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KINETICS OF NICKEL, PALLADIUM AND PLATINUM COMPLEXES*

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CONTENTS

ABBREVIATIONS

en	ethylenediamine	phen	1,10-phenanthroline
dien	diethylenetriamine	pip	piperidine
trien	triethylenetetramine	DMF	dimethylformamide
diars	*o*-phenylenebisdimethylarsine	DMSO	dimethyl sulfoxide
acac	acetylacetonate	EtOAc	ethyl acetate
py	pyridine	MeCN	acetonitrile
bipy	bipyridyl	$MeNO_2$	nitromethane

A. INTRODUCTION

Much work has been reported in recent years dealing with the kinetic behavior of nickel, palladium and platinum complexes, mainly as a consequence of the introduction of new techniques for studying fast reactions[1,2]. The purpose of the present review is to present an up-to-date outline of what has been achieved in this area. The great amount of information now available in the literature is such that some restriction of the material to be reported was necessary. For this reason several kinds of process, such as intramolecular rearrangements, rotation and inversion reactions, catalytic and intramolecular oxidation–reduction reactions[3–22], will not be considered here.

The review is divided in two parts. The first (Sect. B) will consider reactions in which the central metal atom of the complex retains its oxidation state; the second (Sect. C) will

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*No reprints available.

consider oxidation–reduction reactions. The article is further subdivided on the basis of the oxidation state of the central metal atom. This was found convenient because the reaction mechanism, the reactivity and the configuration of the complexes usually change with the oxidation state of the central metal atom.

B. SUBSTITUTION, ISOMERIZATION AND RELATED REACTIONS

(i) Zerovalent metal complexes

A great number of zerovalent metal complexes of the nickel triad are well known[23–28]. The kinetic investigations carried out so far on these compounds are concerned mainly with tetrahedral nickel (0) complexes, whereas those of palladium (0) and platinum (0) have been relatively little studied[29–35].

These complexes undergo substitution reactions through a dissociative mechanism, leading to the formation of a tricoordinate intermediate in the rate-determining step.

$$ML_4 \xrightarrow{\text{slow}} ML_3 + L \tag{1a}$$

$$ML_3 + L' \xrightarrow{\text{fast}} ML_3L' \tag{1b}$$

According to this mechanism the reaction rate is found, in a given solvent, to be first-order in the complex and independent of the concentration of the entering ligand, with rate constants and activation parameters independent of the nature of the entering group (see for example the data for CO exchange and substitution of $Ni(CO)_4$ by PPh_3 in Table 1). The entropies of activation are always positive, also in reasonable agreement with a dissociative mechanism. Evidence for the occurrence of a tricoordinate intermediate has been obtained by means of competition experiments[32] in which $C^{18}O$ and PPh_3 were allowed to react simultaneously with $Ni(C^{16}O)_4$. It was found that the rates of CO exchange and PPh_3 substitution were both lower than the rate of the reaction with either ligand individually. However, the sum of the two rates was equal to the rate of the reaction of $Ni(C^{16}O)_4$ with CO or PPh_3 alone. This is explained by mechanism (1), where CO and PPh_3 react competitively with the tricoordinate intermediate after the rate-determining step.

The rates of substitution reactions of zerovalent metal complexes are very sensitive to the nature of the non-leaving groups coordinated to the central metal atom. For example, the rate of CO exchange in nickel(0) complexes of the type $Ni(CO)_n(PR_3)_{4-n}$ varies in the order $Ni(CO)_4 > Ni(CO)_3(PR_3) > Ni(CO)_2(PR_3)_2$, and this trend is related to an increasing Ni–C strength[30] in going from $Ni(CO)_4$ to $Ni(CO)_2(PR_3)_2$. The rates are also strongly dependent on the nature of the leaving group, as is expected when a dissociative mechanism is operating. Thus, the rate of substitution of phosphines of $Ni(CO)_2(PR_3)_2$ ($PR_3 = PCl_3, P(CH_2CH_2CN)_3, PPh_3, P(n\text{-}Bu)_3, P(OEt)_3, P(OPh)_3$)

TABLE 1

Rate constants and activation parameters for substitution reactions of zerovalent metal complexes of the nickel triad

Complex	Entering group	t (°C)	k (sec^{-1})	ΔH^* ($kcal.mole^{-1}$)	ΔS^* ($cal.deg^{-1}.mole^{-1}$)	Solvent	Ref.
$Ni(CO)_4$	CO	25	1.83×10^{-2}	22.1	7.7	[a]	32
		25	1.07×10^{-2}	24.0	13.1	*n*-Hexane	32
	PPh_3	25	1.02×10^{-2}	24.2	13.5	*n*-Hexane	32
		25	6.87×10^{-3}	26.6	20.9	Cyclohexane	33
		25	1.94×10^{-2}	20.4	2.0	Toluene	33
		25	2.03×10^{-2}	22.3	8.4	Toluene	32
$Ni(PF_3)_4$	$C_6H_{11}NC$	47.2	3.22×10^{-5}	29.1	13.8	*n*-Heptane	35
		47.2	6.16×10^{-5}	28.4	10.7	Toluene	35
$Pt(PF_3)_4$	$C_6H_{11}NC$	13.3	1.1×10^{-2}	24.4	17.6	*n*-Hexane	35
		13.5	2.21×10^{-2}	22.5	12.3	Toluene	35
$Ni(P(OEt)_3)_4$	$C_6H_{11}NC$	40.8	3.77×10^{-6}	32.1	18.8	*n*-Hexane	34
		40.8	9.68×10^{-6}	26.2	1.8	Benzene	34
$Pd(P(OEt)_3)_4$	$P(OEt)_3$	−10.5	8.5	22.4	31.2	Toluene	34
$Pt(P(OEt)_3)_4$	$P(OEt)_3$	51	1.3	26.2	22.3	Toluene	34

[a] Reaction carried out in the gaseous phase.

usually decreases with increasing basicity of the leaving ligand, i.e. $PCl_3 \gg P(CH_2CH_2(CN))_3 \approx PPh_3 > P(n\text{-}Bu)_3$★. Only the complexes with phosphites react more slowly than would be expected on the basis of the basicity of the leaving phosphite. This has been ascribed to an increase of the Ni–P bond strength with respect to that expected from σ-bonding only, possibly due to π-bonding effects[29]. The contribution of σ- and π-bonding to the metal–ligand bond strength is also considered to be responsible for the change in the rate of substitution reactions of $M(PR_3)_4$ (M = Ni, Pd, Pt; $PR_3 = PF_3$, $P(OEt)_3$) with phosphines, phosphites and isocyanides, when M is changed[34,35]. The reactivity of these complexes is in the order Ni < Pd > Pt, and this trend is mainly due to the fact that the enthalpy of activation for the rupture of the M–P bond varies in the order Ni > Pd < Pt. This is also regarded as being the relative order of the M–P bond strength and is considered to arise from σ and π contributions to the M–P bond. The π contribution, which is very important in metal (0) complexes, decreases[36] in the order Ni ≫ Pd > Pt. The strongest σ contribution is expected to be encountered for platinum, regarded as the most electronegative of the triad. Thus, the lowest bond strength encountered for the palladium (0) complex, and therefore its highest reactivity, is attributed to the small tendency of palladium to π-bond and its intermediate tendency to σ-bond. On the other hand, the relatively higher bond strength encountered in the nickel (0) and platinum (0) complexes, and their lower reactivity, is primarily due to the greater tendency of nickel to π-bond and to that of platinum to σ-bond.

Although the specific role of the solvent is not yet clear, it has been ascertained that it affects the rate of substitution reactions of zerovalent metal complexes of the nickel triad. An extensive investigation on the effect of the solvent upon the rate of substitution reactions of $Ni(CO)_4$ with PPh_3 has shown that the rate constants do not show any definite dependence on the dielectric constant of the solvents[33]. The use of better parameters for the solvent polarities[37] does not give any satisfactory correlation. However, a rather significant solvent effect on the activation parameters is observed (see Table 1) on going from aromatic solvents, such as benzene and toluene, to non-aromatic ones, such as hexane and cyclohexane, a lower enthalpy and entropy of activation being observed in the former solvents. It is believed that an interaction of the aromatic solvent with $Ni(CO)_4$ in the transition state does assist the dissociation of a CO group, thus contributing to the lowering of the enthalpy of activation. This interaction also restricts the freedom of the aromatic molecule, thus also lowering the entropy of activation.

(ii) Bivalent metal complexes

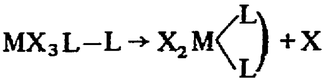
(a) Square-planar complexes

(1) Rate law and mechanism. Many kinetic investigations have been carried out on nucleophilic substitution reactions of square-planar complexes of the nickel (II) triad. The entering group in these reactions can be either a mono- or a multidentate ligand, e.g.

★ However, steric effects can also be important[26].

$$MX_4 + Y \rightarrow MX_3Y + X \tag{2}$$

$$MX_4 + L{-}L \rightarrow MX_3L{-}L + X \tag{3a}$$



$$MX_3L{-}L \rightarrow X_2M\left(\begin{matrix}L\\L\end{matrix}\right) + X \tag{3b}$$

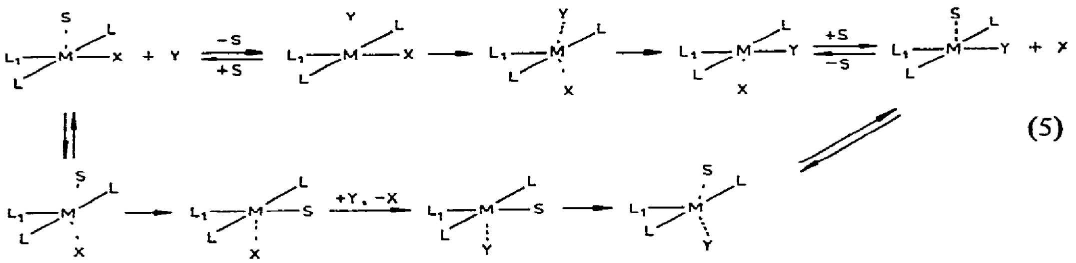
In the latter case the rate-determining step is usually the substitution of the first leaving group, whereas the ring closure is normally a fast step[38,39].

These substitution reactions usually follow a two-term rate law

$$\text{Rate} = k_1\,[\text{complex}] + k_2\,[\text{complex}]\,[Y] \tag{4}$$

where k_1 is the first-order rate constant for a solvolytic path and k_2 is the second-order rate constant for a direct bimolecular substitution path. Rate law (4) can be regarded as typical for square-planar complexes, although some examples of anomalous behavior are reported in the literature[40]. Well documented evidence is now available for the assignment of an associative reaction mechanism to both the k_1 and k_2 pathways[41–43]. A recent evaluation of the volumes of activation for the solvolysis of $[PtCl_4]^{2-}$ (-17 ml.mole^{-1}) and $[Pt(NH_3)Cl_3]^-$ (-14 ml.mole^{-1}) in water[44], and for both solvolytic and bimolecular substitutions of *trans*-$[Pt(PEt_3)_2Cl_2]$ with bromide in methanol or aqueous methanol (-28 ml.mole^{-1} and -27 ml.mole^{-1} for the two pathways)[45] provide further evidence to support an associative mechanism for these reactions. The highly negative values of the volumes of activation show that bond formation is the dominant feature for the transition states of both solvolytic and bimolecular paths.

The reaction mechanism



(5)

implies a five-coordinate transition state generally believed to have a trigonal-bipyramidal structure, with the entering ligand, Y, the leaving ligand, X, and the group L_1, originally *trans* to X, in the trigonal plane. The reaction mechanism is better described in terms of an associative A (or S_N2 lim) mechanism, also implying a labile five-coordinate intermediate which can be formed before (Fig. 1(a)) or after (Fig. 1(b)) the rate-determining step[46,47]. The existence of stable five-coordinate complexes of nickel (II), palladium (II) and platinum (II)[48–51], supports the associative mechanism. Direct evidence of the occurrence of five-coordinate adducts in the course of these reactions has been obtained in the nucleophilic

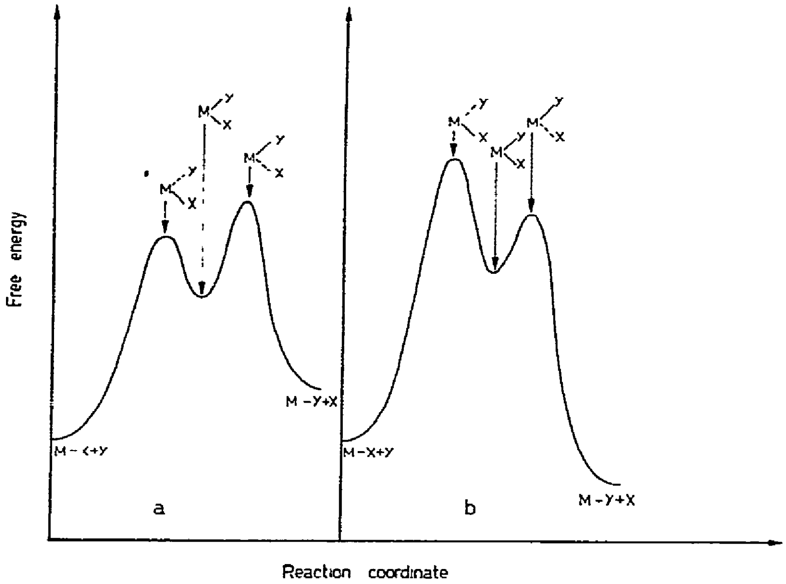


Fig. 1. Reaction profiles for the displacement mechanism of square-planar complexes, involving an unstable five-coordinate intermediate, X—M—Y. (a) Bond breaking is rate-determining; (b) bond making is rate-determining.

substitution by dithiolates[52] of square-planar nickel (II)—dithiolate complexes.

Although an associative mechanism is normally operating in the nucleophilic substitution reactions of square-planar complexes, there are also some cases of sterically hindered complexes whose kinetics are better explained by a dissociative mechanism (see p. 142).

(2) Role of the entering group. Information on this point is mostly available for reactions of platinum (II) complexes. As a general trend, the bimolecular reactivity of the different nucleophiles is mainly related to their polarizability, whereas basicity towards a proton is of little importance. A few attempts to correlate the second-order rate constants, k_2, with nucleophilic reactivity parameters quoted in the literature for the single entering group were not very successful[53,54]. For this reason it has been found convenient to devise a nucleophilic scale for platinum (II) complexes, related to the reactivity of the single nucleophiles towards *trans*-[Pt(pip)$_2$Cl$_2$], taken as a standard substrate, in methanol at 30°C (or 25°C)[53,54]. The nucleophilic reactivity constants, n^0_{Pt}, in this scale are given by

$$n^0_{\text{Pt}} = \log \frac{k_Y}{k^0_s} \tag{6}$$

where k_Y and k^0_s are the second-order rate constants for the direct replacement and for the solvolytic path ($k^0_s = k_1/[\text{MeOH}]$). The values of n^0_{Pt} measured for several nucleophiles are collected in Table 2.

TABLE 2

The values of n^0_{Pt}

Nucleophile	n^0_{Pt}	Nucleophile	n^0_{Pt}
CH_3OH	0.00[a]	$S(C_2H_5)_2$	4.52
α-Picoline	2.2	$P(N(C_2H_5)_2)_3$	4.54
$S(4\text{-}NO_2C_6H_4)_2$	2.4[b]	$S(CH_3)_2$	4.87
Cl^-	3.04	$PO(OCH_3)_2^-$	5.01
NH_3	3.07	$S(CH_2)_5$	5.02
Piperidine	3.13	$S(CH_2)_4$	5.14
Aniline	3.16	$SnCl_3^-$	5.44
Pyridine	3.19	I^-	5.46
$S(4\text{-}ClC_6H_4)_2$	3.21[b]	$Se(CH_2C_6H_5)_2$	5.53
NO_2^-	3.22	$Se(CH_3)_2$	5.70
$S(C_6H_5)_2$	3.22[b]	SCN^-	5.75
$S(C_6H_5)(4\text{-}ClC_6H_4)$	3.25[b]	SO_3^{2-}	5.79
$S(4\text{-}FC_6H_4)_2$	3.30[b]	$C_6H_{11}NC$	6.34
$S(4\text{-}NH_2C_6H_4)(4\text{-}NO_2C_6H_4)$	3.31[b]	$Sb(C_6H_5)_3$	6.79
$S(CH_2C_6H_5)_2$	3.43	$As(C_6H_5)_3$	6.89
Imidazole	3.44	$SeCN^-$	7.11
N_3^-	3.58	CN^-	7.14
$S(C_6H_5)(4\text{-}CH_3OC_6H_4)$	3.64[b]	$C_6H_5S^-$	7.17
$S(4\text{-}CH_3C_6H_4)_2$	3.68[b]	$SC(NH_2)_2$	7.17
$S(4\text{-}CH_3OC_6H_4)_2$	3.73[b]	$P(OCH_3)_3$	7.23
NH_2OH	3.85	$S_2O_3^{2-}$	7.34
$S(4\text{-}OHC_6H_4)_2$	3.85[b]	$As(C_2H_5)_3$	7.68
NH_2NH_2	3.86	$P(C_6H_5)_3$	8.93
C_6H_5SH	4.15	$P(n\text{-}C_4H_9)_3$	8.96
Br^-	4.18	$P(C_2H_5)_3$	8.99
$S(4\text{-}NH_2C_6H_4)_2$	4.27[b]		

[a] Data from ref. 54 except where footnote *b* is indicated.

[b] Data from ref. 55.

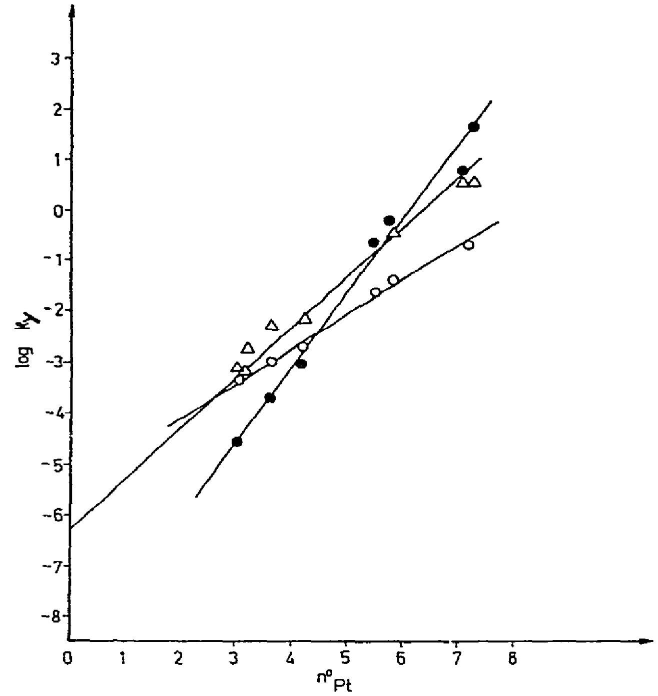


Fig. 2. Correlation of the second-order rate constants, k_Y, of the nucleophilic substitution reactions of platinum (II) complexes with the nucleophilic reactivity constants, n^0_{Pt}, for different nucleophiles: $[Pt(en)Cl_2]$ in H_2O at 35°C (o); *trans*-$[Pt(AsEt_3)_2Cl_2]$ in MeOH at 30°C (•); *trans*-$[Pt(pip)_2Cl_2]$ in MeOH at 30°C (Δ). Data from ref. 53

The values of log k_Y for a great number of uncharged square-planar platinum (II) complexes are correlated with the nucleophilic reactivity constants, n^0_{Pt}, by the relationship

$$\log k_Y = s n^0_{Pt} + \log k^0_s \tag{7}$$

where the constant s, called the *nucleophilic discrimination factor* (N.D.F), is a measure of the discriminating ability of the substrate towards the entering ligands. The consistency of such a relationship is documented by the examples of plots of log k_Y against n^0_{Pt} reported in Fig. 2. The values of s for some complexes are reported in Table 3. Although relationship (7) holds for a large number of complexes and for several nucleophiles, important deviations are met when biphilic nucleophiles, i.e. those able to behave both as nucleophiles and electrophiles, react with complexes either charged or containing good π-acceptor ligands, such as phosphines[40, 59].

