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Kinetics of Ligand Substitution in Platinum(II) Complexes: a Study on the Concept of Nucleophilic Discrimination

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Abstract

Several platinum(II) complexes of the general type [Pt(OND)X] have been prepared and characterized, the ligand (OND) representing the phenolate anion of the tridentate Schiff bases *N*-(2-diethylaminoethyl)-salicylaldimine (D = NEt_2), *N*-(2-ethylaminoethyl)-salicylaldimine (D = NHEt) and *N*-(3-thia-n-pentyl)-salicylaldimine (D = SEt) and X = Cl, NO_3. As shown by conductimetric studies the nitrato complexes [Pt(OND)NO_3] dissociate completely in methanol according to:

$$[\mathrm{Pt(OND)NO_3}] + \mathrm{H_2O}\ (\text{in MeOH}) \rightleftharpoons [\mathrm{Pt(OND)(H_2O)}]^+ + \mathrm{NO_3^-}$$

Spectrophotometry (normal and stopped-flow) has been used to study the kinetics of solvent substitution according to

$$[\mathrm{Pt(OND)(H_2O)}]^+ + \mathrm{Y} \rightleftharpoons [\mathrm{Pt(OND)Y}]^+ + \mathrm{H_2O}$$

with a variety of neutral and anionic nucleophiles Y in methanol at 20 °C and constant ionic strength, $I = 0.2$ M ($NaClO_4$). The substitution follows a one-term rate law, $v = k_{obs}[\mathrm{Pt(OND)(H_2O)^+}] = k_Y[\mathrm{Y}]\cdot[\mathrm{Pt(OND)(H_2O)^+}]$. The k_Y data obtained for 13 (D = NEt_2) and 7 (D = NHEt; SEt) different nucleophiles Y cannot be adequately correlated with their n^0_{Pt} values according to the well-known relationship $\log k_Y = sn^0_{Pt} + \log k_S$. The deviations are strongest for large and bulky nucleophiles such as Y = Ph_3P, Bu_3P, Ph_3As, I^- and for D = NEt_2, from which it is concluded that steric crowding hinders the formation of the 5-coordinate transition state. The rate reducing steric *cis*-effect observed is of the order $k_Y(\mathrm{D = NEt_2}):k_Y(\mathrm{D = NHEt}):k_Y(\mathrm{D = SEt}) = 1:35:63$ for small nucleophiles Y and as large as 1:192:2640 for Y = Ph_3P. The introduction of substituents X in the salicylaldehyde ring in *ortho* (X^3), *meta* (X^4) and *para* position (X^5) to the phenolic oxygen proves the existence of rather small electronic effects (X^4, X^5) and much stronger steric effects of bulky substituents X^3, neighboring the donor oxygen.

With the standard substrate *trans*-[$Ptpy_2Cl_2$] some new n^0_{Pt} values were determined, namely for *N,N'*-dimethylthiourea ($n^0_{Pt} = 7.02$), *N,N'*-diphenylthiourea ($n^0_{Pt} = 7.19$), *N,N,N',N'*-tetramethylthiourea ($n^0_{Pt} = 6.05$) and for the pseudo-halide dicyanoamide ion, $N(CN)_2^-$ ($n^0_{Pt} = 3.05$). The n^0_{Pt} value for the pseudo-halide tricyanomethanide ion, $C(CN)_3^-$, was estimated to be 3.03.

Introduction

Ligand substitution in Pt(II) complexes according to eqn. (1) follows the two-term rate law (eqn. (2))

$$\mathrm{L_3Pt{-}X} + \mathrm{Y} \rightleftharpoons \mathrm{L_3Pt{-}Y} + \mathrm{X} \qquad (1)$$

in which the ligand-dependent contribution $k_Y[\mathrm{Y}]$ (ligand path) is in general much greater than the

$$\text{rate} = (k_S + k_Y[\mathrm{Y}])[\mathrm{L_3PtX}] = k_{obs}[\mathrm{L_3PtX}] \qquad (2)$$

solvent-initiated, ligand-independent contribution k_S (solvent path). Both pathways are associative (A-mechanism) and the reactivity of the nucleophile Y is characterized by its n^0_{Pt} value [1]. This parameter refers to the standard substrate *trans*-[$Ptpy_2Cl_2$] reacting according to eqn. (1) in methanol at 30 °C and is defined by eqn. (3) [1]:

$$n^0_{Pt} = \log(k_Y/k'_S) = \log\left(\frac{k_Y[\mathrm{MeOH}]}{k_S}\right) \qquad (3)$$

The n^0_{Pt} values of more than 40 nucleophiles Y have been determined and range from 3 (Y = Cl^-) to 9 (Y = Ph_3P), thus demonstrating an enormous spread in nucleophilicity.

The significance of the n^0_{Pt} scale is evidenced by the finding that in many cases a relationship (eqn.

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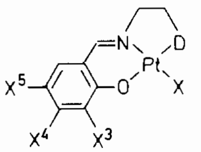
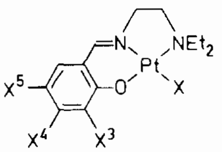
(4)) can be successfully applied to describe the reactivity of nucleophiles Y towards Pt(II) complexes other than the standard substrate *trans*-[Ptpy$_2$Cl$_2$] [1]. The parameter s, which fits rate constant k_Y for a given platinum complex to the n^0_{Pt} scale, is called 'nucleophilic discrimination factor'.

$$\log k_Y = s \cdot n^0_{Pt} + \log k_S \qquad (4)$$

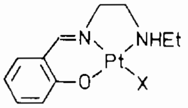
The present study was carried out to test the general applicability of eqn. (4) to several new Pt(II) complexes of type **I** (X = anion) with D representing a NEt$_2$ group (**Ia**), a NHEt group (**Ib**) or a SEt group (**Ic**).



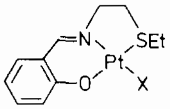
I



Ia



Ib



Ic

As shown for the corresponding Pd(II) complex **Ia** (X = Cl; $X^3 = X^4 = X^5 = H$) by single crystal X-ray analysis, these complexes have an almost square-planar arrangement of the donor atoms around the metal, the phenyl ring being slightly bent off [2]. The following symbols will be used:

I $\hat{=}$ PtX^3, X^4, X^5-OND)X

Ia $\hat{=}$ Pt(ONNEt$_2$)X

Ib $\hat{=}$ Pt(ONNHEt)X

Ic $\hat{=}$ Pt(ONSEt)X

In methanol the nitrato complexes **I** (X = NO$_3$) dissociate according to eqn. (5) (S = solvent):

$$\mathrm{Pt(OND)NO_3 + S \rightleftharpoons Pt(OND)S^+ + NO_3^-} \qquad (5)$$

Reaction (eqn. (6)) was studied in methanol (I = 0.2 M; NaClO$_4$) at 20 °C for a variety of neutral and anionic nucleophiles Y and for substituted and non-substituted complexes **Ia**–**Ic** by normal and stopped-flow spectrophotometry:

$$\mathrm{Pt(OND)S^+ + Y \longrightarrow Pt(OND)Y^+ + S} \qquad (6)$$

In the course of the study it became necessary to determine the hitherto unknown n^0_{Pt} values for the dicyanoamide anion (N(CN)$_2^-$) and for several *N*-alkylated thiourea derivatives according to eqn. (1) (L$_3$Pt–X $\hat{=}$ *trans*-[Ptpy$_2$Cl$_2$]) and eqn. (3).

Experimental

Solvent and Nucleophiles Y

The solvent MeOH (Merck, Darmstadt) was reagent grade and was used without further treatment. The nucleophiles Y applied for the study of the reaction (eqn. (6)) were all commercially available and were either bought in reagent grade quality (Ph–S–Me, thiourea = TU; LiCl; LiBr; NaSCN; [(n-Bu)$_4$N]I = TBAI; NaN(CN)$_2$ = NaDCA) or purified by recrystallization (Ph$_3$P; Ph$_3$As; *N,N'*-dimethylthiourea = DMTU; *N,N'*-diphenylthiourea = DPTU; *N,N,N',N'*-tetramethylthiourea = TMTU) or by fractional distillation (tri-n-butylphosphane = Bu$_3$P). The NaClO$_4$ applied for adjusting the ionic strength to I = 0.2 M was reagent grade.

