The Chemistry of Polynuclear Compounds. Part XXVII.[1] Activation of Chloroethanes by Dodecacarbonyl-*triangulo*-tri-iron and -triruthenium

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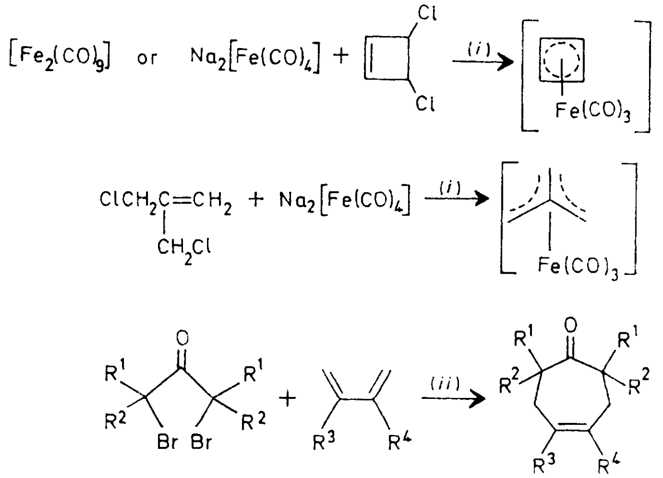
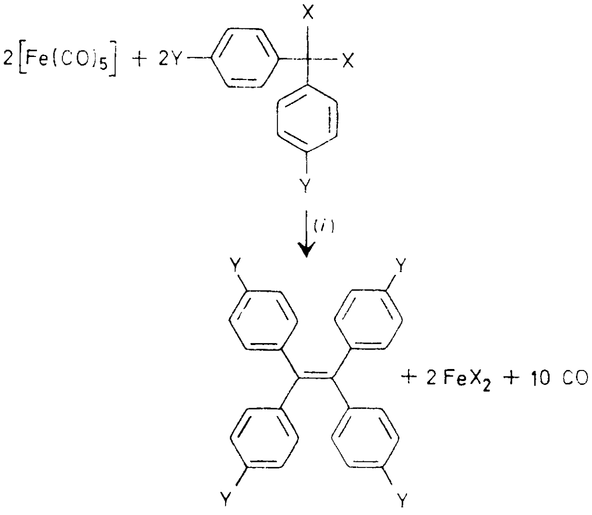
The action of $[Fe_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ on chloroethanes in the presence of alkanes leads to the formation of a large number of organic products the majority of which have been isolated and characterized by various spectroscopic techniques. In general, the chloroethanes are converted into the corresponding chloroethylenes, whilst the alkanes are transformed into the monochloroalkanes and alkenes. Possible mechanisms for these somewhat complex reactions are described.

THE first reaction of a chloroalkane with a metal carbonyl was reported in 1928 by Mittasch,[2] in which he found that $[Fe(CO)_5]$ reacted with carbon tetrachloride to give phosgene, iron(II) chloride, some hexachloroethane, but mostly tars. More recently[3,4] it has been shown that the reaction of $[M_2(CO)_{10}]$ (M = Mn or Re) with carbon tetrachloride leads to the formation in high yield of $[M(CO)_5Cl]$ species. Halogen abstraction by iron carbonyls or their anionic equivalents has been used extensively in both organometallic and organic synthesis (Scheme 1).[5-12] Collman[13,14] in particular has expounded the use of $Na_2[Fe(CO)_4]$ as an inexpensive selective reagent for the high yield conversion, involving halogen abstraction, of aliphatic halides and tosylates into aldehydes and unsymmetrical ketones. A similar type of reaction has been reported by other workers[15] who found that benzyl chloride, when stirred in a benzene solution of $[Fe_2(CO)_9]$ at 30 °C, gives dibenzyl ketone in good yield. However, the same organic chloride, when stirred in a tetrahydrofuran (thf) solution of $[Fe(CO)_5]$ at 30 °C, is quantitatively converted into the hydrocarbon polymer $(CH_2C_6H_4)_n$ (*n ca.* 62). Both groups provide experimental evidence which suggests that ketone synthesis is preceded by the formation of a σ-bonded alkyl iron carbonyl unit and that this, being thermally unstable, decomposes to give the ketone.



SCHEME 1 (*i*) thf; (*ii*) $[Fe_2(CO)_9]$



SCHEME 2 X = Cl, Y = H, Me, Cl, CMe_3, or OMe; X = Br, Y = NO_2

A simple preparation of tetra-arylethylenes involving the treatment of particular *gem*-dihalides with $[Fe(CO)_5]$ in refluxing benzene has been reported by Coffey[16] (Scheme 2). Under similar conditions, no reaction was observed with t-butyl bromide, 2,2-dibromopropane, benzyl chloride, benzal chloride, triphenylmethyl chloride, 1,2-dibromo-1,2-diphenylethane, chloroform, or methylene chloride. Amongst other metal carbonyls which converted dichlorodiphenylmethane to tetraphenylethylene were $[FeHg(CO)_4]$, $[\{Fe(CO)_2(cp)\}_2]$, and $[Ni(CO)_4]$ (cp = η-cyclopentadienyl). This work by

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[14] W. O. Siegl and J. P. Collman, *J. Amer. Chem. Soc.*, 1972, **94**, 2516.

