Effects of Geometric Configuration and Steric Hindrance on Rates and Mechanisms of Oxidation of Diaminedichloroplatinum(II) Complexes by Tetrachloroaurate(III) Ions

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The oxidation reactions of *trans*- and/or *cis*-$[PtCl_2(NH_2R)_2]$ by $[AuCl_4]^-$ in the presence of $[NEt_4]Cl$ have been kinetically investigated in acetonitrile (R = H, Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, CH_2Bu^t, CH_2Ph, or cyclo-C_6H_{11}). The rate law for the oxidation of the *trans* complexes consists mainly of a third-order rate term, $k_c[PtCl_2(NH_2R)_2][AuCl_4^-][Cl^-]$, whereas an additional rate term, $k_a[PtCl_2(NH_2R)_2][AuCl_4^-][Cl^-]/(1 + k_b[Cl^-])$, operates in the case of the *cis* complexes. A reaction scheme is proposed. The oxidation rates of both *cis* and *trans* complexes appear to be reduced by increasing the steric hindrance of the amine, *cis* complexes being more sensitive towards changes of steric hindrance than *trans* analogues. Approximate linear relationships correlate the reactivities (log *k*) of both *cis* and *trans* complexes with an amine steric hindrance parameter.

In previous papers [1-3] I reported that platinum(II) complexes of the type *cis*- or *trans*-$[PtCl_2L_2]$ (L = $AsEt_3$, PEt_3, or substituted pyridines; L_2 = 2,2′-bipyridine or substituted 1,10-phenanthrolines) undergo quantitative oxidation to platinum(IV) by tetrachloroaurate(III) in acetonitrile in the presence of chloride ions. It was found that the σ-donor ability of the substituted pyridines or phenanthrolines did not appreciably affect the rates of oxidation, but on the other hand the oxidation was prevented by ligands such as *ortho*-substituted pyridines (2-methyl- and 2,4-dimethyl-pyridine) as a result of steric effects.

In this paper a kinetic investigation is reported on the oxidation reactions of platinum(II) complexes of the type *trans*- and/or *cis*-$[PtCl_2(NH_2R)_2]$ by $[NEt_4][AuCl_4]$ in acetonitrile at 50 °C (R = H, Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, CH_2Bu^t, CH_2Ph, and cyclo-C_6H_{11}). The amines were chosen in order to provide a set of ligands displaying different steric hindrances [4] but similar σ-donor abilities.[5]

Experimental

Materials.—The *cis*-platinum(II) complexes were prepared following typical literature methods,[6,7] or by reacting aqueous solutions of $K_2[PtCl_4]$ with a slight excess of the amine either at 0 °C (R = Pr^n, Bu^n, Bu^i, or CH_2Ph) or at 20—30 °C (R = Pr^i, Bu^s, CH_2Bu^t, or cyclo-C_6H_{11}). The pale yellow compounds obtained were recrystallized from methanol or (R = CH_2Ph or cyclo-C_6H_{11}) carefully washed with water and methanol. Complexes soluble enough to allow reliable u.v. spectra to be obtained in acetonitrile in the presence of 0.10 mol dm^{-3} $[NEt_4]Cl$ exhibited closely related spectra, with two broad unresolved bands of comparable intensities (Figure 1) with maxima at *ca.* 310 (ε 140—160) and *ca.* 280 nm (ε 140—170 dm^3 mol^{-1} cm^{-1}). Absorbances of rather lower intensities were observed in the 260—310 nm region when $[NEt_4]Cl$ was entirely replaced by $[NEt_4][ClO_4]$ (Figure 1). The absorbances in the above region were found to increase with increasing $[NEt_4]Cl$ content, reaching a saturation value, for the concentration of complexes used (see below), at chloride concentrations of *ca.* 2×10^{-3}—3×10^{-3} mol dm^{-3} at 50 °C and I = 0.10 mol dm^{-3}.

