An Investigation on the Influence of Co-ordinated Aliphatic Amines on the Rates of Reduction of Tetrachlorodiamineplatinum(IV) Complexes

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The reduction reactions of *trans*- and/or *cis*-$[\mathrm{PtCl_4(NRH_2)_2}]$ by $[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]$, NaI, and $[\mathrm{Pt(NEtH_2)_4}][\mathrm{ClO_4}]_2$ in the presence of chloride ions have been kinetically investigated in methanol [R = H, Me, Et, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^n}$, $\mathrm{Bu^i}$, $\mathrm{Bu^s}$, $\mathrm{Bu^t}$, $\mathrm{CH_2Bu^t}$, $\mathrm{CH_2Ph}$, or cyclo-$\mathrm{C_6H_{11}}$]. The rate constants for the *cis* complexes are sensitive to both σ-donor ability and steric hindrance of R, according to relationships of the Taft's type: $\log k_{\mathrm{red}} = a + \rho_{\mathrm{I}}[-\sigma_{\mathrm{I}}(\mathrm{R})] + \rho_{\mathrm{S}}[-E_{\mathrm{S}}(\mathrm{R})]$. The rates are increased by lowering the σ-donor ability of R and by increasing its bulkiness; the *trans* complexes behave similarly.

The mechanism for most reduction reactions of platinum(IV) complexes is now well established.[1-3] However, little information is available on the effect of ' non-leaving ' ligands upon the reactivity of platinum(IV) towards reduction. In this connection it has been found that both σ-donor and π-acceptor abilities of such ligands,[2,4] as well as their steric hindrance,[5,6] may affect the rates of reduction, though only a few systematic kinetic investigations on this subject have been carried out.[1,4]

This paper reports a kinetic study on the reduction of platinum(IV) complexes of the type *trans*- and/or *cis*-$[\mathrm{PtCl_4(NRH_2)_2}]$ (R = H, Me, Et, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^n}$, $\mathrm{Bu^i}$, $\mathrm{Bu^s}$, $\mathrm{Bu^t}$, $\mathrm{CH_2Bu^t}$, $\mathrm{CH_2Ph}$, or cyclo-$\mathrm{C_6H_{11}}$) by ferrocene, sodium iodide, or tetrakis(ethylamine)platinum(II) perchlorate in methanol.

Experimental

Materials.—*cis*- or *trans*-$[\mathrm{PtCl_4(NRH_2)_2}]$ and $[\mathrm{Pt(NEtH_2)_4}][\mathrm{ClO_4}]_2$ were prepared as described elsewhere.[6,7] Reagent grade sodium iodide and tetraethylammonium-chloride and -perchlorate were dried before use. Ferrocene was purified by sublimation. Methanol was dried by refluxing over magnesium methoxide.

Kinetics.—Stock solutions of reactants were prepared by weight and kept in the dark.* The reactions were initiated by mixing appropriate volumes of thermostatted and freshly prepared stock solutions of the reactants in 1-cm silica cells maintained in the thermostatically controlled cell compartment. The progress of the reaction was followed spectrophotometrically by scanning the absorption spectrum of the reacting mixture at suitable time intervals in the wavelength range 280—380 nm {reactions with NaI or with $[\mathrm{Pt(NEtH_2)_4}][\mathrm{ClO_4}]_2$} or 280—320 nm {reactions with $[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]$}. The reactions with ferrocene were occasionally followed also in the range 500—700 nm, using high platinum(IV) concentrations (*ca.* 1×10^{-3} mol dm^{-3}), in order to detect the formation of $[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]^+$ during the reaction. Fast reactions were followed by recording the absorbance against time at constant wavelength.

The concentration of platinum(IV) complexes in the reaction mixture ($<6 \times 10^{-5}$ mol dm^{-3}) was small enough to ensure pseudo-first-order conditions. The reactions with ferrocene and with sodium iodide were carried out without ionic strength control. The reactions with $[\mathrm{Pt(NEtH_2)_4}][\mathrm{ClO_4}]_2$ were carried out in the presence of $[\mathrm{NEt_4}]\mathrm{Cl}$ and at $I = 5.00 \times 10^{-2}$ mol dm^{-3}, using $[\mathrm{NEt_4}][\mathrm{ClO_4}]$ as ionic strength buffer. The concentrations of the reactants were changed in the ranges listed in Table 1.

The observed rate constants, $k_{\mathrm{obs.}}$, were determined from the slope of plots of $\log|A_t - A_\infty|$ against time, where A_t and A_∞ are the absorbance of the reacting mixture at time t and at the end of the reaction, respectively.