[15] I. Rhee, M. Ryang, and S. Tsutsumi, *J. Organometallic Chem.*, 1967, **9**, 361.

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Coffey was taken to suggest that $[Fe(CO)_5]$ will only react with organic halides (under reflux in benzene) if two conditions are met: (*a*) the halogen atom must be activated by at least one, and preferably two, groups such as cyano, alkoxycarbonyl, phenyl, or halogeno (in decreasing order of effectiveness); (*b*) there must be at least two halogens on the same carbon atom. Condition (*b*) suggested that the reactions of *gem*-dihalides with metal carbonyls involved a carbene intermediate and indeed some experimental evidence was available in support of this mechanism. More particularly, the validity of condition (*b*) appeared to be beyond question since in no case was reaction with monohalogenated compounds observed even in the strongly halogen-activated triphenylmethyl chloride. Ketone formation appeared to be negligible.

TABLE 1

$$[Fe_3(CO)_{12}] + \text{chloroethane} \xrightarrow[\text{reflux}]{n\text{-}C_7H_{16}} \text{organic products} + FeCl_2 + [Fe(CO)_5]$$

1,1,1,2-Tetrachloroethane	Hexachloroethane	1,1,1-Trichloroethane
	Organic products	
Mixture of isomeric heptenes (small yield)	mixture of isomeric heptenes (good yield)	mixture of isomeric heptenes (moderate yield)
Vinyl chloride (trace)		1,1-dichloroethane (moderate yield)
1,1-Dichloroethylene (major product)		*trans*-2,3-dichlorobut-2-ene (moderate yield)
cis-1,2-Dichloroethylene (trace but *cis* ≫ *trans*)	*cis*-1,2-dichloroethylene (trace but *cis* ≫ *trans*)	*cis*-2,3-dichlorobut-2-ene (trace)
trans-1,2-Dichloroethylene (trace)	*trans*-1,2-dichloroethylene (trace)	2,2,3-trichlorobutane (small yield)
1,1,2-Trichloroethane (second highest yield)	trichloroethylene (third highest yield)	trichlorobutene (trace, isomer not determined)
	tetrachloroethylene (second highest yield)	2,2,3,3-tetrachlorobutane (moderate yield)
		1,1,3,3-tetrachlorobutane (trace)
1-, 2-, 3-, and 4-Chloroheptane (small yield)	1-, 2-, 3-, and 4-chloroheptane (major product)	1-, 2-, 3-, and 4-chloroheptane (major product)

Thus, despite the existence of a considerable volume of literature associated with halogen abstraction, particularly by iron carbonyl species, very few if any studies of chloroethanes have been made. This obviously represents a large gap in the knowledge of this relatively cheap and simple class of organic compounds. In this paper, apart from providing basic information of relevance to the more significant alkane systems, we describe the reactions of iron and ruthenium carbonyls with chloroethanes and attempt to rationalize most of the products mechanistically.

RESULTS AND DISCUSSION

Dodecacarbonyl-triangulo-*tri-iron*.—When $[Fe_3(CO)_{12}]$ was heated under reflux in n-heptane with 1,1,1,2-tetrachloroethane, hexachloroethane, or 1,1,1-trichloroethane for 24 h a light brown solid was slowly deposited from the deep green solutions. Gas–liquid chromatography (g.l.c.) on the resulting solutions showed a considerable number of organic products (Figure), the majority of which, after separation, were identified by a combination of ^1H n.m.r., i.r., and mass spectroscopic data as well as their standardized g.l.c. retention times. The results of these studies (Table 1) suggest a number of general conclusions. (*a*) Where possible, 1,2-abstraction of two chlorine atoms occurs to give the corresponding ethylene, *e.g.* as in equation (1). This appears to be one of the major reaction paths. (*b*) Chloroethanes

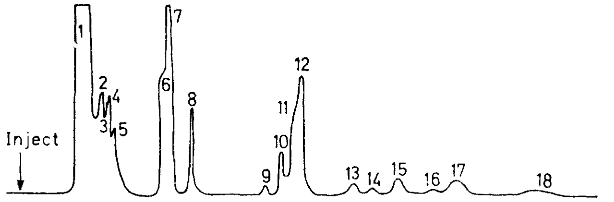
$$[Fe_3(CO)_{12}] + Cl_3CCCl_3 \xrightarrow{n\text{-}C_7H_{16}} Cl_2C{=}CCl_2 + FeCl_2 \quad (1)$$