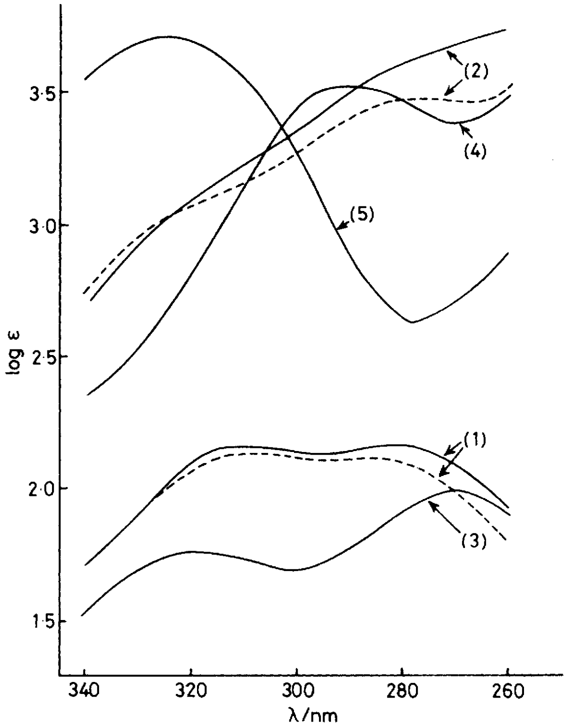

Figure 1. Typical examples of u.v. absorption spectra in acetonitrile at 50 °C and I = 0.10 mol dm^{-3} of (1) *cis*-$[PtCl_2(NH_2Pr^n)_2]$ in $[NEt_4]Cl$ (0.10 mol dm^{-3}) (——) or $[NEt_4][ClO_4]$ (0.10 mol dm^{-3}) (— — —); (2) *cis*-$[PtCl_4(NH_2Pr^n)_2]$ in $[NEt_4]Cl$ (0.10 mol dm^{-3}) (——) or $[NEt_4][ClO_4]$ (0.10 mol dm^{-3}) (— — —); (3) *trans*-$[PtCl_2(NH_2Pr^n)_2]$; (4) *trans*-$[PtCl_4(NH_2Pr^n)_2]$; and (5) $[NEt_4]$-$[AuCl_4]$. Spectra (3), (4), and (5) are not affected by replacement of $[NEt_4]Cl$ with $[NEt_4][ClO_4]$

The *trans*-platinum(II) complexes (R = H, Me, Et, Pr^n, or CH_2Ph) were prepared by reacting $[Pt(NH_2R)_4]Cl_2$ with warm or boiling 3—6 mol dm^{-3} hydrochloric acid. A literature method was used to prepare *trans*-$[PtCl_2\{NH_2(cyclo\text{-}C_6H_{11})\}_2]$.[7] The *trans* form of $[PtCl_2(NH_2Bu^t)_2]$ appeared to be the only species which was recovered when aqueous $K_2[PtCl_4]$ was reacted with an excess of NH_2Bu^t at 40—50 °C. The u.v. spectra of all the complexes in 0.10 mol dm^{-3} $[NEt_4]Cl$ in acetonitrile exhibited a similar pattern, with two rather distinct maxima (Figure 1) at *ca.* 320 (327 for R = Bu^t) (ε 60—80) and *ca.* 270 nm (274 nm for R = Bu^t) (ε 90—120 dm^3 mol^{-1} cm^{-1}).* Replacement of $[NEt_4]Cl$ with $[NEt_4]$-

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* The maximum at the lower wavelength for both *cis* and *trans* complexes with benzylamine was masked by the absorption of the aromatic ring.

[ClO$_4$] gave no clear indication of any changes in absorbance of the solutions.

The platinum(IV) complexes were prepared by reacting hot aqueous suspensions of the related platinum(II) complexes with hydrogen peroxide (5—10 cm^3, 30% aqueous) and concentrated hydrochloric acid. In each case the mixture was heated with stirring for 10—30 min at *ca.* 80 °C and the yellow precipitate obtained was filtered off, washed with cold water, and dried under vacuum. The u.v. spectrum of each *trans*-platinum(IV) complex in acetonitrile containing 0.10 mol dm^{-3} [NEt$_4$]Cl was unaffected by replacement of chloride with perchlorate ions (Figure 1). Conversely, the u.v. spectra of the *cis* complexes were dependent on the [NEt$_4$]Cl content, reaching a saturation value, for the platinum(IV) concentrations used (see below), at [NEt$_4$]Cl concentrations of *ca.* 2×10^{-3}—3×10^{-3} mol dm^{-3} at 50 °C and $I = 0.10$ mol dm^{-3}.

Tetraethylammonium tetrachloroaurate(III) was prepared by the reaction of a stirred aqueous hydrochloric acid solution of hydrogen tetrachloroaurate(III) with tetraethylammonium chloride. The yellow precipitate was filtered off, carefully washed with water, and dried under vacuum. Reagent grade [NEt$_4$]Cl and [NEt$_4$][ClO$_4$] were dried before use. Acetonitrile was purified by standard methods.

