Substitution Reactions of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$ revisited. Mechanistic Elucidation from a Volume-profile Analysis‡

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The complex-formation reactions of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$ with L = imidazole (Him), isonicotinamide (isn) and pyrazine (pyz) were studied in aqueous solution (I = 0.10 mol dm^{-3}, CF_3CO_2Na) as a function of entering ligand concentration and pressure up to 100 MPa, at 25.0 ± 0.1 °C. The volumes of activation for the complex-formation reactions were +4.2 ± 0.2 (pH 8.6), +1.9 ± 0.3 (pH 5.3) and +2.0 ± 0.3 cm^3 mol^{-1} (pH 5.0), for L = Him, isn and pyz, respectively. In the case of isn and pyz as entering ligands the volumes of activation for the reverse aquation reactions were found to be +7.5 ± 0.4 and +10.4 ± 0.3 cm^3 mol^{-1}, respectively. Based on the volume of activation data and the constructed volume profiles a dissociative interchange mechanism is proposed.

In recent years we have developed an interest in tuning the substitution lability of metal complexes *via* a systematic variation of the steric and electronic properties of the coordinated spectator ligands.[1-4] Such variations can cause an increase or decrease of many orders of magnitude in the substitution rate constants.[2] A fundamental question is whether such a drastic change in lability is accompanied by a gradual change in the nature of the substitution mechanism.

Phosphite ligands such as $P(OEt)_3$ are known to labilize the *trans* position, and this is one of the reasons why detailed kinetic studies were performed on complex-formation and the reverse aquation reactions of complexes of the type *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$ for a wide range of organic and inorganic entering ligands in aqueous solution.[5,6] The kinetic behaviour of these reactions is not that straightforward, with the result that mechanistic interpretation of the labilization caused by $P(OEt)_3$ is rather vague.[5,6] For instance, plots of k_{obs} *versus* entering ligand concentrations [L], for complex-formation reactions of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$ exhibit significantly different trends depending on the nature of L. For electrophilic species such as isonicotinamide (isn), nicotinamide, 4-cyanopyridine, 4-cyanopyridinium ion, pyrazine (pyz), 4-methylpyrazinium ion and pyridine a tendency for rate saturation was observed at [L] higher than 0.1 mol dm^{-3}.[5,6] However, for nucleophilic species such as histidine, glycine, NH_3, imidazole (Him), 1-methylimidazole, N_3^-, SCN^-, CN^-, SO_3^{2-}, $S_2O_3^{2-}$ and $CS_2N_3^-$ no such tendency was observed.[5,6] An interchange mechanism was proposed to account for this behaviour.[5,6]

Our earlier experience with detailed studies of ligand-substitution processes clearly demonstrated how volumes of activation and the construction of a reaction volume profile can greatly assist the elucidation of the underlying reaction mechanism.[7-10] Furthermore, such studies can also contribute to a better understanding of the labilization effects of the spectator ligands.[2,3,11] We have therefore revisited a series of typical complex-formation reactions of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$ and have constructed volume profiles in order to resolve the intimate nature of the ligand-substitution process. For this purpose we selected the neutral entering ligands pyz, isn and Him which have different donor–acceptor properties.[5] The results enable an unequivocal assignment of the underlying mechanism.

Experimental

Materials.—Chemicals of analytical reagent grade and deionized water were used throughout. The complex *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)][CF_3SO_3]_2$ was prepared according to a literature procedure.[5] All manipulations were performed under argon by using Schlenk techniques. The salt CF_3CO_2Na was used to adjust the ionic strength of the medium, and CF_3CO_2H–NaOH were used to control the pH of the test solutions.

Kinetic Measurements.—At ambient pressure the substitution reactions were followed spectrophotometrically using a Durrum D110 stopped-flow instrument connected to an on-line computer system for data acquisition and analysis. Kinetic measurements at elevated pressure were performed on a laboratory-made high-pressure stopped-flow unit as described elsewhere.[12] *n*-Heptane was used as pressure-transmitting medium. Subsequent to each pressure increase, the system was thermally equilibrated for 20 min before collecting kinetic data. Absorbance *vs.* time traces were recorded on a Dasar transient recorder and transferred to an on-line computer for calculation of the rate constant. Each experiment consists of a series of kinetic runs using the same freshly prepared solution. All the instruments used for kinetic measurements were thermostatted at 25.0 ± 0.1 °C. All the solutions were transferred with the aid of gas-tight syringes to the stopped-flow units. The kinetics was monitored for at least 10 half-lives at wavelengths corresponding to the maximum absorbance change (350, 366 and 320 nm) for L = isn, pyz and Him, respectively.

