The *cis*- and *trans*-Effects of Cyanide in Substitution at Platinum(II)†

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The *cis*- and *trans*-$[Pt(am)_2Cl_2]$ isomers (am = dimethylamine, pyridine, 4-cyanopyridine, 4-chloropyridine, 2-methylpyridine, 4-methylpyridine, 2,4-dimethylpyridine, 4-ethylpyridine, morpholine or piperidine), react rapidly with excess CN^- in methanol to form the corresponding *cis*- and *trans*-$[Pt(am)_2(CN)_2]$ species which then react further to give $[Pt(CN)_4]^{2-}$. The kinetics of the slow step, $[Pt(am)_2(CN)_2] + CN^- \longrightarrow [Pt(am)(CN)_3]^- + am$, has been studied. In spite of the strong *trans* effect of CN^- the *trans* species are all more reactive than the corresponding *cis* isomers. The second-order rate constants are sensitive to the nature of am; plots of $\log k_2$ against the pK_a of Ham^+ are linear but the slope for the *trans* isomers (−0.27) is much greater than that for the *cis* isomers (−0.07). The rate constants for the displacement of *o*-methyl substituted pyridines are smaller than predicted from their basicity. This steric hindrance effect is much more marked in the *trans* isomers. The complexes with am = NH_3 and NH_2Me are similarly less reactive than might be predicted but the effect is the same in both isomers. The results are explained in terms of the *trans* effect of cyanide and its effect upon the intrinsic reactivities and nucleophilic discriminations of the substrates.

In a recent paper[1] we reported our studies of the nucleophilic displacement of chloride and ammonia from platinum(II) complexes by cyanide, in aqueous solution at 25 °C. An important observation was that the reactivities of *cis*- and *trans*-$[Pt(NH_3)_2(CN)_2]$ towards CN^- were remarkably similar indicating an apparent *cis* labilising effect of the cyanide ligand as large as its well known *trans* effect. Two possible explanations were proposed, one based on transition-state stabilisation arising from π interactions in the linear NC–Pt–CN unit, and the other based on bond weakening by a strong σ donor where, for strong nucleophiles such as CN^-, the high intrinsic reactivity of the *cis* isomer would be fortuitously compensated by the much higher nucleophilic discrimination of the *trans* isomer.

In order to gain further insight into these systems and possibly which, if either, of the above explanations is correct, we decided to see if this similarity in lability was a general phenomenon that accompanied the displacement of nitrogen donors of different basicity and steric hindrance. In this paper we report the results of kinetic experiments carried out with a number of substrates of the type *cis*- and *trans*-$[Pt(am)_2Cl_2]$ (am = neutral nitrogen donor) reacting in methanol–water (95:5 v/v) at 25 °C with an excess of cyanide to produce, by a fast reaction, the corresponding cyano complexes *cis*- and *trans*-$[Pt(am)_2(CN)_2]$, which then lose am in a slower, cyanide dependent, reaction. The change of the solvent from water to methanol was forced, partly because many of the substrates were insufficiently soluble in water, and also to avoid the solvolytic disturbances due to the presence of hydroxide.

Experimental

Materials.—Dipotassium tetrachloroplatinate(II) was prepared from metallic platinum according to standard literature methods. Commercial pyridines were distilled over KOH. Morpholine and piperidine were reagent grade products and used without further purification. The inorganic salts and the solvents were also reagent grade products.

Preparation of the Complexes.—The complexes *trans*-$[PtL_2Cl_2]$ [L = 4-cyanopyridine (4CN-py), 4-chloropyridine (4Cl-py), 4-methylpyridine (4Me-py), 2-methylpyridine (2Me-py), 4-ethylpyridine (4Et-py), 2,4-dimethylpyridine ($2,4Me_2$-py), pyridine (py), morpholine (morph), dimethylamine or piperidine (pip)], were prepared in accordance with the method described by Kong and Rochon,[2] in which 2.1 molar equivalents of the appropriate amine were added to a solution of $K_2[PtCl_4]$ in dimethylformamide (dmf). The mixture was kept at 80 °C for 6 h. The dmf was then evaporated under reduced pressure and the residue crystallised from boiling chloroform. In all cases the yields were above 80%.

