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Recollections of early studies on platinum(II) complexes related to Chatt's contributions to coordination chemistry [1]

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Contents

Abstract

An overview is reported on early research done in our laboratory on ligand substitution reactions of Pt(II) complexes. Some of the research was related to seminal work of Chatt on the subject, and one of our joint publications with him dealt with his view of the kinetic *trans* effect. Rate data on the reactions of *trans*-$PtClL(PEt_3)_2$ (L = alkyl, aryl, or hydride) show that these ligands have a large *trans* effect. Since these ligands do not π bond, the results are explained in terms of the high polarizability of the ligands. Also described are reactions of different nucleophiles with *trans*-$PtCl_2(pyridine)_2$ and its use as a standard to estimate values of nucleophilic constants η^0_{Pt} for substitution reactions of Pt(II) complexes. The data obtained were consistent with Pt(II) being a class b or soft metal and preferring the more polarizable ligand atoms.

Keywords: Platinum(II) complexes; Ligand substitution reactions; *Trans* effect

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[1] Dedicated to the memory of Joseph Chatt.

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1. Introduction

This is intended to be a brief review of some of our early research in areas of coordination chemistry of interest to Chatt and in which he made significant seminal contributions. He and I often had friendly discussions about our researches where there was a mutual interest in the work. Eventually we even collaborated on a joint publication dealing with the *trans* effect in Pt(II) complexes (see Refs. [1–3]).

Although the initial work on the *trans* effect was largely done by Chernyaev [4] and the Russian school, Chatt had to be one of the world experts on the *trans* effect and on platinum chemistry. As a result of the π bonding model for Zeise's salt, Chatt suggested that the Russian polarization theory [3] would not account for the high *trans*-labilizing influence of ligands such as C_2H_4, CO and NO. He wrote [2]

> The operation of the rapid and readily reversible elimination of groups *trans* to ligands A of high *trans*-effect (*i.e.* high double-bonding capacity) is readily explained if we suppose that *trans*-substitution occurs by an S_N2 (bimolecular) mechanism. Increasing double bonding by A increases the electron affinity of the metal atom and hence the ease of nucleophilic attack. Also, because the electron withdrawal occasioned by A occurs from the antinodes remote from A of the d_{xz}-orbital, the attack takes place there, preferentially displacing the ligand *trans* to A.

As stated by Chatt and coworkers, their early speculation on the role of *trans*-π bonding groups in ligand substitution of Pt(II) complexes was based on the assumption that the reactions proceed by an S_N2 mechanism. However, at the time (1955) most of the observations reported on such reactions were qualitative and little had been done in terms of detailed kinetic studies [3] in attempts to elucidate the mechanism of ligand substitution. Since the valence bond theory in use then assigned *dsp*^{2} hybridization to the square planar Pt(II) complexes, coordination chemists believed an entering nucleophile would readily attack the vacant *p* orbital on the metal and substitution would take place by an S_N2 mechanism. A massive amount of kinetic studies now support the S_N2 mechanism, so much so that when Romeo and coworkers [5] discovered S_N1 reactions of Pt(II) complexes, the referees delayed publication because of the strong belief that "all Pt(II) substitutions are S_N2".

It was clear in the 1950s that there was a need for detailed kinetic studies of ligand substitution reactions of Pt(II) complexes, and our laboratory was prepared to do this because it was engaged in such studies of octahedral substitution [6]. Martin and his students [7], at about this time, initiated their investigations of such studies on aquation reactions of chloroammineplatinum(II) complexes. However, only a brief chronological account of our studies is given in this article.

2. Reaction of Pt(II) complexes

2.1. Reactions with different reactants

The initial report from our laboratory on the kinetics and mechanism of ligand substitution reactions of Pt(II) complexes was based on research done by Banerjea et al. [8]. The substrates used in this investigation were *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ and $[PtCl(NH_3)_3]^+$, where Cl^- is the leaving group being replaced by the entering nucleophile Y:

$$[PtCl_2(NH_3)_2] + Y^- \rightarrow [PtClY(NH_3)_2] + Cl^- \qquad (1)$$

Kinetic studies showed that reactants Y fell into two categories: (1) those that are first order in complex but zero order in reactant and all of about the same rate ($^{36}Cl^-$, OH^-, NH_2CH_2COOH, $C_6H_5NH_2$, C_5H_5N); (2) those that are first order in both the complex and the reactant and are faster than those in the first category ($SC(NH_2)_2$, NO_2^-, $CH_2{=}CHCH_2OH$).

