Nucleophilic Discrimination and the *trans* Effect. The Kinetics of Displacement of X from *trans*-$[Pt(L)(X)Cl_2]^{n-}$ (L = Me_2SO, Et_2S, PMe_3, PEt_3, PPh_3, or $AsEt_3$; X = Cl, *n* = 1; X = MeOH, *n* = 0) by Neutral and Anionic Nucleophiles

Martin L. Tobe * **and Andrew T. Treadgold**
Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ
Lucio Cattalini
Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta, 2137, Venezia, Italy

The kinetics of the reaction *trans*-$[Pt(L)(X)Cl_2]^{n-}$ + L′ $\longrightarrow$ *trans*-$[Pt(L)(L')Cl_2]^{n'-}$ + X (X = Cl^-, *n* = 1, L = Me_2SO, Et_2S, PMe_3, PEt_3, PPh_3, or $AsEt_3$, L′ = pyridine (py), Me_2S, Et_2S, PPh_3, Me_2SO, thiourea (tu), or *NNN′N′*-tetramethylthiourea (tmtu), *n′* = 0; L′ = Cl^-, Br^-, I^-, or SCN^-, *n′* = 1; X = MeOH, *n* = 0, L′ = Cl^-, Br^-, I^-, or SCN^-, *n′* = 1) have been studied in 95% methanol + 5% water at 25 °C. The second-order rate constants, k_2, for the anionic substrates do not follow the usual dependence upon n^0_{Pt}, the anionic nucleophiles being much less reactive than predicted. A new nucleophilicity scale, based on $[Pt(Et_3As)Cl_3]^-$ as standard substrate, does give linear relationships for all the anionic substrates. The relationship between the nucleophilic discrimination and the nature of the *trans* ligand is discussed.

The rate at which a ligand is displaced from four-co-ordinate planar complexes of d^8 metal ions is very sensitive to the nature of the ligand *trans* to it. At least two causes have been identified. The first is a ground-state effect whereby a strong σ donor enhances its bonding at the expense of that of the ligand *trans* to it. The effect is mitigated in the transition state and so increases the rate of reaction[1] and, being a ground-state effect, it is also seen as a *trans* influence on bond length,[2,3] stretching frequency and force constant,[3,4] n.m.r. spin–spin coupling,[5–8] and other non-kinetic phenomena. The second effect is a transition-state stabilisation through charge acceptance by a good π acceptor[9,10] which has no parallel *trans* influence and which might, in favourable circumstances, stabilise the five-co-ordinate intermediate to the point where it can be detected directly,[11] or even isolated.[12]

These two effects are not mutually exclusive and it has been our aim for a numbers of years[13–17] to try to develop criteria for assigning the relative contributions from the σ-weakening and π-stabilising effects. We have examined a wide series of complexes of the type $[Pt(L)Cl_3]^-$, where L is a neutral ligand, and have examined the quantitative *trans*-effect sequences for forward and reverse reactions of the type (1) and the

$$[Pt(L)Cl_3]^- + am \rightleftharpoons trans\text{-}[Pt(L)(am)Cl_2] + Cl^- \quad (1)$$

corresponding solvolytic processes in methanol (am is an amine or a heterocyclic nitrogen base). A commonly discussed criterion is the nucleophilic discrimination factor.[18] A good σ donor will favour a more open transition state and, since the binding of the entering nucleophile therein will be relatively weak, the extent to which the second-order rate constants depend upon the nature of the entering group will be small. In the limit, the reaction is dominated by the solvolytic pathway because, in a poorly discriminating system, the high concentration of the solvent gives it precedence. Occasionally, the nucleophilic discrimination will depend upon the nature of the entering group, potential π acceptors being more reactive than predicted.[19] The nucleophilic discrimination is expected to be much greater when there is transition-state stabilisation since bonding to the incoming group in the transition state takes on greater significance.

In our studies with heterocyclic bases we were surprised to find that, in spite of the fact that these were weak nucleophiles, their reactions could be characterised by important contributions from the nucleophile-dependent pathway and, far from being insensitive to the basicity of the entering group as is usual for platinum(II) substrates,[20] the rate constants actually increased as the proton basicity of the nucleophile decreased. Furthermore, studies of the mass-law retardation of the solvent-mediated pathway by chloride suggested that pyridine could be some 10^3 times more effective than chloride in displacing methanol from *trans*-$[Pt(L)(MeOH)Cl_2]$. We have therefore also studied the displacement of Cl^- or methanol from these trichloro- and *trans*-dichloro-methanol complexes in order to determine the relationship between the nature of the entering group, the *trans* ligand, and the leaving group on the reactivity and we report the results in this paper.

