The Reaction of Tetrachloromethane with Oct-1-ene in the Presence of $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$ † and Other Transition-metal Complexes

Reg Davis * **and Ian F. Groves**
School of Chemical and Physical Sciences, Kingston Polytechnic, Penrhyn Road, Kingston-upon-Thames KT1 2EE

A study has been made of the mechanism of the addition reaction between CCl_4 and oct-1-ene in the presence of $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$. On the basis of kinetic and spectroscopic evidence and an examination of the reaction of some related model compounds, it is suggested that the complex $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$ initially acts as a catalyst in a reaction proceeding by a redox catalysed mechanism. Gradual decomposition of all metal–carbonyl-containing species leads to this mechanism being replaced by a radical chain reaction, probably initiated by molybdenum-containing decomposition products. A brief comparison is made of the efficiency of a range of transition-metal complexes in promoting addition of CCl_4 to oct-1-ene in reactions performed under standard conditions.

There has recently been much interest in ' organotransition-metal free radicals.' Such species contain a metal atom in a low oxidation state, together with a ligand array that confers a configuration of 17 or 19 valence electrons. These therefore have one unpaired electron, usually show low kinetic stability and often their modes of reactivity parallel those of organic free radicals.[1] As part of a general study of such species we have been interested in examining organic reactions in which they may play a role as either catalysts or initiators.

One such radical is $[Mo(CO)_3(\eta^5-C_5H_5)]$ which may be generated from its parent dimer. This dimer, together with the related complexes $[Co_2(CO)_8]$ and $[Fe_2(CO)_4(\eta^5-C_5H_5)_2]$, has been shown to be active in promoting the Karasch addition of halogenocarbons to alkenes [equation (1)].[2] Detailed

$$R'X + RCH{=}CH_2 \longrightarrow RCXHCH_2R' \quad (1)$$

mechanistic studies have not been performed on such reactions in the presence of dimeric metal complexes. However, the mechanism shown in Scheme 1 has been tentatively advanced for reactions involving tetrachloromethane.[3] Although this mechanism involves a metal-centred complex acting as a catalyst, the third step [equation (4)] has the nature of a chain propagation step and we shall term this mechanism *chain catalysis*.

Two alternative mechanisms are worthy of consideration for this reaction. The first of these is a classical *radical chain* reaction in which the metal dimer acts simply as an initiator (Scheme 2).[2] At this point we do not write equation (5) in a balanced form, but simply to represent reaction of the complex with tetrachloromethane to form trichloromethyl radicals. Neither have we included all possible chain termination reactions, although a number of such reactions have been previously recognised in addition reactions of this type.[2]

The second alternative is one similar to that established for addition reactions performed in the presence of halides of copper or iron [4] and is shown in Scheme 3. Such a mechanism is clearly catalytic in metal dimer, but unlike the more usual type of catalysis by metal complexes involving oxidative addition, demands only a single change in metal oxidation state between molybdenum(I) and molybdenum(II). Such single redox changes also occur in catalysis by halides of iron and copper and thus we use the same terminology in referring to this mechanism as *redox catalysis*.

The aim of this study was, thus, to elucidate the mechanism of Karasch addition in the presence of $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$. This has been achieved by means of a detailed examination of reaction intermediates and model compounds, as well as by a kinetic study. We also comment briefly on some hitherto unreported side products of the reaction.

Finally, there have been a number of disparate reports of promotion of Karasch addition reactions by low-valent transition-metal complexes,[3,5–7] but as these were often performed under slightly different conditions, we take this opportunity to compare the efficiency of a range of these complexes in reactions performed under standard conditions. Some of these results have been communicated as a preliminary report.[8]

Results and Discussion

(*a*) *Mechanistic Studies.*—In our mechanistic study of Karasch addition in the presence of $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$ we chose to study the reaction of oct-1-ene with tetrachloromethane. Oct-1-ene was chosen as its low volatility enables accurate weighings to be made for quantification and kinetic experiments. The choice of halogenoalkane was dictated by considerations of reactivity, as higher homologues show much lower reactivity despite their advantages in handling. Furthermore, the product of this reaction is tetrachlorononane, a compound which can be analysed by gas–liquid chromatography (g.l.c.) relatively rapidly. The yield of product was good (see Table 1) in reactions carried out both in sealed tubes and under reflux. Low yields of a number of previously unreported side products were observed and a typical g.l.c. trace is shown in Figure 1. The origin of these compounds will be discussed later.

