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Kinetics and Mechanism of Ligand Substitution Reactions of $RuCl_3NOL_2$ Complexes

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A kinetic and mechanistic study on the ligand substitution reactions of $RuCl_3NOL_2$ (L = $AsPh_3$ or $SbPh_3$) complexes is reported. These reactions proceed via a dissociative step. The competition of different ligands for the intermediate $RuCl_3NOL$ has been investigated; steric effects seem to influence the ability of the ligands to attack this pentacoordinated intermediate.

Introduction

The discovery of catalytic properties in ruthenium complexes [1] stimulated several investigations aimed to explore the reactivity [2] and, sometimes, the reaction mechanisms [3–5] of such compounds.

More recently it has been found that an organometallic catalyst can be anchored on polymers to give an insoluble catalyst [6] whose properties, even if not yet thoroughly studied, are comparable to those of the starting compound.

A more extensive knowledge of the reaction mechanisms in ruthenium complexes (even if without catalytic activity) should be useful for a better understanding of the catalytic properties of related systems. Preliminary investigations in this laboratory indicate that it is possible to support complexes like $RuCl_3NOL_2$ on polystyrene–divinylbenzene beads; the study of ligand substitution of the supported complex becomes thus possible.

We have studied the homogeneous reaction

$$RuCl_3NOL_2 + 2L' = RuCl_3NOL'_2 + 2L$$

and here we report the related kinetic data and a possible mechanism. The comparison with the data for the heterogenized reaction* should give useful information on the possible difference of reactivity of the supported complex.

With a better understanding of the influence of the heterogenization on the chemical properties of these complexes it may become possible to transfer this information to structurally related complexes with catalytic activity and to synthesize catalysts with enhanced activity and selectivity.

Experimental

Materials

The complexes $RuCl_3NOL_2$ (L = PPh_3, $AsPh_3$, and $SbPh_3$) have been prepared according to literature procedures [7] and purified by crystallization from CH_2Cl_2–C_2H_5OH mixtures. Complexes containing as ligands $P(OMe)_3$, $P(OEt)_3$ and $P(On\text{-}Bu)_3$ have been prepared from $RuCl_3NO(SbPh_3)_2$ allowing the complex and a 5 molar excess of the appropriate ligand to react for 5 hours in CH_2Cl_2 at room temperature. After evaporation of the solvent the solid residue was washed with pentane and the complex was obtained by crystallization from CH_2Cl_2–C_2H_5OH. $RuCl_3NODPE$ (DPE = 1,2 bis(diphenylphosphinolethane) was obtained from the reaction of $RuCl_3NO(SbPh_3)_2$ with a 10 molar excess of DPE in CH_2Cl_2 at room temperature. Addition of C_2H_5OH to the reaction mixture caused the separation of yellow crystals of $RuCl_3NODPE$ which could be purified by crystallization from CH_2Cl_2–C_2H_5OH. Elemental analyses have been made for $RuCl_3NO[P(OMe)_3]_2$ (C = 15.56%, H = 3.57%, N = 2.8%; calculated values are 14.84, 3.73 and 2.88% respectively) and for $RuCl_3NODPE$ (C = 51.92%, H = 4.41%, P = 9.80%; N = 1.7%; calculated values are 49.11, 3.80, 9.74 and 2.2% respectively).

Table I reports the i.r. data in the ν_{NO} stretching region. The complex $RuCl_3NO[P(OMe)_3]_2$ has been characterized also by means of n.m.r.. The spectrum shows a 1:2:1 triplet centered at 4.05 p.p.m.; signals attributable to phenyl hydrogens are absent. Compounds with the same spectral characteristics have been prepared also starting from $RuCl_3NO(AsPh_3)_2$; in this case 35 °C and 24 hours of reaction are needed. Solvents and ligands used in the kinetic work have been purified according to standard literature methods. The solutions of the complexes suffer extensive modification in their u.v. spectra [8] in presence of light, so that all the manipulations have been performed in the dark.

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*Work in progress in this laboratory.

TABLE I. ν_{NO} in CH_2Cl_2 of $RuCl_3NOL_2$.