Experimental

Preparations.—The following complexes were prepared according to the literature procedures: $[NEt_4][Pt(Et_2S)Cl_3]$,[15] $K[Pt(Me_2SO)Cl_3]$,[21] $[NEt_4][Pt(Ph_3P)Cl_3]$,[16] $[Pt_2(Me_3P)_2(\mu\text{-}Cl)_2Cl_2]$,[16] $[Pt_2(Et_3P)_2(\mu\text{-}Cl)_2Cl_2]$,[22] $[Pt_2(Et_3As)_2(\mu\text{-}Cl)_2Cl_2]$,[16] *trans*-$[Pt(Et_2S)(py)Cl_2]$ (py = pyridine),[23] *trans*-$[Pt(Et_2S)_2Cl_2]$,[24] and *trans*-$[Pt(Me_2SO)(py)Cl_2]$.[21]

Tetraethylammonium trans-*bromodichloro(dimethyl sulphoxide)platinate*(II). A solution of tetraethylammonium bromide (0.21 g, 1 mmol) in dichloromethane was added to a solution of $[Pt_2(Me_2SO)_2(\mu\text{-}Cl)_2Cl_2]$[25] (0.34 g, 0.5 mmol) dissolved in the minimum amount of the same solvent. The solution was stirred overnight and the solvent removed in a rotary evaporator. The residue was washed with a small amount of cold methanol and then diethyl ether.

trans-*Dichloro(dimethyl sulphide)(dimethyl sulphoxide)platinum*(II). Dimethyl sulphide (0.062 g, 0.50 mmol) was dissolved in dichloromethane and the solution added drop by drop over a period of 5 min to a solution of $[Pt_2(Me_2SO)_2(\mu\text{-}Cl)_2Cl_2]$[25] (0.34 g, 0.50 mmol) in dichloromethane. The solvent was then immediately removed in a rotary evaporator and the product washed with cold methanol and diethyl ether. *trans*-Dichloro(dimethyl sulphoxide)(thiourea)platinum(II) was prepared in a similar way using thiourea.

Elemental analyses and relevant i.r. stretching frequencies are collected in Table 1.

Table 1. Analytical data and characteristic metal–ligand stretching frequencies

Compound	Empirical formula	Analysis */%				ν(Pt–L)/cm^{-1}	ν(Pt–Cl)/cm^{-1}
		C	H	N	Cl		
K[Pt(Me_2SO)Cl_3]	$C_6H_6Cl_3KOPtS$	5.7 (5.7)	1.5 (1.4)		25.3 (25.4)	446, 382	346, 331, 309
[Pt_2(Me_3P)$_2$$Cl_4$]	$C_6H_{18}Cl_4P_2Pt_2$	10.8 (10.5)	2.6 (2.7)		20.8 (20.7)	393	346, 329, 260
[Pt_2(Et_3P)$_2$$Cl_4$]	$C_{12}H_{30}Cl_4P_2Pt_2$	18.7 (18.8)	3.9 (3.9)		18.2 (18.4)	442	351, 327, 260
[Pt_2(Et_3As)$_2$$Cl_4$]	$C_{12}H_{30}As_2Cl_4Pt_2$	16.9 (16.8)	3.3 (3.5)				346, 321, 261
[NEt_4][Pt(Et_2S)Cl_3]	$C_{12}H_{30}Cl_3NPtS$	26.9 (27.6)	5.6 (5.8)	2.6 (2.7)	20.2 (20.4)	421	345, 325, 307
[NEt_4][Pt(Ph_3P)Cl_3]	$C_{26}H_{35}Cl_3NPPt$	44.8 (44.5)	5.1 (5.1)	2.2 (2.0)			333, 279
trans-[Pt(Et_2S)(py)Cl_2]	$C_9H_{15}Cl_2NPtS$	24.9 (24.8)	3.5 (3.5)	3.2 (3.2)			347
trans-[Pt(Et_2S)$_2$$Cl_2$]	$C_8H_{20}Cl_2PtS_2$	21.6 (21.5)	4.4 (4.5)				342
trans-[Pt(Me_2SO)(py)Cl_2]	$C_7H_{11}Cl_2NOPtS$	20.0 (19.9)	2.6 (2.6)	3.2 (3.3)			347
[NEt_4][*trans*-Pt(Me_2SO)(Br)Cl_2]	$C_{10}H_{26}BrCl_2NOPtS$	21.7 (21.7)	5.0 (4.8)	2.7 (2.5)			335
trans-[Pt(Me_2S)(Me_2SO)Cl_2]	$C_4H_{12}Cl_2OPtS_2$	11.9 (11.8)	2.9 (3.0)		18.9 (17.5)		348
trans-[Pt(Me_2SO)(tu)Cl_2]	$C_3H_{10}Cl_2N_2S_2$	8.5 (8.6)	2.5 (2.4)	6.7 (6.7)			348

* Calculated values in parentheses.