Very little information is available about the effect of the entering group upon the substitution reaction rates of palladium (II) square-planar complexes. There is, however, some kinetic evidence which seems to indicate that the order of reactivity of the different nucleophiles towards palladium (II) is the same as that found for platinum (II). For example, *trans*-$[Pd(NH_3)_2Cl_2]$, *cis*- and *trans*-$[Pd(NH_3)_2(NO_2)_2]$ and $[Pt(en)Cl_2]$ react with

TABLE 3

Nucleophilic discrimination factors, *s*, of some platinum (II) complexes in methanol

Complex	*t* (°C)	*s*	Ref.
trans-[Pt(py)$_2$Cl$_2$]	30	1.00	53
trans-[Pt(PEt$_3$)$_2$Cl$_2$]	30	1.43	53
trans-[Pt(AsEt$_3$)$_2$Cl$_2$]	30	1.25	53
trans-[Pt(S(*sec*-Bu)$_2$)$_2$Cl$_2$]	55	0.57	53
trans-[Pt(SeEt$_2$)$_2$Cl$_2$]	30	1.05	53
trans-[Pt(pip)$_2$Cl$_2$]	30	0.91	53
trans-[Pt(PEt$_3$) (pip) Cl$_2$]	30	1.15	57
trans-[Pt(4-CNpy)$_2$Cl$_2$]	30	1.1	58
trans-[Pt(4-Clpy)$_2$Cl$_2$]	30	1.033	58
trans-[Pt(4-CH$_3$py)$_2$Cl$_2$]	30	0.955	58
[Pt(en)Cl$_2$]	35	0.64[a]	53
[Pt(bipy)Cl$_2$]	25	0.75	56
[Pt(bipy) (NO$_2$)Cl]	25	0.87	56
[Pt(bipy) (N$_3$)Cl]	25	0 95	56
[Pt(bipy) (SCN)Cl]	25	1.3	56

[a] In water.

some nucleophiles with a rate decreasing in the order[60] thiourea > py > glycine > aniline > H$_2$O. On the other hand a reactivity order[61] SCN$^-$ > I$^-$ > Br$^-$ > Cl$^-$ > H$_2$O is found for [Pd(acac)$_2$]. Both these sequences parallel the order of the nucleophilic reactivity constants, n^0_{Pt}.

It has already been pointed out that the basicity is of little importance in determining the reactivity of the nucleophiles towards the complexes under consideration. However, the extent of its contribution has been determined by reacting platinum (II) and palladium (II) complexes with amines and thioethers. The second-order rate constants[62–72] for amines having the same kind of steric hindrance are related to pK_a according to eqn. (8), and those for thioethers are related to basicity, expressed in terms of the sum of the Taft σ^* values of the radicals bonded to sulfur, according to eqn. (9).

$$\log k_2 = \alpha_{\mathrm{N}} \mathrm{p}K_{\mathrm{a}} + C_{\mathrm{N}} \qquad (8)$$

$$\log k_2 = \alpha_{\mathrm{S}}(-\Sigma\sigma^*) + C_{\mathrm{S}} \qquad (9)$$

A linear relationship has also been found by plotting log k_2 of the reactions of *trans*-

$[Pt(py)_2Cl_2]$ with 4,4′-disubstituted dephenylthioethers in methanol against $\Sigma\sigma_p$, where σ_p are the Hammett substituent parameters of the *para* substituents[55]. Besides basicity, the extent of steric hindrance of the amines is also important in determining their reactivity. Some investigations carried out by using substituted pyridines as entering groups have shown that the kind of steric hindrance does affect only C_N and not α_N. Each 2-substituent is found to change the value of C_N by a constant amount, Δ, so that the relationship operating in these cases is

$$C_{N(n)} - C_{N(n')} = (n' - n)\,\Delta \tag{10}$$

(n and n' are the numbers of 2-substituents (0, 1 or 2); Δ is a measure of the steric effect of one 2-substituent in lowering the bimolecular reactivity of substituted pyridines towards a given complex)[67]. The lower reactivity of 2-substituted pyridines, with respect to the 3- and 4-substituted derivatives, seems to be due to a higher enthalpy of activation related to a greater difficulty experienced in the formation of the five-coordinate intermediate when the entering group exhibits steric hindrance near the pyridine nitrogen[73]. Tables 4 and 5 report data regarding the discrimination parameters, α_S and α_N, together with the steric hindrance parameter, Δ, for some complexes.

TABLE 4

Discrimination parameters, α_S, of some palladium (II) and platinum (II) planar complexes reacting with thioethers at 25°C

Complex	Leaving group	Solvent	α_S	Ref.
$[Pt(bipy)Cl_2]$	Cl^-	Methanol	1.25	68
$[Pt(bipy)(N_3)Cl]$	Cl^-	Methanol	0.47	68
$[Pt(bipy)(NO_2)Cl]$	Cl^-	Methanol	2.7	68
$[Pt(bipy)(NO_2)_2]$	NO_2^-	Methanol	2.6	68
$[Pt(bipy)(NO_2)N_3]$	N_3^-	Methanol	2.6	68
trans-$[Pd(3\text{-}CNpy)_2Cl_2]$	3-CNpy	1,2-Dimethoxyethane	0.8	69
trans-$[Pd(4\text{-}CNpy)_2Cl_2]$	4-CNpy	1,2-Dimethoxyethane	0.8	69
trans-$[Pd(3\text{-}CH_3py)_2Cl_2]$	$4\text{-}CH_3py$	1,2-Dimethoxyethane	0.8	69
trans-$[Pd(py)_2Cl_2]$	py	1,2-Dimethoxyethane	0.76	69
trans-$[Pd(4\text{-}Clpy)_2Cl_2]$	4-Clpy	1,2-Dimethoxyethane	0.29	72
trans-$[Pd(4\text{-}Clpy)_2Br_2]$	4-Cipy	1,2-Dimethoxyethane	0.18	72
trans-$[Pd(4\text{-}Clpy)_2I_2]$	4-Clpy	1,2-Dimethoxyethane	0.02	72
trans-$[Pd(py)_2Br_2]$	py	1,2-Dimethoxyethane	0.28	72
trans-$[Pd(py)_2I_2]$	py	1,2-Dimethoxyethane	0.02	72

TABLE 5

Discrimination (α_N) and steric hindrance (Δ) parameters related to the reactions of amines with some palladium (II) and platinum (II) complexes at 25°C

Complex	Leaving group	Solvent	α_N	Δ	Ref.
$[Pt(bipy)Cl_2]$	Cl^-	Methanol	0.06	1.0	67
$[Pt(PhS(CH_2)_3SPh)Cl_2]$	$PhS(CH_2)_3SPh$	1,2-Dimethoxyethane	0.14		66
$[Pd(PhS(CH_2)_3SPh)Cl_2]$	$PhS(CH_2)_3SPh$	1,2-Dimethoxyethane	0.09		66
$[Pt(PhS(CH_2)_2SPh)Cl_2]$	$PhS(CH_2)_2SPh$	1,2-Dimethoxyethane	0.14	1.6	64
$[Pd(PhS(CH_2)_2SPh)Cl_2]$	$PhS(CH_2)_2SPh$	1,2-Dimethoxyethane	0.22	2.4	71
$[Pd(PhS(CH_2)_2SPh)Br_2]$	$PhS(CH_2)_2SPh$	1,2-Dimethoxyethane	0.28		70
$[Pd(PhS(CH_2)_2SPh)(N_3)_2]$	$PhS(CH_2)_2SPh$	1,2-Dimethoxyethane	0.3		70
$[Pd(PhS(CH_2)_2SPh)I_2]$	$PhS(CH_2)_2SPh$	1,2-Dimethoxyethane	0.36		70
$[Pd(PhS(CH_2)_2SPh)(SCN)_2]$	$PhS(CH_2)_2SPh$	1,2-Dimethoxyethane	0.42		70
trans-$[Pt(i\text{-}Pr_2S)_2Cl_2$	$i\text{-}Pr_2S$	1,2-Dimethoxyethane	0.138	2.48	65
trans-$[Pd(i\text{-}Pr_2S)_2Cl_2]$	$i\text{-}Pr_2S$	1,2-Dimethoxyethane	0.132	2 35	65
$[Pd(dien)I]^+$	I^-	H_2O	~0	1.6	63
$[Pd(dien)N_3]^+$	N_3^-	H_2O	~0	1.75	63
$[Pd(dien)SCN]^+$	SCN^-	H_2O	~0	1.45	63
$[Pd(dien)(NO_2)]^+$	NO_2^-	H_2O	~0	1.4	63
$[PdCl_4]^{2-}$	Cl^-	H_2O	0.25	1.5	62
trans-$[Pd(4\text{-}Clpy)_2Cl_2]$	4-Clpy	H_2O	0.075		72
trans-$[Pd(4\text{-}Clpy)_2Br_2]$	4-Clpy	H_2O	0.24		72
trans-$[Pd(4\text{-}Clpy)_2I_2]$	4-Clpy	H_2O	0.34		72

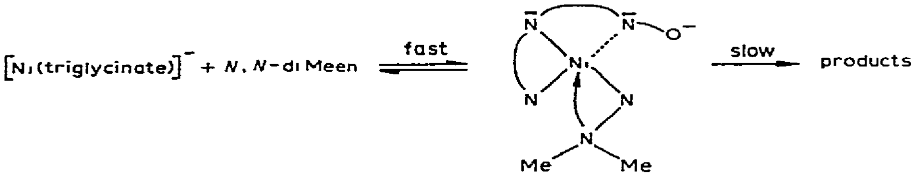
Although the linear free energy relationship (8) has been found to be valid in several cases, it does not always hold[73–77]. For example, the second-order rate constants of the reactions

$$[Pt(dien)X]^+ + am \rightarrow [Pt(dien)(am)]^{2+} + X^- \quad (11)$$

$$[PtCl_4]^{2-} + am \rightarrow [Pt(am)Cl_3]^- + Cl^- \quad (12)$$

do not show any correlation with the basicity of entering amines of constant steric form. Nevertheless, in these cases too, less sterically hindered amines exhibit higher reactivities.

There is little information about the effect of the entering group on the rate of substitution reactions of planar nickel (II) complexes. However, some data are available concerning this effect in the reactions of square-planar nickel (II) complexes yielding octahedral complexes. The mechanism of these reactions is not yet well understood, but it is assumed to involve an associative mechanism, by analogy with the usual kinetic behaviour of d^8 square-planar complexes. The steric hindrance of the entering group also appears to be kinetically very important in these reactions as has been shown in the substitution reactions of planar $[Ni(triglycinate)]^-$ with amines, carboxylates and aminocarboxylates[78]. An interesting chelate kinetic effect has been found in this reaction when the entering group is a multidentate aminocarboxylate ligand. These groups are found to react much more quickly than monodentate ligands[78]. In such a case, the reaction seems to involve a fast reversible substitution of one carboxylic group of triglycinate by one end of the entering ligand, and the rate-determining step is the subsequent reaction of the intermediate so formed, e.g.



(13)

Important chelate kinetic effects have been encountered also in substitution reactions of $[Ni(CN)_4]^{2-}$ with multidentate amine ligands[79].

(3) Role of the leaving group. The importance of the effect of the leaving group on the rate of substitution reactions of square-planar complexes was first recognized in the reactions

$$[Pt(dien)X]^{n+} + py \rightarrow [Pt(dien)py]^{2+} + X^{n-2} \tag{14}$$

whose rates were found to change in the order[80] $NO_3^- > H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$. Further data are now available in this connection. Some of these are reported in Table 6. They are in reasonable agreement with the order of reactivity $Cl^- \simeq Br^- \simeq I^- \simeq N_3^- > SCN^- > NO_2^- > CN^-$. The comparable reactivity for chloride, bromide and iodide as leaving groups has been rationalized in terms of bond making being rate-determining (profile (b) of Fig. 1) so that bond breaking is of little kinetic importance. The large dependence upon X of the reactivity for the other leaving groups is ascribed to bond breaking becoming rate-determining[42]. The influence of the basicity of the leaving group on the reactivity of square-planar complexes of the nickel triad is now well recognized. Examples are the replacement of thioethers from $[Pt(bipy)(RSR')Cl]^+$ by several nucleophiles[85], the substitution of amines from *trans*-$[Pd(am)_2Cl_2]$ by thioethers[69] and the substitution of phosphines[86] from planar *trans*-$[Ni(PR_3)_2(NCS)_2]$ by bipy. It is generally found that the second-order rate constants decrease with increasing basicity of the leaving group. Good linear relationships are generally found between $\log k_2$ and the values of pK_a (or $\Sigma\sigma^*$) of the single leaving group.

TABLE 6

Effect of the leaving group, X, on the second-order rate constants, k_2, of nucleophilic substitution reactions of some planar complexes of Pd^{II} and Pt^{II}

Complex	Entering ligand	Solvent	t (°C)	k_2 (l. mole^{-1} sec^{-1}) for X equal to Cl^-	Br^-	I^-	N_3^-	SCN^-	NO_2^-	CN^-	Ref.
$[Pt(dien)X]^+$	py[a]	H_2O	25	3.48×10^{-5}	2.30×10^{-5}	1.0×10^{-5}	8.33×10^{-7}	3.2×10^{-7}	5×10^{-8}	1.67×10^{-8}	80
	Cl^-	H_2O	25	5.0×10^{-3}	8.8×10^{-4}	2.3×10^{-4}					81
	Thiourea	H_2O	30	5.80×10^{-1}	1.30	1.30	1.5×10^{-2}	2.0×10^{-2}	3.5×10^{-4}		47
	N_3^-	H_2O	30	5.20×10^{-3}	9.20×10^{-3}	1.1×10^{-2}					47
	I^-	H_2O	30	1.70×10^{-1}	3.2×10^{-1}		8.5×10^{-3}				47
	SCN^-	H_2O	30	4.20×10^{-1}	8.80×10^{-1}	8.70×10^{-1}	9×10^{-3}				47
	$SeCN^-$	H_2O	30	2.50	7.00	7.00	5.1×10^{-2}				47
$[Pd(dien)X]^+$	py	H_2O	25	Fast	Fast	3.55×10^{2}	1.30×10^{2}	3.1×10^{1}	6.4		63
	Quinoline	H_2O	25			9	2.4	1.06	0.3		63
	$2\text{-}CH_3py$	H_2O	25			8.8	2.3	1.08	0.25		63
	$2,4\text{-}(CH_3)_2py$	H_2O	25			9.7	2.5	1.09	0.26		63
	$2,6\text{-}(CH_3)_2py$	H_2O	25			1.25×10^{-1}		3×10^{-2}	8×10^{-3}		63
trans-$[Pt(PEt_3)_2(Me)X]$	I^-	MeOH	30	4×10^{-1}	2.6×10^{-1}						82
trans-$[Pt(PEt_3)_2(Ph)X]$	I^-	MeOH	30	6×10^{-2}	8×10^{-2}						82
trans-$[Pt(PEt_3)_2(m\text{-}FC_6H_4)X]$	I^-	MeOH	30	3.2×10^{-2}	9×10^{-2}		5.1×10^{-2}		1.4×10^{-3}		83
	Thiourea	MeOH	30	3.95	3.25	1.70	1.43	4.9×10^{-2}	1.48×10^{-2}		83
$[Pt(bipy)(NO_2)X]$	Cl^- [b]	MeOH	25	1.6×10^{-4}		2.5×10^{-2}	2.2×10^{-5}		1.8×10^{-4}		84
	NO_2^- [b]	MeOH	25	2.6×10^{-3}	3.3×10^{-3}	1×10^{-2}	2.0×10^{-5}				84

[a] k_{obs}, [py] = 5.92×10^{-3} *M.*

[b] The same reactivity sequence has been found for Br^-, N_3^-, I^-, SCN^- and thiourea as entering ligands.

(4) Cis and trans effects. Ligands bound in positions *cis* or *trans* to the leaving group may play an important part in determining the reaction rate. Many experimental data are available in this connection as well as satisfactory theoretical treatments[87-91]. The strongest effect is caused by the *trans* ligand. This *trans effect* was originally intended to describe the *trans directing influence* of a ligand upon the ease of replacement of the ligand *trans* to it. On preparative chemistry grounds only it has been possible to define the following order for the *trans* effect[87]:

$$CN^-, CO, C_2H_4, NO > \text{thiourea}, PR_3, SR_2 > NO_2^- > I^- > SCN^- > Br^- >$$

$$> Cl^- > NH_3, \text{py}, RNH_2 > OH^- > H_2O$$

From a kinetic point of view it is more adequate to consider the effect of a ligand upon the rate of substitution of the group *trans* to it, i.e. the so-called *labilizing trans effect*. A few sequences of the labilizing *trans* effect for platinum (II) complexes are reported in Table 7. These, and other data reported in the literature[41-43], lead one to define the following order for the labilizing *trans* effect for platinum (II) complexes:

$$\text{Olefins} \simeq NO \simeq CO \simeq CN^- > PR_3 \simeq H \simeq \text{thiourea} > CH_3^- > Ph^- > SCN^- >$$

$$> NO_2^- > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O^\star$$

The data available on the labilizing *trans* effect on square-planar palladium (II) and nickel (II) complexes are relatively limited. However, the information available seems to indicate behavior similar to that found for platinum (II). For example, kinetic studies of the ammination of chloroaminepalladium (II) complexes have shown that ammonia exhibits a labilizing *trans* effect about ten times greater than that of chloride[103]. Also, a sequence $NO_2^- > Cl^- > H_2O$ has been derived[104, 105] from a kinetic study of the acid hydrolysis reaction

$$trans\text{-}[Pd(NH_3)_2LCl]^{n+} + H_2O \rightarrow trans\text{-}[Pd(NH_3)_2L(H_2O)]^{n+1} + Cl^- \qquad (15)$$

All these data parallel the order of the *trans* effect found for platinum (II).