Preparation of the Reaction Mixtures and Evaluation of the Observed Rate Constants.—Reactions were carried out at 50 °C in acetonitrile at $I = 0.10$ mol dm^{-3}, using [NEt$_4$][ClO$_4$] to maintain a constant ionic strength. Stock solutions of [NEt$_4$][AuCl$_4$], [NEt$_4$]Cl, [NEt$_4$][ClO$_4$], and platinum(II) complexes were prepared by weight and kept in the dark.* The reactions were followed spectrophotometrically and were initiated by mixing appropriate volumes of thermostatted solutions of the reactants in 1-cm silica cells maintained in the thermostattically controlled cell compartment of the spectrophotometer. The concentrations of the platinum(II) complexes in the reacting mixtures were lower than 1×10^{-4} mol dm^{-3} and always at least ten times lower than that of [NEt$_4$][AuCl$_4$]. The concentration ranges explored for the reactants were as follows: [NEt$_4$][AuCl$_4$], 6.18×10^{-4}—3.29×10^{-3} {1.98×10^{-4} for *cis*-[PtCl$_2$(NH$_2$Et)$_2$] and *trans*-[PtCl$_2$(NH$_2$Bu^t)$_2$]}; [NEt$_4$]Cl, 5.88×10^{-4}—7.35×10^{-2} mol dm^{-3}. A series of reactions were also carried out without added [NEt$_4$]Cl.

The progress of the reactions was followed by scanning the absorption spectrum of the reacting mixture at suitable time intervals in the range 250—350 nm, or 265—295 nm for relatively high gold(III) concentrations. Fast reactions were followed by scanning the absorbance against time at a constant wavelength (270 nm for *cis* complexes; 280 nm for *trans* complexes). During the course of the reactions the spectra exhibited an isosbestic point in the region 302—306 nm (at 312 nm for R = CH$_2$Ph).† Observed rate constants, $k_{obs.}$, were determined from gradients of plots of log $|A_t - A_\infty|$ against time, where A_t and A_∞ are the absorbances of the reacting mixture at time t and at the end of the reaction. The reactions of some *trans* complexes (*i.e.* R = H, Me, or Et), carried out in the absence of [NEt$_4$]Cl, exhibited an apparently autocatalytic behaviour and were not further investigated under these conditions.

At least three sets of kinetic runs were carried out for each complex using different gold(III) concentrations, each set involving at least ten runs in which the [NEt$_4$]Cl concentration was changed.

Results

All the complexes examined were found to react with gold(III) with the consumption of one mol of gold(III) per mol of platinum(II) reacted. The u.v. spectra showed that the oxidation product was usually *cis*- or *trans*-[PtCl$_4$(NH$_2$R)$_2$], according to whether *cis*- or *trans*-platinum(II) complexes were involved in the reaction. However, when the reactions of *cis* complexes were performed at [NEt$_4$]Cl concentrations lower than *ca.* 2×10^{-3} mol dm^{-3}, *cis*-[PtCl$_4$(NH$_2$R)$_2$] was found to be in equilibrium with some other platinum(IV) species which was instantaneously and quantitatively transformed into *cis*-[PtCl$_4$(NH$_2$R)$_2$] by addition of excess [NEt$_4$]Cl to the exhausted reaction mixture. On considering the spectral behaviour displayed by *cis*-[PtCl$_4$(NH$_2$R)$_2$] as a function of [NEt$_4$]Cl concentration (Experimental section, Figure 1), the above observations can be rationalized by assuming the occurrence of equilibrium (1). An equilibrium of the same type [equation (2)] can be invoked to explain the spectral changes observed on changing the [NEt$_4$]Cl concentration in solutions of the *cis*-[PtCl$_2$(NH$_2$R)$_2$] complexes (Experimental section, Figure 1). An approximate value of $K_{eq.}$ has been obtained for equation (2) for some platinum(II) complexes [$K_{eq.}$ within 3×10^2—7×10^2 (R = Pr^n, Bu^n, Bu^i, or CH$_2$Bu^t), or 7×10^2—20×10^2 dm^3 mol^{-1} (R = Bu^s)].

