FREE RADICAL HALOGENATION OF ALKANES INITIATED BY TRANSITION METAL COMPLEXES

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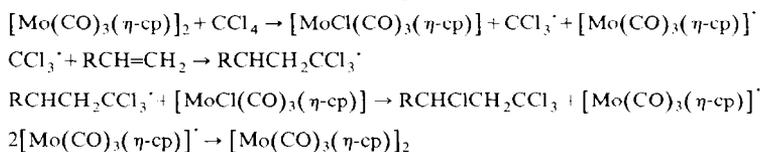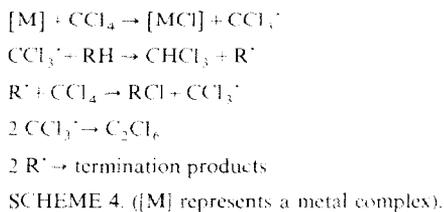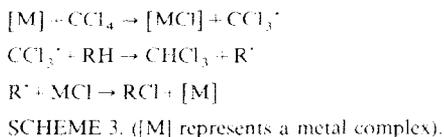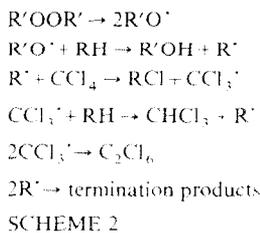
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Summary

Reaction between halocarbons (particularly CCl_4) and hydrocarbons (particularly c-C_6H_{12}) in the presence of a range of low valent metal complexes have been investigated. A detailed study of the reaction involving [$Re_2(CO)_{10}$] has shown it to proceed by a free radical chain route in which the metal complex acts solely as an initiator. Similar behaviour has been confirmed for [$Cr(CO)_6$]. [$Re_2(CO)_{10}$] and [$Cr(CO)_6$] show initiation efficiencies comparable with organic peroxides, but other complexes are less efficient. Factors effecting efficiencies have been studied.

We have previously studied the addition of halocarbons to alkenic double bonds (the Karasch addition reaction) in the presence of transition metal complexes. These studies have shown that in the presence of [$Mo_2(CO)_6(\eta\text{-cp})_2$] [1], [$Fe_2(CO)_4(\eta\text{-cp})_2$] [2], [$RuCl_2(PPh_3)_3$] [3] and [$Cr(CO)_3(\eta\text{-}C_{10}H_8)$] [4] such reactions do not proceed by a free radical chain mechanism of the type encountered in the presence of traditional initiators [5], but follow a route in which the metal complex acts as a catalyst, as opposed to acting simply as an initiator. During the catalytic reaction the metal undergoes an increase in valency by one unit, a change which is reversed at the end of each cycle. Such addition reactions are thus said to follow a "redox-catalysed" mechanism and are exemplified in Scheme 1. These findings led us to consider employing metal-mediated processes for alkane functionalisation.

Alkane functionalisation reactions of the type shown in Scheme 2 have been reported in which the use of organic peroxides or ultraviolet light leads to the initiation of a free radical chain process. These reactions have been employed to

$[Mo(CO)_3(\eta\text{-cp})]_2 + CCl_4 \rightarrow [MoCl(CO)_3(\eta\text{-cp})] + CCl_3^{\cdot} + [Mo(CO)_3(\eta\text{-cp})]^{\cdot}$

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

$RCHCH_2CCl_3^{\cdot} + [MoCl(CO)_3(\eta\text{-cp})] \rightarrow RCHClCH_2CCl_3 + [Mo(CO)_3(\eta\text{-cp})]^{\cdot}$

$2[Mo(CO)_3(\eta\text{-cp})]^{\cdot} \rightarrow [Mo(CO)_3(\eta\text{-cp})]_2$

SCHEME 1

$$R'OOR' \rightarrow 2R'O^{\cdot}$$

$$R'O^{\cdot} + RH \rightarrow R'OH + R^{\cdot}$$

$$R^{\cdot} + CCl_4 \rightarrow RCl + CCl_3^{\cdot}$$

$$CCl_3^{\cdot} + RH \rightarrow CHCl_3 + R^{\cdot}$$

$$2CCl_3^{\cdot} \rightarrow C_2Cl_6$$

$$2R^{\cdot} \rightarrow termination \ products$$

SCHEME 2

$$[M] + CCl_4 \rightarrow [MCl] + CCl_3^{\cdot}$$

$$CCl_3^{\cdot} + RH \rightarrow CHCl_3 + R^{\cdot}$$

$$R^{\cdot} + MCl \rightarrow RCl + [M]$$

SCHEME 3. ([M] represents a metal complex).

$$[M] + CCl_4 \rightarrow [MCl] + CCl_3^{\cdot}$$

$$CCl_3^{\cdot} + RH \rightarrow CHCl_3 + R^{\cdot}$$

$$R^{\cdot} + CCl_4 \rightarrow RCl + CCl_3^{\cdot}$$

$$2 \ CCl_3^{\cdot} \rightarrow C_2Cl_6$$

$$2 \ R^{\cdot} \rightarrow termination \ products$$

SCHEME 4. ([M] represents a metal complex).

bring about the halogenation of a range of alkanes, cycloalkanes and alkyl aromatics employing reagents such as CCl_4, C_2Cl_6 and $CBrCl_3$ [6-9]. There are, however, no reports in the literature of the use of transition metal complexes as either catalysts or initiators for such reactions.

In view of our findings for alkene addition reactions, we wished to explore the possibility that transition metal complexes may either catalyse such reactions (Scheme 3) or act as initiators of radical chain processes (Scheme 4). This would present an alternative route for alkane functionalisation to reactions involving the oxidative addition of alkanes to metal complexes [10]. The latter type of reactions have only been reported relatively recently and have not yet led to the development of processes catalysed by metal complexes.

Some of the results contained in this paper have previously been communicated in preliminary form [11].

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 before use and particular care was taken to ensure that organic reagents were free from peroxide impurities. Solvents were thoroughly degassed by at least 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.

