Chem., 3 (1893) 267; Ann., 386 (1912) 139; Ber., 44 (1911) 879.

4 P. Walden, Ber., 28 (1895) 1287, 2766.

5 F. Basolo, Chem. Rev., 52 (1953) 459.

6 F. Basolo, B.D. Stone and R.G. Pearson, J. Am. Chem. Soc., 75 (1953) 819.

7 R.G. Pearson and F. Basolo, J. Am. Chem. Soc., 78 (1956) 4878; Inorg. Chem., 4 (1965) 1522.

8 D.D. Brown, C.K. Ingold and R.S. Nyholm, J. Chem. Soc., (1953) 2673, 2680, 2696. C.K. Ingold, R.S. Nyholm and M.L. Tobe, J. Chem. Soc., (1956) 1691, 1707.

9 M.L. Tobe, personal communication, 1960.

10 F. Basolo, J.G. Bergmann and R.G. Pearson, J. Phys. Chem., 56 (1952) 22.

11 A.B. Lamb and J.W. Marden, J. Am. Chem. Soc., 33 (1911) 1873.
J.N. Bronsted, Z. Phys. Chem., 122 (1926) 383.
F.J. Garrick, Trans. Faraday Soc., 34 (1938) 1088.
A.W. Adamson, J.P. Welker and M. Volpe, J. Am. Chem. Soc., 72 (1950) 4030.

12 R.G. Pearson, C.R. Boston and F. Basolo, J. Am. Chem. Soc., 75 (1953) 3089.

13 (a) F. Basolo, J.G. Bergmann, R.E. Meeker and R.G. Pearson, J. Am. Chem. Soc., 78 (1956) 2676.
(b) F. Basolo, W.R. Matoush and R.G. Pearson, 78 (1956) 4883.
(c) J.W. Moore and R.G. Pearson, Inorg. Chem., 3 (1964) 1334.

14 F.J. Garrick, Nature (London), 139 (1937) 507.
J.S. Anderson, H.V.A. Briscoe and N.L. Spoor, J. Chem. Soc., (1943) 361.

15 R.G. Pearson, R.E. Meeker and F. Basolo, J. Inorg. Nucl. Chem., 1 (1955) 342; J. Am. Chem. Soc., 78 (1956) 709.

16 K. Linderstrøm-Lang, O. Jacobsen and G. Johnsen, C. R. Trav. Lab. Carlsberg, Ser. Chim., 23 (1938) 17.

17 A.W. Adamson and F. Basolo, Acta Chem. Scand., 9 (1955) 1261.

18 F. Basolo, H.H. Schmidtke and R.G. Pearson, J. Am. Chem. Soc., 82 (1960) 4434.

19 M. Green and H. Taube, Inorg. Chem., 2 (1963) 948.
D.A. Buckingham, I.I. Olsen and A.M. Sargeson, J. Am. Chem. Soc., 88 (1966) 5443.

20 R.G. Pearson, P.M. Henry and F. Basolo, J. Am. Chem. Soc., 79 (1957) 5382; J. Am. Chem. Soc., 79 (1957) 5379.

21 S. Anderson and F. Basolo, J. Am. Chem. Soc., 82 (1960) 4423.
S.A. Johnson and F. Basolo, Inorg. Chem., 1 (1962) 925.

22 R.A. Bauer and F. Basolo, J. Am. Chem. Soc., 90 (1968) 2437; J. Chem. Soc., Chem. Commun., 252 (1968) 458; Inorg. Chem., 8 (1969) 2231.

23 S.A. Johnson, F. Basolo and R.G. Pearson, J. Am. Chem. Soc., 85 (1963) 1741.

24 C.H. Langford and H.B. Gray, Ligand Substitution Processes, Benjamin, New York, 1965.

25 A. Panunzi and F. Basolo, Inorg. Chim. Acta, 1 (1967) 223.

26 F. Basolo, E.J. Bounsall and A.J. Poë, Proc. Chem. Soc., London, (1963) 366.

27 F. Monacelli, F. Basolo and R.G. Pearson, J. Inorg. Nucl. Chem., 24 (1962) 1241.

28 M. Delepine, Bull. Soc. Chim. Fr., 45 (1929) 235; C. R., 236 (1953) 559.

29 J.V. Rund, F. Basolo and R.G. Pearson, Inorg. Chem., 3 (1964) 658.

30 A.F. Messing, Ph.D. Dissertation, Northwestern University, Evanston, IL, 1957.

31 H. Taube, J. Am. Chem. Soc., 77 (1955) 4481.

32 F. Basolo, P.H. Wilks, R.G. Pearson and R.G. Wilkins, J. Inorg. Nucl. Chem., 6 (1958) 161.
F. Basolo, M.L. Morris and R.G. Pearson, Faraday Discuss. Chem. Soc., 29 (1960) 80.

