The *cis* Effect of Phosphines and Phosphites in the Reactions of Chloro(1,2-diaminoethane)phosphine- and Chloro(1,2-diaminoethane)-trimethyl phosphite-platinum(II) Cations with Nucleophiles †

Giuliano Annibale,* Luciano Canovese, Lucio Cattalini, Giampaolo Marangoni, and Gianni Michelon
Instituto di Chimica Generale ed Inorganica, Universita di Venezia, Italy
Martin L. Tobe
C. K. Ingold Laboratory, University College London, London WC1 6BT

The kinetics of the replacement of Cl from $[Pt(PR_3)(en)Cl]^+$ (R = Me, Et, Bu^n, or OCH_3; en = 1,2-diaminoethane) by a range of nucleophiles (H_2O, Br^-, N_3^-, I^-, or SCN^-) have been studied in water at 26.5 °C. Good linear relationships are observed between log k_2^0 (k_2^0 is the nucleophile dependent second-order rate constant, extrapolated to $I = 0$ mol dm^{-3}) and the index of nucleophilicity, relative to the standard +1 cationic substrate, $[Pt(NH_3)(en)Cl]^+$. The nucleophilic discrimination is similar to that of the dimethyl sulphoxide complex but the absolute rates are sensitive to steric hindrance from the *cis* ligand (the reactivity decreases along the sequence $PMe_3 > PEt_3 \geqslant PBu^n_3$). The phosphorus in the $P(OMe)_3$ complex is also subject to nucleophilic attack and unambiguous kinetics could only be obtained in the reactions with Br^- and I^-.

As part of a program comparing the *cis* and *trans* effect of neutral ligands (L) with Group 5 and 6 donors, we have been examining the kinetics of the reactions of $[PtLCl_3]^-$ (as representative substrate for the *trans* effect of L) and $[PtL(en)Cl]^+$ (to examine its *cis* effect) (en = 1,2-diaminoethane). Until now our *trans* effect studies have been confined to reactions between the substrates and a variety of amine ligands with L = dimethyl sulphoxide (dmso),[1] SMe_2,[2] SEt_2,[3] PMe_3, PEt_3, PBu^n_3, PPh_3, $P(OMe)_3$, and $AsEt_3$.[4]

Reactions with stronger nucleophiles require the use of fast reaction techniques and are now in progress. As expected, the sensitivity of the reactivity to the nature of the donor atom of the *trans* ligand is very marked, while substituent variation leads to a comparatively minor effect. The cationic complexes with L *cis* to the leaving group are much less reactive and so the *cis* effect studies could be extended to a much greater range of nucleophiles, indeed the reactions with weak amine nucleophiles are generally too slow to be followed with any accuracy. Variation in the nature of the *cis* donor (NH_3, Me_2S, dmso) leads to far less change in reactivity and the differences in the rate constants for the reaction of a particular nucleophile with the substrates are only significant with strong nucleophiles, indicating that the electronic effects, at least, are seen as a change in nucleophilic discrimination. The other major study of *cis* effect in the literature, *i.e.* the reactions of *trans*-$[PtL_2Cl_2]$,[5] also indicate this nucleophilic discrimination difference but also exhibit a change in the intrinsic reactivity, which, until now, we have not observed. It was therefore important, in the case of phosphorus donor ligands, to see whether substituent effects play an important role in determining overall reactivity patterns. This work is reported in this paper.

Experimental

Preparations.—The precursor bridged complexes $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$ were prepared by literature methods[6] and used without further purification. All other reagents were commercial reagent grade products.

Chloro(1,2-*diaminoethane*)*trimethylphosphineplatinum*(II) *chloride*. The complex $[Pt_2(PMe_3)_2(\mu\text{-}Cl)_2Cl_2]$ (0.35 g, 0.70 mmol) was dissolved in dichloromethane (60 cm^3) and a solution of 1,2-diaminoethane (0.086 g, 1.7 mmol) in dichloromethane (5 cm^3) was added, with stirring, at room temperature. A white precipitate formed immediately and the mixture was stirred for 2 h to ensure complete reaction. The precipitate was filtered off, washed with dichloromethane (3 × 10 cm^3) and diethyl ether (20 cm^3). The crude product was obtained as white crystals by adding diethyl ether (100 cm^3) to a filtered solution in warm methanol (20 cm^3) and leaving to crystallize in an ice-bath. Yield 0.4 g (93%). The other complexes of the type [PtL(en)Cl]Cl [L = PEt_3, PBu^n_3, or $P(OMe_3)_3$] were prepared in a similar manner from the corresponding bridged dimers in similar yield. Analytical data are reported in Table 1.