Most experiments were done at a pH high enough so that the ligands were largely in the basic form: H_2im^+, pK_a = 6.9; $Hisn^+$, pK_a = 3.5; $Hpyz^+$, pK_a = 0.65. Nonetheless, since the pK_a value can change with pressure, a series of experiments at

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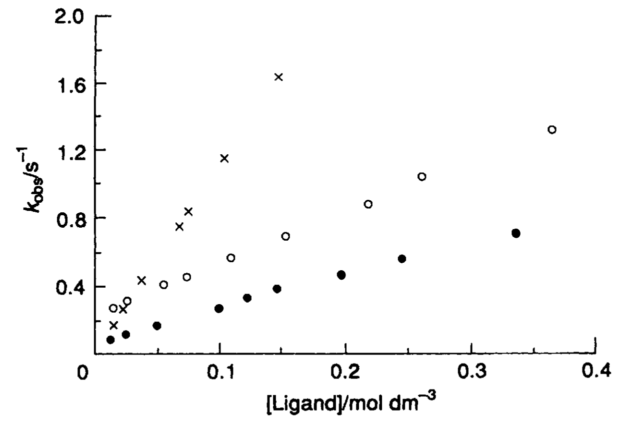

Fig. 1 Dependence of k_{obs} on ligand concentration for the complex-formation reaction of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$ in aqueous solution [$I = 0.10$ mol dm^{-3} (CF_3CO_2Na); 25.0 °C] at ambient pressure with Him (×), pyz (○) or isn (●)

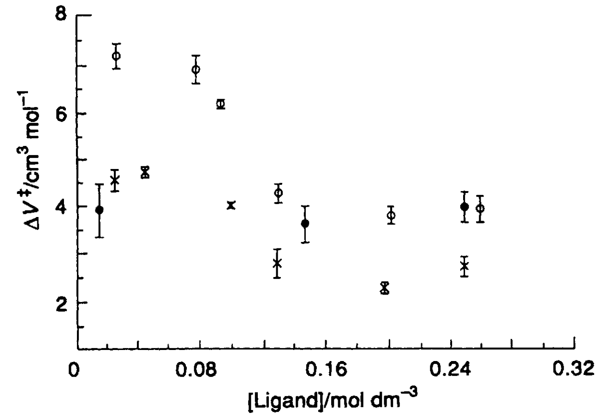

Fig. 2 Dependence of $\Delta V^{\ddagger}$ on ligand concentration for the formation of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}L]^{2+}$ at 25.0 °C, according to data in SUP 57055, where L = pyz (○), isn (×) or Him (●)

different pH were performed in order to check the effect of pH on k_{obs} for the systems where L = isn and Him. The results indicated no significant effect in the range studied (pH 4.2–6.3 and 7.3–9.3 for L = isn and Him, respectively). Therefore, pressure-dependence investigations were performed at selected pH values, where a minor change in pH due to change in pressure will have no significant effect on k_{obs}.

Treatment of Data.—The complex-formation reactions were studied under pseudo-first-order conditions, and the observed rate constants, k_{obs}, were calculated in the usual way[5] using a standard program. The values of k_1 and k_{-1} were estimated by using a linear least-squares treatment according to equation (1).

$$k_{obs} = k_{-1} + k_1[L] \qquad (1)$$

Equilibrium constants, K_{eq}, were calculated from k_1/k_{-1}.

The volumes of activation, $\Delta V^{\ddagger}$, were obtained according to equation (2).[7] Plots of ln k_{obs} *vs.* pressure were linear within the experimental error limits up to 100 MPa.

$$\Delta V^{\ddagger} = -RT[\mathrm{d}(\ln k_{obs})/\mathrm{d}P]_T \qquad (2)$$

Results and Discussion

Studies at Ambient Pressure.—These studies were carried out to check the consistency of the results from the high-pressure experiments as compared to the ambient-pressure results reported before.[5] The kinetic data obtained for reaction (3),

$$trans\text{-}[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4\{P(OEt)_3\}L]^{2+} + H_2O \qquad (3)$$

where L = isn, pyz or Him, are summarized in Table 1. In general, the results are quite consistent with those reported before.[5] Significantly, plots of k_{obs} *vs.* [L] at constant pH, Fig. 1, are linear, except when L = isn (SUP 57055). In the latter case a slight deviation from linearity was observed at [isn] higher than 0.15 mol dm^{-3}, and the rate constants were evaluated from the linear part of the plot ([isn] < 0.15 mol dm^{-3}). The plot of k_{obs} *vs.* [pyz] exhibited a well defined departure from linearity as reported before.[5]