L	ν_{NO}, cm^{-1}
$SbPh_3$	1854 ± 3
$AsPh_3$	1868 ± 3
PPh_3	1868 ± 3
$P(On\text{-}Bu)_3$	1887 ± 3
$P(OEt)_3$	1900 ± 3
$P(OMe)_3$	1898 ± 3
DPE	1870 ± 3

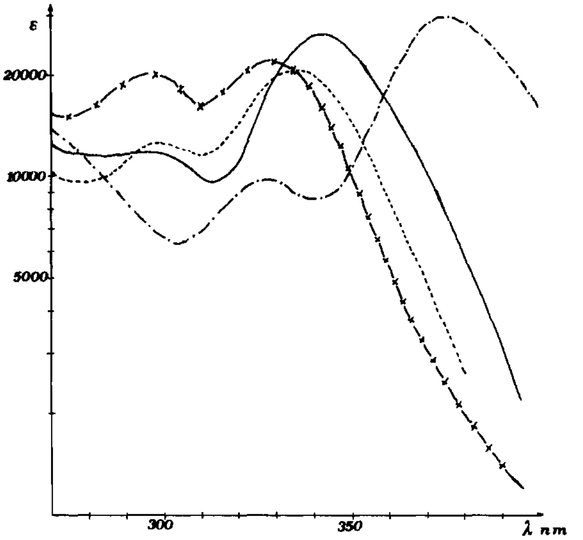

Fig. 1. U.v. spectra of $RuCl_3NOL_2$ complexes; ——— L = $AsPh_3$; ------- L = PPh_3; —·—·— L = $SbPh_3$; –X–X– L_2 = DPE.

Conditions for the Kinetic Work

The kinetics have been followed through the variation of the u.v. absorbance, using an Hitachi Perkin-Elmer mod. 139 spectrometer. Where possible, the results have been tested following the reactions also by i.r. spectrometry with a Perkin-Elmer 337 spectrometer. In those cases the ν_{NO} stretching frequencies of the reagent and product have been monitored. The u.v. spectra of the compounds, shown in Figs. 1 and 2, are stable over time intervals much longer than those used for the kinetic runs. For all the compounds, at the choosen wavelengths, the absorbance is linear with concentration between 5 X 10^{-6} and 5 X 10^{-4} *M*. All reactions go to completion. The reactions of $RuCl_3NO(SbPh_3)_2$ have been followed at 340 and 380 nm, while for the reactions of $RuCl_3NO(AsPh_3)_2$ the chosen wavelengths were 360 and 380 nm. No ligand absorbance is present at these wavelengths. All the kinetics have been made under pseudo-first-order conditions; absorbance values at infinite time have been usually calculated from the

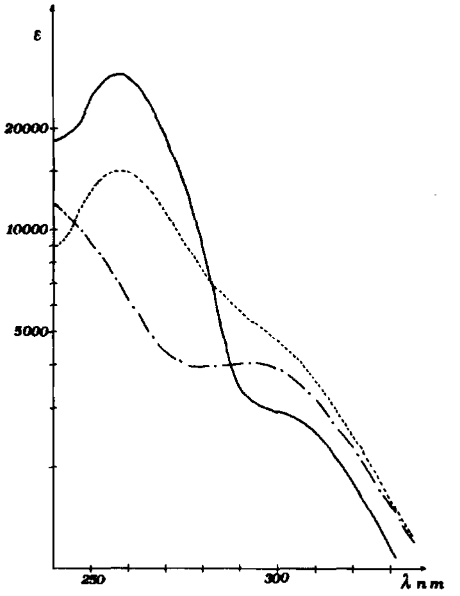

Fig. 2. U.v. spectra of $RuCl_3NOL_2$ complexes; ——— L = $P(OEt)_3$; ------- L = $P(OMe)_3$; —·—·— L = $P(On\text{-}Bu)_3$.

TABLE II. Experimental Results for the Reaction of $RuCl_3NO(AsPh_3)_2$ and PPh_3.

T °C	[Compl.] X 10^4	$[PPh_3]$ X 10^3	$[AsPh_3]$ X 10^3	k_{obs} (sec^{-1}) X 10^6
21	1.08	0.49	–	5.72
21	1.08	1.98	→ –	6.35
21	1.08	6.30	–	5.70 →
21	1.08	20.0	–	5.80
21	1.08	22.5	–	4.95
30	1.14	0.47	–	28.0
30	1.14	1.09	–	32.4
30	1.14	2.06	–	33.2
30	1.14	3.37	–	30.2
30	1.14	5.42	–	32.3
30	1.14	6.52	–	35.2
30	1.14	20.8	–	31.0
30	1.14	21.0	–	36.0
30	1.14	23.7	–	33.7
30	1.14	25.2	–	35.2
30	0.52	20.0	–	31.5
30	0.83	20.0	–	30.0
30	1.04	20.0	–	30.7
30	2.08	20.0	–	34.2
30	4.70	20.0	–	27.6
30	8.16	1.06	–	35.1
30	8.16	2.90	–	36.7
30	8.16	6.13	–	34.5
30	1.28	19.0	0.95	31.5
30	1.28	19.0	2.07	27.2
30	1.28	19.0	8.37	21.2
30	1.28	19.0	25.4	14.4
30	1.28	19.0	36.0	11.4

