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THE MECHANISM OF THE ADDITION OF HALOALKANES TO ALKENES IN THE PRESENCE OF DICHLOROTRIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II), $[RuCl_2(PPh_3)_3]$

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Summary

The addition of haloalkanes to alkenes in the presence of $[RuCl_2(PPh_3)_3]$ has been subjected to a detailed kinetic study. The results of this study, together with an examination of reaction intermediates, suggest a mechanism inolving a non-chain sequence in which $[RuCl_2(PPh_3)_3]$ acts as a catalyst, but which involves free radical intermediates.

We have recently been concerned with a number of reactions of transition metal complexes that proceed by free radical mechanisms. In particular we have examined the addition of halocarbons to alkenes (the Kharasch addition reaction) in the presence of $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$ [1] and $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ ($C_{10}H_8$ = naphthalene) [2]. In the presence of the molybdenum complex, the reaction was found to proceed initially by a redox catalysed mechanism, but gradual decomposition of all metal carbonyl-containing species led to this pathway being replaced by a radical chain route. In the case of the chromium complex, the reaction was shown to proceed via a non-chain catalysed mechanism involving free radical intermediates.

In the presence of both complexes the yields of 1 : 1 adduct were only moderate (yields of 1,1,1,3-tetrachlorononane from a 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 under conditions identical to those used above [1]).

Matsumoto and co-workers have shown I to be efficient in the promotion of a range of reactions involving the addition of $X_3C\text{-}Cl$ to alkenes [3,4] and although no

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detailed mechanistic studies have been reported for these reactions, they have been shown to be inhibited by radical scavengers [3]. Other studies by these workers have shown that the addition of CCl_4 to cyclohexene in the presence of I proceeds in good yield to give 1-chloro-2-trichloromethyl-cyclohexane [4a]. The ratio of *cis*- to *trans*-isomers obtained is 4 to 96, compared to the equimolar mixture of isomers obtained from reactions following free radical chain pathways initiated by either peroxides or ultraviolet light. Furthermore, an examination of the ratio of 1,2- to 1,4-addition of CCl_4 to cyclooctene has shown a marked difference in the ratio of adducts obtained in the presence of I compared to photochemically or thermally initiated chain processes [4c]. These findings together with a consideration of the effect of temperature on these ratios led Matsumoto and co-workers to suggest association between the radical intermediates assumed to be present in the reaction sequence and the ruthenium centre, giving rise to what has been termed "a radical reaction within the coordination sphere".

In an effort to gain further insight into the nature of the Kharasch addition reaction in the presence of I, we have made a study of some aspects of this reaction, including a kinetic study of the addition of CCl_4 to oct-1-ene in the presence of I. A preliminary account of this work has been published [5].

Results

(a) Kinetics of the addition of tetrachloromethane to oct-1-ene in the presence of I

The addition of tetrachloromethane to oct-1-ene was chosen as the system for detailed study for the reasons given in our previous paper [1]. The kinetic study employed the initial rate method and plots of initial rates of reaction vs. concentrations of I, CCl_4, and oct-1-ene are shown in Figs. 1, 2 and 3 respectively. The linearity of the plot of rate vs. [I] indicates a first-order dependence on complex, however, the positive intercept suggests a minor contribution from a reaction not involving I [6]. The dependence on CCl_4 concentration is also first order, however the dependence on [oct-1-ene] is non-linear. A plot of the reciprocal of the rate vs. the reciprocal of the alkene concentration (Fig. 4) is linear indicating an alkene (A) dependence of the type shown in eq. 1. The addition of free triphenylphosphine

$$\text{Rate} = \frac{k[\text{oct-1-ene}]}{1 + k^1[\text{oct-1-ene}]} \qquad (1)$$

causes a decrease in the rate of reaction as shown in Table 1. Addition of a large excess of phosphine over the amount of I present (approximately tenfold) was found to inhibit the reaction almost completely.