It is significant to note the magnitudes of the intercept in the k_{obs} *vs.* [L] plots: close to zero in the case of L = Him, but larger when L = pyz or isn. The plots exhibiting meaningful intercepts indicate that the reactions do not go to completion under the selected conditions. Kinetic measurements of the aquation of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(isn)]^{2+}$ *via* a pH-jump method on the Durrum stopped-flow instrument resulted in a k_{-1} value in good agreement with that extrapolated from the least-squares analysis (Table 1).

High-pressure Experiments.—The kinetic data as a function of pressure and ligand concentration for the formation of the Him-, isn- and pyz-substituted complexes are summarized in SUP 57055. In general the k_{obs} values decreased slightly with increasing pressure for all the systems studied.

The values of $\Delta V^{\ddagger}$ are small and positive in all cases (Fig. 2, SUP 57055). In the case of L = Him, the $\Delta V^{\ddagger}$ values are independent of [L] within the experimental error limits. This is not surprising since the equilibrium constant is such that the reaction goes to completion and equation (1) can be simplified to (4). In order to minimize the errors, three different [Him]

$$k_{obs} = k_1[\mathrm{Him}] \qquad (4)$$

were used. At each concentration a duplicate experiment was performed using a freshly prepared solution. The pressure dependence of k_1 was estimated from the pressure dependence of k_{obs} at different [Him], using the results summarized in SUP 57055. The k_{-1} values could not be extrapolated from such plots, since the error in the intercept is too large to obtain reliable k_{-1} data.

In the cases where L = isn or pyz, K_{eq} is smaller and the reactions do not go to completion, such that the $\Delta V^{\ddagger}$ values depend on [L] (Fig. 2). In these cases the pressure dependence of k_{obs} was studied as a function of [L]. Plots of k_{obs} *vs.* [L] are satisfactorily described by the linear function (1) at every pressure. The pressure dependencies of k_1 and k_{-1} were estimated and the results are included in SUP 57055. The volumes of activation, $\Delta V^{\ddagger}$, were estimated in the usual way [equation (2)], and are summarized in Table 2. According to these data, the values of $\Delta V^{\ddagger}_{cf}$ and $\Delta V^{\ddagger}_{aq}$, cf = complex formation and aq = aquation, seem to be in agreement with a dissociative interchange mechanism (I_d),[7,8] for all the systems studied. Their absolute values are small, and consistent with the small effect of pressure on k_{obs}.

More reliable data for the activation volume of the reverse reaction was obtained in the case of L = isn (see Table 2), following the disappearance of the substituted complex through the pH-jump technique (SUP 57055). The value obtained by this technique (+7.6 ± 0.3 cm^3 mol^{-1}) is in good agreement with that obtained by extrapolation (+7.4 ± 0.5 cm^3 mol^{-1}). This close agreement suggests that the extrapolated value for pyz is also reliable. A similar determination for pyz would require measurements at low [H$^+$], *i.e.* the employment of a

Table 1 Rate data for the formation of *trans*-$[\mathrm{Ru(NH_3)_4\{P(OEt)_3\}L}]^{2+}$[a]

Ligand L	k_1/dm^3 mol^{-1} s^{-1}	10^2k_{-1}/s^{-1}	K_{eq}/dm^3 mol^{-1}	Remarks
Him	11.2 ± 0.1	1.1 ± 0.7	1.06×10^3	This work
	15.2	0.99	1.5×10^3	Ref. 5
pyz	3.00 ± 0.03	23.7 ± 0.6	12.6	This work
	3.8	20	19	Ref. 5
	3.13 ± 0.09	24.4 ± 1.5	12.8	Calculated from data in ref. 5
isn	2.18 ± 0.05	6.2 ± 0.4	35.1	This work
		6.0 ± 0.1	35.8	Determined by a change in $[\mathrm{H^+}]$[b]
	2.24	6.4	36	Ref. 5

[a] $I = 0.10$ mol dm^{-3} ($\mathrm{CF_3CO_2Na}$); 25.0 °C; ambient pressure. [b] First syringe, $[\mathrm{Ru^{II}}] = 0.16$ mol dm^{-3}, [isn] = 0.198 mol dm^{-3}, pH 5.3; second syringe, $[\mathrm{H^+}] = 0.25$ mol dm^{-3} ($\mathrm{CF_3CO_2H}$); mean value from six kinetic runs.