(continued on facing page)

TABLE II. *(continued)*

T °C	[Compl.] × 10^4	[PPh_3] × 10^3	[$AsPh_3$] × 10^3	k_{obs} (sec^{-1}) × 10^6
30	1.45	20.8	16.6	19.1
30	1.45	20.8	19.0	16.7
30	1.45	20.8	19.0	16.7
30	1.45	20.8	34.5	12.0
30	1.45	20.8	50.0	9.7
30	1.57	18.8	4.96	25.8
30	1.57	18.8	14.2	19.2
30	1.57	18.8	20.7	15.0
30	1.57	18.8	30.2	11.6
30	1.48	27.8	2.96	29.8
30	1.48	27.8	8.9	24.9
30	1.48	27.8	16.6	20.2
30	1.48	27.8	20.7	18.0
30	1.48	27.8	29.6	14.6
30	1.42	69.5	10.0	28.5
30	1.42	69.5	23.7	24.0
30	1.42	69.5	39.1	22.0
30	1.42	69.5	64.0	16.0
30	1.42	69.5	89.0	14.1
30	1.50	15.0	19.8	13.8
30	1.50	30.1	19.8	21.2
30	1.50	60.0	19.8	24.0
30	1.50	80.0	19.8	25.0
30	1.50	200.0	19.8	28.5
30	1.54	15.0	35.0	9.0
30	1.54	29.8	35.0	14.8
30	1.54	80.0	35.0	22.4
30	1.54	101.0	35.0	23.5
30	1.54	502.0	35.0	28.3

TABLE III. Experimental Results for the Reaction of $RuCl_3NO(AsPh_3)_2$ and $P(OMe)_3$.

T °C	[Compl.] × 10^4	[$P(OMe)_3$] × 10^3	[$AsPh_3$] × 10^3	k_{obs} (sec^{-1}) × 10^6
32	0.91	4.85	–	41.8
32	0.91	5.26	–	41.6
32	0.91	← 8.50	–	39.8
32	0.91	13.3	–	41.3
32	0.91	17.6	–	37.5
29.5	1.04	2.28	–	27.1
29.5	1.04	3.00	–	26.5
29.5	1.04	6.40	–	28.4
29.5	1.04	9.90	–	28.7
29.5	1.04	18.3	–	27.7
29.5	1.09	21.2	1.78	25.8
29.5	1.09	21.2	7.36	20.0
29.5	1.09	21.2	14.5	16.4
29.5	1.09	21.2	45.2	8.7
29.5	1.00	↙45.2	1.78	24.4
29.5	1.00	45.2	7.37	21.4
29.5	1.00	45.2	14.5	18.7
29.5	1.00	45.2	45.1	11.5

TABLE IV. Experimental Results for the Reaction of $RuCl_3NO(AsPh_3)_2$ and DPE.

T °C	[Compl.] × 10^4	[DPE] × 10^3	[$AsPh_3$] × 10^3	k_{obs} (sec^{-1}) × 10^6
21.5	0.89	1.0	–	5.19
21.5	0.89	2.0	–	4.8
21.5	0.90	4.0	–	5.49
21.5	0.89	8.0	–	5.1
30	0.99	1.0	–	18.5
30	0.99	2.0	–	19.0
30	1.02	4.0	–	19.4
30	0.93	5.0	–	19.9
30	0.90	8.0	–	20.1
30	0.93	10.0	–	20.2
30	0.48	20.0	1.0	18.5
30	0.49	20.0	2.0	18.9
30	0.49	20.0	3.0	19.1
30	0.54	20.0	5.0	16.2
30	0.55	20.0	7.0	16.2
30	0.56	20.0	10.0	15.5
30	0.58	20.0	20.0	11.9
30	0.58	20.0	40.0	8.6
30	0.58	20.0	60.0	7.2
30	0.58	20.0	80.0	5.5
30	0.63	1.0	1.0	12.7
30	0.66	1.0	3.0	8.5
30	0.65	1.0	7.0	4.9
30	0.68	1.0	9.8	2.5
30	0.65	1.0	19.6	1.9
30	0.63	1.0	39.0	0.95
30	0.63	2.3	1.0	16.5
30	0.67	2.3	3.0	12.7
30	0.66	2.3	7.0	8.4
30	0.66	2.3	9.8	7.6
30	0.66	2.3	19.8	4.8
30	0.64	2.3	39.0	2.2
30	0.63	2.3	↙ 59.0	1.5
30	0.64	4.0	1.0	19.0
30	0.63	4.0	3.0	15.8
30	0.64	4.0	7.0	11.0
30	0.64	4.0	9.8	8.7
30	0.63	4.0	19.8	5.4
30	0.64	4.0	39.0	3.3
30	0.64	4.0	59.0	2.2
30	0.63	4.0	78.0	1.7

TABLE V. Experimental Results for the Reaction of $RuCl_3NO(SbPh_3)_2$ and $P(On\text{-}Bu)_3$ at 21 °C.

