The mechanism of the addition of haloalkanes to alkenes in the presence of [RuH$_3$(SiMe$_2$Ph)(PPh$_3$)$_3$] and [RuH$_2$(PPh$_3$)$_4$]

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Abstract

Kinetic and other studies have demonstrated that the addition of haloalkanes to alkenes in the presence of either [RuH$_3$(SiMe$_2$Ph)(PPh$_3$)$_3$] or [RuH$_2$(PPh$_3$)$_4$] has a mechanism very similar to that observed in the presence of [RuCl$_2$(PPh$_3$)$_3$]. The previous report of enhanced catalytic activity for the two hydrides has not been confirmed.

Introduction

We have previously published studies of the mechanism of the addition of halocarbons to alkenes (eq. 1) catalysed by the transition metal complexes, [RuCl$_2$(PPh$_3$)$_3$] [1], [Cr(CO)$_3$(η^6-C$_{10}$H$_8$)] [2], [Fe$_2$(CO)$_4$(η-cp)$_2$] [3], [Mo$_2$-

$$RCH=CH_2 + CX_4 \rightarrow RCHXCH_2CX_3 \qquad (1)$$

(CO)$_4$(η-cp)$_2$] [4] and [Mo$_2$(CO)$_6$(η-cp)$_2$] [5]. The first of these is by far the most active catalyst and is the complex preferred for synthetic applications of such reactions. All these catalysts operate by a broadly similar mechanism, which is detailed in Scheme 1 for [RuCl$_2$(PPh$_3$)$_3$] (I).

Matsumoto *et al.* [5] have reported that ruthenium(IV) complexes of the type [RuH$_3$(SiR$_3$)(PPh$_3$)$_2$] display considerably higher catalytic activity than I, with "catalytic efficiencies" (defined as moles of product/moles of catalyst) up to 32 times that of I. They have also reported that the hydrido–ruthenium(II) complexes [RuH$_2$(PPh$_3$)$_4$] (II) and [RuH(SiR$_3$)(PPh$_3$)$_2$] show somewhat higher efficiency than I, varying from 3-fold in the case of II to 7-fold for [RuH{Si(OMe)$_3$}(PPh$_3$)$_2$].
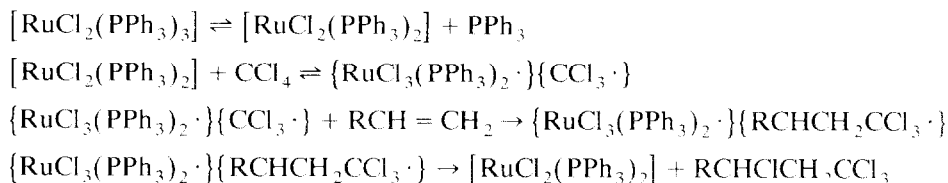

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Table 1

Reaction of tetrachloromethane with oct-1-ene catalysed by I, II and III in the absence and presence of added triphenylphosphine

Catalyst	Conc. ($\times 10^{-5}$ mol)	PPh$_3$ ($\times 10^{-4}$ mol)	% Yield [a]	product : catalyst mol. ratio
I	1.32		79.1	3072
	1.35	1.58	13.8	522
II	1.09		67.4	3144
	1.14	1.71	7.9	353
III	1.27		71.0	2860
	1.35	1.63	14.0	535

[a] Mean of three measurements

$$\left[RuCl_2(PPh_3)_3\right] \rightleftharpoons \left[RuCl_2(PPh_3)_2\right] + PPh_3$$

$$\left[RuCl_2(PPh_3)_2\right] + CCl_4 \rightleftharpoons \left\{RuCl_3(PPh_3)_2\cdot\right\}\left\{CCl_3\cdot\right\}$$

$$\left\{RuCl_3(PPh_3)_2\cdot\right\}\left\{CCl_3\cdot\right\} + RCH=CH_2 \rightarrow \left\{RuCl_3(PPh_3)_2\cdot\right\}\left\{RCHCH_2CCl_3\cdot\right\}$$

$$\left\{RuCl_3(PPh_3)_2\cdot\right\}\left\{RCHCH_2CCl_3\cdot\right\} \rightarrow \left[RuCl_2(PPh_3)_2\right] + RCHClCH_2CCl_3$$

Scheme 1.