Since these results show that the first category of reactants are not involved in the rate-determining step for reaction and since the rates are identical for all of these reagents, it was suggested that the first slow step is a reaction with solvent water to form the aquo complex followed with a fast replacement of water by the entering nucleophile to form the final product:

$$[PtCl_2(NH_3)_2] \xrightarrow[+H_2O,\ -Cl^-]{\text{slow}} [PtClH_2O(NH_3)_2]^+ \xrightarrow[+Y^-,\ -H_2O]{\text{fast}} [PtClY(NH_3)_2] \qquad (2)$$

The point was made that the second category of reactants are ligands known to have large *trans* effects, and the π bonding suggestion of Chatt [2] and of Orgel [9] to account for *trans*-activating ligands was extended to accommodate the reactivities of the reagents in the second category.

The conclusion finally reached was based on square planar complexes in solution believed [10] to have a tetragonal structure with solvent weakly coordinated to the metal above and below the plane. It was suggested that a "dissociation" mechanism may be involved for the solvent pathway. This was envisioned as a departure of the leaving group while the two solvent molecules move in to form a five-coordinate intermediate, which then rapidly reacts with the entering reagent. The more reactive reagents of the second category could involve a similar mechanism, but one which is first order in reagent concentration. This would merely require a rapid pre-equilibrium between the tetragonal disolvated complex and a species where one of the solvent molecules in the axial position is replaced by the entering reagent. In this case loss of the leaving group would result in the direct coordination of the entering nucleophile to form product.

2.2. Reactions in different solvents

Because of the important role of the solvent in ligand substitution reactions of Pt(II) complexes with poor reactants of the first category described above, Gray and coworkers [11] decided to investigate the effect of a variety of solvents. They chose to study the rate of $^{36}Cl^-$ exchange with *trans*-$[PtCl_2(\text{pyridine})_2]$ in 15 different solvents. The most interesting finding of this study was that the most effective solvents for accelerating the rates of Cl^- exchange were not those usually considered to be the best σ bonding coordinating solvents. Among the most effective solvents were nitromethane, dimethyl sulfoxide, acetic acid and boric acid. These solvents have available potentially vacant orbitals of a type capable of bonding with the filled d_{yz} or d_{xz} orbitals of the platinum atom which project above and below the plane of the complex. Such π back bonding may permit these solvent molecules to approach so that their basic oxygen atoms are very near Pt and in a position to displace Cl^- from the complex (Fig. 1). That is, they can both donate electrons to the metal atom and accept electrons from the metal atom. It was proposed that the name "biphilic" reagent be used to describe such molecules, but this term did not achieve wide usage.

2.3. Substitution lability compared with Pd(II) and Ni(II)

In the 1950s few or no quantitative data were available on the relative ligand substitution rates of analogous complexes of the nickel triad. Therefore, Gray and coworkers [12] decided to obtain such data for reactions of the complexes $[M(dien)X]^+$ (M = Ni, Pd, Pt) with pyridine:

$$[M(dien)X]^+ + py \rightarrow [M(dien)py]^2 + X^- \tag{3}$$

$$(M = Ni, Pd, Pt;\ dien = NH_2C_2H_4NHC_2H_4NH_2;\ py = pyridine)$$

For analogous complexes the relative rates of substitution decreased in the order Ni(II) > Pd(II) ≫ Pt(II). For example, the rate of reaction of $[M(dien)SCN]^+$ for Pd(II) is 7×10^5 times faster than that for Pt(II) while the Ni(II) complex reacted too fast to be measured by the conventional experimental method used. However, a subsequent study [13] with Chatt (see Section 2.4) did show that the sterically hindered complexes *trans*-$[MCl(o\text{-tolyl})(PEt_3)_2]$ undergo Cl^- replacement by pyridine at relative rates of $5 \times 10^6 : 1 \times 10^5 : 1$ for Ni(II), Pd(II) and Pt(II) respectively. This order of reactivity, *1st row > 2nd row > 3rd row*, for a given triad of transition metals was expected, because it was known to be the order for substitution reactions of octahedral complexes [6]. A few years later oganometallic chemists were surprised by the discovery that for transition metals in low oxidation states the relative order of reactivity is generally *1st row < 2nd row > 3rd* [14]. Meier et al. [15] reported this reactivity order of the nickel triad for the complexes $M[P(OEt)_3]_4$.