The salt K_2PtCl_4 was loaned by Johnson Matthey plc. Pyridine was refluxed over NaOH pellets and distilled at 116 °C. Dimethyl sulphide (Aldrich) and diethyl sulphide (Koch-Light Ltd) were freed from mercaptan by shaking with HgO and the filtered liquid was fractionally distilled. Fractions boiling at 37 and 92 °C respectively were collected. The purity was confirmed by the ^1H n.m.r. spectrum in CD_2Cl_2 solution. Tetraethylammonium bromide (BDH) was recrystallised from dry ethanol and stored over P_2O_5. Anhydrous $LiClO_4$ (Fluka), anhydrous LiBr (BDH), anhydrous LiI (BDH), and anhydrous LiNCS (Hopkin and Williams) were dried and stored over P_2O_5 in a vacuum desiccator. The other reagents were of AR quality or otherwise the best available and were used without further purification.

Kinetics.—All reactions were followed spectrophotometrically. Those with half-lives greater than 20 s were initiated by adding 0.10 cm^3 of a stock solution of the complex to a methanolic solution of all the other reagents (3.00 cm^3) previously brought to the reaction temperature in a thermostatted cell compartment of a Unicam SP 1750 or Perkin-Elmer 554 spectrophotometer. The temperature control ($\pm$ 0.1 °C) was maintained electrically using a Peltier-effect device or by water circulation from an external thermostat. The temperature of the reaction vessel was monitored by a platinum-resistance thermometer placed in an adjacent cell, and displayed digitally.

Reactions with half-lives of less than 20 s were studied using a Hi-Tec stopped-flow spectrophotometer and the data collected and processed using a Research Machines 380Z microcomputer. The reactions were initiated by mixing equal volumes of separate solutions of the nucleophile and the substrate previously brought to the reaction temperature. The two solutions were made up to the same ionic strength in order to minimise Schlieren effects on mixing. The heat exchanger reservoir coils, mixer, and cuvette were all immersed in the thermostat. A high-speed data acquisition programme, written by J. Cant and A. Griffiths of Johnson Matthey Research Centre, allowed the change in photon multiplier output with time to be digitalised, monitored, and stored. These readings were converted into absorbance *versus* time data which were processed by a linear least-squares regression analysis of the $\ln(A_\infty - A_t)$ *versus* time plots, or by Guggenheim's method[26,27] or Swinbourne's method[28] depending upon the degree of confidence in the value of A_∞ (the absorbance at the end of the first-order process studied) and the extent to which there was interference from consecutive or parallel reactions. The data for the reactions with interference from either consecutive or parallel reactions were also analysed by a non-linear regression using the appropriate expressions[29–31] and the SMDP 3R programme.[32]

Infrared spectra of CsCl discs or Nujol mulls were recorded with a Perkin-Elmer 225 spectrometer. Proton n.m.r. spectra were recorded using a Varian XL 200 FT spectrometer. Solutions were made up in CD_2Cl_2, CD_3OD, or D_2O with tetramethylsilane as standard ($\delta = 0$).

Results

Solutions of complexes of the type [NEt_4][Pt(L)Cl_3] (L = Et_2S, Me_2SO, PMe_3, PEt_3, PPh_3, or $AsEt_3$) are readily solvolysed in methanol and the equilibrium (2) can be rapidly established.

$$[Pt(L)Cl_3]^- + MeOH \rightleftharpoons \textit{trans}\text{-}[Pt(L)(MeOH)Cl_2] + Cl^- \quad (2)$$

established. The equilibrium constant, as well as the rate at which equilibrium is approached, is very sensitive to the nature of L.[16] Dilute solutions of the complex where L = PMe_3, PEt_3, PPh_3, or $AsEt_3$ are fully solvolysed and contain mainly the *trans* methanol species. In order to suppress this solvolysis it was necessary to work in the presence of a known excess of LiCl. Although in the slower reactions it was only necessary to maintain high chloride concentration in the stock solution and the subsequent dilution (30-fold) did allow studies to be made in the presence of *ca.* 10^{-2} mol dm^{-3} Cl^-, the stopped-flow technique only allowed a two-fold dilution. Therefore, in order to be able to compare the data from both sources, all reactions were studied in the presence of 0.25 mol dm^{-3} LiCl in 5% aqueous methanol. Such solutions, with the complex provided as [NEt_4][Pt(L)Cl_3] (except in the case of L = Me_2SO where the potassium salt was used) or the chloro-bridged dimers {[Pt_2(L)$_2$$Cl_4$], L = PMe_3, PEt_3, or $AsEt_3$} which were rapidly converted into the anionic monomers, were completely unchanged 24 h after mixing. With the anionic nucleophiles, entry by way of the solvolytic pathway made a major contribution to the reactions, and in order to correct for the anion-dependent contribution arising from this, a second set of reactions was studied in the presence of 1.25×10^{-2} mol dm^{-3} LiCl.