At least five kinetic runs were carried out for the reactions of each complex with $[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]$ or NaI, using different concentrations of the reducing agent. For the reactions with $[\mathrm{Pt(NEtH_2)_4}][\mathrm{ClO_4}]_2$ at least eight kinetic runs were carried out for the reactions of each complex, using different concentrations of both platinum(II) and chloride ions. The temperatures explored are listed in Tables 2—4.

Results

The reactions of the platinum(IV) complexes with $[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]$ involve the formation of two moles of $[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]^+$ per mole of platinum(IV) consumed. No detectable intermediates appear to be formed and the stoicheiometry of the overall reaction [equation (1)] is the same as that previously found for the reduction of other platinum(IV) complexes by the same reducing agent.[8] The reactions obey a second-order rate law [equation (2)].

$$[\mathrm{PtCl_4(NRH_2)_2}] + 2[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}] \longrightarrow [\mathrm{PtCl_2(NRH_2)_2}] + 2[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]^+ + 2\mathrm{Cl}^- \quad (1)$$

$$-\mathrm{d}[\mathrm{Pt^{IV}}]/\mathrm{d}t = k_{\mathrm{obs.}}[\mathrm{Pt^{IV}}] = k_{\mathrm{ferrocene}}[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}][\mathrm{Pt^{IV}}] \quad (2)$$

When sodium iodide is the reducing agent, the reactions involve the formation of one mole of $\mathrm{I_3}^-$ per mole of platinum(IV) consumed, in agreement with the occurrence of reaction (3), which may be followed by chloride displacement in the platinum(II) complex formed.[2,4] A second-order rate law

$$[\mathrm{PtCl_4(NRH_2)_2}] + 2\mathrm{I}^- \xrightarrow{\mathrm{I}^-} [\mathrm{PtCl_2(NRH_2)_2}] + \mathrm{I_3}^- + 2\mathrm{Cl}^- \quad (3)$$

$$-\mathrm{d}[\mathrm{Pt^{IV}}]/\mathrm{d}t = k_{\mathrm{obs.}}[\mathrm{Pt^{IV}}] = k_{\mathrm{I}^-}[\mathrm{I}^-][\mathrm{Pt^{IV}}] \quad (4)$$

[equation (4)] is also operating for these reactions. The rates are not affected by the presence of sodium chloride in the reaction mixture at least up to 8×10^{-2} mol dm^{-3} and with $[\mathrm{Cl}^-]/[\mathrm{I}^-]$ ratios up to 10, only the u.v. spectra being modified for the formation of other species, such as $\mathrm{I_2Cl}^-$, in conjunction with $\mathrm{I_3}^-$.

The reactions of platinum(IV) complexes with $[\mathrm{Pt(NEtH_2)_4}][\mathrm{ClO_4}]_2$ in the presence of $[\mathrm{NEt_4}]\mathrm{Cl}$ imply quantitative reduction of the starting platinum(IV) complexes and formation of

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* Filtered saturated solutions were used for the ammine complexes.

Table 1. Concentration ranges ($\times 10^{-3}$) of reducing agents explored in the reduction of *cis*- or *trans*-$[PtCl_4(NRH_2)_2]$ in methanol

			Concentration ranges (mol dm^{-3}) explored			
Complex	R	Config.	$[Fe(\eta^5-C_5H_5)_2]$	NaI	$[Pt(NEtH_2)_4][ClO_4]_2$	$[NEt_4]Cl$
(1)	H	*cis*	6.23—30.6	17.7—171	1.71—5.88	7.35—36.8
		trans	6.23—30.6	14.7—176	0.471—2.12	7.35—36.8
(2)	Me	*cis*	4.42—17.6	17.7—171	1.47—5.59	7.35—36.8
		trans	4.42—17.6		0.471—2.12	7.35—36.8
(3)	Et	*cis*	6.23—30.6	17.7—171	1.13—4.94	5.88—35.3
		trans	3.16—15.6		0.471—2.12	7.35—36.8
(4)	Pr^n	*cis*	7.38—30.6	8.82—171	1.13—4.94	5.88—35.3
		trans	7.38—30.6	14.7—176	0.471—2.12	7.35—36.8
(5)	Pr^i	*cis*	4.42—17.6	8.82—171	1.13—4.94	5.88—35.3
(6)	Bu^n	*cis*	4.42—17.6	8.82—171	1.47—4.71	7.35—36.8
(7)	Bu^i	*cis*	4.42—17.6	17.7—171	1.47—4.71	7.35—36.8
(8)	Bu^s	*cis*	7.38--30.6	14.7—176	1.47—4.71	7.35—36.8
(9)	Bu^t	*trans*	3.16—15.6	1.18—17.1	1.13—4.94	7.35—36.8
(10)	CH_2Bu^t	*cis*	3.16—15.6	8.82—171	1.13—4.94	7.35—36.8
(11)	CH_2Ph	*cis*	3.16—15.6	17.7—171	1.47—4.71	7.35—36.8
		trans	3.16—15.6	14.7—176	0.471—2.12	7.35—36.8
(12)	cyclo-C_6H_{11}	*trans*	3.16—15.6	14.7—176	0.471—2.12	7.35—36.8

trans-$[PtCl_2(NEtH_2)_4]^{2+}$ according to equation (5). These reactions follow the well known third-order rate law (6), usually operating in redox reactions involving platinum(IV)–platinum(II) systems.

