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Transition Metal Carbonyls Combined with Hydrogen Donors as Initiators of the Radical Reduction of Trichloromethyl Compounds

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The review is devoted to new redox catalysts of the homolytic reduction of trichloromethyl compounds to dichloromethyl compounds—mononuclear and dinuclear metal carbonyls [$Fe(CO)_5$, $Ni(CO)_4$, $M(CO)_6$ (M = Mo, Cr, W), $Mn_2(CO)_{10}$] in combination with hydrogen donors (secondary alcohols, silicon hydrides, mercaptans, tertiary amines, amides, and tetrahydrofuran).
The results obtained hitherto concerning the development of a new radical-chain method for the reduction of a wide variety of trichloromethyl compounds to the dichloromethyl derivatives are surveyed.
The bibliography includes 78 references.

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I. INTRODUCTION

The ability of $Fe(CO)_5$ to initiate the hydrogenolysis of the C–Cl bond in polychloro-derivatives containing the CCl_3 group under the influence of hydrogen donors with the selective formation of the corresponding dichloromethyl derivatives was discovered by the authors of the present review in 1967;[1,2] since then the reaction based on Scheme (1) has been investigated for a wide range of examples using a wide variety of metal carbonyls (MC) and hydrogen donors (HA).

Scheme 1

$$RCCl_3 + HA \xrightarrow{MC} RCCl_2H.$$

The study of the applications of MC as initiators of radical reactions is a comparatively new field in the chemistry of transition metal carbonyls. The first investigations on these lines date back to 1959–61.[3,4] Many examples of radical addition, telomerisation, polymerisation, cyclisation, disproportionation, and others, initiated by metal carbonyls and their complexes with various ligands, are now known.[5] The evidence for the radical mechanism of the reaction based on Scheme (1), obtained particularly by the EPR method using spin trapping agents (see Section IV), is presented below.

The hydrogenolysis of the C–Cl bond in various polychloro-derivatives has significantly extended the range of applications of various MC and their combinations with nucleophiles for the initiation of radical reactions. We call such systems (MC + nucleophile) coordination initiators based on metal carbonyls; they are also referred to as redox catalysts.[6]

The study of the reduction of trichloromethyl compounds led to the discovery of a number of features of the reactions as a function of the nature of the MC and the hydrogen donor and also as a function of the structure of the trichloromethyl compound.

$Fe(CO)_5$, $Mo(CO)_6$, $Cr(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ have been used as initiators, while secondary alcohols, silicon hydrides, mercaptans, tertiary amines, acid amides, and tetrahydrofuran have been employed as hydrogen donors. $Ni(CO)_4$, $HMo(CO)_4P(C_6H_5)_3$, and $MoH_2(\eta\text{-}C_5H_5)_2$ have also been used.

It is noteworthy that, apart from its interest for the chemistry of metal carbonyls, the reduction of trichloromethyl compounds to the corresponding dichloromethyl derivatives is an urgent synthetic problem, since in recent years trichloromethyl compounds have become available as a result of the addition of polyhalogenomethanes (CCl_3X; X = H, Cl, Pr) to olefins and telomerisation,[7,8] while compounds with dichloromethyl groups are less readily available. Methods for the selective reduction $RCCl_3 \rightarrow RCHCl_2$ have undergone little development in previous investigations. The reaction which would be of greatest interest for the solution of the problem formulated, namely the catalytic hydrogenation of $RCCl_3$ compounds, proceeds as "reductive dimerisation" and not as hydrogenolysis of the C–Cl bond:[9,10]

$$2RCCl_3 \xrightarrow[Pd/C]{H_2} RCCl_2CCl_2R.$$

Dichloromethyl compounds are of interest not only for chemical and physicochemical studies but also for practical purposes. We may mention the reduction of DDT and related compounds,[11] the reduction of α-trichloromethyl compounds to the corresponding dichloromethyl derivatives.[12] Trichloro- and dichloro-methyl compounds have found extensive applications as insecticides, herbicides, and plasticisers and in the synthesis of medicinal preparations.

This review is devoted to a survey of data on the applications of transition metal carbonyls in the initiation of the hydrogenolysis of the C–Cl bond and the justification of a fundamentally new method for the conversion of trichloromethyl compounds into the dichloromethyl derivatives.

The only other review on this problem[13] is devoted solely to the synthetic aspect of these reactions.

II. SYSTEMS BASED ON METAL CARBONYLS AND VARIOUS HYDROGEN DONORS

1. Alcohols

(a) The Reduction of CCl_4 and $CHCl_3$

Since carbon tetrachloride is reduced more readily than chloroform, in the presence of reductants with moderate activity it is possible to carry out a selective reduction to chloroform. The $Fe(CO)_5$ + iso-C_3H_7OH system is a reductant of this kind (Table 1, experiment 1). $Mo(CO)_6$ and

$Mn_2(CO)_{10}$ combined with iso-C_3H_7OH enter into a non-selective reaction with partial reduction to CH_2Cl_2 (Table 1, experiments 2 and 3).

Chloroform is reduced with greater difficulty than CCl_4 and $RCCl_3$. Thus the $Fe(CO)_5$ + iso-C_3H_7OH system hardly reduces $CHCl_3$ at 120–140 °C (experiments 4 and 5). $Mo(CO)_6$ and $Mn_2(CO)_{10}$ combined with iso-C_3H_7OH reduce $CHCl_3$ to CH_2Cl_2 in 72–73% yields.

Table 1. The reduction of polychloromethanes CCl_3X by isopropyl alcohol in the presence of metal carbonyls (3 h).[12]

No.	MC	X	[CCl_3X] : [iso-C_3H_7OH] : [MC]	T, °C	F*, %	Yield, %	
						$CHCl_3$	CH_2Cl_2
1	$Fe(CO)_5$	Cl	1:8:0.05	120	100	100	0
2	$Mn_2(CO)_{10}$	Cl	1:8:0.05	120	100	90	10
3	$Mo(CO)_6$	Cl	1:8:0.05	140	100	64	36
4	$Fe(CO)_5$	H	1:8:0.05	120	0	—	0
5	$Fe(CO)_5$	H	1:8:0.05	140	10	—	10
6	$Mn_2(CO)_{10}$	H	1:8:0.1	120	72	—	72
7	$Mo(CO)_6$	H	1:8:0.05	140	73	—	73

*F = degree of conversion of the initial polychloroalkane.

The data in Table 1 clearly demonstrate the sequence of the reactivities of MC: $Mo(CO)_6 \geq Mn_2(CO)_{10} \gg Fe(CO)_5$.