$$[\mathrm{PtCl_3(NH_2R)_2(MeCN)}]^+ + \mathrm{Cl}^- \underset{+\mathrm{MeCN}}{\overset{-\mathrm{MeCN}}{\rightleftharpoons}} \textit{cis}\text{-}[\mathrm{PtCl_4(NH_2R)_2}] \quad (1)$$

$$[\mathrm{PtCl(NH_2R)_2(MeCN)}]^+ + \mathrm{Cl}^- \underset{+\mathrm{MeCN}}{\overset{-\mathrm{MeCN}}{\rightleftharpoons}} \textit{cis}\text{-}[\mathrm{PtCl_2(NH_2R)_2}] \quad (2)$$

Therefore, on the basis of the above considerations, the general pattern of the oxidation reactions of the investigated platinum(II) complexes by gold(III) can be expressed by equation (3).

$$\textit{trans}\text{-}[\mathrm{PtCl_2(NH_2R)_2}] \text{ or } \left\{\begin{array}{c}[\mathrm{PtCl(NH_2R)_2(MeCN)}]^+ + \mathrm{Cl}^- \\ {\scriptstyle -\mathrm{MeCN}}\downarrow\uparrow{\scriptstyle +\mathrm{MeCN}} \\ \textit{cis}\text{-}[\mathrm{PtCl_2(NH_2R)_2}]\end{array}\right\} + [\mathrm{AuCl_4}]^- \xrightarrow{\mathrm{Cl}^-} \textit{trans}\text{-}[\mathrm{PtCl_4(NH_2R)_2}] \text{ or } \left\{\begin{array}{c}[\mathrm{PtCl_3(NH_2R)_2(MeCN)}]^+ + \mathrm{Cl}^- \\ {\scriptstyle -\mathrm{MeCN}}\downarrow\uparrow{\scriptstyle +\mathrm{MeCN}} \\ \textit{cis}\text{-}[\mathrm{PtCl_4(NH_2R)_2}]\end{array}\right\} + [\mathrm{AuCl_2}]^- \quad (3)$$

The reactions, carried out in the presence of [NEt$_4$]Cl and with an excess of [NEt$_4$][AuCl$_4$], were found to follow a pseudo-first-order rate law. At constant [NEt$_4$]Cl concen-

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* Filtered saturated solutions were used for *cis*- and *trans*-[PtCl$_2$(NH$_3$)$_2$] and for *cis*-[PtCl$_2${NH$_2$(CH$_2$Ph)}$_2$].

† When the [NEt$_4$]Cl concentration employed for the reactions of the *cis* complexes was less than *ca.* 2×10^{-3} mol dm^{-3}, the isosbestic point was located at a lower wavelength, down to *ca.* 300 nm (308 nm for R = CH$_2$Ph) in the absence of [NEt$_4$]Cl.

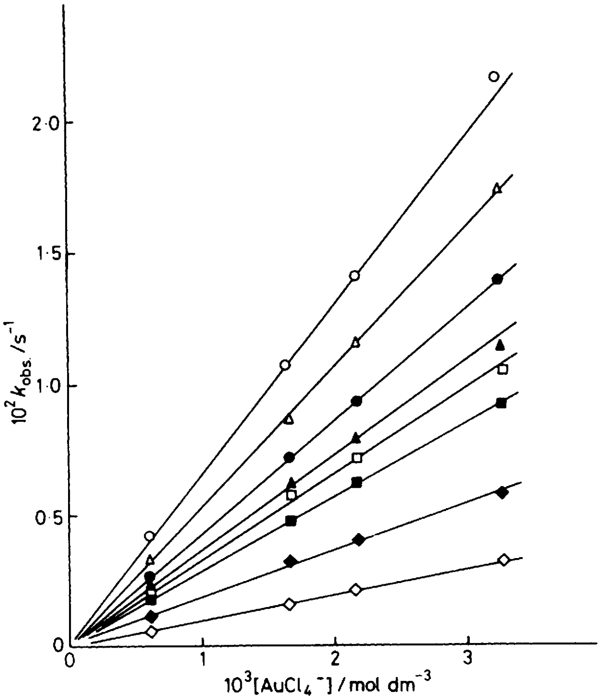

Figure 2. Dependence of the observed rate constants, $k_{obs.}$, on the concentration of gold(III) for the oxidation of *cis*-$[PtCl_2(NH_2Et)_2]$ (filled symbols) and *trans*-$[PtCl_2(NH_2Et)_2]$ (open symbols) by $[NEt_4][AuCl_4]$ in the presence of $[NEt_4]Cl$: 7.35×10^{-2} (○, ●); 5.59×10^{-2} (△, ▲); 3.53×10^{-2} (□, ■); and 8.82×10^{-3} mol dm^{-3} (◇, ◆); in acetonitrile at 50 °C and $I = 0.10$ mol dm^{-3}