$$[PtCl_4(NRH_2)_2] + [Pt(NEtH_2)_4]^{2+} \xrightarrow{Cl^-} [PtCl_2(NRH_2)_2] + trans\text{-}[PtCl_2(NEtH_2)_4]^{2+} \quad (5)$$

$$-d[Pt^{IV}]/dt = k_{obs.}[Pt^{IV}] = k_{Pt^{II}}[Pt(NEtH_2)_4{}^{2+}][Cl^-][Pt^{IV}] \quad (6)$$

The values of the specific rate constants, $k_{ferrocene}$, k_{I^-}, and $k_{Pt^{II}}$, are collected in Tables 2—4, together with related activation parameters.

Discussion

The rate laws operating for the reactions with the reducing agents employed in the present investigation are of the type previously found for the reductions of other platinum(IV) complexes by the same reductants and are accounted for by the occurrence of reaction schemes (7)—(9).[1,2] An outer-sphere redox mechanism has been proposed to operate in the rate-determining step for the reductions by ferrocene,[8] whereas the rate-determining steps for the reductions by I^- or $[PtCl(NEtH_2)_4]^+$ imply an inner-sphere redox mechanism,[1,2] even though the $PtCl \cdots I^-$ bond formation in the activated complex may be scarce.[2,5]

$$[PtCl_4(NRH_2)_2] + [Fe(\eta^5-C_5H_5)_2] \xrightarrow{slow} [PtCl_3(NRH_2)_2] + [Fe(\eta^5-C_5H_5)_2]^+ + Cl^- \quad (7a)$$

$$[PtCl_3(NRH_2)_2] + [Fe(\eta^5-C_5H_5)_2] \xrightarrow{fast} [PtCl_2(NRH_2)_2] + [Fe(\eta^5-C_5H_5)_2]^+ + Cl^- \quad (7b)$$

$$[PtCl_4(NRH_2)_2] + I^- \xrightarrow{slow} [PtCl_2(NRH_2)_2] + ICl + Cl^- \quad (8a)$$

$$ICl + 2I^- \xrightarrow{fast} I_3^- + Cl^- \quad (8b)$$

$$[Pt(NEtH_2)_4]^{2+} + Cl^- \xrightleftharpoons{fast} [PtCl(NEtH_2)_4]^+ \quad (9a)$$

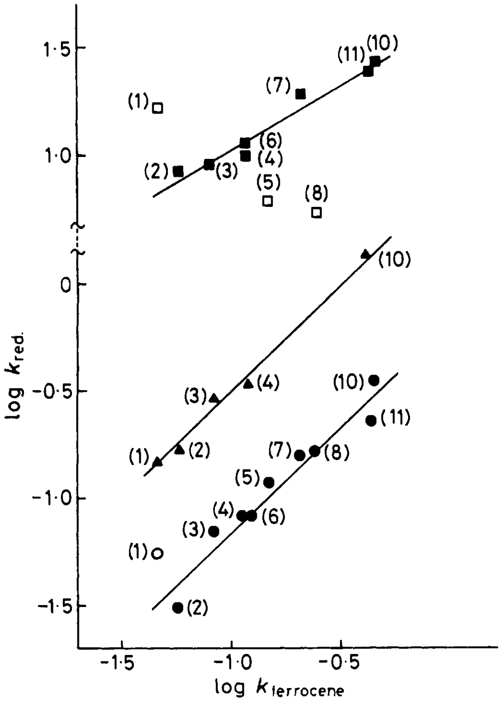

Figure 1. Plots comparing the specific rate constants for the reduction of *cis* tetrachlorodiamineplatinum(IV) complexes by ferrocene at 50.0 °C and NaI at 50.0 °C (●,○) or $[Pt(NEtH_2)_4][ClO_4]_2$ + $[NEt_4]Cl$ at 45.0 °C (■,□); values represented by ▲ are referred to the specific rate constants for the reduction of *trans* complexes by ferrocene at 50.0 °C. Open symbols refer to data not considered in deriving equation (10). For compound numbering see Table 1

$$[PtCl_4(NRH_2)_2] + [PtCl(NEtH_2)_4]^+ \xrightarrow{slow} [PtCl_2(NRH_2)_2] + trans\text{-}[PtCl_2(NEtH_2)_4]^{2+} + Cl^- \quad (9b)$$

