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# PLATINUM(II)-CATALYZED SUBSTITUTIONS OF PLATINUM(IV) COMPLEXES

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CONTENTS

## A. INTRODUCTION

Substitution reactions have been used for many years in the synthesis of octahedral platinum(IV) coordination compounds. Russian chemists particularly have made extensive use of substitutions in the preparation of a large variety of complexes varying in type and complexity from symmetrical complexes with six identical ligands, to some with six distinctly different ligands in the coordination sphere of the platinum(IV) ion[1]. It has only been recently, however, that attempts have been made to understand the mechanisms of substitution reactions of platinum(IV). It was clearly recognized from preparative work that these reactions were generally slow at room temperature and that platinum(IV) complexes were characterized as being inert. This behavior was not surprising since platinum(IV) has the same low-spin $d^6$ electronic configuration as the cobalt(III), rhodium(III), and iridium(III) ions which were also known to form characteristically inert complexes. However, an interesting and distinct feature of a number of platinum(IV) substitutions was noted. The presence of small amounts of four-coordinate platinum(II) complexes, or reducing agents capable of reducing platinum(IV) to platinum(II), produced a marked increase in reaction rates[2-4]. The role of the square-planar platinum(II) complexes was not at all clear until the kinetics of several reactions were investigated in detail[5,6]. From the results of these studies and some recent investigations[7-22] an important reaction path has emerged for substitutions of certain types of platinum(IV) complexes, a path which involves an inner-sphere redox process.

## B. RATE LAWS AND MECHANISM

The first detailed kinetic investigation of a platinum(II)-catalyzed substitution was a study[5] of radio-chloride exchange with the *trans*-dichloro-bis(ethylenediamine)platinum(IV) cation, (1) (en = ethylenediamine).

$$trans\text{-Pt(en)}_2\text{Cl}_2{}^{2+} + {}^*\text{Cl}^- \rightarrow trans\text{-Pt(en)}_2\text{Cl}^*\text{Cl}^{2+} + \text{Cl}^- \qquad (1)$$

The reaction was found to be catalyzed by the $\text{Pt(en)}_2{}^{2+}$ cation, and the kinetics were described by a third-order rate law, eqn. (2).

$$-d[trans\text{-Pt(en)}_2\text{Cl}_2{}^{2+}]/dt = k_3[\text{Pt(en)}_2\text{Cl}_2{}^{2+}][\text{Pt(en)}_2{}^{2+}][{}^*\text{Cl}^-] \qquad (2)$$

Subsequently, a variety of reactions of the general type (3) have been found to exhibit third-order kinetics with rate dependence on the substrate platinum(IV) complex, *trans*-$\text{PtL}_4\text{ZX}$, the entering ligand, Y, and a suitable platinum(II) complex, $\text{PtL}_4$.

$$trans\text{-PtL}_4\text{ZX} + \text{Y} \rightarrow trans\text{-PtL}_4\text{ZY} + \text{X} \qquad (3)$$

The mechanism for platinum(II)-catalyzed substitutions of the type shown in reaction (3) was first postulated by Basolo et al.[5], to explain the radio-chloride exchange (1). The reaction sequence postulated involves the formation of an inner-sphere bridged complex, which is then followed by a ligand-transfer. This is outlined in reactions (4)-(7) in general terms for reaction (3), but is fundamentally the Basolo-Pearson scheme.

$$\text{PtL}_4 + \text{Y} \xrightleftharpoons{\text{fast}} \text{PtL}_4\text{-Y} \qquad (4)$$

$$\text{X-PtL}_4\text{-Z} + \text{PtL}_4\text{-Y} \rightleftharpoons \text{X-PtL}_4\text{-Z-PtL}_4\text{-Y} \qquad (5)$$

$$\text{X-PtL}_4\text{-Z-PtL}_4\text{-Y} \rightleftharpoons \text{X-PtL}_4 + \text{Z-PtL}_4\text{-Y} \qquad (6)$$

$$\text{X-PtL}_4 \xrightleftharpoons{\text{fast}} \text{X} + \text{PtL}_4 \qquad (7)$$

The reaction sequence (4)–(7) is consistent with a third-order rate law provided the formation of the five-coordinate platinum(II) complex with the entering ligand, reaction (4) is a rapidly established equilibrium lying to the left. Either the second or third step of the sequence is assumed to be rate-determining. Further, the sequence predicts a retention of geometric configuration for the *trans* platinum(IV) substrate. Such retention of configuration has been observed in all examples of reaction (3) studied. Also, the sequence predicts platinum exchange between the catalyst and the substrate. This feature was verified for reaction (8) by Cox et al.[8] using a platinum-195 tracer.

$$trans\text{-}^{195}Pt(en)_2Cl_2^{2+} + Cl^- \rightarrow trans\text{-}Pt(en)_2Cl_2^{2+} + {}^{195}Pt(en)_2^{2+} + Cl^- \quad (8)$$

The rate of reaction (8) at 25°C was found to agree, to within experimental error, with the rate of radio-chloride exchange of reaction (1), which had been measured previously[5]. Thus, the reaction sequence of (4)–(7) describes not only a substitution process but also a redox electron transfer process between platinum(II) and platinum(IV).

The purpose of this review is to present the vantage point given the platinum(II)-catalyzed reaction path by recent studies. Such a review is timely not only in developing a mechanistic basis for platinum(IV) substitutions – which is of interest in its own right – but also from two other viewpoints. First, the substitution process outlined in reactions (4)–(7) can be visualized as an oxidative addition reaction of the planar platinum(II) complex in which the entering ligand Y and the ligand Z from the platinum(IV) complex are *added* to the platinum(II). Oxidative addition reactions of complexes of low coordination number have been of considerable interest recently in the study of homogeneous catalysis of certain organic reactions such as olefin hydrogenation and polymerization[23,24]. Second, the reaction sequence (4)–(7) is of interest because of the two-electron redox feature. Inner-sphere processes involving two-electron transfers are presently not well characterized. The platinum(II)–platinum(IV) reactions present themselves as nearly ideal systems in which to study such a process.

The present review is based primarily on comparative rate data resulting from a number of detailed kinetic studies. These data are presented in tables and are followed by discussion of reactivity correlations. Reactivity dependence on the nature of the bridging, entering, leaving, and non-labile *cis* ligands are discussed, followed by solvent and ionic-strength effects. Finally, attention is drawn to certain side reactions observed in several studies.