Before the kinetic studies could be carried out it was necessary to identify the spectrophotometric changes that were observed when the reagents were mixed. Unlike the previously reported reactions of these substrates with amines and heterocyclic bases,[13–17] more than one chloride is replaced and there may even be isomerisation processes. With neutral nucleophiles, L′, the first product, *trans*-$[Pt(L)(L')Cl_2]$ was a non-electrolyte and frequently very easy to prepare, isolate, and characterise. Reactions carried out in the presence of a slight molar excess of ligand L′ were slow enough to be followed by repetitive scanning and gave sets of spectra that were characteristic of a single-stage reaction and a final spectrum that agreed with that of an authentic sample of the *trans* monosubstituted product. The spectrum of the solution at the end of the reaction between $[Pt(Et_2S)Cl_3]^-$ and Me_2SO was identical to that at the end of the reaction between $[Pt(Me_2SO)Cl_3]^-$ and Et_2S.

The kinetics were studied at much higher nucleophile concentrations (>40 times that of the complex) in order to ensure first-order conditions, but the values for the absorbance at the end of the first stage of reaction, A_∞, were always in close agreement with those calculated for the *trans*-$[Pt(L)(L')Cl_2]$ product under identical conditions.

The products of the reactions with anionic nucleophiles were themselves anionic and therefore difficult to isolate in a pure form. The salt $[NEt_4]$[*trans*-$Pt(Me_2SO)(Br)Cl_2]$ was isolated after treating the appropriate chloro-bridged dimer with 2 equivalents of $[NEt_4]Br$ in dichloromethane, but the bulk of the reactions were characterised simply by examining the reactions by repetitive scanning under the slowest conditions that could be achieved and showing that the initial spectrum was indeed that of the trichloro substrate. The spectrum at the end of the observed single-stage process was assumed to be that of the *trans*-$[Pt(L)(X)Cl_2]^-$ anion. The values of A_∞ used in the kinetic analyses, always carried out under first-order conditions, were in close agreement with these spectra. The subsequent stages, whether they were replacement of other chlorides or *trans–cis* isomerisation, were comparatively slow and did not usually interfere with the evaluation of the rate constants for the first stage. However, in the reaction between $[Pt(Me_2SO)Cl_3]^-$ and iodide, a yellow precipitate of $[Pt_2(Me_2SO)_2I_4]$[33] separated and made the study difficult. In no case was there any evidence for the replacement of L, ^1H n.m.r. spectra of the reaction mixture giving no signal for free L even after very long reaction times.

The kinetics were followed at constant ionic strength (0.50 mol dm^{-3}, $LiClO_4$) by measuring the change in absorbance at a single wavelength, chosen as a compromise between the maximum absorbance change for the reaction and the minimum change (ideally an isosbestic point) for the subsequent process.

In the reactions with the neutral nucleophiles, the interference from the mass-law retardation by chloride was minimal and plots of $k_{obs.}$ *vs.* [L′] were linear, the slope being the second-order rate constant for direct entry, k_2. With the anionic nucleophiles, however, it was necessary to take account of the partition of the solvento complex between the reaction with Cl^- and that with X^-. Use of the complicated expression introduced to take account of the situation where a significant amount of the solvento intermediate remained present during the reaction[16] was unwarranted and the simpler expression $k_{obs.} = k_s + k_2[X^-]$, where $k_s = k_1k_X[X^-]/(k_{Cl}[Cl^-] + k_X[X^-])$, was used instead. Values of k_{Cl} and k_X, the rate constants for the reaction of the *trans*-methanol complex were determined independently as described below and inserted in the equation. Values of k_1, the solvolytic rate constant, were taken from the reactions with the stronger nucleophiles. Plots of $(k_{obs.} - k_s)$ *vs.* $[X^-]$ were linear and the slopes were equal to k_2. The validity of the expression was confirmed by using data at two chloride concentrations.

The reactions between *trans*-$[Pt(L)(MeOH)Cl_2]$ and X^- were carried out in acidified methanol in order to prevent complications from deprotonation of the co-ordinated methanol. The substrates were generated by dissolving the trichloro anion or the chloro-bridged dimer in the acidified methanol–water (95:5 v/v) solvent. The most solvolytically resistant substrate, $[Pt(Me_2SO)Cl_3]^-$ ($K = 2.5 \times 10^{-4}$ mol dm^{-3}), is only 75% solvolysed in a 1×10^{-4} mol dm^{-3} solution but with this, and all other species, there is significant formation of the bis(methanol) species under these conditions. Consequently, all reactions were carried out in the presence of a small amount of LiCl, $[Cl^-] = 1.25 \times 10^{-3}$ mol dm^{-3}. This reduces the amount of (mono)methanol complex to some 40% of the total unreacted species but the amount of bis(methanol) complexes is reduced to a negligible 1%; the rest of the substrate is in the form of the trichloro anion. The anionic nucleophiles have two parallel reactions leading to the same product, the faster being the displacement of methanol and the slower the displacement of chloride. The less solvolytically resistant substrates generate a much greater fraction of the (mono)methanol species but the amount of bis(methanol) species, which appears to be less sensitive to the nature of L, is always reduced to negligible amounts. The first-order rate constants, $k_{obs.}$, determined in the usual way, obey the relationship $k_{obs.} = k_2[X^-]$. Values of k_2 are collected in Table 3.