Dependence of the reaction rate upon temperature was examined over a limited range (Table 2) which was dictated by incomplete dissolution of I at temperatures of less than 60°C while at temperatures above 80°C considerable vaporisation of CCl_4 occurred. Such a small temperature variation, together with the occurrence of a minor contribution from a reaction not promoted by I renders activation parameters less meaningful than usual [6]. However, values of E_a, $\Delta H^{\neq\theta}$ and $\Delta S^{\neq\theta}$ of ca. 100 kJ mol^{-1}, ca. 97 kJ mol^{-1} and 0.5 J K^{-1} mol^{-1}, respectively at 353 K were obtained.

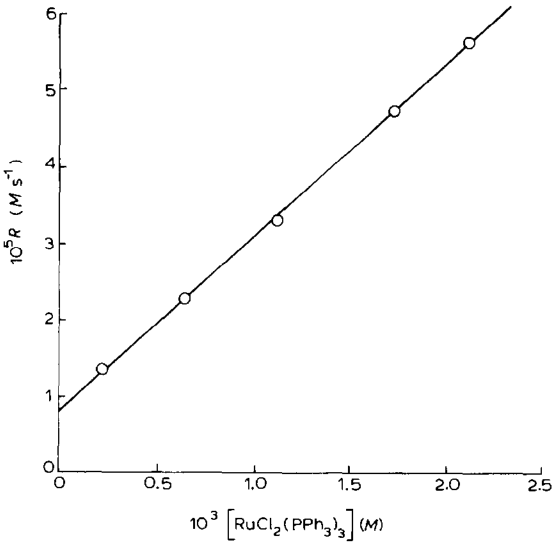

Fig. 1. Variation of initial rate of reaction with [$RuCl_2(PPh_3)_3$] concentration.

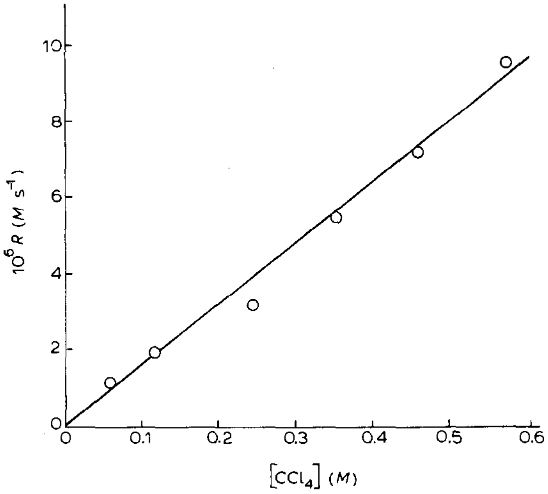

Fig. 2. Variation of initial rate of reaction with CCl_4 concentration.

TABLE 1

DEPENDENCE OF THE RATE OF REACTION UPON THE AMOUNT OF ADDED PPh_3 [a]

PPh_3 concentration ($\times 10^{-3}$ M)	Rate ($\times 10^{-6}$ $M\,s^{-1}$)
0	3.52
3.48	2.75
4.52	2.57

[a] [$RuCl_2(PPh_3)_3$] = 1.1×10^{-3} M, [CCl_4] = 1.1 M, [oct-1-ene] = 0.6 M, 76°C.

TABLE 2

VARIATION OF RATE CONSTANT (k) WITH TEMPERATURE

T(K)	$k(10^{-3} M^2 s^{-1})$
333.2	4.94
343.2	13.10
353.2	36.40

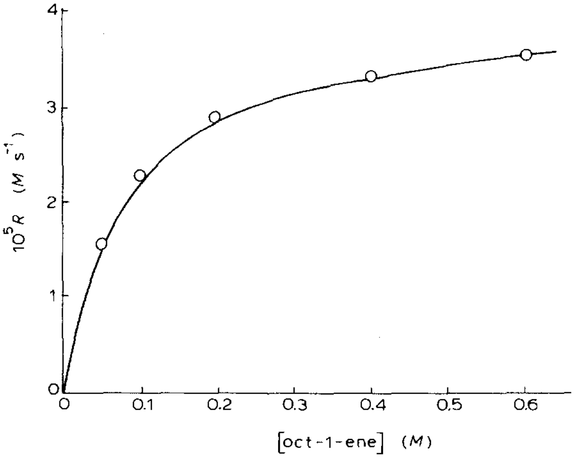

Fig. 3. Variation of initial rate of reaction with oct-1-ene concentration.