[Compl.] × 10^5	[$P(On\text{-}Bu)_3$] × 10^4	[$SbPh_3$] × 10^4	k_{obs} (sec^{-1}) × 10^4
5	10	–	8.76[a] 8.56[b]
5	15	–	8.95[a] 9.42[b]

(continued overleaf)

TABLE V. *(continued)*

[Compl.] × 10^5	[P(On-Bu)$_3$] × 10^4	[SbPh$_3$] × 10^4	k_{obs} (sec^{-1}) × 10^4
5	25	–	10.17[a]
			10.00[b]
5	37.5	–	10.2 [a]
			10.5 [b]
5	50	–	10.3 [a]
			10.4 [b]
400	800	–	9.58[c]
			9.97[d]
5	25	7	6.47[a]
5	25	12.5	5.14[a]
5	25	25	3.5 [a]
5	50	6.5	8.10[a]
5	50	12.5	6.85[a]
5	50	25	5.38[a]

[a] u.v. 380 nm. [b] u.v. 320 nm. [c] i.r. reagent band. [d] i.r. product band.

TABLE VI. Experimental Results for the Reaction of RuCl$_3$NO(SbPh$_3$)$_2$ and P(OEt)$_3$.

[Compl.] × 10^5	[P(OEt)$_3$] × 10^4	[SbPh$_3$] × 10^4	k_{obs} (sec^{-1}) × 10^4	T °C
310	500	–	12.4[a]	25
			14.1[b]	25
500	"	–	13.8[a]	25
			13.4[b]	25
400	200	–	16.0[a]	25
			19.0[b]	25
400	300	–	17.0[a]	25
			19.0[b]	25
400	360	–	14.0[a]	25
			11.0[b]	25
400	400	–	9.4[a]	25
			13.0[b]	25
400	1200	–	13.3[a]	25
			16.2[b]	25
400	2000	–	16.0[a]	25
			18.0[b]	25
5	12.5	–	9.1[c]	21
5	25	–	9.1[c]	21
5	50	–	9.3[c]	21
5	50	6.7	8.28[c]	21
5	50	12.5	7.71[c]	21
5	50	25	6.08[c]	21
5	25	6.7	7.04[c]	21
5	25	12.5	5.72[c]	21
5	25	25	4.17[c]	21

[a] i.r. reagent band. [b] i.r. product band. [c] u.v. 380 nm.

TABLE VII. Experimental Results for the Reaction of RuCl$_3$NO(SbPH$_3$)$_2$ and P(OMe)$_3$ at 21 °C.

[Compl.] × 10^5	[P(OMe)$_3$] × 10^4	[SbPh$_3$] × 10^4	k_{obs} (sec^{-1}) × 10^4
5	5	–	7.42
5	10	–	8.91
5	15	–	8.96
5	25	–	9.59
5	37.5	–	9.59
5	50	–	9.59
5	25	6.2	8.1
5	25	12.5	6.65
5	25	25	5.27
5	50	6.2	8.72
5	50	12.5	7.81
5	50	25	6.42

initial complex concentration for the slowest reactions (to test this procedure, in some cases the calculated value was checked with the experimental one), while for the reactions of RuCl$_3$NO(SbPh$_3$)$_2$ the experimental values have been used. Rate constants were reproducible within 10%; quoted uncertainties are standard deviations.

Results and Discussion

The experimental results are reported in Tables II, III and IV for the reactions of RuCl$_3$NO(AsPh$_3$)$_2$ and in Tables V, VI and VII for those of RuCl$_3$NO(SbPh$_3$)$_2$. In all cases no variation is observed in the pseudo first-order rate constants in a wide range of ligand and complex concentrations; only in the reactions of RuCl$_3$NO(SbPh$_3$)$_2$ with P(On-Bu)$_3$ and P(OMe)$_3$, performed with the lowest [complex]/[ligand] ratios, there is a slight effect of the ligand concentration on the observed rate constant (k_{obs}) which, however, soon reaches an upper limit; average values of k_{obs} are reported in Table VIII. The rate constants decrease in presence of the leaving ligand suggesting the following dissociative mechanism:

$$\mathrm{RuCl_3NOL_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RuCl_3NOL + L} \qquad \text{(a)}$$

$$\mathrm{RuCl_3NOL + L'} \xrightarrow{k_2} \mathrm{RuCl_3NOLL'} \qquad \text{(b)}$$

$$\mathrm{RuCl_3NOLL'} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{RuCl_3NOL' + L} \qquad \text{(c)}$$

$$\mathrm{RuCl_3NOL' + L'} \xrightarrow{k_4} \mathrm{RuCl_3NOL'_2} \qquad \text{(d)}$$