Close observation of this reaction showed some inconsistencies with the chain catalysis mechanism previously proposed (Scheme 1).[3] Thus all metal carbonyl CO stretching bands disappear from the i.r. spectrum of the refluxing reaction mixture after 180 min, indicating complete decomposition of metal carbonyl complexes. Despite this, the product is formed at almost the same rate for a further 210 min. Furthermore, although CCl_4 reacts with $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$ in a separate reaction to form $[MoCl(CO)_3(\eta^5-C_5H_5)]$ in good yield, as

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† Bis(tricarbonyl-η^5-cyclopentadienylmolybdenum).

$$[\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2}] + \mathrm{CCl_4} \xrightarrow{k_2} [\mathrm{MoCl(CO)_3(\eta^5\text{-}C_5H_5)}] + [\mathrm{Mo(CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)}] \quad (2)$$

$$[\mathrm{Mo(CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)}] + \mathrm{RCH{=}CH_2} \xrightarrow{k_3} [\mathrm{Mo(CHRCH_2CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)}] \quad (3)$$

$$[\mathrm{Mo(CHRCH_2CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)}] + \mathrm{CCl_4} \xrightarrow{k_4} \mathrm{RCHClCH_2CCl_3} + [\mathrm{Mo(CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)}] \quad (4)$$

Scheme 1.

$$[\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2}] + \mathrm{CCl_4} \xrightarrow{k_5} [\mathrm{MoCl(CO)_3(\eta^5\text{-}C_5H_5)}] + \mathrm{CCl_3}^{\bullet} \quad (5)$$

$$\mathrm{CCl_3}^{\bullet} + \mathrm{RCH{=}CH_2} \xrightarrow{k_6} \mathrm{R\dot{C}HCH_2CCl_3} \quad (6)$$

$$\mathrm{R\dot{C}HCH_2CCl_3} + \mathrm{CCl_4} \xrightarrow{k_7} \mathrm{RCHClCH_2CCl_3} + \mathrm{CCl_3}^{\bullet} \quad (7)$$

$$2\mathrm{CCl_3}^{\bullet} \xrightarrow{k_8} \mathrm{C_2Cl_6} \quad (8)$$

Scheme 2.

$$[\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2}] + \mathrm{CCl_4} \xrightarrow{k_9} [\mathrm{MoCl(CO)_3(\eta^5\text{-}C_5H_5)}] + [\mathrm{Mo(CO)_3(\eta^5\text{-}C_5H_5)}]^{\bullet} + \mathrm{CCl_3}^{\bullet} \quad (9)$$

$$\mathrm{CCl_3}^{\bullet} + \mathrm{RCH{=}CH_2} \xrightarrow{k_{10}} \mathrm{R\dot{C}HCH_2CCl_3} \quad (10)$$

$$\mathrm{R\dot{C}HCH_2CCl_3} + [\mathrm{MoCl(CO)_3(\eta^5\text{-}C_5H_5)}] \xrightarrow{k_{11}} \mathrm{RCHClCH_2CCl_3} + [\mathrm{Mo(CO)_3(\eta^5\text{-}C_5H_5)}]^{\bullet} \quad (11)$$

$$2[\mathrm{Mo(CO)_3(\eta^5\text{-}C_5H_5)}]^{\bullet} \xrightarrow{k_{12}} [\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2}] \quad (12)$$

Scheme 3.

Table 1. Product yields from addition reactions promoted by various metal-containing species

	Yield [b,c] (%)		
Carbonyl [a] complex	T = 80 °C [d]	T = 100 °C [d]	T = 120 °C [d]
$[\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2}]$	19.6	36.5	47.5
$[\mathrm{Mo_2(CO)_4(PPh_3)_2(\eta^5\text{-}C_5H_5)_2}]$	14.3	16.3	20.2
$[\mathrm{Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2}]$	8.2	12.3	50.3
$[\mathrm{Mn_2(CO)_{10}}]$	8.4	14.7	15.8
$[\mathrm{Re_2(CO)_{10}}]$	2.8	2.6	9.2
$[\{\mathrm{Re(CO)_4(PPh_3)}\}_2]$	4.5	7.9	17.6
$[\mathrm{Co_2(CO)_8}]$	3.9	4.8	4.9
$[\mathrm{Cr(CO)_6}]$	6.4	9.2	20.6
$[\mathrm{Mo(CO)_6}]$	12.1	23.6	23.2
$[\mathrm{RhCl(CO)(PBu^n_3)_2}]$ [e]		4.9	9.1
$[\mathrm{RhCl(CO)(PPh_3)_2}]$	15.1	20.3	23.5
$[\mathrm{Cr(CO)_3(\eta^6\text{-}C_{10}H_8)}]$	12.4	11.6	11.7
$[\mathrm{RuCl_2(PPh_3)_3}]$	74.6	71.3	67.2

[a] In all cases amount of metal complex = 3.88×10^{-5} mol. [b] Yields based on amount of alkene charged rather than consumed. [c] All reactions run in tubes, sealed under vacuum, for 20 h. [d] Reaction temperature. [e] $[\mathrm{RhCl(CO)(PBu^n_3)_2}]$ could not be weighed accurately due to its oily nature, therefore quantification is not accurate.

proposed in equation (2) of Scheme 1, there is no spectroscopic or other evidence for the presence of $[\mathrm{Mo(CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)}]$ (see below), and $[\mathrm{MoCl(CO)_3(\eta^5\text{-}C_5H_5)}]$ rapidly undergoes total decomposition under the reaction conditions.