tration, the pseudo-first-order rate constant, $k_{obs.}$, was linearly dependent on the tetrachloroaurate(III) concentration (Figure 2), according to relationship (4). The occurrence of the

$$k_{obs.} = k'[AuCl_4^-] + k_e \quad (4)$$

k_e rate term could be inferred only by using very low chloride concentrations (usually lower than 1×10^{-3} mol dm^{-3}) and was too small for a reliable evaluation (Table). The k' values were found to depend on the chloride concentration (Figure 3) according to either equation (5) (*cis* complexes) or (6) (*trans* complexes).* The part played by k_d on the overall reaction rate was usually negligible unless very low chloride concentrations were used. Approximate values of such a rate term could be obtained experimentally only for *cis* complexes, by carrying out a series of kinetic runs in the absence of added chloride ions (Table). In the case of the *trans* complexes the value of k_d was best evaluated, together with k_c, from plots of k' against $[Cl^-]$ [equation (6)], since direct determinations were not allowed for the occurrence of some other reaction path in the absence of chloride ions (Experimental section). The values of k_a, k_b, and k_c for the *cis* complexes were obtained from equation (5), knowing the value of k_d. The related values are collected in the Table.

$$k' = \frac{k_a[Cl^-]}{1 + k_b[Cl^-]} + k_c[Cl^-] + k_d \quad (5)$$

$$k' = k_c[Cl^-] + k_d \quad (6)$$

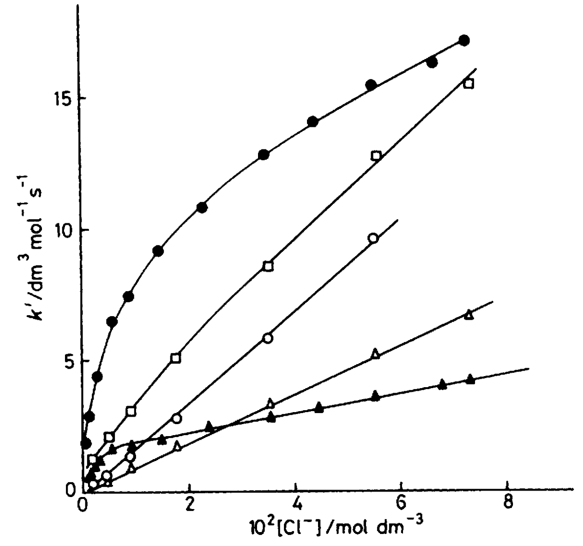

Figure 3. Dependence of k' [slopes of equation (4); $10k'$ for $NH_2(cyclo\text{-}C_6H_{11})$] on the concentration of $[NEt_4]Cl$ for the oxidation of *cis*-$[PtCl_2(NH_2R)_2]$ (filled symbols) or *trans*-$[PtCl_2(NH_2R)_2]$ (open symbols) by $[NEt_4][AuCl_4]$ in acetonitrile at 50 °C and $I = 0.10$ mol dm^{-3}: $NH_2R = NH_3$ (○, ●); NH_2Et (△, ▲); or $NH_2(cyclo\text{-}C_6H_{11})$ (□)

The analytical form of $k_{obs.}$ [equation (7) (*cis* complexes) or (8) (*trans* complexes)] can then be obtained by combining equation (4) with (5) or (6). The poorly characterized and

$$k_{obs.} = \frac{k_a[AuCl_4^-][Cl^-]}{1 + k_b[Cl^-]} + k_c[AuCl_4^-][Cl^-] + k_d[AuCl_4^-] + k_e \quad (7)$$

$$k_{obs.} = k_c[AuCl_4^-][Cl^-] + k_d[AuCl_4^-] + k_e \quad (8)$$

scarcely significant k_d and k_e rate terms can be neglected over a wide range of gold(III) and chloride concentrations and will not be further considered in the following discussion.