The irreversibility of step (d) (and possibly of step (b) also) was verified for L′ = PPh$_3$, since solutions of RuCl$_3$NO(PPh$_3$)$_2$ did not change appreciably their u.v. spectra at 30 °C in presence of up to a 10-fold molar excess of the other ligands, over a 48 hours period.

Apart from the reaction between RuCl$_3$NO(SbPh$_3$)$_2$ and PPh$_3$ (see below), no reaction intermediate

TABLE VIII. Average Values of k_{obs}.

Complex	L'	T (°C)	k_{obs} (sec^{-1})
$RuCl_3NO(AsPh_3)_2$	PPh_3[a]	21.0	$(5.7 \pm 0.9) \times 10^{-6}$
$RuCl_3NO(AsPh_3)_2$	PPh_3[a]	30.0	$(36.2 \pm 3) \times 10^{-6}$
$RuCl_3NO(AsPh_3)_2$	$P(OMe)_3$[a]	29.5	$(27.6 \pm 1.8) \times 10^{-6}$
$RuCl_3NO(AsPh_3)_2$	$P(OMe)_3$[a]	32.0	$(40.4 \pm 1.8) \times 10^{-6}$
$RuCl_3NO(AsPh_3)_2$	DPE	21.5	$(5.1 \pm 0.2) \times 10^{-6}$
$RuCl_3NO(AsPh_3)_2$	DPE	30.0	$(19.5 \pm 0.6) \times 10^{-6}$
$RuCl_3NO(SbPh_3)_2$	$P(On\text{-}Bu)_3$	21.0	1.01×10^{-3} [b]
$RuCl_3NO(SbPh_3)_2$	$P(OEt)_3$	21.0	0.92×10^{-3} [b]
$RuCl_3NO(SbPh_3)_2$	$P(OEt)_3$	25.0	1.47×10^{-3} [b]
$RuCl_3NO(SbPh_3)_2$	$P(OMe)_3$	21.0	0.93×10^{-3} [b]

[a] For these reactions $\Delta H^\ddagger = 33.6 \pm 1.7$ Kcal/mol; $\Delta S^\ddagger = 30 \pm 3$ e.u. [b] Standard deviations are less than 0.1%.

TABLE IX. Kinetic Parameters and Competition Ratios k_{-1}/k_2 for the Reactions of $RuCl_3NOL_2$.

Complex	L'	[L']	B	A[L']	k_{-1}/k_2
$RuCl_3NO(AsPh_3)_2$	PPh_3	1.88×10^{-2}	$(2.8 \pm 0.1) \times 10^4$	$(3.58 \pm 0.08) \times 10^4$	1.17 ± 0.11
		1.90×10^{-2}	$(3.2 \pm 0.2) \times 10^4$	$(2.88 \pm 0.09) \times 10^4$	0.94 ± 0.09
		2.08×10^{-2}	$(3.1 \pm 0.2) \times 10^4$	$(3.05 \pm 0.16) \times 10^4$	0.99 ± 0.10
		2.78×10^{-2}	$(2.9 \pm 0.1) \times 10^4$	$(3.5 \pm 0.08) \times 10^4$	1.14 ± 0.11
		6.95×10^{-2}	$(3.0 \pm 0.2) \times 10^4$	$(3.32 \pm 0.10) \times 10^4$	1.08 ± 0.10
	$P(OMe)_3$	2.12×10^{-2}	$(3.6 \pm 0.1) \times 10^4$	$(3.71 \pm 0.07) \times 10^4$	1.02 ± 0.07
		4.52×10^{-2}	$(3.9 \pm 0.03) \times 10^4$	$(4.82 \pm 0.03) \times 10^4$	1.32 ± 0.09
	DPE	1.0×10^{-3}	$(4.6 \pm 0.3) \times 10^4$	$(2.43 \pm 0.02) \times 10^4$	0.48 ± 0.01
		2.3×10^{-3}	$(4.2 \pm 2.0) \times 10^4$	$(2.36 \pm 0.02) \times 10^4$	0.45 ± 0.01
		4.0×10^{-3}	$(4.4 \pm 0.5) \times 10^4$	$(2.73 \pm 0.10) \times 10^4$	0.53 ± 0.02
		20.0×10^{-3}	$(5.0 \pm 0.3) \times 10^4$	$(3.21 \pm 0.07) \times 10^4$	0.62 ± 0.02
$RuCl_3NO(SbPh_3)_2$	$P(OMe)_3$	2.5×10^{-3}	$(1.0 \pm 0.06) \times 10^3$	$(8.7 \pm 0.7) \times 10^2$	0.82 ± 0.07
		5.0×10^{-3}	$(1.0 \pm 0.005) \times 10^3$	$(1.1 \pm 0.01) \times 10^3$	1.02 ± 0.01
	$P(OEt)_3$	2.5×10^{-3}	$(1.0 \pm 0.02) \times 10^3$	$(1.3 \pm 0.03) \times 10^3$	1.22 ± 0.03
		5.0×10^{-3}	$(1.0 \pm 0.06) \times 10^3$	$(1.22 \pm 0.15) \times 10^3$	1.12 ± 0.14
	$P(On\text{-}Bu)_3$	2.5×10^{-3}	$(1.0 \pm 0.01) \times 10^3$	$(1.90 \pm 0.01) \times 10^3$	1.92 ± 0.01
		5.0×10^{-3}	$(1.0 \pm 0.02) \times 10^3$	$(1.67 \pm 0.07) \times 10^3$	1.72 ± 0.07

