Journal of Organometallic Chemistry, 280 (1985) 95–103
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE MECHANISM OF THE ADDITION OF HALOALKANES TO ALKENES IN THE PRESENCE OF TRICARBONYL-η^6-NAPHTHALENECHROMIUM(0), [$Cr(CO)_3(\eta^6$-$C_{10}H_8)$]

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(Received July 9th, 1984)

Summary

The title reaction has been subjected to a detailed kinetic study, the results of which when taken with an examination of reaction intermediates suggest a mechanism involving a non-chain sequence in which [$Cr(CO)_3(\eta$-$C_{10}H_8)$] acts as a catalyst, but which involves free radical intermediates. A brief comparison is made of the efficiency of a range of complexes of formula [$Cr(CO)_3(\eta^6$-arene)] in promoting addition of CCl_4 to oct-1-ene.

We have recently reported mechanistic studies on the reaction between haloalkanes and alkenes in the presence of [$Mo_2(CO)_6(\eta$-$Cp)_2$] [1] and [$RuCl_2(PPh_3)_3$] [2]. On the basis of kinetic studies, examination of reaction intermediates and model reactions it was proposed that, in the presence of the molybdenum complex, addition follows a redox catalysed mechanism in the early stages of the reaction and that this is replaced by a radical chain pathway as the metal carbonyl-containing species decompose, while in the presence of [$RuCl_2(PPh_3)_3$], a non-chain catalysed sequence involving free radical intermediates obtains.

Such addition reactions are also promoted by [$Cr(CO)_3(\eta^6$-$C_{10}H_8)$] (I) as reported by Gandolfi and Cais [3], although conversions are only moderate for the addition of perhaloalkanes such as CCl_4 to terminal alkenes and cycloalkenes. Higher conversions were observed for addition of CCl_4 to cyclodienes. Gandolfi and Cais proposed the mechanism shown in Scheme 1 for these reactions. This involves oxidative addition of CCl_4 to the metal, followed by alkene insertion into the M–CCl_3 bond. The cycle is then completed by reaction of the alkylmetal with a further molecule of CCl_4, thereby forming the product by a chain sequence. In view

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0022-328X/85/$03.30

$$Cr(CO)_3(\eta^6\text{-}C_{10}H_8)+THF \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cr(CO)_3(THF)(\eta^4\text{-}C_{10}H_8)]$$

$$[Cr(CO)_3(THF)(\eta^4\text{-}C_{10}H_8)]+CCl_4 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [CrCl(CCl_3)(THF)(CO)_3]+C_{10}H_8$$

$$[CrCl(CCl_3)(THF)(CO)_3]+RCH{=}CH_2 \xrightarrow{k_3} [CrCl(CHRCH_2CCl_3)(THF)(CO)_3]$$

$$[CrCl(CHRCH_2CCl_3)(THF)(CO)_3]+CCl_4 \xrightarrow{k_4} [CrCl(CCl_3)(THF)(CO)_3]+RCHClCH_2CCl_3$$

$$[CrCl(CCl_3)(THF)(CO)_3] \xrightarrow{k_5} [CrCl_2(THF)(CO)_3]+{:}CCl_2$$

SCHEME 1

of our findings for similar reactions catalysed by $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$ and $[RuCl_2(PPh_3)_3]$, we wished to examine, in more detail, the role of the chromium complex. A preliminary account of this work has been published [4].

Results

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

The addition of halocarbons to alkenes was previously observed to occur in the presence of tetrahydrofuran (THF) [3]. This kinetic study was carried out upon the reaction between CCl_4 and oct-1-ene for the reasons described in our previous paper [1], but all reactions were performed in the presence of THF. The variation of the rate of reaction was examined as a function of the concentrations of I, CCl_4, oct-1-ene and THF. In the cases of variation of concentrations of I and oct-1-ene, an equimolar ratio of CCl_4 and THF was employed. The data were analysed by the initial rate method and plots of the initial rates of reaction versus concentrations of I, CCl_4 THF and oct-1-ene are shown in Fig. 1–5 respectively.