GC-MS was performed on a Kratos MS3076-Pye 104 system. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. NMR spectra were recorded on a Perkin-Elmer R32 spectrometer. GLC analyses were performed on an FID equipped Pye 204 chromatograph linked to a Spectra-Physics Autolab Minigrator. Analysis of reaction products was accomplished by means of a 2 m, 0.25 in, 5%

OV17 on Chromosorb W 80–100 mesh column (column T 80°C, injector T 100°C, detector T 150°C, nitrogen flow rate 30 cm^3 min^{-1}) Products were identified with the aid of authentic samples. Quantification of CCl$_4$/cyclohexane reaction products from preparative experiments was achieved with the aid of bromocyclohexane as internal standard, whereas methyl octanoate was employed as internal standard from the analysis of products from kinetic experiments. The products of analogous reactions employing other halogenating agents and hydrocarbon substrates were quantified using either bromocyclohexane, iodocyclohexane or benzyl chloride as internal standards. Analysis of the products from the reaction between CCl$_4$ and adamantane was achieved by means of a 2 m, 0.25 in, 12% Carbowax 20, on Chromosorb W 80–100 mesh column (column T 170°C, injector and detector T 200°C, nitrogen flow rate 30 cm^3 min^{-1}) employing methyl palmitate as the internal standard. In all cases response factors were measured three times during each set of analyses.

[Cr(CO)$_6$], [Mo(CO)$_6$], [Mn$_2$(CO)$_{10}$], [Re$_2$(CO)$_{10}$], [Co$_2$(CO)$_8$] and [Fe$_2$(CO)$_4$(η-cp)$_2$] were supplied by Strem Chemicals and were recrystallised prior to use. [Mo$_2$(CO)$_6$(η-cp)$_2$] [12], [MoI(CO)$_3$(η-cp)] [13], [MoMe(CO)$_3$(η-cp)] [14], [Re$_2$(CO)$_8$(PPh$_3$)$_2$] [15], chlorocyclooctane [16] and methyl octanoate [16] were prepared by literature methods.

[MCl(CO)$_5$] (M = Mn, Re) and [FeCl(CO)$_2$(η-cp)] were prepared by reaction between the appropriate dinuclear metal carbonyl complex and SO$_2$Cl$_2$. The details of this reaction have been described elsewhere [17].

Typical conditions for the reactions between halocarbons and hydrocarbons *

In a typical reaction, cyclohexane (8.4 g, 0.1 mol), tetrachloromethane (3.85 g, 2.5 × 10^{-2} mol) and the transition metal complex (4 × 10^{-5} mol) were loaded into a glass ampoule with a restriction in the neck to facilitate sealing. The reaction mixture was degassed by three freeze-pump-thaw cycles 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 the required time. After cooling the tube was broken open and the contents analysed.

Kinetic studies

These were performed in benzene, sufficient solvent being added to maintain the total volume of the solution at 50 cm^3. The reaction mixture, excluding the metal complex, but including the internal standard, methyl octanoate, was placed in a thermostatted vessel connected to a nitrogen-vacuum line and fitted with a rotatable spoon, containing the complex. The spoon was equipped with a loose fitting cover (n.b. In separate experiments, methyl octanoate was shown to be unaffected by treatment with either reagents or catalyst). The vessel also had a side arm sealed with a rubber septum and positioned so as to facilitate the withdrawal of samples by

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* *Important: Potential hazard.* On a few occasions tubes exploded in the oven. There did not appear to be any discernable pattern of reaction temperatures or times or reagent concentrations governing these occurances, and it probably depends on the quality of the seal at the neck. We recommend that the oven devoted to such reactions has a stout door fastener and contains no other glassware or chemicals.

syringe for analysis. The reaction mixture was degassed by three freeze-pump-thaw cycles and allowed to come to a constant temperature of 81°C by pumping hot water through the thermostat lining. The complex was then dropped into the solution and samples were withdrawn at regular time intervals. The samples were immediately quenched by freezing in liquid nitrogen and subsequently analysed by GLC for chlorocyclohexane.

Results and discussion

(a) General considerations

This study is principally concerned with reaction (1), although the use of both alternative hydrocarbons and halocarbons will be considered in section (e).

$$c\text{-}C_6H_{12} + CCl_4 \rightarrow C_6H_{11}Cl + CHCl_3 \tag{1}$$

Reactions of this type have previously been performed in the presence of conventional free radical initiators and have been shown to follow free radical chain mechanisms such as that shown in Scheme 1 [6–9]. There are no previous reports of the use of transition metal complexes to promote reactions of this type, however, the results given in Table 1 show that low-valent metal complexes can afford high yields of chlorocyclohexane (up to 60% based on the amount of CCl_4 charged into the reaction). This is comparable with the yield obtained using an equivalent amount of $(Bu^tO)_2$ under identical conditions. These reactions were carried out under relatively mild conditions, 100 to 120°C for 20 h, with the total exclusion of light. There was thus no photochemical initiation of radical chain reactions and blank reactions performed in the absence of any metal complex never gave yields of chlorocyclohexane higher than 1%, indicating that adventitious initiators did not play an important role. In all cases reactions were performed with carefully purified reagents, particular care having been taken to remove all peroxide-containing impurities. Oxygen was also rigorously excluded from the reactions.

TABLE 1

REACTIONS BETWEEN c-C_6H_{12} AND CCl_4 IN THE PRESENCE OF VARIOUS METAL COMPLEXES

Complex	Yield of c-C_6H_{11}Cl (%)	
	T 100°C	T 120°C
$[Cr(CO)_6]$	42	57
$[Mo(CO)_6]$	0	29
$[Mn_2(CO)_{10}]$	28	36
$[Re_2(CO)_{10}]$	15	50
$[MnCl(CO)_5]$		23
$[ReCl(CO)_5]$	1	15
$[Re_2(CO)_8(PPh_3)_2]$	4	46
$[Fe_2(CO)_4(\eta\text{-cp})_2]$	-	7
$[Mo_2(CO)_6(\eta\text{-cp})_2]$		23
$[FeCl(CO)_2(\eta\text{-cp})]$		3
$[Co_2(CO)_8]$		4
	0.5	0.6
$(Bu^tO)_2$		64

TABLE 2

VARIATION IN YIELD OF c-$C_6H_{11}Cl$ WITH [$Re_2(CO)_{10}$] CONCENTRATION

Amount of $Re_2(CO)_{10}$ (mol $\times 10^5$)	Yield of c-$C_6H_{11}Cl$ (%)
2	34.7
4	50.1
6	60.5
8	64.8

Table 2 shows the variation in the yield of chlorocyclohexane as a function of the amount of metal complex employed, using [$Re_2(CO)_{10}$] as an example. This shows that yields greater than 50% were achieved with as little as 4×10^{-5} mol of complex. This represents a reagent/complex ratio of 6.25×10^2 and a product/complex ratio of 3.13×10^2. The reaction, therefore, is clearly either catalytic in metal complex or involves a chain process with a high kinetic chain length.