is likely to be present in detectable concentration, due to the invariance of the isosbestic points during the reactions.

By a simple steady state treatment one obtains:

$$\text{reaction rate} = k_2k_1 \frac{[RuCl_3NOL_2]\,[L']}{k_{-1}[L] + k_2[L']} \qquad (1)$$

giving:

$$k_{obs} = \frac{k_2k_1[L']}{k_{-1}[L] + k_2[L']} \qquad (2)$$

which in absence of free L and in presence of a large excess of L', reduces to $k_{obs} = k_1$ in accordance with the experimental findings. The proposed mechanism can be easily tested; from eqn. (2) it follows:

$$1/k_{obs} = A[L] + B \text{ where}$$

$$A = \frac{k_{-1}}{k_2k_1[L']} \text{ and } B = 1/k_1 \qquad (3)$$

This last equation predicts a linear relationship between $1/k_{obs}$ and [L] if [L'] is constant, the intercept being $1/k_1$.

Kinetic runs performed to test eqn. (3) gave the results summarized in Table IX, while Figs. 3 and 4 give some examples of the $1/k_{obs}$ *vs.* [L] plots. Additional evidence comes from kinetic runs for the reac-

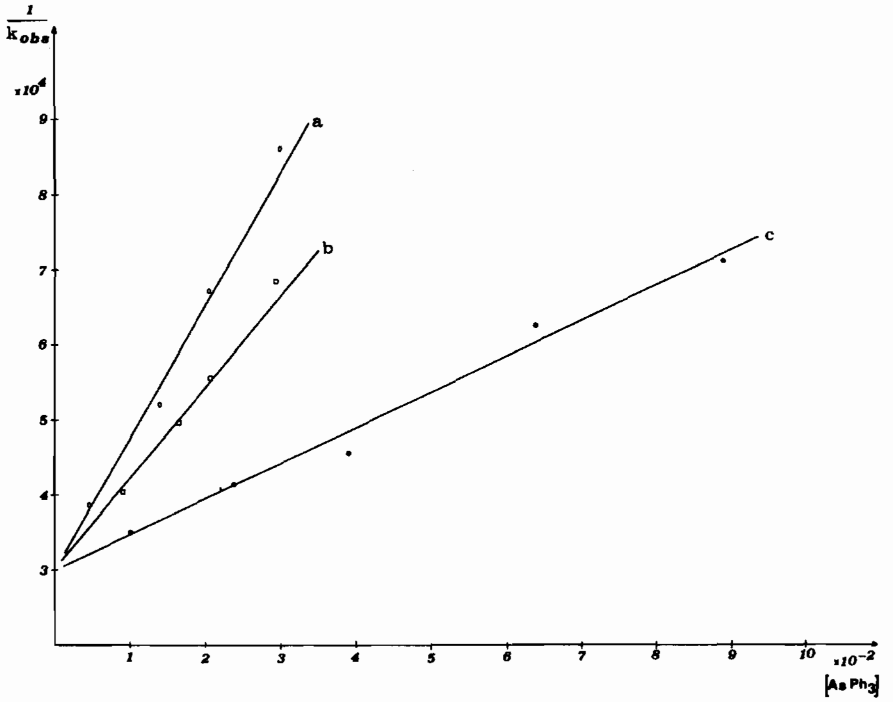

Fig. 3. Plot of $1/k_{obs}$ *vs.* [$AsPh_3$] for the reaction of $RuCl_3NO(AsPh_3)_2$ with PPh_3. [PPh_3] = (a) 18.8 × 10^{-3} *M*, (b) 27.8 × 10^{-3} *M*, (c) 69.5 × 10^{-3} *M*.