The reaction rate shows a first order dependence on I, CCl_4 and THF, however, in the case of the complex, a positive intercept is observed indicating a contribution from a reaction not mediated by I. Similar results were obtained in our previous

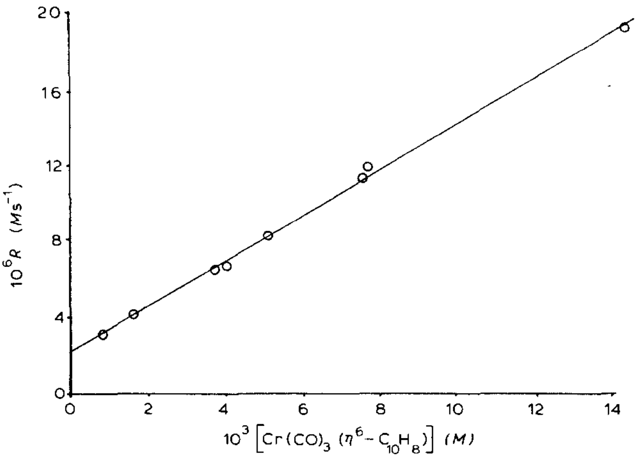

Fig. 1. Variation of initial rate of reaction with $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ concentration.

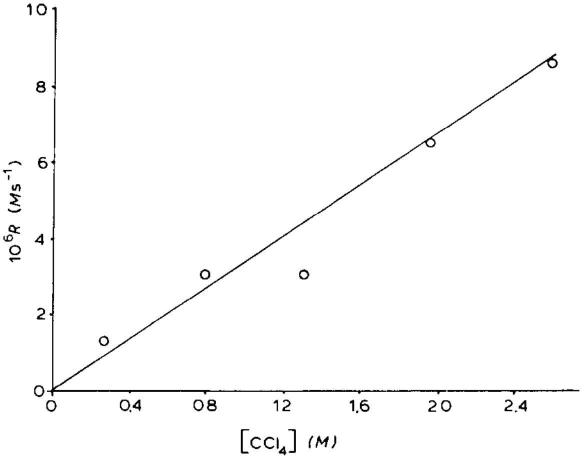

Fig. 2. Variation of initial rate of reaction with CCl_4 concentration.

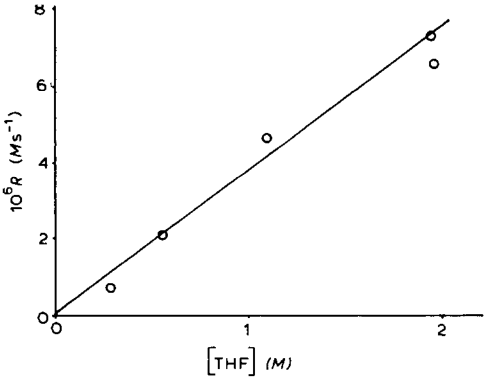

Fig. 3. Variation of initial rate of reaction with THF concentration.

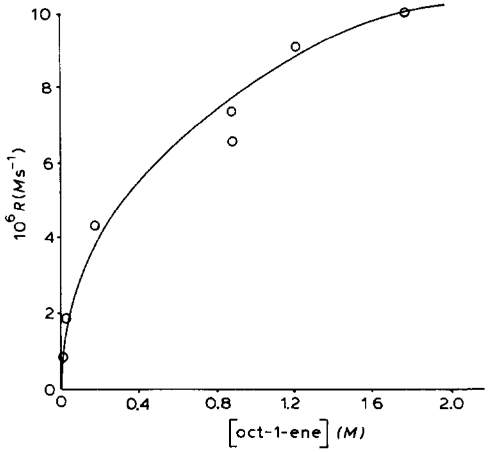

Fig. 4. Variation of initial rate of reaction with oct-1-ene concentration.

studies [1,2]. The dependence on oct-1-ene concentration is non-linear and a plot of the reciprocal of the rate versus the reciprocal of the concentration of alkene is shown in Fig. 6. This is linear and indicates a Michelis–Menton relationship between the reaction rate and the alkene concentration (eq. 1).

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

The rate was observed to be slower when free naphthalene was added to the

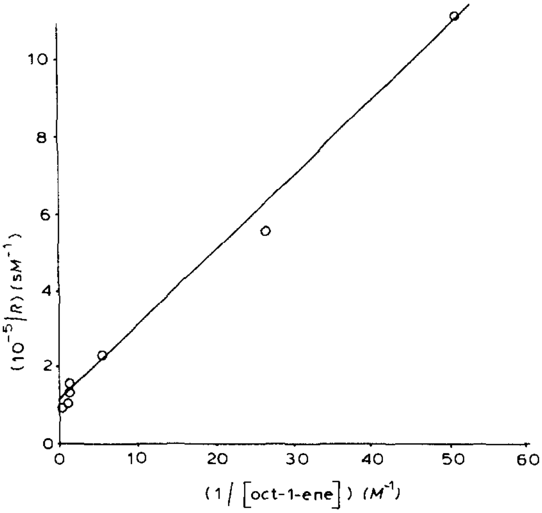

Fig. 5. Variation of the reciprocal of the initial rate of reaction with the reciprocal of the oct-1-ene concentration.

