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KINETICS AND MECHANISM OF LIGAND SUBSTITUTION REACTIONS OF POLYMER-SUPPORTED $RuCl_3NO(SbPh_3)_2$. EVIDENCE FOR CHELATION OF THE ANCHORED COMPLEX

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Summary

A kinetic and mechanistic study on the ligand substitution reaction between polymer-supported $RuCl_3NO(SbPh_3)_2$ and PPh_3 is reported. Three resins with different Sb and Ru contents have been employed, and a comparison with the homogeneous reaction of the $RuCl_3NO[SbPh_2(CH_2)_3SbPh_2]$ chelate complex has been made. The results indicate that the reaction involves two different pathways starting from a common intermediate. Further evidence for the strong tendency to chelation of the Ru complex in the anchoring reaction is found.

Introduction

The anchoring of various species, mainly complexes with catalytic properties, to polymeric supports has been widely studied in the last decade [1]. The use of the heterogeneous phase can overcome difficulties such as the low solubility of the active species and its recovery. Moreover, the electronic and steric effects of the support can enhance properties such as specificity and activity of the supported species compared with those of its homogeneous counterpart. While much preparative work has been done, kinetic and structural data are still meagre. In previous investigations we studied the dependence of the rate of hydrogenation of olefins [2] on the substrate concentration and the solvent, using as catalyst $RhCl(PPh_3)_3$ anchored to polystyrene with varied cross-linking degrees. We also carried out a kinetic study of the anchoring reaction of $RuCl_3NO(SbPh_3)_2$ to resin-supported phosphinic ligands [3], obtaining some insight into the anchoring mechanism and structure of the bound complex, which turned out to be mainly bi-anchored to the functionalized resin. In this paper, we describe study of the ligand substitution reaction between dissolved PPh_3

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and $RuCl_3NO(SbPh_3)_2$, bound to the polymer via the stibine ligands. The results are compared to those for the homogeneous reaction of the chelate complex $RuCl_3NO[SbPh_2(CH_2(_3SbPh_2]$.

Experimental

Materials

Literature procedures were employed for the preparation of the compounds $ClSbPh_2$ (I) [4], $Ph_2Sb(CH_2)_3SbPh_2$ (II) [5] and $RuCl_3NO(SbPh_3)_2$ (III) [6]. Compounds I and II were identified by mass spectrometry, and III by IR and UV spectra. The method used to obtain III was also successful for $RuCl_3NO$-$[Ph_2Sb(CH_2)_3SbPh_2]$ (IV) (found: C, 38.68; H, 3.11; Cl, 13.63; Sb, 31.14. $C_{27}H_{26}Cl_3NOSb_2Ru$ calcd.: C, 39.00; H, 3.15; Cl, 12.79; Sb, 29.28%). The UV spectrum of IV is shown in Fig. 1; the ν(NO) is at 1848 cm^{-1} in CH_2Cl_2. The exchange between III and the ligand II gave a compound with the same spectral characteristics. Polystyrene-divinylbenzene resin (1% cross-linking, 200—400 mesh) was functionalized with -$SbPh_2$ groups, using known procedures [7]. The reaction (3 h in refluxing CH_2Cl_2) between III and this functionalized resin gave the polymer-supported ruthenium complex.