Discussion

Examination of the collection of rate constants in Tables 2 and 3 shows that there is a general pattern of *trans* effect that is independent of the nature of the entering group and the leaving group. In all cases examined the sequence of *trans* effect runs

Table 2. Rate constants for the reaction $[Pt(L)Cl_3]^- + L' \rightarrow$ *trans*-$[Pt(L)(L')Cl_2] + Cl^-$, or $[Pt(L)Cl_3]^- + X^- \rightarrow$ *trans*-$[Pt(L)(X)Cl_2]^- + Cl^-$[a]

	10^2k_1/s^{-1}	10^2k_2/dm^3 mol^{-1} s^{-1}									
L		L′ = py	Et$_2$S	Me$_2$S	tu	tmtu	PPh$_3$	Me$_2$SO	X$^-$ = Br	SCN	I
		(3.19)[b]	(4.52)	(4.87)	(7.17)	(5.83)	(8.93)	(2.56)	(4.18)	(5.75)	(5.46)
Et$_2$S	0.20	9.1	52	300	78	14		13.3	*c*	*c*	*c*
Me$_2$SO	0.62	61.7	550	5 600	1 380		9 000		*c*	12.5	
PMe$_3$	280	1 440	6 300	17 700	4 500				120	500	600
PEt$_3$	504	1 080	4 300	17 000		2 900					
PPh$_3$	230	1 800	6 900	33 000					200	600	*c*
AsEt$_3$	57	360	1 940	9 200	1 440	320		160	10	40	50

[a] In 95% methanol + 5% water at 25.0 °C, $[Cl^-] = 0.25$ mol dm^{-3}, $I = 0.50$ mol dm^{-3} ($LiClO_4$). [b] Values of n^0_{Pt} in parentheses taken from M. L. Tobe, 'Comprehensive Coordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 1, p. 313. [c] $k_{obs.} - k_s$ (see text) does not vary significantly with $[X^-]$.

Table 3. Second-order rate constants ($dm^3 mol^{-1} s^{-1}$) for the reaction *trans*-$[Pt(L)(MeOH)Cl_2] + X^- \longrightarrow$ *trans*-$[Pt(L)(X)Cl_2]^- + MeOH$[a]

	X				
L	Cl	Br	I	SCN	py[b]
Et_2S	1.26	6.1	24.8	43.2	
Me_2SO	12.4	31.2		120	
$AsEt_3$	52.2	152	538	729	7 987
PMe_3	83.6	199	570	1 050	4 514
PPh_3	190	452	1 210	2 350	22 900

[a] In 95% methanol + 5% water at 25.0 °C; I not held constant. [b] Calculated from previously published values of the ratio $k_2(py)/k_2(Cl)$.[16]

thioether < sulphoxide < arsine < phosphine. The sequence within the phosphines may change on changing the nature of the reaction but the difference between trimethyl-, triethyl-, and triphenyl-phosphine never seems to be very great.

In seeking to account for the *trans* effect in terms of the relative contributions of the σ (ground-state bond weakening) and π (transition-state stabilisation) components it is important to be able to measure relative nucleophilic discrimination factors for these substrates, the reasoning being that the greater the nucleophilic discrimination the more developed is bond making with the incoming nucleophile in the rate-determining transition state. It has been the practice to treat this as a linear free-energy relationship and define the nucleophilic discrimination factor as the slope of the plot of log k_2 against the n^0_{Pt} value of the nucleophile.[34] Indeed Belluco *et al.*[35] have already tried to define the *trans* effect in terms of the nucleophilic discrimination factor. Values of n^0_{Pt} for all the nucleophiles used are given in Table 2 and a cursory inspection will show that the sequence is not even qualitatively correct. For example, pyridine, whose n^0_{Pt} value is virtually the same as that of Cl^-, is more reactive than I^-, the most active of the halides. Closer inspection shows that the rate constants for the anionic nucleophiles roughly follow the same order as their n^0_{Pt} values, but they are very close together. The main difference is that they are significantly less reactive, as a group, than neutral nucleophiles towards these anionic substrates. Rate constants have been measured at $I = 0.50$ mol dm^{-3} and no attempt has been made to correct them to $I = 0$ because the extrapolation is too long and the parameters in the equations too uncertain. However, salt effects cannot account for the low reactivity of the anionic reagents since rate constants for reactions between ions of like charge increase as the ionic strength increases and so the effect would be even more pronounced at $I = 0$.

The unsuitability of the n^0_{Pt} scale for cationic substrates has already been discussed and the problem has been overcome by using a nucleophilicity scale derived from a standard substrate of the same charge as the system under examination.[36-38] Provided the charge types correspond, plots of log k_2 for the substrate against log k_2 for the standard are essentially linear. An analogous nucleophilicity scale has been set up for mono-anionic substrates using $[Pt(pyca)Cl_2]^-$ (pyca = pyridine-2-carboxylate) as standard,[39] but the nucleophiles are all anionic and no data exist for the neutral nucleophiles that have been studied in this work. We therefore propose to use one of the substrates used in this work as the standard and have chosen $[Pt(Et_3As)Cl_3]^-$ simply because it was reacted with more nucleophiles than any of the other complexes. There are too few data for adequate comparison to be made between the two scales but it does seem that, in its reactions with $[Pt(pyca)Cl_2]^-$, SCN^- is a much better nucleophile than I^- (by nearly two orders of magnitude) while with $[Pt(Et_3As)Cl_3]^-$, I^- is marginally more effective than SCN^-.