A recent study of the kinetics of substitution reactions of planar nickel (II)—dithiolate complexes with dithiolates and with cyanide has provided important information on the *trans* effect in the reactions of nickel (II) complexes[52]. The order of the *trans* effect has been found to parallel the increase of delocalization of the π-electron density from the nickel $4p_z$ orbital caused by the *trans* ligand. A high π-electron density delocalization is thought to cause a high stability of the five-coordinate adduct which is formed prior to the bond-breaking step. This would then lead to a high rate of reaction.

Pi interactions appear to be an important factor in determining the *trans* effect of a

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★ More detailed information concerning the *trans* effect of the mono-olefins or phosphines can be derived from Table 7.

TABLE 7

Labilizing *trans* effect on the rate of reaction of some platinum (II) complexes

Complex	Entering group	*trans* group	Order of labilizing *trans* effect[a]	Ref.
cis-$[Pt(NH_3)LCl_2]$	py	L	$C_2H_4 \gg NO_2 > Br > Cl$ $>100 \quad 9 \quad 3 \quad 1$	92
cis-$[Pt(PR_3)_2Cl_2]$ or *trans*-$[Pt(PEt_3)_2LCl]$	py	PR_3 or L	$PMe_3 > PEt_3 \simeq H^{(-)} > P(n\text{-}Pr)_3 > CH_3 > Ph \simeq p\text{-}MeOPh$ $>50{,}000 \quad \sim10{,}000 \quad \sim10{,}000 \quad \sim4{,}000 \quad 167 \quad 40 \quad 37$ $\simeq p\text{-}ClPh > 4\text{-}biphenylyl > o\text{-}tolyl > mesityl \simeq Cl$ $33 \quad 24 \quad 4.2 \quad 0.92 \quad 1$	93
trans-$[Pt(PEt_3)_2LCl]$	CN^-	L	$Ph > o\text{-}tolyl > mesityl$ $425 \quad 28 \quad 1$	94
trans-$[Pt(PEt_3)_2LCl]$	Thiourea	L	$Ph > o\text{-}tolyl > mesityl$ $127 \quad 13.2 \quad 1$	94
trans-$[PtL(NH_2Et)Cl_2]$	NH_2Et exch.	L	Olefins, alkynes $\gg SbEt_3 > SbPh_3 > PMe_3 > PET_3 >$ $> P(n\text{-}Pr)_3 > PPh_3 > AsEt_3 > AsPh_3 \gg S(n\text{-}Pr)_2$	95
$[Pt(olefin)Cl_3]^-$	bipy	Olefin	Pent-4-enyl$NH_3^+ >$ allyl$SO_3^- >$ allyl$PEt_3^+ \simeq$ allylNH_3^+ $> Me_2C(OH)C{\equiv}CC(OH)Me_2 > C_2H_4$	96–98
$[Pt(H_2O)_{4-n}X_n]^{2-n}$ and $[Pt(NH_3)_{4-n}Cl_n]^{2-n}$	H_2O and/or NH_3		$Br > Cl > NH_3 > H_2O$	99–102

[a] The figures are ratios of rate constants.

ligand. For example, Table 7 shows that good π-acceptors such as phosphines and olefins exhibit a high *trans* effect. However, π interactions are not the only factors influencing the *trans* effect. For example, H^-, a very weak π-acceptor but a strong σ-donor, exhibits a high *trans* effect. It is now generally accepted that both σ and π contributions play an important role in determining the *trans* effect[90,91].

Much information is also now available on the effect of the ligands bonded *cis* to the leaving group in determining rates of substitution. Although some exceptions are known[99, 102], a ligand usually has a less marked effect on the rate when it occupies a *cis* rather than a *trans* position, provided steric effects are not important.

One of the first investigations of the *cis* effect was a study of the kinetics of the reaction

$$cis\text{-}[Pt(PEt_3)_2RCl] + py \rightarrow cis\text{-}[Pt(PEt_3)_2Rpy]^+ + Cl^- \qquad (16)$$

where R is an organic radical or the chloride ion[93]. The order of the *cis* effect found for R in this reaction is

R:	CH_3 >	*p*-tolyl >	Ph >	Cl >	*o*-tolyl >	mesityl
$\frac{k_{Pt-R}}{k_{Pt-Cl}}$:	3.6	3.0	2.3	1	5×10^{-3}	2.5×10^{-5}

A comparison of the data for the first four ligands with the data of Table 7 shows that the *cis* effect is less marked than the *trans* effect. A more marked *cis* effect is exhibited by the *o*-tolyl and mesityl ligands and is ascribed to the effect of steric hindrance on the reaction center caused by the *ortho* methyls.

Rather interesting information on the *cis* effect has been obtained from kinetic studies of the reactions

$$trans\text{-}[PtL_2X_2] + Y \rightarrow trans\text{-}[PtL_2XY] + X \qquad (17a)$$

$$trans\text{-}[PtL_2XY] + Y \rightarrow trans\text{-}[PtL_2Y_2] + X \qquad (17b)$$

by using several groups L bonded *cis* to the leaving group. It has been found that the order of the *cis* effect is also dependent on the nature of the entering group. For example, the order of the *cis* effect is $PEt_3 < AsEt_3 < py < pip$ when the incoming ligand is a rather poor nucleophile[53], such as NO_2^-, and $pip < py < PEt_3 < AsEt_3$ in the case of good nucleophiles, such as $SeCN^-$ and thiourea[106-108]. This inversion of the trend has been explained on the basis of the effects of the *cis* ligands in labilizing the Pt–Cl bond and in determining the electron density at the reaction center[109, 110]. Measurements of ^{35}Cl nuclear quadrupole resonance frequencies[109] have shown that *cis* ligands progressively weaken the M–Cl bond in *trans*-$[ML_2Cl_2]$ compounds (M = Pd, Pt) in the order $PR_3 < AsR_3 < py < pip$. This is also the order found for reactions with weak nucleophiles, and is consistent with the fact that bond breaking is rate-determining in these cases (profile

(a) of Fig. 1). A nearly opposite trend is found for reactions with good nucleophiles where bond making is rate-determining (profile (b) of Fig. 1). In this case an order $PR_3 > AsR_3 > py > pip$ should be determined by a decrease of the electron density on the reaction center due to π-withdrawal in the order $pip > py > AsR_3 > PR_3$.

The change of *cis* effect order by changing the nucleophilic power of the entering group can be described in terms of different discrimination parameters, s, α_N and α_S, for the substrates, according to eqns.(7), (8) and (9) (see for example Fig.2 and Tables 3, 4 and 5). Analogous behaviour has also been observed for the *trans* effect. For example in reaction (18), where R = CH_3, Ph, Cl,

$$trans\text{-}[Pt(PEt_3)_2RCl] + Y^{n-} \rightarrow trans\text{-}[Pt(PEt_3)_2RY]^{1-n} + Cl^- \qquad (18)$$

the *trans* effect order $CH_3 > Ph > Cl$ is observed with poor nucleophiles (see Fig. 3) whilst with good nucleophiles the order[111] is $Cl > CH_3 > Ph$. In order to avoid the dependence of both *cis* and *trans* effects on the entering group it has been suggested that these effects should be defined in terms of the discrimination parameters. According to this proposal a higher *trans* effect is exhibited by *trans* ligands causing a lower ability of the substrate to discriminate between the entering ligands (i.e. the order of the *trans* effect parallels the values of $1/s$)[111], and a larger *cis* effect is exhibited by *cis* ligands causing a higher ability of the substrate to discriminate between the entering groups (i.e. the order of the *cis* effect parallels the values of s and α_N[*])[58]. Actually, the discrimination parameters can be very useful in gaining information about the effects of *cis* and *trans* ligands upon the kinetic behavior of square-planar complexes, but their use to describe *cis* and *trans* effects is not consistent with the conventional definition of these effects. In fact, the parameters s and α_N do not provide information about the *cis* and *trans* effects in terms of reactivity. For example, the reaction

$$trans\text{-}[Pd(4\text{-}Clpy)_2X_2] + am \rightarrow trans\text{-}[Pd(4\text{-}Clpy)(am)X_2] + 4\text{-}Clpy \qquad (19)$$

shows an order of *cis* effect $I > Br > Cl$ (see Table 5) when expressed in terms of α_N, but the order is $Cl > Br > I$ when expressed in terms of reactivity towards any of the entering amines so far considered[72]. To avoid confusion between the different terminologies it seems much better to retain the usual definition related to reactivity for *cis* and *trans* effects, in spite of the possible changes of order with the entering group. The effects related to the discrimination parameters could be indicated more properly as *cis* and *trans discrimination effects.*

The *cis discrimination effect* seems to depend on the nucleophilic power of the *cis* ligand causing this effect. Indeed, there is a general parallelism between s or α_N for a given complex and the nucleophilic reactivity constants, n^0_{Pt}, assigned to the *cis* ligands[56,70,72]. Also, the basicity of the *cis* ligand is found to play only a small part in determining the ability of the complex to discriminate between the entering groups.

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[*] The discrimination parameter for the thioethers[68,69,72] does not seem to give orders of the *cis* effect consistent with those related to s and to α_N.

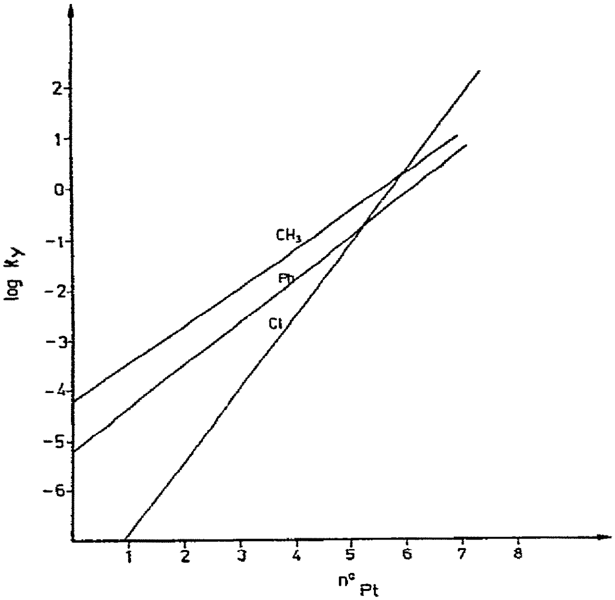


Fig. 3. Effect of the *trans* ligand upon k_Y of *trans*-[Pt(PEt$_3$)$_2$RCl] in methanol at 30° C as a function of the nucleophilic reactivity constants, n_{Pt}, for different nucleophiles. Data from ref. 111.

(5) Steric effects of coordinated ligands. Steric hindrance caused by ligands bonded to the central metal ion strongly affects the rates of reaction of square-planar complexes. For example, the first- and second-order rate constants, k_1 and k_2, of thiocyanate exchange and substitution of [Pt(AA)(SCN)$_2$] complexes with thiourea (AA = diamine) decrease with increasing steric hindrance of the diamine, i.e. in the order[112–114] N,N'-Me$_2$en $>N,N'$-i-Pr$_2$en $>N,N'$-Ph$_2$en. The complex with the unhindered en group occupies an anomalous position in this sequence, being the least reactive member of the series. However, this anomaly disappears when the effect of the steric hindrance is discussed in terms of the enthalpy of activation rather than in terms of reactivity at a given temperature[114]. Other examples of the effect of steric hindrance on the reaction rates are shown in Table 8. From the first two examples it is found that steric hindrance caused by a bulky ligand is kinetically more important when this is bonded *cis* rather than *trans* to the leaving group. An important effect is also exhibited by steric hindrance in the leaving group. This has been shown by studying reaction (20) in methanol or *n*-hexane[120].

$$trans\text{-}[\mathrm{PtCl_2(PR'_3)[^{14}C]NHR''_2}] + \mathrm{NHR'''_2} \rightarrow trans\text{-}[\mathrm{PtCl_2(PR'_3)(NHR'''_2)}] + [^{14}\mathrm{C}]\mathrm{NHR''_2} \qquad (20)$$

In such cases a change in the steric hindrance of the phosphines, *trans* to the leaving group, causes only a small decrease in the first- and second-order rate constants in the order[120] PMe$_3$ > PEt$_3$ > P(n-Pr)$_3$, the total change being less than three-fold in going from PMe$_3$ to P(n-Pr)$_3$. A greater effect is observed by changing the steric hindrance of the leaving group. In fact the rate constants k_1 and k_2 for the reaction of *trans*-[PtCl$_2$(P(n-Pr)$_3$)-

Steric effects on the rate of substitution of some planar complexes of the nickel triad

Reacting mixture	t (°C)	Solvent	Order of steric effect caused by the bulky ligand				Ref.
cis-$[Pt(PEt_3)_2RCl]$ + py	0	EtOH		Ph >	*o*-tolyl >	mesityl	93
				3.84×10^{-2}	8.7×10^{-5}	4.17×10^{-7} [a]	
trans-$[Pt(PEt_3)_2RCl]$ + py	25	EtOH		Ph >	*o*-tolyl >	mesityl	93
				1.3×10^{-4}	1.7×10^{-5}	3.40×10^{-6} [b]	
trans-$[Pt(PEt_3)_2RCl]$ + CN^-	30	MeOH		Ph >	*o*-tolyl >	mesityl	
				3.61	2.34×10^{-1}	8.49×10^{-3} [c]	94, 115
		DMSO		very fast	3.54	3.17×10^{-2} [c]	94, 115
trans-$[Pt(PEt_3)_2RCl]$ + thiourea	30	MeOH		Ph >	*o*-tolyl >	mesityl	
				6.30	6.52×10^{-1}	4.94×10^{-2} [c]	94, 111, 115
		DMSO		5.32×10^{-1}	1.057×10^{-1}	9.525×10^{-3} [c]	94, 115
trans-$[Ni(PEt_3)_2RCl]$ + py	25	EtOH			*o*-tolyl >	mesityl	93
					33.4	2×10^{-2} [a]	
$[Ni(\alpha\text{-amineoxime})_2\text{-}H]^+ + EDTA^{4-}$	25.3	H_2O		AO >	MeAO >	$\frac{1}{2}$enAO	116
				1.58×10^{-3}	1.92×10^{-5}	1.25×10^{-5} [d]	
$[Ni(AA)_2]^{2+}$ + aqueous HCl	0	H_2O		TetraMeen >	ethyltriMeen >	diethyldiMeen	117
				282	900	3,000[e]	
$[Pd(AAA)Cl]^+ + Y^-$	25	H_2O	dien >	Me_5dien >	Et_4dien >	$MeEt_4$dien	118
			1.0×10^2	3×10^{-1}	2×10^{-3}	8×10^{-4} [a]	

[a] k_1 (sec^{-1}).

[b] k_{obs} (sec^{-1}), [py] = 6.2×10^{-3} *M*, derived from Table 3, ref. 93.

[c] k_2 ($l.mole^{-1}.sec^{-1}$).

[d] k_{obs} (sec^{-1}) at pH 9.48 0.025 *M* EDTA. A similar order is found in the exchange of α-amineoximes[119]. (AO = 2-amino-2methyl-3-butaneoxime; MeAO = 2-methylamino-2-methyl-3-butaneoxime; enAO = 2,2'-ethylenediaminobis-2-(methylbutanone) dioxime).

[e] $t_{\frac{1}{2}}$ in seconds

$(NHMe_2)]$ with $NHEt_2$ are respectively 15.7 and 60.5 times higher than those of the complex *trans*-$[PtCl_2(P(n\text{-}Pr)_3(NHEt_2)]$.

Steric hindrance can also modify the reaction mechanism. For example, reaction (21), (X = Cl, Br, I; Y = Br, I, SCN, NO_2, N_3; AAA = substituted diethylenetriamines) follows a simple first-order rate law, without any bimolecular contribution[118,121], when AAA is a strongly hindering ligand such as Me_5 dien, Et_4dien, $MeEt_4$dien.

$$[Pd(AAA)X]^+ + Y^- \rightarrow [Pd(AAA)Y]^+ + X^- \qquad (21)$$

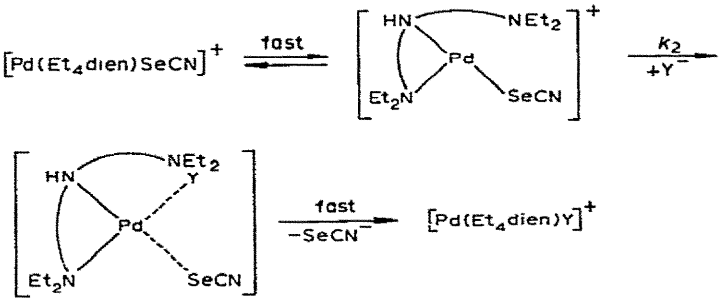
The first-order rate law for these sterically hindered complexes is better explained on the basis of an interchange dissociative mechanism, rather than an associative mechanism involving a molecule of solvent in the rate-determining step. Square-planar complexes displaying such behavior are called *pseudo-octahedral* complexes.

Pseudo-octahedral behavior is also exhibited by *trans*-$[Pt(PEt_3)_2RCl]$ (R = *o*-tolyl, mesityl), and is ascribed, at least partially, to the steric hindrance caused by the *ortho* methyls at the reaction center[94, 115]. In fact these complexes have rates of reaction which are independent of the entering group even when this is a good nucleophile such as I^-, SCN^-, PhS^-, $S_2O_3{}^{2-}$. However, a contribution dependent on the entering group is operating in methanol and in DMSO when the incoming ligand is cyanide, selenocyanide and thiourea. The fact that such a contribution is absent when other good nucleophiles are used has been taken as an indication that the pseudo-octahedral behavior of these complexes does not come only from steric hindrance. It is believed that a strong σ-donation of R^- also contributes towards preventihg a bimolecular attack. Biphilic nucleophiles, such as CN^-, $SeCN^-$ and thiourea, would still react through associative pathways, owing to their ability to delocalize the charge from the reaction center through π-interactions[115]. $[Pd(Et_4dien)Br]^+$ also reacts with $S_2O_3{}^{2-}$ in water[122] and with chloride and iodide in MeCN (ref. 123) showing a second-order contribution to the rate. In the first case the high nucleophilic reactivity of thiosulfate ($n^0_{Pt} = 7.34$) and the formation of an ion-pair are believed to overcome the steric strain caused by the bulky ligand. In the second case the bimolecular contribution is probably favored by a high reactivity of chloride and iodide in MeCN, due to their lower degree of solvation under these conditions.

There are several other cases in which reactions of sterically hindered complexes display second-order rate laws. However, an associative mechanism does not operate in these cases. For example, the second-order rate law observed for the reaction

$$[Pd(Et_4dien)(H_2O)]^{2+} + Y^{n-} \rightarrow [Pd(Et_4dien)Y]^{2-n} + H_2O \qquad (22)$$

has been explained in terms of an ion-pair associative ligand interchange mechanism (S_N2IP)[122]. $[Pd(Et_4dien)SeCN]^+$ also reacts with several nucleophiles through a second-order contribution to the rate[124]. However, the order of the rate constants does not parallel the nucleophilic power of the entering ligands, measured in terms of n^0_{Pt}, showing that this is not the determining factor for the rate of the k_2 path. This also makes an associative mechanism rather unlikely. The mechanism operating in these reactions is thought to involve the formation of an intermediate by the fast reversible opening of one or more of the chelate rings owing to the steric strain caused by the large selenium atom bonded to palladium (II) near the bulky Et_2N– ends of Et_4dien. A nucleophilic attack of the incoming ligand on such an intermediate would be the rate-determining step.