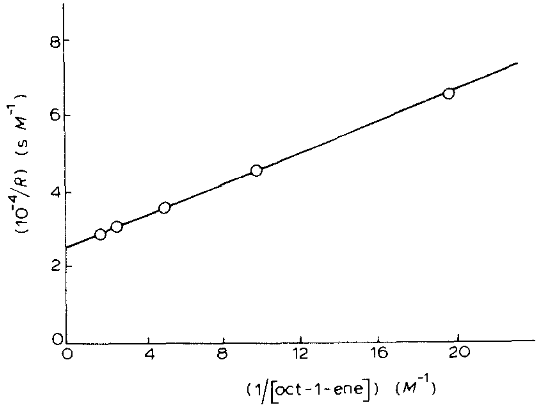

Fig. 4. Variation of the reciprocal rate of reaction with the reciprocal of the oct-1-ene concentration.

(b) Other mechanistic studies

(i) The reaction between [$RuCl_2(PPh_3)_3$] and alkenes. The reaction between [$RuCl_2(PPh_3)_3$] and alkenes was examined under various conditions. These included passing ethene through a heated solution of I and heating a suspension of I in oct-1-ene. Samples were removed at intervals and examined by IR and NMR

spectroscopy, however there was no indication of complex formation between I and the alkenes.

(ii) The reaction between $[RuCl_2(PPh_3)_3]$ and CCl_4. The solubility of I in CCl_4 was low and thus the interaction between these reagents was examined in toluene. After refluxing the mixture for some hours, hexachloroethane was identified by GLC. Addition of a large excess of PPh_3 to a solution of I in CCl_4, followed by refluxing for several hours, resulted in precipitation of a light orange brown solid. Analytical data for this material were close to that expected for $[RuCl_3(PPh_3)_3 \cdot CCl_4]$. The magnetic moment of this compound was determined to be 1.4 μ_β, considerably less than that expected for the spin-only value for ruthenium(III) of 1.73 μ_β. This may arise as a consequence of contamination with a small amount of a ruthenium(II) material. Addition of a large excess of triphenylphosphine to a reaction mixture containing I, CCl_4 and oct-1-ene under reflux also produced a light orange brown solid. Analytical data for this material were closest to that for $[RuCl_3(PPh_3)_3 \cdot 0.67CCl_4]$ and in this case the magnetic moment was 1.67 μ_β.

(iii) Cross addition reactions. Both CCl_4 and CBr_4 afford high yields of the respective 1 : 1 adducts when reacted with oct-1-ene in the presence of I. Treatment of the alkene with a mixture of these two halocarbons in the presence of I yielded not only 1,1,1,3-tetrachloro- and 1,1,1,3-tetrabromononane, but also 3-bromo-1,1,1-trichlorononane and 3-chloro-1,1,1-tribromononane. The ratio of tetrabromo-/bromotrichloro-/chlorotribromo-/tetrachlorononane was 14/2/5/1 as estimated by GLC.

(iv) ESR spectral studies. As it appeared likely that these reactions involved the formation of free radical intermediates, attempts were made to identify such species by ESR spectroscopy. Variable temperature spin trapping experiments in the presence of nitrosodurene failed to show any evidence for radical formation in the case of mixtures of $[RuCl_2(PPh_3)_3]$ and CCl_4 and $[RuCl_2(PPh_3)_3]$, CCl_4 and oct-1-ene. It is however, noteworthy that a related study of the reaction of *cis*-$[M(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ ($M = Cr$, Mo) with several halocarbons (RX) exhibited spectra consistent with the formation of spin adducts for $R = PhCH_2$, Ph_2CH, Ph_3C, but no signal was produced for $R = CCl_3$ [7].