containing a CCl_3 group undergo exchange presumably with the n-heptane and this leads to the formation of chloroheptanes and the corresponding CCl_2H group; this, if possible, will once again undergo 1,2-abstraction of two chlorine atoms to give the ethylene, *e.g.* as in equation (2). (*c*) Products corresponding to dehydrochlorination of the

$$\begin{tikzcd} ClCH_2CCl_3 + n\text{-}C_7H_{16} \arrow[r, "{[Fe_3(CO)_{12}]}"] & CH_2{=}CCl_2,\ C_7H_{15}Cl,\ ClCH_2CHCl_2 \arrow[d, "{[Fe_3(CO)_{12}]}"'] \\ & CH_2{=}CHCl \end{tikzcd} \quad (2)$$

chloroethane are formed in only trace amounts, *e.g.* as in equation (3). (*d*) Where 1,2-abstraction of two chlorine

$$[Fe_3(CO)_{12}] + CH_3CCl_3 \not\xrightarrow{n\text{-}C_7H_{16}} CH_2{=}CCl_2 \quad (3)$$



Gas–liquid chromatograph of the solution resulting from the reaction of $[Fe_3(CO)_{12}]$ with 1,1,1-trichloroethane in n-heptane. Stationary phase, LAC 1R 296. Peaks: (1) n-heptane (solvent); (2) *trans*-hept-3-ene; (3) *cis*-hept-3-ene; (4) *trans*-hept-2-ene; (5) *cis*-hept-2-ene; (6) 1,1-dichloroethane; (7) unchanged 1,1,1-trichloroethane; (8) *trans*-2,3-dichlorobut-2-ene; (9) 1,2-dichloroethane (original impurity); (10) 4-chloroheptane; (11) 3-chloroheptane; (12) 2-chloroheptane; (13) *cis*-2,3-dichlorobut-2-ene; (14) 1-chloroheptane; (15) 2,2,3-trichlorobutane; (16) a trichlorobutene; (17) 2,2,3,3-tetrachlorobutane; and (18) 1,1,3,3-tetrachlorobutane atoms is not possible, dimerization occurs and the product is then subject to 2,3-abstraction of two chlorine atoms, *e.g.* as in equation (4). This accounts for the formation of 2,2,3,3-tetrachlorobutane (dimerization of

$$\begin{tikzcd}[Fe_3(CO)_{12}] + CH_3CCl_3 \arrow[r, "n\text{-}C_7H_{16}"] & CH_3CCl_2CCl_2CH_3 \arrow[d, "{[Fe_3(CO)_{12}]}"] \\ & CH_3CCl{=}CClCH_3\end{tikzcd} \qquad (4)$$

1,1,1-trichloroethane), the 2,3-dichlorobut-2-ene isomers, and the 2,2,3-trichlorobutane (coupling of 1,1,1-trichloroethane and 1,1-dichloroethane). A number of the minor products are probably the result of positional isomerism within the chlorobutenes.[17]

The validity of conclusion (*a*) was further demonstrated by independently synthesizing 2,2,3,3-tetrachlorobutane and then reacting this with $[Fe_3(CO)_{12}]$ in n-heptane. *trans*-2,3-Dichlorobut-2-ene was the major product of the reaction together with a trace amount of the corresponding *cis* isomer. The heptenes remain the only significant products which are not encompassed by conclusions (*a*)—(*d*). Contrasting directly with conclusion (*c*), it was found that each of the four isomeric monochloroheptanes, when heated separately under reflux in n-heptane with $[Fe_3(CO)_{12}]$, gave a mixture of heptenes the isomeric yields of which were identical and corresponded to the ratio shown in the Figure. Such a mixture of heptenes could be expected since it is now well established that $[Fe_3(CO)_{12}]$ is capable of isomerizing olefins to give mainly the *trans* internal isomers.[18,19] Furthermore, whereas 1-chloroheptane gave only trace amounts of isomeric heptenes together with unchanged 1-chloroheptane, the reaction separately of either 2-, 3-, or 4-chloroheptane gave much higher yields of isomeric heptenes together with a mixture of unchanged 2-, 3-, and 4-chloroheptane, *e.g.* as in equations (5) and (6).

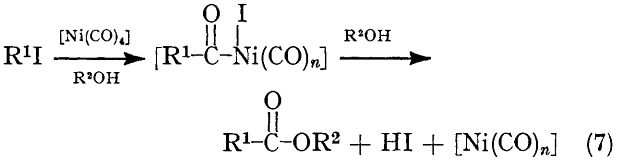
$$C_7H_{15}Cl\text{-}1 + [Fe_3(CO)_{12}] \xrightarrow[\text{reflux}]{n\text{-}C_7H_{16}} \begin{array}{c}\text{trace amounts}\\ \text{of isomeric}\\ \text{heptenes}\end{array} + \text{unchanged } C_7H_{15}Cl\text{-}1 \qquad (5)$$

$$C_7H_{15}Cl\text{-}3 + [Fe_3(CO)_{12}] \xrightarrow[\text{reflux}]{n\text{-}C_7H_{16}} \begin{array}{c}\text{moderate}\\ \text{yield of}\\ \text{isomeric}\\ \text{heptenes}\end{array} + \text{unchanged } C_7H_{15}Cl\text{-2, -3, and -4} \qquad (6)$$

Thus $[Fe_3(CO)_{12}]$ appears to be capable of reversibly dehydrochlorinating and isomerizing alkyl halides.