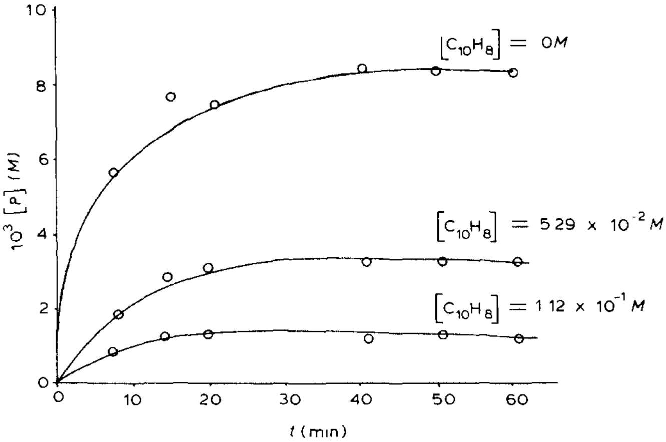

Fig. 6. Effect on the rate of reaction of added naphthalene ([P] = concentration of $C_9H_{16}Cl_4$).

reaction mixture (Fig. 6), but there was only a very slight reduction in rate when the reactions were performed under CO (5.8×10^{-6} M s^{-1}) rather than nitrogen (7.0×10^{-6} M s^{-1}).

(b) Other mechanistic studies

(i) The reaction between I and CCl_4. A solution of I in an equimolar mixture of CCl_4 and THF was stirred at room temperature, for several hours. During this time the colour of the solution changed from yellow to purple. The purple solution was shown to contain $Cr(CO)_6$ (infrared spectroscopy) and C_2Cl_6 (GLC).

(ii) Cross addition reactions. Norbornadiene was treated with a mixture of CCl_4 and CBr_4 in the presence of I at room temperature. After 17 h, GC/MS analysis indicated the presence of $C_8H_8Cl_4$, $C_8H_8Br_4$ and $C_8H_8Br_3Cl$ (ratio, 1/100/5). Although Gandolfi and Cais identified two isomers of $C_8H_8Cl_4$ produced from norbornadiene and CCl_4 [3], no attempt was made to identify isomers in these cross addition reactions.

(c) Comparative efficiency of [$Cr(CO)_3(\eta^6$-arene)] complexes in promoting CCl_4 addition to oct-1-ene

A range of complexes [$Cr(CO)_3(\eta^6$-arene)], were examined as mediators of the reaction between CCl_4 and oct-1-ene. These reactions were carried out under standard conditions and yields of 1/1 adduct are reported in Table 1.

Discussion

(a) Mechanistic studies

The rate law for the addition of CCl_4 to oct-1-ene in the presence of I and THF is given in eq. 2. Furthermore, the reaction is retarded in the presence of excess

$$\text{rate} = \frac{k[\text{I}][\text{THF}][\text{CCl}_4][\text{oct-1-ene}]}{k' + k''[\text{oct-1-ene}]} \qquad (2)$$

naphthalene, but the rate is independent of added CO. Such behaviour is clearly inconsistent with a reaction proceeding by a free radical chain mechanism in which I acts solely as an initiator. Such a reaction would be expected to show half order

TABLE 1

YIELDS OF 1/1 ADDUCT FORMED FROM CCl_4 AND OCT-1-ENE IN THE PRESENCE OF [$Cr(CO)_3(\eta^6$-arene)] [a]

Arene	Concentration (M)	Yield (%)
C_6H_6	0.0448	60.4
C_6H_5Cl	0.0432	62.1
C_6H_5OMe	0.0422	76.6
C_6H_5Me	0.0416	52.2
p-$C_6H_4Me_2$	0.0398	57.3
$C_{10}H_8$	0.0389	53.2
$C_{10}H_8$	0.0353	45.2
2-$MeC_{10}H_7$	0.0506	60.6