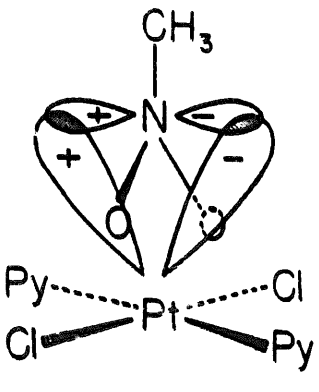


Fig. 1. Molecule of solvent CH_3NO_2 π back bonded to Pt(II) for the complex *trans*-$PtCl_2(pyridine)_2$.

One further observation was that the order of decreasing reactivity of different X groups in the Pt(dien)X$^+$ series is

$$NO_3^- > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$$

This nicely parallels both the order of increasing bond strength [16,17] and the position of these ligands in the *trans* effect series [3]. Thus, at least in these examples, strongly *trans*-activating groups are difficult groups to dislodge.

The total separation in rate is about 2000 in going from Pt(dien)Cl$^+$ to Pt(dien)CN$^+$. This is approximately the same spread as is found for octahedral cobalt(III) complexes where the order of reactivity is [6]

$$NO_3^- > I^- > Br^- > Cl^- > SCN^- > NO_2^-$$

It is of considerable interest that the order of reactivity for halide complexes is reversed in going from Co(III) to Pt(II). Thus, the changes in stability parallel the changes in lability in both cases since from equilibrium data [6] cobalt(III) holds the halogens in the order $Cl^- > Br^- > I^-$. This indicates that Pt(II) is a class b or soft metal, whereas Co(III) is a class a or hard metal.

For Pd(dien)X$^+$ the general order of reactivity seems to be the same as for platinum but the rates are much closer together. For example, there is only a 7-fold difference in rate between Pd(dien)I$^+$ and Pd(dien)NO$_2^+$, whereas for platinum the factor is 200. This supports the view that π bonding is less important for Pd(II) than for Pt(II) complexes.

2.4. Collaboration with Chatt on trans effect

By the late 1950s, Chatt and Shaw [18] had succeeded in preparing several alkyl-, aryl-, and hydrido-metal complexes of the nickel triad. Because of our mutual interest in the kinetic *trans* effect of Pt(II) complexes, Chatt and I decided to examine the rates of ligand substitution of these new organometallics. Shaw prepared the compounds and Gray did the kinetic studies. Years later Chatt [19] gave the following 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 so fast; as soon as he had done one the next compound was waiting'.

The results of this joint venture were reported [13] for the reaction in ethanol solution between pyridine and several planar compounds of the general formula *trans*-[MClL(PEt$_3$)$_2$]:

$$trans\text{-}[MClL(PEt_3)_2] + py \rightarrow trans\text{-}[MLpy(PEt_3)_2]^+ + Cl^- \qquad (4)$$

(M = Ni, Pd, Pt; L = alkyl, aryl, hydride)

The relative rates of reaction of *trans*-[MCl(*o*-tolyl)(PEt_3)$_2$] are approximately 5×10^6 for Ni, 1×10^5 for Pd, and 1 for Pt. The large difference in lability between Pt(II) and Ni(II) is in accord with a mechanism where ligands above and below the plane move in to displace Cl^-, since Ni(II) more readily expands its coordination number than does Pt(II) [6b]. In further support is the observation that *trans*-[NiCl(mesityl)(PEt_3)$_2$] reacts only about 2×10^4 times faster than the corresponding Pt(II) compound, because the mesityl ligand blocks the coordination sites above and below the plane and retards the reaction of Ni(II) more than of Pt(II). In fact the differences in rates for the mesityl systems resemble those between octahedral Co(II) and Ir(III) complexes.

Results of this study show that the *trans*-labilizing ability of the ligands L examined in this study (Eq. (4)) decrease in the order $PMe_3 > H > Me >$ pheyl ≈ *p*-methoxyphenyl ≈ *p*-chlorophenyl > biphenyl > *o*-tolyl > mesilyl ≈ Cl.