Isopropyl alcohol is not an inert medium for the reaction under consideration. Being a hydrogen atom donor, it is oxidised to acetone and in addition it enters into a series of side processes, which lead to the formation of isopropyl chloride, di-isopropyl ether, propene, and water:[14]

$$RCCl_3 + (CH_3)_2CHOH \xrightarrow{MC} RCCl_2H + (CH_3)_2CO + HCl,$$
$$(CH_3)_2CHOH + HCl \rightarrow (CH_3)_2CHCl + H_2O,$$
$$(CH_3)_2CHCl + (CH_3)_2CHOH \rightarrow [(CH_3)_2CH]_2O + H_2O,$$
$$(CH_3)_2CHOH \rightarrow C_3H_6 + H_2O.$$

The formation of propene leads in a number of instances to the appearance of adducts of the type of $RCCl_2CH_2CHClCH_3$.[14]

(b) The Reduction of ααα-Trichloroalkanes

The reduction of ααα-trichloroalkanes by different MC in isopropyl alcohol has been investigated for molecules with a chain length ranging from two to ten carbon atoms. Table 2 presents the results of the reduction of 1,1,1-trichloropentane. The choice of this compound is associated with the fact that it contains no other functional groups and the length of the hydrocarbon chain is such that it cannot lead to lateral displacements of hydrogen in the radical.[15] On the other hand, the chain is not so short that the C–Cl bond energy depends on it, since the reactivity of CCl_4 and CCl_3CH_3 is significantly higher than that of ααα-trichloroalkanes with longer chains. According to the data in Table 2, it is possible to set up the following activity series of MC in the reaction investigated:

$$Mo(CO)_6 > Mn_2(CO)_{10} > Fe(CO)_5 \gg W(CO)_6 > Cr(CO)_6 \gg Re_2(CO)_{10}.$$

Thus the MC used have been divided into two groups—the active initiators $Mo(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, and the relatively ineffective $W(CO)_6$, $Cr(CO)_6$, and $Re_2(CO)_{10}$. The reactions involving the active MC have a chain mechanism and the yield of 1,1-dichloropentane under the chosen conditions ranged from 5.6 to 9.2 moles per mole of the MC (Table 2). The Table also shows that the best [$C_4H_9CCl_3$] : [iso-C_3H_7OH] ratio for $Fe(CO)_5$ or $Mn_2(CO)_{10}$ is 1 : 8 (experiments 3 and 5). In the presence of $Mo(CO)_6$ a high yield is obtained at an even lower dilution (experiment 1).

Table 2. The reduction of 1,1,1-trichloropentane (3 mmol) by isopropyl alcohol in the presence of metal carbonyls (0.3 mmol) (3 h).[16]

No.	MC	[iso-C_3H_7OH]/[$C_4H_9CCl_3$]	T, °C	F, %	Yield %	Q*
1	$Mo(CO)_6$	3	140	96	90	9.0
2	$Mn_2(CO)_{10}$	3	120	72	65	6.5
3	$Mn_2(CO)_{10}$	8	120	97	84	8.4
4	$Fe(CO)_5$	3	120	63	56	5.6
5	$Fe(CO)_5$	8	120	92	92	9.2
6	$W(CO)_6$	3	140	30	26	2.6
7	$W(CO)_6$	8	140	27	27	2.7
8	$Cr(CO)_6$	3	140	20	11	1.1
9	$Cr(CO)_6$	8	140	44	12	1.2
10**	$Re_2(CO)_{10}$	3	140	0	0	0

*Q = [$RCHCl_2$] : [MC], i.e. the yield of the reduction product in moles per mole of the metal carbonyl ("value").
**0.15 mmol of $Re_2(CO)_{10}$ was employed.

Table 3. The reduction of ααα-trichloroalkanes* $RCCl_3$ by isopropyl alcohol in the presence of metal carbonyls.

No.	MC	R	[$RCCl_3$] : [iso-C_3H_7OH] : [MC]	T, °C	τ**	F, %	Yield, %	Q	Refs.
1	$Fe(CO)_5$	C_5H_{11}	1:9.5:0.14	145	5	100	84	6.0	[18]
2	$Fe(CO)_5$	C_7H_{15}	1:8:0.15	120	3	96	65	4.3	[20]
3	$Mo(CO)_6$	C_7H_{15}	1:8:0.075	140	3	93	72	9.6	[20]
4	$Mn_2(CO)_{10}$	C_7H_{15}	1:8:0.1	120	3	88	79	7.9	[20]
5	$Mn_2(CO)_{10}$	C_8H_{17}	1:8:0.1	120	3	95	68	6.8	[20]
6	$Mo(CO)_6$	$C_{10}H_{21}$	1:8:0.05	140	3	95	74	14.7	[20]

*The reduction of $C_4H_9CCl_3$ (see Table 2); for other examples of the reduction of ααα-trichloroalkanes, see also Refs. 17, 19, and 21.
**τ = reaction time in hours.

Table 3 presents examples of the reduction of ααα-trichloroalkanes with different chain lengths. The data in this Table demonstrate the wide-scale applicability of the proposed method to the reduction of a wide variety of ααα-trichloroalkanes and confirm the high activity of $Mo(CO)_6$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ in combination with isopropyl alcohol. The amount of MC can be varied within fairly wide limits depending on its nature. The smallest amount of MC has been used in the case of $Mo(CO)_6$ (Table 3, experiments 3 and 6).

(c) The Reduction of Polychloroalkanes

αααω-Tetrachloroalkanes can be obtained by the telomerisation of ethylene with CCl_4; ααάγ-tetrachloroalkanes are obtained by the addition of CCl_4 to α-olefins. The reduction of tetrachloroalkanes containing from 3 to 11 carbon atoms in the molecule by active MC in combination with alcohols has

Table 4. The reduction of αααω-tetrachloroalkanes $CCl_3(CH_2CH_2)_nCl(RCCl_3)$ by alcohols with initiation by metal carbonyls.