## C. RATE DATA

Platinum(II)-catalyzed substitutions of platinum(IV) complexes exhibit characteristic third-order kinetics, first-order each in the platinum(IV) substrate, an entering ligand Y, and the platinum(II) complex. Table 1 includes rate constants and activation parameters for reactions in which the four in-plane ligands in the platinum(IV) complex and those in the platinum(II) complex are identical, as in reaction (9).

$$trans\text{-}PtL_4ZX + Y + PtL_4 \rightarrow trans\text{-}PtL_4ZY + X + PtL_4 \quad (9)$$

The platinum(II) complex is regenerated during the course of the reaction and thus is a catalyst in a strict sense. Table 2 presents rate constants and activation parameters for some related reactions in which the in-plane ligands in the platinum(IV) complexes are different from those in the platinum(II) complexes. This is shown in reaction (10).

$$trans\text{-}PtL_4ZX + Y + PtL_4' \rightarrow trans\text{-}PtL'_4ZY + X + PtL_4 \quad (10)$$

The kinetics of these reactions are also third-order and the mechanism of reactions (4)–(7) is still applicable. In fact, the exchange of the in-plane ligands may be offered as evidence of platinum exchange.

**TABLE 1**

Rate data for *trans*-$PtL_4ZX + Y + PtL_4 \rightarrow$ *trans*-$PtL_4ZY + X + PtL_4$

| Z | Y | X | $\Delta H^*$ (kcal $mol^{-1}$) | $\Delta S^*$ (cal $deg^{-1} mol^{-1}$) | $k_3(25°)$ ($M^{-2} sec^{-1}$) | $\mu$ ($M$) | Ref. |
|---|---|---|---|---|---|---|---|
| $Pt(NH_3)_5Z^{3+} + Y^- + Pt(NH_3)_4{}^{2+} \rightarrow$ *trans*-$Pt(NH_3)_4ZY^{2+} + NH_3 + Pt(NH_3)_4{}^{2+}$ | | | | | | | |
| I | $I^-$ | $NH_3$ | 6 | −29 | $3.9\times10^{2}$ | 0.016 | 10 |
| I | $Br^-$ | $NH_3$ | 8 | −15 | $1.2\times10^{4}$ | 0.016 | 10 |
| I | $Cl^-$ | $NH_3$ | 11 | −10 | $5.6\times10^{2}$ | 0.016 | 10 |
| Br | $Br^-$ | $NH_3$ | 10 | −19 | $1.2\times10^{1}$ | 0.32 | 10 |
| Cl | $Cl^-$ | $NH_3$ | 18 | −13 | $1.2\times10^{-3}$ | 0.32 | 10 |
| OH | $Cl^-$ | $NH_3$ | | | Very slow | 0.01 | 39 |
| *trans*-$Pt(NH_3)_4ZX^{2,3+} + Y^{0,-} + Pt(NH_3)_4{}^{2+} \rightarrow$ *trans*-$Pt(NH_3)_4ZY^{2,3+} + X^{0,-} + Pt(NH_3)_4{}^{2+}$ | | | | | | | |
| Cl | $Br^-$ | $Cl^-$ | 8 | −24 | $1.1\times10^{2}$ | 0.20 | 12 |
| Br | $Br^-$ | $Cl^-$ | 3 | −30 | $1.9\times10^{4}$ | 0.20 | 12 |
| Br | $Br^-$ | $I^-$ | 8 | −16 | $5.0\times10^{3}$ | 0.20 | 41 |
| Cl | $Cl^-$ | $Cl^-$ | | | 6.5 | 0.015 | 6 |
| Cl | $Cl^-$ | $Br^-$ | 11 | −20 | 6.3 | 0.20 | 12 |
| Br | $Cl^-$ | $Br^-$ | 6 | −22 | $4.2\times10^{3}$ | 0.20 | 12 |
| Cl | $NH_3$ | $Cl^-$ | 6 | −37 | 1.2 | 0.37 | 11 |
| Cl | $Cl^-$ | $SCN^-$ | 10 | −20 | 2.7 | 1.10 | 13 |
| SCN | $Cl^-$ | $SCN^-$ | 5 | −30 | $1.8\times10^{2}$ | 0.20 | 13 |
| Cl | $Cl^-$ | Py | | | $6.2\times10^{1}$ | 0.20 | 14 |
| Cl | Py | $Cl^-$ | | | $\sim5\times10^{-1}$ | 0.20 | 14 |
| Cl | $NO_2{}^-$ | $Cl^-$ | | | 3.3(50°) | 0.235 | 9 |
| *trans*-$Pt(CH_3NH_2)_4Cl_2{}^{2+} + 2\,Br^- + Pt(CH_3NH_2)_4{}^{2+} \rightarrow$ *trans*-$Pt(CH_3NH_2)_4Br_2{}^{2+} + 2\,Cl^- + Pt(CH_3NH_2)_4{}^{2+}$ | | | | | | | |
| Cl | $Br^-$ | $Cl^-$ | 7 | −26 | $9.6\times10^{1}$[a] | 0.066 | 20 |
| *trans*-$Pt(C_2H_5NH_2)_4Cl_2{}^{2+} + 2\,Br^- + Pt(C_2H_5NH_2)_4{}^{2+} \rightarrow$ *trans*-$Pt(C_2H_5NH_2)_4Br_2{}^{2+} + 2\,Cl^- + Pt(C_2H_5NH_2)_4{}^{2+}$ | | | | | | | |
| Cl | $Br^-$ | $Cl^-$ | 7.3 | −29 | $1.6\times10^{1}$ | 0.066 | 20 |
| *trans*-$Pt(en)_2Cl_2{}^{2+} + Y^- + Pt(en)_2{}^{2+} \rightarrow$ *trans*-$Pt(en)_2ClY^{2+} + Cl^- + Pt(en)_2{}^{2+}$ | | | | | | | |
| Cl | $Cl^-$ | $Cl^-$ | 7 | −24 | $3.9\times10^{1}$(20°) | 1.0 | 38 |
| Cl | $NO_2{}^-$ | $Cl^-$ | | | $1.0\times10^{1}$(50°) | 0.235 | 9 |
| Cl | $Br^-$ | $Cl^-$ | 6 | −27 | $3.0\times10^{2}$ | 0.066 | 20 |
| Cl | $I^-$ | $Cl^-$ | 2.5 | −29 | $4.0\times10^{4}$ | 1.00 | 35 |
| *trans*-$Pt(en)(tet)Cl_2{}^{2+} + 2\,Br^- + Pt(en)(tet)^{2+} \rightarrow$ *trans*-$Pt(en)(tet)Br_2{}^{2+} + 2\,Cl^- + Pt(en)(tet)^{2+}$ | | | | | | | |
| Cl | $Br^-$ | $Cl^-$ | 9 | −32 | $1.7\times10^{-1}$ | 1.00 | 35 |
| *trans*-$Pt(C\text{-}Me_4en)_2Cl_2{}^{2+} + Y^- + Pt(C\text{-}Me_4en)_2{}^{2+} \rightarrow$ *trans*-$Pt(C\text{-}Me_4en)_2ClY^{2+} + Cl^- + Pt(C\text{-}Me_4en)_2{}^{2+}$ | | | | | | | |
| Cl | $Cl^-$ | $Cl^-$ | | | Very slow | 0.02 | 6 |
| Cl | $NO_2{}^-$ | $Cl^-$ | | | Very slow | 0.235 | 9 |
| *trans*-$Pt(en)(NO_2)_2ZX + Y^- + Pt(en)(NO_2)_2 \rightarrow$ *trans*-$Pt(en)(NO_2)_2ZY + X^- + Pt(en)(NO_2)_2$ | | | | | | | |
| Cl | $Br^-$ | $Cl^-$ | 6 | −29 | $1.6\times10^{2}$ | 0.10 | 21 |
| Cl | $Cl^-$ | $Br^-$ | | | $8.8\times10^{-2}$ | 0.10 | 21 |
| Br | $Cl^-$ | $Br^-$ | | | $8.4\times10^{1}$ | 0.005 | 21 |