Ligands

The tridentate Schiff base ligands were prepared by reacting substituted or non-substituted salicylaldehyde with H$_2$N–CH$_2$–CH$_2$–NEt$_2$ (Aldrich, Steinheim), H$_2$N–CH$_2$–CH$_2$–NHEt (Aldrich, Steinheim) or H$_2$N–CH$_2$–CH$_2$–SEt (as prepared from phthalimide, 1,2-dibromoethane and ethanethiol according to a modified procedure described in the literature [3]). The substituted salicylaldehydes were either commercially available (4-methoxysalicylaldehyde, 5-methoxysalicylaldehyde) or prepared according to standard procedures (5-methylsalicylaldehyde [4], 5-bromosalicylaldehyde [5], 5-iodosalicylaldehyde [6], 5-nitrosalicylaldehyde [7], 3,5-diiodosalicylaldehyde [8], 3-t-butyl-5-methylsalicylaldehyde [9]).

The following standard procedure was applied for the formation of the various Schiff bases. A solution of 50 mmol amine in 15 ml EtOH is added to a stirred solution of 49 mmol salicylaldehyde in 100 ml EtOH, whereupon the mixture turns yellow immediately. After 30 min of further stirring at slightly elevated temperature the solution is evaporated to dryness by vacuum distillation, finally at 90 °C, to remove excess amine and water. The residual red–brown, oily Schiff base is reacted with PtCl$_2$ without further purification.

Complexes

trans-[Ptpy$_2$Cl$_2$] was prepared from K$_2$PtCl$_4$ according to a standard procedure [10] and characterized by elemental analysis.

The complexes [Pt(OND)NO$_3$] were prepared by the following standard procedure: 0.8 g PtCl$_2$ (3 mmol; Degussa, Frankfurt), 0.42 g Na$_2$CO$_3$ (4 mmol),

TABLE I. Results of Elemental Analysis for the Nitrato Complexes **Ia–Ic**

Complex	Melting point[a] (°C)	C(%)		H(%)		N(%)	
		calc.	found	calc.	found	calc.	found
$Pt(ONNEt_2)NO_3$	210–213	32.78	32.61	4.02	3.80	8.82	8.73
$Pt(ONNHEt)NO_3$	215(dec)	29.47	29.61	3.77	3.34	9.37	9.18
$Pt(ONSEt)NO_3$	112–115	28.39	28.46	3.03	2.94	6.02	5.69
$Pt(5\text{-}Br\text{-}ONNEt_2)NO_3$	213(dec)	28.12	28.25	3.27	3.33	7.57	7.51
$Pt(5\text{-}I\text{-}ONNEt_2)NO_3$	195(dec)	25.92	25.94	3.01	3.06	6.98	6.84
$Pt(3{,}5\text{-}I_2\text{-}ONNEt_2)NO_3$	171(dec)	21.44	22.18	2.35	2.62	5.77	6.00
$Pt(5\text{-}NO_2\text{-}ONNEt_2)NO_3$	236(dec)	29.95	29.42	3.48	3.41	10.75	10.45
$Pt(5\text{-}Me\text{-}ONNEt_2)NO_3$	210(dec)	34.29	34.02	4.31	4.18	8.57	8.37
$Pt(3\text{-}t\text{-}Bu\text{-}5\text{-}Me\text{-}ONNEt_2)NO_3$	192–195	39.56	39.79	5.35	5.43	7.69	7.56
$Pt(4\text{-}MeO\text{-}ONNEt_2)NO_3$	224(dec)	33.20	33.41	4.18	4.11	8.30	8.04
$Pt(5\text{-}MeO\text{-}ONNEt_2)NO_3$	124(dec)	33.20	33.24	4.18	4.26	8.30	7.69

[a] dec, decomposition.

3 mmol tridentate Schiff base and 35 ml DMSO are heated in a two-neck-flask to 80–85 °C for 30 min under vigorous stirring (the flask is equipped with a cooler and an inner thermometer). After that a small sample of the reaction mixture is withdrawn and added to water; the formation of a yellow precipitate indicates the formation of the complex [Pt(OND)Cl]. The reaction mixture is then filtered, reduced to 10 ml by vacuum distillation and poured into 60 ml of water saturated with NaCl. The yellow precipitate of [Pt(OND)Cl] formed is filtered, washed with water and dissolved in chloroform. The chloroform solution is dried with anhydrous $CaCl_2$ and evaporated to dryness; the residual chloro complex is recrystallized from EtOH.

To convert the chloro complex [Pt(OND)Cl] into the nitrato complex $[Pt(OND)NO_3]$, 1.75 mmol of [Pt(OND)Cl] are dissolved in slightly warmed EtOH (approx. 100 ml or more, if necessary) and 1.75 mmol solid $AgNO_3$ are added. The reaction mixture is kept at 40 °C for 30 min in the dark and the precipitate of AgCl formed is then filtered off. The volume of the yellow filtrate is reduced by vacuum distillation and the crystals of pure $[Pt(OND)NO_3]$ formed are filtered off and dried at 80 °C. Further recrystallization from EtOH is not necessary as long as the precipitate of AgCl is coarse enough not to pass the filter upon filtration.

Table I presents the results of elemental analysis. The complexes were additionally characterized by their ^1H NMR spectra, IR spectra and UV–Vis spectra (see Table II).

In the solid state the nitrato complexes $[Pt(OND)NO_3]$ are stable towards air and light. Their methanol solutions, however, should be kept in the dark to avoid slow decomposition. The methanol solutions of $[Pt(5\text{-}Me\text{-}ONNEt_2)NO_3]$ and $[Pt(5\text{-}NO_2\text{-}ONNEt_2)NO_3]$ begin to decompose even in the dark after 4–5 h.

UV–Vis Spectra and Conductance Data

The spectra were recorded with a double beam UV–Vis spectrophotometer (Zeiss, type DMR-22 WL, or Perkin-Elmer, type PE 554) in quartz cells.

Conductivity data were obtained with the conductometer type E 365 B (Metrohm) connected to cells with cell constants of 0.805 and 0.673 cm^{-1}. The equivalent conductance of the nitrato complexes $[Pt(OND)NO_3]$ (see Table III) was determined for the concentration range 5×10^{-3} to 1×10^{-4} M. When ligand substitution in *trans*-$[Ptpy_2Cl_2]$ by neutral nucleophiles Y was followed conductimetrically the conductometer was connected to a recorder to register the κ/t curves (κ = specific conductance).

Kinetic Measurements

Most of the kinetic runs were monitored spectrophotometrically, either by standard spectrophotometry (reactions with a half life of $t_{1/2} > 1$ min) or by 'stopped-flow' spectrophotometry ($t_{1/2} < 1$ min). The equipment used for the latter technique has been described earlier [11]. The measurement of the absorbance $A = f(t)$ was carried out under pseudo-first-order conditions ([Y] $\gg$ [complex]) at a wavelength with a maximum difference ΔA between initial complex and product (see Table V). Some kinetic runs were monitored conductimetrically (see Table IV).

To evaluate the experimental rate constant k_{obs} a total of approximately 50 A/t or κ/t data points were fitted to the function $(A - A_\infty)/(A_0 - A_\infty) = \exp(-k_{obs} \cdot t)$ or to the function $(\kappa - \kappa_\infty)/(\kappa_0 - \kappa_\infty) = \exp(-k_{obs} \cdot t)$ with a computer program based on the least-squares method. The deviation from ideal first-order kinetics was smaller than 2%.