The analogous *cis* complexes were prepared according to the literature procedure[3] in which 2.64 mmol of the appropriate amine dissolved in the minimum amount of water or methanol was added to a stirred solution of $K_2[PtCl_4]$ (0.5 g, 1.205 mmol) in distilled water (20 cm^3). The stirring was continued for several hours and then the mixture was allowed to stand in the refrigerator until the precipitation seemed to be complete. The precipitate was filtered off and washed twice respectively with ice–water, ice–ethanol and ether, and finally dried in vacuum over P_2O_5.

The isomeric purity of the dichloro species was established from the far infrared spectrum and the compounds were recrystallised if necessary. Isomeric mixtures were sometimes obtained when am was a sterically hindered pyridine and the *trans* isomer could be separated from the *cis* species by extraction with boiling benzene.[3]

trans-Dicyanobis(pyridine)platinum(II) was prepared by the method of Avshu and Parkins.[4] The complex *trans*-$[Pt(py)_2Cl_2]$ (1.00 g, 2.36 mmol) and silver nitrate (0.802 g, 4.72 mmol) were added to boiling water (50 cm^3) in a flask covered with aluminium foil to exclude light and the mixture was shaken for 1 h. The precipitated silver chloride was filtered off and the filtrate treated with potassium cyanide (0.307 g, 4.72 mmol). The colourless product, which precipitated immediately, was filtered off, washed with cold water, ethanol and diethyl ether,

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† *Supplementary data available* (No. SUP 56914, 6 pp.): first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical data for the complexes of the type [Pt(am)$_2$Cl$_2$] (calculated values in parentheses)