(b) Mechanistic study

In view of the novelty of the metal complex-promoted reactions described above we engaged in a detailed study of the reaction mechanism. We chose to study the reaction between cyclohexane and CCl_4 in the presence of [$Re_2(CO)_{10}$]. The choice of organic reagents was based on reaction yields, ease of purification and ease of handling in a kinetic study. [$Re_2(CO)_{10}$] was chosen because it brought about high yields of product and also because it was the only metal carbonyl complex examined that was converted entirely into metal carbonyl-containing products by the end of the reaction. These were [$ReCl(CO)_5$], together with a small amount of [$ReCl(CO)_4$]$_2$. The latter presumably arose by thermal decomposition of the former. In the case of all other complexes employed, the final metal-containing product was a higher oxidation state metal chloride. The formation of such chlorides presumably arose from reaction of the metal species with CCl_4 after the initial interaction with the metal carbonyl. It was felt that this may complicate the kinetic study.

The kinetic study was carried out by the initial rate method and this involved varying the concentration of one component while maintaining the other two constant. The total volume of the reaction mixture was kept constant during studies of the effects of variation of cyclohexane and CCl_4 by adding appropriate amounts of benzene. Control reactions showed that benzene did not react with any combination of reagents and the metal complex. Figures 1, 2 and 3 show the variation of the initial rate of reaction plotted against [$Re_2(CO)_{10}$]$^{1/2}$, [CCl_4]$^{1/2}$ and [C_6H_{12}], respectively. In each case a good straight line is obtained. It should be noted that there is a small positive intercept to Fig. 1, which is in accord with the findings, discussed in section (a), that there is a small contribution from a reaction which is not promoted by [$Re_2(CO)_{10}$]. For this reason, no attempt was made to obtain activation parameters for the reaction [18]. It is, however, possible to obtain values for the second order rate constant, k, as defined in the rate expression (eq. 2). Values of 1.19×10^{-3}, 1.22×10^{-3} and 1.35×10^{-3} dm^3 mol^{-1} s^{-1} were ob-

$$\text{Rate} = k \left[Re_2(CO)_{10} \right]^{1/2} [CCl_4]^{1/2} [C_6H_{12}] \tag{2}$$
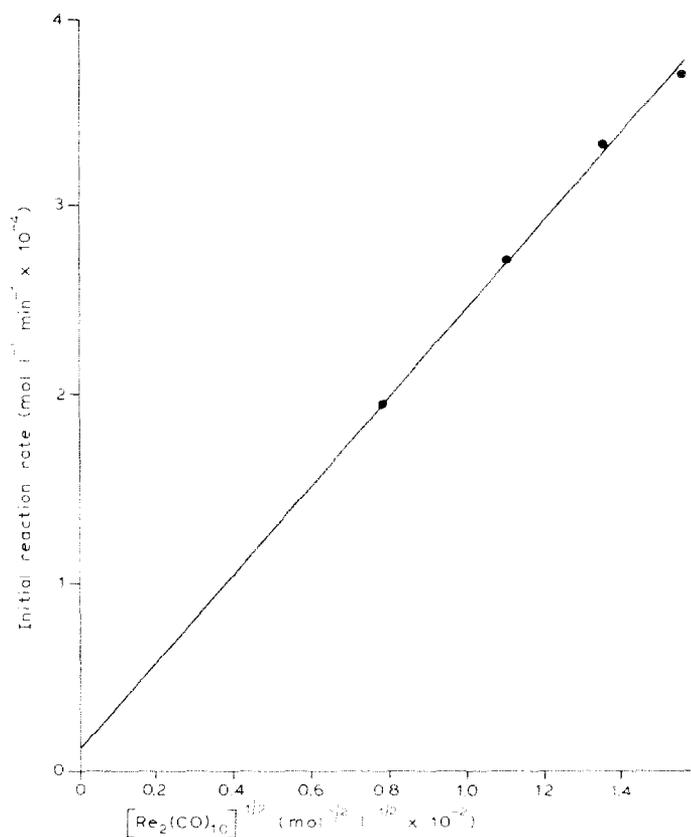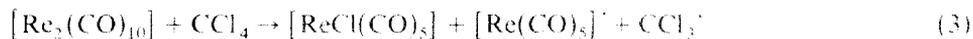
Fig. 1. Initial reaction rate vs $[Re_2(CO)_{10}]^{1/2}$

tained from studies of the variation in concentrations of $[Re_2(CO)_{10}]$, CCl_4 and C_6H_{12}, respectively. In view of the fact that these values were obtained employing the initial rate method, which can be subject to considerable error due to the difficulty in estimating the correct tangent to the rate curve, the agreement between them is satisfactory.

In view of previous studies, we believed two mechanisms were worthy of consideration for this reaction. Scheme 4 represents a conventional radical chain process in which the metal complex (depicted as [M] plays the role of an initiator. Our previous findings [1,3,4], that reactions between CCl_4 and alkenes in the presence of low valent metal complexes follow redox catalysed routes, led us to consider the possibility of a similar mechanism in this case. Such a mechanism is shown in Scheme 3. The exact form of the rate equations for the mechanisms shown in Schemes 3 and 4 depends upon the stoichiometry of the initial reaction between the metal complex and CCl_4. Thus, $[Re_2(CO)_{10}]$ could react with either one or two moles of CCl_4 as shown in eqs. 3 and 4, respectively.
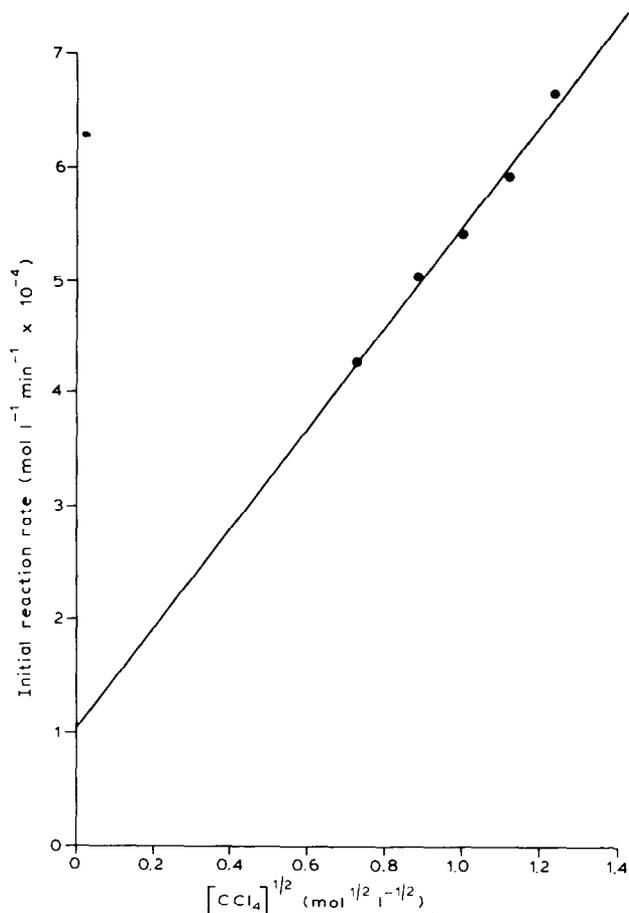
$$[Re_2(CO)_{10}] + CCl_4 \rightarrow [ReCl(CO)_5] + [Re(CO)_5]^{\cdot} + CCl_3^{\cdot} \tag{3}$$