Calculation of the n^0_{Pt} Values

The n^0_{Pt} values were calculated on the basis of eqn. (3). Both k_Y and k_S follow from plotting k_{obs}

TABLE II. UV–Vis Absorption Data[a] for Complexes [Pt(OND)NO_3] and [Pt(OND)Y][b] in Methanol

Complex	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)
Pt($ONNEt_2$)NO_3	6640	290	5010	306(sh)	3290	393
Pt($ONNEt_2$)(Ph-S-Me)$^+$					3020	393
Pt($ONNEt_2$)SCN	5640	290(sh)			2730	395
Pt($ONNEt_2$)(TMTU)$^+$					1710	394
Pt($ONNEt_2$)(DMTU)$^+$					2620	390
Pt($ONNEt_2$)(DPTU)$^+$					1940	390
Pt($ONNEt_2$)(Bu_3P)$^+$	8200	281			2960	387
Pt($ONNEt_2$)Cl	5350	301	3930	324(sh)	2790	398
Pt($ONNEt_2$)py$^+$					3050	388
Pt($ONNEt_2$)Br	5300	305	3700	328(sh)	2560	400
Pt($ONNEt_2$)I	5410	318			2390	395
Pt($ONNEt_2$)(Ph_3As)$^+$			4160	312(sh)	3020	388
Pt($ONNEt_2$)(TU)$^+$					2450	388
Pt($ONNEt_2$)(Ph_3P)$^+$					2960	392
Pt(5-Br-$ONNEt_2$)NO_3	5750	292	4440	309(sh)	3380	404
Pt(5-I-$ONNEt_2$)NO_3	5730	290(sh)	4270	310(sh)	3050	406
Pt(3,5-I_2-$ONNEt_2$)NO_3	5520	300(sh)	4380	320(sh)	3470	412
Pt(5-NO_2-$ONNEt_2$)NO_3	14860	258	11100	288	13000	354
Pt(5-Me-$ONNEt_2$)NO_3	7500	292	5240	310(sh)	3400	405
Pt(3-t-Bu-5-Me $ONNEt_2$)NO_3	6320	290	4780	310(sh)	3360	409
Pt(4-MeO-$ONNEt_2$)NO_3	10700	297			4960	377
Pt(5-MeO-$ONNEt_2$)NO_3	5640	294	4440	310(sh)	3420	425
Pt(ONNHEt)NO_3	11790	291	9600	306(sh)	6410	394
Pt(ONNHEt)Cl	10470	300	8400	310(sh)	5200	400
Pt(ONNHEt)py$^+$					6150	392
Pt(ONNHEt)Br	10490	304	8350	320(sh)	5700	401
Pt(ONNHEt)I					4590	398
Pt(ONNHEt)(Ph_3As)$^+$					6100	389
Pt(ONNHEt)(TU)$^+$					4880	391
Pt(ONNHEt)(Ph_3P)$^+$					5640	393
Pt(ONSEt)NO_3	14350	287			5640	391
Pt(ONSEt)Cl	13050	298			5140	396
Pt(ONSEt)py$^+$					5400	386
Pt(ONSEt)Br	13000	302			4910	398
Pt(ONSEt)I					4040	394
Pt(ONSEt)(Ph_3As)$^+$					5370	386
Pt(ONSEt)(TU)$^+$					4700	388
Pt(ONSEt)(Ph_3P)$^+$					5170	388

[a] Standard conditions: [complex] = 10^{-4} M; [$NaClO_4$] = 0.2 M; T = 20 °C. [b] Data refer to final spectra obtained after addition of an at least 100 fold excess of the nucleophile Y to the nitrato complex [Pt(OND)NO_3].

versus the concentration of entering nucleophile Y, rate constant k_S representing the intercept at [Y] = 0. Especially for very nucleophilic ligands Y (*i.e.*, for $k_Y \gg k_S$) extrapolation to [Y] = 0 produces k_S values with a large error. Therefore, the value $k_S = 6.67 \times 10^{-6}$ s^{-1} ($k'_S = 2.7 \times 10^{-7}$ M^{-1} s^{-1}) was taken from the literature [12].

The n_{Pt}^0 values applied for correlating the observed rate constants according to eqn. (4) are those stemming from the pioneering work done by Belluco *et al.* [13] and Pearson *et al.* [12], except for the nucleophile Ph–S–Me (n_{Pt}^0 = 4.30 [14]*).

Results and Discussion

UV–Vis Spectra

The absorption data for the nitrato complexes **Ia**–**Ic** as obtained from their methanol solutions in the presence of $NaClO_4$ (0.2 M) at 20 °C are compiled in Table II together with the spectra resulting in the presence of excess nucleophile Y.

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*The n_{Pt}^0 value obtained is slightly smaller than n_{Pt}^0 (Ph–S–Me) = 4.45, which can be derived from the work carried out by Hoover and Zipp [15].

It follows from Table II that the spectra of all substituted and non-substituted complexes [Pt(OND)X] are very similar indeed. There is one absorption band in the range $\lambda = 290–305$ nm ($\epsilon \approx 5000–13\,000$ M^{-1} cm^{-1}) with a shoulder in the range $\lambda = 305–320$ nm and another absorption band in the range $\lambda = 385–410$ nm ($\epsilon \approx 2000–6000$ M^{-1} cm^{-1}). The latter one is probably due to a $n \rightarrow \pi^*$ transition at the phenolate oxygen, whereas the others refer to charge transfer and inner ligand transitions. There is practically no absorption beyond λ = 420 nm and the spectra do not provide any indication for bridged species, which is in agreement with the finding that the corresponding palladium complex [$Pd(ONNEt_2)Cl$] is monomeric in the solid state [2].

Substituents X^5 on the aromatic ring clearly affect the lowest energy absorption in the sense that an electron withdrawing substituent such as the nitro group causes a blue shift ($\lambda_{max} = 354$ nm) and that an electron releasing substituent such as the methoxy group causes a red shift ($\lambda_{max} = 425$ nm). A simple correlation of λ_{max} with the corresponding Hammett parameters is not possible, however.

Any variation of or at the donor atom D affects neither λ_{max} of the lowest energy absorption (393, 394 and 391 nm for D = NEt_2, NHEt and SEt) nor λ_{max} of the highest energy absorption significantly (290, 291 and 287 nm), which thus proves that any Pt–D charge transfer does not occur in this wavelength range.

The data compiled in Table II were taken as the basis for finding the optimum wavelength for the spectrophotometrically monitored substitution reactions.

Solubility and Dissociation

The nitrato complexes [$Pt(OND)NO_3$] are easily soluble in acetone, MeOH, EtOH and DMSO, less soluble in t-BuOH, water and chloroform and only sparingly soluble in solvents such as benzene and 2,4-dimethylpentanol-3.

Table III presents the data obtained for the equivalent conductance Λ in MeOH at ambient temperature. The values for Λ (corrected for solvent conductance) lie in the range 79–91 Ω^{-1} cm^2 mol^{-1}. According to Geary's review [16] on conductance data of different electrolytes in MeOH the 1:1 and 1:2 electrolytes produce an equivalent conductance in the range 80–115 and 160–220 Ω^{-1} cm^2 mol^{-1}, respectively. This means that the nitrato complexes studied (see Table III) behave as 1:1 electrolytes, *i.e.*, dissociate completely. It is of interest to note that the corresponding chloro complexes [Pt(OND)Cl] dissociate to a much lesser extent.

The complete dissociation of the nitrato complexes according to eqn. (5) raises the question as to what the solvent S really is. Considering the fact that the reagent grade MeOH applied contains residual water ($[H_2O]_{max} = 0.025$ M) the ratio [complex]/[H_2O] is approximately 1:250 and the ratio [H_2O]/[MeOH] corresponds to 1:1250. So, there is much more water than complex and much more methanol than water. If in eqn. (5) the solvent S were MeOH, any increase in the water concentration should shift the equilibrium (eqn. (7)) towards the aquo species $[Pt(OND)(H_2O)]^+$:

TABLE III. Equivalent Conductance Λ of the Nitrato Complexes in Methanol

Complex[a]	Λ^b (Ω^{-1} cm^2 mol^{-1})
$Pt(ONNEt_2)NO_3$	88.5
$Pt(ONNHEt)NO_3$	85.4
$Pt(ONSEt)NO_3$	90.1
$Pt(5\text{-}Br\text{-}ONNEt_2)NO_3$	91.0
$Pt(5\text{-}I\text{-}ONNEt)_2)NO_3$	89.0
$Pt(3,5\text{-}I_2\text{-}ONNEt_2)NO_3$	86.9
$Pt(5\text{-}NO_2\text{-}ONNEt_2)NO_3$	83.8
$Pt(5\text{-}Me\text{-}ONNEt_2)NO_3$	88.5
$Pt(3\text{-}t\text{-}Bu\text{-}5\text{-}Me\text{-}ONNEt_2)NO_3$	83.4
$Pt(4\text{-}MeO\text{-}ONNEt_2)NO_3$	80.2
$Pt(5\text{-}MeO\text{-}ONNEt_2)NO_3$	79.0

[a]Concentration range $5 \times 10^{-3}–1 \times 10^{-4}$ M. [b]Averaged values.

