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**Preliminary communication**

# THE MECHANISM OF THE ADDITION OF TETRAHALOALKANES TO ALKENES IN THE PRESENCE OF $RuCl_2(PPh_3)_3$

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## Summary

The addition of tetrahaloalkanes to alkenes in the presence of $[RuCl_2(PPh_3)_3]$ has been examined in detail and it is suggested that it proceeds by a non-chain catalysed mechanism involving free radical intermediates.

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We have recently carried out mechanistic studies on the addition of halocarbons across alkenic bonds in the presence of both $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$ [1] and $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ [2]. Reaction sequences have been proposed in both cases. In the presence of both complexes the yields of 1/1 adduct were only moderate (Yields of 1,1,1,3-tetrachlorononane from reaction between $CCl_4$ and oct-1-ene: 19.6% at 80°C, 47.5% at 120°C in the presence of $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$; 12.4% at 80°C, 11.7% at 120°C in the presence of $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$). However, use of $[RuCl_2(PPh_3)_3]$ (I) has been shown to give much higher yields of the 1/1 adduct [3] (74.6% at 80°C, 67.2% at 120°C in our hands under conditions identical to those used above).

Matsumoto and co-workers have shown I to be efficient in the promotion of a range of reactions involving the addition of $X_3CCl$ to alkenes and although no detailed mechanistic studies have been reported for any of these reactions, they have been shown to be inhibited by radical scavengers [3,4]. Other studies by these workers of the addition of $CCl_4$ to cyclohexene and cyclooctene in the presence of I have suggested that these reactions do not follow the well established free-radical chain route and have led to the proposal of a "radical reaction within the coordination sphere" (Scheme 1) [5], in which free radicals are in some way associated with the metal centre, such that their reactivity is modified.

We have carried out a kinetic study of the reaction between $CCl_4$ and oct-1-ene in the presence of I, using the initial rate method. This yielded a rate law of the type shown in eqn. 1.

$$\mathrm{Ru^{II} + CCl_4 \rightarrow Ru^{III}Cl + CCl_3^{\bullet}}$$

$$\mathrm{CCl_3^{\bullet} + RCH{=}CH_2 \rightarrow RCH{\cdot}CH_2CCl_3^{\bullet}}$$

$$\mathrm{RCH{\cdot}CH_2CCl_3^{\bullet} + Ru^{III}Cl \rightarrow RCHCl{\cdot}CH_2CCl_3 + Ru^{II}}$$

SCHEME 1

$$\text{Rate} = \frac{k[\mathrm{I}][\mathrm{CCl_4}][\mathrm{C_8H_{16}}]}{(k'[\mathrm{C_8H_{16}}] + k'')} \tag{1}$$

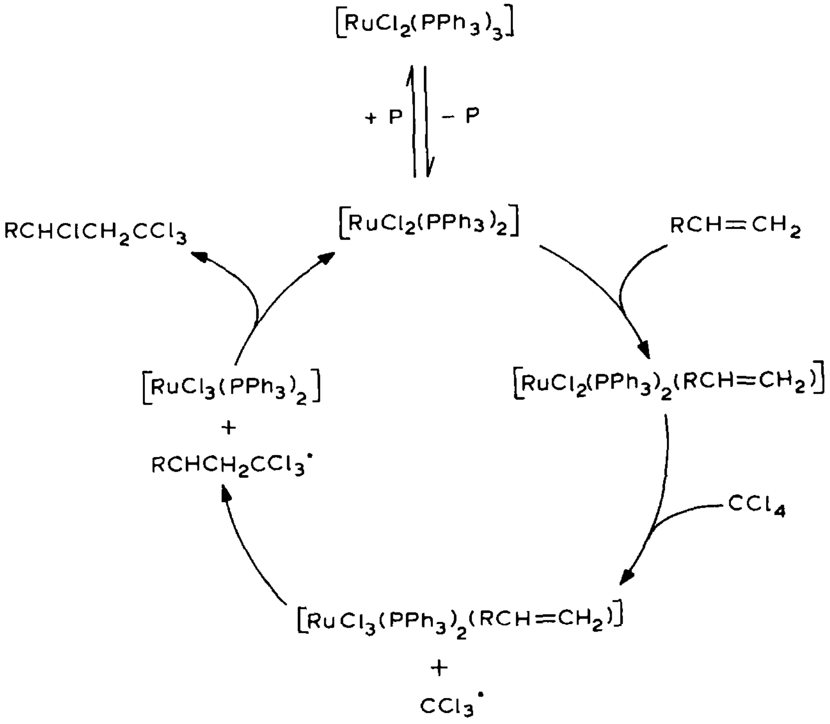
The reaction rate is retarded by the addition of triphenylphosphine and this is in accord with dissociation of $PPh_3$ from I, as has been reported previously [6].