$$[Re_2(CO)_{10}] + 2CCl_4 \rightarrow 2[ReCl(CO)_5] + 2CCl_3^{\cdot} \tag{4}$$

Fig. 2. Initial reaction rate vs. $[CCl_4]^{1/2}$.

Furthermore, eq. 3 could also be expressed in the form shown in eq. 5.

$$[Re_2(CO)_{10}] + CCl_4 \rightarrow [ReCl(CO)_5] + [Re(CCl_3)(CO)_5] \tag{5}$$

Our approach to the determination of the stoichiometry of this reaction, involved allowing a known amount of $[Re_2(CO)_{10}]$ to react, to completion, with excess halocarbon and to determine the amount of $[ReCl(CO)_5]$ and other products formed employing infrared spectroscopy. We have previously successfully used this technique in studying the reaction between $[Mo_2(CO)_6(\eta\text{-cp})_2]$ and C_3F_7I [1]. However direct study of the reaction between $[Re_2(CO)_{10}]$ and CCl_4 posed a number of problems. Reaction did not proceed cleanly to completion in a convenient time at room temperature. Elevated temperatures thus had to be employed and it is unlikely that one possible product, $[Re(CCl_3)(CO)_5]$, would be stable at elevated temperatures [19]. Furthermore, $[ReCl(CO)_5]$ readily undergoes thermal decarbonylation and thus a mixture of this compound and $[Re_2Cl_2(CO)_8]$ was obtained, making the quantitation of product [5] complex. In order to overcome this
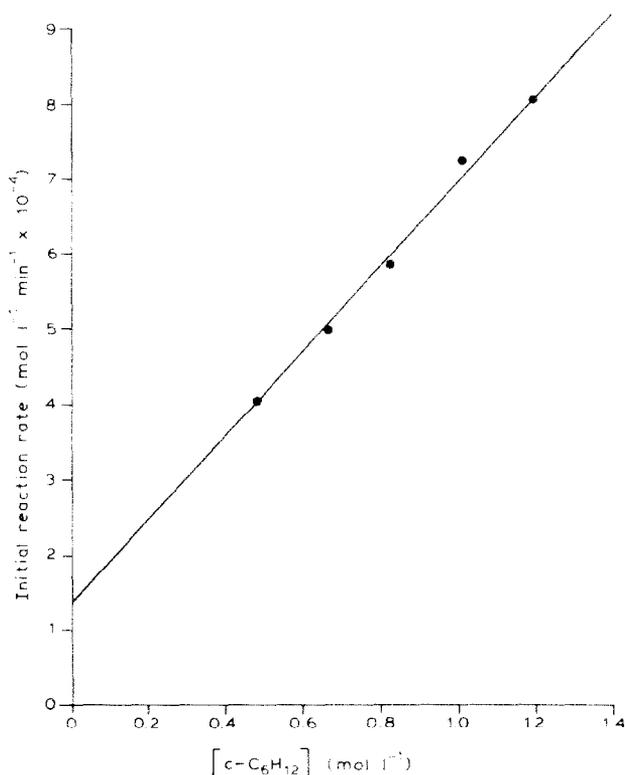
Fig. 3. Initial reaction rate vs. [c-C$_6$H$_{12}$].

problem the reaction between [Re$_2$(CO)$_{10}$] and CH$_3$I was investigated, however, the infrared spectra of the possible products, [Re(CH$_3$)(CO)$_5$] and [ReI(CO)$_5$] are almost indistinguishable thus rendering the investigation impossible.