TABLE 1 (*continued*)

| Z | Y | X | ΔH* (kcal mol$^{-1}$) | ΔS* (cal deg$^{-1}$ mol$^{-1}$) | $k_3$(25°) (M$^{-2}$sec$^{-1}$) | μ (M) | Ref. |
|---|---|---|---|---|---|---|---|
| *trans*-$Pt(dien)NH_3ZX^{2+} + Y^- + Pt(dien)NH_3^{2+} \rightarrow$ *trans*-$Pt(dien)NH_3ZY^{2+} + X^- + Pt(dien)NH_3^{2+}$ | | | | | | | |
| Cl | $Br^-$ | $Cl^-$ | 4 | −33 | $3.0 \times 10^2$ | 0.10 | 21 |
| Br | $Cl^-$ | $Br^-$ | | | $1.4 \times 10^2$ | 0.0025 | 21 |
| *trans*-$Pt(dien)BrCl_2^+ + Br^- + Pt(dien)Br^+ \rightarrow$ *trans*-$Pt(dien)BrClBr^+ + Cl^- + Pt(dien)Br^+$ | | | | | | | |
| Cl | $Br^-$ | $Cl^-$ | 6 | −27 | $2.0 \times 10^2$ | 0.20 | 18 |
| *trans*-$Pt(diars)_2Cl_2^{2+} + 2Br^- + Pt(diars)_2^{2+} \rightarrow$ *trans*-$Pt(diars)_2Br_2^{2+} + 2Cl^- + Pt(diars)_2^{2+}$ | | | | | | | |
| Cl | $Br^-$ | $Cl^-$ | 6.1 | −22 | $3.2 \times 10^3$ | 0.066 | 20 |
| *trans*-$Pt(CN)_4ZX^{2-} + Y^- + Pt(CN)_4^{2-} \rightarrow$ *trans*-$Pt(CN)_4ZY^{2-} + X^- + Pt(CN)_4^{2-}$ | | | | | | | |
| Cl | $Br^-$ | $Cl^-$ | 2 | −48 | 4.5 | 1.01 | 22 |
| Br | $Br^-$ | $Cl^-$ | 0 | −44 | $4.2 \times 10^3$ | 1.01 | 22 |
| Cl | $Cl^-$ | $Br^-$ | 6 | −48 | $2.0 \times 10^{-2}$ | 1.01 | 22 |
| Br | $Cl^-$ | $Br^-$ | 2 | −42 | $7.2 \times 10^1$ | 1.01 | 16 |
| Br | $Br^-$ | $CN^-$ | | | Very slow | 1.01 | 40 |
| *trans*-$Pt(NO_2)_4Br_2^{2-} + Cl^- + Pt(NO_2)_4^{2-} \rightarrow$ *trans*-$Pt(NO_2)_4ClBr^{2-} + Br^- + Pt(NO_2)_4^{2-}$ | | | | | | | |
| Br | $Cl^-$ | $Br^-$ | −1 | −64 | $7.6 \times 10^{-1}$ | 1.01 | 16 |

[a] Extrapolated value from rates at higher temperatures.

TABLE 2

Rate data for *trans*-$PtL_4ZX + Y + PtL'_4 \rightarrow$ *trans*-$PtL'_4ZY + X + PtL_4$

| $PtL'_4$ | ΔH* (kcal mol$^{-1}$) | ΔS* (cal deg$^{-1}$ mol$^{-1}$) | $k_3$(25°) ($M^{-2}$sec$^{-1}$) | μ ($M$) | Ref. |
|---|---|---|---|---|---|
| *trans*-$Pt(NH_3)_4Cl_2^{2+} + Cl^- + PtL'^{2+}_4 \rightarrow$ *trans*-$PtL'_4Cl_2^{2+} + Cl^- + Pt(NH_3)_4^{2+}$ | | | | | |
| $Pt(C_2H_5NH_2)_4^{2+}$ | | | 0.5 | 0.066 | 19 |
| $Pt(en)_2^{2+}$ | 8.6 | −21 | $1.5 \times 10^2$(35°) | 0.066 | 19 |
| $Pt(diars)_2^{2+}$ | 14.5 | −11 | 1.5(35°) | 0.066 | 19 |
| *trans*-$Pt(NH_3)_4Cl_2^{2+} + Br^- + PtL'^{+,2+}_4 \rightarrow$ *trans*-$PtL'_4ClBr^{+,2+} + Cl^- + Pt(NH_3)_4^{2+}$ | | | | | |
| $Pt(CH_3NH_2)_4^{2+}$ | 7.8 | −25 | $4.1 \times 10^1$ | 0.066 | 20 |
| $Pt(en)_2^{2+}$ | 6.6 | −23 | $9.6 \times 10^2$ | 0.066 | 20 |
| $Pt(dien)NH_3^{2+}$ | 5.9 | −27 | $4.0 \times 10^2$ | 0.20 | 18 |
| $Pt(dien)Br^+$ | 7.6 | −23 | $1.3 \times 10^2$ | 0.20 | 18 |
| $Pt(dien)NO_2^+$ | 8.4 | −21 | $1.2 \times 10^2$ | 0.20 | 18 |
| $Pt(diars)_2^{2+}$ | 9.5 | −18 | $8.7 \times 10^1$[a] | 0.066 | 20 |
| *trans*-$Pt(NH_3)_4Br_2^{2+} Cl^- + PtL'^{2+}_4 \rightarrow$ *trans*-$PtL'_4ClBr^{2+} + Br^- + Pt(NH_3)_4^{2+}$ | | | | | |
| $Pt(CH_3NH_2)_4^{2+}$ | 6.6 | −22 | $1.6 \times 10^3$ | 0.066 | 20 |
| $Pt(C_2H_5NH_2)_4^{2+}$ | 7.0 | −24 | $3.3 \times 10^3$ | 0.066 | 20 |
| $Pt(en)_2^{2+}$ | 4.9 | −23 | $5.3 \times 10^4$ | 0.066 | 20 |
| $Pt(diars)_2^{2+}$ | 9.2 | −10 | $7.5 \times 10^3$ | 0.066 | 20 |