No.	n	MC	Alcohol	[$RCCl_3$] : [alcohol] : [MC]	T, °C	τ	F, %	Yield, %	Refs.
1	1	$Fe(CO)_5$	iso-C_3H_7OH	1 : 3—8 : 0.05—0.16	140	3—5	73—100	55—70	[14,17,22, 23]
2	1	$Fe(CO)_5$	cyclo-$C_6H_{11}OH$	1 : 3 : 0.1	140	3.5	83	81	[24]
3	1	$Fe(CO)_5$	$C_6H_5CH_2OH$	1 : 2.6 : 0.11	145	5	100	76	[14]
4	1	$Mo(CO)_6$	iso-C_3H_7OH	1 : 8 : 0.05	140	3	100	98	[23]
5	1	$Mo(CO)_6$	cyclo-$C_6H_{11}OH$	1 : 3 : 0.02	140	3.5	47	45	[24]
6	1	$Mn_2(CO)_{10}$	iso-C_3H_7OH	1 : 8 : 0.05	140	3	78	74	[23]
7	2	$Fe(CO)_5$	iso-C_3H_7OH	1 : 3.3—8 : 0.02—0.15	120—145	3—5	100	67—97	[14,16,22] [25]
8	2	$Mo(CO)_6$	iso-C_3H_7OH	1 : 3 : 0.05	140	3	88	86	[16]
9	2	$Mn_2(CO)_{10}$	iso-C_3H_7OH	1 : 8 : 0.1	120	3	97	85	[16]
10	3	$Fe(CO)_5$	iso-C_3H_7OH	1 : 3.3 : 0.04	145	3	100	42—50	[26]

Table 5. The reduction of αααββ-pentachloro- and αααγ-tetrachloro-alkanes $RCCl_3$ by alcohols in the presence of metal carbonyls.

No.	MC	R	Alcohol	[$RCCl_3$] : [alcohol] : [MC]	T, °C	F, %	Yield, %	Refs.
1	$Fe(CO)_5$	$CHCl_2$	iso-C_3H_7OH	1 : 8 : 0.1	120	35	14*	[20]
2	$Mo(CO)_6$	$CHCl_2$	iso-C_3H_7OH	1 : 8 : 0.1	140	73	23*	[20]
3	$Mn_2(CO)_{10}$	$CHCl_2$	iso-C_3H_7OH	1 : 8 : 0.1	120	64	40*	[20]
4	$Fe(CO)_5$	$C_6H_{13}CHClCH_2$	iso-C_3H_7OH	1 : 3 : 0.15	130	79	40	[28]
5	$Fe(CO)_5$	$C_6H_{13}CHClCH_2$	cyclo-$C_6H_{11}OH$	1 : 3 : 0.15	130	93	52	[28]

*CCl_2 = CHCl was also obtained in yields of 14% (experiment 1), 42% (experiment 2), and 18% (experiment 3).

been investigated. The results are compiled in Tables 4 and 5. They show that the presence of the chlorine atom in the chain does not have a significant influence on the yields of the corresponding ααγ- and ααω-trichloroalkanes compared with the reduction of the unsubstituted ααα-trichloroalkanes. In all cases high yields of the reduced compounds have been obtained under favourable conditions, where the $[CCl_3C_nH_{2n}Cl] : [ROH] : [MC]$ ratios are close to 1 : 8 : 0.1 and the chain reaction proceeds selectively via one chlorine atom of the CCl_3 group.

The formation of the products of the 1,5- and 1,6-shifts of hydrogen in the long-chain radical as side products has been noted in the reduction of ααα-trichloro- and αααγ-tetrachloroalkanes with long chains (with more than 5 carbon atoms) and also of ααaω-tetrachloroalkanes starting with $CCl_3(CH_2CH_2)_2Cl$.[19] In the reduction of *gem*-trichloroalkanes with $Fe(CO)_5$ or $Mo(CO)_6$ in combination with isopropyl alcohol such rearrangement proceeds to equal extents, while in the presence of $Mn_2(CO)_{10}$ under the same conditions the rearrangement does not take place.[20]

It is known that the CCl_3 group αααβ-tetrachloroalkanes exhibits a number of characteristic features in chemical reactions. In particular catalytic reduction leads in this instance mainly to dechlorination to 1,1-dichloroalk-1-enes;[9] the reduction of 1,1,2-tetrachloropentane with triethylsilane in the presence of t-butyl peroxide is also accompaned by the formation of $CCl_2 = CHC_3H_7$.[27]

The formation of the dechlorination product has been explained by the fact that the $\dot{C}Cl_2CCl_2H$ radical can be stabilised not only by the abstraction of hydrogen but also by fragmentation with elimination of the chlorine atom in the β-position relative to the radical centre:

$$CCl_3CCl_2H \rightarrow \dot{C}Cl_2CCl_2H \begin{cases} \xrightarrow{HA} CHCl_2CCl_2H, \\ \xrightarrow{-Cl} CCl_2{=}CClH. \end{cases}$$

The fragmentation of radicals with ejection of the β-chlorine atom is a general property of such radicals and has been described in numerous examples of radicals of this type generated by different procedures in various reactions.[29]

As can be seen from Table 5, a dechlorination product, namely trichloroethylene, was obtained in all cases from αααββ-pentachloroethane together with the reduced product. The ratio of the two reaction pathways depends on the nature of the MC. Thus in the presence of $Mn_2(CO)_{10}$ the yields of the reduced product (*sym*-tetrachloroethane) reach 40%, while those of the dechlorinated product (trichloroethylene) are 15–18%. On the other hand, the use of $Mo(CO)_6$ favours the preferential formation of trichloroethylene.

Thus the presence of chlorine in the α-position relative to the CCl_3 group results in the reduction process, which proceeds with a yield of 20–40% and is complicated by the concomitant dechlorination to 1,1-dichloroalk-1-enes.

(d) The Reduction of Trichloromethylcarbinols

The practical importance of the reduction of DDT and trichloromethylcarbinols stimulated the study of its possibility. The results are compiled in Table 6.

ααα-Trichloromethyldimethylmethanol (chlorobutol) and aryl-ααα-trichloromethylmethanols, listed in Table 6, are polyfunctional compounds and are formally capable of a series of side reactions. For example, the reduction of chlorobutol involves also the formation of 1,1-dichloro-2-methylpropene, whose yields depend on the nature of the MC (experiments 1 and 3). Aryltrichloromethylmethanols are secondary alcohols and, by analogy with the reactions of isopropyl alcohol (or cyclohexanol), one may expect the formation of the corresponding ketones.

Table 6 shows, for chlorobutol, that aliphatic α-trichloromethylcarbinols are successfully reduced by isopropyl alcohol in combination with $Fe(CO)_5$, $Mo(CO)_6$, and $Mn_2(CO)_{10}$, the

yields being significantly higher in the presence of the last two MC than in the presence of the first (experiments 1–3).

Aryl-α-trichloromethylmethanols can also be successfully reduced to aryl-α-dichloromethylmethanols by the MC + iso-C_3H_7OH system (Table 6, experiments 4–8). It has been shown that the nature of the substituent in the aromatic ring and the MC employed exert a significant influence on the direction of the process. The reaction proceeds in accordance with the scheme

$$\underset{(I)}{XC_6H_4CH(OH)CCl_3} + \text{iso-}C_3H_7OH \xrightarrow{MC} \rightarrow \underset{(II)}{XC_6H_4CH(OH)CHCl_2} + \underset{(III)}{XC_6H_4CH(CHCl_2)OCH(CH_3)_2};$$

X = H (a), *o*-Cl (b), *n*-CH_3O (c).