Other observations are that one of the side products is $\mathrm{C_2Cl_6}$, presumably formed by dimerisation of $\mathrm{CCl_3}^{\cdot}$ radicals [2] and that tetrachlorononane is produced in one major and two minor isomeric forms. The minor forms may well be the 1,1,1,5- and 1,1,1,7-isomers arising by 1,3- and 1,5-hydrogen migrations of intermediate $\mathrm{Cl_3CCH_2\dot{C}H(CH_2)_5CH_3}$ radicals, while the major form is presumably the 1,1,1,3-isomer. N.m.r. spectra of a purified tetrachlorononane mixture are consistent with those previously reported for the 1,1,1,3-isomers,[9] but show other peaks too weak for detailed analysis.

We also observed that, despite a previous report to the contrary,[3] the reaction is inhibited by both oxygen and the radical scavenger, phenothiazine. In the latter case, complete consumption of an added aliquot of scavenger is followed by the reaction returning to its normal rate for the production of tetrachlorononane.

It thus seemed to us that at least two mechanisms are operating, presumably concurrently, in this reaction. Initial interaction of $[\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2}]$ with $\mathrm{CCl_4}$ must lead to formation of product by a mechanism such as one of those outlined in Schemes (1)—(3). However, a second process must come into operation upon decomposition of metal–carbonyl-containing compounds. This later reaction is presumably of radical chain nature and may be initiated by molybdenum-containing decomposition products. In order to examine the nature of the initial reaction, a kinetic study was undertaken by the initial rate method.

Application of steady-state considerations to the intermediates $[\mathrm{Mo(CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)}]$ and $[\mathrm{Mo(CHRCH_2CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)}]$ in Scheme 1 leads to the kinetic expression shown [equation (13)].

$$\mathrm{d[RCHClCH_2CCl_3]}/\mathrm{d}t = k_2[\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2}][\mathrm{CCl_4}] \quad (13)$$

Similar treatment of $\mathrm{R\dot{C}HCH_2CCl_3}$ and $\mathrm{CCl_3}^{\cdot}$ in Scheme 2 gives the expression (14), and a steady-state consideration of $\mathrm{R\dot{C}HCH_2CCl_3}$ and $\mathrm{CCl_3}^{\cdot}$ in Scheme 3 leads to equation (15). Thus initial reaction by a radical chain process should be readily distinguished from chain or redox catalysis, although reaction orders do not differentiate between these later mechanisms.

$$\frac{\mathrm{d[RCHClCH_2CCl_3]}}{\mathrm{d}t} = \frac{k_6 k_5^{\frac{1}{2}}}{k_8^{\frac{1}{2}}}[\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2}]^{\frac{1}{2}}[\mathrm{CCl_4}]^{\frac{1}{2}}[\mathrm{RCH{=}CH_2}] \quad (14)$$

$$\frac{\mathrm{d[RCHClCH_2CCl_3]}}{\mathrm{d}t} = k_9[\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2}][\mathrm{CCl_4}] \quad (15)$$

A plot of initial rate *versus* concentration of $[\mathrm{Mo_2(CO)_6}$-

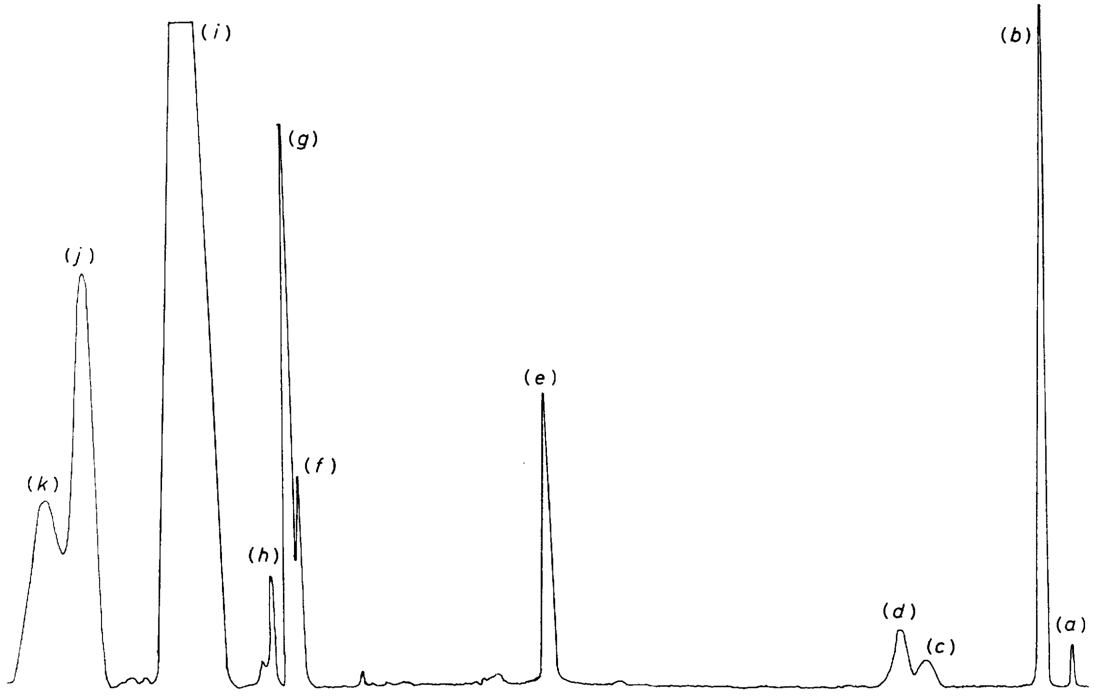


Figure 1. G.l.c. trace of reaction mixture separated on an Apiezon-L column: $CHCl_3$ (*a*); CCl_4 (*b*); oct-1-ene (*c*); oct-2-ene (*d*); unknown, C_8H_{16} (*e*); dichlorononadienes (*f*)—(*h*); 1,1,1,3-tetrachlorononane (*i*); other tetrachlorononane isomers (*j*), (*k*)