Chemical analysis

The functionalized resin was destroyed with a sulphuric-nitric acid mixture,

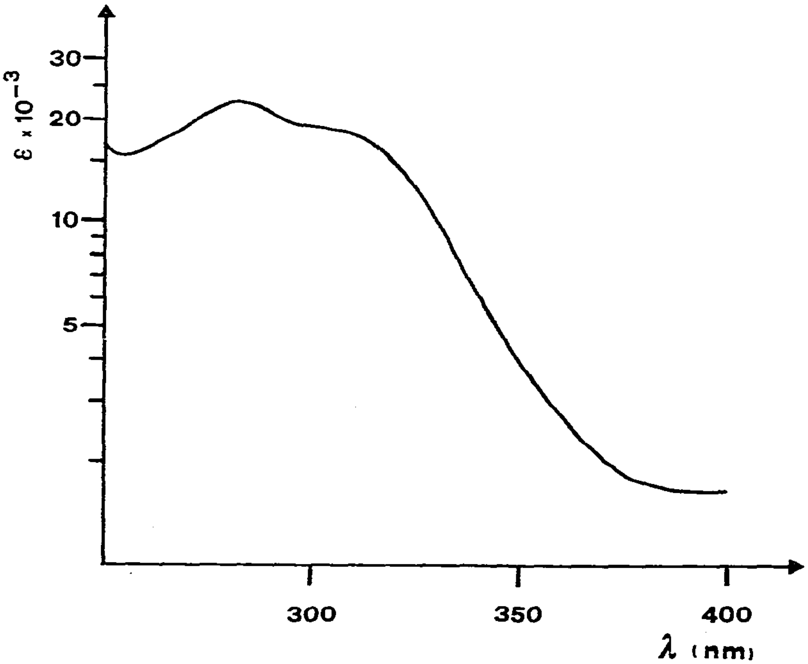


Fig. 1. UV spectrum of $RuCl_3NO[Ph_2Sb(CH_2)_3SbPh_2]$ complex in CH_2Cl_2.

the final oxidation being accomplished with perchloric acid. Dilution of the resulting clear liquid gave a solution suitable for the atomic absorption determination of antimony. For ruthenium determination, the resin was destroyed with sulphuric-perchloric acid mixture; the resulting RuO_4 was distilled into 10% NH_2OH/HCl, 3 *M* to give a solution suitable for atomic absorption analysis.

Conditions for the kinetic measurements

A few preliminary runs showed that (a) the reaction between the supported complex and PPh_3 in CH_2Cl_2 solution gives $RuCl_3NO(PPh_3)_2$ quantitatively in solution; (b) the same product is obtained in the homogeneous reaction of IV with PPh_3 in CH_2Cl_2; (c) solutions of IV in CH_2Cl_2 obey the Lambert-Beer law at least between 3×10^{-5} and 15×10^{-5} *M* (ϵ at 340 nm is 6400). The heterogeneous reaction kinetics were studied by suspending a known amount of resin in a constant volume (120 ml) of CH_2Cl_2. This suspension was magnetically stirred and excess PPh_3 was added; small aliquots of the clear solution were withdrawn at suitable intervals and their UV absorbances were read at 340 nm; these aliquots were then returned to the reaction vessel. The large excess of PPh_3 always employed ensured that the final readings depended only on the amount of resin present, and so absorbances at infinite time were measured only once for each set of kinetic runs. The homogeneous kinetics were studied under pseudo-first order conditions in the thermostated cell compartment of a Unicam SP 1800 UV-vis spectrophotometer. The kinetics were always followed for at least 20% reaction and good pseudo-first order plots were obtained throughout. All the kinetic data were obtained by weighted mean-square analysis [8]; the uncertainties shown are the standard errors.

Results and discussion

The first resin used had an antimony content of 9.33% by weight, corresponding to almost one $-SbPh_2$ group every ten benzene rings. After the introduction of the ruthenium complex the analysis gave 7.66 and 3.40% for Sb and Ru, respectively (Sb/Ru molar ratio = 1.90). This indicates that all the anchored stibine groups are saturated with Ru atoms, since otherwise the expected Sb/Ru molar ratio would be >2. Moreover, the Sb content found is close to that (8.5%) expected for a resin in which the stibine groups are saturated by chelate Ru complex. For a partially monoanchored Ru complex, the Sb content would be higher (up to 12.7%). The kinetic data for the reaction of this resin (R_1) and PPh_3 at 28°C are reported in Table 1. The values of k_{obs} are very low compared with those for the homogeneous reaction between $RuCl_3NO(SbPh_3)_2$ and PPh_3 [9]. There is a linear correlation between k_{obs} and the PPh_3 concentration (see Fig. 2). A single regression line holds for the kinetics performed with 0.1 and 0.2 g of resin; the experimental points fit the equation:

$$k_{obs} = (2.35 \times 10^{-6} \pm 1.5 \times 10^{-7}) + (1.49 \times 10^{-3} \pm 0.7 \times 10^{-4})[PPh_3] \qquad (1)$$