$$Pt(OND)(MeOH)^+ + H_2O \rightleftharpoons Pt(OND)(H_2O)^+ + MeOH \qquad (7)$$

The kinetic finding, however, that the stepwise increase of the water concentration up to [H_2O] = 0.2 M does not affect the rate of solvent replacement in the species $[Pt(ONNEt_2)S]^+$ by iodide ions is very much in favor of the interpretation given by eqn. (8) with water being coordinated instead of methanol:

$$Pt(OND)NO_3 + H_2O(\text{in MeOH}) \rightleftharpoons Pt(OND)(H_2O)^+ + NO_3^- \qquad (8)$$

The more correct description of ligand replacement in the nitrato complexes according to eqn. (6) is therefore given by eqn. (9), with coordinated water being replaced by neutral and anionic nucleophiles Y:

$$Pt(OND)(H_2O)^+ + Y \rightleftharpoons Pt(OND)Y^+ + H_2O \qquad (9)$$

The attempt to isolate the aquo complex as perchlorate $[Pt(OND)(H_2O)]ClO_4$ was not successful. The product obtained was not uniform, which indicates that in the solid state the formation of the neutral substrate [Pt(OND)X] instead of the salt $[Pt(OND)(H_2O)]X$ is obviously preferred. In addi-

TABLE IV. Kinetic Data for the Reaction of *trans*-[Ptpy$_2$Cl$_2$] with Various Nucleophiles Y in Methanol at 30 °C

Nucleophile Y	[complex] (M)	[Y] × 10^3 (M)	k_{obs} × 10^4 (s^{-1})	k_Y[d] (M^{-1} s^{-1})	n_{Pt}^0 [e]
DCA^- [a]	1.5 × 10^{-4}	1.5	0.15	(3.03 ± 0.3) × 10^{-4}	3.05
		4.0	0.17		
		10.0	0.19		
		25.0	0.25		
		50.0	0.30		
DMTU[b]	1 × 10^{-4}	0.5	16	2.5 ± 0.23	7.02
		2.5	74		
		5.0	141		
		10.0	341		
		12.5	357		
		25.0	598		
DPTU[b]	1 × 10^{-4}	0.5	21	4.15 ± 0.04	7.19
		2.5	100		
		5.0	200		
		6.3	254		
		12.5	526		
		25.0	1030		
TMTU[c]	1 × 10^{-4}	1.0	1.73	0.30 ± 0.006	6.05
		2.5	8.38		
		5.0	14.7		
		7.5	23.0		
		10.0	30.7		

[a]Reaction was followed spectrophotometrically at λ = 280 nm; I = 0.1 M ($NaClO_4$). [b]Reaction was followed conductimetrically; I = 0. [c]Reaction was followed spectrophotometrically at λ = 360 nm; I = 0.1 M ($NaClO_4$). [d]As determined from the slope of the plot k_{obs} = f([Y]). [e]As calculated from eqn. (3) with k'_S = 2.7 × 10^{-7} M^{-1} s^{-1}.

tion, the product obtained upon addition of equivalent amounts of a strong base (NaOH, KOR with R = t-Bu) to the methanol solution of [Pt(OND)NO$_3$] could not be identified as the hydroxo complex [Pt(OND)OH]. Again, the yellow to deep-brown product was not uniform and of low solubility, which is not surprising when one considers the well-known lability of Schiff bases towards strong bases and the tendency of Pt(II) hydroxo complexes to form bridged species.

New n_{Pt}^0 Values

The kinetics of ligand replacement in the standard complex *trans*-[Ptpy$_2$Cl$_2$] according to the reaction (eqn. (10)) were studied with several nucleophiles Y, the n_{Pt}^0 values of which are hitherto unknown.

$$trans\text{-}Ptpy_2Cl_2 + Y \rightleftharpoons trans\text{-}Ptpy_2ClY^+ + Cl^- \qquad (10)$$

The nucleophiles investigated were the tricyanomethanide ion ($C(CN)_3^-$ = TCM^-)*, the dicyanoamide ion ($N(CN)_2^-$ = DCA^-), *N,N'*-dimethylthiourea (DMTU), *N,N'*-diphenylthiourea (DPTU) and *N,N,N',N'*-tetramethylthiourea (TMTU).

Even in the presence of a large excess of the anion TCM^- in the system *trans*-[Ptpy$_2$Cl$_2$]/TCM^-/MeOH no spectral changes were to be observed within 12 h. This could mean that either the chloride ion is not replaced or the spectra of *trans*-[Ptpy$_2$Cl$_2$] and *trans*-[Ptpy$_2$Cl(TCM)] are very similar. The latter explanation is preferred since the TCM^- ion is able to displace water from the complex [Pt(ONNEt$_2$)(H$_2$O)]$^+$ (see below).

The data obtained for the nucleophiles DCA^-, DMTU, DPTU and TMTU are compiled in Table IV. One learns that the dicyanoamide anion DCA^- is a poor nucleophile with a n_{Pt}^0 value (3.05) very close to that of the chloride ion (3.04). When the nucleophile thiourea (= TU; n_{Pt}^0 = 7.17 [13]) is *N*-alkylated, the change in nucleophilicity is small for *N,N'*-dimethylthiourea (= DMTU; n_{Pt}^0 = 7.02) and *N,N'*diphenylthiourea (= DPTU; n_{Pt}^0 = 7.19) and more significant (decrease in k_Y by a factor of 13) only for *N,N,N',N'*-tetramethylthiourea (= TMTU; n_{Pt}^0 = 6.05). It could well be that the fourfold methylation of

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*The salt K[C(CN)$_3$] = KTCM was prepared as described in the literature [17].

thiourea causes steric crowding in the transition state.

Kinetics of Ligand Substitution in the Complexes [Pt(OND)NO₃]

As discussed above the nitrato complexes [Pt(OND)NO_3] dissociate completely in MeOH to form the cationic aquo species [Pt(OND)(H_2O)]$^+$.

It is well known that the rate of reactions between cationic and anionic species decreases with increasing ionic strength. It was not surprising, therefore, to find for the substitution reaction (eqn. (11)) ($Y^- = I^-$, Cl^-) a non-linear relationship between

$$Pt(ONNEt_2)(H_2O)^+ + Y^- \longrightarrow Pt(ONNEt_2)Y + H_2O \qquad (11)$$

the experimental rate constant k_{obs} and the anion concentration $[Y^-]$. At higher concentration of Y^- (*i.e.*, at higher ionic strength of the medium) the values obtained for k_{obs} became apparently smaller than expected according to the relationship $k_{obs} = k_Y[Y^-]$. To avoid this effect the ionic strength of the medium was adjusted to $I = 0.2$ M with $NaClO_4$ and this standard condition was maintained throughout all kinetic experiments.

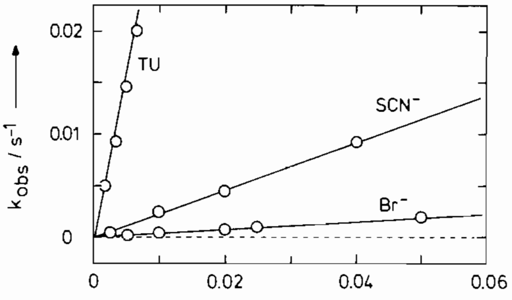

Fig. 1. The dependence of rate constant k_{obs} on the excess concentration of the entering nucleophile Y for solvent substitution in the complex $[Pt(ONNEt_2)(H_2O)]^+$ at 20 °C in methanol ($I = 0.2$ M ($NaClO_4$); TU = thiourea).

Figure 1 presents some typical data obtained for replacement of water in the species $[Pt(ONNEt_2)(H_2O)]^+$ by the nucleophiles Br^-, SCN^- and TU (= thiourea) under standard conditions ($I = 0.2$ M; $T = 20$ °C; [complex] = 10^{-4} M). In all cases the time dependence of the change in absorbance can be fitted to a single exponential function (see 'Experimental') and the experimental rate constant k_{obs} increases linearly with the concentration of the nucleophile according to the rate eqn. (12). Rate constant k_Y is obtained from the slope of the curves shown in Fig. 1 by least-squares fitting. The finding

$$\text{rate} = k_{obs}[\text{complex}] = k_Y[Y][\text{complex}] \qquad (12)$$

that there is no intercept (*i.e.*, no solvent path) corresponds convincingly to the fact that the nitrato complex introduced dissociates to form the solvento species $[Pt(ONNEt_2)(H_2O)]^+$. The data obtained for rate constant k_Y are compiled in Table V.