(1,2-*Diaminoethane*)*iodotriethylphosphineplatinum*(II) *tetraphenylborate*. An equimolar amount of sodium iodide was added to a saturated aqueous solution of $[Pt(PEt_3)(en)Cl]Cl$ and the resultant mixture stirred for several hours. The spectrum of the solution at this time corresponded closely with that of the reaction product obtained under kinetic conditions. Addition of an aqueous solution of sodium tetraphenylborate precipitated a white powder which was filtered off, washed with water, and dried under vacuum. Analytical data are shown in Table 1.

Kinetics.—The reactions were followed spectrophotometrically using methods described elsewhere.[7] The fast reactions were followed with a Durrum D110 stopped flow spectrophotometer with the output from the log amplifier connected directly to the Servoscribe pen recorder.

Results and Discussion

With the exception of the reactions of $[Pt\{P(OMe)_3\}(en)Cl]^+$ with OH^-, N_3^-, and SCN^-, the changes of absorbance follow a pseudo-first-order rate equation, the initial spectrum corresponding to that of the substrate and the final spectrum (tested in the case of L = PMe_3, X = SCN and L = PEt_3, X = I) to that of an independently prepared and characterized sample of $[PtL(en)X][BPh_4]$. The observed changes correspond to the reaction below.

$$[PtL(en)Cl]^+ + X^- \longrightarrow [PtL(en)X]^+ + Cl^-$$

In the reactions of the trimethly phosphite complexes with

---

† *Supplementary data available* (No. SUP 23497, 4 pp.): a listing of $k_{obs.}$ as a function of $[X^-]$. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

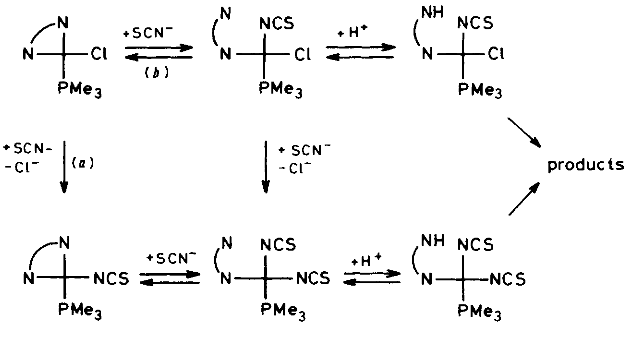
Table 1. Analytical data for the complexes

Compound	Empirical formula	Analysis * (%) C	H	N	Cl
$[Pt(PMe_3)(en)Cl]Cl$	$C_5H_{17}Cl_2N_2PPt$	14.95 (14.95)	4.25 (4.25)	6.90 (6.95)	17.55 (17.65)
$[Pt(PEt_3)(en)Cl]Cl$	$C_8H_{23}Cl_2N_2PPt$	21.55 (21.65)	5.25 (5.20)	6.40 (6.30)	16.35 (15.95)
$[Pt(PBu^n{}_3)(en)Cl]Cl$	$C_{14}H_{35}Cl_2N_2PPt$	31.50 (31.80)	6.60 (6.70)	5.40 (5.30)	13.05 (13.40)
$[Pt\{P(OMe)_3\}(en)Cl]Cl$	$C_5H_{17}Cl_2N_2O_3PPt$	13.10 (13.35)	3.70 (3.80)	6.25 (6.20)	15.30 (15.75)
$[Pt(PMe_3)(en)(SCN)][BPh_4]$	$C_{30}H_{37}BN_3PPtS$	50.80 (50.85)	5.40 (5.25)	5.85 (5.95)	
$[Pt(PEt_3)(en)I][BPh_4]$	$C_{32}H_{43}BIN_2PPt$	47.10 (46.90)	5.35 (5.30)	3.35 (3.40)	

* Calculated values in parentheses.