The reduction of arylcarbinols (I, a and b) result mainly in the formation of aryl-α-dichloromethylmethanols (II, a and b) (experiments 4 and 5). In the case of the carbinol (Ic) under the same conditions the carbinol (IIc) is hardly formed and the reaction is accompanied by pronounced charring. In order to prevent this, a fiftyfold excess of isopropyl alcohol was employed and $Mo(CO)_6$ or $Mn_2(CO)_{10}$ were used in addition to $Fe(CO)_5$ (experiments 6–8). The product ratio (IIc):(IIIc) then depends on the nature of the MC: in the presence of $Fe(CO)_5$ mainly the ether (IIc) is obtained, while the presence of $Mn_2(CO)_{10}$ the main product is the carbinol (IIc).

Table 6. The reduction of trichloromethylmethanols and DDT by isopropyl alcohol in the presence of metal carbonyls (140 °C, 3 h).

No.	MC	$RCCl_3$	$[RCCl_3]:[iso\text{-}C_3H_7OH]:[MC]$	*F*, %	Yield, %	Refs.
1	$Fe(CO)_5$	$(CH_3)_2C(OH)CCl_3$	1 : 8 : 0.26	100	38*	[32]
2	$Mo(CO)_6$	$(CH_3)_2C(OH)CCl_3$	1 : 8 : 0.26	80	76	[32]
3	$Mn_2(CO)_{10}$	$(CH_3)_2C(OH)CCl_3$	1 : 8 : 0.13	100	75*	[32]
4	$Fe(CO)_5$	$C_6H_4CH(OH)CCl_3$ (Ia)	1 : 5 : 0.1	70	52	[12]
5	$Fe(CO)_5$	*o*-$ClC_6H_4CH(OH)CCl_3$ (Ib)	1 : (5–50) : (0.1–0.15)	80–100	74–93	[12]
6	$Fe(CO)_5$	*p*-$CH_3OC_6H_4CH(OH)CCl_3$ (Ic)	1 : 50 : 0.15	50	7**	[12]
7	$Mo(CO)_6$	ditto	1 : 50 : 0.15	89	45**	[12]
8	$Mn_2(CO)_{10}$	»	1 : 50 : 0.15	91	72**	[12]
9***	$Fe(CO)_5$	(*p*-$ClC_6H_4)_2CHCCl_3$	1 : 12 : 0.05	100	91	[11]

*$(CH_3)_2C = CCl_2$ is also formed in yields of 17% (experiment 1) or 3% (experiment 3); $Cr(CO)_6$, $W(CO)_6$, and $Re_2(CO)_{10}$ give rise to low yields of reaction products.

**p-$CH_3OC_6H_4CH(CHCl_2)OCH(CH_3)_2$ (IIIc) is also formed in yields of 35% (experiment 6), 34% (experiment 7) or 10% (experiment 8).

***135 °C, 6 h.

Thus the reduction of α-trichloromethylcarbinols by the MC + iso-C_3H_7OH system can be undoubtedly used to synthesise α-dichloromethylcarbinols.

DDT was successfully reduced to DDD by secondary alcohols in the presence of MC with a yield of 70–90%.

Among the *gem*-trichloromethyl compounds with aromatic substituents, trichloromethylbenzene occupies a special place. The presence of the phenyl group in the α-position relative to the CCl_3 group is responsible for the specific features of its chemical behaviour. Thus it has been found that the reduction of $C_6H_5CCl_3$ by $Fe(CO)_5$ is the presence of isopropyl or ethyl alcohol does not lead to the formation of $C_6H_5CHCl_2$. The products are $(C_6H_5CCl_2)_2$ or $C_6H_5CCl = CClC_6H_5$.[11] The synthesis of $C_6H_5CHCl_2$ from $C_6H_5CCl_3$ in a nearly quantitative yield has been described. The reaction proceeds without a catalyst in ethanol in the presence of $P[N(C_2H_5)_2]_3$ [30] or $(C_2H_5)_3N$ and $HPO(OC_2H_5)_2$.[31]

In conclusion of the discussion of the use of alcohols in combination with various MC for the reduction of trichloromethyl compounds, one may note that isopropyl alcohol is most suitable for preparative purposes. In certain cases cyclohexanol is more convenient, since it is possible to use it at atmospheric pressure. Benzyl alcohol is also active in these reactions. It has been shown in relation to the reaction with 1,1,1,3-tetrachloropropane that alcohols such as CH_3OH and C_2H_5OH combined with $Fe(CO)_5$ are in principle capable of reducing the trichloromethyl group to the dichloromethyl group, but 1,1,3-trichloropropane is formed only in a low yield. In the presence of $Fe(CO)_5$, $(CH_3)_3COH$ does not reduce 1,1,1,3-tetrachloropropane.[14]

2. Silicon Hydrides

Reactions are known where, in the presence of catalysts ($AlCl_3$, $ZnCl_2$, etc), silicon hydrides reduce a series of organic compounds—acid chlorides, amides, nitriles, lactones, carbonyl compounds, and monochloroalkanes.[33] This review deals with the results of the use of silicon hydrides in combination with metal carbonyls to reduce the CCl_3 group to $CHCl_2$. Examples of such reactions are presented in Tables 7–9.

Table 7. The reduction of compounds with the trichloromethyl group ($RCCl_3$)* by silicon hydrides ($HSiX_3$) in the presence of iron pentacarbonyl

No.	X	R	$[RCCl_3]:[HSiX_3]:[MC]$	*T*, °C	τ	*F*, %	Yield, %	*Q*	Refs.
1	C_2H_5	Cl	1 : 3 : 0.1	105	5	93	70**		[27]
2	C_2H_5	H	1 : 1 : 0.07	145	5	88	84	12	[27]
3	C_2H_5	CH_3	1 : 1 : 0.1	145	5	98	73	7.3	[34]
4	C_2H_5	C_8H_{17}	1 : 1.1 : 0.06	145	5	—	62	10.3	[35]
5	C_2H_5	$CHClC_3H_7$	1 : 1 : 0.067	145	5	33	13***	—	[27]
6	C_2H_5	$CH_2CHClCH_3$	1 : 1 : 0.1	145	4	80	71	7.1	[17]
7	C_2H_5	$CH_2CHClC_3H_7$	1 : 1.1 : 0.06	145	5	—	55	9.1	[35]
8	C_2H_5	$CH_2CHClC_6H_{13}$	1 : 3 : 0.15	130	3	100	72	5	[28]
9	C_2H_5	$(CH_2CH_2)_2Cl$	1 : 1.1 : 0.1	145	4	99	88	8.8	[17]
10	C_2H_5	$(CH_2CH_2)_2Cl$	1 : 1–1.6 : 0.035–0.13	150	3	98	82–89	23–7	[25,35]
11	C_2H_5	$(CH_2CH_2)_2Cl$	1 : 1.3 : 0.007	145	3	100	92	131	[2]
12	OC_2H_5	$(CH_2CH_2)_2Cl$	1 : 1.3 : 0.007	145	3	47	36****	51	[2]
13	Cl	$(CH_2CH_2)_2Cl$	1 : 1.3 : 0.07	145	3	68	12****	18	[2]
14	*****	$(CH_2CH_2)_2Cl$	1 : 1.3 : 0.11	140	5	73	71	6.5	[26]

*For the reduction of 1,1,1-trichloro-octane, see Table 8.