		Analysis (%)			
Complex	Empirical formula	C	H	N	Cl
cis-[Pt(4CN-py)$_2$Cl$_2$]	$C_{12}H_8Cl_2N_4Pt$	30.35 (30.40)	1.70 (1.70)	11.75 (11.80)	14.85 (14.95)
cis-[Pt(4Cl-py)$_2$Cl$_2$]	$C_{10}H_8Cl_4N_2Pt$	24.20 (24.35)	1.70 (1.65)	5.70 (5.70)	28.70 (28.75)
cis-[Pt(py)$_2$Cl$_2$]	$C_{10}H_{10}Cl_2N_2Pt$	28.30 (28.30)	2.45 (2.40)	6.60 (6.60)	16.70 (16.70)
cis-[Pt(2Me-py)$_2$Cl$_2$]	$C_{12}H_{14}Cl_2N_2Pt$	31.85 (31.85)	3.10 (3.10)	6.15 (6.20)	15.60 (15.70)
cis-[Pt(4Et-py)$_2$Cl$_2$]	$C_{14}H_{18}Cl_2N_2Pt$	34.90 (35.00)	3.70 (3.80)	5.85 (5.85)	14.70 (14.75)
cis-[Pt(4Me-py)$_2$Cl$_2$]	$C_{12}H_{14}Cl_2N_2Pt$	31.65 (31.85)	3.15 (3.10)	6.20 (6.20)	15.60 (15.70)
cis-[Pt(2,4Me$_2$-py)$_2$Cl$_2$]	$C_{14}H_{18}Cl_2N_2Pt$	35.10 (35.00)	3.70 (3.75)	5.80 (5.85)	14.75 (14.75)
cis-[Pt(morph)$_2$Cl$_2$]	$C_8H_{18}Cl_2N_2O_2Pt$	21.95 (21.85)	4.00 (4.10)	6.30 (6.35)	16.15 (16.10)
cis-[Pt(NH$_2$Me)$_2$Cl$_2$]	$C_2H_{10}Cl_2N_2Pt$	7.15 (7.30)	3.10 (3.05)	8.60 (8.55)	21.70 (21.60)
cis-[Pt(NHMe$_2$)$_2$Cl$_2$]	$C_4H_{14}Cl_2N_2Pt$	13.40 (13.50)	3.95 (3.95)	7.80 (7.85)	20.00 (19.90)
cis-[Pt(pip)$_2$Cl$_2$]	$C_{10}H_{22}Cl_2N_2Pt$	27.65 (27.55)	5.10 (5.10)	6.50 (6.40)	16.30 (16.25)
cis-[Pt(py)$_2$(CN)$_2$]	$C_{12}H_{10}N_4Pt$	35.50 (35.55)	2.40 (2.50)	13.5 (13.8)	
trans-[Pt(4CN-py)$_2$Cl$_2$]	$C_{12}H_8Cl_2N_4Pt$	30.15 (30.40)	1.80 (1.70)	11.85 (11.80)	14.85 (14.95)
trans-[Pt(4Cl-py)$_2$Cl$_2$]	$C_{10}H_8Cl_4N_2Pt$	24.45 (24.35)	1.70 (1.65)	5.80 (5.70)	28.90 (28.75)
trans-[Pt(py)$_2$Cl$_2$]	$C_{10}H_{10}Cl_2N_2Pt$	28.30 (28.30)	2.35 (2.40)	6.60 (6.60)	16.70 (16.70)
trans-[Pt(2Me-py)$_2$Cl$_2$]	$C_{12}H_{14}Cl_2N_2Pt$	31.90 (31.85)	3.05 (3.10)	6.20 (6.20)	15.65 (15.70)
trans-[Pt(4Et-py)$_2$Cl$_2$]	$C_{14}H_{18}Cl_2N_2Pt$	34.90 (35.00)	3.70 (3.80)	5.85 (5.85)	14.70 (14.75)
trans-[Pt(4Me-py)$_2$Cl$_2$]	$C_{12}H_{14}Cl_2N_2Pt$	31.55 (31.85)	3.04 (3.10)	6.20 (6.20)	15.75 (15.70)
trans-[Pt(2,4Me$_2$-py)$_2$Cl$_2$]	$C_{14}H_{18}Cl_2N_2Pt$	34.90 (35.00)	3.70 (3.75)	5.80 (5.85)	14.70 (14.75)
trans-[Pt(morph)$_2$Cl$_2$]	$C_8H_{18}Cl_2N_2O_2Pt$	21.80 (21.85)	4.10 (4.10)	6.35 (6.35)	16.15 (16.10)
trans-[Pt(NH$_2$Me)$_2$Cl$_2$]	$C_2H_{10}Cl_2N_2Pt$	7.30 (7.30)	3.10 (3.05)	8.50 (8.55)	21.55 (21.60)
trans-[Pt(NHMe$_2$)$_2$Cl$_2$]	$C_4H_{14}Cl_2N_2Pt$	13.30 (13.50)	4.00 (3.95)	7.80 (7.85)	20.00 (19.90)
trans-[Pt(pip)$_2$Cl$_2$]	$C_{10}H_{22}Cl_2N_2Pt$	27.65 (27.55)	5.05 (5.10)	6.50 (6.40)	16.30 (16.25)
trans-[Pt(py)$_2$(CN)$_2$]	$C_{12}H_{10}N_4Pt$	35.10 (35.55)	2.40 (2.50)	13.9 (13.8)	

air-dried and recrystallised from boiling water. Yield 0.809 g, 89%. IR: ν(CN) 2120 cm^{-1}; lit.,[4] 2120 cm^{-1}.