$(\eta^5-C_5H_5)_2]$ is shown in Figure 2, clearly demonstrating that the reaction is first order in complex.

A similar dependence on CCl_4 concentration is evident from Figure 3. The reaction rate was found to be independent of concentration of oct-1-ene. The small positive intercept of Figure 2 indicates a minor contribution from a reaction not promoted by $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$ and, for this reason, no attempt was made to obtain activation parameters for the reaction.[10] Examination of reaction rates *versus* initial concentrations at reaction times of 5 min and longer showed marked deviations from the orders given above, a finding consistent with the observations detailed earlier. However, it is not possible to perform accurate quantitative analysis of these data.

Second-order rate constants of 1.93 ± 0.14 $dm^3 mol^{-1} s^{-1}$ and 2.22 ± 0.16 $dm^3 mol^{-1} s^{-1}$ were obtained from the variation in initial rates with $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$ concentration and CCl_4 concentration respectively. In view of the fact that these results were obtained by the initial rate method which can be subject to considerable error in estimation of the correct tangent to the rate curve, the agreement between rate constants is satisfactory. The Figures are also comparable with a second-order rate constant of 2×10^{-2} $dm^3 mol^{-1} s^{-1}$ at 34 °C for reaction between $[Mo(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ and CCl_4.[11] However, there is a marked discrepancy with the observation of Poe and co-workers [12] that reaction between $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$ and both $C_2H_2Cl_4$ and $CHBr_3$ is first order in complex and second order in halogenocarbon. No reasons for this difference are obvious.

This kinetic analysis, therefore, excludes an initial reaction in which the $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$ acts as an initiating species for a radical chain reaction. It does not, however, distinguish between chain and redox catalysis. The important differences between these mechanisms (Schemes 1 and 3) rest in the formation of the metal–trichloromethyl complex, followed by insertion into the Mo–C bond (Scheme 1), compared with a reaction involving the formation and reaction with the alkene

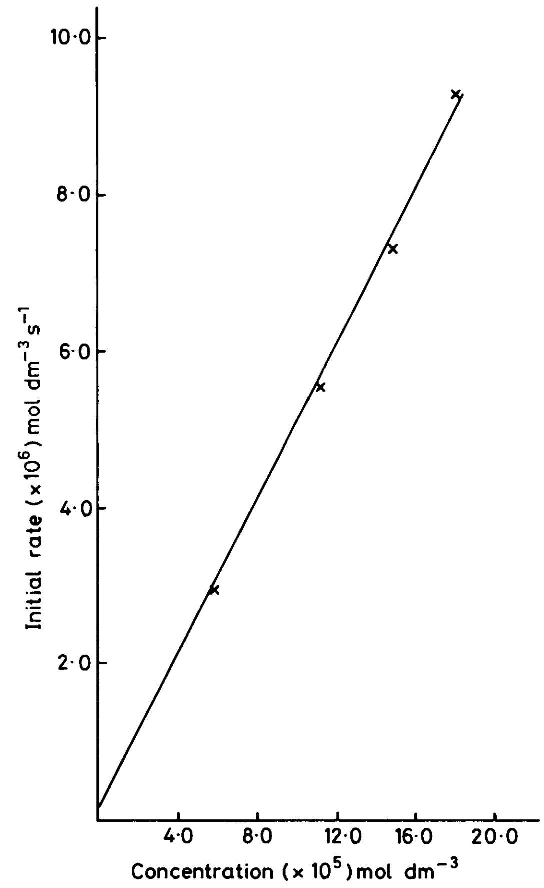


Figure 2. Plot of initial rate *versus* concentration of $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$