Table 2 Summary of activation parameters for the systems[a] *trans*-$[\mathrm{Ru(NH_3)_4\{P(OEt)_3\}(H_2O)}]^{2+} + \mathrm{L} \rightleftharpoons$ *trans*-$[\mathrm{Ru(NH_3)_4\{P(OEt)_3\}\,L}]^{2+} + \mathrm{H_2O}$

	L		
	Him	isn	pyz
$\Delta V^{\ddagger}_{cf}$[b]	+4.2 ± 0.2	+1.9 ± 0.3	+2.0 ± 0.3
$\Delta V^{\ddagger}_{aq}$[c]		+7.4 ± 0.5 +7.6 ± 0.3[d]	+10.4 ± 0.3
$\Delta \bar{V}$[e]		−5.6 ± 0.8 −5.7 ± 0.6	−8.4 ± 0.6
$\Delta H^{\ddagger}_{cf}$[f]	16.1 ± 0.01	17.4 ± 1.0	19.3 ± 2.3
$\Delta S^{\ddagger}_{cf}$[f]	+0.85 ± 0.04	+1.4 ± 3.3	+8.6 ± 7.8
$\Delta H^{\ddagger}_{aq}$[f]	22.4 ± 1.0	24.1 ± 0.2	21.4 ± 0.3
$\Delta S^{\ddagger}_{aq}$[f]	7.5 ± 3.4	+16.8 ± 0.6	+11.1 ± 1.1

[a] Volumes in cm^3 mol^{-1}, $\Delta H^{\ddagger}$ in kcal mol^{-1}, $\Delta S^{\ddagger}$ in cal K^{-1} mol^{-1}, where cal = 4.184 J. [b] Calculated from k_1 in SUP 57055. [c] Calculated from k_{-1} in SUP 57055. [d] Obtained from rate data for the aquation of the isonicotinamide complex through variation in $[\mathrm{H^+}]$ as a function of pressure (SUP 57055). [e] $\Delta \bar{V} = \Delta V^{\ddagger}_{cf} - \Delta V^{\ddagger}_{aq}$. [f] Calculated from data in ref. 5 (see text).

buffer. The $\Delta V^{\ddagger}_{aq}$ for L = Him cannot be measured on the stopped-flow time-scale.

Two representative volume profiles are shown in Fig. 3, from which it follows that the transition state has a significantly higher partial molar volume than either that of the reactant or product states, in agreement with the dissociative character of the intrinsic reaction mechanism. The overall reaction volumes ($\Delta \bar{V}$) are negative and indicate an overall volume collapse during the substitution process. This is understandable since the small $\mathrm{H_2O}$ molecule is substituted by a significantly larger L in reaction (3).

The more positive $\Delta V^{\ddagger}$ values found for some of the aquation reactions (L = isn or pyz) are related to the larger size of the leaving group in a process involving partial bond breakage ($\mathrm{I_d}$ mechanism). This is consistent with the sensitivity of $\Delta V^{\ddagger}$ to the size of the leaving and entering ligands, which in fact tunes the intimate nature of the substitution process at the metal centre.[7,8] A tentative explanation for such behaviour can be found in the large *trans* influence of the $\mathrm{P(OEt)_3}$ ligand.[5,6,13] Thus, the competition for the $4d_{\pi}$ electrons of the ruthenium(II) centre, between the $\mathrm{P(OEt)_3}$ and the ligand L *trans* to it in the co-ordination sphere, will weaken the Ru–L bond, favouring a dissociative pathway. This conclusion is in agreement with the experimental order[5] of decreasing K_{eq} values for the substituted complexes (Him $\gg$ isn > pyz), which is consistent with the order of increasing π-acid character of these ligands (Him $\ll$ isn < pyz). On the basis of this ground-state argument, we could expect a less positive value of $\Delta V^{\ddagger}$ for the aquation of *trans*-$[\mathrm{Ru(NH_3)_4\{P(OEt)_3\}(Him)}]^{2+}$, assigning the following order of $\Delta V^{\ddagger}$ for the aquation of the substituted ruthenium complexes: Him < isn < pyz. The complex-formation reactions for L = pyz and isn, which are good π acceptors, can be understood in terms of the π-competition proposal mentioned above and used to interpret the substitution lability in the ground state of the substituted complex during the aquation reaction.

