Preliminary communication

HALOGENATION OF ALKANES PROMOTED BY TRANSITION METAL COMPLEXES

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Summary

The reaction between cycloalkanes and halocarbons, such as CCl_4, to yield cycloalkyl halides proceeds in good yield in the presence of a range of metal carbonyl complexes. Kinetic evidence suggests that the metal complexes act as efficient initiators of radical chain processes.

The activation of hydrocarbons by transition metal complexes remains a topic of considerable interest and, in particular, there is great attraction in employing such complexes in reactions of alkanes [1]. Oxidative addition of alkanes to transition metal complexes has only recently been reported [2] and, as yet, there is no example of alkane functionalisation employing metal complexes as catalysts that involve such a reaction. Our studies of the addition of halocarbons across alkenic bonds in the presence of transition metal complexes [3] have led us to consider employing metal-mediated one-electron (free radical) processes for alkane functionalisation.

Thus, we have found that heating cyclo-C_6H_{12} with CCl_4 in the presence of various metal carbonyl complexes, with the rigorous exclusion of oxygen, leads, in most cases, to moderate to good yields of chlorocyclohexane in a remarkably clean reaction employing low levels of metal complex (Table 1). Only in the case of $[Re_2(CO)_{10}]$ is there any evidence for metal carbonyl containing products at the end of the reaction. These are $[ReCl(CO)_5]$ and $[ReCl(CO)_4]_2$, the latter presumably formed by thermolysis of the former. In other cases metal chlorides are formed (e.g. $[MnCl_2]$ and $[CoCl_2]$ from $[Mn_2(CO)_{10}]$ and $[Co_2(CO)_8]$, respectively).

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TABLE I

YIELDS OF CHLOROCYCLOHEXANE FROM THE REACTION OF CYCLOHEXANE AND TETRA-CHLOROMETHANE IN THE PRESENCE OF VARIOUS METAL CARBONYL COMPLEXES[a]

Complex	Amount (mol)	Temperature ($^\circ$C)	Reaction time (h)	Yield (%)
$[Mo(CO)_6]$	4×10^{-5}	120	20	41.7
$[Mn_2(CO)_{10}]$	4×10^{-5}	120	20	46.3
$[Co_2(CO)_8]$	4×10^{-5}	120	20	4.1
$[Fe_2(CO)_4(\eta\text{-}cp)_2]$	4×10^{-5}	120	20	7.0
$[Mo_2(CO)_6(\eta\text{-}cp)_2]$	4×10^{-5}	120	20	23.3
$[Cr(CO)_6]$	4×10^{-5}	100	20	42.0
$[Cr(CO)_6]$	4×10^{-5}	120	20	78.3
$[Re_2(CO)_{10}]$	4×10^{-5}	120	20	50.1
$[Re_2(CO)_{10}]$	4×10^{-5}	100	20	13.0
$[Re_2(CO)_{10}]$	2×10^{-5}	120	20	34.7
$[Re_2(CO)_{10}]$	6×10^{-5}	120	20	60.5
$[Re_2(CO)_{10}]$	8×10^{-5}	120	20	64.8
$[Re_2(CO)_{10}]$	4×10^{-5}	120	40	74.2
$[Re_2(CO)_{10}]$	4×10^{-5}	120	65	73.0

[a] 10^{-1} mol of C_6H_{12} and 2.5×10^{-2} mol of CCl_4 in all cases.

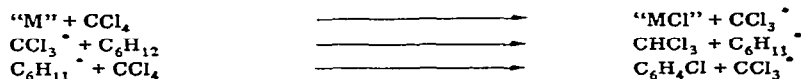Other cycloalkanes (C_5H_{10}, C_7H_{14}, C_8H_{16}) also undergo reactions in good yield. However, toluene, benzene and acetonitrile are all unreactive and n-hexane gives only a small yield of hexyl chloride (isomeric distribution, as yet, undetermined).