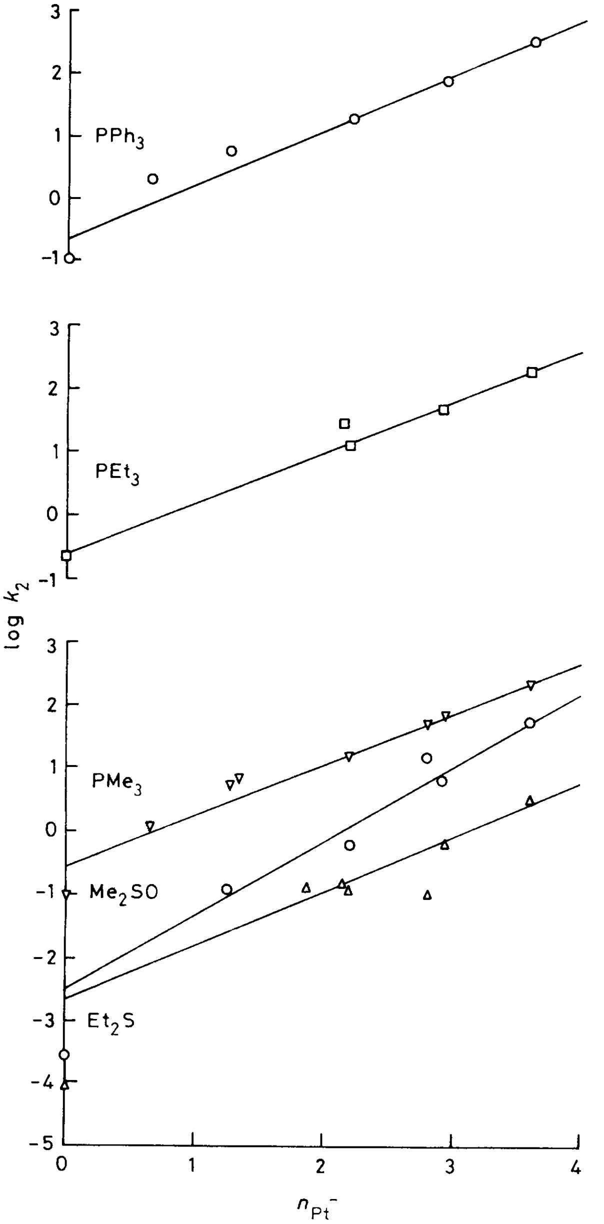

Figure 1. Plots of log k_2 *versus* n_{Pt}^- (as defined in text) for reactions of $[Pt(L)Cl_3]^-$ with nucleophiles in methanol–water (95:5) at 25.0 °C. Each line is labelled with the appropriate L

Using the equation, $n_{Pt}^- = \log(k_2/k_1) + 1.40$* {where k_2 and k_1 are the appropriate rate constants for the reaction between the standard $[Pt(Et_3As)Cl_3]^-$ and the reagents in methanol–water (95:5) at 30 °C}, the nucleophilicities of the reagents used are: methanol–water 0.00 (0.00); Br^- 0.64 (4.18); SCN^- 1.25 (5.75); I^- 1.34 (5.46); Me_2SO 1.85 (2.56); *NNN'N'*-tetramethylthiourea (tmtu) 2.15 (5.83); py 2.20 (3.19); tu 2.80 (7.17); Et_2S 2.93 (4.52); and Me_2S 3.61 (4.87) (n^0_{Pt} values in parentheses). Apart from the low reactivity of the anionic nucleophiles which has already been mentioned, the relatively low reactivity of

---

* The addition of 1.40, *i.e.* log[MeOH], enables the solvolysis to be represented by a second-order rate constant and serves to make the expression in the logarithm dimensionless.