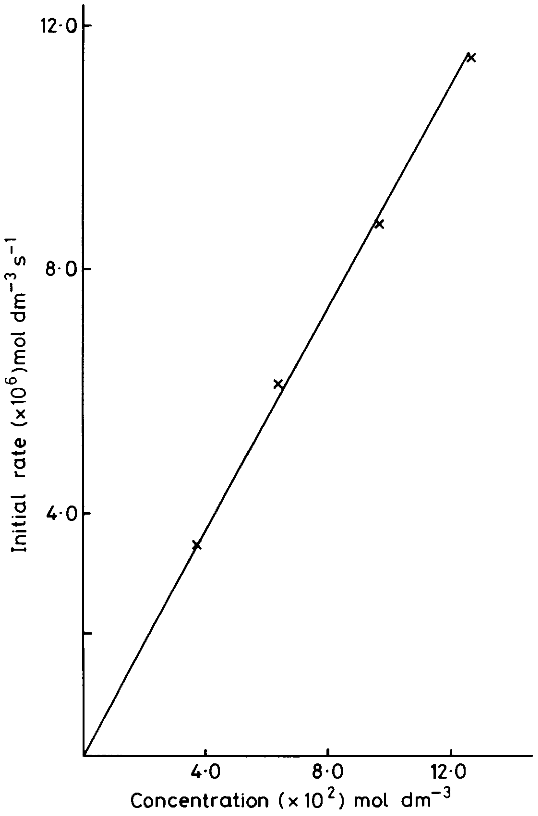


Figure 3. Plot of initial rate *versus* concentration of CCl_4

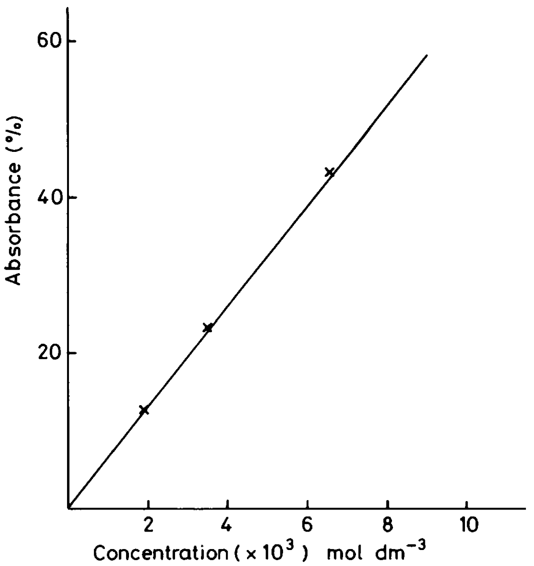
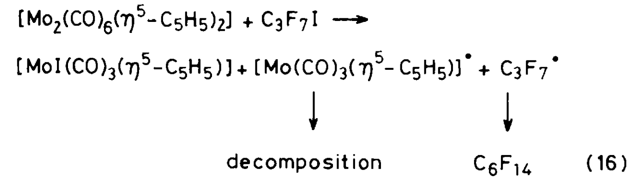


Figure 4. Plot of absorbance of the CO stretching band at 2 040 cm^{-1} *versus* concentration for $[MoI(CO)_3(\eta^5\text{-}C_5H_5)]$



of free trichloromethyl radicals (Scheme 3). In seeking to differentiate between these two, it is therefore important to obtain evidence concerning formation of the intermediate metal halogenoalkyl complex. It is noteworthy, at this stage, that $[Mo(CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)]$ has not been previously reported and, indeed, well characterised examples of metal–trichloromethyl complexes are scarce.[13]

As stated above, when $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ reacts with CCl_4 either in the presence of alkene or in a separate reaction, an i.r. spectrum characteristic of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ is observed. The reaction is complete after 24 h at room temperature. At no stage during this reaction is there i.r. evidence for the presence of any metal–carbonyl-containing species other than the starting material and the chloro-complex. This does not, however, rule out the chance coincidence of the i.r. absorptions of $[Mo(CCl_3)(CO)_3(\eta^5\text{-}C_5H_5)]$ with those of the chloro-complex. Neither does it preclude transient existence of the complex in the addition reaction and, indeed, the low kinetic stability of such a compound would favour efficient catalysis.

The compound $[Mo(C_3F_7)(CO)_3(\eta^5\text{-}C_5H_5)]$ is, however, well known [14] and may serve as a model for formation of the trichloromethyl complex in a parallel addition of n-C_3F_7I to oct-1-ene. This addition reaction has been previously reported as proceeding in good yield in the presence of copper(I) chloride and 2-aminoethanol.[9] 1,1,1,2,2,3,3-Heptafluoro-5-iodoundecane was therefore prepared by this method and was identical to the product of an analogous reaction promoted by $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$. Thus, if addition of C_3F_7I to oct-1-ene proceeds by the mechanism shown in Scheme 1, the formation of $[Mo(C_3F_7)(CO)_3(\eta^5\text{-}C_5H_5)]$ should be observed. This compound was prepared by the literature method and its i.r. data obtained [ν(CO) 2 055m, 1 982s, and 1 972m cm^{-1}] in a C_3F_7I–oct-1-ene mixture. The reaction between the two compounds was then performed in the presence of $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$. Monitoring the i.r. spectrum showed clearly the gradual disappearance of the dimer and formation of $[MoI(CO)_3(\eta^5\text{-}C_5H_5)]$ [ν(CO) 2 040m, 1 979s, and 1 963m cm^{-1}]. However, there was no evidence for formation of the perfluoropropyl complex. In a separate experiment it was shown that this compound was stable under the reaction conditions in that its i.r. spectrum remained unchanged after refluxing for 3 h at 80 °C. Finally, in order to eliminate the possibility that the i.r. bands arising from the dimer and the iodo-complex were obscuring those of the perfluoroalkyl complex, a synthetic mixture of the three compounds was examined. While the spectrum resulting from this mixture showed some of the carbonyl bands below 2 000 cm^{-1} to merge, the bands at 2 040 and 2 055 cm^{-1} from the iodo and perfluoroalkyl complexes respectively were clearly distinguishable.