Reactions of $[RuCl_2(PPh_3)_2(C_7H_8)]$ (II)

No simple alkene complexes of the type $[RuCl_2(PR_3)_2(alkene)]$ are known [8], however the six-coordinate norbornadiene complex II, has been reported [9] and it was felt that despite the fact that this was coordinatively saturated examination of its reaction with CCl_4 was worthwhile. Accordingly, II was treated with CCl_4 at both room temperature and under reflux. In neither case was any isomer of the 1 : 1 adduct of CCl_4 and norbornadiene formed.

Discussion

The kinetic data clearly exclude a free radical chain process in which I acts solely as an initiator. Such a process would be expected to show half order dependence on concentrations of both I and CCl_4 and first-order dependence on the alkene concentration. Furthermore, a simple redox catalysed process analogous to that oberved in the case of reactions involving $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$ [1] (Scheme 1) gives

SCHEME 1

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

$$[RuCl_2(PPh_3)_2]+CCl_4 \xrightarrow{k_2} [RuCl_3(PPh_3)_2]+CCl_3^{\cdot}$$

$$CCl_3^{\cdot}+RCH{=}CH_2 \xrightarrow{k_3} RCHCH_2CCl_3^{\cdot}$$

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

rise to the rate expression shown in eq. 2. This is also inconsistent with the observed kinetic data.

$$\text{Rate} = \frac{k_1k_2[I][CCl_4]}{k_{-1}[PPh_3]+k_2[CCl_4]} \tag{2}$$

A number of alternative mechanisms can be proposed which are consistent with the observed kinetic data. One of these, which is related to that shown in Scheme 1, but involves radicals bound within the coordination sphere of the metal atom (Scheme 2) gives rise to the rate expression shown in eq. 3 and this in accord with

SCHEME 2

$$RuCl_2(PPh_3)_3 \overset{K_1}{\rightleftharpoons} RuCl_2(PPh_3)_2+PPh_3$$

$$RuCl_2(PPh_3)_2+CCl_4 \overset{K_2}{\rightleftharpoons} [RuCl_3(PPh_3)_2\ldots CCl_3]$$

$$[RuCl_2(PPh_3)_2\ldots CCl_3]+RCH{=}CH_2 \xrightarrow{k_3} [RuCl_3(PPh_3)_2\ldots CHRCH_2CCl_3]$$

$$[RuCl_3(PPh_3)_2\ldots CHRCH_2CCl_3] \xrightarrow{k_4} RCHClCH_2CCl_3+[RuCl_2(PPh_3)_2]$$

the experimental results.

$$\text{Rate} = \frac{k_1k_2k_3[I][CCl_4][RCH{=}CH_2]}{[PPh_3]\{k_{-2}+k_3[RCH{=}CH_2]\}} \tag{3}$$

It is not clear from the previous work [3,4] how $[RuCl_3(PPh_3)_2(\ldots CCl_3)]$ in which the CCl_3 group is held within the coordination sphere, differs from $[Ru(CCl_3)Cl_3(PPh_3)_2]$ in which CCl_4 has undergone oxidative addition to the ruthenium(II) centre and thus a related mechanism involving such an oxidative addition step also obeys the observed rate law.

A further mechanism involving initial coordination of the alkene to the reactive intermediate $[RuCl_2(PPh_3)_2]$ is shown in Scheme 3. The rate equation for this process is shown in eq. 4 and this also is in accord with observed reaction orders.

$$\text{Rate} = \frac{K_2k_3[I][CCl_4][A]}{1+[PPh_3]/K_1+K_2[A]} \tag{4}$$

In all the above sequences we suggest dissociation of a triphenylphosphine ligand as the initial step. This is in accord with the inhibition of the reaction in the presence of excess PPh_3. Such dissociation of I has received detailed study elsewhere in which