As mentioned above there are two main hypotheses used to account for the *trans* effect. One is that of the Russian school [1] which considers it to be mostly electrostatic in origin, depending largely on the polarizability of the ligand. The more polarizable the ligand, the greater its *trans* effect. The second hypothesis is that of the English school [2,9] which suggests that large *trans* effects are produced by ligands able to π back bond to the metal. This π back bonding lowers the electron density on the metal which enhances nucleophilic attack on the metal and/or stabilizes a 5-coordinate transition state for reaction. The results of our study with Chatt further support there being two types of ligands that have high kinetic *trans* effects: those that seem to function via the polarization theory and those that involve π bonding. For example, the relative rates of reaction of compounds with the *trans* ligands H, Me, phenyl, and Cl are approximately 100000:200:30:1. Since π back bonding is of no importance for these ligands, it follows that this rapid rate decrease must be mainly electrostatic in origin. This is supported by the rapid decrease in dipole moment for changes in the *trans*-ligand L = H (4.2*D*), Me (3.4*D*), phenyl (2.6*D*), and Cl (0*D*). However, good π bonding ligands such as C_2H_4 and CO do not have this polarization effect, but they do have a large kinetic *trans* effect best explained by the π backbonding concept.

2.5. *Nucleophilic reactivity constants*

During the 1960s several different laboratories investigated the kinetics and mechanism of ligand substitution reactions of Pt(II) complexes [6b]:

$$[PtA_3X] + Y \rightarrow [PtA_3Y] + X \tag{5}$$

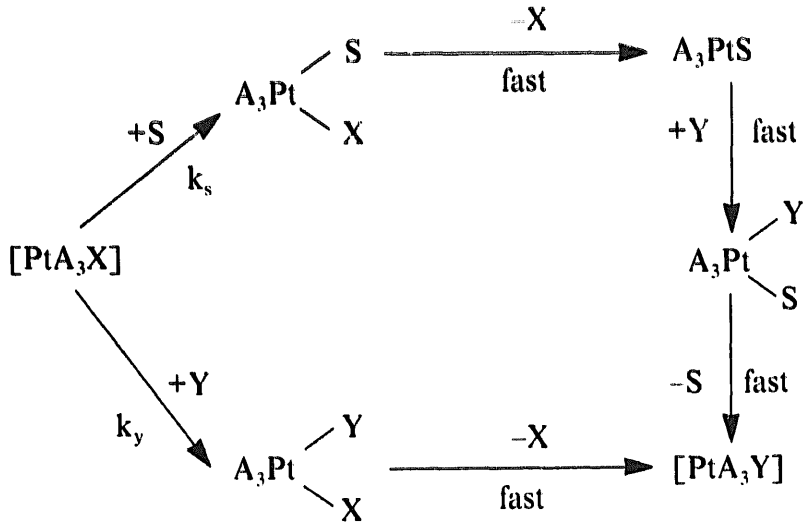
The bottom line of all these studies was that the reactions follow a two-term rate law:

$$\text{rate} = k_s[PtA_3X] + k_y[PtA_3X][Y] \tag{6}$$

where k_s is the rate constant for the solvent pathway which is first order in substrate but zero order in entering nucleophile concentrations, whereas k_y is the rate constant for the direct nucleophilic attack pathway which is first order in both substrate and nucleophile concentrations. Plots of rates of reaction are linear with the same non-zero intercept representing the solvent pathway (k_s), and the slopes of the lines allowing estimates of the direct nucleophilic displacement rate constants k_y (Fig. 2). The mechanism proposed, now widely accepted, that is in keeping with the experimental data is represented in Scheme 1. All of the steps in this mechanism are believed to proceed by S_N2 pathways as had earlier been assumed by Chatt et al. [2] and others [6b].

Physical organic chemists for years attempted to evaluate and quantify the strengths of nucleophiles in S_N2 reactions towards carbon. One approach that met with some success was that reported by Swain and Scott [20]. They determined a large number of nucleophilic reactivity constants η_c using CH_3Br as a standard. Although this proved reasonably satisfactory for nucleophilic displacement reactions at carbon, it is well known that no one scale of nucleophilicity exists and that the substrate is important in any determination of nucleophilic strengths. Quantitative evaluation of the nucleophilic properties of various reagents generally brings in their basicities toward the proton and a characteritic which may be loosely defined as polarizability or electronegativity. The nature of the electrophilic substrate determines which of the properties makes the greatest contribution.

Chatt [16] and others [21], including even Berzelius, made the point years ago that certain metals (class a, hard) prefer less polarizable ligand atoms whilst other metals (class b, soft) prefer more polarizable ligand atoms. For example, Pt(II) is a class b or soft metal. Unfortunately there is no suitable way to quantify polarizability. Although Edwards [22] has had success with the use of electrode potentials to estimate nucleophilic strengths, one disadvantage is that E^0 values are not known



Scheme 1.