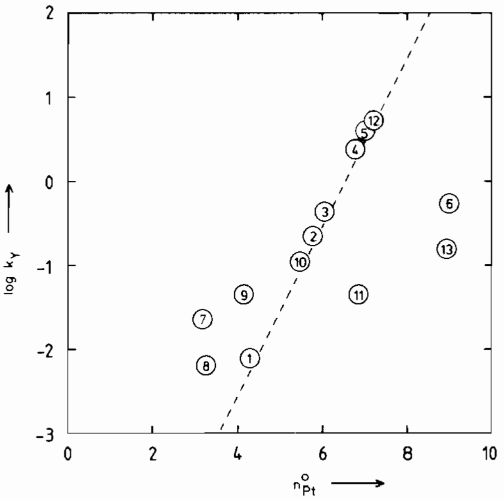

Fig. 2. The dependency log $k_Y = f(n^0_{Pt})$ for solvent substitution in the complex cation $[Pt(ONNEt_2)(H_2O)]^+$ (the numbering of the nucleophiles Y corresponds to that in Table V).

Looking first at water replacement in the aquo complex $[Pt(ONNEt_2)(H_2O)]^+$ one recognizes that there is a wide spread in nucleophilicity for the thirteen nucleophiles studied. Rate constant k_Y is smallest for Y = py (0.683×10^{-2} M^{-1} s^{-1}) and largest for Y = TU = thiourea (531×10^{-2} M^{-1} s^{-1}). Figure 2 shows a plot of log k_Y versus the parameter n^0_{Pt} with a numbering of the ligands corresponding to that given in Table V. The overall impression is that a linear correlation between log k_Y and n^0_{Pt} according to eqn. (4) does not exist. Although seven nucleophiles (**1**–**5**, **10**, **12**) fall nicely on the dashed line corresponding to $s = 1$ (s = nucleophilic discrimination factor; see eqn. (4)), nucleophiles **6**–**9**, **11** and **13** deviate strongly. One could argue, of course, that the n^0_{Pt} scale refers to the neutral substrate *trans*-$[Ptpy_2Cl_2]$ whereas the aquo complex $[Pt(ONNEt_2)(H_2O)]^+$ is cationic. It follows from this argument that the equilibrium constant K_{os} for outer-sphere complex formation according to eqn. (13) is certainly

$$Pt(OND)(H_2O)^+ + Y^- \overset{K_{os}}{\rightleftharpoons}$$

$$Pt(OND)(H_2O)^+, Y^- \xrightarrow{k'_Y} Pt(OND)Y + H_2O \qquad (13)$$

greater for anionic nucleophiles Y^- than for neutral nucleophiles Y and that the experimental rate constants $k_Y = k'_Y K_{os}$ (see Table V) should be corrected for this electrostatic interaction. One can estimate that the ratio K_{os} (Y = anion)/K_{os} (Y = neutral) is

TABLE V. Kinetic Data for Solvent Substitution in the Complex Cations $[Pt(OND)(H_2O)]^+$ as Studied in Methanol[a] According to Reaction (eqn. (11))

Nucleophile Y (number)	λ[b] (nm)	$[Y] \times 10^3$ (M)	$k_{obs} \times 10^4$ (s^{-1})	$k_Y \times 10^2$ [c] ($M^{-1}\ s^{-1}$)
Complex $[Pt(ONNEt_2)(H_2O)]^+$				
Ph–S–Me	316	4.0	0.345	0.80 ± 0.5%
(1)		7.5	0.622	
		10	0.818	
		20	1.58	
		30	2.37	
		40	3.15	
		50	3.77	
SCN^-	400	1.0	2.30	22.2 ± 0.5%
(2)		2.5	5.35	
		5.0	14.2	
		10	25.6	
		20	41.1	
		30	60.1	
		40	90.9	
TMTU	400	1.0	4.66	44.7 ± 1%
(3)		2.5	11.7	
		5.0	22.3	
		7.5	33.8	
		10	44.4	
DMTU	330	1.0	29	251 ± 1%
(4)		2.5	61	
		5.0	125	
		7.5	183	
		10	255	
DPTU	400	1.0	41	386 ± 1%
(5)		2.5	102	
		5.0	195	
		7.5	283	
		10	388	
Bu_3P	320	1.0	8.0	55 ± 1%
(6)		2.5	13.2	
		5.0	27.6	
		7.5	38.5	
Cl^-	320	5.0	1.35	2.19 ± 0.5%
(7)		25	5.33	
		40	9.77	
		50	10.5	
		70	15.3	
		80	16.7	
		100	20.9	
py[d]	304	2.5	0.16	0.683 ± 1%
(8)		5.0	0.39	
		10	0.73	
		25	1.63	
		50	3.32	
Br^-	320	1.25	0.64	4.18 ± 0.5%
(9)		5.0	2.25	

(continued on facing page)

TABLE V. *(continued)*

Nucleophile Y (number)	λ^b (nm)	$[Y] \times 10^3$ (M)	$k_{obs} \times 10^4$ (s^{-1})	$k_Y \times 10^2$ [c] (M^{-1} s^{-1})
		10	4.38	
		12.5	4.82	
		20	8.40	
		25	9.18	
		50	19.8	
I^-	400	2.5	3.48	11.2 ± 0.5%
(10)		10	11.6	
		25	28.0	
		30	28.1	
		40	42.3	
		50	65.0	
		60	72.0	
Ph_3As	315	2.5	1.13	4.16 ± 1%
(11)		5.0	2.17	
		7.5	3.28	
		10	4.26	
		20	8.47	
		25	10.1	
TU	320	1.0	64.1	531 ± 2%
(12)		5.0	290	
		12.5	576	
		25	1380	
		50	2650	
Ph_3P	410	2.5	3.46	15.5 ± 0.5%
(13)		5.0	6.91	
		10	14.7	
		20	33.1	
		30	50.3	
Complex $[Pt(ONNHEt)(H_2O)]^+$				
Cl^-	330	5.0	24.2	48.6 ± 1%
(7)		10	49.8	
		15	70.0	
		20	101	
		25	120	
py	300	2.5	9.82	38.0 ± 1%
(8)		7.5	28.2	
		12.5	47.9	
		20	74.4	
		25	96.1	
Br^-	330	1.0	10.5	131 ± 1%
(9)		5.0	67.5	
		10	132	
		15	194	
		20	263	
I^-	395	1.0	106	851 ± 1%
(10)		3.0	285	
		5.0	496	

(continued overleaf)

TABLE V. *(continued)*

Nucleophile Y (number)	λ^b (nm)	$[Y] \times 10^3$ (M)	$k_{obs} \times 10^4$ (s^{-1})	$k_Y \times 10^2$ c (M^{-1} s^{-1})
		20	1770	
		40	3360	
Ph_3As	320	3.0	72.1	241 ± 0.5%
(11)		5.0	118	
		7.5	185	
		10	240	
		15	362	
TU	395	1.0	1420	14950 ± 2%
(12)		3.0	4000	
		5.0	5780	
		20	31400	
		40	59300	
Ph_3P	410	1.0	274	2980 ± 2%
(13)		3.0	810	
		5.0	1360	
		15	4110	
		30	9140	
Complex $[Pt(ONSEt)(H_2O)]^+$				
Cl^-	330	1.0	10.0	106 ± 0.5%
(7)		5.0	52.9	
		10	106	
		15	158	
		20	212	
py	300	2.5	11.8	48.9 ± 0.5%
(8)		7.5	38.3	
		12.5	60.9	
		20	98.0	
		25	122	
Br^-	330	1.0	32.5	345 ± 1%
(9)		2.5	92.0	
		5.0	165	
		7.5	264	
		10	344	
I^-	385	1.0	346	1630 ± 7%
(10)		3.0	780	
		5.0	1410	
		20	3050	
Ph_3As	310	1.0	43.3	125 ± 12%
(11)		2.5	48.2	
		4.0	59.0	
		5.0	51.2	
		10	120	
TU	405	1.0	950	26750 ± 5%
(12)		3.0	6940	
		5.0	11300	

(continued on facing page)

TABLE V. *(continued)*

Nucleophile Y (number)	λ^b (nm)	$[Y] \times 10^3$ (M)	$k_{obs} \times 10^4$ (s^{-1})	$k_Y \times 10^2$ ^{c} (M^{-1} s^{-1})
		20	64300	
		40	102000	
Ph_3P (13)	410	1.0	4280	40960 ± 2%
		3.0	12000	
		5.0	16600	
		15	64500	
		30	122000	

[a]Standard conditions: $I = 0.2$ M ($NaClO_4$), $T = 20$ °C, [complex] $= 10^{-4}$ M. [b]Wavelength for observation. [c]As obtained from the slope of the plot $k_{obs} = k_Y[Y]$ according to eqn. (12) by least-squares fitting. [d]The kinetic runs were carried out in buffered solution (0.05 M 2,6-lutidine; 0.1 M 2,6-lutidinium perchlorate; 0.1 M $NaClO_4$).

of the order 3.3–4.0*. The correction for electrostatic effects would mean, therefore, that the experimentally obtained rate constants k_Y for the anions $Y = SCN^-$, Cl^-, Br^-, I^- (**2**, **7**, **9**, **10**; see Table V and Fig 2) have to be divided by a factor of approximately 3.5 to make them compatible with the rate constants obtained for neutral nucleophiles Y. It can be easily seen from Fig. 2 that such a correction reduces the degree of scattering of the data slightly but does not eliminate it.