For these reasons, we were unable to determine the stoichiometry of an [Re$_2$(CO)$_{10}$]-halocarbon reaction. Our previous studies of the reaction between [Mo$_2$(CO)$_6$(η-cp)$_2$] and C$_3$F$_7$I had shown it to have a 1 : 1 stoichiometry. In the present work we have examined the reaction between this molybdenum complex and CH$_3$I in tetrahydrofuran at room temperature. The only carbonyl-containing product was [MoI(CO)$_3$(η-cp)] (in a separate experiment, it was established that [Mo(CH$_3$)(CO)$_3$(η-cp)] is stable under the reaction conditions) and using the Lambert-Beer law plot for this compound shown in Fig. 4, it was found that the reaction between [Mo$_2$(CO)$_6$(η-cp)$_2$] and CH$_3$I adopted 1 : 1 stoichiometry. It was felt necessary to perform this study, in case the identical stoichiometry observed for [Mo$_2$(CO)$_6$(η-cp)$_2$] and C$_3$F$_7$I was unique to perfluorocarbon compounds. Recently, as a part of a separate study, we have also found that the reaction between [Fe$_2$(CO)$_4$(η-cp)$_2$] and CCl$_4$ also adopts a 1 : 1 stoichiometry [2]. On the basis of this evidence and the known similar chemistries of [Re$_2$(CO)$_{10}$], [Mo$_2$(CO)$_6$(η-cp)$_2$] and [Fe$_2$(CO)$_4$(η-cp)$_2$], it appears reasonable to infer that the reaction between [Re$_2$(CO)$_{10}$] and CCl$_4$ also adopts a 1 : 1 stoichiometry (eq. 3).
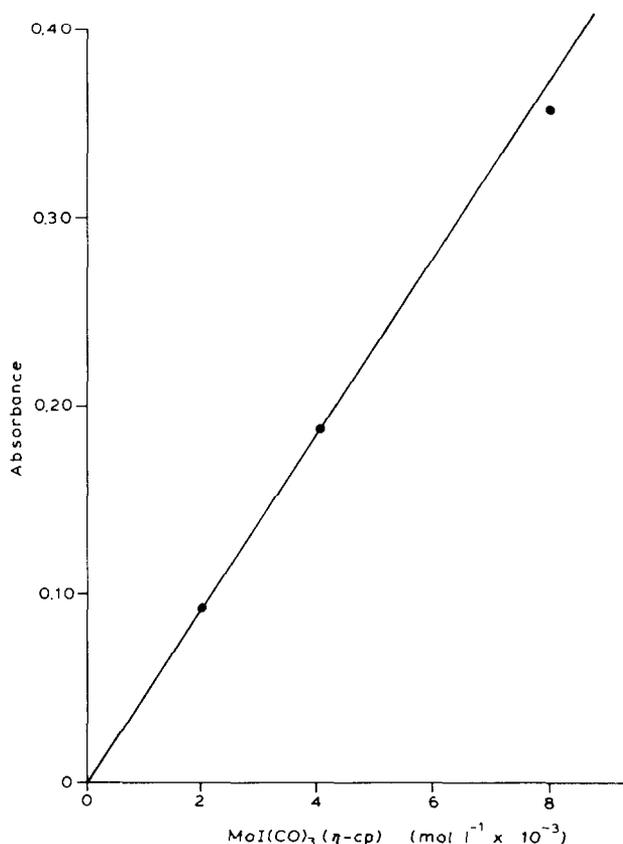
Fig. 4. Lambert-Beer law plot of absorbance of infrared band at 2040 cm^{-1} of [MoI(CO)$_3$(η-Cp)] vs. concentration.

Using eq. 3 as the first step in Schemes 3 and 4 leads to the rate equations shown in eqs. 6 and 7, respectively. Thus, the observed orders of reaction clearly distin-

$$\text{Rate} = k[\text{Re}_2(\text{CO})_{10}][\text{CCl}_4] \tag{6}$$

$$\text{Rate} = k[(\text{Re}_2(\text{CO})_{10}]^{1/2}[\text{CCl}_4]^{1/2}[\text{C}_6\text{H}_{12}] \tag{7}$$

guish between the two mechanisms and demonstrate, unequivocally, that the reaction proceeds by a free radical chain route (Scheme 4).

We also carried out a somewhat less rigorous kinetic study upon the cyclohexane-CCl$_4$ reaction in the presence of [Cr(CO)$_6$], in order to ascertain whether a similar mechanism obtained in the presence of a mononuclear metal carbonyl complex. In this study we examined the effect of varying [Cr(CO)$_6$] concentrations upon the yield of chlorocyclohexane obtained from reactions carried out concurrently under identical conditions (10 h, 100°C) in sealed tubes. The results of these experiments are shown in Table 3 and it can be seen that the ratio of the concentration of chlorocyclohexane to the square root of the concentration of [Cr(CO)$_6$] is approximately constant. This half-order dependance of concentration of [Cr(CO)$_6$] is also in accord with a radical chain mechanism initiated by the metal complex.

TABLE 3

VARIATION IN YIELD OF c-$C_6H_{11}Cl$ WITH $[Cr(CO)_6]$ CONCENTRATION

Amount of $Cr(CO)_6$ $(mol \times 10^5)$	Amount of c-$C_6H_{11}Cl$ $(mol \times 10^3)$	Ratio of c-$C_6H_{11}Cl/[Cr(CO)_6]^{1/2}$
2.09	5.35	1.17
6.14	8.59	1.10
8.05	10.04	1.12

Clearly, these experiments should not be viewed as a definitive kinetic study, but since care was taken to ensure that the reactions were performed under identical conditions and that they had not proceeded to completion, the results are mechanistically useful.

(c) Reaction products

Production of chlorocyclohexane by reaction 1 was a particularly clean process, the only other major product being trichloromethane. Thus, the products were easily purified on a preparative scale by distillation. GLC analysis showed the production of trace quantities (less than 2%) of hexachloroethane and cyclohexene. The former presumably arose as a consequence of coupling of $CCl_3^.$ radicals, a termination process for the chain sequence. The latter could be formed, together with cyclohexane by disproportionation of cyclohexyl radicals, a known termination step in reactions involving these radicals, or by dehydrochlorination of chlorocyclohexane. We favour the second of these processes, as a small quantity of HCl was always observed when the reaction tubes were opened and for the reasons expounded in section (d) below. There was no evidence of the formation of polychlorocyclohexanes.

The product yield and specificity of these metal complex-initiated reactions was compared with that of a reaction initiated by di-t-butylperoxide (4×10^{-5} mol) performed under identical conditions. The yield of chlorocyclohexane from the peroxide initiated reaction was 64% compared to 50 and 57% in the presence of $[Re_2(CO)_{10}]$ and $[Cr(CO)_6]$, respectively. All three reactions led to the formation of similar quantities of C_2Cl_6 and cyclohexene and none showed any evidence for the presence of polychlorocyclohexanes. Thus, as expected for a free radical chain process, the selectivity of the reaction arises as a consequence of the reactivity of the chain carrying species, $CCl_3^.$, rather than from the nature of the initiator.

The selectivity effect of $CCl_3^.$ was further demonstrated by examination of the reactivity of CCl_4 with adamantane in benzene in the presence of both $[Re_2(CO)_{10}]$ and $(Bu^tO)_2$. In both reactions the major products were 1-chloro- and 2-chloro-adamantane, the yields being 40.6 and 4.8%, respectively in the presence of the metal complex and 55.2 and 6.5%, respectively in the presence of the peroxide. These results yield identical statistically corrected tertiary C–H to secondary C–H reactivity ratios of 25.4. This figure compares favourably with the published value of 28.75 [20].