Discussion

The *cis*-platinum(II) complexes examined herein display a behaviour which differs from that of the *trans* analogues mainly for two reasons. Firstly, only for *cis* complexes are equilibria of type (2) clearly observed and secondly, only for *cis* isomers is the oxidation reaction path responsible for the k_a rate term unambiguously involved. The occurrence of both k_a and k_c rate terms for the oxidation of the *cis* complexes can be accounted for by assuming that both *cis*-$[PtCl_2(NH_2R)_2]$ and $[PtCl(NH_2R)_2(MeCN)]^+$ undergo oxidative attack by $[AuCl_4]^-$ through reaction steps (9) and (10).

$$[PtCl_2(NH_2R)_2] + [AuCl_4]^- + Cl^- \xrightarrow{k_3} [PtCl_4(NH_2R)_2] + [AuCl_2]^- + Cl^- \quad (9)$$

$$[PtCl(NH_2R)_2(MeCN)]^+ + [AuCl_4]^- + Cl^- \xrightarrow{k_3'} [PtCl_3(NH_2R)_2(MeCN)]^+ + [AuCl_2]^- + Cl^- \quad (10)$$

Such steps, together with fast equilibria (1) and (2), lead to the overall pattern of the oxidation reactions. The pseudo-first-order rate constant, $k_{obs.}$ [equation (11)], is consistent with the

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* Despite some doubts as to its actual weight, a small contribution to k' appears to be given by the k_a rate term for *trans* complexes bearing the bulky $NH_2(C_6H_{11})$ and NH_2Bu^t (Figure 3).

Table. Rate constants,[a] according to equations (5) and (6), for the oxidation of *trans*- and/or *cis*-$[PtCl_2(NH_2R)_2]$ complexes by $[NEt_4]$-$[AuCl_4]$ in acetonitrile at 50 °C and $I = 0.10$ mol dm^{-3}

NH_2R	Geometric configuration	k_a / $dm^6\ mol^{-2}\ s^{-1}$	k_b / $dm^3\ mol^{-1}$	k_c / $dm^6\ mol^{-2}\ s^{-1}$	k_d / $dm^3\ mol^{-1}\ s^{-1}$	k_e / s^{-1}
NH_3	*cis*	2.3×10^3	2.4×10^2	105	0.2	$<1.5 \times 10^{-4}$
	trans	—	—	166	—	$<6 \times 10^{-5}$
NH_2Me	*cis*	2.9×10^3	5.4×10^2	90.8	0.2	$<1.5 \times 10^{-4}$
	trans	—	—	235	—	$<7 \times 10^{-5}$
NH_2Et	*cis*	7.2×10^2	4.9×10^2	36.1	0.25	2.2×10^{-4}
	trans	—	—	93.2	—	$<7 \times 10^{-5}$
NH_2Pr^n	*cis*	1.2×10^3	6.7×10^2	41.3	0.1	$<1 \times 10^{-4}$
	trans	—	—	108	—	$<1 \times 10^{-4}$
NH_2Pr^i	*cis*	60 [b]	1×10^3 [c]	1.0 [b]	6×10^{-2}	$<6 \times 10^{-5}$
NH_2Bu^n	*cis*	1.2×10^3	6.3×10^2	37.6	8×10^{-2}	$<1 \times 10^{-4}$
NH_2Bu^i	*cis*	1.4×10^3	5.2×10^2	53.6	0.1	$<1.5 \times 10^{-4}$
NH_2Bu^s	*cis*	80 [b]	1×10^3 [c]	1.5 [b]	5×10^{-2}	$<8 \times 10^{-5}$
NH_2Bu^t	*trans*	4 [d]	20 [d]	1.93	1.5×10^{-2}	$<1 \times 10^{-5}$
$NH_2(CH_2Bu^t)$	*cis*	2.1×10^3	5.4×10^2	32.1	0.2	$<2 \times 10^{-4}$
$NH_2(CH_2Ph)$	*cis*	1.4×10^3	6.8×10^2	114	0.3	$<2 \times 10^{-5}$
	trans	—	—	220	6×10^{-2}	$<5 \times 10^{-5}$
$NH_2(cyclo\text{-}C_6H_{11})$	*cis*	58 [b]	8.3×10^2 [c]	2.25 [b]	6×10^{-2}	$<6 \times 10^{-5}$
	trans	40 [d]	3.8×10^2 [d]	20.3	4×10^{-2}	$<1 \times 10^{-5}$