The presence of a second-order term in the rate-law indicates there must be a contribution from a mechanism different from that of the previously studied

TABLE 1

THE RATES OF REACTION OF RESIN (R_1) WITH PPh_3 AT 28°C

g. Resin	$[PPh_3] \times 10^4$ (M)	$[SbPh_3] \times 10^4$ (M)	$k_{obs} \times 10^6 \pm s \times 10^7$ (s^{-1})
0.1	6.31		3.68 ± 0.5
0.1	15.90		4.52 ± 0.2
0.1	15.90		4.78 ± 0.2
0.1	31.80		6.70 ± 1.3
0.1	31.80		6.96 ± 0.9
0.1	47.71		10.00 ± 0.9
0.1	63.61		12.00 ± 1.5
0.2	6.31		3.51 ± 0.3
0.2	31.80		7.26 ± 0.7
0.2	47.71		9.55 ± 0.6
0.1	6.31	11.80	4.50 ± 0.6
0.1	15.90	11.80	7.04 ± 0.8
0.1	31.80	11.80	8.82 ± 0.8
0.1	31.80	11.80	8.35 ± 0.8
0.1	41.35	11.80	9.67 ± 0.8
0.1	63.61	11.80	11.68 ± 1.9
0.1	63.61	11.80	11.22 ± 1.2
0.1	9.54	11.80	5.38 ± 0.4

homogeneous reaction.

Another striking difference between the homogeneous and heterogeneous reactions is bounded by the effect of free $SbPh_3$.

In the homogeneous system addition of leaving ligand lowers k_{obs}, whereas here (see Table 1) the presence of $SbPh_3$ in solution increases the k_{obs} values. A

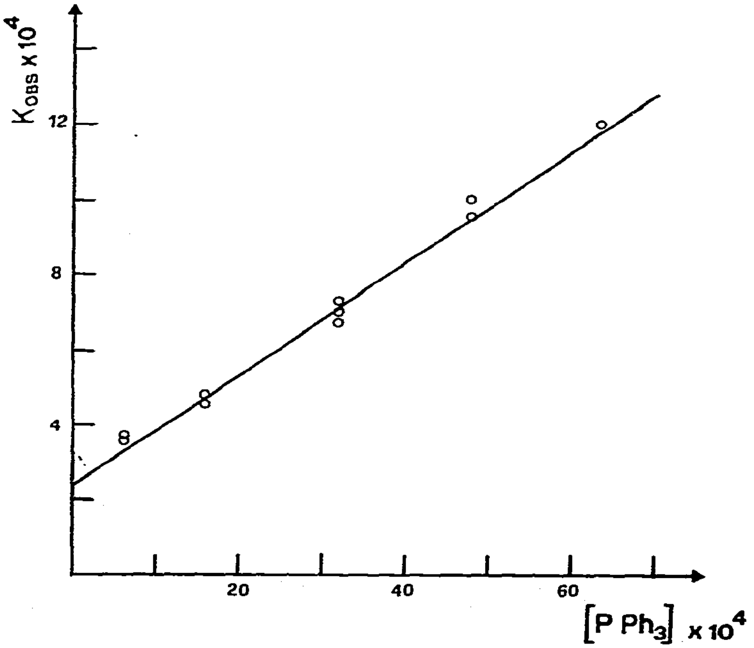


Fig. 2. Plot of k_{obs} (s^{-1}) vs. $[PPh_3]$ ($\times 10^4$ M) for the reaction of resin R_1 with PPh_3.