No kinetic results were obtained for the reaction of C_3F_7I with oct-1-ene in the presence of $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$. However, the stoicheiometry of the reaction between the dimer and C_3F_7I was confirmed by quantitative i.r. spectroscopy. Thus a Beer-Lambert plot of the intensity of the band at 2 040 cm^{-1} of $[MoI(CO)_3(\eta^5\text{-}C_5H_5)]$ was constructed (Figure 4) and following complete reaction of $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ with excess C_3F_7I, the iodo-complex produced was quantified. In this experiment, 0.0034 mol of dimer produced 0.0033 mol of iodo-complex. Furthermore, at the end of the reaction there had formed a small amount of precipitated material containing molybdenum, and C_6F_{14} was identified by g.l.c. comparison with an authentic sample. This is consistent with equation (16) and is in accord with the first step of the redox catalysis mechanism (Scheme 3).

In summary, the evidence is in favour of a mechanism in-

Table 2. Mixtures examined by e.s.r.[a]

(*i*) CCl_4–C_8H_{16}–$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$
(*ii*) CCl_4–$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$
(*iii*) C_8H_{16}–$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$
(*iv*) $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ [b]
(*v*) CCl_4–C_8H_{16}
(*vi*) C_3F_7I–C_8H_{16}–$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$
(*vii*) C_3F_7I–$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$
(*viii*) C_3F_7I–C_8H_{16}

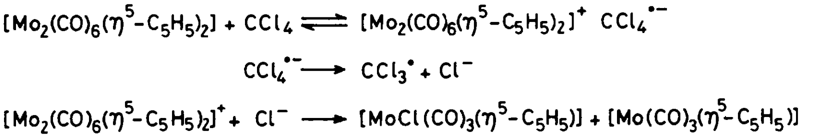
[a] C_8H_{16} = oct-1-ene; all mixtures in the presence of nitrosodurene. [b] Cyclohexane solvent.

volving redox catalysis and as such a mechanism encompasses the generation of free radicals, attempts were made to identify such species by e.s.r. spectroscopy. The mixtures shown in Table 2 were examined at both ambient temperature and at 80 °C, all in the presence of the radical trapping agent, nitrosodurene. In none of these were spectra observed consistent with formation of $CCl_3^\bullet$, $C_3F_7^\bullet$, or $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]^\bullet$ radicals. It is, however, noteworthy that a related study of the reactions between *cis*-$[M(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ (M = Cr or Mo) and several halogenoalkanes (RX) exhibited spectra consistent with formation of spin adducts with nitrosodurene when R = $PhCH_2$, Ph_2CH, or Ph_3C but no signal was observed in comparable reactions with CCl_4.[13]

Finally, a brief consideration is made of the nature of the initial interaction of halogenoalkane with $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$. There exist several possible modes of such interaction that would eventually lead to production of radicals such as $CCl_3^\bullet$.

The analogous dimer $[Cr_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ has been shown by n.m.r. spectroscopy to undergo reversible dissociation into the mononuclear radicals $[Cr(CO)_3(\eta^5\text{-}C_5H_5)]^\bullet$ at temperatures above ambient [15] and e.s.r. evidence has been presented for the existence of the radicals in *ca.* 1% concentration at room temperature.[16] Similar e.s.r. studies of the molybdenum and tungsten dimers yielded no evidence for metal–metal bond homolysis at room temperature [17] and in this study we have examined the variable-temperature n.m.r. spectrum of the molybdenum complex. The low-temperature spectrum was consistent with that previously reported [18] and is indicative of hindered rotation about the Mo–Mo bond. However, no peak broadening consistent with production of paramagnetic species was observed at high temperatures. Furthermore, $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ is indefinitely stable in CCl_4 solution, even at 60 °C *in the dark*, although exposure to daylight leads to immediate production of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$. It is therefore not likely that thermally induced metal–metal bond homolysis plays a significant role in the reaction. Initial interaction may be *via* charge-transfer complex formation, radical production being achieved as a consequence of photolytic decomposition of such a complex (Scheme 4). Similar behaviour has been noted in reactions of ferrocene and ruthenocene with CCl_4.[19] However, none of the usual spectroscopic methods [20] gave any indication of the formation of such a complex at room temperature. Finally, others have suggested the formation of an I_2 bridged complex in the reaction of $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ and iodine [21] and such an intermediate cannot be excluded in the case of CCl_4.