Under conditions necessary for the reactions in Table 1 to occur, $[Fe_3(CO)_{12}]$ decomposes quite readily to give metallic iron. It is possible that, like metallic zinc or nickel,[20] metallic iron rather than an organometallic species could dechlorinate the organic molecule. In an attempt to clarify this situation, two reactions were studied: (*a*) the reaction of metallic iron, produced by heating $[Fe_3(CO)_{12}]$ under reflux in n-nonane for 24 h, with 1,1,1,2-tetrachloroethane at 80 °C; and (*b*) the reaction of $[Fe(CO)_5]$ with 1,1,1,2-tetrachloroethane in n-heptane. No reaction was observed in (*a*) whereas in (*b*) 1,1-dichloroethylene remained the major product of the reaction. Furthermore, for all reactions described in this paper, control experiments, omitting the metal carbonyl, were carried out and in each case the only detectable products were minute traces of the monochloroalkanes (*e.g.* monochloroheptanes). These results suggest that iron carbonyl units {possibly $[Fe(CO)_4]$} are significant species in the reactions discussed in this section. The use of n-hexane rather than n-heptane as solvent gave products which generally satisfied conclusions (*a*)—(*d*) presented earlier.

Dodecacarbonyl-triangulo-*triruthenium*.—Whereas aryl halides show low thermal reactivity towards $[Fe(CO)_5]$ [*e.g.* iodobenzene fails to react [15] at 30—60 °C], $[Ni(CO)_4]$ is far more reactive towards halogen-containing molecules. Thus Bauld [21] reported that aryl iodides can be converted into arylcarboxylic acid esters by nickel carbonyl in the presence of alcoholic solvents [equation (7)]. These results suggested that the choice of metal



$$R^1I \xrightarrow[R^2OH]{[Ni(CO)_4]} [R^1\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\overset{\overset{\displaystyle I}{|}}{Ni}(CO)_n] \xrightarrow{R^2OH} R^1\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OR^2 + HI + [Ni(CO)_n] \qquad (7)$$

carbonyl can be critical and that possibly the use of $[Ru_3(CO)_{12}]$ rather than $[Fe_3(CO)_{12}]$ may lead to a substantially more active system.

A detailed examination of the organic products formed in the reaction of $[Ru_3(CO)_{12}]$ with selected chloroethanes was therefore undertaken and these results are presented in Table 2. They show that in the case of 1,1,1,2-tetrachloroethane little difference exists between the use of iron or ruthenium carbonyls, whilst with hexachloroethane no 1,2-dichloroethylenes or trichloroethylene could be detected. With 1,1,1-trichloroethane, dimerization products (chlorobutanes and butenes) were absent. In general, reactions with $[Ru_3(CO)_{12}]$ gave g.l.c. spectra consistent with a large number of very low yield organic products the characterization of which in many cases was not possible. Significantly, the ruthenium residues of these reactions gave complex i.r. spectra in the carbonyl-stretching region and t.l.c. revealed at least six major components. Their further identification was not effected because of the already highly complex nature of the organic products. However, reactions of $[Co_2(CO)_8]$ with organic halides of the form RCX_3 result in the formation of a

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[17] G. Henrici-Olivé and S. Olivé, *J. Organometallic Chem.*, 1971, **29**, 307.

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[21] N. L. Bauld, *Tetrahedron Letters*, 1963, 1841.

series of novel cobalt clusters based on the $[Co_3C(CO)_9]$ unit.[22] It is possible therefore that the reactions presented in this section could lead to similar ruthenium clusters.

Although it would be unwise to try and compare categorically the reactions of iron and ruthenium carbonyls on the basis of their organic products, since in the case of ruthenium some of these ' products ' could still remain co-ordinated to the metal, it does appear that the use of $[Ru_3(CO)_{12}]$ rather than $[Fe_3(CO)_{12}]$ does not lead to a distinctively different and more active system.