TABLE 2

THE RATES OF REACTION OF $RuCl_3NO(SbPh_2(CH_2)_3SbPh_2)$ WITH PPh_3 AT 28°C

[Complex] × 10^4 (*M*)	[PPh_3] × 10^3 (*M*)	[$SbPh_3$] × 10^3 (*M*)	$k_{obs} \times 10^7 \pm s \times 10^8$ (s^{-1})
1.22	6.95		6.44 ± 0.9
1.30	7.90		7.13 ± 0.8
1.22	13.90		9.77 ± 1.5
1.30	15.34		8.17 ± 1.1
1.30	23.40		9.78 ± 1.6
1.30	35.92		11.95 ± 3.0
1.22	6.95	12.06	8.36 ± 1.0
1.22	13.90	12.06	12.81 ± 2.3

linear correlation still holds, and the data fit (2).

$$k_{obs} = (2.73 \times 10^{-6} \pm 3.8 \times 10^{-7}) + (1.26 \times 10^{-3} \pm 1.1 \times 10^{-4})([PPh_3] + [SbPh_3]) \quad (2)$$

This is very similar to eq. 1. The 90% confidence intervals calculated [8] for the slopes of eq. 1 and 2 ($\pm 1.3 \times 10^{-4}$ and $\pm 2.2 \times 10^{-4}$, respectively), indicate that they must be considered equal within the experimental error. We therefore conclude that $SbPPh_3$ is as effective as PPh_3 in the detachment reaction; the stibine complex then undergoes a fast ligand exchange in the homogeneous phase, to give $RuCl_3NO(PPh_3)_2$.

Previous indications [3] of a tendency to chelation in the anchoring reaction suggested comparison of the above results with data for the homogeneous ligand substitution reaction of a similar complex containing a chelate ligand. The results obtained for the reaction between IV and PPh_3 are summarized in Table 2; the equation relating k_{obs} with PPh_3 is

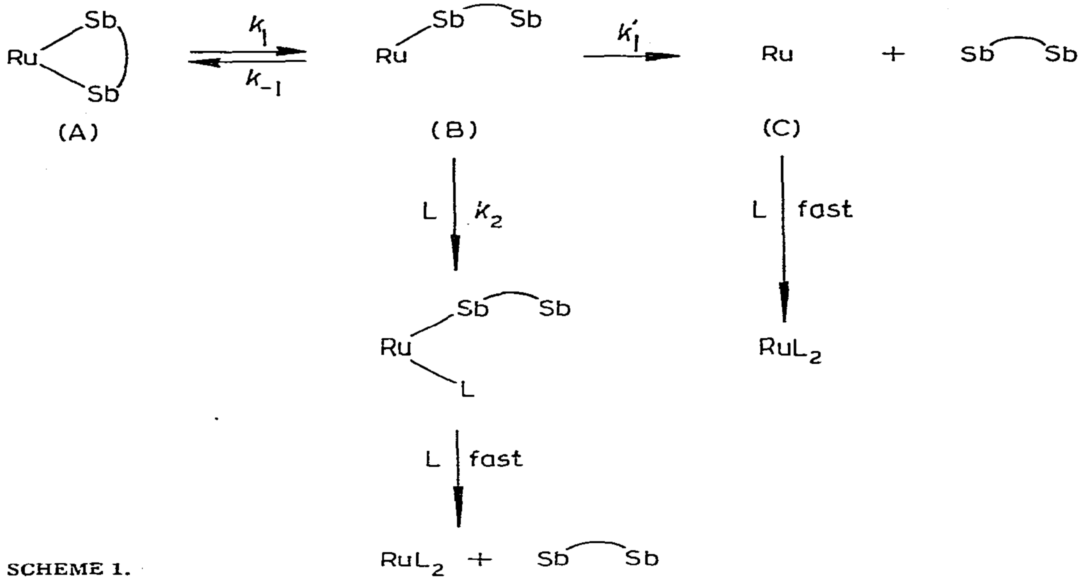
$$k_{obs} = (5.32 \times 10^{-7} \pm 6.3 \times 10^{-8}) + (2.22 \times 10^{-5} \pm 4.8 \times 10^{-6})[PPh_3] \quad (3)$$

i.e., there is a marked decrease of the overall rate but the two term rate law still applies. In this case once again, the presence of $SbPh_3$ in solution increases the rate (see Table 2). The presence in the complex of a chelate ligand is incompatible with the simplest reaction mechanism suggested by eq. (3), i.e. a dissociative first order pathway and a parallel associative second-order one.