tion between $RuCl_3NO(AsPh_3)_2$ and PPh_3, performed at constant [$AsPh_3$) and variable [PPh_3]. In these conditions it follows from eqn. (2):

$$1/k_{obs} = \frac{A'}{[PPh_3]} + B \text{ where}$$

$$A' = \frac{k_{-1}}{k_2k_1}[AsPh_3] \text{ and } B = 1/k_1 \qquad (4)$$

Good linear plots of $1/k_{obs}$ *vs.* $1/[PPh_3]$ have been obtained (see Fig. 5) with a common intercept at 3 × 10^4; from the slopes it is possible to calculate the values of k_{-1}/k_2k_1 which are 3.1 × 10^4 and 3.2 × 10^4 sec, in agreement with the results from eqn. (3). The proposed mechanism implies that the rate constants observed in absence of free leaving ligand be independent of the nature of the entering ligands, as is experimentally found within 10%. The reactions with DPE show a larger deviation on this respect, which is difficult to rationalize; even if the steps (c) and (d) of the proposed mechanism are likely to become a single rapid concerted step, as is usual in a chelation reaction, the analytical expression of the rate law remains the same as already discussed. At this stage one cannot be sure that this difference (which is just outside the limit of the experimental error) is significant; in similar situations, found in the literature for reaction mechanisms of the same type [9, 10], this point does not seem to have been emphasized.

During the reaction of $RuCl_3NO(SbPh_3)_2$ with PPh_3 a variation of the isosbestic point at 352.5 nm is observed; the absorbance increases at the beginning of the reaction and then decreases to the initial value, showing that an intermediate product is formed in appreciable concentration. Kinetic runs performed at 21 °C in pseudo-first order conditions have been analyzed by the method suggested by Mocak *et al.* [11]:

For the reaction

$$RuCl_3NO(SbPh_3)_2 + PPh_3 \xrightarrow{k_1}$$

$$\text{Intermediate} \xrightarrow[PPh_3]{k_2} RuCl_3NO(PPh_3)_2$$

we found k_1 = 0.9 × 10^{-3} and k_2 = 0.4 × 10^{-3} sec^{-1}.

There are some arguments to indicate the reliability of these data which, however, are less accurate than those obtained for the other reactions:

a) the k_1 value is in agreement with the values found for the other reactions;

b) the knowledge of the k_1 and k_2 allows the calculation of the molar absorbance coefficient ϵ for the intermediate. The value so calculated at several times up to 65 minutes of reaction, is fairly constant both at 380 nm (12,700 with a 3% maxi-