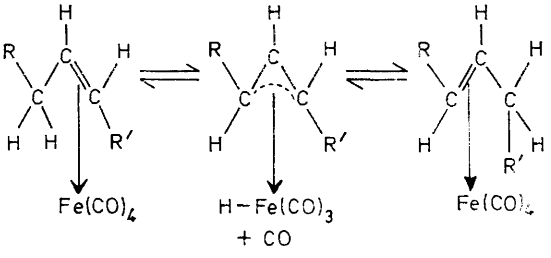
Tetracarbonylironmercury.—The use of $[Fe_3(CO)_{12}]$ as a chlorine abstracting reagent under reflux conditions leads readily to the formation of $[Fe(CO)_5]$. The toxicity of this species together with its undesirable effect on g.l.c. detectors makes it necessary to either devise suitable methods for its removal or to use alternative reagents. For this reason an investigation of some analogous reactions of $[FeHg(CO)_4]$ [23] was undertaken. In the case of, for example, 1,1,1,2-tetrachloroethane, using n-octane rather than n-heptane as solvent, the major product was trichloroethylene (*i.e.* dehydrochlorination) in high yield (70%) together with a trace amount of 1,1-dichloroethylene (*i.e.* 1,2-dechlorination). This reagent therefore significantly contrasts with $[Fe_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$, but a number of reagents particularly $FeCl_3$ or $AlCl_3$ [24-26] are equally efficient and more readily available dehydrochlorinating reagents. No carbonyl-stretching frequencies were observed in the i.r. spectrum of the solid residue, but the formation of $FeCl_2$ and metallic mercury suggested that the $[FeHg(CO)_4]$ had been converted into $[Fe(CO)_4(HgCl)_2]$ [27] which decomposed under the reaction conditions.[28]

TABLE 2

$$[Ru_3(CO)_{12}] + \text{chloroethane} \xrightarrow[\text{reflux}]{n\text{-}C_7H_{16}} \text{organic products} + \text{organoruthenium complexes}$$

1,1,1,2-Tetrachloroethane	Hexachloroethane	1,1,1-Trichloroethane
	Organic products	
Mixture of isomeric heptenes (moderate yield)	mixture of isomeric heptenes (moderate yield)	mixture of isomeric heptenes (major product)
1,1-Dichloroethylene (major product)	tetrachloroethylene (major product)	1,1-dichloroethane (moderate yield)
cis-1,2-Dichloroethylene (trace)		
1,1,2-Trichloroethane (second highest yield)		
1-, 2-, 3-, and 4-Chloroheptane (small yield)	1-, 2-, 3-, and 4-chloroheptane (trace)	1-, 2-, 3-, and 4-chloroheptane (trace)

Possible Mechanisms.—A number of papers describing reactions somewhat similar to some of those presented here have appeared during the course of this work. Thus $[Ni(CO)_4]$ is also capable of converting a CCl_3 group into a $CHCl_2$ group,[29] whilst Petrova and Freidlina [30] were able to effect a similar transformation using $[Fe(CO)_5]$ and a thiol, the latter giving an organic disulphide. However, a mechanistic dilemma still exists amongst the various research groups and significantly a recently published extensive review of the area deals only superficially with the role of the metal carbonyl.[31] Whilst some research groups believe that reactions of metal carbonyls with organochlorine compounds involve co-ordination mechanisms,[13-15,32] others are firmly convinced of free-radical routes.[4,16,33] Bamford favours a route in which radicals are produced by a co-ordination mechanism,[34] whereas Webb and Borcherdt [35] suggested that the coupling of allylic halides by $[Ni(CO)_4]$ could proceed through either type of mechanism but consider the free-radical route to be the most plausible.



SCHEME 3

Similar arguments apply equally well to the reactions discussed herein. Thus, the addition of various types of standard free-radical inhibitors to some of the reactions of $[Fe_3(CO)_{12}]$ with chloroethanes does not in general alter the product distribution and yield. However, this observation should be interpreted with care since (*a*) the free-radical inhibitors may co-ordinate to the iron carbonyl units; and (*b*) very ' hot ' free radicals like

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[22] R. R. Penfold and B. H. Robinson, *Accounts Chem. Res.*, 1973, **6**, 73.

[23] H. Hock and H. Stuhlmann, *Chem. Ber.*, 1929, **B62**, 431.

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[32] R. F. Heck and C. R. Boss, *J. Amer. Chem. Soc.*, 1964, **86**, 2580.