(23)

The importance of the steric effect of selenium in operating this mechanism is also inferred from the fact that the thiocyanato complex, $[Pd(Et_4dien)SCN]^+$, does not react through any bimolecular path, thus behaving as a pseudo-octahedral complex[125]. This behavior is consistent with the fact that the sulfur atom, smaller than selenium, does not create sufficient steric strain.

(6) Solvent effect. The solvent plays a double role in the reactions of planar complexes, being a reaction medium as well as a nucleophile (for the k_1 reaction path of unhindered complexes). Most information on this subject relates to the reactions of platinum (II) complexes.

The solvent effect on the k_1 term is documented in Table 9. No correlation is found with either the polarity or the solvating ability of the solvents, thus showing that these factors are not the most important in determining the rate of the k_1 path. Nucleophilicity, however, is an important factor, as expected for an associative mechanism. For example, a general trend $DMSO > H_2O \simeq MeNO_2 > ROH$ is encountered for k_1. The relatively high value found for DMSO is ascribed to the fact that this solvent is a good nucleophile* towards platinum (II). On the other hand $MeNO_2$ also gives relatively high values of k_1

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* The occurence of strong $\mathrm{Pt{-}\overset{\overset{O}{\|}}{S}(CH_3)_2}$ bonds in platinum (II) complexes supports this interpretation.

TABLE 9

Solvent effect on the rate of the solvolytic path at 25°C of the reactions of some platinum (II) complexes

Complex	Solvent	k_1 (sec^{-1})	Ref.
trans-$[Pt(py)_2Cl_2]$	DMSO	3.8×10^{-4}	126
	H_2O[a]	3.5×10^{-5}	126
	$MeNO_2$	3.2×10^{-5}	126
	EtOH	1.4×10^{-5}	126
	MeOH[b]	1×10^{-5}	106
	n-PrOH	4.2×10^{-6}	126
trans-$[Pt(pip)_2Cl_2]$	DMSO	7×10^{-4}	128
	$(CH_3)_2CO$	8×10^{-5}	128
	DMF	4×10^{-5}	128
	AcCN	3×10^{-5}	128
	$MeNO_2$	2.5×10^{-5}	128
	MeOH	1.2×10^{-5}	127
	EtOH	7×10^{-6}	129
	t-BuOH[c]	1.2×10^{-4}	129
	MeOH[c]	5×10^{-5}	129
	EtOH[c]	3×10^{-5}	129
trans-$[Pt(PEt_3)_2Cl_2]$	DMSO	2×10^{-5}	130
	$(CH_3)_2CO$	$\sim 10^{-6}$	130
	MeOH	$\sim 2 \times 10^{-7}$	53

[a] These data refer to *trans*-$[Pt(NH_3)_2Cl_2]$.
[b] Values at 30°C.
[c] Values at 40°C.

owing to its biphilic behavior, which makes it able to interact via π-bonding with the central metal atom. The lower values found for water and alcohols are in agreement with the weak nucleophilic nature of their oxygen atoms towards platinum (II). There is now little doubt that the solvent effect on the k_1 of unhindered complexes is related to the occurrence of an associative mechanism for the solvolytic reaction path. There are, however, a few recent results on the aquation of *trans*-$[Pt(NH_3)_2Cl_2]$ (ref. 131) and *cis*-$[Pt(NH_3)_2Cl_2]$ and $[Pt(en)Cl_2]$ (ref. 132) in aqueous organic solvents which are believed to be better explained in terms of a dissociative mechanism.

Data on the effect of the solvent upon the second-order rate constant, k_2, were origi-

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nally obtained by measuring the rate of chloride exchange in *trans*-[Pt(py)$_2$Cl$_2$] in a variety of solvents[126]. The bimolecular rate constants were found to decrease in the order $CCl_4 > C_6H_6 >$ *m*-cresol $\simeq$ *t*-BuOH $\simeq CH_2ClCH_2Cl >$ EtOAc $\simeq (CH_3)_2CO$ $>$ MeCN $>$ DMF. Such a trend was explained by assigning a higher reactivity to Cl^- in a solvent with poor ion solvating ability, such as CCl_4 or C_6H_6. In good solvents, such as DMF or MeCN, the chloride ion would be less reactive, being more solvated. An extensive investigation on the solvent effect has been carried out by reacting *trans*-[PtL$_2$X$_2$] with several nucleophiles in protic[129] as well as in dipolar aprotic solvents[128,130]. A rather interesting result is that the nucleophilic reactivity order remains the same regardless of the nature of the solvent, showing that the polarizability of the nucleophile is much more important than the nature of the solvent in determining the rate of substitution of platinum (II) complexes. The solvent, however, does influence the nucleophilic discrimination factor, *s*, which is lowered in going from protic to dipolar aprotic solvents, regardless of the platinum (II) complex employed*. This last consideration suggests that the change in *s* arises mainly from changes of solvation of the entering group. Although there are indications in favor of this hypothesis[82], it is not certain, for example, that the solvation of the leaving group on changing the solvent is kinetically unimportant when bond breaking rather than bond making is rate-determining. On the other hand, indications in favor of a kinetically important solvation of the leaving group appear to have been obtained by studying the rate of the substitution reaction of *trans*-[Pt(py)$_2$Cl$_2$] with bromide in H_2O—DMSO mixtures[133]. This is at least an indication of how a complete understanding of the effect of the solvent upon the bimolecular reaction pathways of planar complexes is far from achieved. It is not yet clear what the different factors contributing to the overall effect are. For example, the conformation of the solvated complex in solution is not yet definitively known. Although this is usually believed to contain two molecules of solvent above and below the molecular plane, some evidence seem to indicate that in many cases only one molecule of solvent is present in the fifth position[134]. Among the several factors that can influence the rate, and one that has not yet been properly investigated, is the profile of the reaction which can change from (a) of Fig. 1 to (b) when the solvent is changed.

(7) Effect of the central metal ion. Few data are available concerning the effect of changing the central metal ion on the rates of reaction of square-planar complexes of nickel (II), palladium (II) and platinum (II). The most significant of these are collected in Table 10. It is apparent that the rates of substitution of similar complexes decrease in the order Ni $>$ Pd $\gg$ Pt approximately in the ratios 10^{5-7}: 10^{3-5}: 1. Although these ratios are largely dependent on the particular substrate and also on the particular entering group, the order Ni $>$ Pd $\gg$ Pt is always observed in the nucleophilic substitution reactions of low-spin square-planar complexes under consideration. This order is likely to be due primarily to the greater ability relative to platinum (II) of nickel (II) and palladium (II) to add a fifth

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* No data are available relating the solvent effect to discrimination parameters α_N and α_S.

TABLE 10

Second-order rate constants, k_2, of some reactions of similar square-planar complexes of nickel (II), palladium (II) and platinum (II) at 25°C

Reacting mixture	M	Solvent	k_2 (l. mole^{-1}. sec^{-1})	Ref.
$[MCl_4]^{2-} + NH_3$	Pd	H_2O^a	33	103
	Pt	H_2O^b	$< 4 \times 10^{-5}$	40
$[MCl_4]^{2-}$ + phen	Pd	H_2O^c	2.23	135
	Pt	H_2O^d	2×10^{-3}	136
trans-$[M(NH_3)_2Cl_2] + NH_3$	Pd	H_2O^a	4	103
	Pt	H_2O^b	7.8×10^{-4}	40
$[M(dien)Cl]^+ + H_2O$	Pd	H_2O	1×10^2 [e]	118
	Pt	H_2O^f	1×10^{-5} [e]	47
trans-$[M(i\text{-}Pr_2S)_2Cl_2]$ + py	Pd	$(CH_3OCH_2)_2$	7.4×10^1	65
	Pt	$(CH_3OCH_2)_2$	5.28×10^{-3}	65
trans-$[M(PhSCH_2CH_2SPh)Cl_2]$ + py	Pd	$(CH_3OCH_2)_2$	6.8	71
	Pt	$(CH_3OCH_2)_2$	1.15×10^{-2}	64
trans-$[M(PEt_3)_2$(*o*-tolyl)Cl] + py	Ni	EtOH	3.3×10^1 [e]	93
	Pd	EtOH	5.8×10^{-1} [e]	93
	Pt	EtOH	6.7×10^{-6} [e]	93
trans-$[M(PEt_3)_2$(mesityl)Cl] + py	Ni	EtOH	2×10^{-2} [e]	93
	Pt	EtOH	1.24×10^{-6} [e]	93

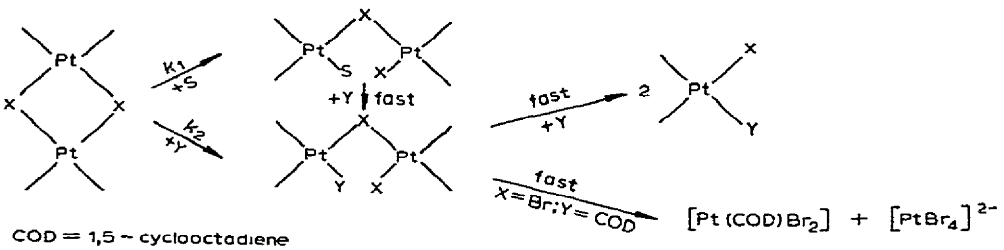
[a] Ionic strength 1 *M.*
[b] Ionic strength 0.318 *M.*
[c] Ionic strength 0.279 *M.*
[d] Values at 45°C; ionic strength 2.46×10^{-2} *M.*
[e] k_1 (sec^{-1}).
[f] Ionic strength 0.1 *M.*

ligand. The formation of five-coordinate intermediates, prior to the rate-determining step, in the nucleophilic substitution of nickel (II)–dithiolates by dithiolates[52], supports this interpretation.

(8) Binuclear complexes. Several binuclear complexes of palladium (II) and platinum (II) are well known and characterized[137–139] but few of these have been subjected to kinetic investigation[140–142]. Some attention has been devoted to the reactions of binuclear platinum (II) complexes with amines and with olefins. These reactions are found to obey a two-term rate law similar to that followed by square-planar complexes; viz.

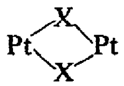
$$\text{Rate} = k_1\,[\text{complex}] + k_2\,[\text{complex}]\,[\text{Y}] \tag{24}$$

Such a rate law is consistent with the fact that both the metal ions in these binuclear complexes are involved in a square-planar configuration. Both k_1 and k_2 reaction paths are thought to involve a binuclear process in which a solvent molecule or the incoming nucleophile, respectively, participates in the rate-determining step by attacking one platinum, leading to the cleavage of one Pt–X–Pt bridge.



(25)

The reaction rates are affected by the same factors found to be operating in the square-planar complexes. For instance, higher rates are found for olefins rather than for amines as entering groups. Also, the *trans* effect is qualitatively the same. This is shown, for example by the fact that the reaction rate of $[\text{Pt}_2(\text{P}(n\text{-Bu})_3)_2\text{Cl}_4]$ is higher than that of $[\text{Pt}_2(\text{pip})_2\text{Cl}_4]$, the first containing a phosphine *trans* to the leaving group with a higher *trans* effect than piperidine. In these complexes, however, this effect is less important than in mononuclear planar complexes, as appears from the fact that $[\text{Pt}_2\text{Br}_6]^{2-}$ reacts with pyridine more quickly than $[\text{Pt}_2\text{I}_6]^{2-}$, although iodide usually exhibits a higher *trans* effect than bromide. This result is also an indication of the importance of the Pt–X bond strength in determining the reactivity of the substrate[140]. A general feature of the binuclear complexes is their higher reactivity compared with that of the corresponding mononuclear compounds. This is because the four-membered ring



is rather strained, so that the cleavage of one Pt–X–Pt bridge is easier than the breaking of a single Pt–X bond.

The chloride exchange of $[\text{Pt}_2(\text{C}_2\text{H}_4)_2\text{Cl}_4]$ in ethanol has a rather peculiar mechanism[143]. In this case the complex is completely solvated in solution according to reaction (26), thus behaving as though it were mononuclear. Moreover, in the presence of free chloride it is in equilibrium with $[Pt(C_2H_4)Cl_3]^-$ according to reaction (27).

$$[Pt_2(C_2H_4)_2Cl_4] + 2\,C_2H_5OH \rightarrow 2\ \textit{trans}\text{-}[Pt(C_2H_4)Cl_2(C_2H_5OH)] \tag{26}$$

$$\textit{trans}\text{-}[Pt(C_2H_4)Cl_2(C_2H_5OH)] + Cl^- \rightarrow [Pt(C_2H_4)Cl_3]^- + C_2H_5OH \tag{27}$$

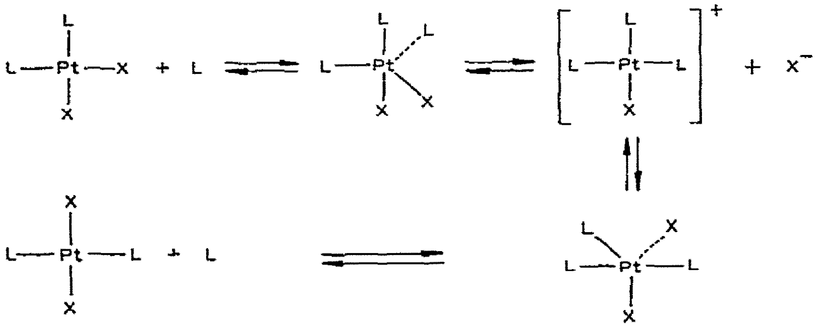
Although binuclear species do not appear to be present in solution in detectable amounts, they must be involved in some step of the overall reaction, as suggested by the form of the rate law for the chloride exchange

$$\text{Rate}_{\text{ex}} = k[Pt(C_2H_4)Cl_3{}^-]\,[\textit{trans}\text{-}Pt(C_2H_4)Cl_2(C_2H_5OH)] \tag{28}$$

Other examples in which binuclear platinum (II) complexes are thought to participate in reactions of platinum (II) complexes are represented by the $[PtBr_4]^{2-}$-catalyzed bromide exchange of both $[PtBr_4]^{2-}$ (ref. 144) and $[Pt(dien)Br]^+$ (ref. 145).

(9) Cis–trans isomerization. Square-planar complexes of formula $[ML_2X_2]$ and $[M(LL')_2]$ are known to occur as geometric isomers, with the possibility of interconversion of the two forms, *cis* and *trans*. The best examples are found in platinum (II) complexes, where because of their stability and inertness it is possible to isolate both the *cis* and *trans* forms. Examples of geometric isomers are also known for nickel (II) and palladium (II)[146,147], but in these cases the separation of the two forms is usually very difficult because of the high lability of these complexes leading to the isolation of only the more stable or the more easily separable isomer.

Until very recently data for *cis–trans* isomerization of planar complexes referred only to thermodynamic[148–151] and photochemical studies[152,153]. It was known that isomerization can occur only in the presence of catalysts, which are usually uncharged ligands identical to those coordinated to the central metal ion[147,154]. Such a catalyzed *cis–trans* isomerization was believed to occur through a double displacement mechanism. The first stage was thought[155] to involve the replacement of an X^- group by a molecule of catalyst, L, to form $[PtL_3X]^+X^-$, and the second stage the entry of X^- with displacement of L.



(29)

The amine-catalyzed isomerization of *cis*–[Pd(am)$_2$Cl$_2$] (am = substituted pyridines) in 1,2-dimethoxyethane has been found recently to follow a second-order rate law, first-order either in palladium (II) and in free amine, and has been regarded[156] as evidence in favor of mechanism (29). However, very recent kinetic investigations of *cis–trans* isomerization carried out on reaction (30) (L = phosphine; X = Cl) do not support such a mechanism[157].

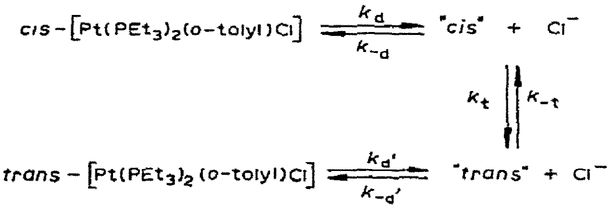
$$cis\text{-}[\mathrm{PtL_2X_2}] \xrightarrow{L'} trans\text{-}[\mathrm{PtL_2X_2}] \tag{30}$$

In this investigation the free phosphine, L′, present in catalytic amount, was either the same as or different from that contained in the complex. Analysis of the kinetic results has indicated that the isomerization must proceed much faster than the phosphine exchange. Therefore, the double displacement mechanism (29) cannot be operating in these cases because it would imply ligand exchange at every isomerization. An alternative mechanism for the catalyzed isomerization has thus been proposed to account for the results obtained[157]. It involves an association of the catalyst, L′, with the complex and formation of five-coordinate a distorted five-coordinate state in which L′ occupies a unique position, perhaps due to a long Pt–L′ bond. This distorted state undergoes fluxional change which interconverts the position of L and X and leads to isomerization, whereas the catalyst, L′, retains its identity.

Uncatalyzed *cis–trans* isomerizations usually do not occur. However, *cis*-[Pt(PEt$_3$)$_2$-(*o*-tolyl)Cl] is also found to undergo isomerization in the absence of any catalyst[158]. Its isomerization follows a first-order rate law and is lowered when free chloride is added to the reaction mixture. The rate constant in the presence of chloride is given by

$$k_I = \frac{k_d}{k[\mathrm{Cl^-}] + 1} \tag{31}$$

In order to explain the effect of added chloride on the reaction rate, a two-stage mechanism involving two labile three-coordinate intermediates of unknown structure, "*cis*" and "*trans*", has been suggested.



(32)

(b) Tetrahedral complexes

Only tetracoordinate nickel (II) provides examples of high-spin tetrahedral as well as low-spin planar complexes, with possible interconversion between the two forms. While much work[159–162] has been done on the stability of the two structures and on the equilibrium of the interconversion

$$\text{Tetrahedral (paramagnetic)} \rightleftharpoons \text{planar (diamagnetic)} \qquad (33)$$

few kinetic investigations have been carried out on substitutions of tetrahedral complexes and on the dynamics of the interconversion. In this connection, some quantitative information is available for complexes of formula $[Ni(PR_3)_2X_2]$. These complexes are known to be square-planar or tetrahedral according to whether trialkyl- or triarylphosphines are coordinated to the central metal ion, while complexes bearing dialkylarlyl- or diarylalkylphosphines can lead to the coexistence in solution of both diamagnetic and paramagnetic forms[159,163].