OH^-, N_3^-, and SCN^- two overlapping changes are observed and the kinetics could not be properly analyzed. It is suggested that there is a parallel and interfering reaction involving attack by the nucleophile at the co-ordinated phosphorus and these systems were not measured further. The rate of substitution of the *trans* chloride in $[Pt\{P(OMe)_3\}Cl_3]^-$ is too fast for attack at phosphorus to interfere with, or even to be observed in, the reactions of these substrates with OH^- or amines.[4] A more serious problem that might arise in the studies of the reactions of $[Pt(PR_3)(en)Cl]^+$ is the opening of the diamine chelating ring under the *trans* influence of the phosphine. The relevance of this possible pathway was examined in detail for the reaction of $[Pt(PMe_3)(en)Cl]^+$ with thiocyanate ions. Within the range of $[SCN^-]$ used for the study of the substitution reaction (10^{-3}—10^{-1} mol dm^{-3}) the fastest spectrophotometric change is consistent with a single-stage first-order conversion of a species whose spectrum is that of the starting material in the absence of SCN^- to another whose spectrum is identical to that of an independently prepared and characterized sample of $[Pt(PMe_3)(en)(SCN)]^+$ but this is followed by a slower second stage, which corresponds to an increase in absorbance over the whole range of wavelength studied. The final spectrum depends on the concentration of thiocyanate studied and is suppressed by the addition of small amounts of hydroxide before the reaction is initiated. The reaction appears to be reversible and, if the hydroxide is added at the end of the reaction, the spectrum changes rapidly to that of $[Pt(PMe_3)(en)(SCN)]^+$. Studies carried out at much higher concentrations of SCN^- and followed in a Durrum D110 stopped flow spectrophotometer show that the first step is still present and has the rate expected for the concentration of thiocyanate used. Because of the large difference in rate it is not possible to say, unambiguously, whether the second stage is parallel to, or consecutive with, the first reaction.

The extent of the second reaction can be much enhanced if acid is present. For a constant SCN^- the rate increases to a H^+ independent value for $[H^+] = 1.5 \times 10^{-2}$ mol dm^{-3}. At constant H^+ the dependence of $k_{obs.}$ upon SCN^- approaches linearity with increasing nucleophile concentration, the limiting slope at $[H^+] = 1.4 \times 10^{-2}$ mol dm^{-3} being 0.2 dm^3 mol^{-1} s^{-1}. The system has not yet been examined in sufficient detail for a full analysis but everything is consistent with the Scheme.* The rate constants are such that the direct pathway (*a*) predominates for the first stage, the replacement of Cl by SCN, and the second stage is an interesting but irrelevant side reaction. The ring opening reaction (*b*) appears to be much slower than might have been predicted from a calculation based on the rate constants for ring opening in the $[Pt(dmso)(en)Cl]^+$ cation in its reaction with HCl,[8] the enhanced *trans* effect of PMe_3 when compared to dmso,[4] and the greater nucleophilicity of SCN^-. It is suspected that the *trans* effect of phosphine lowers the nucleophilic discrimination of the platinum and k_2 for ring opening by thiocyanate may not be very much greater than that for Cl^-. This remains speculative and indicates a need for a careful examination of the relationship between *trans* effect and nucleophilic discrimination.



Scheme.

The pseudo-first-order rate constants were obtained from the slopes of plots of ln $(A_t - A_\infty)$ *versus* time *t*, where A_t and A_∞ are the absorbances after time *t* and six half-lives respectively. These plots were linear for at least four half-lives. Interference from subsequent stages was either not serious or else could be minimized by a suitable choice of wavelength.