The adamantane-CCl_4 reaction initiated by $[Re_2(CO)_{10}]$ showed two other minor products when performed in benzene. GC-MS analysis of these showed one to be adamantylbenzene (m/z 212), whose isomeric nature could not be definitively

established. However, since reaction between cyclohexane and CCl_4 in benzene in the presence of $[Re_2(CO)_{10}]$ did not yield cyclohexylbenzene, it can be inferred that adamantylbenzene is the 1-isomer formed via reaction of the more labile tertiary C–H bond. The highest mass ion observed in the spectrum of the second product was at m/z 169. This corresponds to (chloroadamantane $-$ H)$^+$, but most probably arises from (dichloroadamantane $-$ Cl)$^+$. Some dichlorination might be expected in the case of adamantane since mono-chloroadamantanes will still contain relatively reactive tertiary C–H bonds.

(d) The reaction between tetrachloromethane and cyclohexane in the presence of various metal complexes

Table 1 shows the yield of chlorocyclohexane from reactions performed under identical conditions, but involving a range of low valent metal complexes as initiators. We have not found it possible to rationalise the yields of these reactions in terms of a single common phenomenon. A number of features of reactions of this type must play a role in determining yields.

Thus, it is likely that the initial interaction between the metal complex and the halocarbon is of the charge-transfer type (eqs. 8 and 9). There is evidence for

$$[ML_n] + CCl_4 \rightleftharpoons [ML_n]^+ + CCl_4^{\cdot -} \tag{8}$$

$$CCl_4^{\cdot -} \rightarrow CCl_3^{\cdot} + Cl^- \tag{9}$$

such interactions both in the case of reactions, between $[M(CO)_2i(dpme)_2]$ (M = Cr, Mo: dpme = $Me_2PCH_2CH_2PMe_2$) and alkyl halides [21] and in the case of reactions between $[M(\eta\text{-cp})_2]$ (M = Fe, Ru) and CCl_4 [22]. Indeed, we have found that when $[Re_2(CO)_{10}]$ was heated in CCl_4, the initially colourless solution became pale yellow and exhibited a new band at 435 nm in its UV-VIS spectrum (Fig. 5). This change is not accompanied by any change in either the position, the relative intensities or the absolute intensities of the CO stretching frequencies and $[Re_2(CO)_{10}]$ could be recovered on removal of the solvent. The new absorption at 435 nm is too close to an intense band arising from the solvent to make it possible to apply the usual techniques to define more precisely its origin, but it is possible that a charge transfer complex is being formed. Others have previously noted this colour change [23]. We have also observed a new band in the spectrum of $[Re_2(CO)_{10}]$ in $CHCl_3$ at 425 nm, after reflux. This shift to shorter wavelength compared to that with CCl_4 has been observed previously for $[Fe_4(CO)_4(\eta\text{-cp})_4]$ and has been taken as evidence for charge transfer since it is in accord with the halfwave reduction potentials for the two halocarbons [24].

If charge transfer is important, then the oxidation potentials of the metal complexes must be taken into account in discussing reactivities. However, one electron oxidation and charge transfer cannot be the only factor governing overall yields. This is well illustrated by examination of the behaviour of $[M(CO)_6]$ (M = Cr and Mo). These complexes have identical oxidation potentials [25], but gave markedly different overall yields of chlorocyclohexane. As discussed in section (b), $[Re_2(CO)_{10}]$ was the only one of the complexes examined that gave a chloro-metal carbonyl at the end of the reaction. All other compounds produced higher oxidation state metal chlorides such as $[MnCl_2]$ and $[CrCl_3]$. It was not possible to unequivocally identify the chloride formed in each case, as removal of the last traces
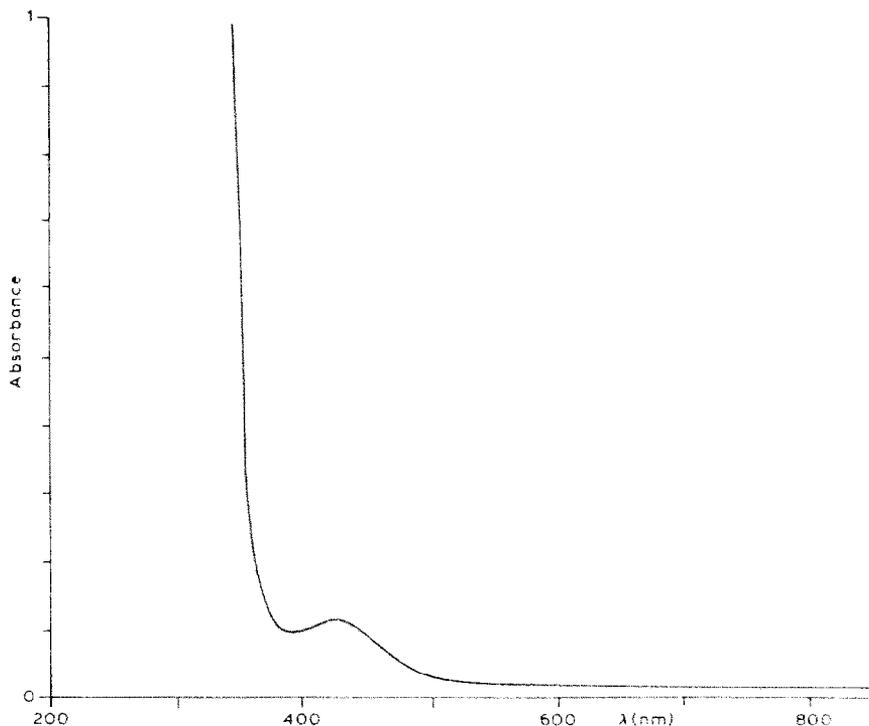
Fig. 5. UV-VIS spectrum of [Re$_2$(CO)$_{10}$] after heating in CCl$_4$.

of CCl$_4$ from these products proved very difficult and this rendered the results of quantitative analysis meaningless. Nevertheless, presumably these higher chlorides were formed by stepwise reactions between CCl$_4$ and the metal carbonyl complexes, followed by similar reactions involving CCl$_4$ and the intermediate low valent chlorides. Should at least some of these latter reactions be free radical in nature, then new product forming chains would be initiated. This is exemplified by the reactions involving [Mn$_2$(CO)$_{10}$] and [MnCl(CO)$_5$], both of which ultimately yielded [MnCl$_2$] and both of which gave significant yields (36 and 13%, respectively) of chlorocyclohexane.