The fact that eqn. (4) is not able to correlate the rate data satisfactorily has to be due to arguments other than electrostatic. Looking at Fig. 2 the most striking result is the high nucleophilicity of TU, DPTU and DMTU (**12**, **5** and **4**) as compared to the unexpectedly low nucleophilicity of Bu_3P, Ph_3As and Ph_3P (**6**, **11** and **13**). Considering the fact that the ligand replaced in these studies is a water molecule *cis*-coordinated to a phenolic oxygen one could imagine that hydrogen bonding is a rate-increasing factor in the case of thiourea (TU) and its di-alkylated derivatives DPTU and DMTU. All of these three nucleophiles can form N–H···O bonds either with the leaving water molecule (transition state more easily formed) or with the phenolic oxygen (product ground state stabilized). As a matter of fact, the nucleophile TMTU (*N,N,N′,N′*-tetramethylthiourea) is not capable of forming this type of hydrogen bond and reacts much slower (k_Y(TU)/k_Y(TMTU) = 12:1).

The finding that the nucleophile $Y = Ph_3P$ with one of the highest n^0_{Pt} values known ($n^0_{Pt} = 8.93$) reacts rather slowly with the complex $[Pt(ONNEt_2)(H_2O)]^+$ strongly indicates that steric problems are involved. The formation of the five-coordinate transition state is obviously hindered when the bulky ligand Ph_3P (**13**) approaches the metal carrying the diethyl ammonium group in *cis*-position. The same is probably true for the nucleophiles Ph_3As (**11**) and Bu_3P (**6**). If so, the variation of the steric demands of the donor group D should be a good indicator (see below).

Table V also presents the rate data obtained for the reaction of the complex cations $[Pt(ONNHEt)(H_2O)]^+$ and $[Pt(ONSEt)(H_2O)]^+$ with a variety of nucleophiles Y. It should be pointed out that water substitution in these two complexes follows rate law (eqn. (12)) as well. As shown in Figs. 3a–3c, qualitatively the patterns of reactivity appear to be very similar for the nitrato complexes **Ia**, **Ib** and **Ic**. In all three systems there is strong scattering of the data when plotted according to eqn. (4). A closer look at the rate constants k_Y obtained (see Table V) reveals, however, some interesting details, namely: (i) for a given nucleophile Y rate constant k_Y follows the sequence k_Y(**Ia**) < k_Y(**Ib**) < k_Y (**Ic**), and, (ii) the relative nucleophilicity of a bulky nucleophile such as Ph_3P seems to increase when the *cis* donor group NEt_2 (**Ia**) is replaced by NHEt (**Ib**) and SEt (**Ic**).

Table VI presents relative rate constants which indeed prove the trends described above. For relatively small nucleophiles such as Cl^-, Br^-, py and TU the relative ratio of rate constants averages to approximately 63:35:1, which means that the rate of solvent substitution is approximately 35 fold and 63 fold enhanced when the *cis* donor group $D = NEt_2$ in the complex species $[Pt(OND)(H_2O)]^+$ is replaced by D = NHEt and D = SEt, respectively. This behavior has to be attributed to steric '*cis*-blocking' (*i.e*, the bulkier $-NEt_2$ donor group blocks more than the NHEt donor group) and to the *cis*-effect

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*The calculation of an outer-sphere complex formation constant K_{os} is carried out according to the expression theoretically deduced by Fuoss [18]:

$$K_{os} = \frac{4\pi N a^3}{3000} \exp(-U/kt)$$

The interionic potential $U = Z_1 Z_2 e^2/aD$ as well as K_{os} depend on the parameter *a*, the distance of closest approach of two ions. For $a = 400$ pm and $a = 600$ pm, the ratio K_{os} ($Z_1 = +1$; $Z_2 = -1$)/K_{os} ($Z_1 = +1$; $Z_2 = 0$) comes out to be 3.3 and 4.0, respectively.

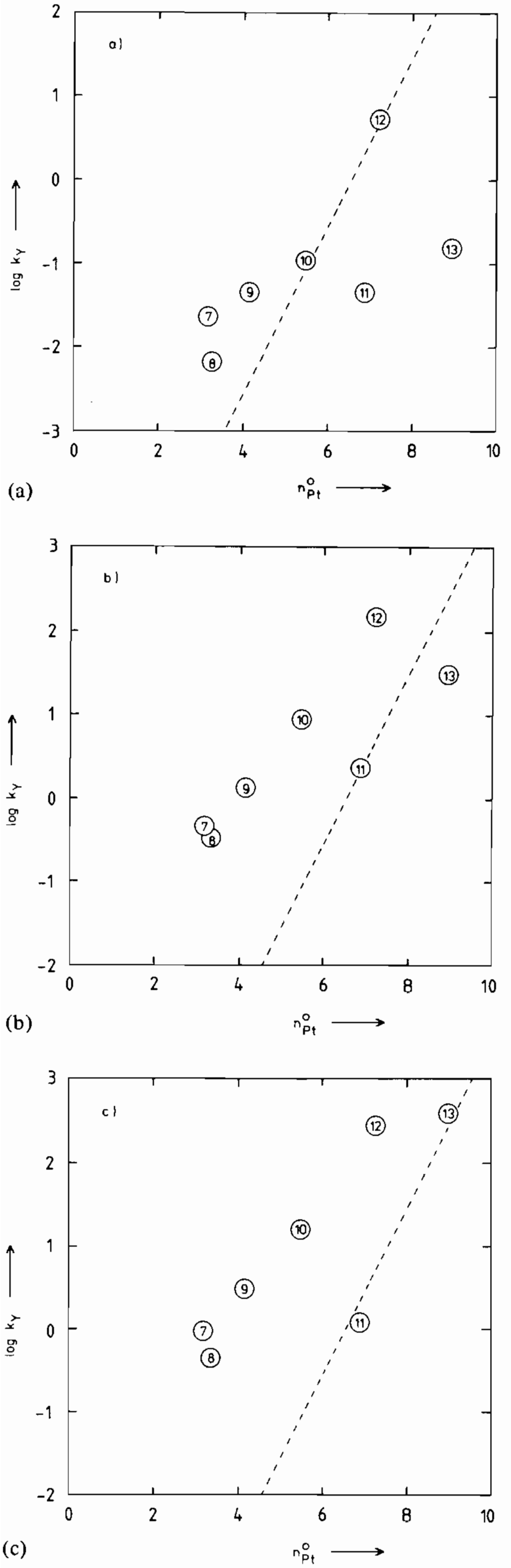

Fig. 3. The dependency log k_Y = f(n^0_{Pt}) for solvent substitution in the cations $[Pt(OND)(H_2O)]^+$ with D = NEt_2 (a), D = NHEt (b) and D = SEt (c) (the numbering of the nucleophiles Y corresponds to that in Table V).

of the SEt group instead of the NHEt group. When it comes to sterically more demanding nucleophiles, however, the effects become more drastic. For the large anion I^- the relative ratio of rate constants amounts to 146:75:1 and for the very bulky ligand Ph_3P an even higher ratio is obtained, namely 2640:192:1. These results are clearly indicative of steric crowding in the transition state following the order:

$NEt_2 > NHET > SEt$ (*cis*-effect of D)

$Ph_3P \gg I^- > Br^-$, TU, py, Cl^- (effect of entering nucleophile Y)

So, the combination Y = Ph_3P and D = $-NEt_2$ yields for steric reasons a drastically reduced rate of solvent substitution, although Ph_3P is known to be a very strong nucleophile.