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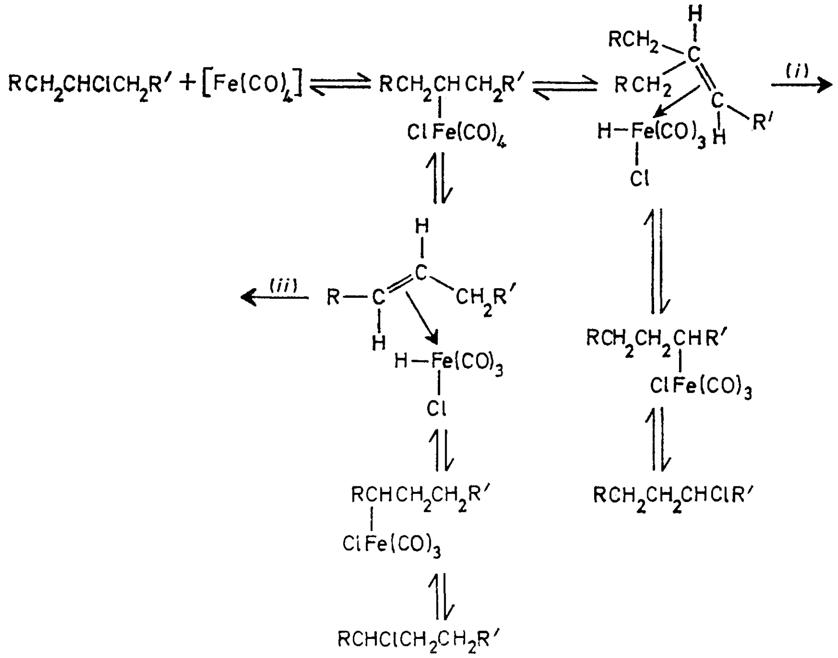
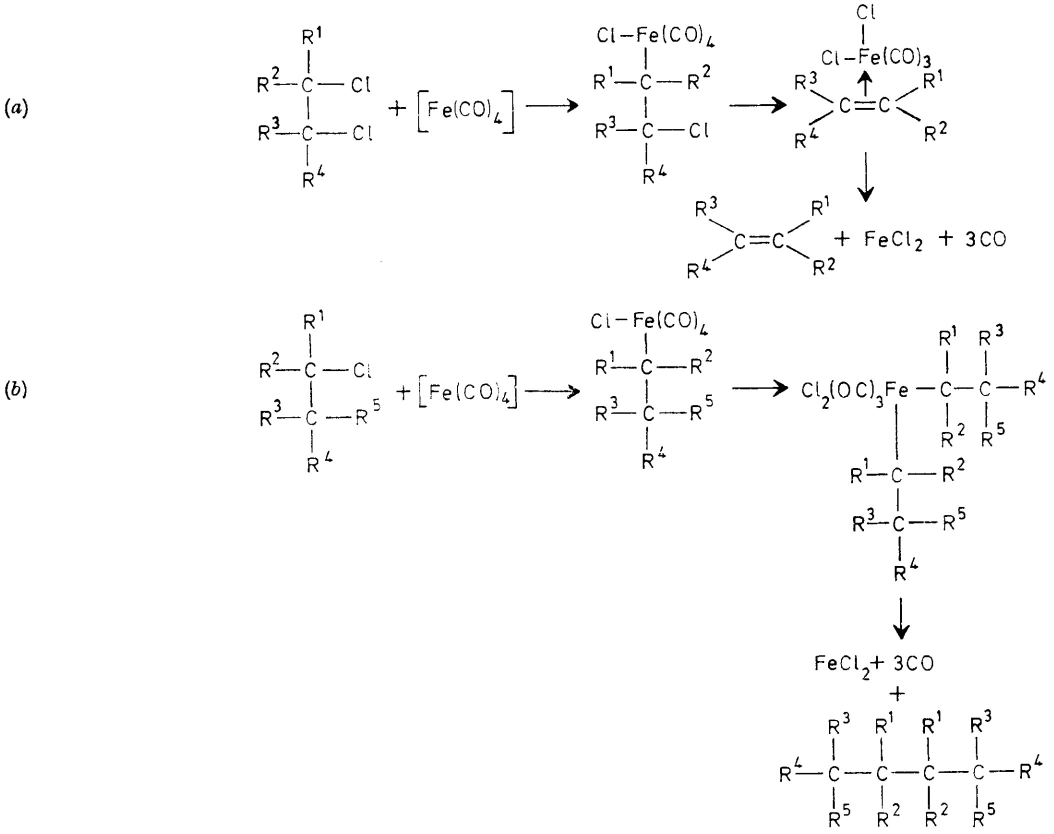
[34] C. H. Bamford, G. C. Eastmond, and D. Whittle, *J. Organometallic Chem.*, 1969, **17**, P33.

[35] I. D. Webb and G. T. Borcherdt, *J. Amer. Chem. Soc.*, 1951, **73**, 2654.



SCHEME 4 (*i*), Decomposition to alkene, $RCH_2CH{=}CHR'$; (*ii*), decomposition to alkene, $RCH{=}CHCH_2R'$



SCHEME 5 Route (*b*) is regarded as less likely since it involves an iron(IV) intermediate

Cl· are not easily quenched.[36] Precedent would suggest,[18,37,38] however, that alkene isomerism is likely to involve a co-ordination mechanism in which an (η-allyl)tricarbonylhydrido-iron (or -ruthenium) intermediate is formed, the *trans* internal isomers being preferentially produced purely on steric grounds since they will be the most unreactive (Scheme 3). The observed isomerization of the alkyl halides is probably the result of a similar type of mechanism; one such possibility (Scheme 4) also provides an alternative route to heptene formation and isomerism.