SCHEME 3

$$[\mathrm{RuCl_2(PPh_3)_3}] \overset{K_1}{\rightleftharpoons} [\mathrm{RuCl_2(PPh_3)_2}] + \mathrm{PPh_3}$$

$$\mathrm{RuCl_2(PPh_3)_2} + \mathrm{RCH{=}CH_2} \overset{K_2}{\rightleftharpoons} [\mathrm{RuCl_2(PPh_3)_2(RCH{=}CH_2)}]$$

$$[\mathrm{RuCl_2(PPh_3)_2(RCH{=}CH_2)}] + \mathrm{CCl_4} \xrightarrow{k_3} [\mathrm{RuCl_3(PPh_3)_2(RCH{=}CH_2)}] + \mathrm{CCl_3^{\cdot}}$$

$$\mathrm{RuCl_3(PPh_3)_2(RCH{=}CH_2)} + \mathrm{CCl_3^{\cdot}} \xrightarrow{k_4} [\mathrm{RuCl_3(PPh_3)_2}] + \mathrm{RCHCH_2CCl_3^{\cdot}}$$

$$\mathrm{RuCl_3(PPh_3)_2} + \mathrm{RCHCH_2CCl_3^{\cdot}} \xrightarrow{k_5} [\mathrm{RuCl_2(PPh_3)_2}] + \mathrm{RCHClCH_2CCl_3^{\cdot}}$$

formation of the dimer, $[\{\mathrm{RuCl(PPh_3)_2}\}_2(\mu\text{-Cl})_2]$ has been demonstrated [10]. Such dimer formation undoubtedly occurs in the reactions under investigation here and this is more important at higher initial concentrations of $[\mathrm{RuCl_2(PPh_3)_3}]$. This effect may be responsible for the degradation of the plot of reaction rate vs. $[\mathrm{RuCl_2(PPh_3)_3}]$ concentration from linearity at concentrations of complex greater than 2×10^{-3} *M*.

In an effort to distinguish between the above mechanistic possibilities, a number of further studies were performed. In a search for possible intermediates in the sequence, the reaction between I and alkenes was examined. As has been reported by others [8], we were unable to identify any complexation of I by monoalkenes such as ethene and oct-1-ene.

The related norbornadiene complex, $[\mathrm{RuCl_2(PPh_3)_2(C_7H_8)}]$, (II) [9] does not react with CCl_4, even under reflux, to give the 1 : 1 adduct, $C_8H_8Cl_4$, although such an adduct is formed when norbornadiene is treated with CCl_4 in the presence of I. Even though II is not a true model for the reaction of $[\mathrm{RuCl_2(PPh_3)_2}]$ with monoalkenes, these observations do indicate that coordination of the diene to the metal does not lead to marked activation towards reaction with CCl_4. In an effort to activate coordinated norbornadiene to attack, an analogous complex containing more basic phosphines, $[\mathrm{RuCl_2(PMe_2Ph)_2(C_7H_8)}]$ [11] was also examined. This also showed no reaction towards CCl_4. I reacts with CCl_4 yielding C_2Cl_6, presumably formed from $\mathrm{CCl_3^{\cdot}}$ radicals, and ruthenium(III) complexes. Complete identification of the ruthenium(III) species did not prove possible and although analytical data were close to that calculated for adducts of $[\mathrm{RuCl_3(PPh_3)_3}]$ with CCl_4, the magnetic moments of the products were below those expected for ruthenium(III). This may be due to the presence of some unreacted diamagnetic ruthenium(II) complex.

These results indicate that $[\mathrm{RuCl_2(PPh_3)_2}]$ reacts readily with CCl_4 under the reaction conditions and it is thus likely that this step precedes any reaction with the alkene. We therefore favour the reaction sequences such as that shown in Scheme 2 and rather than Scheme 3, but these experiments do not distinguish between a mechanism involving oxidative addition of CCl_4 to ruthenium(II) and one in which there is some other interaction between the $\mathrm{CCl_3^{\cdot}}$ radical and the metal. In an effort to distinguish between these two possibilities, we carried out a cross-over experiment in which oct-1-ene was treated with a mixture of CCl_4 and CBr_4 in the presence of I. Oxidative addition of the halocarbons to the metal centres would be expected to lead to formation of tetrachlorononane and tetrabromononane only, whereas the reaction yielded a mixture of the four possible products from cross-over reactions. Thus $C_9H_{16}Cl_4$, $C_9H_{16}Br_4$, $C_9H_{16}BrCl_3$ and $C_9H_{16}Br_3Cl$ were formed in a 1/14/2/5 ratio. Such cross-over reactions are indicative of a reaction sequence involving free radical intermediates.