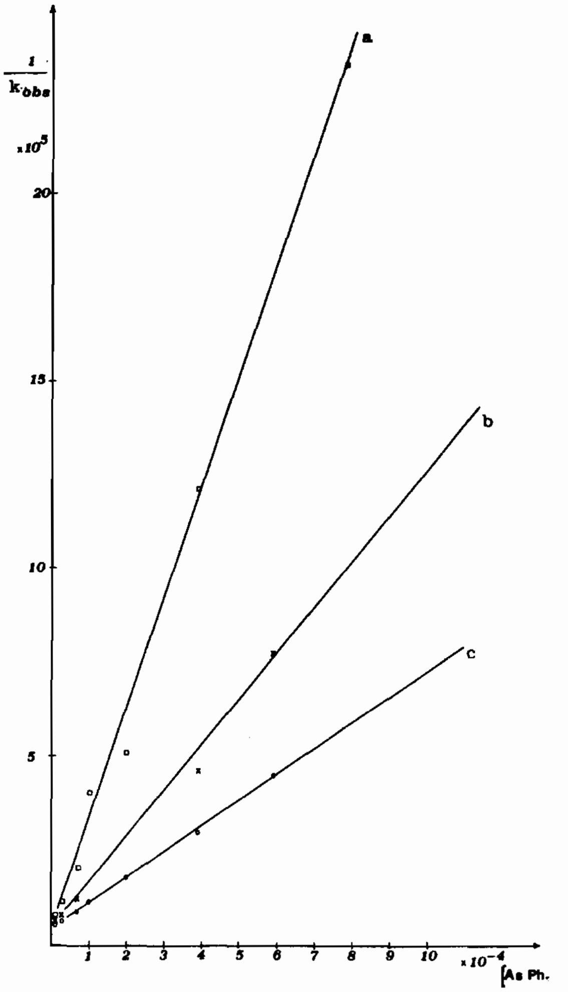

Fig. 4. Plot of $1/k_{obs}$ *vs.* $[AsPh_3]$ for the reaction of $RuCl_3NO(AsPh_3)_2$ with DPE. [DPE] = (a) 1×10^{-3} *M*, (b) 2.3×10^{-3} *M*, (c) 4×10^{-3} *M*.

mum deviation) and at 340 nm (20,200 with a 5% maximum deviation;

c) the available data allow also to calculate the variation of absorbance during the reaction, giving values in good agreement with the experimental ones (see Fig. 6).

We propose that the intermediate is $RuCl_3NOSbPh_3PPh_3$; it is also obvious that the results for this reaction agree with the previously proposed mechanism.

The ratio k_{-1}/k_2 (see data in Table IX) is a relative measure for the competition of ligands L and L′ towards a common pentacoordinate intermediate. The main effect is a lack of selectivity (common to other Ru complexes [5]) possibly due to the coordinative unsaturation which levels off any difference in the ligand reactivity; steric [9] and electronic effects [12] are reported to influence the competition ratio k_{-1}/k_2 and our results could indicate a predominance of steric effects, since the order of preference for the intermediate $RuCl_3NOSbPh_3$ is $P(On\text{-}Bu)_3 > P(OEt)_3 > P(OMe)_3$, following the order of decreasing phosphine cone angles [13].

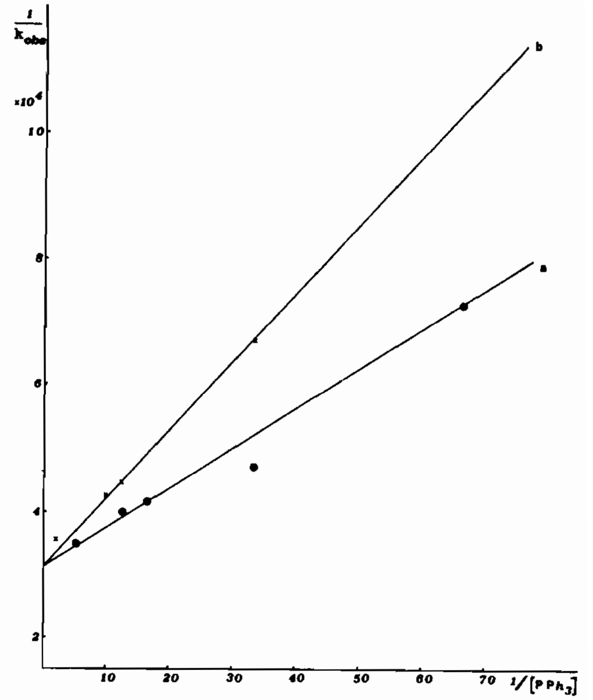

Fig. 5. Plot of $1/k_{obs}$ *vs.* $1/[PPh_3]$ for the reaction of $RuCl_3NO(AsPh_3)_2$ with PPh_3. $[AsPh_3]$ = (a) 19.8×10^{-3} *M*, (b) 35.0×10^{-3} *M*.

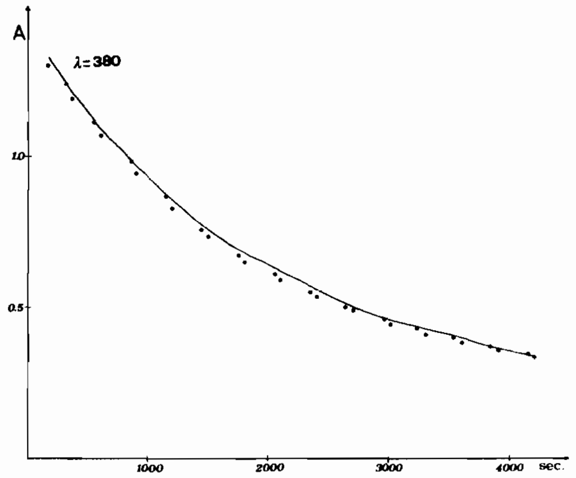

Fig. 6. Calculated (continuous line) and experimental (dots) values of absorbance in the reaction of $RuCl_3NO(SbPh_3)_2$ with PPh_3.

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