The observation of a rate law of the same form for the ligand exchange reactions of the complex IV and the polymer-supported complex III indicate that the supported complex is mainly in a chelate form. A similar mechanism must thus operate in the homogeneous and heterogeneous exchange reactions.

A possible scheme which can account for the experimental finding is Scheme 1, where the bidentate ligand is indicated by SbSb and the entering ligand as L; other ligands are not shown. In this scheme the reaction proceeds via two parallel pathways, both starting from the intermediate B. The reaction rate is therefore given by

$$v = k_1'[B] + k_2[B][L] = (k_1' + k_2[L])[B]$$



SCHEME 1.

Applying the steady-state treatment to B, gives

$$v = (k'_1 + k_2[\mathrm{L}])\left(\frac{k_1[\mathrm{A}]}{k_{-1} + k'_1 + k_2[\mathrm{L}]}\right)$$

so that, under the pseudo-first order conditions used,

$$k_{\mathrm{obs}} = k_1\frac{k'_1 + k_2[\mathrm{L}]}{k_{-1} + k'_1 + k_2[\mathrm{L}]} \qquad (4)$$

The intermediate B reacts in three different ways; the fastest reaction is likely to be that corresponding to the closing of the chelate ring, so that one can assume $k_{-1} >> (k'_1 + k_2[\mathrm{L}])$. Then eq. 4 becomes

$$k_{\mathrm{obs}} = \frac{k_1}{k_{-1}}k'_1 + \frac{k_1}{k_{-1}}k_2[\mathrm{L}] \qquad (5)$$

which agrees with the observed dependence of k_{obs} on the entering ligand concentration. The supported complex, however, undergoes the ligand exchange reaction faster than complex IV. This increased reactivity might arise from a steric effect; it is likely that since the -SbPh$_2$ groups are bound to a cross-linked polymeric chain, the final geometry of the supported complex will be somewhat distorted compared with that in the unsupported chelate complex. According to this interpretation, in a polymer containing a lower concentration of -SbPh$_2$ groups this steric strain would increase, and the supported complex would be more reactive.

To test this hypothesis, we prepared a resin with a lower Sb content (1.98% by weight, corresponding to about 1 functionalized ring in every 60), and allowed it to react with excess complex III. The final product (resin R$_2$) con-

TABLE 3

RATES OF REACTION OF THE RESIN (R_2) WITH PPh_3 AT 28°C

Resin (g)	$[PPh_3] \times 10^4$ (*M*)	$k_{obs} \times 10^6 \pm s \times 10^7$ (s^{-1})
0.1	6.31	8.97 ± 2.2
0.1	15.90	12.96 ± 2.1
0.1	47.71	25.88 ± 3.7
0.1	63.61	32.12 ± 6.4

TABLE 4

RATES OF REACTION OF RESIN (R_3) WITH PPh_3 AT 28°C

Resin (g)	$[PPh_3] \times 10^4$ (*M*)	$k_{obs} \times 10^6 \pm s \times 10^7$ (s^{-1})
0.1	6.31	8.47 ± 2.1
0.1	15.90	10.17 ± 5.6
0.1	31.80	15.18 ± 5.9
0.1	47.71	19.13 ± 5.7
0.1	63.61	25.73 ± 8.2

tained 1.88% and 0.8% of Sb and Ru, respectively (Sb/Ru molar ratio = 1.94). The kinetic data, obtained as before, for R_2 are shown in Table 3; the relation between k_{obs} and $[PPh_3]$ is given by the equation

$$k_{obs} = (6.45 \times 10^{-6} \pm 0.7 \times 10^{-7}) + (4.06 \times 10^{-3} \pm 0.2 \times 10^{-4})\,[PPh_3] \qquad (6)$$

Both the first and second order terms are higher in R_2 as expected. A closer inspection of eqs. 1 and 6 reveals that the ratios of the overall first and second order rate constants are almost equal (2.74 and 2.72, respectively). According to the proposed mechanism, the reaction paths denoted by k'_1 and k_2 should not be influenced by the different steric situation of the supported complex in the two resins, because these steps follow the loss of chelation. Any difference in reactivity between R_1 and R_2 must be ascribed to the first dissociative step. In fact, according to eq. 5, a variation of the ratio k_1/k_{-1} changes the first and second order terms by the same factor, as found experimentally *.