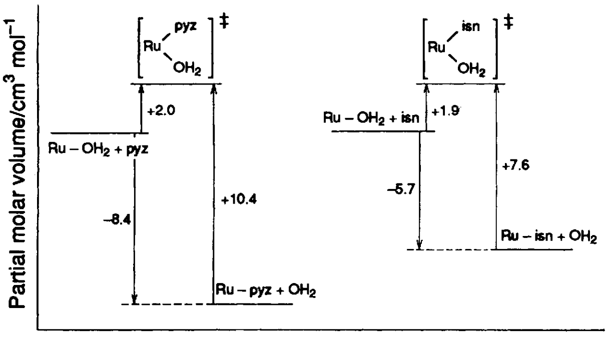

Fig. 3 Volume profiles for the reactions *trans*-$[\mathrm{Ru(NH_3)_4\{P(OEt)_3\}(H_2O)}]^{2+} + \mathrm{L} \rightleftharpoons$ *trans*-$[\mathrm{Ru(NH_3)_4\{P(OEt)_3\}L}]^{2+} + \mathrm{H_2O}$ where L = pyz (left) or isn (right). The metal complexes are shown in abbreviated form

A point of interest is the question of how the imidazole ligand and the aqua complex could have the same degree of bond formation in the transition state as indicated by the low value of $\Delta V^{\ddagger}$. Most probably, the formation of the transition state for nucleophilic ligands will differ from electrophilic ligands (pyz and isn). This may be due to the presence of the biphilic $\mathrm{P(OEt)_3}$ ligand, acting as σ and π 'electron pump' in the co-ordination sphere. Thus, when electron density is withdrawn from the ruthenium(II) centre, the attack of the σ-donor ligand will be facilitated over one of the low-electron-density orbitals. The nucleophilic attack will be on the $4d_{\pi}$ orbitals of the metal the electron density of which will be partially localized over the phosphorus $3d_{\pi}$ orbital.

For the proposed $\mathrm{I_d}$ mechanism, reaction (1) should proceed according to the simplified reaction scheme (5).[14] Under

$$\begin{array}{ccc} [\mathrm{Ru(H_2O)}]^{2+} + \mathrm{L} & \overset{K_{os}}{\rightleftharpoons} & \{[\mathrm{Ru(H_2O)\cdot L}]\}^{2+} \\ & & k_b \upharpoonleft\downharpoonright k_a \\ & & [\mathrm{RuL}]^{2+} + \mathrm{H_2O} \end{array} \qquad (5)$$

pseudo-first-order conditions, *i.e.* an excess of L, the observed first-order rate constant can be expressed as in equation (6)

$$k_{obs} = \frac{k_a K_{os}[L]}{1 + K_{os}[L]} + k_b \quad (6)$$

where K_{os} is the ion-pair or encounter-complex formation constant and k_a and k_b are the forward and reverse interchange rate constants, respectively. When plots of k_{obs} *versus* [L] are curved it is possible to separate k_a and K_{os}, and therefore also their pressure dependencies. Under our experimental conditions no meaningful curvature in the k_{obs} *versus* [L] plots was observed, which means that K_{os} is small and $1 + K_{os}[L] \approx 1$, such that equation (6) simplifies to $k_{obs} = k_a K_{os}[L] + k_b$. It follows that $\Delta V^{\ddagger}_{cf}$ is a composite of the effect of pressure on k_a and K_{os} as shown in equation (7). We were unable to separate these contributions experimentally and have therefore treated $\Delta V^{\ddagger}_{cf}$ in an overall way.

$$\Delta V^{\ddagger}_{cf} = \Delta \bar{V}(K_{os}) + \Delta V^{\ddagger}(k_a) \quad (7)$$

The activation parameters are summarized in Table 2. The quantities $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were taken from experiments described earlier,[5] but were recalculated to improve the accuracy. It follows that all the $\Delta S^{\ddagger}$ values are small and positive, consistent with an I_d mechanism and the activation volumes. The volume of activation data reported here strongly support the earlier proposal[5] of a dissociative interchange mechanism being operative for the substitution reactions in *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}Y]^{2+}$, where Y = H_2O, isn, pyz or Him. The present results suggest that bond breaking is more important than bond making in the transition state, independent of the nature of the entering ligand, *viz.* nucleophile or electrophile. In general, it is always good practice to have as much evidence as possible in support of a proposed mechanism.

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