In a search for possible intermediates in this addition reaction, the reaction between I and alkenes was examined. As has been reported by others [7], we were unable to identify any products with monoalkenes such as ethene and oct-1-ene.

The solubility of I in $CCl_4$ is low and thus the direct reaction between these two species was first examined in toluene. After refluxing such a mixture for some hours, $C_2Cl_6$ was produced, but we were unable to obtain reproducible analyses for the ruthenium containing product. In a separate reaction, a $CCl_4$ suspension of I was refluxed for several hours in the presence of a large excess of $PPh_3$. This resulted in formation of a material, the analytical data for which was close to that expected for $[RuCl_3(PPh_3)_3 \cdot CCl_4]$. However, the magnetic moment of this compound was found to be 1.4 $\mu_B$, considerably less than that expected for ruthenium(III). This may arise as a consequence of contamination with a small amount of ruthenium(II)-containing material. Thus, the product of this reaction could not be characterised unambiguously, however, it is clear that reaction between I and $CCl_4$ leads to a ruthenium(III) containing product and $C_2Cl_6$, presumably formed by dimerisation of $CCl_3^{\bullet}$ radicals.

A cross-over experiment was also performed in which oct-1-ene was treated with a mixture of $CCl_4$ and $CBr_4$ in the presence of I. This yielded $C_9H_{16}Cl_4$, $C_9H_{16}Br_4$, $C_9H_{16}BrCl_3$ and $C_9H_{16}Br_3Cl$ (product ratio: 1/14/2/5). As in the study of similar reactions promoted by $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ [2], these findings are inconsistent with a reaction proceeding by a route involving oxidative addition of $CX_4$ to the ruthenium(II) centre. The kinetic data clearly exclude a free radical chain reaction.

Alternative mechanisms can be proposed which are consistent with the kinetic data. In particular, the Michaelis—Menton behaviour with respect to alkene concentration might suggest reversible alkene coordination to ruthenium(II) as detailed in Scheme 2. However, in view of the findings outlined above, we believe it unlikely that reaction between ruthenium(II) and $CCl_4$ does not precede reaction with the alkene. Furthermore, the norbornadiene complex $[RuCl_2(PMe_2Ph)_2(C_7H_8)]$ does not react with $CCl_4$, even under reflux, to give the 1/1 adduct $C_8H_8Cl_4$, and although this coordinatively saturated compound does not provide a true model for the mono-alkene intermediates formed from $[RuCl_2(PPh_3)_2]$, it does indicate that coordination of the diene does not markedly activate it towards reaction with $CCl_4$.



SCHEME 2

In view of our proposals for the promotion of reactions of this type by $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ [2], we suggest that the reaction in the presence of I follows the route outlined in Scheme 3, the rate law for which is given in eq. 2.

$$\underset{(I)}{[RuCl_2(PPh_3)_3]} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(II)}{[RuCl_2(PPh_3)_2]} + PPh_3$$

$$[RuCl_2(PPh_3)_2] + CCl_4 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(III)}{\{RuCl_3(PPh_3)_2{}^{\bullet}\}\{CCl_3{}^{\bullet}\}}$$

$$\{RuCl_3(PPh_3)_2{}^{\bullet}\}\{CCl_3{}^{\bullet}\} + RCH{=}CH_2 \xrightarrow{k_3} \underset{(IV)}{\{RuCl_3(PPh_3)_2{}^{\bullet}\}\{RCHCH_2CCl_3{}^{\bullet}\}}$$

$$\{RuCl_3(PPh_3)_2{}^{\bullet}\}\{RCHCH_2CCl_3{}^{\bullet}\} \xrightarrow{k_4} [RuCl_2(PPh_3)_2] + RCHClCH_2CCl_3$$

SCHEME 3

$$\text{Rate} = \frac{K_1 k_2 k_3 [RuCl_2(PPh_3)_3][CCl_4][RCH{=}CH_2]}{[PPh_3]\{k_{-2} + k_3[RCH{=}CH_2]\}} \tag{2}$$

This mechanism involves formation of the four coordinate intermediate II, which reacts with $CCl_4$ to give the radical pair III. We represent the reaction of III with the alkene as yielding a similar radical pair IV. This step may involve prior coordination of the alkene to the five coordinate ruthenium(III) centre, but we have no way of investigating the details of this step. The mechanism shown in Scheme 3 is consistent with the evidence cited above, however, we have been unable to identify any radical intermediates by ESR spectroscopy, a difficulty we and others have encountered previously in reactions of $CCl_4$ with transition metal complexes [1,2,8].

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