**CH_2Cl_2 is also formed in 19% yield.

***$CCl_2 = CHC_3H_7$ was also obtained in 15% yield.

****1,1,5-Trichloropent-1-ene was also obtained in yields of 5% (experiment 12) and 56% (experiment 13).

*****CH_3SiCl_2H was used as the hydrogen donor.

In the absence of metal carbonyls, silicon hydrides do not reduce the trichloromethyl group.[2] The reduction of trichloromethyl compounds by the $Fe(CO)_5$ + silicon hydride system has been studied in greatest detail. The data in Table 7 demonstrate the high effectiveness of this system in the reduction of the trichloromethyl group to the dichloromethyl group in polychloromethanes, ααα-trichloroalkanes, αααγ-tetrachloroalkanes, and αααω-tetrachloroalkanes. The reaction has a chain mechanism in all cases—the yield of

reduced compounds varies from 5 to 12.5 moles per mole of $Fe(CO)_5$. The high effectiveness of this system is illustrated by the ease of the reduction of chloroform (Table 7, experiment 2) [the $Fe(CO)_5$ + iso-C_3H_7OH system is ineffective in this reaction (Table 1, experiment 4)] and also by the fact that CCl_4 is reduced with the formation of a mixture of chloroform and methylene chloride (Table 7, experiment 1). The reduction of all the polychloroalkanes containing the CCl_3 group investigated (except ααaβ-tetrachloroalkanes) by $Fe(CO)_5$ and $(C_2H_5)_3SiH$ (Table 7, experiments 3, 4, and 6–11) or CH_3SiCl_2H (experiment 14) proceeds selectively with a high yield of the reduced products:

$$RCCl_3 + HSiX_3 \xrightarrow{Fe(CO)_5} RCCl_2H + ClSiX_3.$$

In the majority of the examples investigated, it was sufficient to use 1–1.3 moles of silicon hydride per mole of the initial polychloroalkane and 5 mole % of $Fe(CO)_5$ (relative to $RCCl_3$) in order to obtain high yields of products. The use of $HSi(OC_2H_5)_3$ and $HSiCl_3$ gives rise to low yields of the reduction products (Table 7, experiments 12 and 13).

Table 8. The reduction of n-$C_7H_{15}CCl_3$ (3 mmol) by $(C_2H_5)_3SiH$ (4 mmol) in the presence of metal carbonyls (0.15 mmol).[36]

No.	MC	T, °C	F, %	Yield, %	Q
1	$Fe(CO)_5$	120	62	60	12
2	$Fe(CO)_5$	140	89	83	16
3	$Mo(CO)_6$	120	53	42*	8.4
4	$Mo(CO)_6$	140	97	67*	13
5	$Mn_2(CO)_{10}$	120	100	100	20

*n-$C_6H_{13}CH = CCl_2$ was also obtained in yields of 10 and 30% at 120° and 140 °C respectively.

Table 9. The reduction of perchloropropene and 1,1,2,3,3-pentachloropropene by silicon hydrides in the presence of $Fe(CO)_5$ (5 mole % for C_3Cl_6 and 7.5 mole % for C_3Cl_5H).[36]

No.	Polychloropropene	$[(C_2H_5)_3SiH]/[C_3Cl_n]$	T, °C	τ	F, %	Yield, %	
						C_3Cl_4H	$C_3Cl_4H_2$
1	C_3Cl_6	1.1	105–110	4	90	52	9
2	C_3Cl_6	1	120	3	91	43	24
3	C_3Cl_6	2	140	6	100	4	50
4	C_3Cl_6	*	140	7	100	5	43
5	C_3Cl_5H	1.7	140	4	85	—	30**

*GKZh-94, a siloxane having the structure $[-Si(C_2H_5)(H)O-]_n$ (32 g), was employed.
**$CCl_2 = CClCH_3$ was obtained in addition in ~1% yield.

The hydrogenolysis of the C–Cl bond by $Fe(CO)_5$, $Mo(CO)_6$, or $Mn_2(CO)_{10}$ in combination with triethylsilane has been investigated for 1,1-trichlorooctane (Table 8).[20] The data in Table 8 show that the most active metal carbonyl is $Mn_2(CO)_{10}$ in combination with triethylsilane. $Mo(CO)_6$ proved to be less effective owing to the occurrence of a dehydrochlorination side reaction. The reactions discussed have a chain mechanism.

It has been shown that, in the reduction of long-chain *gem*-trichloro-alkanes by the MC + $(C_2H_5)_3SiH$ systems a rearrangement with 1,5- and 1,6-migration of hydrogen, noted previously for the reduction of the same compounds by isopropyl alcohol in combination with metal carbonyls, does not occur.[36]

The reduction of trichloromethyl compounds containing a multiple bond proceeds in a more complex manner. It has been shown for 5,5,5-trichloropent-1-ene that the interaction of unsaturated trichloromethyl compounds with various metal carbonyls in combination with isopropyl alcohol or triethylsilane leads to a reduction product in a very low yield at high conversions of the initial polychloroalkene.[36] The reduction of perchloropropene and 1,1,2,3,3-pentachloropropene was more successful;[36] the results are presented in Table 9.