TABLE 2 (*continued*)

| $PtL'_4$ | $\Delta H^*$ (kcal mol$^{-1}$) | $\Delta S^*$ (cal deg$^{-1}$ mol$^{-1}$) | $k_3(25^\circ)$ ($M^{-2}$ sec$^{-1}$) | $\mu$ ($M$) | Ref. |
|---|---|---|---|---|---|
| *trans*-$Pt(CH_3NH_2)_4Cl_2^{2+} + Cl^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4Cl_2^{2+} + Cl^- + Pt(CH_3NH_2)_4^{2+}$ | | | | | |
| $Pt(diars)_2^{2+}$ | 13 | −16 | $8.5 \times 10^{-1}$ (35°) | 0.066 | 19 |
| *trans*-$Pt(CH_3NH_2)_4Cl_2^{2+} + Br^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4ClBr^{2+} + Cl^- + Pt(CH_3NH_2)_4^{2+}$ | | | | | |
| $Pt(NH_3)_4^{2+}$ | 7.0 | −24 | $2.1 \times 10^2$ | 0.066 | 20 |
| $Pt(en)_2^{2+}$ | 6.8 | −21 | $1.8 \times 10^3$ | 0.066 | 20 |
| $Pt(diars)_2^{2+}$ | 7.9 | −22 | $1.6 \times 10^{2a}$ | 0.066 | 20 |
| *trans*-$Pt(C_2H_5NH_2)_4Cl_2^{2+} + Cl^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4Cl_2^{2+} + Cl^- + Pt(C_2H_5NH_2)_4^{2+}$ | | | | | |
| $Pt(NH_3)_4^{2+}$ | 10 | −20 | $1.3 \times 10^1$ | 0.066 | 19 |
| $Pt(diars)_2^{2+}$ | 9.6 | −24 | 6.6(35°) | 0.066 | 19 |
| *trans*-$Pt(C_2H_5NH_2)_4Cl_2^{2+} + Br^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4ClBr^{2+} + Cl^- + Pt(C_2H_5NH_2)_4^{2+}$ | | | | | |
| $Pt(NH_3)_4^{2+}$ | 5.8 | −29 | $1.4 \times 10^2$ | 0.066 | 20 |
| $Pt(CH_3NH_2)_4^{2+}$ | 5.6 | −30 | $1.0 \times 10^{2a}$ | 0.066 | 20 |
| $Pt(en)_2^{2+}$ | 5.7 | −25 | $1.1 \times 10^2$ | 0.066 | 20 |
| $Pt(diars)_2^{2+}$ | 7.6 | −22 | $2.6 \times 10^2$ | 0.066 | 20 |
| *trans*-$Pt(en)_2Cl_2^{2+} + Cl^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4Cl_2^{2+} + Cl^- + Pt(en)_2^{2+}$ | | | | | |
| $Pt(NH_3)_4^{2+}$ | 8.5 | −29 | 2.4(35°) | 0.066 | 19 |
| $Pt(diars)_2^{2+}$ | 15.8 | −14 | $4.3 \times 10^{-2}$ (35°) | 0.066 | 19 |
| *trans*-$Pt(en)_2Cl_2^{2+} + Br^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4ClBr^{2+} + Cl^- + Pt(en)_2^{2+}$ | | | | | |
| $Pt(NH_3)_4^{2+}$ | 8.9 | −24 | $1.6 \times 10^1$ | 0.066 | 20 |
| $Pt(CH_3NH_2)_4^{2+}$ | 9.5 | −23 | 6 | 0.066 | 20 |
| *trans*-$Pt(diars)_2Cl_2^{2+} + Cl^- + PtL'_4 \rightarrow$ *trans*-$PtL'_4Cl_2^{2+} + Cl^- + Pt(diars)_2^{2+}$ | | | | | |
| $Pt(NH_3)_4^{2+}$ | 5.0 | −34 | $6.9 \times 10^1$ (35°) | 0.066 | 19 |
| $Pt(CH_3NH_2)_4^{2+}$ | 4.8 | −36 | $3.2 \times 10^1$ (35°) | 0.066 | 19 |
| $Pt(C_2H_5NH_2)_4^{2+}$ | 3.9 | −41 | $1.4 \times 10^1$ (35°) | 0.066 | 19 |
| $Pt(en)_2^{2+}$ | 6.1 | −30 | $9.8 \times 10^1$ (35°) | 0.066 | 19 |
| *trans*-$Pt(diars)_2Cl_2^{2+} + Br^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4ClBr^{2+} + Pt(diars)_2^{2+}$ | | | | | |
| $Pt(NH_3)_4^{2+}$ | 3.6 | −32 | $1.1 \times 10^3$ | 0.066 | 20 |
| $Pt(CH_3NH_2)_4^{2+}$ | 4.9 | −30 | $3.2 \times 10^2$ | 0.066 | 20 |
| $Pt(C_2H_5NH_2)_4^{2+}$ | 5.4 | −28 | $4.3 \times 10^2$ | 0.066 | 20 |
| $Pt(en)_2^{2+}$ | 4.0 | −32 | $8.3 \times 10^2$ | 0.066 | 20 |
| *trans*-$Pt(dien)NH_3Cl_2^{2+} + Br^- + Pt(dien)Br^+ \rightarrow$ *trans*-$Pt(dien)BrClBr^+ + Cl^- + Pt(dien)NH_3^{2+}$ | | | | | |
| $Pt(dien)Br^+$ | 8.0 | −21 | $1.7 \times 10^2$ | 0.20 | 18 |
| *trans*-$Pt(dien)NO_2Cl_2^+ + Br^- + Pt(dien)Br^+ \rightarrow$ *trans*-$Pt(dien)BrClBr^+ + Cl^- + Pt(dien)NO_2^+$ | | | | | |
| $Pt(dien)Br^+$ | 5.0 | −28 | $9.3 \times 10^2$ | 0.20 | 18 |
| *trans*-$Pt(NH_3)_2Cl_4 + Cl^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4Cl_2^{2+} + Cl^- +$ *trans*-$Pt(NH_3)_2Cl_2$ | | | | | |
| $Pt(NH_3)_4^{2+}$ | 8.1 | −22 | $1.1 \times 10^2$ | 0.066 | 17 |
| $Pt(CH_3NH_2)_4^{2+}$ | 7.4 | −23 | $2.4 \times 10^2$ | 0.066 | 17 |
| $Pt(C_2H_5NH_2)_4^{2+}$ | 7.7 | −26 | $2.9 \times 10^2$ | 0.066 | 17 |
| $Pt(en)_2^{2+}$ | 7.7 | −18 | $2.0 \times 10^3$ | 0.066 | 17 |
| $Pt(diars)_2^{2+}$ | 8.5 | −12 | $6.5 \times 10^3$ | 0.066 | 17 |