The mechanism whereby a CCl_3 group exchanges with hydrogen atoms of the alkane to give the corresponding $CHCl_2$ group and the monochloroalkane is probably free radical. This is because: (*a*) the monochloroalkanes are formed in minute traces in the absence of any metal carbonyl and the $[M(CO)_4]$ unit (M = Fe or Ru) is liable to be involved in the initial formation of radicals;[31] (*b*) the isomer distribution of monochloroalkanes is similar to that observed in the liquid-phase elemental chlorination of alkanes.[39] This proposed free-radical hydrogen–chlorine exchange could be accomplished according to equations (8)—(10).

$$RCCl_3 + [Fe(CO)_4] \longrightarrow [Fe(CO)_4Cl] + RCCl_2\cdot \qquad (8)$$

$$RCCl_2\cdot + C_7H_{16} \longrightarrow RCCl_2H + C_7H_{15}\cdot \qquad (9)$$

$$C_7H_{15}\cdot + RCCl_3 \longrightarrow C_7H_{15}Cl + RCCl_2\cdot \qquad (10)$$

The dimerization or 1,2-abstraction of chlorine atoms in chloroethanes, using iron and ruthenium carbonyls, could proceed along co-ordination routes somewhat similar to those proposed by Alper [40] (Scheme 5). However, the experimental results are not completely consistent with such a mechanism since it could be expected that this should also lead to ketone formation.[13-15] Moreover, it might be expected that by such a mechanism the nature and distribution of organic products should change dramatically as the metal is changed. Thus, consistent with the reported ease of dechlorination of radicals like $\cdot CCl_2CCl_2H$, the following free-radical mechanism could effect the experimentally observed transformations.

$$(a)\ \begin{cases} RCCl_3 + [Fe(CO)_4] \longrightarrow \\ \qquad\qquad RCCl_2\cdot + [Fe(CO)_4Cl] & (8) \\ 2RCCl_2\cdot \longrightarrow RCl_2CCCl_2R & (11) \end{cases}$$

$$(b)\ \begin{cases} RCl_2CCCl_2R + [Fe(CO)_4] \longrightarrow \\ \qquad\qquad [Fe(CO)_4Cl] + RCl_2C\dot{C}ClR & (12) \\ RCl_2C\dot{C}ClR \longrightarrow RClC{=}CClR + Cl\cdot & (13) \\ RCl_2C\dot{C}ClR + [Fe(CO)_4Cl] \longrightarrow \\ \qquad\qquad RClC{=}CClR + FeCl_2 + 4CO & (14) \end{cases}$$

As a result of this chloroethane study, it could be inferred that Coffey's proposal (*b*), and particularly of a carbene intermediate in the formation of tetraphenylethylene from dichlorodiphenylmethane and $[Fe(CO)_5]$, was incorrect.[16] It would be expected that the intermediate 1,2-dichloro-1,1,2,2-tetraphenylethane could be isolated from this reaction and indeed, in the case of 1,1,1-trichloroethane and $[Fe_3(CO)_{12}]$, 2,2,3,3-tetrachlorobutane was isolated and shown to be an intermediate in the formation of *cis*- and *trans*-2,3-dichlorobut-2-ene.

In conclusion therefore it appears that the reactions of chloroethanes with iron and ruthenium carbonyls are highly complex and it is necessary to rationalize the many products by a number of mechanisms. However, the results suggest that monochloroalkanes can be activated by such metal carbonyls and this is, at the very least, not unfavourable towards us achieving our goal of alkane activation by metal complexes. Indeed it cannot be unequivocally stated that chloroheptane formation is not the result of metal carbonyl interactions, and this suggests that a study of the alkanes themselves with metal carbonyls is appropriate.[41]

EXPERIMENTAL

The complexes $[Fe_3(CO)_{12}]$,[42] $[Ru_3(CO)_{12}]$,[43] $[FeHg(CO)_4]$ and $[Fe(CO)_4(HgCl)_2]$ [23,27,44] were prepared by the literature methods. Whilst hexachloroethane was purified by sublimation and recrystallization (hexane), the other chloroethanes were fractionally distilled using a heated vacuum-jacketed distillation column (3 ft, glass beads). G.l.c. on the middle fractions showed 100% purity for all of the compounds except 1,1,1-trichloroethane which contained 1% 1,2-dichloroethane as impurity. Alkanes were purified by stirring over concentrated sulphuric acid for 24 h, treating with sodium hydrogencarbonate solution and water, and then degassing with nitrogen followed by distillation over calcium hydride through a Vigreux column. G.l.c. confirmed the complete absence of alkenes. All reactions were carred out under dry oxygen-free nitrogen.

Infrared spectra were recorded as solutions in 0.5 mm NaCl cells using a Perkin-Elmer 257 spectrometer with polystyrene as calibrant. Mass spectra were obtained using an A.E.I. M.S.12 instrument operating at 70 eV ionizing potential.* G.l.c. spectra were recorded on a Perkin-Elmer F11 FI machine (analytical) and an F.M. machine (preparative) using 0.125- and 0.25-in diameter columns respectively. ^1H N.m.r. spectra were recorded at 100 MHz on a Varian Associates HA 100 spectrometer.