cis-Dicyanobis(pyridine)platinum(II) was prepared by the method of Arshu and Parkins.[4] Anhydrous platinum(II) cyanide (0.300 g, 1.21 mmol) was added to boiling pyridine (30 cm^3) and the suspension was stirred for 30 min. The solution was filtered hot and the product separated as colourless crystals on cooling. These were filtered off, washed with ethanol and diethyl ether and dried *in vacuo*. The complex could not be recrystallised without extensive decomposition and could not be stored for long periods. Yield 0.085 g, 28%. IR: ν(CN) 2121 and 2140 cm^{-1}.

cis- and *trans*-[Pt(NH$_3$)$_2$Cl$_2$] were from the sample used in the previous study[1] and the methylamine complexes were kindly donated by Professor A. Khokhar of the University of Texas. The analytical data are reported in Table 1.

Kinetics.—In order to start the reaction, a known volume of a solution of the appropriate complex in methanol–water (95:5 v/v) was mixed with an equal volume of another containing the other reagents, both solutions having been brought to the reaction temperature in a thermostat. The mixture was transferred to a cuvette which was placed in the constant temperature cell compartment of a Perkin Elmer Lambda 5 spectrophotometer. Spectra were scanned at suitable intervals in order to characterise the nature of the change and the wavelengths most suitable for studying the kinetics were established. After an initial rapid change, the absorbance changed with time in a first-order fashion and the rate constant, k_{obs}, was obtained using an iterative non-linear least-squares program that determined the values of k_{obs}, A_0 and A_∞ which best fit the A_t *versus* t data to the first-order rate expression, $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A_t is the measured absorbance at time t.

Results

The Nature of the Reaction.—In aqueous solution it has been shown that, on mixing basic aqueous solutions of KCN and *cis*- or *trans*-[Pt(NH$_3$)$_2$Cl$_2$], the substrates are rapidly converted into the corresponding [Pt(NH$_3$)$_2$(CN)$_2$] species which then loses ammonia to form [Pt(CN)$_4$]$^{2-}$. The slow spectrophotometric stage is the displacement of the first ammonia to give the [Pt(NH$_3$)(CN)$_3$]$^-$ anion.[1] In order to minimise the disturbance to the kinetics from the solvolytic processes that led to the formation of almost inert hydroxy species and to enable us to extend our studies to complexes that were insoluble in water we have changed the solvent to methanol containing 5% by volume of water. Preliminary experiments with *cis*- and *trans*-[Pt(NH$_3$)$_2$Cl$_2$] show that the spectral changes closely resemble those observed in water; the first spectrum measured after mixing the reagents is that of the corresponding *cis*- or *trans*-[Pt(NH$_3$)$_2$(CN)$_2$] species whose preparations have been described elsewhere.[1] The solvolytic disturbances observed in aqueous solution and ascribed to the formation of small quantities of unreactive hydroxo complexes are less evident in methanol. The spectral changes observed with the other substrates of the type *cis*- and *trans*-[Pt(am)$_2$Cl$_2$], where am is a nitrogen-donor ligand, follow a similar pattern, although when am is pyridine or one of its derivatives, the characteristic absorbances of co-ordinated and free am contribute significantly to the observed spectra. In all cases the conversion of the dichloro to the corresponding dicyano species is complete before the first measurement is made and the observed spectrophotometric changes, frequently with one or more isosbestic points, are characteristic of a single stage of reaction and correspond to the displacement of the first am from the [Pt(am)$_2$(CN)$_2$] species [equation (1)], followed

$$\textit{cis-}\text{ or }\textit{trans-}[\mathrm{Pt(am)_2(CN)_2}] + \mathrm{CN^-} \longrightarrow \textit{cis-}\text{ or }\textit{trans-}[\mathrm{Pt(am)(CN)_3}]^- + \mathrm{am} \qquad (1)$$

by the relatively fast displacement of the second am ligand, to form the tetracyanoplatinate(II) anion. This is confirmed by the observation that the rate constants are essentially independent of ionic strength. The first-order rate constants, measured at different cyanide concentrations with the various complexes are available as supplementary material (SUP 56914). The *cis* and *trans* isomers of [Pt(py)$_2$(CN)$_2$] have been prepared and characterised and their spectra agree closely with those of the first initial product of the reaction of the corresponding [Pt(py)$_2$Cl$_2$] complexes with KCN. The spectral changes and rate constants for their subsequent reaction with KCN agree