TABLE 2 (*continued*)

| $PtL'_4$ | ΔH* (kcal $mol^{-1}$) | ΔS* (cal $deg^{-1} mol^{-1}$) | $k_3$(25°) ($M^{-2} sec^{-1}$) | μ ($M$) | Ref. |
|---|---|---|---|---|---|
| *trans*-$Pt(NH_3)_2Cl_4 + Br^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4ClBr + Cl^-$ + *trans*-$Pt(NH_3)_2Cl_2$ | | | | | |
| $Pt(NH_3)_4{}^{2+}$ | 6.0 | −24 | $1.3 \times 10^3$ | 0.056 | 17 |
| $Pt(CH_3NH_2)_4{}^{2+}$ | 5.5 | −25 | $1.6 \times 10^3$ | 0.066 | 17 |
| $Pt(C_2H_5NH_2)_4{}^{2+}$ | 5.3 | −29 | $2.9 \times 10^2$ | 0.066 | 17 |
| $Pt(en)_2{}^{2+}$ | 5.2 | −21 | $2.4 \times 10^4$ | 0.066 | 17 |
| $Pt(diars)_2{}^{2+}$ | 6.3 | −11 | $6.3 \times 10^5$ | 0.066 | 17 |
| *trans*-$Pt(CH_3NH_2)_2Cl_4 + Cl^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4Cl_2{}^{2+} + Cl^-$ + *trans*-$Pt(CH_3NH_2)_2Cl_2$ | | | | | |
| $Pt(NH_3)_4{}^{2+}$ | 6.5 | −27 | $8.6 \times 10^1$ | 0.066 | 17 |
| $Pt(CH_3NH_2)_4{}^{2+}$ | 6.2 | −28 | $1.7 \times 10^2$ | 0.066 | 17 |
| $Pt(diars)_2{}^{2+}$ | 8.0 | −15 | $4.9 \times 10^3$ | 0.066 | 17 |
| *trans*-$Pt(CH_3NH_2)_2Cl_4 + Br^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4ClBr^{2+} + Cl^-$ + *trans*-$Pt(CH_3NH_2)_2Cl_2$ | | | | | |
| $Pt(NH_3)_4{}^{2+}$ | 5.8 | −26 | $8.1 \times 10^3$ | 0.066 | 17 |
| $Pt(CH_3NH_2)_4{}^{2+}$ | 4.9 | −28 | $1.2 \times 10^3$ | 0.066 | 17 |
| $Pt(diars)_2{}^{2+}$ | 6.2 | −13 | $2.9 \times 10^5$ | 0.066 | 17 |
| *trans*-$Pt(NH_3)_2Br_4 + Cl^- + PtL'_4{}^{2+} \rightarrow$ *trans*-$PtL'_4ClBr^{2+} + Br^-$ + *trans*-$Pt(NH_3)_2Br_2$ | | | | | |
| $Pt(CH_3NH_2)_4{}^{2+}$ | 4.8 | −24 | $1.2 \times 10^4$ | 0.066 | 17 |
| $Pt(C_2H_5NH_2)_4{}^{2+}$ | 4.2 | −29 | $2.1 \times 10^3$ | 0.065 | 17 |
| $Pt(en)_2{}^{2+}$ | 3.7 | −21 | $3.1 \times 10^5$ | 0.066 | 17 |
| $Pt(diars)_2{}^{2+}$ | | | $\sim 1 \times 10^7$ | 0.066 | 17 |

[a] Extrapolated value from rates at higher temperature.

## D. REACTIVITY CORRELATIONS

### *(i) Effect of the bridging ligand*

One of the characteristic features of inner-sphere reactions is the sensitivity of rates to the nature of the bridging ligand[25,26]. The platinum(IV) redox substitutions are no exception. Indeed, the dependence of reactivity on the bridging ligand Z of reactions (5) and (6) is quite striking. Comparative data from Table 1 for reactions involving the same leaving ligands X, entering ligands Y, and in-plane ligands L, but differing bridging ligands Z give the following order of reactivity for Z: $I^- \gg Br^- > -SCN^- > Cl^- \gg OH^-$. The relative rates for $L = NH_3$ at 25°C and $\mu = 0.2\ M$ are approximately $4.7 \times 10^5$: 400: 30: 1: $\sim 10^{-3}$ for these ligands. A similar order among the three halide ligands is observed for reactions (11)[27] and (12)[28] which are also believed to proceed by an inner-sphere ligand transfer process. The relative rates are much smaller however: $I^- > Br^- > Cl^-$ with relative rates 100:15:1 and 5:2:1 for reactions (11) and (12) respectively.

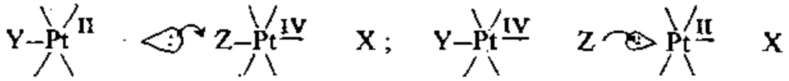
$$Cr(NH_3)_5X^{2+} + Cr(Aq)^{2+} + 5\,H_2O \rightarrow Cr(H_2O)_5X^2 + Cr(Aq)^{2+} + 5\,NH_3 \qquad (11)$$

$$Co(NH_3)_5X^{2+} + Cr(Aq)^{2+} + 5\,H_2O \rightarrow Cr(H_2O)_5X^{2+} + Co(Aq)^{2+} + 5\,NH_3 \qquad (12)$$

As Taube[29] and others[5,6] have pointed out, the effect of the bridging ligand on the rate of inner-sphere redox reactions is related to the ability of the bridging ligand to "mediate" the electron transfer process. The ligands with lighter donor atoms possess empty orbitals to facilitate electron transfer only at relatively high energy. The heavier and more polarizable ligands in contrast have lower energy available orbitals which can participate in bridge bonding and thus provide an effective path for the electron transfer process. Indeed, ligands such as $NH_3$ or $H_2O$ would not be expected to bridge at all, while an iodine atom should be quite effective.

The activation parameters collected in Table 1 show that the reactions are characterized by negative entropies of activation and relatively small enthalpies of activation. This behavior has also been noted[29] as a characteristic feature of the inner-sphere process involving a bridged transition state. It may be pointed out that the marked rate dependence on the nature of the bridging ligand Z results primarily from a favorable $\Delta H^*$. This behavior is consistent with stronger bridge bonding in a transition state involving a good bridging ligand.

An alternate[10], but perhaps helpful way to visualize the redox ligand transfer process is to consider the formation of the bridged complex, the redox electron transfer and the subsequent dissolution of the complex as a nucleophilic displacement on the bridging ligand Z by the five-coordinate platinum(II) species of reaction (4). This is illustrated in (13).



(13)

The more readily Z will expand its coordination number to accommodate the electron pair, the more stable will be the bridged transition state for such a process. Formally, the process can be considered[30] as the transfer of $Z^+$ from one platinum center to the other rather than an electron transfer.