(*b*) *Side Products.*—G.l.c. analysis of the reaction product on an Apiezon-L column showed that the peak attributed to tetrachlorononane could be resolved into one major and two minor components. Subsequent gas chromatography–mass spectra (g.c.–m.s.) examination showed these to have virtually identical mass spectra and these spectra were also in good agreement with that obtained from a bulk sample of tetrachlorononane purified by fractional distillation. It therefore appears that these represent isomeric forms of tetrachlorononane. Such isomers presumably arise by 1,3- and 1,5-hydrogen migrations of the initially formed $CCl_3CH_2\dot{C}H(CH_2)_5CH_3$ radical.[2] Attempts to separate these isomers by preparative g.l.c. and distillation were unsuccessful.



$$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2] + CCl_4 \rightleftharpoons [Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]^+\ CCl_4^{\bullet-}$$
$$CCl_4^{\bullet-} \longrightarrow CCl_3^\bullet + Cl^-$$
$$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]^+ + Cl^- \longrightarrow [MoCl(CO)_3(\eta^5\text{-}C_5H_5)] + [Mo(CO)_3(\eta^5\text{-}C_5H_5)]$$

Scheme 4.

Preparative reactions left for *ca.* 20 h produced hydrogen chloride and showed small peaks in the g.l.c. trace, which, on subsequent g.c.–m.s. analysis, all gave spectra consistent with dichlorononadienes [*m*/*e* 192(relative intensity 9), 194(6), 196(1)]. It was not possible to assign unique structures to each component based on fragmentation behaviour, but presumably these isomers arise by dehydrochlorination of the isomeric tetrachlorononanes. In a separate reaction, a bulk sample of tetrachlorononane was subjected to dehydrochlorination by ethanolic KOH. The products of this reaction were identical (g.c.–m.s.) to those discussed above.

A further side product was hexachloroethane which arises as a consequence of termination of the radical chain mechanism by coupling of $CCl_3^\bullet$. Trichloromethane and oct-2-ene were also identified and it is suggested that these arise as a consequence of a small amount of allylic hydrogen abstraction from oct-1-ene by $CCl_3^\bullet$ radicals,[2] accompanied by subsequent formation of a delocalised 1-pentylallyl radical, which reforms oct-2-ene by hydrogen abstraction by the unsubstituted terminal carbon atom of the radical. Other sources of oct-2-ene, namely alkene isomerisation promoted by $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ or HCl, were eliminated by independent reactions.

Finally, a minor component was observed of molecular formula C_8H_{16} (g.c.–m.s.). The fact that this was not a fragment ion of some higher molecular weight species was confirmed by chemical ionisation mass spectrometry. Again, the fragmentation pattern did not allow unique identification and besides the fact that g.l.c. comparison showed the compound not to be any of the octene isomers or ethylcyclohexane, its identification remains unconfirmed.

(*c*) *A Comparison of the Efficiency of Various Metal Complexes in promoting Reaction between* CCl_4 *and Oct-*1*-ene.*—There have been a number of independent reports of the promotion of addition of CCl_4 to alkenes by transition-metal complexes. However, there has been no previous comparison of the relative efficiency of these complexes in reactions performed under standard conditions. Furthermore, there exist reports of compounds such as $[M_2(CO)_{10}]$ [22] (M = Mn or Re) and $[RhCl(CO)(PBu^n{}_3)_2]$[23] reacting with CCl_4 and thus displaying potential for promotion of addition reactions. Here we briefly survey the efficiency of a number of these compounds in promoting the addition of CCl_4 to oct-1-ene at three temperatures (Table 1). We do not wish to draw detailed mechanistic inferences from the yields obtained and, indeed, the range of possible contributory factors would render this unwarranted. However, it is noteworthy that, with the exception of $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$, $[Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$, and $[RuCl_2(PPh_3)_3]$, yields of addition product are poor to moderate. We have examined, and will be reporting in detail elsewhere on the mechanism of one such low yield reaction, that performed in the presence of $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$.[24] Based on our findings in this case, it is likely that these low yield reactions proceed entirely by a radical chain mechanism in which the metal complex acts simply as an initiator. It seems likely that reaction in the presence of $[Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ parallels the mechanistic pathway followed by the molybdenum dimer. The high efficiency of such reactions in the presence of $[RuCl_2(PPh_3)_3]$ has been the subject of a number of studies by Matsumoto *et al.*[5,25] and these workers have advanced a redox catalysis mechanism operating in the co-ordination sphere. We have also examined this reaction in detail and will also be reporting separately upon it.[24]

Experimental

All reactions and kinetic experiments were carried out under an atmosphere of dry oxygen-free 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.

G.c.–m.s. was performed on a Kratos MS 3076–Pye 104 system. Chemical ionisation g.c.–m.s. were performed on a V.G. Micromass ZAB machine. Organometallic samples were examined on an AEI MS9 machine using the direct insertion probe. Infra-red spectra were recorded on a Perkin-Elmer 457 spectrometer, n.m.r. spectra on a Perkin-Elmer R32, and e.s.r. spectra on a Varian E.4.

G.l.c. analyses were performed on F.I.D. equipped Pye GCD and 204 instruments as detailed below.