The results collected in Tables 2—4 show that variation of NRH_2 has a definite, albeit not pronounced, effect on the rates of reduction of both *cis*- and *trans*-$[PtCl_4(NRH_2)_2]$ complexes. For the outer-sphere reductions by $[Fe(\eta^5-C_5H_5)_2]$, in particular, the reactivity towards reduction increases in the

Table 2. Rate constants[a] and activation parameters[b] for the reduction reactions of *cis*- or *trans*-$[\mathrm{PtCl_4(NRH_2)_2}]$ by $[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]$ in methanol

R	Config.	θ_c/°C	$k_{\mathrm{ferrocene}}$/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
H	*cis*	30.0	5.60×10^{-3}		
		40.0	1.63×10^{-2}		
		50.0	4.60×10^{-2}	83.1	−14
	trans	30.0	1.62×10^{-2}		
		40.0	5.22×10^{-2}		
		50.0	1.47×10^{-1}	87.3	8
Me	*cis*	30.0	6.85×10^{-3}		
		40.0	2.14×10^{-2}		
		50.0	5.85×10^{-2}	84.8	−7
	trans	30.0	1.91×10^{-2}		
		40.0	5.70×10^{-2}		
		50.0	1.65×10^{-1}	85.3	3
Et	*cis*	30.0	1.00×10^{-2}		
		40.0	3.02×10^{-2}		
		50.0	8.38×10^{-2}	84.1	−6
	trans	30.0	3.14×10^{-2}		
		40.0	9.96×10^{-2}		
		50.0	2.85×10^{-1}	87.3	14
$\mathrm{Pr^n}$	*cis*	30.0	1.40×10^{-2}		
		40.0	4.35×10^{-2}		
		50.0	1.18×10^{-1}	84.2	−3
	trans	30.0	4.59×10^{-2}		
		40.0	1.25×10^{-1}		
		50.0	3.35×10^{-1}	78.4	−12
$\mathrm{Pr^i}$	*cis*	30.0	2.09×10^{-2}		
		40.0	5.96×10^{-2}		
		50.0	1.49×10^{-1}	77.4	−22
$\mathrm{Bu^n}$	*cis*	30.0	1.46×10^{-2}		
		40.0	4.41×10^{-2}		
		50.0	1.20×10^{-1}	83.2	−6
$\mathrm{Bu^i}$	*cis*	30.0	2.73×10^{-2}		
		40.0	8.01×10^{-2}		
		50.0	2.08×10^{-1}	80.2	−11
$\mathrm{Bu^s}$	*cis*	30.0	3.35×10^{-2}		
		40.0	9.22×10^{-2}		
		50.0	2.41×10^{-1}	77,9	−16
$\mathrm{Bu^t}$	*trans*	30.0	1.74×10^{-1}		
		40.0	4.75×10^{-1}		
		50.0	1.20	77.7	−4
$\mathrm{CH_2Bu^t}$	*cis*	30.0	6.14×10^{-2}		
		40.0	1.79×10^{-1}		
		50.0	4.50×10^{-1}	78.6	−9
$\mathrm{CH_2Ph}$	*cis*	30.0	5.53×10^{-2}		
		40.0	1.62×10^{-1}		
		50.0	4.38×10^{-1}	81.7	0
	trans	30.0	1.84×10^{-1}		
		40.0	5.17×10^{-1}		
		50.0	1.36	78.9	1
cyclo-$\mathrm{C_6H_{11}}$	*trans*	30.0	6.98×10^{-2}		
		40.0	1.96×10^{-1}		
		50.0	5.17×10^{-1}	79.0	−7

[a] Average errors ±3%. [b] $\Delta H^\ddagger$ values ±4 kJ mol^{-1}, $\Delta S^\ddagger$ values ±12 J K^{-1} mol^{-1} (from average errors in rate constants).

order of R = H < Me < Et < $\mathrm{Pr^n}$, $\mathrm{Bu^n}$ < $\mathrm{Pr^i}$ < $\mathrm{Bu^s}$ < $\mathrm{CH_2Ph}$, $\mathrm{CH_2Bu^t}$ for *cis* complexes and H < Me < Et < $\mathrm{Pr^n}$ < cyclo-$\mathrm{C_6H_{11}}$ < $\mathrm{Bu^t}$, $\mathrm{CH_2Ph}$ for *trans* complexes.