No explanation was offered for this enhanced activity and we therefore thought it of interest to establish the mechanistic features of these catalysts.

Results and discussion

Table 1 shows the effect of the catalysts I, II and [RuH$_3$(SiMe$_2$Ph)(PPh$_3$)$_3$] [III] on the addition of CCl$_4$ to oct-1-ene. Under strictly comparable reaction conditions and catalyst concentrations we observed no marked difference between the efficiency (as defined above) of the three complexes. This clearly contrasts with the earlier findings [5] and we were unable to find conditions under which II and III showed enhanced activity in reactions carried out under preparative conditions (5 h of reflux). A kinetic study of the reaction of CCl$_4$ and oct-1-ene by the initial rate method showed both II and III to obey a rate law comparable with that of I (eq. 2) [1]. Comparison of the variation of reaction rate with catalyst concentration shows I and III to be similar, while II is somewhat lower (Fig. 1). There is also a notable increase in the size of intercept with II and III compared to I.

$$\text{Rate} = \frac{k[\text{I}][CCl_4][RCH=CH_2]}{[PPh_3](1 + [RCH=CH_2])} \tag{2}$$

The data given in Table 1 show that PPh$_3$ dissociation is important in all three cases. Additions of SiHMe$_2$Ph to reactions catalysed by III did not lead to a reduction in reaction rate, suggesting that reductive elimination of the silane is not involved in generating the active catalyst. However, addition of SiClMe$_2$Ph does slow the reaction (Fig. 2), complete inhibition being achieved in the presence of a 35-fold excess of chlorosilane. A combination of a 10-fold excess of PPh$_3$ and a 10-fold excess of chlorosilane also quenched the reaction completely.
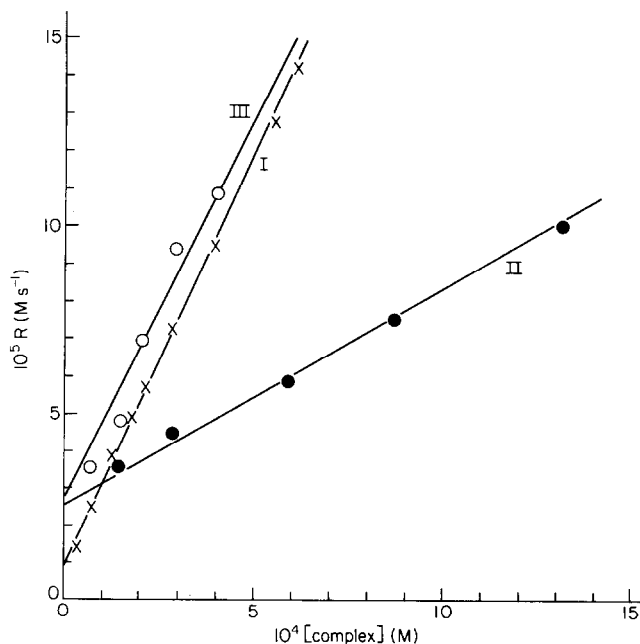
Fig. 1. Variation of initial rate of reaction with complex concentration for I, II and III.

When the alkene–halocarbon addition reaction was carried out in the presence of either II or III under and atmosphere of H_2 rather than N_2 there was no reduction in rate. However, the effect on this type of reaction of placing the solution under hydrogen at a pressure of 1 atm might be expected to be small, since the concentration of gas in the solution would be low. It was not possible to
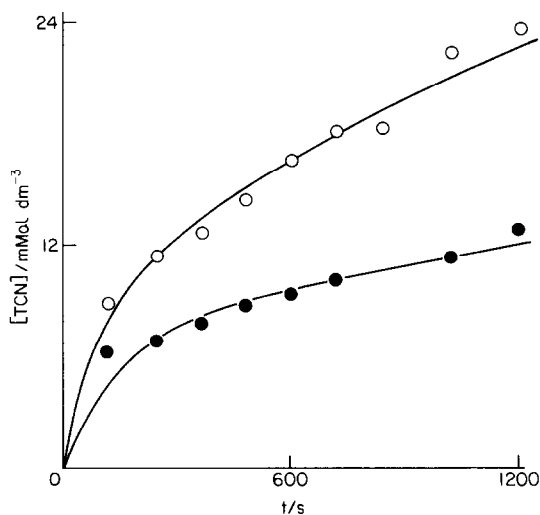