Thus this study suggests a reaction scheme in which free radicals play an important role. In view of the earlier findings of Masumoto and co-workers that normal free radical reactivity is modified by the presence of the ruthenium complex, we suggest that a mechanism related to that shown in Scheme 2 obtains. In this sequence, better elaborated in Scheme 4, the four-coordinate intermediate,

SCHEME 4

$$[RuCl_2(PPh_3)_3] \overset{K_1}{\rightleftharpoons} [RuCl_2(PPh_3)_2] + PPh_3$$

$$[RuCl_2(PPh_3)_2] + CCl_4 \overset{K_2}{\rightleftharpoons} \{RuCl_3(PPh_3)_2^{\cdot}\}\{CCl_3^{\cdot}\}$$

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

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

$[RuCl_2(PPh_3)_2]$ reacts with CCl_4 to form the ruthenium(III) containing radical pair $\{RuCl_3(PPh_3)_2\}^{\cdot}\{CCl_3\}^{\cdot}$ and reaction of this with the alkene generates a second radical pair, $\{RuCl_3(PPh_3)_2\}^{\cdot}\{C_8H_{16}CCl_3\}^{\cdot}$. This step may involve prior interaction between the alkene and the five coordinate metal centre, but we have not found a method of investigating this possibility. The final step of the cycle, chlorine atom transfer from ruthenium(III), leads to the product and regeneration of $[RuCl_2(PPh_3)_2]$. The rate law for this sequence is that given in eq. 3.

Experimental

All reactions and kinetic experiments were carried out under an atmosphere of dry nitrogen. All solvents and reagents were purified by standard techniques and all solvents thoroughly degassed by three freeze-pump-thaw cycles immediately prior to use. Transfer of solvents between vessels and all other manipulations were carried out with the rigorous exclusion of air.

Infrared spectra were recorded on a Perkin–Elmer 457 spectrometer, NMR spectra on a Perkin–Elmer R32 spectrometer and ESR spectra on a Varian E4 instrument. GLC analyses were performed on FID equipped Pye GCD and 204 instruments. Details of GLC columns and conditions have been published previously [1].

The compounds $[RuCl_2(PPh_3)_3]$ [12], $[RuCl_2(PPh_3)_2(C_7H_8)]$ [9] and $[RuCl_2(PMe_2Ph)_2(C_7H_8)]$ [11] were prepared by literature methods. All showed satisfactory analytical and spectroscopic data.

Reaction between $[RuCl_2(PPh_3)_3]$ and CCl_4

(a) In toluene. $[RuCl_2(PPh_3)_3]$ (0.1 g, 1×10^{-4} mol) and CCl_4(10 g, 6.5×10^{-2} mol) were added to toluene (50 cm^3) and the mixture degassed by the freeze-pump-thaw method. The solution was then refluxed for 6 h. After this time, an aliquot of the solution was analysed by GLC and C_2Cl_6 was identified by comparison with an authentic sample.

(b) In tetrachloromethane. A large excess of Ph_3P (2 g, 7.6×10^{-3} mol) was

added to a solution of $[RuCl_2(PPh_3)_3]$ (0.1 g, 1×10^{-4} mol) in CCl_4 (20 cm^3). After boiling this solution under reflux, a light orange-brown precipitate formed. This was filtered off, washed twice with CCl_4 (5 cm^3) and dried.

(Found: C, 57.18; H, 4.11; Cl, 21.47; P, 8.20; $[RuCl_3(PPh_3)_3 \cdot CCl_4]$ calcd.: C, 57.52; H. 3.92; Cl, 21.66; P, 8.11%).