[a] THF 5.0 cm^3 (6.2 M), CCl_4 4.0 cm^3 (4.2 M), Oct-1-ene 1.0 cm^3 (6.8 M), Reaction time 17 h.

dependences on the concentrations of I, THF and CCl_4 and first order dependence on the concentration of oct-1-ene. Furthermore, a simple redox catalysed mechanism such as that observed for this reaction in the presence of $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$ [1] can be eliminated as the rate of such a reaction should be independent of alkene concentration. I did not show any interaction with alkenes under thermal conditions in the absence of CCl_4 and this observation, together with a lack of inhibition of the reaction by CO suggests that an initial interaction between I and the alkene is not occurring. This is in accord with previous studies that have shown that $[Cr(CO)_2(\eta^2\text{-alkene})(\eta^6\text{-arene})]$ is only produced under UV irradiation [5].

The exact form of the rate law for the chain mechanism proposed by Gandolfi and Cais (Scheme 1) depends upon the nature of the termination sequence which converts the chain carrying species, $[CrCl(CCl_3)(THF)(CO)_3]$, into the inactive product, $[CrCl_3(THF)_3]$. We have assumed a unimolecular decomposition of the chain carrier to $[CrCl_2(THF)(CO)_3]$ and $:CCl_2$ as the first step. This reaction is analogous to that suggested for decomposition of $[Co(CCl_3)(CO)_3]$ [6]. Further reactions of the above dichloro complex involving replacement of CO by THF and oxidation to chromium(III) are probably fast. Thus, the sequence shown in Scheme 1 leads to the rate expression given in eq. 3, which is not in agreement with the observed orders of reaction.

$$\text{rate} = \frac{k_1 k_2 k_3 [\text{I}][CCl_4][\text{THF}][\text{oct-1-ene}]}{k_{-1} k_{-2}[\text{oct-1-ene}] + k_2 k_5 [CCl_4] + k_{-1} k_5} \tag{3}$$

An alternative mechanism involves a non-chain catalysed sequence similar to that proposed for reactions in the presence of $[RuCl_2(PPh_3)_3]$ [2]. This is shown in Scheme 2. The rate expression for this sequence is shown in eq. 4 and this is consistent with the observed behaviour.

$$[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)] + THF \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cr(CO)_3(THF)(\eta^6\text{-}C_{10}H_8)]$$

$$[Cr(CO)_3(THF)(\eta^4\text{-}C_{10}H_8)] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Cr(CO)_3(THF)] + C_{10}H_8$$

$$[Cr(CO)_3(THF)] + CCl_4 \underset{k_{-1}}{\overset{k_3}{\rightleftharpoons}} [\{CrCl(THF)(CO)_3\}\{CCl_3\}]$$

$$[\{CrCl(THF)(CO)_3\}\{CCl_3\}] + RCH{=}CH_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [\{CrCl(THF)(CO)_3(RCH{=}CH_2)\}\{CCl_3\}]$$

$$[\{CrCl(THF)(CO)_3(RCH{=}CH_2)\}\{CCl_3\}] \xrightarrow{k_5} [\{CrCl(THF)(CO)_3\}\{(RCHCH_2CCl_3\}]$$

$$[\{CrCl(THF)(CO)_3\}\{RCHCH_2CCl_3\} \xrightarrow{k_6} [Cr(CO)_3(THF)] + RCHClCH_2CCl_3$$

SCHEME 2

$$\text{rate} = \frac{K_1 K_2 k_3 k_4 k_5 [\text{I}][CCl_4][\text{THF}][\text{oct-1-ene}]}{[C_{10}H_8]\{k_{-3}k_{-4} + k_{-3}k_{-5} + k_4 k_5[\text{oct-1-ene}]\}} \tag{4}$$