As far as the *cis* complexes are concerned, for which more data are available, the above sequence of reactivity also holds for most of the data related to the reactions with iodide as well as with tetrakis(ethylamine)platinum(II). Exceptions to the above trend are due to the comparatively high reactivity of *cis*-$[\mathrm{PtCl_4(NH_3)_2}]$ and by the low reactivity of *cis*-$[\mathrm{PtCl_4(NPr^iH_2)_4}]$ and *cis*-$[\mathrm{PtCl_4(NBu^sH_2)_2}]$ complexes towards $[\mathrm{Pt(NEtH_2)_4}]^{2+}$ + $\mathrm{Cl^-}$. With the exceptions of such cases, it can be stated that the reactivity of all *cis* complexes towards both $\mathrm{I^-}$ and $[\mathrm{Pt(NEtH_2)_4}]^{2+}$ + $\mathrm{Cl^-}$ are linearly related to their reactivity towards $[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]$ by the log–log relationship (10) (Figure 1) [$\alpha = 0.987$ (for $k_{\mathrm{I^-}}^{50\,°\mathrm{C}}$) and 0.612 (for $k_{\mathrm{Pt^{II}}}^{45\,°\mathrm{C}}$); $\beta = -0.179$ (for $k_{\mathrm{I^-}}^{50\,°\mathrm{C}}$) and 1.62 (for $k_{\mathrm{Pt^{II}}}^{45\,°\mathrm{C}}$)]. The occurrence of such relationships suggests that the same factors are responsible for changes in reactivity by changes of $\mathrm{NRH_2}$ ligands, whatever the reducing agent used. Reaction free-energy changes are recognised to play an important part in causing changes of free energy of activation in both inner- and outer-sphere redox processes.[9] In this connection, thermodynamic information (*e.g.* standard potentials) is not available for the platinum(IV) complexes considered in the present paper, in order to verify the occurrence of any relationship between

$$\log k_{\mathrm{red.}} = \alpha \log k_{\mathrm{ferrocene}}^{50\,°\mathrm{C}} + \beta \qquad (10)$$

Table 3. Rate constants [a] and activation parameters [b] for the reduction reactions of *cis*- or *trans*-$[PtCl_4(NRH_2)_2]$ by NaI in methanol

R	Config.	θ_c/°C	k_{I^-}/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
H	*cis*	35.0	1.27×10^{-2}		
		50.0	5.48×10^{-2}	78.1	−28
	trans	35.0	8.93×10^{-3}		
		50.0	3.83×10^{-2}	77.8	−32
Me	*cis*	35.0	7.00×10^{-3}		
		50.0	3.09×10^{-2}	79.4	−29
	trans [c]	35.0	6.8×10^{-3}		
		50.0	3.1×10^{-2}	81.1	−24
Et	*cis*	35.0	1.67×10^{-2}		
		50.0	6.95×10^{-2}	76.1	−32
	trans [c]	35.0	2.15×10^{-2}		
		50.0	8.6×10^{-2}	73.9	−37
Pr^n	*cis*	35.0	1.96×10^{-2}		
		50.0	8.19×10^{-2}	76.3	−30
	trans	35.0	2.24×10^{-2}		
		50.0	9.04×10^{-2}	74.4	−35
Pr^i	*cis*	35.0	3.03×10^{-2}		
		50.0	1.16×10^{-1}	71.5	−42
Bu^n	*cis*	35.0	1.98×10^{-2}		
		50.0	8.06×10^{-2}	74.9	−35
Bu^i	*cis*	35.0	3.93×10^{-2}		
		50.0	1.54×10^{-1}	72.8	−36
Bu^s	*cis*	35.0	3.90×10^{-2}		
		50.0	1.60×10^{-1}	75.3	−28
Bu^t	*trans*	35.0	1.50		
		50.0	4.89	62.6	−39
CH_2Bu^t	*cis*	35.0	9.05×10^{-2}		
		50.0	3.50×10^{-1}	72.1	−31
CH_2Ph	*cis*	35.0	5.40×10^{-2}		
		50.0	2.18×10^{-1}	74.4	−28
	trans	35.0	7.49×10^{-2}		
		50.0	2.92×10^{-1}	72.5	−32
cyclo-C_6H_{11}	*trans*	35.0	5.88×10^{-2}		
		50.0	2.22×10^{-1}	70.7	−39

[a] Average errors ±3%. [b] $\Delta H^\ddagger$ values ±4 kJ mol^{-1}, $\Delta S^\ddagger$ values ±12 J K^{-1} mol^{-1} (from average errors in rate constants). [c] Data taken from A. Peloso, G. Dolcetti, and R. Ettorre, *Inorg. Chim. Acta*, 1967, **1**, 403.