(c) In the presence of oct-1-ene. Oct-1-ene (5 g) and CCl_4 (10 g) were heated in the presence of $[RuCl_2(PPh_3)_3]$ (0.1 g). After 20 min, excess PPh_3 (2 g, 7.6×10^{-3} mol) was added. Production of tetrachlorononane ceased (GLC) and a light red-brown solid was precipitated. The precipitate was filtered off, washed with methanol in order to remove any free PPh_3 and dried.

(Found: C, 60.32; H, 4.13; Cl, 17.43; P, 8.85. $[RuCl_3(PPh_3)_3 \cdot 0.67\ CCl_4]$ calcd.: C, 59.82; H, 4.10; Cl, 18.4; P, 8.48%).

Typical reaction conditions for the addition of haloalkanes to oct-1-ene

Oct-1-ene (3.4 g, 0.03 mol), haloalkane (0.06 mol) and $[RuCl_2(PPh_3)_3]$ (0.01 g, 1×10^{-5} mol) were loaded into a glass tube with a restriction in the neck to facilitate sealing. The reaction mixture was degassed three times by the freeze-pump-thaw method and the tube was then sealed under vacuum. The tube was then heated to the desired temperature in an oven for times varying between 1.5 and 20 h, after which time it was opened and the contents analysed by GLC.

Kinetic studies

The method employed for the kinetic studies has been described previously [1].

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References

1 R. Davis and I.F. Groves, J. Chem. Soc., Dalton Trans., (1982) 2281.
2 W.J. Bland, R. Davis and J.L.A. Durrant, J. Organomet. Chem., 260 (1984) C75.
3 H. Matsumoto, T. Nakano and Y. Nagai, Tetrahedron Lett., (1973) 5147.
4 (a) H. Matsumoto, T. Nakano and Y. Nagai, Tetrahedron Lett., (1975) 899; (b) H. Matsumoto, T. Nakano and Y. Nagai, J. Org. Chem., 41 (1976) 396; (c) H. Matsumoto, T. Nakano, K. Takasu and Y. Nagai, J. Org. Chem., 43 (1978) 1734; (d) H. Matsumoto, T. Nakano, K. Ohkawa and Y. Nagai, Chem. Lett., (1978) 363. (e) H. Matsumoto, T. Nakano, T. Nikaido and Y. Nagai, Chem. Lett., (1978) 115; (f) H. Matsumoto, T. Nakano, M. Kato and Y. Nagai, Chem. Lett., (1978) 223; (g) T. Nakano, H. Arai, H. Matsumoto and Y. Nagai, Org. Prep. Proced. Int., 10 (1978) 55; (h) H. Matsumoto, T. Nakano, Y. Nagai and H. Kono, Bull. Chem. Soc. Japan, 51 (1978) 2445; (i) H. Matsumoto, K. Ohkawa, S. Ikemori, T. Nakano and Y. Nagai, Chem. Lett., (1979) 1011; (j) H. Matsumoto, T. Motegi, T. Nakano and Y. Nagai, J. Organomet. Chem., 174 (1979) 157; (k) T. Nakano, Y. Shimada, R. Sako, M. Kayama, H. Matsumoto and Y. Nagai, Chem. Lett., (1982) 1255.
5 W.J. Bland, R. Davis and J.L.A. Durrant, J. Organomet. Chem., 267 (1984) C45.
6 G.A. Moelwyn-Hughes Chemical Statics and Kinetics of Solutions, Academic Press, London and New York, 1971, p. 340.
7 J.A. Connor and P.I. Riley, J. Chem. Soc., Dalton Trans., (1979) 1318.
8 S. Cenini, A. Fusi and F. Porta, Gazz. Chim. Ital., 108 (1978) 109; L. Ruiz-Ramirez, T.A. Stephenson and E.S. Switkes, J. Chem. Soc., Dalton Trans., (1973) 1770.

9 S.D. Robinson and G. Wilkinson, J. Chem. Soc. A, (1966) 300.
10 P.R. Hoffman and K.G. Caulton, J. Am. Chem. Soc., 97 (1975) 4221.
11 L. Ruiz-Ramirez and T.A. Stephenson, J. Chem. Soc., Dalton Trans., (1974) 1640.
12 T.A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., 28 (1966) 945.