Kinetic investigations on the tetrahedral complexes have been concerned with the exchange of phosphines of $[Ni(PR_3)_2X_2]$ in $CDCl_3$ (PR_3 = P(*o*-tolyl)$_3$, PPh_3; X = Cl, Br, I)[164–166]. These reactions obey a second-order rate law, first-order both in the complex and in the free phosphine. A bimolecular process involving a five-coordinate activated complex, probably with trigonal-bipyramidal structure, accounts for this reaction order. The entropies of activation, always highly negative (–20 to –25 cal.deg^{-1} mole^{-1}, except in one case) are in agreement with such a mechanism. There is still little information about the effect of the phosphines in determining the reaction rates. The effect of X is better known, the reactivities of complexes with different X being found to decrease in the order $Cl > Br > I$ in all the cases examined. This order is thought[167] to be determined by increased Ni–P π-bonding in going from chloride to iodide, as a consequence of increased π-donation from the halogen to the nickel in the order $Cl < Br < I$. However, some doubts on the full validity of this interpretation arise from the fact that the enthalpies of activation are in the order $Cl > I > Br$, whereas an order $I > Br > Cl$ would be expected in terms of π effects[166].

The kinetic behavior of the tetrahedral–planar interconversion of $[Ni(PR_3)_2X_2]$ complexes (PR_3 = several phosphines; X = Cl, Br, I) in $CDCl_3$ or CD_2Cl_2 is now well documented[168–171]. When these interconversions are carried out without addition of free phosphine a first-order rate law is observed. The addition of phosphine to the reaction mixture increases the rate of interconversion, owing to the operation of a reaction path dependent on the free phosphine. This is thought to be an associative process involving a five-coordinate activated complex similar to that found in the ligand exchange of tetrahedral complexes, whereas the mechanism of the reaction path independent of phosphine is believed to involve an intramolecular torsional distorsion process[171]. The rates of interconversion are dependent both on X and on the phosphine coordinated to the central metal atom. The order of the rate constants on changing X is $Br < Cl < I$, which is rather different from the order found for the ligand exchange of the tetrahedral complexes. For a given X the reaction rates change with the coordinated phosphine in the order $MePPh_2 < (n\text{-}Pr)PPh_2 < (n\text{-}Bu)PPh_2 < EtPPh_2$ (ref. 171) and $MeP(p\text{-}MeOPh)_2 < < MeP(p\text{-}ClPh)_2 < MePPh_2$ (ref. 170). Neither of these sequences shows any correlation with either the steric and/or electronic properties of the ligands, This is very likely because both these effects are simultaneously operative in such a way that their contributions are inseparable.

(c) Five-coordinate complexes

Very little work has been done so far on the kinetics of five-coordinate compounds of the nickel triad. In this connection only the five-coordinate complexes $[M(QAS)X]^+$ (QAS = tris-(*o*-diphenylarsinophenyl)arsine; M = Pt, Pd; X = Cl, Br) seem to have received much attention[172]. $[Pt(QAS)X]^+$ reacts in methanol with several nucleophiles in the presence of a large excess of the entering ligand obeying a two-term rate law similar to that observed for square-planar complexes.

$$\text{Rate} = k_1\,[\text{complex}] + k_2\,[\text{complex}]\,[Y] \tag{34}$$

In this case, however, the value of k_1 varies with the nucleophile employed and, therefore, it cannot be interpreted in terms of either a solvolytic or dissociative reaction path. Moreover, the rate law (34) does not hold at low nucleophile concentrations, a reaction rate lower than expected being observed in these conditions. It seems that the mechanism which best fits the experimental data does involve a bimolecular attack of the nucleophile both on the free complex and on an ion-pair formed by association of the complex with the nucleophile.

$$[Pt(QAS)X]^+ + Y^- \overset{K}{\rightleftharpoons} [Pt(QAS)X]^+\,Y^- \tag{35a}$$

$$[Pt(QAS)X]^+ + Y^- \xrightarrow{k'_2} [Pt(QAS)Y]^+ + X^- \tag{35b}$$

$$[Pt(QAS)X]^+, Y^- + Y^- \xrightarrow{k'_{2\,IP}} [Pt(QAS)Y]^+\,Y^- + X^- \tag{35c}$$

The pseudo-first-order rate constant related to such a mechanism, viz.

$$k_{obs} = \frac{k'_2\,[Y^-] + k'_{2\,IP}K[Y^-]^2}{1 + K\,[Y^-]} \tag{36}$$

explains the non-linear dependence of k_{obs} on the entering-group at low concentrations of entering group. Moreover, in the presence of free nucleophile in excess large enough that $K\,[Y^-] \gg 1$, the form of k_{obs} becomes the same as that found experimentally

$$k_{obs} = \frac{k'_2}{K} + k'_{2\,IP}\,[Y^-] \tag{37}$$

The entering group is found to affect the reaction rate in a way similar to that noticed for square-planar complexes. In fact, the second-order rate constants vary with the entering ligand in the order $CN^- >$ thiourea $> SCN^- \simeq I^- \simeq PPh_3 > N_3^- > NO_2^- \gg$ pip, which is also roughly the order of the nucleophilic reactivity for square-planar platinum (II) complexes, with the exception of PPh_3 and, in part, piperidine (see Table 2). The effect of the central metal ion has not been examined extensively. However, a qualitative experiment carried out by reacting $[Pd(QAS)Br]^+$ with azide has shown that this substrate reacts about 10^4 times faster than the corresponding platinum complex. The result seems to indicate that the kinetic effect of the central metal ion is also similar to that found for square-planar complexes.

(d) Metal (II) octahedral complexes

Octahedral complexes of nickel (II) are well known, and have been subjected to a great deal of kinetic investigation so that their kinetic behavior is now fairly well understood. The basic results will be reported here, while further general information is available in several recent reviews dealing directly or indirectly with this topic[173–176]. Particular attention will be devoted to the most recent literature.

(1) Ligand exchange kinetics. Solvent exchange is perhaps the most important example of this kind of reaction.

$$[L_m NiS_n]^{a+} + {}^*S \rightleftharpoons [L_m NiS_{n-1}\,{}^*S]^{a+} + S \tag{38}$$

The kinetics of this kind of reaction have been studied both in pure solvents and in mixtures of coordinating and non-coordinating solvents.

Exchange in pure solvents is found to obey a first-order rate law

$$\text{Rate} = nk_{ex}\,[L_m NiS_n{}^{a+}] \tag{39}$$

where n is the number of molecules of solvent present in the complex, and k_{ex} is the specific rate for the exchange of a single molecule of that solvent. Some kinetic data for the solvent exchange of $[NiS_6]^{2+}$ complexes (S = solvent) are reported in Table 11*.

The dependence of the rate of solvent exchange on the entering group, which remains undetermined when pure solvents are used, has been determined by following the solvent exchange of $[NiS_6]^{2+}$ complexes in DMSO–$MeNO_2$, DMSO–CH_2Cl_2 (ref. 193) and

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* Data are also available on the exchange of L′, where this may be a solvent molecule[175,177,178,180] or any other exchangeable ligand[194,195], in complexes of formula $[L_m NiL'_n]^{a+}$. It is generally found that non-participating ligands affect the rate of exchange.

TABLE 11

Kinetic data for the solvent exchange of some octahedral nickel (II) complexes in pure solvents at 25°C

Complex	k_{ex} (sec^{-1})	ΔH^*_{ex} ($kcal.mole^{-1}$)	ΔS^*_{ex} ($cal.deg^{-1}.mole^{-1}$)	Ref.
$[Ni(H_2O)_6]^{2+}$	4.4×10^4	10.3	− 5.2	177
	3.6×10^4	12.3	+ 3.6	178
	3.0×10^4	10.8	− 1.7	179
	2.7×10^4	11.6	+ 0.6	180
$[Ni(MeOH)_6]^{2+}$	1.0×10^3	15.8	+ 8	181
$[Ni(EtOH)_6]^{2+}$	1.1×10^4	10.8	− 4	182
$[Ni(NH_3)_6]^{2+}$	1×10^5	9.9	− 2	183
	0.47×10^5	10.0	− 3	184
$[Ni(DMF)_6]^{2+}$	6.9×10^3	14.0	+ 6	185
	3.8×10^3	15.0	+ 8	186
$[Ni(MeCN)_6]^{2+}$	12.4×10^3	11.8	− 0.2	187
	3.9×10^3	10.9	− 8.8	188
	2.8×10^3	11.7	− 3.6	189
$[Ni(DMSO)_6]^{2+}$	9.3×10^3	7.3	− 16	190
	7.5×10^3	8	− 16	191
	5.2×10^3	12.1	− 1.3	192
	3.2×10^3	13.0	+ 1.4	193

DMF–$MeNO_2$ (ref. 185) mixtures. The nickel (II) in these solutions is present as $[Ni(DMSO)_6]^{2+}$ and $[Ni(DMF)_6]^{2+}$ respectively; nitromethane and methylene chloride are not present in the coordination sphere because of their inability to coordinate to nickel (II). The exchange rate constant and the activation parameters are found to be independent of the concentration of the exchanging solvent present in the bulk solution. This fact has been considered to be good evidence for a dissociative mechanism involving a true five-coordinate intermediate (S_N1 lim or D mechanism)[185]. Similar conclusions concerning the mechanism have also been reached for the exchange of several other ligands. Examples are the exchange of 3-picoline-*N*-oxide (3-*N*-picO) in $[Ni(3\text{-}N\text{-}picO)_6]^{2+}$ in nitromethane–acetone mixtures[196], and the exchange of 4-picoline-*N*-oxide and 4-picoline in bis(picoline) adducts[194,195] of bis(β-diketonato)nickel (II) complexes in $CDCl_3$.

The data reported in Table 11 show that the enthalpies and entropies of activation are largely dependent on the exchanging solvent, although little effect is observed at 25°C on the exchange rate constant, k_{ex}. Several factors are believed to contribute to the solvent effect. Among these the most important are: (*i*) the metal–ligand bond energies; (*ii*) the ability of the ligands to provide electronic stabilization for a tricoordinate state; (*iii*) the steric requirements of the different ligands; (*iv*) the solvation differences between ground and transition states, and (*v*) the structural properties of the solvents[197,198]. In the older literature most attention was paid to the crystal field contributions to the enthalpy of the activation, while other contributions were scarely considered. In terms of crystal field alone, the enthalpy of activation should parallel the crystal field splitting parameter Dq. This is known to lie in the order $\text{MeCN} > \text{NH}_3 > \text{H}_2\text{O} > \text{MeOH} > \text{DMF} > \text{DMSO}$[192], which does not correspond to the order of ΔH^* (Table 11) for the same ligands, implying that other factors are also important. Consequently it has been thought that among these may be the solvation differences between ground and transition states. The total enthalpy of activation has been considered[192] to be made up of a crystal field contribution, ΔH^*_{CF}, and of a solvation contribution, ΔH^*_{sol}. On this basis the experimental order of the enthalpies of activation would be the consequence of a contribution of Δ^*_{sol} increasing in the order $\text{NH}_3 < \text{MeCN} < \text{H}_2\text{O} < \text{DMSO} < \text{DMF} < \text{MeOH}$. A rather different treatment of the data, based on the occurrence of a general relation between enthalpy and entropy of activation in a wide variety of solvents, has indicated that the structural properties of the solvents, in addition to the breaking of a metal–solvent bond, are also important in determining the observed reactivities as well as the activation parameters[198]. A very interesting theory of the solvent effect has been derived from this treatment, based essentially on an extension to non-aqueous solvents of the Frank and Wen model of the solvated ion. According to this theory solvent exchange is a concerted motion of molecules involving several stages which can be summarized as follows (see Fig. 4): stage (a), a molecule of solvent leaves the bulk solvent and enters the intermediate disordered region lying between the bulk solvent and the first coordination layer of the ion; stage (b), a molecule takes its place in the first coordination layer if an empty site is available there; stage (c), a molecule leaves this innermost region to enter the intermediate disordered region; stage (d), a molecule leaves this region to go into a hole in the bulk solvent, while in stage (e), the motion of the molecules in the bulk solvent must make stages (a) and (d) mutually dependent[198]. This reaction mechanism, defined as a "solvent-modified dissociative process", is also capable of explaining some results for the kinetics of complexation reactions of nickel (II) in non-aqueous solvents[198].

(2) Formation reactions of nickel (II) complexes. The kinetics of the reactions

$$[\text{L}_m\text{NiS}_n]^{a+} + \text{L}^{b-} \underset{k_\text{d}}{\overset{k_\text{f}}{\rightleftharpoons}} [\text{L}_{(m+1)}\text{NiS}_{(n-x)}]^{a-b} + x\,\text{S} \tag{40}$$

are among the most fully investigated in the chemistry of nickel (II) octahedral complexes. The rate law obeyed by these reactions has the general form

$$\text{Rate} = k_\text{f}[\text{L}_m\text{NiS}_n{}^{a+}]\,[\text{L}^{b-}] - k_\text{d}[\text{L}_{(m+1)}\text{NiS}_{(n-x)}{}^{a-b}] \tag{41}$$

so that the pseudo-first-order rate constant for the forward reaction (complex formation) is

$$k_\text{obs} = k_\text{f}[\text{L}^{b-}] \tag{42}$$

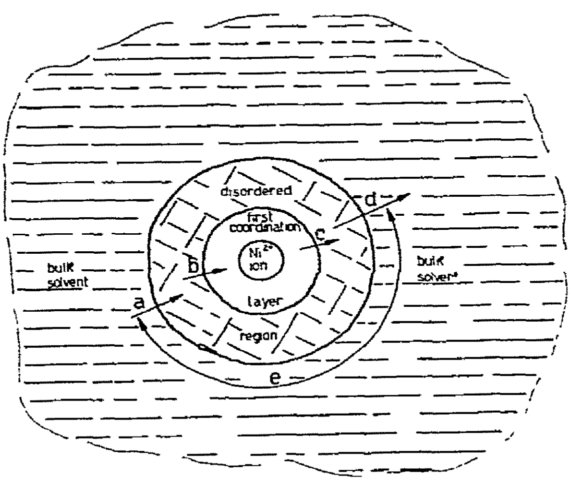

Fig. 4. Model of the solvated nickel (II) ion and schematic indication of the reaction pathways involved in the solvent exchange, according to ref. 198. For comments see text.

Some values of k_f for the formation of $[NiL(H_2O)_n]^m$ complexes are reported in Table 12*. It is apparent from these data that very different entering groups exhibit roughly constant values of k_f, provided they bear the same electrical charge. This behavior is not consistent with an associative mechanism. Rather it supports a dissociative mechanism in which the entering ligand plays a relatively minor role in the rate-determining loss of a molecule of solvent. The occurrence of a dissociative mechanism is also consistent with the values of the volumes of activation (7–9 ml.mole^{-1}) for the reaction of nickel (II) ion with some uncharged ligands in water[212]. The generally accepted mechanism of complex formation was originally proposed by Eigen and Tamm[213–216]. It involves the preliminary diffusion-controlled formation of an outer-sphere complex between nickel (II) and the incoming ligand. The rate-determining step of the overall process is the loss of a solvent molecule from the first coordination layer of this outer-sphere complex**. The mechanism for reactions with a monodentate entering group is

$$[L_m NiS_{(6-m)}]^{a+} + L^{b-} \overset{K_{os}}{\rightleftharpoons} [L_m NiS_{(6-m)}]^{a+}L^{b-} \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} [L_{m+1}NiS_{(5-m)}]^{a-b} + S \tag{43}$$

where K_{os} is the equilibrium constant for the formation of the outer-sphere complex, k_0 is the rate constant for the loss of a solvent molecule from the outer-sphere complex and k_{-0} is the rate constant for the reverse process. According to this mechanism the rate constant for complex formation, k_f, is

$$k_f = \frac{k_0 K_{os}}{1 + K_{os}[L^{b-}]} \tag{44}$$

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* More extensive documentation can be found, for example, in refs. 173 and 174.

** For a more complete discussion, see refs. 173 and 174.

TABLE 12

Specific rate constants, k_1, for the formation of some $[\mathrm{NiL(H_2O)}_n]^m$ complexes in water at 25°C

L	$10^{-3}k_f$ (l. mole^{-1}.sec^{-1})	$10^{-4}k_0 = 10^{-4}\ k_f/K_{os}$ (sec^{-1})	Ref.
NH_3	4.6	3	199
py	4.0	3	200
Imidazole	5.0	1.6	201
SCN^-	6	0.6	202
$HC_2O_4^-$	5	0.3	203
$HO_2CCH_2CO_2^-$	3.1	0.16	204
Glycinate$^-$	15	0.9	201
Diglycinate$^-$	21	1.2	201
Triglycinate$^-$	8	0.46	205
$C_2O_4^{2-}$	75	0.6	203
$CH_2(CO_2)_2^{2-}$	70	0.54	204
$CH_3PO_4^{2-}$	280	0.7	206
SO_4^{2-}		1.5 (at 20°C)	207
NTA$^{3-\,a}$	2,000		208
$HP_2O_7^{3-}$	2,100	1 2	209
EDTA^{4-}	6,000		210
$HP_3O_{10}^{4-}$	6,800	1.2	209
ATP$^{4-\,b}$	4,000	1.0	211

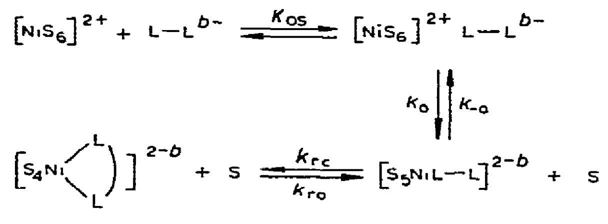
[a] NTA^{3-} = nitrilotriacetate.
[b] ATP^{4-} = adenosine triphosphate.

which becomes

$$k_f = k_0 K_{os} \tag{45}$$

when $K_{os}[\mathrm{L}^{b-}] \ll 1$.

When the entering group is a multidentate ligand, the Eigen mechanism still holds. However, a much more complicated situation can arise in this case because it can happen[217-222] that the rate-determining step is the chelate ring closure rather than the loss of the first solvent molecule from the outer-sphere complex. For the relatively simple case of an incoming bidentate ligand the reaction mechanism can be indicated as


(46)

According to this mechanism the specific rate constant for complex formation, k_f, is

$$k_f = \frac{K_{os}k_0k_{rc}}{k_{-0}+k_{rc}} \tag{47}$$

This becomes equivalent to eqn. (45) only if the ring closure is a fast step ($k_{rc} \gg k_{-0}$); if the ring closure is rate-determining ($k_{rc} \ll k_{-0}$) it becomes

$$k_f = K_{os}\frac{k_0k_{rc}}{k_{-0}} = K_{os}K_1k_{rc} \tag{48}$$

On the basis of the Eigen mechanism the rate-determining step of the formation reaction, involving the loss of a solvent molecule, is affected little by the incoming ligand so that the value of k_0 in a given solvent is expected to be roughly independent of the entering group and very close to the value of the rate constant for solvent exchange, k_{ex}.

$$k_f = k_0K_{os} \simeq k_{ex}K_{os} \tag{49}$$

Therefore, the large variety of values of k_f found with different ligands (see Table 12) arises mainly from the K_{os} term. Unfortunately this statement cannot be tested directly because the values of K_{os} can only be determined experimentally in a few particular cases[206]. However, values of K_{os} can be calculated using the Fuoss equation[223], and their introduction into eqn. (45) or (49) makes it possible to evaluate k_0, which should be roughly independent of the incoming ligand. This is indeed found, as documented by the data collected in the third column of Table 12. Moreover, the values of k_0 obtained in this way are consistent with the rate constant for water exchange, k_{ex}, according to eqn. (49) (see Table 11). The agreement is fairly general in water, although it sometimes fails. For instance, when the entering group is a polyamine, an abnormally high rate of formation is found[199]. In this case the Eigen mechanism is thought still to be essentially operating, but hydrogen bond formation between the hexaaquonickel (II) ion and the polyamine increases the value of K_{os} and also enhances the rate of water loss.