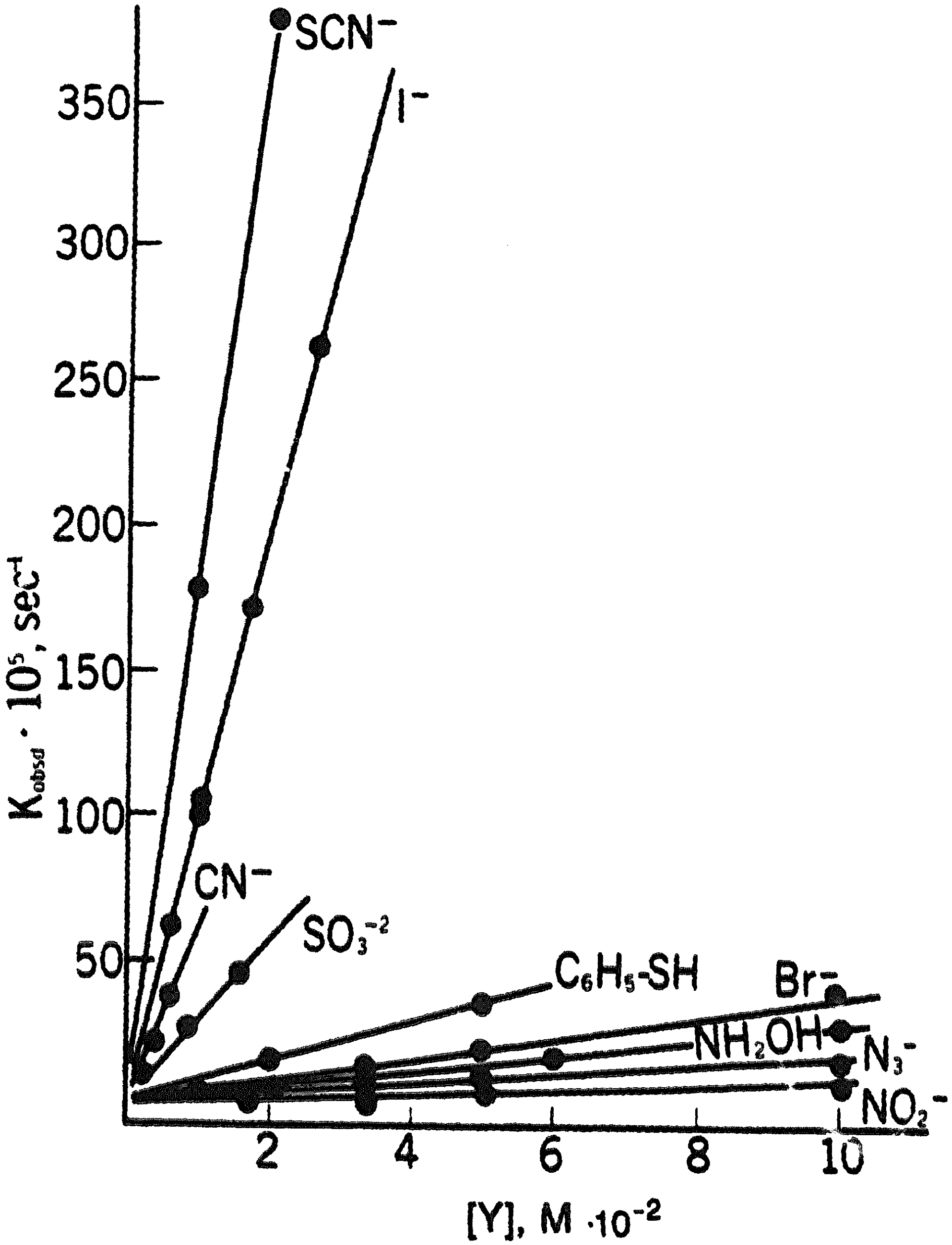


Fig. 2. Rates of reaction (Eq. (8)) of *trans*-$PtCl_2(pyridine)_2$ with different nucleophiles in CH_3OH solvent at 30 °C.

for many common reagents. Other attempts to quantify nucleophilicities towards metals were less successful, so finally Belluco et al. [23] decided to use the rate constants for Cl^- displacement from *trans*-[$PtCl_2(pyridine)_2$] by different nucleophiles as standards. The procedure followed was essentially that used by organic chemists [20] to standardize reactivities towards CH_3Br.