Fig. 2. Effect of added $SiClMe_2Ph$ on the rate of formation of tetrachlorononane in the presence of III. (○ normal reacton; ● in the presence of $SiClMe_2Ph$).

carry out such experiments under a higher pressure of hydrogen since the complexes also catalyse hydrogenation of the alkene. However, evidence for elimination of H_2 was obtained from a study of the reaction of III with CCl_4. Over a period of 4 h, 0.91 moles of H_2 and 0.59 moles of $CHCl_3$ were formed per mole of III. This suggests that reductive elimination of H_2 is occurring, together with reaction of the ruthenium (II) monohydride so formed with CCl_4 (eqs. 3 and 4). The latter reaction might be expected, as production of $CHCl_3$ from metal

$$[RuH_3(SiMe_2Ph)(PPh_3)_3] \rightarrow [RuH(SiMe_2Ph)(PPh_3)_3] + H_2 \qquad (3)$$

$$[RuH(SiMe_2Ph)(PPh_3)_3] + CCl_4 \rightarrow [RuCl(SiMe_2Ph)(PPh_3)_3] + CHCl_3 \qquad (4)$$
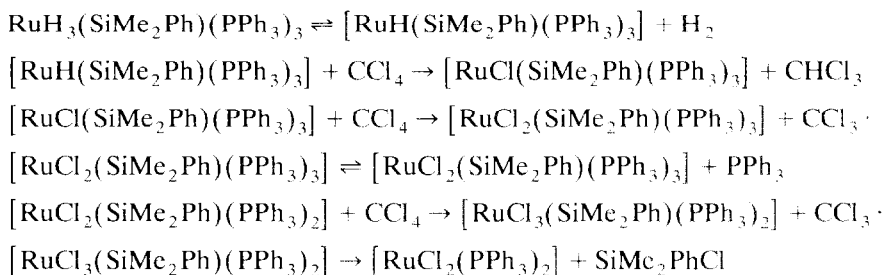
hydrides and CCl_4 has long been used as qualitative evidence for the existence of hydride ligands [6]. The formation of less than one equivalent of $CHCl_3$ is probably a consequence either of loss of $CHCl_3$ during the intermediate replacement of the atmosphere above the solution or of incomplete reaction. C_2Cl_6 was also obtained from the reaction of III with CCl_4. II also reacts with CCl_4 giving both $CHCl_3$ and C_2Cl_6. Both II and III reacted more rapidly with CCl_4 than did I.
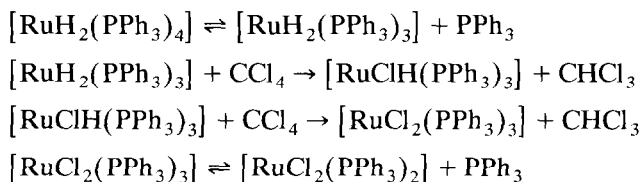
The mechanism of reactions of metal hydrides with CCl_4 has not been established; however, they are likely to be free radical processes which could therefore act as initiating steps in halocarbon-alkene addition reactions proceeding by a radical chain mechanism. As a consequence, reactions in the presence of the metal hydrides II and III might be expected to show a larger intercept to the plot of the reaction rate *versus* catalyst concentration that does I.

Suggested mechanisms for the reactions of II and III with CCl_4 are given in Schemes 2 and 3. Each of these leads to $[RuCl_2(PPh_3)_2]$. This species is also the active catalyst in the reaction catalyst by I [1]. Scheme 2 also shows why reaction in the presence of III is inhibited by added $SiClMe_2Ph$. Furthermore, the reduced reaction rate in the presence of II (Fig. 1) is a consequence of the presence of an extra mole of free PPh_3 in this case (Scheme 3).

Further evidence for the formation of a common species from I, II and III was obtained by ^{31}P NMR spectroscopy. Thus, solutions of the three complexes in benzene in the presence of oct-1-ene and CCl_4 each gave rise to a single absorption of 46 ppm. This is assigned to the species $[RuCl_2(PPh_3)_2]$ [7]. All three solutions slowly produce tetrachlorononane at 30°C in the NMR spectrometer, but no change was observed in the peak at 46 ppm.