Reaction of C_6H_{12} with n-C_3F_7I gives a 33% yield of $C_6H_{11}I$ and use of $CBrCl_3$ gives $C_6H_{11}Br$ in 26% yield with only a trace (ca. 0.1%) of $C_6H_{11}Cl$.

In view of our mechanistic findings for the reaction of CCl_4 with alkenes in the presence of $[Mo_2(CO)_6(\eta\text{-}cp)_2]$ [3], we believe two mechanisms are worthy of consideration for these reactions. These are a radical chain process (Scheme 1), in which the metal complex acts simply as an initiating species and a redox catalysed reaction (Scheme 2). In both of these mechanisms we represent the metal complexes simply as "M" and their corresponding chloro complexes or chlorides as "MCl" and we have excluded a termination step from Scheme 1, although coupling of $CCl_3 \cdot$ radicals or disproportionation of $C_6H_{11} \cdot$ radicals would seem the most likely processes. We have, in fact, observed cyclohexene formation, but the fact that a small quantity of HCl fumes is always present at the end of the reaction suggest that dehydrochlorination of $C_6H_{11}Cl$ is also taking place.

Similar reactions between perchloralkanes and both alkanes and alkyl aromatics have been observed in the presence of the usual free radical initiators, both in the gas phase and in solution, and these certainly follow a free radical chain mechanism [4—6]. However, we are unaware of any such reactions involving promotion by metal complexes although the selective side-chain chlorination of alkyl aromatics by SO_2Cl_2 in the presence of $[Pd(PPh_3)_4]$ has been reported [7]. The alternative mechanisms outlined in the schemes should be easily distinguished by kinetic means. Thus, inclusion of the coupling of $CCl_3 \cdot$ radicals as the termination step in Scheme 1 and application of steady state theory yields a rate expression that shows a first order dependence on

SCHEME 1

$$"M" + CCl_4 \longrightarrow "MCl" + CCl_3{}^{\bullet}$$
$$CCl_3{}^{\bullet} + C_6H_{12} \longrightarrow CHCl_3 + C_6H_{11}{}^{\bullet}$$
$$C_6H_{11}{}^{\bullet} + CCl_4 \longrightarrow C_6H_4Cl + CCl_3{}^{\bullet}$$

SCHEME 2

$$"M" + CCl_4 \longrightarrow "MCl" + CCl_3{}^{\bullet}$$
$$CCl_3{}^{\bullet} + C_6H_{12} \longrightarrow CHCl_3 + C_6H_{11}{}^{\bullet}$$
$$C_6H_{11}{}^{\bullet} + "MCl" \longrightarrow "M" + C_6H_{11}Cl$$
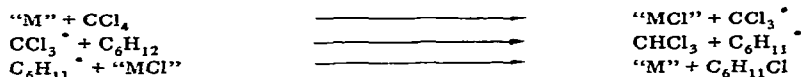
alkane, while the dependence on both CCl_4 and "M" is half order. Similarly, treatment of Scheme 2 suggests a first order dependence on both "M" and CCl_4 and an independence of alkane concentration. Kinetic studies, employing the initial rate method, of the reaction of cyclo-C_6H_{12} and CCl_4 in the presence of $[Re_2(CO)_{10}]$ yield orders of reaction for all three components entirely consistent with a free radical chain mechanism. Thus, $[Re_2(CO)_{10}]$, and presumably the other complexes listed in Table 1, are acting solely as initiators of a radical chain reaction. That metal carbonyl initiation is efficient is evidenced by the fact that initiation of this reaction with di-t-butyl peroxide at levels comparable to those of the metal carbonyls (4×10^{-5} M) gives a 64% yield of cyclo-$C_6H_{11}Cl$ compared to yields of 50 and 78% employing $[Re_2(CO)_{10}]$ and $[Cr(CO)_6]$, respectively.

Although others have used reactions of metal carbonyls with chlorocarbons in the formation of 1 : 1 addition products with alkenes [8] and the formation of alkene telomers and polymers [9] this represents the first use of these systems in alkane functionalisation reactions. Investigations into the synthetic scope of these and related reactions is continuing.

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