33 H.R. Ellison, F. Basolo and R.G. Pearson, J. Am. Chem. Soc., 83 (1961) 3943.

34 R.C. Johnson, F. Basolo and R.G. Pearson, J. Inorg. Nucl. Chem., 24 (1962) 59.

35 J.A. Broomhead, F. Basolo and R.G. Pearson, Inorg. Chem., 3 (1964) 826.
36 A.D. Allen and C. Senoff, J. Chem. Soc., Chem. Commun., (1965) 61.
A.D. Allen and F. Bottomely, Acc. Chem. Res., 1 (1968) 360.
37 K. Gleu and K. Rehm, Z. Anorg. Allg. Chem., 227 (1936) 237.
38 L.A.P. Kane-Maguire, P.S. Sheridan, F. Basolo and R.G. Pearson, J. Am. Chem. Soc., 90 (1968) 5295.
L.A.P. Kane-Maguire, F. Basolo and R.G. Pearson, J. Am. Chem. Soc., 91 (1969) 4609.
39 R.G. Pearson, R.A. Munson and F. Basolo, J. Am. Chem. Soc., 80 (1958) 504.
40 P. Moore, F. Basolo and R.G. Pearson, Inorg. Chem., 5 (1966) 223.
41 M. Ardon, Inorg. Chem., 4 (1965) 372.
42 D. Banerjea, F. Basolo and R.G. Pearson, J. Am. Chem. Soc., 79 (1957) 4055.
43 R.G. Pearson, H.B. Gray and F. Basolo, J. Am. Chem. Soc., 82 (1960) 787.
44 U. Belluco, L. Cattalini, F. Basolo, R. Pearson and A. Turco, J. Am. Chem. Soc., 87 (1965) 241.
45 R.G. Pearson, J. Am. Chem. Soc., 85 (1963) 3533.
46 A. Werner, Z. Anorg. Allg. Chem., 3 (1893) 267.
I.I. Chernyoev, Ann. Inst. Platine (USSR), 4 (1926) 243, 261.
47 A.A. Grinberg, Ann. Inst. Platine (USSR), 10 (1932) 58.
Y.K. Syrkin, Isv. Akad. Nauk (SSSR) Otd. Khim. Nauk, (1948) 69 (Chem. Abs., 42 (1948) 5368.
J. Chatt, L.A. Duncanson and L.M. Venanzi, J. Chem. Soc., (1955) 4456.
L.E. Orgel, J. Inorg. Nucl. Chem., 2 (1956) 137.
48 F. Basolo, J. Chatt, H.B. Gray, R.G. Pearson and B.L. Shaw, J. Chem. Soc., (1961) 2207.
49 J. Chatt, Adv. Organomet. Chem., 12 (1974) 2.
50 F. Basolo, H.B. Gray and R.G. Pearson, J. Am. Chem. Soc., 82 (1960) 4200.
51 H.G. Schuster-Woldan and F. Basolo, J. Am. Chem. Soc., 88 (1966) 1657.
M. Meier, F. Basolo and R.G. Pearson, Inorg. Chem., 8 (1969) 795.
52 G.W. Parshall, Homogeneous Catalysis, Wiley, New York, 1980.
53 W.H. Baddley and F. Basolo, J. Am. Chem. Soc., 86 (1964) 2075; 88 (1966) 2944.
54 J.B. Goddard and F. Basolo, Inorg. Chem., 7 (1968) 936; 7 (1968) 2456.
55 W.H. Baddley and F. Basolo, Inorg. Chem., 3 (1964) 1087.
C.F. Weick and F. Basolo, Inorg. Chem., 5 (1966) 576.
56 F. Basolo, Chem. Eng. News, 39 (1961) 86.
57 R.G. Pearson, P.M. Henry, J.G. Bergmann and F. Basolo, J. Am. Chem. Soc., 76 (1954) 5920.
58 A.T. Austin, E.D. Hughes, J.H. Ridd and C.K. Ingold, J. Am. Chem. Soc., 74 (1952) 555.
59 R.K. Murmann and H. Taube, J. Am. Chem. Soc., 78 (1956) 4886.
R.K. Murmann, J. Am. Chem. Soc., 77 (1955) 5190.
60 F. Basolo and G.S. Hammaker, Inorg. Chem., 1 (1962) 1.
61 S.M. Jorgensen, Z. Anorg. Allg. Chem., 5 (1893) 169.
62 R.L. Carlin and J.O. Edwards, J. Inorg. Nucl. Chem., 6 (1958) 217.
63 F. Basolo, J.L. Burmeister and A.J. Poë, J. Am. Chem. Soc., 85 (1963) 1700.
J.L. Burmesiter and F. Basolo, Inorg. Chem., 3 (1964) 1587.
64 A. Haim and N. Sutin, J. Am. Chem. Soc., 88 (1966) 434.
65 J.L. Burmeister, Coord. Chem. Rev., 3 (1968) 225.
66 F. Basolo, W.H. Baddley and J.L. Burmeister, Inorg. Chem., 3 (1964) 1202.
F. Basolo, W.H. Baddley, and K.J. Weidenbaum, J. Am. Chem. Soc., 88 (1966) 1576.
67 R.C. Johnson and F. Basolo, J. Inorg. Nucl. Chem., 13 (1960) 36.
68 F. Rubinstein, USSR C. R., 28 (1940) 55; Izv. Plat., 20 (1947) 53, 56.