$\Delta G^\ddagger$ and $\Delta G^\ominus$. However, it is known that the reductions of *cis*-$[PtBr_4(NRH_2)_2]$ by Fe^{2+} are thermodynamically favoured in the order R = H < Me < Et < Pr^n.[10] Moreover, the standard potentials of *cis*-$[PtCl_2(NH_3)_2(NRH_2)_2]^{2+}$ in 1 mol dm^{-3} KCl are found to increase in the order R = H (0.612 V) < Me (0.625 V) < Et (0.634 V) < Pr^n (0.643 V) < Pr^i (0.701 V).[11] All these data strongly suggest that aliphatic amines should affect the thermodynamics of reduction reactions of the platinum(IV) complexes considered in this paper in the right direction required to give the observed kinetic reactivity trend.

In attempting to find out which properties of the NRH_2 ligands may be responsible for the observed reactivity trend, it should be recalled that both σ-donor ability and steric hindrance of co-ordinated ligands have been often found to affect the reaction rates in both inner- and outer-sphere redox processes.[4,12–19] In this connection, the negative values of the Taft's inductive parameters of the R substituents, $-\sigma_I(R)$ [ranging between −0.036 (CH_2Ph) and 0.074 (Bu^t)],[20,21] can be used as a measure of the σ-donor ability of R, and also of NRH_2, whereas negative values of either the Taft's steric constants of the R substituents, $-E_S(R)$ [ranging between −1.24 (H) and 1.74 (CH_2Bu^t)],[22] or the steric constants $-E_N(NRH_2)$, equivalent to $-E_S(CRH_2)$,[23] can be tested as a measure of the steric hindrance associated with NRH_2.* It is found that the reactivity towards reduction of *cis* platinum(IV) complexes under consideration is satisfactorily related to σ-donor ability and steric hindrance of R by the Taft's type equation (11) (Table 5, Figure 2), the main deviation being found for the reduction of *cis*-$[PtCl_4(NH_3)_2]$ by I and by $[Pt(NEtH_2)_4]^{2+}$ + Cl^-. In general it appears that negative values for ρ_I and positive values for ρ_S are

$$\log k_{red.} = a + \rho_I[-\sigma_I(R)] + \rho_S[-E_S(R)] \quad (11)$$

observed, whatever the reducing agent is used, thus indicating that the reactivity of platinum(IV) complexes is decreased by increasing the σ-donor ability of R and by decreasing its steric hindrance. A decrease of reactivity with increasing σ-donor ability of R (*i.e.* of NRH_2) is attributable to the related enhancement of the electron density on platinum(IV) which consequently becomes less prone to accept electrons in a reductive act.[4,13] As far as steric hindrance of R is concerned, if its effect derived from direct interactions with the reducing agent, it would be expected, at least for inner-sphere reductions, that an inhibiting effect on the rate would result as the consequence of a higher energy requirement to attain a more sterically hindered bridged activated complex. Thus, in most cases of both inner- and outer-sphere reduction reactions of cobalt(III) complexes, the steric hindrance of the ligands causes

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* Negative values of $\sigma_I(R)$, $E_S(R)$, and $E_N(NRH_2)$ are preferred in order to have more positive values for better σ-donor or more sterically hindered ligands. No satisfactory relationships could be envisaged in terms of $-E_N(NRH_2)$ values, though these were previously found to be good parameters to correlate the rates of oxidation of *cis*- or *trans*-$[PtCl_2(NRH_2)_2]$ complexes by $AuCl_4^-$ with steric hindrance of the amines.

Table 4. Rate constants [a] and activation parameters [b] for the reduction reactions of *cis*- or *trans*-$[\mathrm{PtCl_4(NRH_2)_2}]$ by $[\mathrm{Pt(NEtH_2)_4}][\mathrm{ClO_4}]_2$ in the presence of $[\mathrm{NEt_4}]\mathrm{Cl}$ in methanol at $I = 5.00 \times 10^{-2}$ mol dm^{-3}

R	Config.	θ_c/°C	$k_{\mathrm{Pt^{II}}}$/ dm^6 mol^{-2} s^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}
H	*cis*	25.0	4.00		
		45.0	16.3	52.9	−56
	trans	25.0	2.74		
		45.0	10.5	50.4	−68
Me	*cis*	25.0	2.23		
		45.0	8.12	48.4	−76
	trans	25.0	1.37		
		45.0	4.34	42.9	−98
Et	*cis*	25.0	2.72		
		45.0	8.43	42.1	−96
	trans	25.0	1.91		
		45.0	6.10	43.2	−95
Pr^n	*cis*	25.0	3.10		
		45.0	10.0	43.6	−89
	trans	25.0	2.29		
		45.0	6.86	40.7	−102
Pr^i	*cis*	25.0	1.86		
		45.0	6.00	43.6	−94
Bu^n	*cis*	25.0	3.70		
		45.0	10.8	39.7	−101
Bu^i	*cis*	25.0	6.15		
		45.0	18.6	41.1	−92
Bu^s	*cis*	25.0	1.89		
		45.0	5.36	38.6	−110
Bu^t	*trans*	25.0	7.40		
		45.0	15.9	27.6	−136
$\mathrm{CH_2Bu^t}$	*cis*	25.0	8.10		
		45.0	25.7	43.0	−83
$\mathrm{CH_2Ph}$	*cis*	25.0	6.99		
		45.0	24.1	46.3	−74
	trans	25.0	6.28		
		45.0	19.9	42.9	−86
cyclo-$\mathrm{C_6H_{11}}$	*trans*	25.0	2.03		
		45.0	6.08	40.7	−103