[a] Errors: $k_a \pm 5\%$, $k_b \pm 10\%$, $k_c \pm 3\%$, $k_d \pm 20\%$. [b] ±20%. [c] ±30%. [d] Qualitative.

experimental one, provided that $k_3' = k_a + k_c$, $K_{eq.} = k_b$, and $k_3 = k_c$. The validity of this reaction scheme is supported by the fact that the values of k_b of equation (7) (Table) are consistent, as expected from equation (11), with the approximate values of $K_{eq.}$ obtained spectrophotometrically (see above). According to this mechanism, the k_3 and k_3' reaction steps are expected to imply a similar mode of activation. On this basis the higher values (*ca.* ×10) found for k_3' with respect to k_3 can be ascribed to the fact that negatively charged reactants ($[AuCl_4]^- + Cl^-$) can approach more easily the cationic complex $[PtCl(NHR_2)_2(MeCN)]^+$ than the uncharged complex *cis*-$[PtCl_2(NH_2R)_2]$.

$$k_{obs.} = \frac{k_3'[AuCl_4^-][Cl^-]}{1 + K_{eq.}[Cl^-]} + \frac{k_3K_{eq.}[AuCl_4^-][Cl^-]^2}{1 + K_{eq.}[Cl^-]} \qquad (11)$$

The above reaction scheme can also account for the kinetic behaviour displayed by the *trans* complexes. In these cases, it is likely that the absence of detectable solvolytic dissociations of *trans*-$[PtCl_2(NH_2R)_2]$ implies a negligible kinetic contribution of the first rate term of relationship (11). Accordingly, only the k_3 reaction path is expected to be operative in the cases of *trans*-platinum(II) complexes.*

The oxidation rates of both *cis*- and *trans*-platinum(II) complexes are markedly dependent on the amine bound to the central metal atom. Just as found for the oxidation of platinum(II) complexes containing pyridines or phenanthrolines, in the cases examined here the σ-donor abilities of the amines do not appear to be responsible for the observed reactivity trend. In fact, no regular relationships are found between reactivity and σ-donor ability, no matter how the latter is measured (*e.g.* in terms of pK_a,[8] gas-phase basicity, or polar parameters of the groups bonded to nitrogen [9,10]). Thus, *cis* complexes containing NH_2Et, NH_2Pr^n, or NH_2Bu^n react *ca.* 30 times faster than those containing NH_2Pr^i, NH_2Bu^s, or $NH_2(cyclo\text{-}C_6H_{11})$, whose σ-donor abilities are similar to those of the former [*e.g.* pK_a in the range [5] 10.56—10.67; $-\Sigma\sigma^*$ (Taft induction parameter) in the range 0.77—0.88]. The steric hindrance of ligands is also an important parameter which can affect the rates of either inner-sphere or outer-sphere redox reactions.[11-16] It has been previously proposed that the Taft steric constant, E_s, for hydrocarbon substituents, CH_2R, is a parameter suitable for quantifying the steric hindrance (E_N) of isosteric amines, NH_2R,[4,13,17-19] On this assumption it is found that, except for the complexes with benzylamine, linear relationships of type (12) roughly correlate the reactivities of both *cis* and *trans* complexes to the steric parameter of the amines.†

$$\log k = \alpha + \delta(-E_N) \qquad (12)$$

In my opinion the degree of linearity can be considered very satisfactory in view of the degree of uncertainty sometimes ascribed to the reliability of E_s values,[20,21] and also considering that the platinum(II) reaction centre is different both in size and in its geometric environment from the reaction centre implied in the determination of the values of E_s.

It is found (Figure 4) that an increase in the steric hindrance of amines lowers the k_3 rate term for the *cis* complexes ($\delta = -1.94$) more efficiently than for the *trans* analogues ($\delta = -1.17$). This behaviour suggests that during the activation process *trans*-bonded amines interact with the approaching $[AuCl_4]^- + Cl^-$ more weakly than *cis*-positioned amines. A bridged-activated complex having the Pt–Cl–Au bridge approximately perpendicular to the plane of the platinum(II) complex would justify such expectation since $[AuCl_4]^-$ (or $[AuCl_5]^{2-}$) [1] would find a better location in *trans* rather than in *cis* isomers. This expectation is also supported, for instance, by the known structure of *cis*- and *trans*-$[PtCl_2\{NH_2(cyclo\text{-}C_6H_{11})\}_2]$.[22,23]

It is worth noting that if the difference of reactivity between *cis* and *trans* complexes arises only from the relative influence of steric hindrance of amines, the *cis* and *trans* isomers should have the same reactivity when NH_2R has the same steric hindrance as the chloride ions, since in such a case the

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* The probable small contribution of the k_3' rate term to the overall rate for the oxidation of *trans* complexes bearing the bulky $NH_2(cyclo\text{-}C_6H_{11})$ and NH_2Bu^t might arise from some contribution of these ligands in helping the solvolytic dissociation, although unequivocal evidence corroborating this statement is lacking.