The initial steps of this mechanism are totally in accord with those proposed by Gandolfi and Cais [3] and this is based upon our confirmation of the reported infrared spectral changes when I is dissolved in a THF/CCl_4 mixture. Thus, the first step of the sequence involves partial displacement of the arene ligand by THF leading to the η^4-complex $[Cr(CO)_3(THF)(\eta^4\text{-}C_{10}H_8)]$. This is followed by the displacement of the arene and the interception of the coordinatively unsaturated intermediate by CCl_4. This reaction could proceed either by oxidative addition of CCl_4 to the metal centre leading to $[Cr(CCl_3)Cl(CO)_3(THF)]$ [7] or to formation of the radical pair, $[\{CrCl(CO)_3(THF)^{\cdot}\}\{CCl_3^{\cdot}\}]$, similar to that proposed in the case of $[RuCl_2(PPh_3)_3]$ [2]. In the case of the ruthenium complex cross addition reactions, employing a CCl_4/CBr_4 mixed reagent, were used to resolve this point. However, such reactions using oct-1-ene could not be employed, as $[Cr(CO)_6]$ is generated in the decomposition of I and this is known to mediate addition of haloalkanes to alkanes at 70°C [8]. Thus, the reaction between a CCl_4/CBr_4 mixture and norbornadiene in the presence of I was performed at room temperature. This led to the formation of $C_8H_8Cl_4$, $C_8H_8Br_4$ and $C_8H_8Br_3Cl$ (ratio, 1/100/5). Control reactions showed that $[Cr(CO)_6]$ was unable to promote reactions between norbornadiene and either CCl_4 or CBr_4 at this temperature. These results, together with the production of C_2Cl_6 from reaction of I with CCl_4 in THF suggest the generation of $CCl_3^{\cdot}$ radicals.

Subsequent reaction of $[\{CrCl(CO)_3(THF)^{\cdot}\}\{CCl_3^{\cdot}\}]$ with the alkene leads to the radical pair $[\{CrCl(CO)_3(THF)^{\cdot}\}\{RCHCH_2CCl_3^{\cdot}\}]$ and although we have no way of investigating intermediates in this step, we suggest that the alkene may initially bind to the coordinatively unsaturated chromium I moiety prior to formation of the trichlorononyl radical. The sequence is completed by chlorine atom transfer from chromium to the alkyl radical and regeneration of $[Cr(CO)_3(THF)]$. Attempts to identify any free radical intermediates by ESR spectroscopy were unsuccessful, but we [1,2] and others [9] have encountered similar difficulties in related reactions between CCl_4 and transition metal complexes.

(b) A comparison of the efficiency of $[Cr(CO)_3(\eta^6\text{-arene})]$ complexes in promoting the reaction between CCl_4 and oct-1-ene

Previous comparisons of the efficiency of $[Cr(CO)_3(\eta^6\text{-arene})]$ and related complexes in promoting addition of haloalkanes to alkenes have been published. Gandolfi and Cais reported that the yield of 1/1 adducts from reaction between norbornadiene and CCl_4 at room temperature for 5.5 h was 95% in the presence of I, 23% in the presence of the phenanthrene analogue and 0% in the presence of the mesitylene and dimethylterephthalate complexes [3]. Simonneaux et al. report a 67% yield of the 1/1 adduct from reaction between cyclooctene and CCl_4 in refluxing THF (6 h) in the presence of tricarbonyl(*endo*-7-phenylcycloheptatriene)chromium-(0), but no reaction in the presence of $[Cr(CO)_3(\eta\text{-}C_6H_6)]$ [10]. Under reaction conditions similar to those of Simonneaux et al. but with reactions carried out in sealed tubes, we obtained the yields shown in Table 1 for the addition of CCl_4 to oct-1-ene.

Particularly noteworthy is the fact that under our conditions $[Cr(CO)_3(\eta\text{-}C_6H_6)]$ produces moderate yields of 1/1 adduct and that in no case were yields particularly low. There is some variation in yields between the complexes, that of the anisole complex being the highest at 76.6% whereas the others varied between 52.2 and 62.1%. However, in view of the facts that it was not possible to add exactly the same molar quantity of catalyst to each reaction and that in the case of I, a 10% increase in catalyst concentration led to an 8% increase in the yield of 1/1 adduct, no mechanistic significance is placed on the results obtained.

(c) General comments

This study shows that there is a marked similarity in the mechanisms proposed for addition of haloalkanes to alkenes in the presence of both I and [$RuCl_2(PPh_3)_3$]. There are, however, some differences that are worthy of note.

(i) The yields of 1/1 adduct from CCl_4 and oct-1-ene are higher in the presence of [$RuCl_2(PPh_3)_3$] than in the presence of I and THF (74.6% versus 53.2%). In the absence of THF, the difference in yields is more marked (74.6% versus 12.4%) [1] and this probably indicates a different mechanism is followed by reactions in the presence of I-THF to those in the presence of I alone.