It is noteworthy that the hydrogenation of perchloropropene over PtO_2 (like the hydrogenation of trichloromethylalkanes) leads to a dimeric product—perchlorohexadiene.[37] An analogous result has been obtained also on treatment with CuCl in ethanol.[38]

The reduction of perchloropropene by the $Fe(CO)_5$ + $HSi(C_2H_5)_3$ system takes place non-selectively with formation of a mixture 1,1,2,3,3-pentachloropropene and 1,1,2,3-tetrachloropropene. An increase of temperature and an increase of the $(C_2H_5)_3SiH/C_3Cl_6$ ratio improve the yield of $C_3Cl_4H_2$. Table 9 shows that the reaction can be carried out both with formation of C_3Cl_5H as the main product (experiment 2) and with the preferential formation of $C_3Cl_4H_2$ (experiments 3 and 4). The stepwise course of the process is confirmed by the fact that 1,1,2,3,3-pentachloropropene is capable of being reduced under the same conditions to 1,1,2,3-tetrachloropropene (experiment 5). The attempts to reduce perchloropropene by $Fe(CO)_5$, $Mo(CO)_6$, $Mn_2(CO)_{10}$, and $Mo(N_2)_2 \cdot [(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ in isopropyl alcohol were unsuccessful.[36]

3. Mercaptans

Mercaptans are of interest as hydrogen donors becuase of their ready availability, the possible wide variety of their structures, and, in particular, the ease of homolysis of the S–H bond. The interaction of polychloroalkanes with various mercaptants in the presence of $Fe(CO)_5$, $Fe_2(CO)_6(SC_2H_5)_2$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ has been investigated in a wide range of examples, namely CCl_4, ααα-trichloroalkanes, ααaω-tetrachloroalkanes, and ααaβω-pentachloropentane.[39–41] The results of the reduction of 1,1,1,7-tetrachloroheptane by n-butanethiol or toluene-α-thiol in the presence of the metal carbonyls enumerated are presented in Table 10. $Re_2(CO)_{10}$ proved to be ineffective in this series too (experiment 8), while the effectiveness of $W(CO)_6$ is low (experiments 4 and 7). A significant difference was discovered between the $Fe(CO)_5$ + R'SH system and the analogous systems with $Mo(CO)_6$ or $Mn_2(CO)_{10}$. In the first instance the reaction has a distinct chain mechanism and the yield of $RCCl_2H$ in moles per mole of the metal carbonyl reaches 16 (experiment 1), while in the other two systems the yield is close to unity. With increase of the molar ratio $[MC]:[Cl(CH_2)_6CCl_3]$ to 0.5, a satisfactory yield of 1,1,7-trichloroheptane is attained (experiments 9 and 10). The increase of the molar ratio $[R'SH]:[RCCl_3]$ from 3:1 to 9:1 (experiments 2 and 5 and also 3 and 6) does not affect the yield of the reduced product. Carbon tetrachloride is smoothly reduced by $Fe(CO)_5$ in combination with butanethiol.[40] The same system does not

reduce chloroform under the same conditions.[40] In all cases the reduction of $RCCl_3$ proceeds selectively to $RCCl_2H$. It has been shown for a series of examples that the process considered obeys the equation

$$RCCl_3 + 2R'SH \xrightarrow{MC} RCCl_2H + R'SSR' + HCl.$$

The following mercaptans have been tested as hydrogen donors: C_4H_9SH,[39-41] $C_6H_5CH_2SH$,[39,41] t-C_4H_9SH[39,41] and C_6H_5SH.[39] The best results were obtained with butanethiol; the use of other mercaptans, in particular of toluene-α-thiol, results in an increase of the yield of side products (cf experiments 1, 9, and 10 with experiments 12–14). The reduction of other ααaω-tetrachloroalkanes (containing 3, 5, and 9 carbon atoms in the molecule) and also of 1,1,1-trichloroheptane[41] leads to results similar to those obtained for 1,1,1,7-tetrachloroheptane.

Table 10. The reduction of 1,1,1,7-tetrachloroheptane by mercaptans in the presence of metal carbonyls (140 °C, 3 h).[39,41]

No.	MC	$[Cl(CH_2)_6CCl_3] : [R'SH] : [MC]$	F, %	Yield, %	Q
		$n\text{-}C_4H_9SH$			
1	$Fe(CO)_5$	1 : 3 : 0.05	86	83	16.6
2	$Mn_2(CO)_{10}$	1 : 3 : 0.05	10	10	2.0
3	$Mo(CO)_6$	1 : 3 : 0.05	13	12	2.4
4	$W(CO)_6$	1 : 3 : 0.05	9	7	1.4
5	$Mn_2(CO)_{10}$	1 : 9 : 0.05	13	10	2.0
6	$Mo(CO)_6$	1 : 9 : 0.05	18	11	2.2
7	$W(CO)_6$	1 : 9 : 0.1	7	6	0.6
8	$Re_2(CO)_{10}$	1 : 3 : 0.1	3	1*	—
9	$Mn_2(CO)_{10}$	1 : 3 : 0.5	70	63*	1.2
10	$Mo(CO)_6$	1 : 3 : 0.5	46	42*	0.8
11	$Fe_2(CO)_6(SC_2H_5)_2$	1 : 2.5 : 0.02	—	80	33
		$C_6H_5CH_2SH$			
12	$Fe(CO)_5$	1 : 3 : 0.14	90	69*	4.9
13	$Mn_2(CO)_{10}$	1 : 3 : 0.51	86	68*	1.3
14	$Mo(CO)_6$	1 : 3 : 0.49	60	17*	0.3

*1,1,7-Trichlorohept-1-ene is also formed in yields of 1–3% (experiments 8–10), 16% (experiment 12), 7% (experiment 13), and 26% (experiment 14).

Table 11. The reduction of $CCl_3CHCl(CH_2)_3Cl$ (IV) and $CCl_3CH_2CH(CH_3)CH_2CH_2Cl$ (V) by n-buthanethiol in the presence of metal carbonyls (140 °C, 4 h).[41]

No.	MC	Compound	$[RCCl_3] : [n\text{-}C_4H_9SH] : [MC]$	F, %	Yield of $RCHCl_2$, %
1	$Fe(CO)_5$	(IV)	1 : 2.7 : 0.15	100	51*
2	$Fe(CO)_5$	(IV)	1 : 5.6 : 0.18	100	53*
3	$Mn_2(CO)_{10}$	(IV)	1 : 2.7 : 0.48	66	42*
4	$Fe(CO)_5$	(V)	1 : 2.7 : 0.15	100	68**
5	$Mn_2(CO)_{10}$	(V)	1 : 2.8 : 0.50	77	59

*$Cl(CH_2)_3CH = CCl_2$ (VII) was also obtained in yields of 42% (experiment 1), 30% (experiment 2), and 19% (experiment 3) as well as $Cl(CH_2)_3CCl = CCl_2$ (VIII) in yields of 4–5% (experiments 1 and 2).
**$CH_3CHClCH_2CH(CH_3)CH = CCl_2$ (X) was also obtained in 18% yield.