† A negative value ($-E_N$) is used in equation (12) since the values of E_N decrease with increasing steric hindrance of NH_2R.

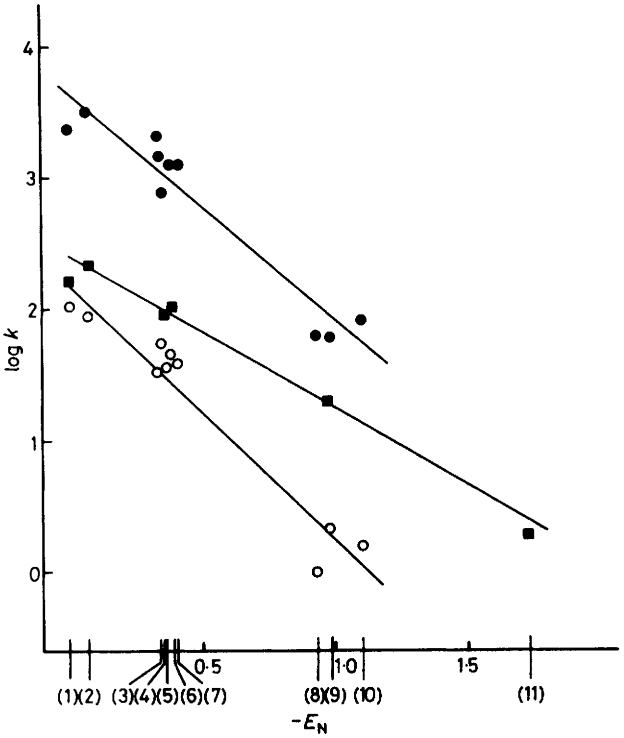

Figure 4. Dependence of rate constants on steric hindrance of NH_2R for the oxidation of *cis*-$[PtCl_2(NH_2R)_2]$ [k_3 (○) and k_3' (●)] or *trans*-$[PtCl_2(NH_2R)_2]$ [k_3 (■)] by $[NEt_4][AuCl_4]$ in acetonitrile at 50 °C and $I = 0.10$ mol dm^{-3}: R = H (1), Me (2), CH_2Bu^t (3), Bu^i (4), Et (5), Pr^n (6), Bu^n (7), Pr^i (8), cyclo-C_6H_{11} (9), Bu^s (10), or Bu^t (11)

two isomers are sterically equivalent. According to relationship (12) (see Figure 4) this situation is expected to be met for $E_N = E_s = +0.23$. This value agrees, probably not just by accident, with the E_s value (+0.18) ascribed to chloride ions.[24]

The effect of steric hindrance on the k_3' rate term ($\delta = -1.73$) for *cis* complexes is rather similar to that found for k_3. This result is well understood in terms of the reasonable assumption that the amines in $[PtCl(NH_2R)_2(MeCN)]^+$ are still *cis* positioned as in the parent *cis*-dichloro-complex.

Both *cis* and *trans* complexes with benzylamine react 2—3 times faster than what would be expected from relationship (12). The inductive effect of the benzyl group is inadequate to account for the higher reactivity observed. Reliable explanations for such behaviour cannot be formulated at the present. It might be that the phenyl groups of benzylamine play a peculiar role in stabilizing the transition state. However, it can be pointed out that $[PtL_4]^{2+}$ has a higher thermodynamic tendency to undergo oxidation to $[PtCl_2L_4]^{2+}$ when L is benzylamine rather than another primary aliphatic amine [E°(HCl 1 mol dm^{-3}) = 0.571, $NH_2(CH_2Ph)$; 0.600, NH_3; 0.622, NH_2Me; 0.691 V, NH_2Et)].[25] Thus, the observed abnormally high reactivities for the complexes with benzylamine are also probably connected to more favourable thermodynamics for the oxidative process.

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