### *(ii) Effect of the entering and leaving ligands*

The variation of reactivity as a function of the nature of the entering and leaving ligands is not nearly as striking as the dependence of reactivity on the nature of the bridging ligand. From suitable comparisons among the reactions of Table 1 the order of reactivity for entering ligands Y is $SCN^- > Br^- > Cl^- > I^- > NH_3 \sim NO_2^- \sim Py$. The relative rates for $L = NH_3$ at 25°C and $\mu \sim 0.2\,M$ are approximately 800:85:4:3:1:~1:~0.5. The order of reactivity for leaving ligands X is $Py > Br^- > SCN^- > Cl^- > I^- > NH_3 \gg CN^-$ while relative rates for $L = NH_3$ at 25°C and $\mu \sim 0.2\,M$ is approximately $5 \times 10^4 : 5 \times 10^3 : 2 \times 10^3 : 1.7 \times 10^3 : 450 : 1 : < 10^{-3}$. Aside from the rather large effects for $NH_3$ and $CN^-$ as leaving ligands, the reactivity dependence on both the entering and leaving ligands is small compared to the dependence on the bridging ligand. The lower reactivity of $NH_3$ and $CN^-$ leaving ligands is likely due to the strength of the Pt-$NH_3$ and Pt-CN bonds. Examination of activation parameters for comparative reactions in Table 1 reveals that the difference in both entering and leaving ligand reactivity are often a result of nearly compensating differences in $\Delta H^*$ and $\Delta S^*$. Such behavior suggests that a combination of effects including differences in solvation, bond strengths and donor capability, are responsible for the reactivity variations, rather than any fundamental features of the bridged redox pathway. For example, the order of leaving ligands generally correlates with the stability of the platinum(IV) substrate with the more stable complexes being the less reactive. The order of entering ligands is similar to the reactivity of Y in planar platinum(II) substitution reactions (with the exception of a lower reactivity for iodide). The order of the rates for chloride replacement by Y in *trans*-$Pt(py)_2Cl_2$[31] is $SCN^- > I^- > Br^- > Cl^- \sim NO_2^- \sim NH_3 \sim$ py. Perhaps the similarity is not too surprising in view of the associative first step of the redox substitution mechanism, reaction (4), and the associative pathway presumed for platinum(II) substitutions[32].

*(iii) Effect of the non-labile cis ligands*

Although the ligands L *cis* to the X-Pt-Z-Pt-Y axis in the bridged complex of reactions (5) and (6) are formally "non-participating" ligands in the redox substitutions, they exert an influence on reactivity nevertheless. Both steric and inductive electronic effects of these ligands appear to be important. The former is a direct consequence of the geometry of the bridged complex; bulky in-plane ligands are expected to hinder bridge formation. In the case of the latter, bonding to the entering, bridging, and leaving ligands are all affected by inductive effects, particularly those which serve to alter the net charge on the platinum centers.

The steric effect of L can be seen from a comparison of the reactivity of ethylenediamine (en), N,N,N'N'-tetramethylethylenediamine ethylenediamine (en)(tet), and tetramethylethylenediamine (C-$Me_4$en) complexes in Table 1. The large differences can be ascribed to blocking of bridge formation by the bulky N-methyl or C-methyl groups[6,9,35]. It seems reasonable to presume that steric blocking is more important for the platinum(II) complex than the platinum(IV). The $Pt(C\text{-}Me_4en)_2^{2+}$ cation is probably an ineffective reductant for all platinum(IV) complexes. On the other hand, *trans*-$Pt(C\text{-}Me_4en)_2X_2^{2+}$ complexes may well be quite reactive, either with an unhindered platinum(II) complex, or by another reaction pathway. The $Pt(en)(tet)Cl_2^{2+}$ complex, for example, reacts with bromide by a non-catalyzed path. This latter reaction has been ascribed to a direct reductive attack on coordinated chloride by bromide[35].

The data of both Table 1 and Table 2 show that reactivity differences among a variety of complexes containing nitrogen donor amines are fairly small. For example, comparable reactions of complexes with $L_4 = 4C_2H_5NH_2$, $4CH_3NH_2$, 2en, $4NH_3$, (dien)A (dien = diethylenetriamine; A = $NH_3$, $NO_2^-$ or $Br^-$), $(NO_2)_2(NH_3)_2$, and $X_2(NH_3)_2$ (X = $Cl^-$ or $Br^-$) span a factor of about 20 in rate. It is also noteworthy that the effect of charge on the substrate and catalyst complexes is small[18]. This is shown by comparisons among reactions of (dien)A, $(NO_2)_2(NH_3)_2$, and $X_2(NH_3)_2$ complexes. Some representative data are collected in Table 3.

If the donor atom of L is changed, or if the electronic structure of the ligand is altered from the simple σ-donor type in the case of the amine complexes, a pronounced effect on reactivity is observed. Comparisons from Table 1 show the following reactivity order for L: ½(diars) > $NH_3$ > $CN^-$ > $NO_2^-$. The relative reactivity at 25°C is approximately $8 \times 10^5 : 3 \times 10^4 : 70 : 1$. The enhanced reactivity of the *o*-phenylenebis(dimethylarsine), (diars), complexes has been ascribed to the formation of a more stable five-coordinate

TABLE 3

Rate constants at 25°C for some amine complexes
*trans*-$PtL_4Cl_2^n + PtL'_4{}^m + Br^- \rightarrow$ *trans*-$PtL'_4BrCl^m + PtL_4{}^n + Cl^-$

| Pt(IV) substrate | $PtL'_4{}^m$ | $10^{-2}k_3(25°)$ ($M^{-2}sec^{-1}$) | $\mu$ ($M$) | Ref. |
|---|---|---|---|---|
| $Pt(dien)NH_3Cl_2{}^{2+}$ | $Pt(dien)NH_3{}^{2+}$ | 3.0 | 0.10 | 21 |
| $Pt(dien)NH_3Cl_2{}^{2+}$ | $Pt(dien)Br^+$ | 1.7 | 0.20 | 18 |
| $Pt(dien)NO_2Cl_2{}^+$ | $Pt(dien)Br^+$ | 9.3 | 0.20 | 18 |
| $Pt(dien)BrCl_2{}^+$ | $Pt(dien)Br^+$ | 2.0 | 0.20 | 18 |
| $Pt(NO_2)_2(NH_3)_2Cl_2$ | $Pt(NO_2)_2(NH_3)_2$ | 1.6 | 0.10 | 21 |
| $Pt(NH_3)_2Cl_2Cl_2$ | $Pt(NH_3)_4{}^{2+}$ | 1.1 | 0.066 | 17 |
| $Pt(CH_3NH_2)_2Cl_2Cl_2$ | $Pt(NH_3)_4{}^{2+}$ | 8.6 | 0.066 | 17 |

complex between the entering ligand and the platinum(II) complex[17]. In fact, some kinetic evidence has been found for the $Pt(diars)_2Br^+$ complex in methanol solution[33]. The lower reactivity in the case of the $CN^-$ and $NO_2^-$ complexes is a result of the highly unfavorable entropy of activation (~ –40 cal deg$^{-1}$ mol$^{-1}$ for $CN^-$ and ~ -60 cal deg$^{-1}$ mol$^{-1}$ for $NO_2^-$). This is likely partly due to the greater solvation requirements of the activated complex which would have a 5- charge compared to a 3+ charge for ammine complexes involving dipositive substrate and catalyst complexes and uninegative entering ligands.