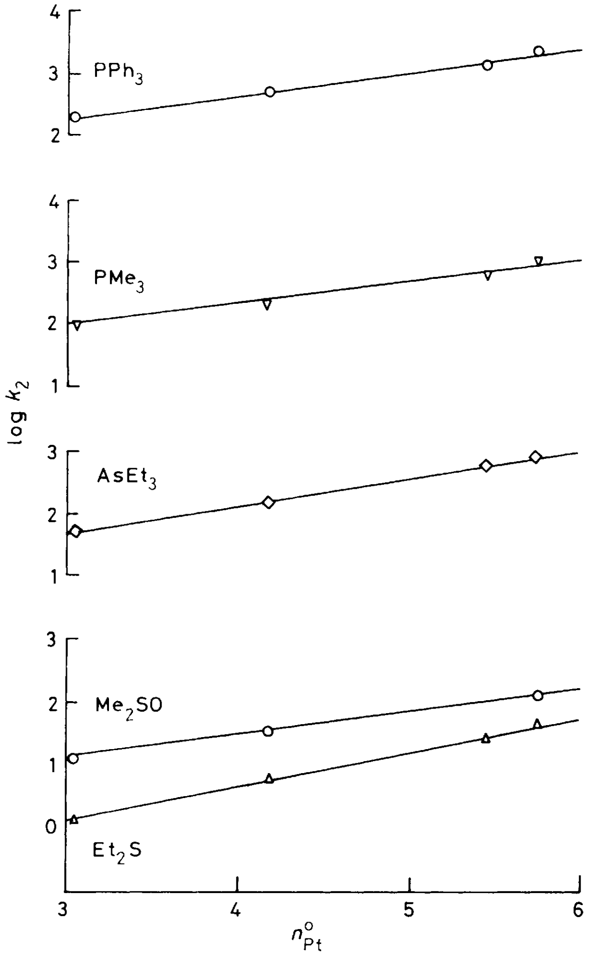

Figure 2. Plots of log k_2 *versus* n^{0}_{Pt} for displacement of MeOH from *trans*-[Pt(L)(MeOH)Cl$_2$] by nucleophiles in methanol–water (95:5) at 25.0 °C. Each line is labelled with the appropriate L

thiourea comes as a surprise. It would appear that for reasons which are not immediately apparent it is unable to exert its full biphilicity on these substrates even though pyridine is unusually effective.

Plots of log k_2 against n_{Pt}^{-} for the reactions of these nucleophiles with the anionic trichloro complexes are shown in Figure 1 and they appear to be substantially linear. The best-fit straight lines drawn through these points give nucleophilic discrimination factors (slopes) for the *trans* ligands, L: Et$_2$S, 0.86; Me$_2$SO, 1.16; AsEt$_3$, 1.00; PMe$_3$, 0.85; PEt$_3$, 0.81; PPh$_3$, 0.88. The scatter of data does not allow any significance to be given to the small differences between the different phosphine ligands, especially as the point for methanol exerts a strong influence on the final slope and yet can be the least accurate data point. Indeed, the points for reactions with MeOH lie so far off the best lines through the other data points for the [Pt(Et$_2$S)Cl$_3$]$^-$ and [Pt(Me$_2$SO)Cl$_3$]$^-$ substrates that they have been left out of the calculation for the best straight line as can be seen from a comparison of the calculated intercepts, -2.68 and -2.47, with the values of (log k_1 $-$ 1.40) = -4.11 and -3.62 for the Et$_2$S and Me$_2$SO trichloro complexes respectively. This cannot be ascribed to error in the determination of k_1 and makes any argument based on small differences in the slopes of the best lines of little value. It would nevertheless seem that the presence of Et$_2$S, PMe$_3$, PEt$_3$, or PPh$_3$ in the *trans* position has much the same effect on the nucleophilic discrimination, AsEt$_3$ produces a greater discrimination, and Me$_2$SO produces the strongest discrimination of all. This is in keeping with conclusions reached elsewhere that the *trans* effect of sulphoxides owes much to their ability to act as π-acceptor transition-state stabilisers. The use of the arsine complex as the standard gives an impression that the nucleophilic discrimination of the dimethyl sulphoxide complex is unusually high. This is purely relative and if one compares the nucleophilicity scale based on the triethylarsine complex with the n^{0}_{Pt} scale the much lower discrimination of the former becomes obvious. The transition states for all the substrates studied are reasonably open, that for the dimethyl sulphoxide complex, however, being somewhat less so than those for the others. It is of interest that the least-discriminating substrates have the largest negative slope for the plot of log k_2 for reaction with heterocyclic bases, am, *versus* the pK_a of Ham$^+$.[16] This adds further weight to the suggestion that these substituted pyridines assist their bonding in the transition state by a π-acceptor contribution.

The reactions of the methanol complex could only be studied with the non-basic anionic nucleophiles. The need to work in acid solution prevented the direct study of the reaction with pyridine and other heterocyclic bases and it was necessary to use the values for k_2 for pyridine derived from previous studies of the mass-law retardation of the solvolytic path for substitution by am into the trichloro complex in the presence of chloride. Clearly pyridine is much more reactive than might have been predicted from its n^{0}_{Pt} value but, until a wider range of nucleophiles, both neutral and anionic, are studied, we cannot distinguish between the possibilities that (*a*) the n^{0}_{Pt} scale cannot be applied to this substrate, in spite of the fact that it is uncharged, and (*b*) the pyridines are acting as biphilic species.