Table 2 Second-order rate constants (k_2/dm^3 mol^{-1} s^{-1}) for the displacement, by cyanide, of ligand am from substrates of the type *trans*- and *cis*-$[Pt(am)_2(CN)_2]$*

am	pK_a of Ham$^+$	*trans* Substrates	*cis* Substrates
4-Cyanopyridine	1.90	38.9 ± 0.09	0.094 ± 0.004
4-Chloropyridine	3.84	8.71 ± 0.05	0.066 1 ± 0.000 8
Pyridine	5.25	3.77 ± 0.01	0.061 9 ± 0.000 9
4-Ethylpyridine	5.87	2.19 ± 0.01	0.049 9 ± 0.000 2
2-Methylpyridine	5.94	0.161 ± 0.005	0.026 ± 0.003
4-Methylpyridine	6.02	2.09 ± 0.02	0.042 ± 0.005
2,4-Dimethylpyridine	6.77	0.025 2 ± 0.000 8	0.0190 ± 0.000 3
Morpholine	8.33	0.44 ± 0.01	0.036 1 ± 0.000 4
Ammonia	9.25	0.006 5 ± 0.000 1	0.001 57 ± 0.000 09
Methylamine	10.66	0.018 ± 0.003	0.009 5 ± 0.000 3
Dimethylamine	10.73	0.053 7 ± 0.000 2	0.023 4 ± 0.000 1
Piperidine	11.12	0.074 ± 0.001	0.016 9 ± 0.000 4

* In MeOH–H_2O (95:5 v/v), $[OH^-] = 10^{-3}$ mol dm^{-3}, $\mu = 0.2$ mol dm^{-3} (NaCl) at 25 °C.

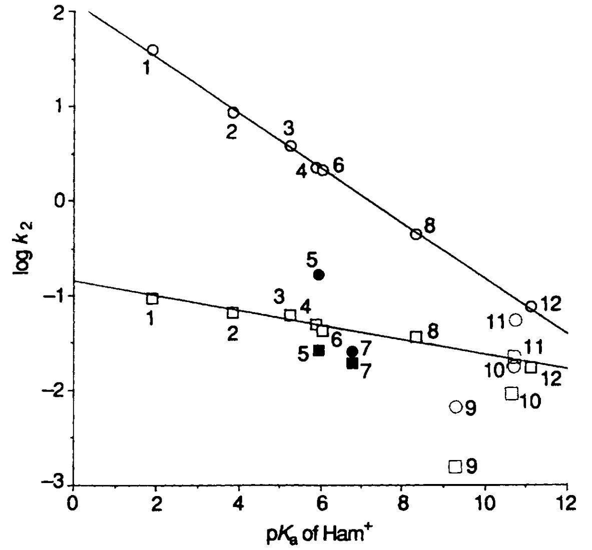

Fig. 1 Plots of log k_2 for the reaction $[Pt(am)_2(CN)_2] + CN \longrightarrow [Pt(am)(CN)_3]^- +$ am in methanol–water (95:5 v/v) at 25.0 °C against pK_a of Ham$^+$: unhindered am, *trans* isomer (○); unhindered am, *cis* isomer (□); hindered am, *trans* isomer (●); hindered am, *cis* isomer (■). 4CN-py (1), 4Cl-py (2), py (3), 4Et-py (4), 2Me-py (5), 4Me-py (6), 2,4Me_2-py (7), morpholine (8), ammonia (9), methylamine (10), dimethylamine (11), piperidine (12)

closely with those of the second stage of the reaction of the dichloro complex with cyanide. All processes obey the general two-term rate law $k_{obs} = k_1 + k_2[CN^-]$, typical for square-planar substitution, but the k_1 term is quite small and of the same order of magnitude as the experimental error. The second-order rate constants, k_2, are summarised in Table 2.