The evidence supporting mechanism (43) or (46) for the formation of nickel (II) complexes is mainly derived from reactions in aqueous solution, whereas relatively little information is available for non-aqueous solvents. Some data obtained using methanol as a solvent are reported in Table 13 and show that at least in this solvent the results are also consistent

TABLE 13

Specific rate constants, k_f, for the formation of some $[\mathrm{NiL(MeOH)}_n]^m$ complexes in methanol at 25°C

L	$10^{-3}k_f$ ($\mathrm{l.mole^{-1}.sec^{-1}}$)	$10^{-3}k_0 = 10^{-3}\,k_f/K_{os}$ ($\mathrm{sec^{-1}}$)	Ionic strength ($\mathrm{mole.l^{-1}}$)	Ref.
MeOH		1.0 (k_{ex})		181
bipy	0.08	0.8		224
$\mathrm{SeCN^-}$	5.3	0.53	0.1	225
$\mathrm{SCN^-}$	7.4	0.74	0.1	225
$\mathrm{SCN^-}$	150	1	→ 0	226
$\mathrm{Cl^-}$	70 (20°C)	0.4	→ 0	227
$\mathrm{MNT^{2-}}$[a]	200	1.5	0.1	225
$\mathrm{DTO^{2-}}$[b]	250	1.9	0.1	225

[a] $\mathrm{MNT^{2-}}$ = maleonitriledithiolate.
$\mathrm{DTO^{2-}}$ = dithiooxalate.

with the proposed mechanism. However, the results of an extensive investigation of the kinetics of reactions of nickel (II) ion with bipyridyl in several non-aqueous solvents seem to point out the need for modifying the commonly accepted mechanism of complexation in order to explain the observed solvent effect[198,224,228–230]. Results obtained in different solvents have been discussed in terms of a quantity n

$$n = \frac{k_f}{k_0 K_{os}} \tag{50}$$

which has been defined as the change of a ligand entering the primary solvation shell of the nickel (II) ion when a solvent molecule leaves it[228]. Values of K_{os} have been estimated to be 0.1 $\mathrm{l.mole^{-1}}$ and are supposed to be the same in all solvents. Thus, if the Eigen mechanism is operating in non-aqueous solvents, one obtains

$$n = \frac{k_f}{k_0 K_{os}} \simeq \frac{k_f}{k_{ex} K_{os}} = 10\frac{k_f}{k_{ex}} \tag{51}$$

Moreover, according to eqn. (49), n should be unity for every solvent. It is seen from the data in Table 14 that n, derived from eqn. (51), is usually very different from unity and strongly dependent on the solvent. This is against the expectation based on the Eigen mechanism for non-aqueous solvents. The occurrence of a general linear correlation between the values of log n and the fluidity of the solvent has led to the suggestion that the structural properties of the solvent must also be taken into account in order to elucidate the substitution mechanism[228]. A reaction mechanism similar to that proposed to explain the solvent effect in solvent exchange reactions is now also thought to operate in complexation reactions in non-aqueous solvents[198].

TABLE 14

Second-order rate constant, k_f, for the formation of $[NiS_4(bipy)]^{2+}$ in several solvents, and fluidity of these solvents at 25°C (data taken from ref. 224)

Solvent	$10^{-3}k_f$ (l.mole^{-1}.sec^{-1})	$10^{-3}k_{ex}$ (sec^{-1})	$n = 10k_f/k_{ex}$	Fluidity (g.ml^{-1}.cP^{-1})
MeCN	4.7	2.8	17	2.27
MeOH	0.083	1.0	0.8	1.43
DMF	0.54	7.7	0.7	1.19
H_2O	1.63	30	0.54	1.12
DMSO	0.069	7.5	0.09	0.55
Etgly[a]	0.033	24	0.08	0.61
DMMP[b]	0.21	4.4[c]	0.09	0.58

[a] Etgly = ethylene glycol
[b] DMMP = dimethylmethyl phosphonate.
[c] Value at 27°C.

(3) Dissociation reactions of nickel (II) complexes. Mechanisms (43) and (46) also account for the dissociation reactions of nickel (II) complexes, that are, of course, the reverse of the complexation reactions (see eqn. (40)). According to these mechanisms the rate constants for the dissociation of complexes bearing mono- or bidentale ligands are respectively

$$k_d = k_{-0} \tag{52}$$

$$k_d = \frac{k_{ro}k_{-0}}{k_{-0} + k_{rc}} \tag{53}$$

It is apparent from the latter relationship that the dissociation rate constant, k_d, in the case of bidentate leaving groups depends only on the opening of the chelate ring, when $k_{-0} \gg k_{1c}$, or also on the rupture of the second metal–ligand bond, when $k_{-0} \ll k_{rc}$[*]. The rate constant, k_d, becomes equal to k_{ro} or to $k_{ro}k_{-0}/k_{rc}$ according to whether ring opening or rupture of the second metal–ligand bond is rate-determining. Both these situations have been detected several times with bi- and also multidentate leaving groups[200,231–233]. In some cases it has also been possible to follow the rupture of the single Ni–ligand bonds of coordinated polydentate ligands ligands[234].

Many data are available on the kinetics of dissociation reactions of octahedral nickel (II) complexes. They have been obtained either directly or by means of the equilibrium constant of complex formation[200,201,218,231,233–242], $K_{eq} = k_f/k_d$, and the rate constant of complex formation, k_f. Correlations between the kinetic effects of either the leaving group or the other bonded ligands and extrakinetic parameters have sometimes been obtained. In

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[*] Similar conclusions can be drawn for multidentate leaving groups. In such a case, however, there are many possible rate-determining steps.

this connection, the effect of the leaving group is well documented by a series of systematic investigations which have shown that the basicity of the leaving group is very important in determining the rate of dissociation. For instance, the rate of dissociation of $[Ni(X\text{–}py)(H_2O)_5]^{2+}$ (X = 3- and 4-CN, -Me, -Br and -OMe; 3-$CONH_2$; 3-NH_3^+) in acid solution increases with decreasing basicity of the leaving amine, according to the linear relationship[243] $\log k_d = 1.58–0.21\ pK_a$. A rather similar relationship has also been obtained for the dissociation of complexes of the type $[Ni(5\text{-}Xphen)(H_2O)_5]^{2+}$ (ref. 244) and $[NiL(H_2O)_5]^{n+}$ (L = carboxy-anion)[222]. Also the non-leaving ligands can strongly affect the rate of release of the leaving group. This is shown, for instance, by the fact that the rate of dissociation of $[NiS_5(SCN)]^+$ and $[NiS_5Cl]^+$ (S = solvent) is strongly dependent upon the type of solvent coordinated to nickel (II). In these two cases the dissociation rate constants[226] for NH_3, H_2O, MeOH are in the approximate ratios $10^7 : 10^3 : 1$. Extensive information on the effect of non-leaving groups has been recently obtained from the kinetics of the dissociation reaction[245]

$$[Ni(H_2O)_nXY] + m\,H_2O \rightarrow [Ni(H_2O)_{n+m}X] + Y \qquad (54)$$

where X = thirteen different groups of ligands and Y = malonate, NH_3, H_2O. The rate of dissociation is found to be strongly affected by X and increases in the order $H_2O <$ bipy $<$ $(py)_2 <$ acac $<$ en $<$ 2,2′-aminoethylpy $<$ 2-aminomethylpy $<$ pn $<$ dien $<$ $(en)_2 \simeq$ trien $\simeq$ $\simeq$ 3,3′-iminobispropylamine $<$ $(pn)_2$. A rather peculiar correlation has been found in these cases between $\log k_d$ and the observed spectral shift in the optical absorption peaks for the *d–d* orbital transitions in the various nickel complexes examined. It is found that for a given leaving group linear relationships are obtained by plotting $\log k_d$ against the spectral shifts when the non-leaving ligands, X, form only σ-bonds. In such cases the value of $\log k_d$ increases sharply with a shift to shorter wavelengths. On the other hand, although those ligands X which simultaneously act as σ-donors and π-acceptors still produce substantial spectral shifts, they produce only small effects on the rate of dissociation. This behavior is ascribed to the fact that only σ-donor ligands can greatly affect the charge density on the central metal ion. σ-donor, π-acceptor ligands do not greatly affect this electron density because of the balancing effects of σ-donation and π-acceptance. Thus, the dissociation rate, which is expected to depend strongly on the charge density of the central ion, is influenced strongly only by σ-donor non-leaving ligands.

(4) Ligand substitution reactions of nickel (II) chelate complexes. A typical feature of this kind of reaction is the rupture and formation of several nickel–ligand bonds. Moreover, a rather common characteristic of these reactions is the fact that they proceed through intermediate mixed-ligand complexes, in which the central metal ion is simultaneously bonded to both leaving and entering ligands. The rate-determining step of the overall reaction is the cleavage of any one of the several bonds between nickel (II) and the leaving group which must be broken in the course of the reaction. This rate-determining step is not necessarily the cleavage of the first bond and formation of the mixed-ligand complex.

For instance, $Ni(dien)^{2+}$ reacts with $EDTA^{4-}$ rapidly, giving a mixed-ligand complex $Ni(dien)(EDTA)^{2-}$. This undergoes successive rate-determining unwrapping of dien and increasing coordination of EDTA, finally yielding[246] $Ni(EDTA)^{2-}$. On the other hand, the formation of the mixed-ligand intermediate complex in the chelate substitution reactions of Ni(EDDA) and $Ni(NTA)^{-}$ with PAR^{2-} ($EDDA^{2-}$ = ethylenediamine-*N,N'*-diacetate; NTA^{3-} = nitrilotriacetate; H_2PAR = 4-(2-pyridylazo) resorcinol) is a relatively slow step[247]. Mixed-ligand complexes have been experimentally recognized or kinetically inferred as reaction imtermediates in several other cases of chelate substitution reactions[79,248–251].

Nickel (II) complexes in which the chelate ligands occupy all six coordination positions usually undergo substitution through the cleavage of one or more metal–ligand bonds before the incoming ligand enters the first coordination sphere. Complexes of this kind and formula $[NiL_2]$ are usually found to lose one ligand L before the entering group participates in the reaction. For instance, the reaction of $[Ni(dien)_2]^{2+}$ with $EDTA^{4-}$ involves[246] the preliminary release of one molecule of dien and the subsequent attack of $EDTA^{4-}$ to $Ni(dien)^{2+}$.

$$[Ni(dien)_2]^{2+} \overset{\text{slow}}{\rightleftharpoons} Ni(dien)^{2+} + dien \qquad (55a)$$

$$Ni(dien)^{2+} + EDTA^{4-} \rightleftharpoons Ni(dien)EDTA^{2-} \xrightarrow{\text{slow}} products \qquad (55b)$$

Rather similar reaction pathways, but involving the release of the ligand as a fast step, have been found in several other reactions of this kind of complex, $[NiL_2]$, with multidentate aminocarboxylate as entering ligand [252–256]. In these cases the reaction rates are found to be strongly affected by the acidity of the medium according to a rate law which is satisfactorily accounted for by the following reaction scheme.

$$[NiL_2]^{a-} \overset{\text{fast}}{\rightleftharpoons} NiL^{2-m} + L^{m-} \qquad (56a)$$

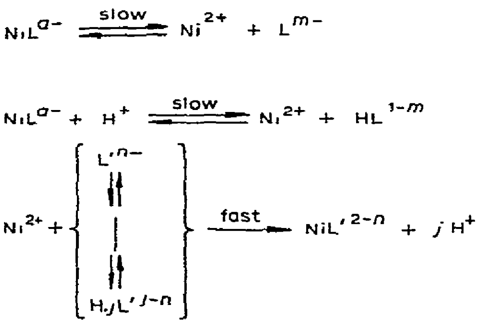
$$NiL^{2-m} + L'^{n-} \overset{\text{slow}}{\rightleftharpoons} NiL'^{2-n} + L^{m-} \qquad (56b)$$

$$NiL^{2-m} + HL'^{1-n} \overset{\text{slow}}{\rightleftharpoons} NiL'^{2-n} + HL^{1-m} \qquad (56c)$$

Pathways (56b) and (56c) are also found to occur for ligand substitutions of several monoligand nickel (II) chelate complexes, NiL[252,257–259].

It has already been pointed out that all the reactions reported above involve mixed-ligand complexes as reaction intermediates. This is because the incoming ligand enters the first coordination sphere of nickel (II) before the substrate has fully released its ligands. However, some examples are also reported in the literature where the complex fully dissociates before the incoming ligand can coordinate to nickel (II)[259, 260].

The form of the rate law, and in particular the role played by the acidity, were found to be consistent with the reaction scheme (57) for the reactions



$$NiL^{a-} \xrightleftharpoons{\text{slow}} Ni^{2+} + L^{m-} \tag{57a}$$

$$NiL^{a-} + H^+ \xrightleftharpoons{\text{slow}} Ni^{2+} + HL^{1-m} \tag{57b}$$

$$Ni^{2+} + \left\{ \begin{array}{c} L'^{n-} \\ \rightleftharpoons \\ | \\ \rightleftharpoons \\ H_jL'^{j-n} \end{array} \right\} \xrightarrow{\text{fast}} NiL'^{2-n} + jH^+ \tag{57c}$$

(iii) Tetravalent metal complexes

Only palladium (IV) and platinum (IV) are well represented in this class of compounds, and only platinum (IV) has provided examples so far of genuine nucleophilic substitution reactions. Several reactions involving platinum (IV) complexes are sometimes regarded as substitution reactions on the basis only of the stoichiometry of the reaction.

$$[L_{6-n}PtX_n] + Y \rightarrow [L_{6-n}PtX_{n-1}Y] + X \tag{58}$$

However, in almost all cases this assignment is incorrect because the reaction mechanism involves redox steps rather than nucleophilic substitution reaction paths. The platinum (II)-catalyzed substitution of platinum (IV) is the most common kind of redox reaction that leads to "formal nucleophilic substitution" of platinum (IV) complexes. In such cases substitution arises from an atom-transfer redox reaction between the starting platinum (IV) and a five-coordinate adduct of the platinum (II) parent, present in solution as an impurity or added to the reaction mixture, e.g.

$$Pt^{II}L_4 + Y \overset{\text{fast}}{\rightleftharpoons} Pt^{II}L_4Y \tag{59a}$$

$$XPt^{IV}L_4X + Pt^{II}L_4Y \rightleftharpoons XPtL_4{-}X{-}PtL_4Y \tag{59b}$$

$$XPtL_4{-}X{-}PtL_4Y \rightleftharpoons XPt^{II}L_4 + XPt^{IV}L_4Y \tag{59c}$$

$$XPt^{II}L_4 \overset{\text{fast}}{\rightleftharpoons} Pt^{II}L_4 + X \tag{59d}$$

This process cannot be considered as a nucleophilic substitution reaction of platinum (IV). Indeed, focusing attention on the bridging atom, X, it is better regarded as a bimolecular nucleophilic substitution in which the nucleophilic $Pt^{II}L_4Y$ replaces $Pt^{II}L_4X$ from the reaction center, X^+. It can also conveniently be considered as an oxidative addition reaction of the platinum (II) complex or a reductive elimination of platinum (IV). This extremely interesting class of reactions will not be discussed further here since an excellent review of this system has recently been published[261]

Other formal substitutions of platinum (IV) complexes include the platinum (III)-catalyzed substitution of platinum (IV)[262]. These reactions are also redox processes. Finally, several other cases of reactions of formal substitution on platinum (IV) complexes, involving other kinds of redox pathways, will be reported in Sect. C of this review (see p. 164).

From the above considerations the need to proceed cautiously in assigning the mechanism of reactions of platinum (IV) complexes which apparently take place by nucleophilic substitution stages becomes apparent. Actually, only a few reactions of base hydrolysis seem to be genuine examples of nucleophilic substitutions of platinum (IV) complexes, ruling out all the reactions originally reported as examples of this[262–264], and later explained more suitably on the basis of redox models[265–267]. The base hydrolyses of $[Pt(NH_3)_5Cl]^{3+}$, *cis*-$[Pt(NH_3)_4Cl_2]^{2+}$ and *trans*-$[Pt(NH_3)_3Cl_3]^+$ represent examples of nucleophilic substitution reactions[268]. These reactions are found to follow a rate law which is first-order in the complex, whereas the hydroxide dependence is intermediate between zero- and first-order. The absence of any catalytic effect of $[Pt(NH_3)_4]^{2+}$, at least for the reactions of *cis*-$[Pt(NH_3)_4Cl_2]^{2+}$, makes the occurrence of the reaction mechanism (59) unlikely. The dependence of the reaction rate on the hydroxide concentration has been explained on the basis of an S_N1CB reaction mechanism involving the rapid production of conjugate bases of these complexes, which are known to behave as weak polybasic acids. The rate-determining step is the release of one chloride from either the starting complex or its conjugate bases. This mechanism has also been proposed[269] to operate in the base hydrolysis of *cis*- and *trans*-$[Pt(NH_3)_2Cl_4]$. However, the base hydrolysis of *trans*-$[Pt(NH_3)_2Br_4]$ and *trans*-$[Pt(NH_3)_2I_4]$ has recently been inferred to occur through the redox mechanism (59), with *trans*-$[Pt(NH_3)_2X_2]$ ($X = Br, I$) acting as a catalyst[270].

A rather interesting case of the substitution reactions of platinum (IV) complexes is the base hydrolysis of *trans*-$[Pt(CN)_4Br_2]^{2-}$ in the presence of free bromide[271]. The rate law for this reaction is

$$\text{Rate} = k_1 [\text{Pt}^{\text{IV}}][\text{OH}^-] + k_2 [\text{Pt}^{\text{IV}}][\text{Br}^-] \tag{60}$$

The reaction path dependent on hydroxide concentration cannot be explained in this case in terms of an S_N1CB mechanism, since the complex does not contain acidic protons. On the other hand, the reaction is not catalyzed by $[Pt(CN)_4]^{2-}$, thus making a redox mechanism of the type (59) very unlikely. Moreover, an ion pairing mechanism should also be unlikely from an electrostatic point of view. Highly positive entropies of activation (from 38 to 50 cal.deg^{-1}.mole^{-1}) suggest instead a dissociative mechanism for this reaction path. In such a case the first-order dependence of the rate on hydroxide has been proposed to arise from the presence of the hydroxide near the platinum (IV) complex as a result of some sort of outer-sphere complexation (see however p. 170). The reaction pathway dependent on bromide is instead believed to involve an association of free bromide with a coordinated bromide, yielding an intermediate of the type $Br{-}Br{-}Pt(CN)_4Br^{3-}$, in which the associated bromide assists the hydrolysis. Such an assisted reaction mechanism also believed to occur in some anation reactions of platinum (IV) complexes[272].