Thus, it is not surprising that [Mo(CO)$_6$] and [Cr(CO)$_6$] gave different overall yields of cyclohexane as the final metal chlorides formed are believed to be [Mo$_6$Cl$_{12}$] and [CrCl$_3$]. As can be seen from Table 1, [Cr(CO)$_6$] gave the higher yield after 20 h, however, examination of the relative reaction rates over shorter periods of time (Fig. 6) showed that the initial rates of reaction were comparable, in line with the oxidation potentials of the two complexes.

The [Mo(CO)$_6$]-initiated reaction also illustrates one final point. Figure 6 shows the yield to decrease slightly between reaction times of 4 and 8 h. Presumably either [Mo(CO)$_6$] or one of its reaction products reacted slowly with chlorocyclohexane.

(e) The reaction of other halocarbons and hydrocarbons in the presence of [Re$_2$(CO)$_{10}$]

A brief study was performed of the effectiveness of [Re$_2$(CO)$_{10}$] in initiating both reactions between cyclohexane and a range of halocarbons and those between CCl$_4$ and a range of hydrocarbons.

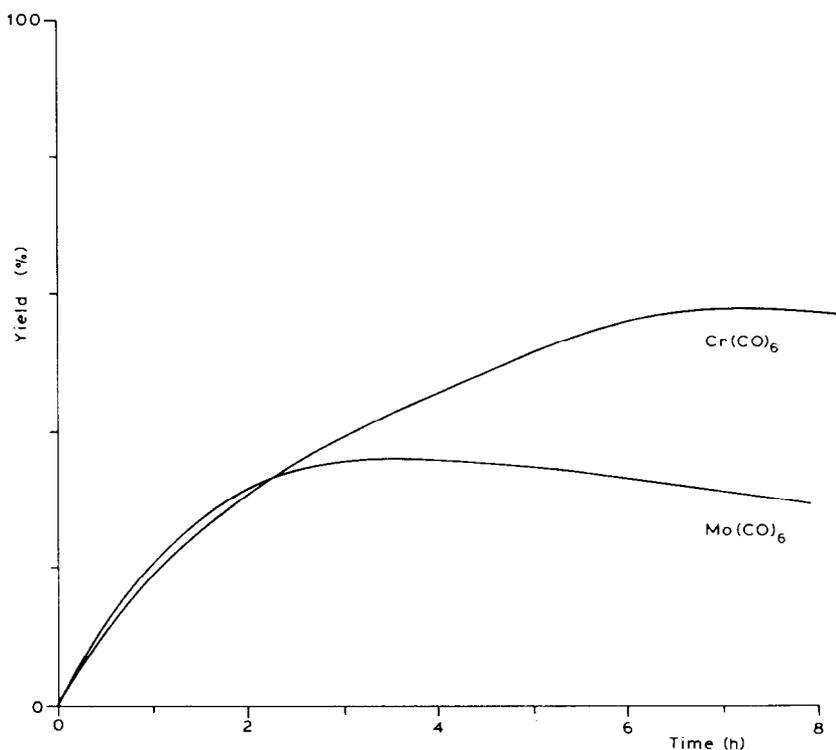Fig. 6. Rates of reaction of c-C_6H_{12} and CCl_4 in the presence of $[M(CO)_6]$ (M = Cr, Mo).

(i) Reactions of cyclohexane with other halocarbons

The results of reactions between cyclohexane and a range of halocarbons are shown in Table 4. Included in this study is the halogenating agent, SO_2Cl_2 which has been employed by others in highly efficient and selective side chain chlorination of toluene in the presence complexes such as $[Pd(PPh_3)_4]$ [26].
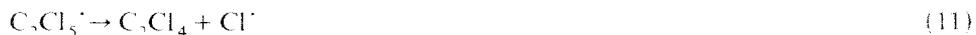
In all cases the yields of halocyclohexanes were inferior to those obtained with CCl_4. In particular, C_2Cl_6 led to yields about one half that obtained with CCl_4. This is in contrast to the results obtained by others using peroxide initiators, where

TABLE 4

REACTIONS BETWEEN c-C_6H_{12} AND VARIOUS HALOGENATING AGENTS IN THE PRESENCE OF $[Re_2(CO)_{10}]$

Halogenating agent	Reaction temp. (°C)	Reaction product(s)	Yield (%)
CCl_4	120	c-$C_6H_{11}Cl$	50
CCl_4	100	c-$C_6H_{11}Cl$	13
C_2Cl_6	120	c-$C_6H_{11}Cl$	23
SO_2Cl_2	100	c-$C_6H_{11}Cl$	41
$CBrCl_3$	120	c-$C_6H_{11}Br$	26
		c-$C_6H_{11}Cl$	0.1
C_3F_7I	120	c-$C_6H_{11}I$	7

C_2Cl_6 proved to be more effective than CCl_4 for halogenation of methylcyclohexane. In the $[Re_2(CO)_{10}]$-initiated reaction employing C_2Cl_6, no C_2HCl_5 was observed among the products, which included C_2Cl_4 and HCl, a finding which parallels the earlier work in the presence of peroxide. Although this implies that the alternative propagation sequence suggested earlier [6] and shown in eqs. 10 and 12 is in operation in both reactions, it does not explain the difference between the two

$$C_6H_{11}{}^{\cdot} + C_2Cl_6 \rightarrow C_6H_{11}Cl + C_2Cl_5{}^{\cdot} \tag{10}$$

$$C_2Cl_5{}^{\cdot} \rightarrow C_2Cl_4 + Cl^{\cdot} \tag{11}$$

$$Cl^{\cdot} + C_6H_{12} \rightarrow C_6H_{11}{}^{\cdot} + HCl \tag{12}$$

initiators. We suggest that this may arise as a consequence of direct reaction between C_2Cl_6 and $[Re_2(CO)_{10}]$ leading to C_2Cl_4 and $[ReCl(CO)_5]$. This has been observed in an independant reaction and if at least a proportion of encounters between the metal carbonyl dimer and C_2Cl_6 resulted in a concerted reaction rather than a stepwise process, less chains will be initiated.