The nulceophilic reactivity constants η^0_{Pt} were defined

$$\log(k_Y/k_S)_0 = \eta^0_{Pt} \qquad (7)$$

Table 1
Values of η^{0}_{Pt} and of pK_a of some nucleophiles

Nucleophile	η^{0}_{Pt}	pK_a
CH_3O^-	<2.4	15.8
Cl^-	3.04	−5.74
NH_3	3.06	9.25
NO_2^-	3.22	3.33
I^-	5.42	−10.7
SCN^-	6.65	−1.8
$S{=}C(NH_2)_2$	7.17	−0.96
$S_2O_3^{2-}$	7.34	1.9
PPh_3	8.79	2.61

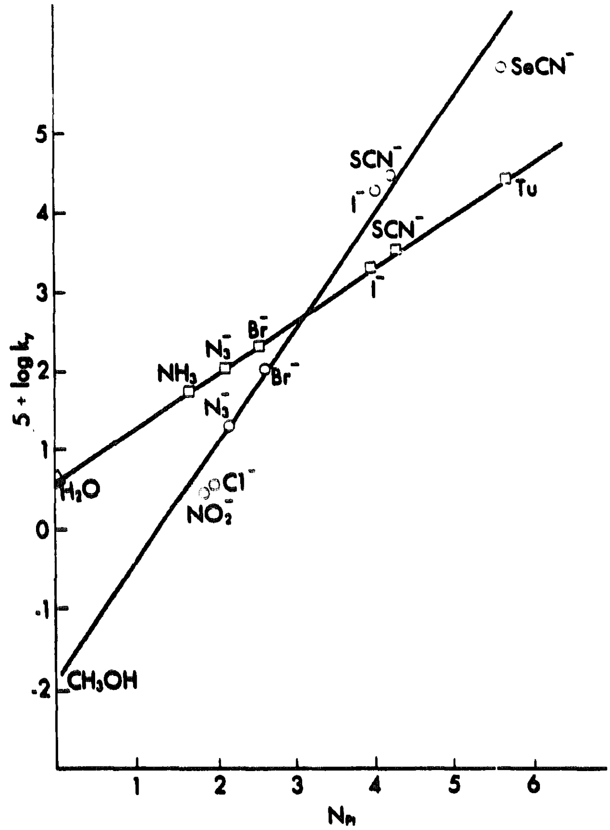


Fig. 3. Correlation of the rates of reaction of Pt(II) complexes with η^{0}_{Pt} for various nucleophiles: ○, *trans*-$PtCl_2(PEt_3)_2$ in methanol at 30 °C; □, $PtCl_2(en)$ in water at 35 °C.

where k_Y and k_S refer to the rate constants for reactions of *trans*-[$PtCl_2$(pyridine)] in CH_3OH at 30 °C:

$$trans\text{-}[PtCl_2(py)_2] + Y^- \xrightarrow[30\,^{\circ}C]{CH_3OH} trans\text{-}[PtClY(py)_2] + Cl^- \qquad (8)$$

Table 1 gives values of η_{Pt}^{0} for several nucleophilic reagents. A plot of $\log k_{\mathrm{Y}}$ for other Pt complexes against η_{Pt}^{0} gives reasonably good straight lines (Fig. 3), which supports the linear free energy relationship

$$\log k_{\mathrm{Y}} = D\eta_{\mathrm{Pt}}^{0} + \log k_{\mathrm{S}} \tag{9}$$

The intercepts of plots such as Fig. 3 are close to the values of k_{S} for each substrate, and the constant D is dependent on the nature of the substrate. It is a nucleophilic discrimination factor, and a large value of D means the complex is very sensitive to changes in the nature of the nucleophilic reagent. Finally the most significant point that can be made from the values of η_{Pt}^{0} (Table 1) is that Pt(II) is a class b [16] or soft [21] metal. The strongest protonic base CH_3O^- in CH_3OH solvent has the smallest η_{Pt}^{0}, whereas some of the weakest protonic bases which are highly polarizable (I^-, $S{=}C(NH_2)_2$, $S_2O_3^{2-}$) have the largest η_{Pt}^{0} values. This came as no surprise, but it was important to quantify the fact and to have a standard for values of nucleophilic strengths of reagents towards Pt(II) complexes.

Acknowledgments

I wish to thank Noel McAuliffe and Jeff Leigh for inviting me to write this article dedicated to the memory of Professor Joseph Chatt. He and I had long been personal friends, and he certainly deserves to be so honored for his many contributions to inorganic chemistry. I thank my former students and postdoctorates who are named in the text and referenced, and I particularly thank my former colleague Professor Ralph G. Pearson. The research was supported by grants from the USA National Science Foundation and the Atomic Energy Commission.

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