[a] Average errors ±3%. [b] $\Delta H^‡$ values ±4 kJ mol^{-1}, $\Delta S^‡$ values ±12 J K^{-1} mol^{-1} (from average errors in rate constants).

Table 5. Influence of steric hindrance and σ-donor ability of amines on the reactivity towards reduction of *cis*- or *trans*-tetrachlorodiamine-platinum(IV) complexes, according to equation (11)

Reducing agent	Config. of Pt$^{\mathrm{IV}}$ complex	θ_c/°C	N*	a	ρ_I	ρ_S	Correlation coeff. r
$[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}]$	*cis*	50.0	10	−0.768	−5.94	0.491	0.975
		40.0	10	−1.20	−5.90	0.508	0.974
		30.0	10	−1.67	−6.00	0.517	0.968
	trans	50.0	7	−0.279	−6.26	0.510	0.966
		40.0	7	−0.712	−6.45	0.535	0.963
		30.0	7	−1.18	−6.61	0.568	0.967
NaI	*cis*	50.0	9	−1.05	−4.25	0.534	0.928
		35.0	9	−1.67	−4.29	0.556	0.919
	trans	50.0	5	−1.10	−4.53	1.01	0.921
		35.0	5	−1.73	−4.65	1.09	0.912
$[\mathrm{Pt(NEtH_2)_4}]^{2+}$	*cis*	45.0	7	1.12	−3.66	0.339	0.983
		25.0	7	0.583	−3.22	0.349	0.960
	trans	45.0	5	0.961	−4.88	0.398	0.974
		25.0	5	0.433	−4.52	0.506	0.984

* N is the number of complexes whose data were used in deriving equation (11).

a lowering in the rate.[12,14,16,17] On the contrary, for the reductions examined herein the steric hindrance of R favours the reactivity of platinum(IV) complexes towards reduction, irrespective of the mechanism operating. It is likely that the observed effect of steric hindrance has a thermodynamic origin, the reaction free energy, which is correlated to the free energy of activation,[9] being lowered by more bulky R groups. Indeed, the steric hindrance of R appears to favour thermodynamic reactions of this kind. For instance, the ΔG° values of the reduction reactions of $[\mathrm{PtBr_4(NRH_2)_2}]$ by $\mathrm{Fe^{3+}}$ decrease in the order R = H > Me > Et > Pr^n.[6] Moreover, the higher standard potentials in 1 mol dm^{-3} KCl found for *cis*- or *trans*-$[\mathrm{PtCl_2(NH_3)_2(NPr^iH_2)_2}]^{2+}$ (0.701 and 0.698 V) with respect to *cis*- or *trans*-$[\mathrm{PtCl_2(NH_3)_2(NPr^nH_2)_2}]^{2+}$ (0.643 and