Discussion

Examination of the data in Table 2 shows that in all twelve pairs of isomers studied, covering a range of basicity of the leaving group, 1.9 < pK_a of Ham$^+$ < 11, the rate constant k_2 for reaction (1) is always greater for the *trans* isomer than it is for the *cis*. Since the ligand *trans* to the leaving group, am, is CN in the *cis* species and am in the *trans* isomer, it would appear at first sight that the relative reactivity of the isomers runs contrary to any simple-minded prediction based on the classic *trans* effect (CN having a much larger *trans* effect than these nitrogen-donor ligands[5]). This has already been noted for the *cis*- and *trans*-$[Pt(NH_3)_2(CN)_2]$ isomers in aqueous solution[1] and now appears to be a general behaviour.

In addition, the relationship between log k_2 and the pK_a of Ham$^+$ shows that the reactivities of the *cis* and *trans* isomers respond in markedly different ways both to the basicity of the leaving group and to its bulk, Fig. 1. There is a reasonably linear relationship between log k_2 and pK_a provided there is no significant steric hindrance but the response of the *cis* isomer is far less sensitive (slope = −0.07) than that of the corresponding *trans* isomer (slope = −0.29). Because of the differences in the slopes of these plots, the difference in the reactivity of the isomers is greatest when the basicity of am is least so that the ratio of the rate constants for the displacement of 4-cyanopyridine from *trans*- and *cis*-$[Pt(4CN\text{-}py)_2(CN)_2]$, $k_2(trans)/k_2(cis) = 410$. As well as being less sensitive to the basicity of the leaving group, the reactivities of the *cis* isomers are less sensitive to the presence of bulky substituents adjacent to the donor nitrogen of am.

Previous studies of the leaving-group and spectator-ligand effects of nitrogen-donor ligands in planar d^8 systems indicate a negligible *trans* effect, a significant *cis* effect and a very strong dependence of the rate constants for the displacement of amines and heterocyclic nitrogen bases from d^8 metal ions upon their proton basicities. For example, the plot of log k_2 against pK_a of Ham$^+$ for the displacement of cycloalkylamines of the type $C_nH_{2n-1}NH_2$ (n = 2–8) by Cl^- under the *trans* effect of dimethyl sulfoxide (dmso) in *cis*-$[Pt(am)_2(dmso)Cl]^+$ has a slope of −0.91, the effect being due to roughly equal contributions from the leaving group effect and the *cis* effect.[6] The slope of the corresponding plot for the displacement of am from *trans*-$[PtCl_2(am)(dmso)]$ by MeOH is −0.55[7] and that for its displacement by Cl^- is *ca.* −0.42. The slope of the log k *versus* pK_a plot for the displacement of pyridine derivatives from $[AuCl_3(R\text{-}py)]$ by Cl^- in methanol is −0.58[8] but this is reduced to −0.27 in the corresponding bromide system.[9] Therefore, the presence of cyanide, either as a spectator ligand or entering group serves to reduce the dependence of rate constant on the basicity of the leaving group. This is most marked when CN is *trans* to the leaving group.