The reactions of 1,1,1,2,5-pentachloropentane (IV) and 1,1,1,5-tetrachloro-3-methylhexane (V) require special consideration (Table 11). As shown above, ααaβ-tetrachloro- and ααaββ-pentachloro-alkanes undergo two types of reactions with metal carbonyls—reduction and dechlorination. Table 11 shows that, on interaction with both $Fe(CO)_5$ and $Mn_2(CO)_{10}$ in the presence of butanethiol, compound (IV) also gives rise to the reduction product (VI) and the dechlorination product (VII) in comparable yields. The reaction of compound (V), containing in the α-position a methyl side group, with $Fe(CO)_5$ and C_4H_9SH affords, together with the reduction product (IX), also the dehydrochlorination product (X) in a significant yield. Dehydrochlorination does not occur in the presence of $Mn_2(CO)_{10}$.

It is noteworthy that the iron carbonyl complex containing RS ligands, namely $Fe_2(CO)_6(SC_2H_5)_2$, combined with n-butanethiol constitutes a system which is just as effective as the system comprising $Fe(CO)_5$ and n-butanethiol (Table 10, experiments 1 and 11).

4. Tertiary Amines and Amides

Triethylamine, dimethylaniline (DMA), pyridine, and quinoline have been tested as hydrogen donors in the $Fe(CO)_5$ + tertiary amine systems (Table 12). It has been shown for the reaction with 1,1,1-trichloro-octane (Table 12) that dimethylaniline (experiments 1, 2, 6, and 7) and triethylamine (III) are active as hydrogen donors in the reactions investigated, while pyridine (experiment 4) and quinoline (experiment 5) are not, as was to be expected.

Table 12. The reduction of trichloromethyl compounds $RCCl_3$ by tertiary amines in the presence of $Fe(CO)_5$ (130–140 °C).

No.	R	Amine	$[RCCl_3] : [amine] : [Fe(CO)_5]$	τ	Yield, %	Refs.
1	CH_3CH_2	DMA	1 : 2.5 : 0.04	18*	68	[35]
2**	$CH_3(CH_2)_6$	DMA	1 : 10.8 : 0.075	18	67	[1]
3**	$CH_3(CH_2)_6$	$(C_2H_5)_3N$	1 : 17 : 0.120	18	69	[1]
4**	$CH_3(CH_2)_6$	pyridine	1 : 11 : 0.075	18	12	[1]
5**	$CH_3(CH_2)_6$	quinoline	1 : 10.9 : 0.076	18	7	[1]
6	$CH_3COO(CH_2)_4$	DMA	1 : 2 : 0.046	5	66	[35]
7	$C_2H_5O(CH_2)_4$	DMA	1 : 2 : 0.073	10	61	[35]

*The reaction was continued until the complete conversion of the initial $RCCl_3$ (gas–liquid chromatographic analysis).
**The experiments were performed in chloroform.

An advantage of this system is the possibility of reducing trichloromethyl compounds containing substituents which are not inert in an acid medium. Thus 5-acetoxy-1,1,1-trichloropentane was reduced by $Fe(CO)_5$ + dimethylaniline with formation of 5-acetoxy-1,1-dichloropentane in 66% yield (experiment 6). 1,1,1-Trichloro-5-ethoxypentane is also reduced smoothyl (experiment 7).

The chemical reactions of dimethylaniline in the process investigated have been elucidated[35] in the reduction of 1,1,1-trichloropropane by the $Fe(CO)_5$ + DMA system. It was found that the main DMA reaction product is the diamine $(CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2$ (XI). The dimer $(CH_3)_2$. .$NC_6H_4CH_2N(CH_3)C_6H_5$ (XII), the trimer $(CH_3)_2NC_6H_4CH_2$. .$N(CH_3)C_6H_4CH_2N(CH_3)C_6H_5$, and methylaniline are also formed in low yields. It has been suggested that compound (XII) is formed initially and is then converted into compound

(XI) and methylaniline according to data of Braun and Kruber:[42]

$$(CH_3)_2NC_6H_4CH_2N(CH_3)C_6H_5 + C_6H_5N(CH_3)_2 \xrightarrow{H^+} (XI) + C_6H_5NHCH_3.$$
(XII)

Indeed it has been shown in a special experiment that heating of compound (XII) with DMA in the presence of diemthylaniline hydrochloride at 140 °C (i.e. under the conditions of the reduction experiments) leads to the formation of compound (XI).[35] On the basis of the foregoing, it is possible to describe the reduction of a *gem*-trichloromethyl compound by DMA + $Fe(CO)_5$ in terms of Scheme 2:

Scheme 2

$$RCCl_3 + 3C_6H_5N(CH_3)_2 \rightarrow RCCl_2H + (CH_3)_2NC_6H_4CH_2N(CH_3)C_6H_5 + \underset{(XII)}{} + C_6H_5N(CH_3)_2 \cdot HCl;$$

$$(XII) + C_6H_5N(CH_3)_2 \rightarrow (CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2 + C_6H_5NH(CH_3).$$
(XI)

Thus it has been demonstrated experimentally that the hydrogen donors in the processes investigated are indeed tertiary amines containing alkyl substituents. Scheme 2 shows that an equimolar amount of the hydrochloride of the amine employed is formed together with the dichloromethyl compound. The formation of the solid amine hydrochloride, which is difficult to separate from the reaction products, complicates their isolation and is an obstacle to the wide-scale employment of tertiary amines as components of the reduction system.

The $Fe(CO)_5$ + DMF system is active in the initiation of radical reactions, but DMF is a comparatively ineffective hydrogen donor. The above system can therefore be used conveniently in the study of the addition, telomerisation, and rearrangement of radicals in reactions involving trichloromethyl compounds where the reduction of the latter becomes a side process.[43]

Table 13. The reduction of polychloroalkanes $RCCl_3$ by DMF in the presence of $Fe(CO)_5$ (135–145 °C, 3–4 h).

No.	R	$[RCCl_3]:[DMF]:[Fe(CO)_5]$	*F*, %	Yield, %	Refs.
1	$Cl(CH_2)_2$	1 : 3 : 0.1	76	24	[17]
2	$Cl(CH_2)_4$	1 : 1 : 0.08	11	7*	[25]
3	$n\text{-}C_6H_{13}CHClCH_2$	1 : 1 : 0.15	72	28**	[28]

*$CHCl_2(CH_2)_3CHCl_2$ is also formed in 1.7% yield.
**The products of the 1,5-H, 1,6-H, 1,7-H, and 1,8-H rearrangements are also formed in an overall yield of 33%.

Certain data obtained in the study of the reactions of $RCCl_3$ with $Fe(CO)_5$ + DMF are presented in Table 13, which shows that, even in reactions with a high degree of conversion of the initial polychloroalkanes (experiments 1 and 3) and for the molar ratio $[RCCl_3]:[DMF] = 1:3$ (experiment 1) the yields of the reduced compound are 24–28% and the yields of the product formed as a result of the rearrangement of hydrogen in the long-chain tetrachloroalkanes is comparable to the yield of the reduced products.