Analysis of the product mixture from addition of tetrachloromethane to oct-1-ene was accomplished by means of both a 2 m, $\frac{1}{4}$ in, 10% PEGA on Chromosorb W 80/100 mesh column (column $T = 165$ °C, injector and detector $T = 250$ °C, nitrogen flow rate 30 cm^3 min^{-1}) and a 2 m, $\frac{1}{4}$ in, 10% Apiezon-L on Chromosorb W 80/100 mesh column (column $T = 185$ °C, injector and detector $T = 250$ °C, nitrogen flow rate 30 cm^3 min^{-1}). Quantification of tetrachlorononane was performed on a 2 m, $\frac{1}{4}$ in, 3% OV17 on Chromosorb W 80/100 mesh column (column $T = 200$ °C injector and detector $T = 250$ °C, nitrogen flow rate 40 cm^3 min^{-1}) employing methyl myristate as an internal standard. Response factors were measured three times during each set of analyses. The C_6F_{14} was identified on a 2 m, $\frac{1}{8}$ in, Poropak Q on Chromosorb W 80/100 mesh column (column $T = 200$ °C, injector and detector $T = 250$ °C, nitrogen flow rate 30 cm^3 min^{-1}). Analysis of the reaction mixture from addition of n-C_3F_7I to oct-1-ene was performed on an Apiezon-L column as detailed above. The compounds $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$,[26] $[MoI(CO)_3(\eta^5\text{-}C_5H_5)]$,[27] $[Mo(C_3F_7)(CO)_3(\eta^5\text{-}C_5H_5)]$,[14] $[RhCl(CO)(PPh_3)_2]$,[28] and $[RhCl(CO)(PBu^n{}_3)_2]$[23] were prepared by literature methods. Both $[RuCl_2(PPh_3)_3]$ and $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$ were prepared by literature methods by Mr. J. L. A. Durrant of these laboratories. All these complexes showed satisfactory analytical and spectroscopic data. Preparation of 1,1,1,2,2,3,3-heptafluoroundecane and dehydrochlorination of tetrachlorononane were performed by the methods of Burton and Kehoe.[9]

$[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$.—The compound $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ (0.1 g) was allowed to stand in CCl_4 (15 cm^3) in daylight. The i.r. spectrum of the solution was monitored periodically and when all bands due to the dimer had disappeared, the solution was evaporated to dryness under vacuum. The resulting red-orange solid was taken up in a minimum quantity of CH_2Cl_2 and passed down a silica column [eluant: ethyl acetate–light petroleum (b.p. 40—60 °C) (3 : 1)]. This produced, on evaporation, an orange-red crystalline solid [0.03 g 53% yield, i.r. spectrum: ν(CO) at 2 055m, 1 988s, and 1 964s cm^{-1} (CCl_4 solution)].[21] Mass spectrum *m/e* 282 (M^+, based on ^{35}Cl, ^{98}Mo), 254, 226, 198, 163.

$[Mo_2(CO)_4(PPh_3)_2(\eta^5\text{-}C_5H_5)_2]$.—$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ and PPh_3 (1 : 2 molar ratio) were refluxed in hexane for 17 h. After this time a dull purple crystalline solid had precipitated. This was removed by filtration and exhibited an i.r. spectrum in agreement with that of $[Mo_2(CO)_4(PPh_3)_2(\eta^5\text{-}C_5H_5)_2]$ [ν(CO) at 1 850 (sh), and 1 834s cm^{-1} (Nujol mull)].[29] The remaining red solution produced a red solid on evaporation which exhibited an i.r. spectrum similar to that of $[Mo_2(CO)_5(PPh_3)(\eta^5\text{-}C_5H_5)_2]$ [ν(CO) at 1 970s, 1 900s, and 1 836s cm^{-1} ($CHCl_3$ solution)].[29,30]

*Typical Reaction Conditions for the Addition of Halogenoalkanes to Oct-*1-*ene.*—Oct-1-ene (3.0 g, 2.68×10^{-2} mol), tetrachloromethane (7.0 g, 4.54×10^{-2} mol), and the appropriate metal complex (3.88×10^{-5} mol) were loaded into a glass ampoule with a restriction in the neck to facilitate sealing. The mixture was degassed three times by the freeze-pump-thaw method and the tube was then sealed under vacuum. This was then heated to the desired temperature in an oven (*i.e.* in the dark) for 20 h, after which time the tube was cooled, broken open, and the contents analysed by g.l.c.

Reactions were also performed under reflux both in the dark and in daylight.

Kinetic Studies.—Kinetic studies were performed in toluene, sufficient solvent being added to maintain the total volume of the solution at 100 cm^3. The reaction mixture, excluding catalyst, was placed in a thermostatted vessel connected to a nitrogen-vacuum line and fitted with a rotatable spoon containing solid catalyst. The vessel also had a side arm sealed with a rubber septum cap and positioned so that samples may be withdrawn by syringe for analysis. The reaction mixture was degassed three times by the freeze-pump-thaw method and then allowed to come to a constant temperature of 83 °C by pumping hot water through a thermostat lining. The solution was stirred with a magnetic stirrer. The catalyst was then dropped into the solution and samples were withdrawn at regular time intervals. These samples were immediately frozen in liquid nitrogen and subsequently analysed by g.l.c. for tetrachlorononane.

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