The reactivities of the complexes in which am has an *o*-methyl substituent are less than predicted from the relationship between log k_2 and the basicity of am, the deviation being much more marked in the *trans* isomers. This steric effect runs counter to what is usually observed in the substitution reactions of d^8 metal complexes where the effect of *ortho* substituents in an aryl spectator ligand that is *cis* to the leaving group is much more marked than that in the corresponding *trans* isomer. This has been cited as evidence for a trigonal-bipyramidal transition state since, in this geometry, the steric hindrance from *ortho* substituents in the axial ligands (which were *cis* to the leaving group in the substrate) will be much greater than if they lie in the trigonal plane.[10] The magnitude of the effect can be seen in the rate constants for the displacement of anionic ligand, X, from complexes of the type $[Pt(PEt_3)_2(aryl)X]$. On going from aryl = phenyl, through 2-methylphenyl to 2,4,6-trimethylphenyl, the solvolytic rate constant in methanol decreases by a factor of 32 000 for the *cis* isomer and only 25-fold for the *trans* (X = Cl).[11] The second-order rate constant for reaction with the strong nucleophile CN^- decreases by a factor of 69 000 for the *cis* isomer and 810 for the *trans* (X = Br).[12] One would expect *ortho*-substituted pyridines to behave in a similar way unless a specific orientation of the π system of the nitrogen base is required in the transition state. In the reactions of $[Pt(am)_2(CN)_2]$ with CN^- the effect of the spectator ligand is not separable from that of the leaving group and while it is not impossible that the combination of the two steric effects might account for the observations, there are no suitable published studies for comparison.

In seeking an explanation for these observations it is necessary to remember, (*i*) that cyanide is a strong σ donor and possibly a good π acceptor, and (*ii*) it is a strong nucleophile ($n^0_{Pt} = 7.14$[13,14]). If the main role of the cyanide spectator ligand is that of a strong σ donor whose destabilisation of the ground state (high *trans* influence) is reduced in the transition state one might expect it to behave like Me or PMe_3 and form an 'open' transition state. In the case of *cis*-$[PtR_2L_2]$ (R = Me or Ph; L = Me_2S or dmso) this effect is strong enough to promote a dissociative mechanism in the absence of strong nucleophiles.[15] When the mechanism remains associative, the intrinsic reactivity is high but the nucleophilic discrimination is much diminished and a characteristic feature of complexes with a σ-bonded alkyl or aryl group, as for example *cis*- and *trans*-$[Pt(PEt_3)_2(X)Cl]$ (where X is an anionic ligand with a strong *trans* influence) is that the solvent, by virtue of its high concentration, becomes the dominant nucleophile and weak to moderate nucleophiles enter by way of a rate-limiting solvolysis. The contrast between such complexes and *trans*-$[Pt(PEt_3)_2Cl_2]$ (*i.e.*, X = Cl) is enormous. In the latter case, the nucleophilic discrimination is extremely high, whereas the intrinsic reactivity is very low.[13] As a result, the rate constant for the methanolysis of *trans*-$[Pt(PEt_3)_2(X)Cl]$ follows the expected *trans* influence of X and the rate constant for the solvolytic displacement of Cl under the *trans* effect of H is some 4×10^6 times greater than it is under the *trans* effect of Cl. However, when the chloride is displaced by the strong nucleophile thiourea, the difference in nucleophilic discrimination becomes important and the second-order rate constant for *trans*-$[Pt(PEt_3)_2Cl_2]$ is greater than that for all other species except *trans*-$[Pt(PEt_3)_2(H)Cl]$. The value of k_2 for the *trans* dichloro complex is three times larger than that for *trans*-$[Pt(PEt_3)_2(Et)Cl]$, the second most solvolytically labile species in the series studied.[16]

Applying this reasoning to the *cis* and *trans* isomers of $[Pt(CN)_2(am)_2]$ we would predict that the *cis* isomer, with the strong *trans* influence ligand cyanide opposite to the leaving group would have a high intrinsic reactivity and exert a low nucleophilic discrimination. The *trans* isomer, on the other hand, would resemble *trans*-$[Pt(PEt_3)_2Cl_2]$ with its low intrinsic reactivity and high nucleophilic discrimination. In the reactions with the strong nucleophile cyanide, whose nucleophilicity is very similar to that of thiourea, the advantage gained from the higher intrinsic reactivity of the *cis* isomer is lost to the higher nucleophilic reactivity of the *trans* isomer. This reasoning can also account for the low dependence of k_2 on the basicity of the leaving group in the *cis* isomer since, in the presence of the high *trans*-influence CN ligand the Pt–N bond will be weakened in the ground state and the extent to which this bond is further weakened in the transition state may be small.[17] The dependence of log k_2 on the basicity of the leaving group and the *cis* ligand will therefore be much diminished. In the *trans* isomers, where there is no ground-state destabilisation, the effect of reactivity on ligand basicity is expected to be much greater. It is also suggested that steric effects are less important in the more open transition state belonging to the *cis* substrates.