Activation Parameters

The temperature dependence of solvent substitution in the complex species $[Pt(ONNEt_2)(H_2O)]^+$ was studied for the nucleophiles TU, DMTU, TMTU, DPTU and Ph_3P. The activation parameters derived from this study are presented in Table VII. The values obtained for the enthalpy of activation range from 48 (Y = TMTU) to 62 (Y = DMTU) kJ mol^{-1} and do not differ strongly. The spread in $\Delta S^{\ddagger}$ is greater and the limits of error for this parameter as well. All values obtained for $\Delta S^{\ddagger}$ are clearly negative, however, thus corroborating the associative character of the substitution reactions studied.

Substituent Effects

It is to be expected that the kinetic effects caused by substituents introduced in the aromatic ring of the Schiff base ligand depend significantly on their posi-

TABLE VI. Relative Rate Constants[a] for Solvent Substitution in the Complex Cations $[Pt(OND)(H_2O)]^+$ Formed by the Nitrato Complexes **Ia**, **Ib** and **Ic**

Nucleophile Y	(number)	k_Y (**Ic**):k_Y(**Ib**):k_Y(**Ia**)[b]
Cl^-	(7)	48:22:1
py	(8)	72:57:1
Br^-	(9)	83:31:1
I^-	(10)	146:76:1
Ph_3As	(11)	(30)[c]:58:1
TU	(12)	50:28:1
Ph_3P	(13)	2640:192:1

[a] Based on the rate constants k_Y compiled in Table V; T = 20 °C, solvent methanol, I = 0.2 M ($NaClO_4$). [b] Relative ratio obtained by setting arbitrarily k_Y (**Ia**) ≡ 1. [c] This number is not very reliable due to the large error in k_Y (see Table V).

TABLE VII. Activation Parameters for Solvent Substitution in the Complex Cation $[Pt(ONNEt_2)(H_2O)]^+$ as Studied in Methanol[a] According to Reaction (eqn. (11))

Nucleophile Y	λ^b (nm)	T (°C)	$k_Y{}^c$ ($M^{-1}\ s^{-1}$)	$\Delta H^\ddagger$ ($kJ\ mol^{-1}$)	$\Delta S^\ddagger$ ($J\ K^{-1}\ mol^{-1}$)
TU	320	20.0	5.31 ± 2%	55.0 ± 4.0	−43.2 ± 13.4
TU	320	25.0	7.5 ± 3%		
TU	320	27.7	9.56 ± 2%		
TU	320	31.7	13.9 ± 1%		
DMTU	330	14.5	1.57 ± 3%	61.6 ± 0.6	−26.9 ± 2.1
DMTU	330	20.0	2.51 ± 1%		
DMTU	330	30.0	5.99 ± 1%		
DMTU	330	44.0	18.8 ± 1%		
TMTU	400	14.5	0.289 ± 1%	48.3 ± 0.7	−87.0 ± 2.2
TMTU	400	20.0	0.447 ± 1%		
TMTU	400	30.0	0.855 ± 1%		
TMTU	400	40.0	1.65 ± 1%		
DPTU	400	15.0	2.96 ± 4%	60.3 ± 3.5	−27.3 ± 11.7
DPTU	400	20.0	3.86 ± 1%		
DPTU	400	30.0	9.39 ± 1%		
DPTU	400	44.0	30.9 ± 1%		
Ph_3P	410	20.0	0.155 ± 1%	60.8 ± 4.8	−53.2 ± 16.1
Ph_3P	410	25.0	0.175 ± 10%		
Ph_3P	410	30.0	0.404 ± 5%		
Ph_3P	410	35.0	0.59 ± 3%		

[a] Standard conditions: $I = 0.2$ M ($NaClO_4$), [complex] $= 10^{-4}$ M; at each temperature five kinetic runs were carried out to obtain five rate constants k_{obs} at different concentrations of the nucleophile Y in the range $[Y] = 1 \times 10^{-3}$–5×10^{-2} M. [b] Wavelength for observation. [c] As obtained from the slope of the plot $k_{obs} = k_Y[Y]$ according to eqn. (12) by least-squares fitting.

tion relative to the donor atoms O(phenolic oxygen) and N(aldimine nitrogen).

Substituents X^5 are in *para* position to the phenolic oxygen and will decrease or increase the electron density at the donor oxygen and, hence, at the metal. Since the nucleophilic attack of the entering ligand is supposed to occur at the metal, rate constant k_Y should follow the electron releasing or electron withdrawing nature of substituents X^5. Table VIII summarizes the data obtained and Fig. 4 presents a plot of log k_Y ($Y = Br^-$) *versus* Hammett's substituent constant σ_p, which indeed proves this correlation. Despite some scattering of the data the electron withdrawing substituents $X^5 = NO_2$, Br, I clearly enhance the rate of solvent substitution by bromide ions and the reaction constant ρ amounts to +0.71 ± 0.1*. The overall kinetic effect of substituents X^5 is small, however, and even for $X^5 = NO_2$ the increase in rate is only fivefold for $Y = Br^-$ and sevenfold for $Y = SCN^-$ (see Table VIII). In addition, it should be pointed out that the order of nucleophilicity of the entering ligands Y is not substantially changed by substituents X^5 (see Table VIII).

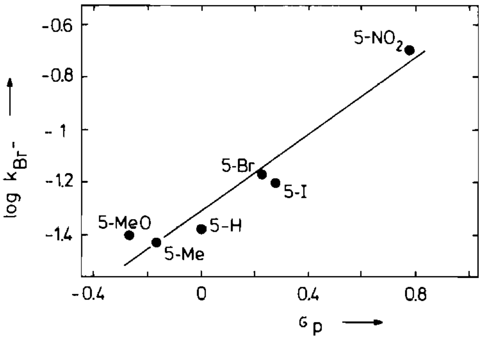

Fig. 4. The dependence of rate constant k_Y for solvent substitution in the cation $[Pt(X^5\text{-}ONNEt_2)(H_2O)]^+$ by bromide ions on Hammett's substituent constant σ_p.

Substituents X^4 are in *meta* position to the phenolic oxygen but could, in principle, act as *para* substituents for the donor nitrogen of the aldimine group, located *trans* to the leaving water molecule. For X^4 = MeO (with $\sigma_m = +0.12$ and $\sigma_p = -0.27$) and for $Y = Br^-$ the kinetic substituent effect is, however, very small. As compared to the non-substituted complex ($X^3 = X^4 = X^5 = H$) the rate is reduced only by 7% (see Table VIII).

The kinetic data obtained for solvent substitution in the complex $[Pt(ONNEt_2)(H_2O)]^+$ carrying substituents X^3 (*i.e.*, in *ortho* position to the phenolic oxygen) are interesting in the sense that they again

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*The parameter ρ is obtained from the slope of the solid line (as calculated by least-squares fitting) in Fig. 4.