(ii) Matsumoto and co-workers report that addition of CCl_4 to cyclohexene in the presence of [$RuCl_2(PPh_3)_3$] produces *cis*- and *trans*-adducts in the ratio of 4/96, whereas addition proceeding by a free radical chain mechanism initiated by peroxides or UV light gives an equimolar mixture of isomers [11]. It is thus noteworthy that these *cis*- and *trans*-isomers are produced in equal amounts in the presence of I and THF [3]. This may presumably reflect two effects. A much stronger interaction between the partners of the radical pairs in the case of [$RuCl_2(PPh_3)_3$] than in the case of I, would lead to a stereochemical preference in reactions catalysed by the ruthenium complex. It should, however, be noted there must be radical pair formation in the case of I, even if the interaction is weak, in order to satisfy the observed reaction kinetics. Preparative reactions in the presence of I are further complicated by formation of [$Cr(CO)_6$]. Although this does not invalidate the above kinetic study, performed by the initial rate method, it does pose the possibility of a second mechanism intervening during the reaction. A mechanism has recently been published for the formation of the hexacarbonyl from [$Cr(CO)_3(\eta^6$-arene)] complexes under photolysis. This involves formation of a multicentre complex formed from photoexcited [$Cr(CO)_3(\eta^6$-arene)] [12]. Similar intermediates could be formed by [$Cr(CO)_3(THF)(\eta^4$-$C_{10}H_8)$] and [$Cr(CO)_3(THF)$].

[$Cr(CO)_6$] is known to promote addition of haloalkanes to alkenes and this reaction is believed to proceed via a free radical chain mechanism in which the hexacarbonyl acts simply as an initiator [8]. This may detract from the synthetic value of some reactions performed in the presence of I.

Experimental

All reactions and kinetic experiments were performed under dry nitrogen. General techniques and reagent purifications were carried out as described earlier [1,2]. 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 spectrometer. GLC analyses were performed by FID equipped Pye GCD and 204 instruments. Details of GLC columns and conditions have been published previously [1]. GC/MS analyses were performed on a Kratos MS 3076 linked to a Pye 104 chromatography and a DS 50 data system.

The compounds [$Cr(CO)_3(\eta^6$-arene)] listed in Table 1 were prepared by the same general method with a modification of published procedures [13]. This is illustrated below for I. All compounds gave satisfactory analytical data and showed the expected infrared, ^1H NMR and mass spectra.

Preparation of [$Cr(CO)_3(\eta^6$-$C_{10}H_8)$]

[$Cr(CO)_6$] (4.0 g, 0.018 mol) and naphthalene (4.0 g, 0.031 mol) were dissolved in di-t-butyl ether (200 cm^3) and tetrahydrofuran (20 cm^3) added. The flask was fitted with a wide-neck condenser and connected to a vacuum/nitrogen line. The mixture was degassed three times by the freeze-pump-thaw method and then heated under reflux for 12 h. During this time the solution developed a deep red colour.

After cooling, the reaction mixture was filtered through a pad of alumina and the solvent removed under vacuum at 60°C to yield a deep orange solid. This solid was placed on the top of a dry silica gel column (0.5 m × 4 cm) and eluted with n-heptane until no more free naphthalene could be detected in the eluant (TLC). The complex was then eluted with toluene. The toluene was removed under vacuum at 60°C to yield deep red crystals of $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ (3.6 g, 76% yield).

Kinetic studies

The method employed for the kinetic studies has been described previously [1]. In the reaction system employing I, both CCl_4 and THF are present and in all cases the total reaction volume was kept constant at 50 cm^3 using toluene to make up the volume. The temperature was maintained at 46°C.

Typical reaction conditions for the addition of CCl_4 to alkenes

I (0.1 g, 3.8×10^{-4} mol), CCl_4 (4.0 cm^3, 0.04 mol), alkene (6×10^{-3} mol) and THF (5.0 cm^3, 0.06 mol) were placed in 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 then sealed under vacuum. The tube was then maintained at either 70°C (oct-1-ene reactions) or room temperature (norbornadiene reactions) in the dark for 17 h. After this time the tube was opened and the mixture analysed by GLC.

Acknowledgements

We thank Professor M.J. Perkins of Chelsea College, University of London for making e.s.r. facilities available to us and the S.E.R.C. for award of a studentship to J.L.A.D.

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