$RuH_3(SiMe_2Ph)(PPh_3)_3 \rightleftharpoons [RuH(SiMe_2Ph)(PPh_3)_3] + H_2$

$[RuH(SiMe_2Ph)(PPh_3)_3] + CCl_4 \rightarrow [RuCl(SiMe_2Ph)(PPh_3)_3] + CHCl_3$

$[RuCl(SiMe_2Ph)(PPh_3)_3] + CCl_4 \rightarrow [RuCl_2(SiMe_2Ph)(PPh_3)_3] + CCl_3\cdot$

$[RuCl_2(SiMe_2Ph)(PPh_3)_3] \rightleftharpoons [RuCl_2(SiMe_2Ph)(PPh_3)_3] + PPh_3$

$[RuCl_2(SiMe_2Ph)(PPh_3)_2] + CCl_4 \rightarrow [RuCl_3(SiMe_2Ph)(PPh_3)_2] + CCl_3\cdot$

$[RuCl_3(SiMe_2Ph)(PPh_3)_2] \rightarrow [RuCl_2(PPh_3)_2] + SiMe_2PhCl$

Scheme 2.

$$[RuH_2(PPh_3)_4] \rightleftharpoons [RuH_2(PPh_3)_3] + PPh_3$$

$$[RuH_2(PPh_3)_3] + CCl_4 \rightarrow [RuClH(PPh_3)_3] + CHCl_3$$

$$[RuClH(PPh_3)_3] + CCl_4 \rightarrow [RuCl_2(PPh_3)_3] + CHCl_3$$

$$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2] + PPh_3$$

Scheme 3.

The evolution of H_2 and the formation of $CHCl_3$ from the reaction between III and CCl_4 may possibly suggest two different forms of ligated hydrogen in III and its reformulation as $[Ru(\eta\text{-}H_2)(H)(SiMe_2Ph)(PPh_3)_3]$ [8]. In an effort to resolve this point the metal hydrogen T_1 values for the complex were determined at $-60°C$. A single value of 626 ms was obtained and while this result is equivocal, it is consistent with the formulation of III as a ruthenium (IV) trihydride rather than a ruthenium (II) monohydride dihydrogen complex [9].

In conclusion, all the evidence presented here is consistent with I, II and III forming a common intermediate on treatment with CCl_4 and with catalysis of CCl_4 addition to oct-1-ene in the presence of these complexes following a common pathway.

Experimental

$[RuCl_2(PPh_3)_3]$ [1], $[RuH_2(PPh_3)_4]$ [10] and $[RuH_3(SiMe_2Ph)(PPh_3)_3]$ [11] were prepared by published methods. General experimental conditions were as described previously [1].

Reaction of CCl_4 with oct-1-ene in the presence of I, II or III

Preparative conditions. The catalyst (approximately 1×10^{-5} mol) and the standard, methyl myristate (approximately 0.2 g) were accurately weighed into a round-bottom flask (50 cm³). CCl_4 (15 cm³) and oct-1-ene (8 cm³) were added from burettes. The mixture was degassed by three freeze-pump-thaw cycles and then refluxed under nitrogen for 5 h. The solution was cooled and samples analysed by GLC (5% OV17 column at 180°C; FID at 250°C; injector port at 225°C). Standard mixtures of methyl myristate and tetrachlorononane were used to determine response factors. These were checked regularly before and after sample analysis.

Kinetic measurements. The kinetic studies were carried out with the apparatus and method previously described [1].

Reaction of II and III with CCl_4

The complex III $(6 \cdot 8 \times 10^{-5}$ mol) was accurately weighed out and was added, together with CCl_4, to a vessel which was subsequently sealed under N_2 and stirred for 2 h. The gas phase was analysed (molecular sieves at 80°C, catherometer detector, N_2 carrier gas at 60 cm³ min^{-1}) and found to contain 4.3×10^{-5} mol of H_2. The gas phase was then pumped out and replaced with N_2. After a further 2 hours, analysis of the gas phase revealed a further 1.9×10^{-5} mol of H_2. Analysis

of the liquid phase (3% APL at 25°C, detector at 62°C, injector at 40°C) revealed 4×10^{-5} mol of $CHCl_3$.

From separate reactions of II and III under reflux both $CHCl_3$ and C_2Cl_6 were identified, although the amounts of these were not determined.

Acknowledgment

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