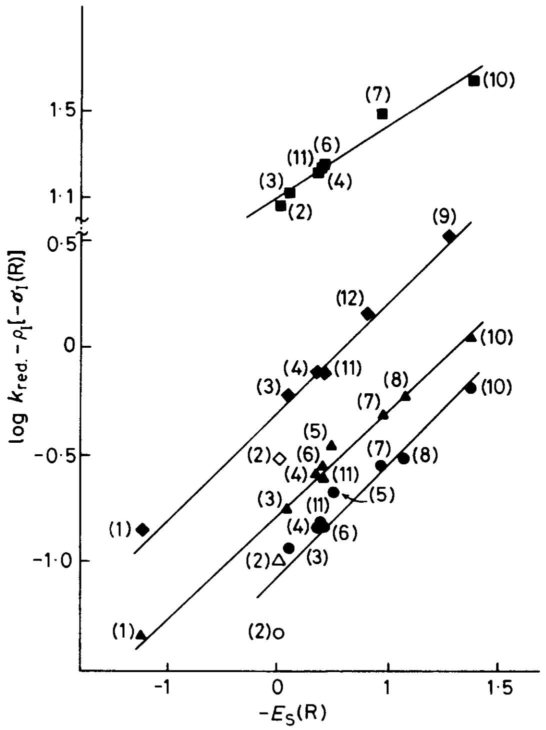

Figure 2. Correlations between the reactivity towards reduction of *cis*-$[PtCl_4(NRH_2)_2]$ and inductive and steric characteristics of R; $k_{red.}$ are the specific rate constants for the reductions of *cis* complexes by ferrocene at 50.0 °C (▲,△), NaI at 50.0 °C (●,○), or by $[Pt(NEtH_2)_4]^{2+}$ + Cl^- at 45.0 °C (■), and for the reductions of *trans* complexes by ferrocene at 50.0 °C (◆,◇). Open symbols represent data which poorly fit equation (11). For compound numbering see Table 1

0.642 V) are attributed to the higher steric hindrance of Pr^i with respect to Pr^n.[11]

The steric hindrance of R plays a smaller role in the reactivity of *cis*-$[PtCl_4(NRH_2)_2]$ towards $[Pt(NEtH_2)_4]^{2+}$ in the presence of chloride ion than that experienced in the case of other reducing agents (*i.e.* lower values of ρ_S; Table 5). Moreover, *cis*-$[PtCl_4(NH_3)_2]$ displays a reactivity towards such reductants which is higher than that required to fit relationship (10) (Table 4, Figure 1) or (11); on the other hand a lower reactivity is exhibited by *cis*-$[PtCl_4(NPr^iH_2)_2]$ and *cis*-$[PtCl_4(NBu^sH_2)_2]$ (Table 4, Figure 1). These anomalous behaviours may be ascribed to different specific interactions between the ethyl group on $[Pt(NEtH_2)_4]^{2+}$ and the immediate surroundings of nitrogen in NRH_2 on platinum(IV).

Only a rough qualitative analysis is possible for the reactions of *trans* complexes, owing to the small number of complexes examined. Nevertheless, a reactivity order towards ferrocene similar to that found for the *cis* analogues can be inferred. For instance, the reactivities of *trans* complexes are related to those of *cis* homologues by equation (10) (α = 1.00, β = 0.488), suggesting that, at least for outer-sphere redox reactions, reactivity changes are not affected by the co-ordination positions of NRH_2. In such a case, relationship (11) also fits the data for NBu^tH_2 and $N(cyclo\text{-}C_6H_{11})H_2$, and the related values of ρ_I and ρ_S (Table 5) are close to those found for the *cis* complexes. Most *trans* complexes display reactivity trends towards iodide or platinum(II) which are also satisfactorily correlated by equation (10) to their reactivity towards ferrocene [α = 1.0 (for $k_{I^-}^{50 °C}$) and 0.70 (for $k_{Pt^{II}}^{45 °C}$)], exceptions being found for the reactions of *trans*-$[PtCl_4(NH_3)_2]$ and *trans*-$[PtCl_4\{N(C_6H_{11})H_2\}_2]$ with $[Pt(NEtH_2)_4][ClO_4]_2$, and for the reactions of *trans*-$[PtCl_4(NBu^tH_2)_2]$ with sodium iodide. The specific rate constant for the last reaction is comparatively too high to fit equation (10). On the other hand, in the case of the reactions with $[Pt(NEtH_2)_4][ClO_4]_2$ equation (10) also holds for *trans*-$[PtCl_4(NBu^tH_2)_2]$ in spite of the fact that the tertiary carbon bonded to nitrogen would be expected to reduce the rate for the above mentioned reasons. It is worth commenting that *trans*-$[PtCl_4\{N(C_6H_{11})H_2\}_2]$, which bears a secondary carbon atom bonded to nitrogen, displays a reactivity towards the platinum(II) complex somewhat lower than that required to fit a common equation (10) with the other *trans* complexes. No straightforward explanations are found for the kinetic behaviour of *trans*-$[PtCl_4(NBu^tH_2)_2]$. The occurrence of some indefinite contribution (*e.g.* different solvation requirements) enhancing the reactivity of this complex towards inner-sphere redox reactions could account for both the high reactivity towards NaI and for a contribution balancing the lowering effect caused by steric interactions in the reactions with $[Pt(NEtH_2)_4][ClO_4]_2$.

Equation (11) gives values of ρ_I and ρ_S for the reactions of the *trans* complexes with NaI and with $[Pt(NEtH_2)_4][ClO_4]_2$ which are in the same direction as that found for the *cis* complexes (Table 5). However, such values are not suitable for a confident quantitative comparison with those of the *cis* complexes because of the rather poor correlation coefficients found for the restricted number of complexes considered.

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Received 11th April 1983; *Paper* 3/573