In an attempt to extend $[Re_2(CO)_{10}]$-initiated reactions to the preparation of other halocyclohexanes, reaction between $CBrCl_3$ and cyclohexane was examined. $CBrCl_3$ is a very selective brominating agent and has been widely employed in photochemically- and peroxide-initiated reactions with a variety of hydrocarbons [7-9]. In such reactions, $CCl_3{}^{\cdot}$ acts as the chain-carrying species. Reaction in the presence of $[Re_2(CO)_{10}]$ demonstrated that $CCl_3{}^{\cdot}$ acted as the main chain propagator in this reaction, the ratio of $C_6H_{11}Br$ to $C_6H_{11}Cl$ produced being 263/1. However, the yield of $C_6H_{11}Br$ (26.3%) was considerable lower than that obtained in the presence of conventional initiators. This presumably arises as a consequence of the enhanced reactivity to $[Re_2(CO)_{10}]$ toward $CBrCl_3$ compared to CCl_4. In separate reactions between $[Re_2(CO)_{10}]$ and the two halocarbons carried out under identical conditions (120°C) the formation of $[ReBr(CO)_5]$ had gone to completion in a little under 9 h, while complete reaction between $[Re_2(CO)_{10}]$ and CCl_4 was only just attained in 20 h. The consequences of these effects are illustrated in Table 5 which compare the yields of $C_6H_{11}Cl$ and $C_6H_{11}Br$ from reactions performed under identical conditions for 8 and 18 h. It is clear that the rapid rate of initiation in the $CBrCl_3$ reaction led to reaction being almost complete in 8 h, while in the CCl_4 reaction only 50% of the final yield had been achieved in that time. The lower yields of $C_6H_{11}Br$ after both 8 and 18 h reactions compared to those of $C_6H_{11}Cl$ is presumably a consequence of the fact that the more facile production of $CCl_3{}^{\cdot}$

TABLE 5

COMPARATIVE REACTIONS BETWEEN c-C_6H_{12} AND EITHER CCl_4 OR $CBrCl_3$ IN THE PRESENCE OF $[Re_2(CO)_{10}]$

Halocarbon	Reaction time (h)	Yield of product (%)
CCl_4	18	49
$CBrCl_3$	18	21
CCl_4	8	26
$CBrCl_3$	8	16

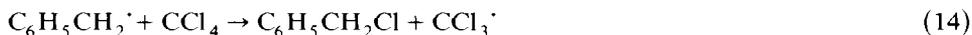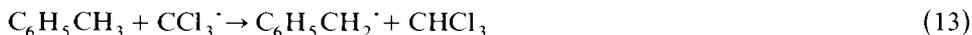radicals from $CBrCl_3$ leads to a higher termination rate and thus to lower kinetic chain lengths.

Iodination of cyclohexane was attempted utilising C_3F_7I in the presence of $[Re_2(CO)_{10}]$. We have not been able to reproduce the yield of $C_6H_{11}I$ reported in our earlier paper [11] and only obtained this product in 7% yield.

Finally in this section, use of SO_2Cl_2 in the presence of $[Re_2(CO)_{10}]$ led to a 41% yield of $C_6H_{11}Cl$ (no polychlorinated products formed) from a reaction performed at 100°C (c.f. 13% yield of $C_6H_{11}Cl$ from reaction between C_6H_{12} and CCl_4 at 100°C). This is to be compared with a 98% conversion to chloro- and dichloro-cyclohexane (9/1) in 6 h employing an organic peroxide initiator (1×10^{-3} mol) [27]. Clearly the metal complex is more selective but less reactive than peroxides in this reaction.

(ii) Reactions of tetrachloromethane with other hydrocarbons

The $[Re_2(CO)_{10}]$-initiated reaction between CCl_4 and n-hexane was investigated. In this case 1-, 2-, and 3-chlorohexanes were formed. 1-Chlorohexane was identified by comparison with an authentic sample GLC. 2- and 3-Chlorohexane were identified by NMR spectroscopy after removal of starting materials from the reaction mixture by distillation. A signal centred at 3.85δ was assigned to the CHCl absorption and its complexity clearly indicated the presence of two overlapping multiplets arising from the 2- and 3-isomers. It was not possible to calculate the relative yields of these two isomers by NMR spectroscopy. GLC analysis show 2- and 3-chlorohexane, together to be formed in 15.3% yield, while only 0.3% of the 1-isomer was present. These results yield a statistically corrected primary/secondary C–H bond reactivity ratio of 68, compared to a literature value of 80 [20]. The reactions of cyclooctane and cyclopentane were also examined and the results are given in Table 6.

The reaction between CCl_4 and $C_6H_5CH_3$ was also performed in the presence of $[Re_2(CO)_{10}]$, however no benzyl chloride was formed. A similar reaction employing $(Bu^tO)_2$ also failed to yield any of this product. The lack of reactivity was therefore not a consequence of the initiator and must depend on the propagation steps (eqs. 13 and 14). Thus, either the $CCl_3{}^{\cdot}$ radical is incapable of abstracting a hydrogen atom from toluene (eq. 13) or the benzyl radical does not react with CCl_4 (eq.

$$C_6H_5CH_3 + CCl_3{}^{\cdot} \rightarrow C_6H_5CH_2{}^{\cdot} + CHCl_3 \tag{13}$$

$$C_6H_5CH_2{}^{\cdot} + CCl_4 \rightarrow C_6H_5CH_2Cl + CCl_3{}^{\cdot} \tag{14}$$

14). If the former is the case, then $CCl_3{}^{\cdot}$ radicals will be consumed in production of C_2Cl_6 and if the latter reaction does not occur then benzyl radicals will be

TABLE 6

REACTIONS BETWEEN CYCLOALKANES AND CCl_4 IN THE PRESENCE OF $[Re_2(CO)_{10}]$

Cycloalkane	Yield of $c\text{-}C_nH_{2n-1}Cl$ (%)
C_5H_{10}	13
C_6H_{12}	50
C_8H_{16}	16

converted in $PhCH_2CH_2Ph$. GLC analysis of the reaction mixture showed the presence of $PhCH_2CH_2Ph$, but no evidence for C_2Cl_6, indicating that benzyl radicals cannot abstract $Cl^{\cdot}$ from CCl_4 (eq. 14).

Changes in either reactant led to some reaction. Thus, the reaction between $PhCH_3$ and $CBrCl_3$ in the presence of $[Re_2(CO)_{10}]$ gave a 5% yield of $PhCH_2Br$. Similarly, reaction between CCl_4 and either ethyl- or isopropyl-benzene in the presence of $[Re_2(CO)_{10}]$ also gave low yields (less than 5%) of monochlorinated products (isomer distribution not established).

Acknowledgement

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