TABLE VIII. Substituent Effects on Rate Constant k_Y for Solvent Substitution in the Complex Cation $[Pt(ONNEt_2)(H_2O)]^+$ According to Reaction (eqn. (11))[a]

Substituents			λ^b (nm)	Nucleophile Y	$k_Y \times 10^2$ [c] ($M^{-1}\ s^{-1}$)	k_Y (rel)[d]
X^3	X^4	X^5				
H	H	Br	330	TU	497 ± 2%	0.936
H	H	Br	330	Br^-	6.74 ± 1%	1.61
H	H	Br	320	Ph_3As	5.0 ± 1%	1.20
H	H	I	330	TU	594 ± 1%	1.12
H	H	I	410	Ph_3P	36.7 ± 2%	2.37
H	H	I	330	Br^-	6.23 ± 2%	1.49
H	H	I	330	Cl^-	3.63 ± 1%	1.66
H	H	I	320	TCM^- [e]	3.18 ± 1%	1.49
I	H	I	410	Ph_3P	5.82 ± 2%	0.375
I	H	I	330	Br^-	3.32 ± 2%	0.794
H	H	NO_2	380	SCN^-	153 ± 6%	6.89
H	H	NO_2	380	Br^-	20.9 ± 1%	5.00
H	H	Me	320	Bu_3P	44.7 ± 1%	0.813
H	H	Me	330	SCN^-	17.5 ± 2%	0.788
H	H	Me	420	Ph_3P	18.9 ± 1%	1.22
H	H	Me	330	Br^-	3.75 ± 1%	0.897
H	H	Me	330	Cl^-	2.09 ± 1%	0.954
H	H	Me	302	py	0.592 ± 1%	0.867
H	H	Me	320	TCM^- [e]	2.09 ± 1%	0.98
t-Bu	H	Me	330	SCN^-	17.6 ± 1%	0.793
t-Bu	H	Me	330	Br^-	2.18 ± 1%	0.522
t-Bu	H	Me	330	Cl^-	0.903 ± 1%	0.412
t-Bu	H	Me	325	TCM^- [e]	3.76 ± 1%	1.76
t-Bu	H	Me	410	Ph_3P	0.310 ± 1%	0.020
H	MeO	H	375	Ph_3P	18.3 ± 2%	1.18
H	MeO	H	300	Br^-	3.87 ± 1%	0.926
H	H	MeO	420	Ph_3P	14.6 ± 3%	0.942
H	H	MeO	330	Br^-	3.98 ± 2%	0.952

[a] Standard conditions: $I = 0.2$ M ($NaClO_4$), $T = 20$ °C, [complex] $= 10^{-4}$ M; for each nucleophile Y five kinetic runs were carried out to obtain five rate constants k_{obs} in the concentration range $[Y] = 1 \times 10^{-3}$–0.1 M. [b] Wavelength for observation. [c] As obtained from the slope of the plot $k_{obs} = k_Y[Y]$ according to eqn. (12) by least-squares fitting. [d] The parameter k_Y(rel) is a relative rate constant as obtained by dividing k_Y for the substituted complex by k_Y for the non-substituted complex (with $X^3 = X^4 = X^5 = H$). [e] The tricyanomethanide ion TCM^- was introduced as NaTCM, prepared from KTCM [17] by reaction with $NaClO_4$.

point to the major role of steric effects. For substituents $X^3 = I$ and $X^3 =$ t-Bu and for $Y = Ph_3P$ and Br^-, rate constant k_Y is more strongly reduced than expected on the basis of purely electronic effects. The rate of solvent substitution by Ph_3P in $[Pt(3,5\text{-}I_2\text{–}ONNEt_2)(H_2O)]^+$ is sixfold slower than in $[Pt(5\text{-}I\text{–}ONNEt_2)(H_2O)]^+$ and for the couple $[Pt(3\text{-t-Bu-}5\text{-Me–}ONNEt_2)(H_2O)]^+/[Pt(5\text{-Me–}ONNEt_2)(H_2O)]^+$ the rate reducing factor is even 61 (see Table VIII). It is obvious that these findings demonstrate steric difficulties in the formation of the transition state, due to the proximity of substituents X^3 to the reaction centre.

Further Studies and Results

Solvent substitution in the complex cation $[Pt(ONNEt_2)(H_2O)]^+$ according to eqn. (11) was not only studied with the thirteen nucleophiles Y listed in Table V, but in addition with a variety of others.

Although it was not possible (see above) to determine the n^0_{Pt} value for the pseudo-halide ion TCM^- (tricyanomethanide, $C(CN)_3^-$), reaction (eqn. (14))

$$\mathrm{Pt(ONNEt_2)(H_2O)^+ + TCM^- \longrightarrow Pt(ONNEt_2)TCM + H_2O} \qquad (14)$$

could be followed spectrophotometrically under standard conditions and led to $k_Y = 2.13 \times 10^{-2} \pm 0.5\%$ M^{-1} s^{-1}. This rate constant is very close to the one obtained for $Y = Cl^-$ ($k_Y = 2.19 \times 10^{-2}$ M^{-1} s^{-1}; see Table V) and one can classify, therefore, the TCM^- ion as a poor nucleophile with an estimated n^0_{Pt} value of 3.03. Much less nucleophilic are the anions NO_3^- and ClO_4^-, for which no changes in the spectrum of the cation $[Pt(ONNEt_2)(H_2O)]^+$ could be observed, even in the presence of a large excess of these anions.

The nucleophiles Y = AcO^-, OH^-, piperidine and 2,6-lutidine represent an interesting group of ligands in the sense that their reaction with the complex $[Pt(ONNEt_2)(H_2O)]^+$ is too fast to be measured by stopped-flow techniques ($k > 100$ s^{-1}). What one observes with these nucleophiles is a very fast jump in the spectrum, obviously associated with the deprotonation of the complex according to eqn. (15):

$$\mathrm{Pt(ONNEt_2)(H_2O)^+ + Y \longrightarrow Pt(ONNEt_2)(OH) + HY^+} \qquad (15)$$

The hydroxo complex formed appears to be kinetically inert, *i.e.*, there is no further reaction to be observed. The formation of bridged dinuclear platinum species cannot be excluded under these conditions.

While a strong base such as the OH^- ion obviously deprotonates the coordinated water completely, there is another group of ligands Y (namely, Y = DCA^-, py, NO_2^-, imidazol, N_3^-, CN^-, *N*-methylimidazol and $HCOO^-$) which only partially deprotonate the aquo complex $[Pt(ONNEt_2)(H_2O)]^+$ according to eqn. (15). The experimental observation with these less basic nucleophiles is a small, but fast jump in the spectrum (too fast for stopped-flow monitoring), followed by a slower, observable reaction. In the case of the anion DCA^- (= dicyanoamide ion) the slower reaction leads to $k_Y = 1.6 \times 10^{-2} \pm 3\%$ M^{-1} s^{-1} under standard conditions. This k_Y value is in line with $k_Y = 2.19 \times 10^{-2}$ M^{-1} s^{-1} for $Y = Cl^-$ and the fact that the corresponding n^0_{Pt} values are very similar ($n^0_{Pt}(DCA^-) = 3.05$; $n^0_{Pt}(Cl^-) = 3.04$).

It should be pointed out that the k_Y value presented in Table V for Y = py was obtained in the presence of a buffer system to avoid partial deprotonation of the aquo complex according to eqn. (15).

Conclusions

The concept of nucleophilic discrimination as based on eqn. (4) correlates the second-order rate constant k_Y for bimolecular ligand substitution in 4-coordinate Pt(II) complexes with the n^0_{Pt} scale as derived for the standard substrate *trans*-$[Ptpy_2Cl_2]$. Although for certain nucleophiles Y (such as thiourea, $SeCN^-$, NO_2^-, SCN^-), and certain platinum complexes (differing in charge, e.g.) deviations from eqn. (4) were [1] and are [19] reported, the relationship (eqn. (4)) was successfully applied to several Pt(II) complexes other than *trans*-$[Ptpy_2Cl_2]$ [1]. The attempt to apply eqn. (4) to solvent substitution in Pt(II) complexes of the type **Ia–Ic** according to $[Pt(OND)(H_2O)]^+ + Y \rightarrow [Pt(OND)Y]^+ + H_2O$ fails in the sense that the k_Y data obtained for a series of nucleophiles Y cannot be fitted to eqn. (4) adequately, even after correction for electrostatic effects. It follows from the present study that steric effects hindering the formation of the 5-coordinate transition state are obviously controlling the deviations observed. The type of steric hindrance occurring has to be classified as a steric *cis* effect which arises for rather bulky attacking nucleophiles Y (such as Ph_3P, Bu_3P, Ph_3As) from sterically demanding *cis* donor groups D (such as D = NEt_2 and, to a lesser extent, D = NHEt, SEt). The rate-reducing effect of the *cis* donor group D is of the order $k_Y(D = SEt):k_Y(D = NHEt):k_Y(D = NEt_2)$ = 63:35:1 for small nucleophiles Y and as large as 2640:192:1 for Y = Ph_3P. Additional steric crowding is created by bulky substituents X^3 (= t-Bu, I) neighboring the phenolic oxygen, which is coordinated in *cis* position to the leaving ligand. The kinetic effects of substituents X^4 and X^5 in *meta* and *para* position to the phenolic oxygen are rather small.

The hitherto unknown nucleophilicity of the pseudo-halide ions DCA^- (= $N(CN)_2^-$) and TCM^- (= $C(CN)_3^-$) proves to be low and close to that of the Cl^- ion.

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