C. OXIDATION–REDUCTION REACTIONS

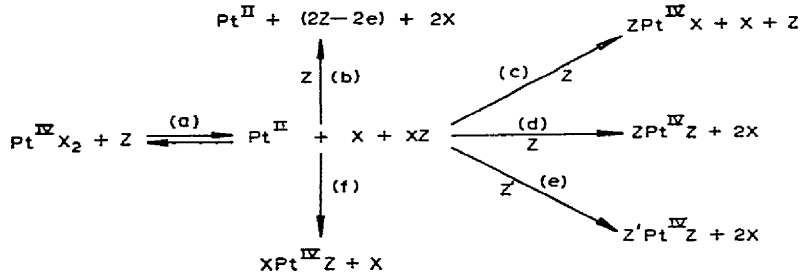
This section will deal mainly with reduction reactions of platinum (IV) and the oxidation of platinum (II) complexes. The kinetics of redox reactions of nickel and palladium complexes so far have only been studied occasionally, so that very little information is available about them[273–279].

The platinum complexes show high versatility with respect to redox processes. The redox reactions so far reported in the literature can be conveniently collected into two classes, according to whether a bielectronic or a monoelectronic redox species reacts with the platinum complex (i.e. complementary and non-complementary redox reactions, respectively).

(i) Complementary redox reactions

Complementary redox reactions involving platinum complexes are fairly well known, the reduction reactions of platinum (IV) being the best documented. Some oxidations of platinum (II) are also known to involve complementary processes.

All reactions belonging to this class are found to involve an inner-sphere atom-transfer oxidation–reduction path. The variety of situations encountered so far in the reactions of platinum (IV) complexes is shown in the reaction scheme (61), in which the charges on the species involved in the reaction are omitted.

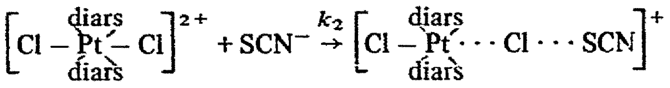


(61)

The likelihood of a given reaction occurring along any one of the paths (b) – (f) depends on several factors such as the relative stability of the particular reaction products and the relative rates of the reactions of each individual path.

It can be seen that path (a) is fundamental to each reaction path, and can be regarded as a reductive elimination reaction of platinum (IV). Of the subsequent paths, only (b) leads to a net redox reaction, whereas in the other cases a net formal substitution reaction of platinum (IV) occurs. The redox step in these latter cases can be regarded as an oxidative addition to the platinum (II) complex formed through the previous reductive elimination reaction (step (a)). Thus, the overall reactions of scheme (61) leading to formal substitution of platinum (IV) complexes can be classified as reactions of *reductive elimination oxidative addition* (REOA reactions).

The reducing agent, Z, in the reactions under consideration, can be any one of a great variety of cationic, anionic and uncharged species. The case of anionic reductants is perhaps the most important, and certainly the best documented in the literature. The first example of clean platinum (IV) reduction by an anionic reductant was observed by reacting $[\mathrm{Pt(diars)_2Cl_2}]^{2+}$ with thiocyanate ions[280]. In such a case the platinum (IV) complex is found to be quantitatively reduced by SCN^- to $[\mathrm{Pt(diars)_2}]^{2+}$ according to a second-order rate law, first-order in platinum (IV) and in thiocyanate. The rate law together with the stoichiometry of the reaction are fully consistent with an inner-sphere atom-transfer redox mechanism in which a chloride atom is transferred from platinum to thiocyanate.



$$\left[\mathrm{Cl}-\overset{\text{diars}}{\underset{\text{diars}}{\mathrm{Pt}}}-\mathrm{Cl}\right]^{2+} + \mathrm{SCN}^- \xrightarrow{k_2} \left[\mathrm{Cl}-\overset{\text{diars}}{\underset{\text{diars}}{\mathrm{Pt}}}\cdots\mathrm{Cl}\cdots\mathrm{SCN}\right]^{+}$$

$$\rightarrow [\mathrm{Pt(diars)_2}]^{2+} + \mathrm{Cl}^- + \mathrm{ClSCN} \qquad (62a)$$

$$\mathrm{ClSCN} \xrightarrow{\text{fast}} \mathrm{Cl}^- + (\mathrm{SCN}^- + 2\,\mathrm{e}) \qquad (62b)$$

Rather similar behavior is exhibited by $[\mathrm{Pt(diars)_2Br_2}]^{2+}$ reacting with thiocyanate and nitrite. However, in this case a simultaneous platinum (II)-catalyzed reaction path is also operating[281].

An extensive kinetic investigation of reactions leading to a net reduction of platinum(IV) complexes has been carried out by reacting *cis*- and *trans*-$[\mathrm{PtL_2X_4}]$ complexes (L = several uncharged ligands; $\mathrm{X_4} = \mathrm{Cl_4}, \mathrm{Br_2Cl_2}, \mathrm{Br_4}$) with SCN^-, I^-, SeCN^- and $\mathrm{S_2O_3}^{2-}$ in methanol[282–286] or other non-aqueous solvents[287]. The stoichiometry of these reactions is

$$(\textit{cis-}\text{ or})\ \textit{trans-}[\mathrm{PtL_2X_4}] + 2\,Z^{n-} \rightarrow (\textit{cis-}\text{ or})\ \textit{trans-}[\mathrm{PtL_2X_2}] + (2\,Z^{n-} - 2\,\mathrm{e}) + 2\,\mathrm{X}^- \qquad (63a)$$

$$(\textit{cis-}\text{ or})\ \textit{trans-}[\mathrm{PtL_2X_2}] + 2\,Z^{n-} \rightarrow (\textit{cis-}\text{ or})\ \textit{trans-}[\mathrm{PtL_2Z_2}]^{2-2n} + 2\,\mathrm{X}^- \qquad (63b)$$

The reactions follow a second-order rate law, first-order with respect to both platinum (IV) and reductant. The mechanism is believed to be an inner-sphere atom-transfer redox mechanism.

$$\mathrm{XPt^{IV}X} + \mathrm{Z}^{n-} \rightleftharpoons \mathrm{XPt^{IV}-X}\cdots\mathrm{Z}^{n-} \rightarrow \mathrm{Pt^{II}} + \mathrm{XZ}^{1-n} + \mathrm{X}^- \qquad (64a)$$

$$\mathrm{XZ}^{1-n} + \mathrm{Z}^{n-} \rightarrow \mathrm{X}^- + (2\,\mathrm{Z}^{n-} - 2\,\mathrm{e}) \qquad (64b)$$

The reactivity of the anionic reductants towards the same platinum (IV) complex increases in the order $\mathrm{SCN}^- < \mathrm{I}^- < \mathrm{SeCN}^- < \mathrm{S_2O_3}^{2-}$, roughly paralleling the order of their standard potentials[289]. On the other hand, the reactivity of different complexes towards the same reductant is found to depend on the ligands L and X as well as on the geometric configuration of the complex. This is documented by the examples reported in Table 15. The enthalpies of activation appear to be most important in determining the relative reactivities of the different substrates towards a given reductant. A linear free energy relationship

$$\log k_2 = r(\mathrm{X}) + r_\mathrm{s} \qquad (65)$$

is found to correlate the second-order rate constants of the reactions of substrates *trans*–$[\mathrm{PtL_2Cl_4}]$ with the different reducing anions in methanol at 40°C. In this relationship k_2 is the second-order rate constant for the reaction of the substrate under investigation with a given reducing anion, $r(\mathrm{X})$ is the value of $\log k_2$ for the corresponding reaction of *trans*-$[\mathrm{Pt(P(}n\text{-}\mathrm{Pr)_3)_2Cl_4}]$, selected as a standard substrate, and r_s is a constant dependent upon the nature[285] of the ligand L.

Values of $r(\mathrm{X})$ (from ref. 283)

Reducing anion	$r(\mathrm{X})$
$\mathrm{SCN^-}$	−5.22
$\mathrm{I^-}$	−2.40
$\mathrm{SeCN^-}$	−1.50
$\mathrm{S_2O_3{}^{2-}}$	0.16

Values of r_s (from ref. 286)

Ligand	r_s
$\mathrm{AsEt_3}$	−0.4
$\mathrm{P(}n\text{-}\mathrm{Pr)_3}$	0.00
$\mathrm{PEt_3}$	0.2
py	1.5
pip	1.95
$\mathrm{SEt_2}$	3.35
$\mathrm{SMe_2}$	3.4

Equation (65) is represented graphically in Fig. 5. This figure also shows that a linear relationship of type (65) also holds for reactions of *cis* isomers as well as for bromo complexes*. This kind of relationship has been taken as indicative that in these reactions each agent makes a contribution to the free energy of activation independent of the nature of the substrate. In other words, bond making and bond breaking are believed to be kinetically independent in these processes. On the other hand, the occurrence of a linear free energy relationship of the type

$$\Delta G^* = a + c\Delta G^0 \qquad (66)$$

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*Deviations from relationship (65) have been found when the ligand L is a primary amine[286].

TABLE 15

Rate constants, k_2 (l.mole^{-1} .sec^{-1}), at 40°C and activation parameters, ΔH^* (kcal.mole^{-1}) and ΔS^* (cal.deg^{-1}.mole^{-1}) for the reduction of some platinum (IV) complexes in methanol

Complex	Reducing anion and kinetic data												Ref.
	SCN^-			I^-			$SeCN^-$			$S_2O_3^{2-}$			
	k_2	ΔH^*	ΔS^*	k_2	ΔH^*	ΔS^*	k_2	ΔH^*	ΔS^*	k_2	ΔH^*	ΔS^*	
trans-[$Pt(AsEt_3)_2Cl_4$]				8.0×10^{-4}	19.5	−11	8.8×10^{-3}	14.5	−22	1.28	14.9	−10	282, 285
trans-[$Pt(PPr_3)_2Cl_4$]	6.00×10^{-6}	13.1	−20	3.90×10^{-3}	14.7	−21	3.10×10^{-2}	14.4	−22	1.46	14.1	−13	283
trans-[$Pt(PEt_3)_2Cl_4$]	1.0×10^{-5}	17.3	−26	5.3×10^{-3}	15.6	−19	4.3×10^{-2}	14.0	−20	3.0	13.9	−12	282, 285
trans-[$Pt(py)_2Cl_4$]				1.7×10^{-1}						36	12.5	−11	286
trans-[$Pt(pip)_2Cl_4$]				2.9×10^{-1}	13.8	−17				1.6×10^{2}			286
trans-[$Pt(SEt_2)_2Cl_4$]	1.26×10^{-2}	15.6	−18	9.25	11.8	−17	78	9.0	−21	2.2×10^{3}	9.7	−12	286
trans-[$Pt(SMe_2)_2Cl_4$]	1.10×10^{-2}	13.2	−25	9.5	10.5	−21				5.4×10^{3}	10.5	− 8	286
trans-[$Pt(PEt_3)_2Br_2Cl_2$]	6.6×10^{-2}	14.5	−18	36.9	9.2	−19	2.87×10^{2}	9.0	−18	2.3×10^{4}	11.2	− 7	284
trans-[$Pt(PEt_3)_2Br_4$]	8.82×10^{-2}	15.0	−15	60.2	10.6	−17	3.78×10^{2}	9.0	−18	2.8×10^{4}	10.0	− 7	285
cis-$Pt(PPr_3)_2Cl_4$]	1.13×10^{-3}	16.0	−21	6.72×10^{-2}	14.6	−17	1.78	12.3	−18	27.9	13.2	−10	283

between the free energy of activation, ΔG^*, and the standard free energy of these reactions (ref. 288) is thought to indicate that a considerable degree of bond making and breaking occurs in the transition state.

The reactivity of *trans*-$[PtL_2X_4]$ upon changing L is in the order $AsEt_3 < P(n\text{-}Pr)_3 < < PEt_3 < py < pip < SEt_2 \simeq SMe_2$. This sequence has been explained by assuming that the reactivity of platinum (IV) complexes towards reduction increases with increasing π-acceptor ability of the ligand L and with decreasing σ-donor ability. The π-withdrawal of electrons should favor the reactivity in the order N < P, As, S, whereas the σ-withholding of electrons should favor an order[289] As, P < S < N. The net balance of these contributions produces the observed[286] order of reactivity, i.e. As, P < N < S. The occurrence of π interactions is also thought to be responsible for the higher reactivity of *cis*-$[Pt(PR_3)_2X_4]$ compared with the *trans* isomers. The π interactions of *cis* isomers are more pronounced than those of the *trans* homologs because two different d_π orbitals of platinum are involved in the first case, against only one in the second case[283]. This makes the *cis* structure more reactive.

The halides coordinated to the central metal ion are also very important in determining the reactivity of the substrate. The most appreciable effect is displayed by the halide which acts as a bridge in the activated complex, whereas the other halides seem to play a less important role. This is inferred by the fact that the rate of reduction of *trans*-$[Pt(PEt_3)_2Br_2Cl_2]$, in which bromide is the bridging atom in the activated complex, is very near to that of *trans*-$[Pt(PEt_3)_2Br_4]$ (see Table 15), but is about 5,000 times higher than that of *trans*-$[Pt(PEt_3)_2Cl_4]$. However, the effect of the bridging halide also depends on the reducing agent used. For example, the tetrabromo complexes react with SCN^-, I^-, $SeCN^-$, $S_2O_3^{2-}$ (ref. 284) and with $[Pt(diars)_2Y]^+$ (Y = Cl, Br, I)[290] about 5,000 times faster than the corresponding tetrachloro complexes, but only 50–200 times faster when the reducing agent is $[Ni(diars)_2Y]^+$ (Y = Cl, Br)[291].

Kinetic investigations carried out on other platinum (IV) complexes shed considerable light on the reaction mechanism of these compounds. The most significant results were obtained by studying the reactions of *trans*-$[Pt(AA)_2X_2]^{2+}$(AA = en, $\frac{1}{2}$*N,N,N′,N′*-tetramethylethylenediamine; X=Cl, Br) with bromide and iodide[288], and *trans*-$[Pt(CN)_4X_2]^{2-}$ (X = Cl, Br, I) with iodide[292]. In these cases the linear free energy relationship (66) is also found to hold, thus showing a close parallel between kinetic and thermodynamic parameters for these kinds of reaction. On this basis, a rather pronounced degree of bond making and breaking is thought to occur in every activated complex of these reactions.

Several cases of REOA reactions do occur with platinum (IV) complexes. These reactions are believed to be responsible for several cases of uncatalyzed formal substitutions of platinum (IV). For instance, the multi-stage hydrolysis of $[PtI_6]^{2-}$ in the presence of free iodide is thought to include reaction (67) as the most important stage[293]*.

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* The letters above the arrows indicate the corresponding reaction path of the scheme (61).

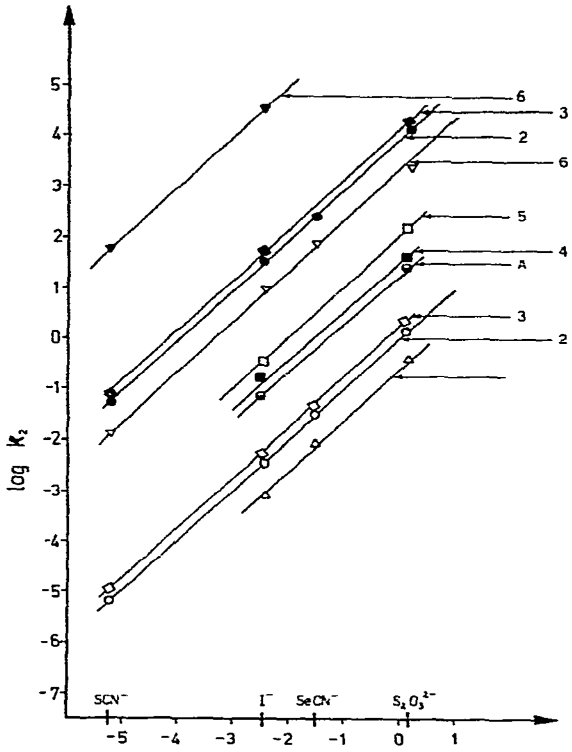
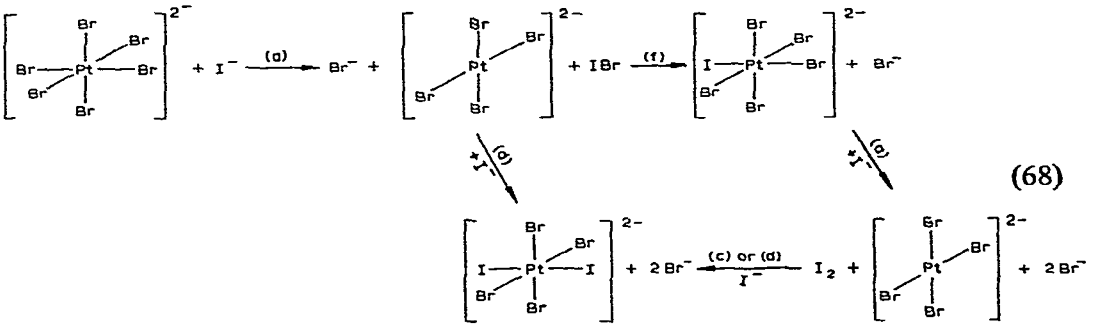


Fig. 5. Correlation of the second-order rate constants, k_2, of the reduction of *trans*-[PtL_2X_4] complexes in methanol at 40°C, with $r(X)$. Open symbols, X = Cl; closed symbols, X = Br. L = $AsEt_3$ (1); $P(n\text{-}Pr)_3$ (2); PEt_3 (3); py (4); pip (5); SEt_2 (6). A = *cis*-[$Pt(P(n\text{-}Pr)_3)_2Cl_4$]. Data from refs. 282–286.

$$[PtI_6]^{2-} + I^- \xrightarrow{(a)} [PtI_4]^{2-} + I^- + I_2 \xrightarrow[H_2O]{(e)} [H_2OPtI_5]^- + 2\,I^- \qquad (67)$$

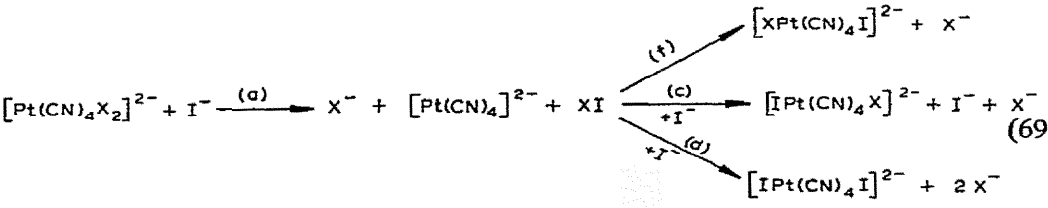
The $[PtBr_6]^{2-}$—I^- interchange reaction has also been adequately explained in terms of a sequence of REOA reactions[265]



(68)

Similar reaction mechanisms are thought to occur in the uncatalyzed path of $[PtCl_6]^{2-}$–I^- and $[PtI_6]^{2-}$–Br^- halide interchanges.