Synthesis of authentic samples of some of the organic products was achieved using adaptations of literature routes. Thus, 2,2,3,3-tetrachlorobutane was prepared by the chlorination of but-2-yne using $SbCl_5$ as a catalyst.[45] 1-Chlorohexane and chloroheptane were prepared by heating n-hexanol or n-heptanol under reflux with thionyl

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* 1 eV ≈ 1.60×10^{-19} J.

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chloride.[46] The remaining isomers could not be prepared by this method and the triphenylphosphine–carbon tetrachloride reagent was used instead.[47,48]

Typical Reaction of a Chloroethane with $[Fe_3(CO)_{12}]$ *in n-Heptane.*—This is well illustrated by the 1,1,1-trichloroethane reaction. The complex $[Fe_3(CO)_{12}]$ (6.3 g, 0.012 mol) was heated under reflux in n-heptane (35 cm^3) with 1,1,1-trichloroethane (5.0 g, 0.037 mol) for 24 h. The reaction mixture was regularly monitored by i.r. spectroscopy [ν(CO)] and this showed the slow decomposition of $[Fe_3(CO)_{12}]$ into $[Fe(CO)_5]$; no other bands could be observed in the carbonyl-stretching region (1 800—2 200 cm^{-1}). The reaction mixture was then partially separated by a bulb to bulb distillation to give a light brown solid and a yellow liquid. The solid residue showed no bands in the carbonyl-stretching region but gave qualitative analysis tests consistent with the presence of both Fe^{2+} and Cl^-. The yellow colouration in the liquid fraction was due to $[Fe(CO)_5]$ and, whereas conventional oxidants such as ammonium cerium(IV) sulphate, bromine, or iodine were not capable of selectively removing this metal carbonyl, treatment with water (10 cm^3) and mercury(II) chloride (5 g) removed the $[Fe(CO)_5]$ as $[Fe(CO)_4(HgCl)_2]$; formation of the latter species takes place selectively in the water layer in which only $[Fe(CO)_5]$ and $HgCl_2$ are soluble.

G.l.c. was the only technique available for the separation of the resulting dry n-heptane layer. Three different stationary phases were used: tricresyl phosphate, M.S. 550, and LAC 1R 296, of which the latter proved to be the most successful particularly for preparative work (oven temperature 70 °C). The complete characterization of the various compounds isolated from the reactions of chloroethanes with metal carbonyls depended on published data on mass spectroscopy,[49-51] n.m.r. spectroscopy,[52] and g.l.c. (retention times).[53-55] In particular, the monochloroheptanes did not show molecular ions in their mass spectra but in the case of 1-chloroheptane a Pr group was ejected to give a five-membered ring containing a chlorine heteroatom, whilst 2-chloroheptane gave a small amount of the methyl-substituted ring with corresponding ejection of an Et group. Instead of ring formation, 3- and 4-chloroheptane gave ions corresponding to loss of HCl.

Typical Reaction of a Chloroethane with $[Ru_3(CO)_{12}]$ *in n-Heptane.*—This is well illustrated by the hexachloroethane reaction. The complex $[Ru_3(CO)_{12}]$ (0.53 g, 0.83 mmol) was heated under reflux in n-heptane (6 cm^3) with hexachloroethane (0.59 g, 2.5 mmol) for 24 h during which time the solution gradually changed from orange to reddish brown. After a bulb to bulb distillation, the solid residue was chromatographed using thin-layer silica plates (2% ethyl acetate–cyclohexane as eluant) whilst the liquid fraction was analysed by g.l.c. as previously described.

Reaction of $[FeHg(CO)_4]$ *with* 1,1,1,2-*Tetrachloroethane in n-Octane.*—The complex $[FeHg(CO)_4]$ (3.6 g, 0.01 mol) was heated under reflux with 1,1,1,2-tetrachloroethane (5.0 g, 0.03 mol) and n-octane (50 cm^3) for 24 h. The yellow colour of $[FeHg(CO)_4]$ was slowly replaced by the light grey of metallic mercury. The mixture was centrifuged and the heptane layer separated off and analyzed by g.l.c.

Gaseous Products.—The use of a bladder to maintain an inert atmosphere permitted a convenient analysis of gaseous products. The complete absence in all cases of hydrogen chloride was confirmed, but this result must be treated with caution since it has been reported that $[Fe(CO)_5]$ will react thermally or photochemically with hydrogen halides to give dimeric halogen-bridged iron carbonyls which can then decompose to $FeCl_2$.[56]

Yields of Reactions.—The major difficulty associated with this study of metal carbonyls and chloroalkanes was its complexity. G.l.c. was the only technique which could separate the large number of organic products and even then not completely satisfactorily. Collection methods were used which gave only small amounts of pure material and unfortunately they were not suitable for the calculation of quantitative yields. In most cases therefore only relative yields are given but some indication of quantitative yields can be derived from Tables 1 and 2 and the Figure.

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