Plotting log k_2 for the anionic reagents against their n^{0}_{Pt} values gives reasonably good straight lines, the slopes of which indicate low discrimination: PPh$_3$ (0.33) ≈ PMe$_3$ (0.35) ≈ Me$_2$SO (0.35) < AsEt$_3$ (0.42) < Et$_2$S (0.53) (Figure 2). There are inadequate data for the reactions of the anionic [Pt(L)Cl$_3$]$^-$ with anions to make a proper comparison of discrimination using the n^{0}_{Pt} scale but from what little trends that can be observed the slopes for the methanol complexes are no higher than those for the anionic chloro analogues.

The unusual behaviour of the dimethyl sulphoxide complex is puzzling. In all other reactions the presence of a sulphoxide *trans* to the leaving group produces higher nucleophilic discrimination than other ligands exerting a strong *trans* influence. The cause for this is far from clear and is a further reason why more studies are required on this system.

Acknowledgements

We thank NATO (Grant No. 593/84) for financial assistance. M. L. T. thanks Johnson Matthey plc for providing the stopped-flow spectrometer, for the loan of materials, and for their continuing encouragement, and A. T. T. thanks the S.E.R.C. for an award.

References

1 C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' W. A. Benjamin, New York, 1965, p. 24.
2 F. B. Hitchcock, B. Jacobsen, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2043.
3 A. N. Coldwell, L. Manojlovic-Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1977, 2265.
4 F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science Publishers, London, 1973, p. 242.
5 H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 2749.
6 M. J. Church and M. Mays, *J. Chem. Soc. A*, 1970, 1938.
7 F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc. A*, 1970, 2087.

8 T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, 1978, **17**, 738.
9 J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 1955, 4455.
10 L. E. Orgel, *J. Inorg. Nucl. Chem.*, 1956, **2**, 137.
11 G. Natile, L. Maresca, and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1977, 658.
12 L. Maresca, G. Natile, M. Calligaris, P. Delise, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1976, 2386.
13 R. Romeo and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1991.
14 B. P. Kennedy, R. Gosling, and M. L. Tobe, *Inorg. Chem.*, 1977, **16**, 1744.
15 R. Gosling and M. L. Tobe, *Inorg. Chim. Acta*, 1980, **42**, 223.
16 R. Gosling and M. L. Tobe, *Inorg. Chem.*, 1983, **22**, 1235.
17 L. Canovese, M. L. Tobe, and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1985, 27.
18 U. Belluco, M. Graziani, and P. Rigo, *Inorg. Chem.*, 1966, **5**, 1123.
19 M. Cusumano, P. Marricchi, R. Romeo, V. Ricevuto, and U. Belluco, *Inorg. Chim. Acta*, 1979, **34**, 169.
20 L. Cattalini, *M.T.P. Int. Rev. Sci., Inorg. Chem. Ser. 1*, 1973, **9**, 269.
21 Y. N. Kukushkin, Y. E. Vyazmenskii, and L. I. Zorina, *Russ. J. Inorg. Chem.*, 1968, **13**, 1573.
22 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 2787.
23 J. Chatt and A. D. Westland, *J. Chem. Soc. A*, 1968, 88.
24 G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 1960, **6**, 211.
25 G. Annibale, M. Bonivento, L. Canovese, L. Cattalini, G. Michelon, and M. L. Tobe, *Inorg. Chem.*, 1985, **24**, 797.
26 E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.
27 J. H. Espenson, 'Chemical Kinetics and Reaction Mechanisms,' McGraw-Hill, New York, 1986.
28 E. F. Swinbourne, 'The Analysis of Kinetic Data,' Nelson, London, 1971.
29 N. W. Alcock, D. J. Benton, and P. Moore, *Trans. Faraday Soc.*, 1970, **66**, 2210.
30 W. G. Jackson and J. McB. Harrowfield, *Int. J. Chem. Kinet.*, 1977, **9**, 535.
31 L. Volk, W. Richardson, K. H. Lau, M. Hall, and S. N. Lin, *J. Chem. Educ.*, 1977, **54**, 95.
32 S. Chasen, 'BDMP Biochemical Computer Programs, P. Series,' ed. W. J. Dickson, University of California Press, 1977, p. 480.
33 P. C. Kong and F. D. Rochon, *Inorg. Chim. Acta*, 1979, **34**, L457.
34 U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, 1965, **87**, 241.
35 U. Belluco, M. Graziano, and P. Rigo, *Inorg. Chem.*, 1966, **5**, 1123.
36 M. Bonivento, L. Cattalini, G. Michelon, A. P. Schwab, and M. L. Tobe, *Inorg. Chem.*, 1980, **19**, 1743.
37 M. Bonivento, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon, and M. L. Tobe, *Inorg. Chem.*, 1981, **20**, 3728.
38 R. Romeo and M. Cusumano, *Inorg. Chim. Acta*, 1981, **49**, 167.
39 G. Annibale, L. Cattalini, G. Chessa, G. Marangoni, B. Pitteri, and M. L. Tobe, *Gazz. Chim. Ital.*, 1985, **115**, 279.

Received 30*th December* 1987; *Paper* 7/2269