The occurrence of REOA reactions represents a general feature of several platinum-(IV) formal substitutions. For example, the reaction of *trans*-$[Pt(CN)_4X_2]^{2-}$ (X = Cl, Br) with iodide leads to substituted platinum (IV) complexes through the REOA reaction mechanism (69).



(69)

The hydrolysis of $[Pt(CN)_4Br_2]^{2-}$ in the presence of free bromide (see p. 163) has also been recently interpreted on the basis of the occurrence of REOA reactions[288].

A rather peculiar complementary redox reaction is the reduction of $[Pt(NH_3)_5Cl]^{3+}$ by aquochromium (II)[294]. Chromium (II), a rather common monoelectronic reductant, behaves in this case as a bielectronic reagent. The reaction obeys a second-order rate law, first-order either in platinum (IV) or chromium (II), and yields a chromium (IV) intermediate, which rapidly reacts with chromium (II) forming a dimeric chromium (III) compound. This then slowly decomposes to $CrCl^{2+}$ and Cr^{3+}.

$$[Pt(NH_3)_5Cl]^{3+} + Cr^{2+} \xrightarrow{\text{slow}} [Pt(NH_3)_4]^{2+} + NH_3 + Cr^{IV}Cl^{3+} \tag{70a}$$

$$Cr^{IV}Cl^{3+} + Cr^{2+} \xrightarrow{\text{fast}} Cr^{III}_2Cl^{5+} \rightarrow CrCl^{2+} + Cr^{3+} \tag{70b}$$

A different reductive elimination[295] mechanism involving platinum (IV) complexes is found to operate in the reaction

$$[Pt(PEt_3)_2Ph_2I_2] \rightarrow [Pt(PEt_3)_2PhI] + PhI \tag{71}$$

This reaction follows the rate law

$$\text{Rate} = \frac{k[Pt^{IV}]}{[I^-]} \tag{72}$$

when carried out in the presence of excess of free iodide. The mechanism accounting for this rate law is believed to involve a fast reversible solvolysis of the initial platinum (IV) complex and a subsequent slow unimolecular reduction of the cationic platinum (IV) complex formed.

$$[Pt(PEt_3)_2Ph_2I_2] + S \overset{K}{\rightleftharpoons} [Pt(PEt_3)_2Ph_2I(S)]^+ + I^- \tag{73a}$$

$$[\mathrm{Pt(PEt_3)_2Ph_2I(S)}]^+ \xrightarrow[-\mathrm{S}+\mathrm{I}^-]{k_1} [\mathrm{Pt(PEt_3)_2PhI}] + \mathrm{PhI} \tag{73b}$$

The reactions reported above have all been concerned with the reduction of platinum (IV). Complementary reactions of oxidation of $\mathrm{Pt^{II}}$ have so far been carried out mainly by using platinum (IV) complexes as oxidizing agents, and have been reviewed elsewhere[261]. A number of attempts to study the kinetics of oxidation of platinum (II) with bromine failed because of the extremely high reaction rates[296]. However, a recent kinetic investigation of the oxidation of $[\mathrm{PtCl_4}]^{2-}$ with chlorine in water has provided direct information on the mechanism of oxidation of platinum (II) complexes by halogens[297]. The oxidation of $[\mathrm{PtCl_4}]^{2-}$ is found to produce hydroxypentachloroplatinate (IV), which subsequently reacts with chloride ion to yield $[\mathrm{PtCl_6}]^{2-}$.

$$[\mathrm{PtCl_4}]^{2-} + \mathrm{Cl_2} + \mathrm{H_2O} \rightarrow [\mathrm{PtCl_5OH}]^{2-} + \mathrm{H^+} + \mathrm{Cl^-} \tag{74a}$$

$$[\mathrm{PtCl_5OH}]^{2-} + \mathrm{H^+} + \mathrm{Cl^-} \rightarrow [\mathrm{PtCl_6}]^{2-}\ \mathrm{H_2O} \tag{74b}$$

The oxidation step (74a) follows the rate law

$$\mathrm{Rate} = (k_1 + k_2[\mathrm{PtCl_4}^{2-}])[\mathrm{PtCl_4 \cdot Cl_2}^{2-}] \tag{75}$$

where $[\mathrm{PtCl_4 \cdot Cl_2}]^{2-}$ is a platinum (II)–chlorine adduct formed in a fast precursor step. The form of the rate law, together with the stoichiometry of the redox step, suggests the redox mechanism (76) for the oxidation of platinum (II) by chlorine.

$$[\mathrm{PtCl_4}]^{2-} + \mathrm{Cl_2} \xrightarrow{\text{fast}} [\mathrm{PtCl_4 \cdot Cl_2}]^{2-} \tag{76a}$$

$$[\mathrm{PtCl_4 \cdot Cl_2}]^{2-} + \mathrm{H_2O} \xrightarrow{k_a} [\mathrm{PtCl_5OH}]^{2-} + \mathrm{H^+} + \mathrm{Cl^-} \tag{76b}$$

$$[\mathrm{PtCl_4 \cdot Cl_2}]^{2-} + [\mathrm{PtCl_4}]^{2-} \overset{K}{\rightleftharpoons} [\mathrm{Cl_4Pt{-}Cl_2{-}PtCl_4}]^{4-} \tag{76c}$$

$$[\mathrm{Cl_4Pt{-}Cl_2{-}PtCl_4}]^{4-} + \mathrm{H_2O} \xrightarrow{k_b} [\mathrm{PtCl_5OH}]^{2-} + [\mathrm{PtCl_4}]^{2-} + \mathrm{H^+} + \mathrm{Cl^-} \tag{76d}$$

There is now evidence suggesting that this mechanism is also operating in the oxidation of other platinum (II) complexes and when bromine is used as an oxidizing agent[297,298]. The substitution reaction (74b) is instead thought to proceed through a platinum (II)-catalyzed substitution reaction of type (59).

Some information on the reactivity of similar nickel (II), palladium (II) and platinum-(II) complexes towards oxidation has been obtained by studying the kinetics of reaction (77) (M = Ni, Pd, Pt; X and Y are halides)[290,291].

$$\begin{aligned} &\textit{trans-}[\mathrm{Pt(PEt_3)_2X_4}] + [\mathrm{M(diars)_2}]^{2+} + \mathrm{Y^-} \rightarrow \\ &\qquad\qquad \textit{trans-}[\mathrm{Pt(PEt_3)_2X_2}] + [\mathrm{M(diars)_2XY}]^{2+} \end{aligned} \tag{77a}$$

$$[\mathrm{M(diars)_2XY}]^{2+} \xrightarrow{\mathrm{Y^-}} \text{products} \tag{77b}$$

The rate law for these reactions has the form

$$\text{Rate} = \frac{k_f K[\mathrm{M(diars)_2}^{2+}]_{\mathrm{tot}}[\mathrm{Y^-}][\mathrm{Pt^{IV}}]}{1 + K[\mathrm{Y^-}]} = k_f[\mathrm{Pt^{IV}}][\mathrm{M(diars)_2Y^+}] \tag{78}$$

and is consistent with the mechanism

$$[\mathrm{M(diars)_2}]^{2+} + \mathrm{Y^-} \overset{K}{\rightleftharpoons} [\mathrm{M(diars)_2Y}]^+ \tag{79a}$$

$$\mathrm{XPt^{IV}X} + [\mathrm{M(diars)_2Y}]^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\mathrm{XPt{-}X{-}M(diars)_2Y}]^+ \xrightarrow{k_3}$$

$$\mathrm{X^-} + \mathrm{Pt^{II}} + [\mathrm{XM(diars)_2Y}]^{2+} \tag{79b}$$

$$[\mathrm{M(diars)_2XY}]^{2+} \xrightarrow{\mathrm{Y^-}} \text{products} \tag{79c}$$

with $k_f = k_1k_3/(k_2 + k_3)$. The second-order rate constant for the reaction of $[\mathrm{M(diars)_2Cl}]^+$, k_f, at 50°C in methanol changes with M in the order Ni $\simeq$ Pt $>$ Pd, the enthalpy of activation for the nickel complex being much higher[291] than that of the platinum (II) complex (10.6 kcal.mole^{-1} against 3.4 kcal.mole^{-1}). This trend is believed to be due to the influence upon the overall free energy of activation of both the relative stability of the oxidation products, $[\mathrm{M(diars)_2XY}]^{2+}$, and the relative stability of the bridged intermediate percursor of the rate-determining step. The nature of the halide bonded to the metal (II) complex, $[\mathrm{M(diars)_2Y}]^+$, has little effect upon the reactivity of these complexes towards oxidation. For instance, the second-order rate constant, k_f, of the oxidation of $[\mathrm{Pt(diars)_2Y}]^+$ is almost independent of the nature of $\mathrm{Y^-}$ ($k_{f(\mathrm{Cl^-})} = 0.705$ l.mole^{-1}.sec^{-1}; $k_{f(\mathrm{Br^-})} = 1.31$ l.mole^{-1}.sec^{-1}; $k_{f(\mathrm{I^-})} = 4.39$ l.mole^{-1}.sec^{-1} in methanol at 50°C and 3.85×10^{-2} molar ionic strength)[290]. Under the same conditions the stability constants of the five-coordinate platinum (II) adduct are on the other hand, strongly dependent on the halide ($K_{(\mathrm{Cl^-})} = 18$ l.mole^{-1}; $K_{(\mathrm{Br^-})} = 340$ l.mole^{-1}; $K_{(\mathrm{I^-})} = 1.4 \times 10^4$ l.mole^{-1}). These results are helpful towards understanding the effect of the entering group in the platinum (II)-catalyzed substitutions of platinum (IV) complexes. In fact they suggest that the dependence of the reactivity on the entering ligand usually encountered in the platinum (II)-catalyzed substitutions of platinum (IV) complexes, which is in the order $\mathrm{I^-} \gg \mathrm{Br^-} \gg \mathrm{Cl^-}$, is mainly related to the thermodynamic stability of the five-coordinate adduct, and thus to its effective concentration in solution, whereas the direct effect of $\mathrm{Y^-}$ upon the tendency of platinum (II) to undergo oxidation is of little importance.

(ii) Non-complementary redox reactions

A general feature of these reactions, in which platinum reacts with monoelectronic reactants, is to undergo oxidation–reduction with formation of labile platinum (III) intermediates. The stoichiometry of these reactions is shown by

$$\mathrm{Pt^{II}} + 2\mathrm{X^-} + 2\,\mathrm{Z}^n \rightleftharpoons \mathrm{Pt^{IV}X_2} + 2\,\mathrm{Z}^{n-1} \qquad (80)$$

(a) Reduction of platinum (IV) complexes

The reduction of platinum (IV) complexes has been carried out by using outer-sphere as well as inner-sphere monoelectronic reductants. The first example of a possible non-complementary outer-sphere redox process has been found[299] in the reduction of several platinum (IV) complexes by $[\mathrm{Cr(bipy)_3}]^{2+}$. The reduction of one molecule of platinum (IV) requires two molecules of chromium (II), only one of which is present in the rate-determining step. In fact, the reaction follows a second-order rate law, first-order with respect to both platinum (IV) and chromium (II). This is consistent with a non-complementary redox process. However, a bielectronic complementary redox mechanism cannot be ruled out owing to the ability of chromium (II) to undergo two-electron oxidation by platinum (IV). On the other hand, the lack of identification of the reaction products prevents a reliable assignment of the reaction mechanism. The reduction of *cis*- and *trans*-$[\mathrm{Pt(am)_2X_4}]$ (am = amine; X = Cl, Br) by ferrocyanide in water[300] and that of *trans*-$[\mathrm{PtL_2X_4}]$ (L = uncharged ligands; $\mathrm{X_4} = \mathrm{Cl_4}, \mathrm{Br_2}, \mathrm{Cl_2}, \mathrm{Br_4}$) by ferrocene in hydroxylic solvents[301] appear to be good examples of outer-sphere redox reactions occurring through an outer-sphere redox mechanism involving two one-electron steps. Platinum (IV) undergoes reduction by both these outer-sphere reductants according to a second-order rate law, first-order in platinum (IV) and in the reductant. The reaction rate is found to depend on the nature of the ligands bonded to the central metal ion. It is found, for example, that the second-order rate constants for the reduction of *trans*-$[\mathrm{PtL_2X_4}]$ by ferrocene[301] increase in the order $\mathrm{AsEt_3} < \mathrm{P}(n\text{-Pr})_3 < \mathrm{PEt_3} < \mathrm{pip} < \mathrm{SEt_2}$, and parallel the values of r_s of the different L. The bromo complexes react with either ferrocyanide or ferrocene with a rate 10–20 times higher than the corresponding chloro complexes. This fact has been ascribed mainly to the lower energy required to deform the bromo complexes in order to make them available for the electron transfer.

Non-complementary inner-sphere reductions of platinum (IV) have been found by using $\mathrm{Fe^{2+}}$ as a reducing agent (see p. 174).

(b) Oxidation of platinum (II)

Several monoelectronic oxidants are expected to oxidize platinum (II) to platinum (IV) with the intermediate formation of platinum (III) complexes. In some cases these intermediates have been invoked to account for the stoichiometry of the reaction and the form of the rate law[302]. These elements are not, however, sufficient for the postulation of platinum (III) intermediates and the definition of a satisfactory mechanism of non-complementary oxidations of platinum (II). Important information for this purpose can be gained from the effects caused by the reaction products on the rate of reaction. The oxidation of $[PtCl_4]^{2-}$ and $[Pt(en)_2]^{2+}$ by $[IrCl_6]^{2-}$ in the presence of free chloride, viz.

$$Pt^{II} + 2\,IrCl_6{}^{2-} + 2\,Cl^- \rightarrow Pt^{IV}Cl_2 + 2\,IrCl_6{}^{3-} \tag{81}$$

appears to be the first example where an adequate mechanism of non-complementary oxidation of platinum (II) could be derived[303]. The intermediate formation of platinum (III) complexes in these cases is inferred from the form of the rate laws of the reactions carried out in the presence of added $[IrCl_6]^{3-}$

$$-\frac{d[PtCl_4{}^{2-}]}{dt} = \frac{k_1 k_3 [PtCl_4{}^{2-}][IrCl_6{}^{2-}]^2[Cl^-]}{k_2[IrCl_6{}^{3-}] + k_3[IrCl_6{}^{2-}][Cl^-]} \tag{82}$$

$$-\frac{d[Pt(en)_2{}^{2+}]}{dt} = \frac{k_1' k_3' [Pt(en)_2{}^{2+}][IrCl_6{}^{2-}]^2[Cl^-]^2}{k_2'[IrCl_6{}^{3-}] + k_3'[IrCl_6{}^{2-}][Cl^-]^2} \tag{83}$$

These rate laws are consistent with a mechanism involving a platinum (III) intermediate and two one-electron redox steps.

$$PtCl_4{}^{2-} + IrCl_6{}^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} PtCl_4{}^{-} + IrCl_6{}^{3-} \tag{84a}$$

$$PtCl_4{}^{-} + IrCl_6{}^{2-} + Cl^- \xrightarrow{k_3} PtCl_5{}^{-} + IrCl_6{}^{3-} \tag{84b}$$

$$PtCl_5{}^{-} + Cl^- \rightarrow PtCl_6{}^{2-} \tag{84c}$$

$$Pt(en)_2{}^{2+} + IrCl_6{}^{2-} \xrightarrow[k'_2]{k'_1} Pt(en)_2{}^{3+} + IrCl_6{}^{3-} \tag{85a}$$

$$Pt(en)_2{}^{3+} + IrCl_6{}^{2-} + 2\,Cl^- \xrightarrow{k'_3} Pt(en)_2Cl_2{}^{2+} + IrCl_6{}^{3-} \tag{85b}$$

(c) Reversible non-complementary redox reactions

A full kinetic investigation of non-complementary redox reactions involving platinum complexes has been carried out on reaction (86) in perchloric acid solutions[304,305]

$$(\textit{cis}\text{ or}) \textit{ trans-}[Pt(am)_2Br_2] + 2\,Fe^{3+} + 2\,Br^- \rightleftharpoons (\textit{cis}\text{ or})$$

$$\textit{trans-}[Pt(am)_2Br_4]^4 + 2\,Fe^{2+} \tag{86}$$

The equilibrium constant of these reactions is such that both the forward and the reverse reactions could be examined. The general rate law (87) was found to operate in these reactions.

$$-\frac{\mathrm{d}[\mathrm{Pt^{II}}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Pt^{IV}}]}{\mathrm{d}t} = \frac{k_1k_3K^2[\mathrm{Pt^{II}}][\mathrm{Fe^{3+}}]^2[\mathrm{Br^-}]^2 - k_2k_4[\mathrm{Pt^{IV}}][\mathrm{Fe^{2+}}]^2}{k_2[\mathrm{Fe^{2+}}] + k_3K[\mathrm{Fe^{3+}}][\mathrm{Br^-}]} \qquad (87)$$

Such a rate law is consistent with an inner-sphere atom-transfer redox mechanism involving once again two one-electron redox steps

$$\mathrm{Fe^{3+} + Br^-} \overset{K}{\rightleftharpoons} \mathrm{FeBr^{2+}} \qquad (88a)$$

$$\mathrm{Pt^{II} + FeBr^{2+}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Pt^{III}Br + Fe^{2+}} \qquad (88b)$$

$$\mathrm{Pt^{III}Br + FeBr^{2+}} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{Pt^{IV}Br_2 + Fe^{2+}} \qquad (88c)$$

This mechanism is also consistent with the values of the equilibrium constant of the reaction. According to such a mechanism the equilibrium constant of equation (86) is related to the specific rate constants of the single steps by the relationship $K_{\mathrm{eq}} = k_1k_3K^2/k_2k_4$. The values of the equilibrium constants for these reactions, derived from kinetic data, are always found to be very close to those derived from concentrations of the different species present at equilibrium.

The reactivity of $[\mathrm{Pt(am)_2Br_4}]$ towards reduction by $\mathrm{Fe^{2+}}$ is independent of the isomeric form, provided that the correction for the statistical effects is made. This behavior is different from that found in the reduction of *cis*- and *trans*-$[\mathrm{Pt(PR_3)_2X_4}]$ by anionic reductants (see p. 168). This is explained by the fact that the amine ligands are not involved in π interactions, which are believed to be responsible for higher reactivity of the *cis* isomer in the phosphine complexes.

The effect of the halide, X, on the rate of reduction is found to be rather unusual in this kind of reaction. In fact, the chloro complexes are found to react with $\mathrm{Fe^{2+}}$ 5–15 times faster than the corresponding bromo complexes, whereas a trend Br > Cl is usually observed in the reduction of platinum (IV) complexes. The higher thermodynamic stability of $\mathrm{FeCl^{2+}}$ with respect to $\mathrm{FeBr^{2+}}$, which are the oxidation products in the two cases, is believed to be the most important factor related to the higher reactivity exhibited by the chloro complexes.

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