The values of $k_{obs.}$ are linearly dependent upon the concentration of nucleophile. The values of intercepts and gradients, calculated from unweighted least-squares fits with quoted uncertainties at 95% confidence level, are reported in Table 2. The dependence is consistent with the usual two terms rate law, $k_{obs.} = k_1 + k_2[X]$, but as is common in reactions of this sort with the stronger nucleophiles, the errors in the determination of the value of k_1 are large (often larger than the value itself). For this reason we determined k_1 independently from the first-order change in the presence of hydroxide which leads to a stable product but does not introduce a OH^- dependent contribution to the rate law.

In this work all nucleophiles except the solvent have the same charge but the extrapolation of k_2 to $I = 0$ (k_2^0) allows direct comparison with previous works. The values of k_2^0 were calculated from the expression[9] $\log k_2 = \log k_2^0 + 1.03\, z_A z_B I^{\frac{1}{2}} (1 + I^{\frac{1}{2}})^{-1}$ and are reported in Table 2 (k_2^0 for the solvent path is $k_1/[H_2O]$).

Plots of log k_2^0 for the phosphine complexes against log k_2^0 for the standard substrate, $[Pt(NH_3)(en)Cl]^+$ are linear (Figure) and of the same slope, within experimental error (slope = 1.24 ± 0.07 for PMe_3, 1.21 ± 0.04 for PEt_3, and

---

* The type of bonding (Pt–S or Pt–N) in the reaction scheme is not solved.

Table 2. (*a*) Slopes (k_2) and intercepts (k_1) from the linear least-squares analysis of $k_{obs.}$ *versus* $[X^-]$ for the reaction $[PtL(en)Cl]^+ + X^- \rightarrow [PtL(en)X]^+ + Cl^-$ at 26.5 °C and $I = 0.1$ mol dm^{-3} ($NaClO_4$) in water. k_2^0 is k_2 extrapolated to $I = 0$

L	X	10^3k_2/ dm^3 mol^{-1} s^{-1}	$10^3k_2^0$/ dm^3 mol^{-1} s^{-1}	10^5k_1/s^{-1}
PMe_3	N_3^-	7.52 ± 0.10	13.3	2.80 ± 0.63
	Br^-	10.0 ± 0.2	17.7	3.12 ± 1.36
	I^-	651 ± 9	1 150	−44 ± 29
	SCN^-	1 020 ± 110	1 803	30 ± 369
PEt_3	N_3^-	2.11 ± 0.08	3.73	1.63 ± 0.38
	Br^-	2.26 ± 0.06	4.00	1.61 ± 0.36
	I^-	154 ± 3	272	−53 ± 12
	SCN^-	257 ± 12	454	14 ± 50
PBu^n_3	N_3^-	1.41 ± 0.04	2.49	0.85 ± 0.26
	Br^-	1.37 ± 0.08	2.42	0.90 ± 0.51
	I^-	96.6 ± 1.2	171	16 ± 71
	SCN^-	256 ± 10	453	17 ± 48
$P(OMe)_3$	Br^-	6.42 ± 0.42	11.3	1.25 ± 2.54
	I^-	484 ± 32	856	−8 ± 194

(*b*) Values of $k_{obs.}(= k_1)$ for the reaction $[PtL(en)Cl]^+ \rightarrow [PtL(en)(OH)]^+$ under the same conditions

L	$10^5k_{obs.}$/s^{-1}
PMe_3	4.24
PEt_3	1.51
PBu^n_3	1.00

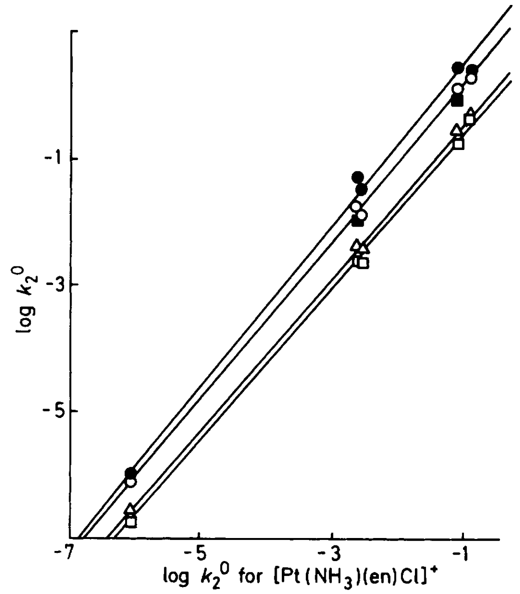


Figure. Values of log k_2^0 for the reactions of the complexes $[PtL(en)Cl]^+$ where L = PBu^n_3 (□), PEt_3 (△), $P(OMe)_3$ (■), PMe_3 (○), and dmso (●) plotted against the values of log k_2^0 for the standard complex $[Pt(NH_3)(en)Cl]^+$