The ligands L also affect the relative reactivity in another way. Comparison between the relative reactivity of a bromine and chlorine atom bridging ligands for corresponding ammine and cyano complexes show that the rate ratio $Br^-:Cl^-$ for the ammine complexes is 350:1 while that for the cyano complexes is 1800:1. Similar behavior has been noted[20], for reactions of the *trans*-$Pt(NH_3)_4X_2{}^{2+}$ or *trans*-$Pt(NH_3)_2X_4$ ($X = Cl^-$ or $Br^-$) complexes with chloride in the presence of different platinum(II) complexes (Table 2). The relative rates for $Br^-:Cl^-$ for several ammine complexes are 440–660 for the former, and 50–170 for the latter, while relative rates for $Pt(diars)_2{}^{2+}$ are 12,000 and 1800 respectively[20]. The greater sensitivity of the rates on the nature of the bridging ligand for the cyano and diarsine complexes has been interpreted[20,22] in terms of electronic inductive effects. The cyano and diarsine ligands by virtue of their $\pi$ acceptor capabilities tend to increase the positive charge at the platinum centers and thus enhance binding of the anionic bridging ligand in the bridged complex. The greater bridge bonding would certainly place more stringent requirements on the nature of the bridging ligand.

An interesting linear free energy correlation has been presented recently for several reactions of the type in reaction (9) employing several different ligands L[19]. Values of $\Delta G^*$ from rate studies were plotted against $\Delta G^0$ obtained from some equilibrium measurements; these plots were linear with slopes of about 0.5. This correlation was interpreted as indicating a similarity between the bridged activated complex and products when the products are less stable than reactants[19].

### E. SOLVENT AND IONIC-STRENGTH EFFECTS

Most kinetic studies on platinum(II)-catalyzed reactions of platinum(IV) complexes have been in aqueous solution. Where ionic-strength effects have been investigated, they have been consistent with primary salt effects, viz. increasing the ionic strength causes an increase in reaction rates. Ionic-strength effects are generally fairly small for reactions of cationic amine complexes but appear to be somewhat larger for reactions of anionic cyano and nitro complexes[16,22]. This is consistent with the higher charge on the activated complexes in the latter cases.

TABLE 4

Solvent effects on rate constants at 25°C[a]

| Solvent | $k_3(25°)$ $(M^{-2} sec^{-1})$ |
|---|---|
| *trans*-$Pt(en)(NO_2)_2Cl_2 + Br^- \rightarrow$ *trans*-$Pt(en)(NO_2)_2ClBr + Cl^-$ | |
| $H_2O$ | 160 |
| $CH_3OH$-$H_2O$(50:50 by vol.) | 26 |
| $CH_3OH$-$H_2O$(89:11 by vol.) | 4.4 |
| dioxane-$H_2O$(50:50 by vol.) | 4.8 |
| *trans*-$Pt(en)(NO_2)_2BrCl + Cl^- \rightarrow$ *trans*-$Pt(en)(NO_2)_2Cl_2 + Br^-$ | |
| $H_2O$ | 8.8 |
| $CH_3OH$-$H_2O$(50:50 by vol.) | 2.0 |
| *trans*-$Pt(en)(NO_2)_2Br_2 + Cl^- \rightarrow$ *trans*-$Pt(en)(NO_2)_2BrCl + Br^-$ | |
| $H_2O$ | $8.4 \times 10^3$ |
| $CH_3OH$-$H_2O$(50:50 by vol.) | $1.3 \times 10^3$ |
| *trans*-$Pt(dien)NH_3Cl_2^{2+} + Br^- \rightarrow$ *trans*-$Pt(dien)NH_3ClBr^{2+} + Cl^-$ | |
| $H_2O$ | 300 |
| $CH_3OH$-$H_2O$(99:1 by vol.) | 3200 |
| *trans*-$Pt(dien)NH_3Br_2^{2+} + Cl^- \rightarrow$ *trans*-$Pt(dien)NH_3BrCl^{2+} + Br^-$ | |
| $H_2O$ | $1.4 \times 10^4$ |
| $CH_2OH$ | $4.2 \times 10^5$ |

[a] Data taken from ref. 21.

Studies in non-aqueous solvents are limited. Some data gathered by Syamal and Johnson[21] for reactions in water, water–methanol and water–dioxane mixtures are collected in Table 4. The reactions of the *trans*-$Pt(en)(NO_2)_2X_2$ complexes decrease in rate as the solvent polarity is lowered while the rates of the reactions of *trans*-$Pt(dien)NH_3X_2^{2+}$ increase as the polarity is decreased. These data have been interpreted[21] in terms of the extent of association of the entering ligand with the platinum(II) complex, the rate enhancement for reactions of the cationic complex suggesting an appreciable degree of association. However, from the observed rate law, no appreciable fraction of the platinum(II) complex was associated even at 0.10 *M* halide concentration in 99% methanol.

## F. SIDE REACTIONS

In several kinetic studies of the platinum(II)-catalyzed replacements of platinum(IV) complexes, rate laws obtained contained an additional term beyond the usual third-order term. Under conditions used to study the platinum(II)-catalyzed paths, these additional terms were generally small in their contribution to the overall reactions. Nevertheless, the products of these other pathways appear to be the same as for the catalyzed path. The side reactions noted to the present have been of three characteristic types: (i) platinum(II)-independent reactions, (ii) entering ligand independent reactions, and (iii) reactions greater than first-order in entering ligand. These three types of side reactions will be discussed briefly in turn.

TABLE 5

Platinum(II)-independent reactions

| Reaction | $k_2(25^\circ)$ ($M^{-1}\,\mathrm{sec}^{-2}$) | $\mu$ ($M$) | Ref. |
|---|---|---|---|
| $\mathrm{Pt(NH_3)_5I^{3+} + Cl^- \rightarrow}$ *trans*-$\mathrm{Pt(NH_3)_4ICl^{2+} + NH_3}$ | $1.0\times10^{-2}$ ($35^\circ$) | 0.016 | 10 |
| $\mathrm{Pt(NH_3)_5I^{3+} + Br^- \rightarrow}$ *trans*-$\mathrm{Pt(NH_3)_4IBr^{2+} + NH_3}$ | $5.0\times10^{-1}$ | 0.016 | 10 |
| $\mathrm{Pt(NH_3)_5I^{3+} + I^- \rightarrow}$ *trans*-$\mathrm{Pt(NH_3)_4I_2{}^{2+} + NH_3}$ | $4.0\times10^{-2}$($38^\circ$) | 0.016 | 10 |
| *trans*-$\mathrm{Pt(NH_3)_4ClBr^{2+} + Br^- \rightarrow}$ *trans*-$\mathrm{Pt(NH_3)_4Br_2{}^{2+} + Cl^-}$ | $1.0\times10^{-2}$ | 0.200 | 12 |
| *trans*-$\mathrm{Pt(NH_3)_4(SCN)Cl^{2+} + Cl^- \rightarrow}$ *trans*-$\mathrm{Pt(NH_3)_4Cl_2{}^{2+} + SCN^-}$ | $2.7\times10^{-4}$($35^\circ$) | 1.10 | 13 |
| *trans*-$\mathrm{Pt(CN)_4ClBr^{2-} + Br^- \rightarrow}$ *trans*-$\mathrm{Pt(CN)_4Br_2{}^{2-} + Cl^-}$ | $2.5\times10^{-1}$ | 1.01 | 22 |
| *trans*-$\mathrm{Pt(en)\,(tet)Cl_2{}^{2+} + 2\,Br^- \rightarrow}$ *trans*-$\mathrm{Pt(en)\,(tet)Br_2{}^{2+} + 2\,Cl^-}$ | 2.0($54^\circ$) | 1.00 | 35 |