In order to confirm that these observations are due to the opposing effects of high intrinsic reactivity and low nucleophilic discrimination when the leaving group is displaced under the strong *trans* effect of cyanide we are trying to examine the kinetics of the displacement of am from *cis*- and *trans*-$[Pt(am)_2(CN)_2]$ by a wide range of nucleophiles. The detailed study will be reported elsewhere when completed but it is noteworthy that a methanolic solution of *trans*-$[Pt(py)_2(CN)_2]$ containing NH_3 (0.5 mol dm^{-3}) can be kept for very long periods at 25 °C without any significant change in its spectrum, whereas the spectrum of the *cis* isomer, under similar conditions, changes to that of a mixture of *cis*-$[Pt(NH_3)_2(CN)_2]$ and free pyridine within an hour.

The systems that depart from the simple linear relationship between log k_2 and pK_a of Ham^+ deserve closer examination. Apart from the effect of steric crowding already discussed, the most prominent departures are found when am = NH_3, where both isomers are some 1.5 orders of magnitude less reactive than predicted from the basicity of the leaving group and am = NH_2Me, where the decrease in reactivity is about one order of magnitude. The data for am = dimethylamine are much closer to the values predicted and those for am = morpholine and piperidine actually lie on the same lines as those for am = R-py (a non-bulky pyridine derivative).

This apparent anomaly, which affects the *cis* and *trans* isomers to much the same extent, is of considerable interest and is now being studied in detail. Preliminary experiments indicate that the intrinsic reactivities of substrates with ammonia and primary amines as leaving groups are much more sensitive to the nature of the solvent than those where the leaving group has fewer hydrophilic substituents on the donor atom and that this applies to both *cis*- and *trans*-$[Pt(am)_2(CN)_2]$ isomers. This work will be reported elsewhere.

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References

1 L. Cattalini, F. Guidi and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1992, 3021.
2 P. C. Kong and F. D. Rochon, *Can. J. Chem.*, 1978, **56**, 441.
3 G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 1965, **7**, 249.
4 A. Avshu and A. W. Parkins, *J. Chem. Res.*, 1984, (*M*), 2201.
5 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1967, p. 398.
6 P. D. Braddock, R. Romeo and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1170.
7 R. Romeo and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1991.
8 L. Canovese, L. Cattalini, M. Tomaselli and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1991, 307.
9 L. Cattalini, G. Chessa, B. Michelon, B. Pitteri, M. L. Tobe and A. Zanardo, *Inorg. Chem.*, 1985, **28**, 3409.
10 F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.
11 R. Romeo, D. Minniti and M. Trozzi, *Inorg. Chem.*, 1976, **15**, 1134.
12 G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, *J. Chem. Soc., Dalton Trans.*, 1974, 1377.
13 U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *J. Am. Chem. Soc.*, 1965, **87**, 241.
14 J. B. Goddard and F. Basolo, *Inorg. Chem.*, 1968, **7**, 936.
15 D. Minniti, G. Alibrandi, M. L. Tobe and R. Romeo, *Inorg. Chem.*, 1987, **26**, 3956.
16 M. Cusumano, P. Marricchi, R. Romeo, V. Ricevuto and U. Belluco, *Inorg. Chim. Acta*, 1979, **34**, 169.
17 C. H. Langford and H. B. Gray, *Ligand Substitution Processes*, Benjamin, New York, 1965, p. 165.

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