Another test of the above suggestions comes from the study of the kinetic behaviour of a third resin (R_3). This resin had the same initial Sb content as R_2, but the anchoring reaction was performed with a deficiency of the ruthenium complex. The final Ru content was 0.37%. Table 4 shows the kinetic data; the experimental values fit the equation

$$k_{obs} = (4.50 \times 10^{-6} \pm 2.8 \times 10^{-7}) + (3.23 \times 10^{-3} \pm 1.2 \times 10^{-4})[PPh_3] \qquad (7)$$

which is significantly different from eq. 6 and indicates a lower overall reaction rate. Once again, the ratio of the overall rate constants for the corresponding

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* According to the proposed mechanism the corresponding ratios of rate constants between the homogeneous (eq. 3) and the heterogeneous reaction should be equal. However, these ratios are different, and the results seem to indicate a significant relative decrease of the k_2 rate constant for the homogeneous reaction. The reason for this is unknown.

TABLE 5

REGRESSION LINES FOR PLOTS OF THE OBSERVED KINETIC CONSTANTS VS. THE CONCENTRATION OF ENTERING LIGAND USING R_1, R_2, R_3 AND $[SbPh_2(CH_2)_3SbPh_2]RuCl_3NO$ (IV)

R_1	$k_{obs} = (2.35 \times 10^{-6} \pm 1.5 \times 10^{-7}) + (1.49 \times 10^{-3} \pm 0.7 \times 10^{-4})\ [PPh_3]$
R_1	$k_{obs} = (2.73 \times 10^{-6} \pm 3.8 \times 10^{-7}) + (1.26 \times 10^{-3} \pm 1.1 \times 10^{-4})\ ([PPh_3] + [SbPh_3])$
R_2	$k_{obs} = (6.45 \times 10^{-6} \pm 0.7 \times 10^{-7}) + (4.06 \times 10^{-3} \pm 0.2 \times 10^{-4})\ [PPh_3]$
R_3	$k_{obs} = (4.05 \times 10^{-6}\ b\ 2.8 \times 10^{-7}) + (3.23 \times 10^{-3} \pm 1.2 \times 10^{-4})\ [PPh_3]$
IV	$k_{obs} = (5.32 \times 10^{-7} \pm 6.3 \times 10^{-8}) + (2.22 \times 10^{-5} \pm 4.8 \times 10^{-6})\ [PPh_3]$

terms of eqs. 7 and 1 are almost equal (1.91 and 2.16, respectively). The lower reactivity of R_3 than of R_2 (Table 5) can be rationalized in terms of the previous suggestions, the lower Ru content favours the chelation since the complex has a relatively higher number of available anchoring points. It can be argued that the presence of free-$SbPh_2$ groups and the claimed "high mobility" of the polymeric chains [10] would produce the same effect. However, if the free-$SbPh_2$ groups in the polymer chains are effective in lowering the reaction rate, their influence should be detectable also in every kinetic run as a marked departure from linearity of the pseudo-first order kinetic plot.

The above results give further information about the strong tendency to chelation in the anchoring reactions, and the possible reasons for changes of reactivity of an anchored complex. Transfer of this information to catalytic systems is straightforward: a decrease in catalytic activity is to be expected whenever the complex is in a chelate form on the supporting polymer, and the catalytic process involves a step involving the detachment of the ligand acting as anchoring group. Further investigations on substitution reactions of ligands not involved in the anchoring of complexes to the resins should help to optimize the conditions for catalytic reactions.

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