### *(i) Platinum(II)-independent reactions*

Platinum(II)-independent terms have been found in the rate laws for the reactions listed in Table 5. For these reactions rate laws of the type given in eqn. (14) were found.

$$d[\mathrm{Pt(IV)}]/dt = \{k_2 + k_3\,[\mathrm{Pt(II)}]\}\;[\mathrm{Y}]\;[\mathrm{Pt(IV)}] \tag{14}$$

Values of $k_2$ are listed in Table 5. In many cases it was acknowledged that they are less precise than values of $k_3$, and in some cases the observed platinum(II)-independent path was of such magnitude that it could have been caused by a platinum(II) impurity of only a few percent in the platinum(IV) samples. However, where temperature dependence was investigated, the $k_2$ platinum(II)-independent path showed considerably larger values of $\Delta H^*$ than the corresponding $k_3$ path [10,22]. In these cases also it is not completely certain that the paths are simply first-order in Y. Clearly, additional careful study of these reactions is required.

A mechanistic interpretation of the platinum(II)-independent path is admittedly speculative in view of the available rate data. The data are consistent with a direct replacement reaction, though the dependence on the nature of $\mathrm{Y^-}$ is puzzling. It is interesting that the magnitude of $k_2$ is largest for $Y = Br^-$. A direct reductive attack on coordinated halide by the entering halide has also been suggested for these platinum(II)-independent reactions[35].

### *(ii) Entering-ligand-independent reactions*

The rate law for the bromide replacement of reaction (15)

$$trans\text{-}Pt(CN)_4Br_2^{2-} + Cl^- \rightarrow trans\text{-}Pt(CN)_4ClBr^{2-} + Br^- \qquad (15)$$

contained[16] a term which was independent of $Cl^-$. This rate law is given in eqn. (16);

$$-d[trans\text{-}Pt(CN)_4Br_2^{2-}]/dt = \{k_2 + k_3[Cl^-]\}[Pt(CN)_4^{2-}][trans\text{-}Pt(CN)_4Br_2^{2-}] \qquad (16)$$

the value of $k_2$ was found to be 7.8 $M^{-1}\,sec^{-1}$ at 25°C and $\mu = 1.01\,M$. A related kinetic behavior was observed[17] for reaction (17) where $k_2$ was reported as less than $4 \times 10^{-2}\,M^{-1}$ at 25°C and $\mu = 0.066\,M$.

$$trans\text{-}Pt(NH_3)_2Cl_4 + Pt(py)_4^{2+} + Br^- \rightarrow trans\text{-}Pt(py)_4ClBr^{2+} + trans\text{-}Pt(NH_3)_2Cl_2 + Cl^- \qquad (17)$$

The chloride-independent term for reaction (15) was interpreted as solvent (water) participating as an entering ligand[16]. This perhaps is not unreasonable since the activated complex would be reduced in charge. Solvation requirements would thus be less stringent for a complex of 4– charge compared to 5– for $Y = Cl^-$. The replacement of the water molecule must be rapid, leading to product. This process could be a direct replacement of water by chloride, although a platinum(II)-catalyzed path cannot be ruled out. The only requirement is that this replacement be faster than the incorporation of solvent. The behavior for reactions (17) was ascribed[17] to unfavorable desolvation of the $Pt(py)_4^{2+}$ complex.

### *(iii) Reactions greater than first-order in entering ligand*

Two examples of reactions which exhibit a greater than first-order dependence on the entering ligand Y have been reported[13,21]. Both of these reactions involved cationic platinum(IV) substrates. Reaction (18) was studied[13] in water while reaction (19) was studied[21] in water and water-methanol solutions. These reactions showed rate laws of the type in eqn. (20).

$$trans\text{-}Pt(NH_3)_4(SCN)_2^{2+} + Cl^- \rightarrow trans\text{-}Pt(NH_3)_4(SCN)Cl^{2+} + SCN^- \qquad (18)$$

$$trans\text{-}Pt(dien)NH_3Cl_2^{2+} + 2\,Br^- \rightarrow trans\text{-}Pt(dien)NH_3Br_2^{2+} + 2\,Cl^- \qquad (19)$$

$$-d[Pt(IV)]/dt = \{k_3 + k_4[Y^-]\}\;[Pt(II)][Y^-][Pt(IV)] \qquad (20)$$

Values reported for $k_4$ at 25°C for reactions (18) and (19), respectively, are $2.5 \times 10^2\,M^{-3}$ $sec^{-1}$ ($\mu = 0.20\,M$) and $1.7 \times 10^3\,M^{-3}\,sec^{-1}$ ($\mu = 0.10\,M$). The greater than first-order dependence on the entering ligand for these reactions was attributed[13,21] to the formation of platinum(IV), $Y^-$ ion pairs of the type $trans\text{-}Pt(NH_3)_4(SCN)_2^{2+}, Cl^-$ or $trans\text{-}Pt(dien)NH_3Cl_2^{2+}, Br^-$. Ion pairs have been reported in related systems[6,12,34], for example $trans\text{-}Pt(en)_2Cl_2^{2+}, Cl^-$, $trans\text{-}Pt(en)_2Br_2^{2+}, Br^-$ and $trans\text{-}Pt(NH_3)_4Br_2^{2+}, Br^-$.

## G. CONCLUSIONS

The relatively wide variety of platinum(II)-platinum(IV) systems which are susceptible to investigation have provided considerable data for reactivity correlations. These correlations focus attention on the more intimate features of the redox ligand-transfer reaction pathway. Considerable information has thus been obtained from the platinum(II)–platinum(IV) systems. Indeed these reactions may be of the nature of prototypes for possible redox substitution pathways in other metal complex systems. For example, several reactions of rhodium(III) have been found[36,37] to be accelerated by reducing agents, and bridged reaction paths involving unstable rhodium(I) complexes have been postulated. Other possible systems where such a pathway might be important include iridium(I)–iridium(III), palladium(II)–palladium(IV), and gold(I)–gold(III).

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