1.29 ± 0.07 for PBu^n_3). Since only two nucleophiles were examined with L = $P(OMe)_3$ it is rash to talk of a slope, but the points lie fairly close to those for L = PMe_3. The lower reactivities of the PEt_3 and PBu^n_3 complexes are seen to arise from downward displacement of the whole plot, with the PBu^n_3 complex marginally less reactive than that of PEt_3.

The nucleophilic discrimination of the phosphine complexes is therefore greater than that of the thioether complexes (slope = 1.14 ± 0.05 for L = SMe_2 [2]) but is no greater than that for L = dmso (1.26 ± 0.05), indeed the absolute values for k_2^0 for the L = PMe_3 and L = dmso complexes are very similar. The absence of adequate data for the L = $P(OMe)_3$ complex does not allow any firm statement as to the consequences of the enhanced π-acceptor properties of the phosphorus (a factor invoked to explain the difference between the behaviour of the Me_2S and dmso complexes) but the two points we have been able to obtain suggest that the effect is not likely to be large.

The main cause of the substituent *cis* effect in these complexes is therefore steric in origin. It is well known that steric hindrance from ligands *cis* to the leaving group, which will sit in the axial position in the quasi trigonal bipyramidal transition state, has a very large effect upon reactivity [10] and we suggest that this work presents a further example of this phenomenon. The results can be compared to the extensive studies of the nucleophilic discrimination of the neutral *trans*-$[PtL_2Cl_2]$ species.[5] The effects are smaller, partly due to the presence of the *cis* donor undergoing change and partly we suspect because the effect is less important as the charge of the substrate increases. Current studies with 2+ cations suggest that variation of the *cis* ligands does not change the nucleophilic discrimination to any great extent but the work is far from complete and any such statement must remain speculative. There has not been any systematic examination of the *cis* substituent effect in these systems but we suspect that the considerably lower reactivity of *trans*-$[Pt(PEt_3)_2Cl_2]$ when compared to *trans*-$[Pt(py)_2Cl_2]$ (py = pyridine) is due to steric effects and predict that the reactions of *trans*-$[Pt(PMe_3)_2Cl_2]$ will be significantly faster.

Acknowledgements

We thank the Italian Council for Research (C.N.R., Rome) and the British Council for financial support of a bilateral research project. $K_2[PtCl_4]$ was generously loaned by Johnson Matthey Ltd. M. L. T. thanks the Central Research Fund of the University of London for an equipment grant. G. A. thanks NATO for a scholarship.

References

1 R. Romeo and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1991.
2 B. P. Kennedy, R. Gosling, and M. L. Tobe, *Inorg. Chem.*, 1977, **16**, 1744.
3 R. Gosling and M. L. Tobe, *Inorg. Chim. Acta*, 1980, **42**, 223.
4 R. Gosling and M. L. Tobe, *Inorg. Chem.*, submitted for publication; R. Gosling, Ph.D. Thesis, University of London, 1979.
5 U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, 1965, **87**, 241.
6 R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc.*, 1965, 7533 and refs. therein.
7 M. Bonivento, L. Cattalini, G. Marangoni, G. Michelon, A. Schwab, and M. L. Tobe, *Inorg. Chem.*, 1980, **19**, 1743.
8 R. Romeo, S. Lanza, and M. L. Tobe, *Inorg. Chem.*, 1977, **16**, 785.
9 A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, p. 150.
10 L. Cattalini, *Prog. Inorg. Chem.*, 1970, **13**, 302.

Received 7*th June* 1982; *Paper* 2/947