5. Tetrahydrofuran Combined with Nickel Carbonyl

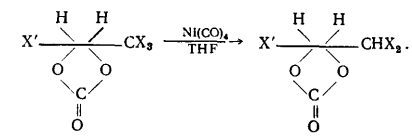
Nickel carbonyl occupies a special place among the metal carbonyls as a component of the reduction system.[44,45] Reduction of the $CHal_3$ group by an excess of $Ni(CO)_4$ under mild conditions in tetrahydrofuran (T) has been investigated (Table 14). The reduction of trichloro- and tribromo-diarylethanes proceeds in accordance with the following scheme:

$$Ar_2CHCX_3 \xrightarrow[THF]{Ni(CO)_4} Ar_2CHCHX_2;$$
(XIII, a and b) (XIV, a and b)
X=Br, Ar=C_6H_5 (a), X=Cl, Ar=*p*-ClC_6H_4 (b)

Table 14. The reduction of the CX_3 group by $Ni(CO)_4$ and THF {40 °C, $[RCX_3]:[THF] = 1:247$}.[45]

No.	RCX_3	X′	$[RCX_3]:[Ni(CO)_4]$	τ	$RCHX_2$	Yield, %
1	(XIIIa)	—	1:2	5	(XIVa)	86
2	(XIIIb)	—	1:2	48	(XIVb)	86
3	(XVa)	H	1:2	24	(XVIa)	38
4	(XVb)	Cl	1:2	48	(XVIb)	53
5	(XVc)	Br	1:2	48	(XVIc)	62
6	(XVd)	CN	1:5	28	(XVId)	48
7	(XVe)	CO_2CH_3	1:3.3	64	(XVIe)	70
8	(XVf)	OCH_3	1:2	48	(XVIf)	59
9	(XVIIa)	Br	1:3	5	(XVIIIa)	69
10	(XVIIb)	CO_2CH_3	1:2.5	2.5	(XVIIIb)	63
11	(XIX)	—	1:2.2	20	(XX)	60

Together with *gem*-trihalogenodiarylethanes, *gem*-trihalogenodioxilans have been reduced by this method. These labile compounds give rise to *gem*-dihalogenodioxolans under the selected conditions (40 °C), which gives rise to the possibility of a transition to aldehydosugars:



X=Cl: (XV,a—e) (XVI,a—e)
X=Br: (XVII, a and b) (XVIII, a and b)

The $Ni(CO)_4$ + THF system makes it possible to reduce selectively the CBr_3 group to $CHBr_2$ (Table 14, experiment 11). Thus 1,1,1,3-tetrabromo-5-phenylpentane (XIX) is reduced to 1,1,3-tribromo-5-phenylpentane (XX) in 60% yield. The reduction of the CBr_3 group, activated by aryl substituents as in compounds (XIIIa), proceeds under mild conditions with a high yield. When other solvents are used (isopropyl alcohol, dioxan, tetrahydrothiophen, cyclohexane, and benzene), there is virtually no reduction. When the reaction was carried out in DMF, the reduction product was obtained in a low yield and the reaction proceeded in a complex manner. An important difference of the reduction reaction in the presence of $Ni(CO)_4$ involves the use of a (2–5)-fold excess of $Ni(CO)_4$ relative to the trihalogenomethyl compound, which hinders the practical application of this method.

III. SYSTEMS BASED ON OTHER TRANSITION METAL COMPOUNDS

Apart from metal carbonyls, metal chlorides,[46] $H_2PtCl_6 \cdot 6H_2O$,[27,46] and $RuCl_2[(C_6H_5)_3P]$[47] can be used in combination with hydrogen donors (silicon hdyrides and secondary

alcohols). The results obtained are presented in Tables 15 and 16. Table 15 shows that copper, cobalt, and chromium chlorides and $H_2PtCl_6.6H_2O$ combined with triethylsilane reduce CCl_4 to $CHCl_3$ in satisfactory yields but not selectively—1–3% of CH_2Cl_2 is also formed despite the presence of an excess of CCl_4. The reduction of both CCl_4 and ααα-trichloroalkanes by $RuCl_2[(C_6H_5)_3P]_3$ in combination with isopropyl alcohol (Table 16) proceeds selectively and with a quantitative yield.

Table 15. The reduction of polychloromethanes ($XCCl_3$) by transition metal complexes and salts (TMS) in combination with hydrogen donors (HA)*.

No.	TMS	HA	X	[$XCCl_3$] : [HA] : [TMS]	T, °C	τ	Yield, %		Refs.
							$CHCl_3$	CH_2Cl_2	
1**	$CuCl_2 \cdot 2H_2O$	$(C_2H_5)_3SiH$	Cl	1 : 0.5 : 0.005	140	5	85	2	[46]
2**	$CoCl_2$	$(C_2H_5)_3SiH$	Cl	1 : 0.5 : 0.005	120	5	49	1	[46]
3**	$CrCl_2 \cdot xH_2O$	$(C_2H_5)_3SiH$	Cl	1 : 0.5 : 0.005	140	10	69	3	[46]
4**	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	Cl	1 : 0.5 : 0.005	75	10	58	2	[46]
5	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	Cl	1 : 3 : 0.0075	105	5	65	35	[27]
6	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	H	1 : 3 : 0.0075	145	5	—	93	[27]
7	$RuCl_2[P(C_6H_5)_3]_3$	iso-C_3H_7OH	Cl	1 : 5 : 0.003	145	2.5	98	—	[47]

*The degree of conversion of the initial polychloromethane was 100%.
**The yield was calculated relative to $(C_2H_5)_3SiH$.

Transition metal hydrides are frequently used for the hydrogenolysis of the C–Cl bond in CCl_4, mainly in order to demonstrate the presence of hydride hydrogen in the molecule. For example, $HMn(CO)_4P(C_6H_5)_3$ [48] and $MoH_2(\eta\text{-}C_5H_5)_2$ have been used as reducing agents.[49] It has been shown that $HMn(CO)_4P(C_6H_5)_3$ reduces CCl_4, taken in a large excess, to $CHCl_3$ at room temperature and the latter is reduced quantitatively to CH_2Cl_2 under the same conditions relative to $HMn(CO)_4P(C_6H_5)_3$. Coordination unsaturated $MoH_2(\eta\text{-}C_5H_5)_2$ reduces CCl_4 stepwise: to $CHCl_3$ at −10 °C and to CH_2Cl_2 at 30 °C. However, reactions of this type are of no preparative value, because they require an equimolar amount of the metal hydride.

Thus is has been established that the transition metal carbonyls $Fe(CO)_5$, $M(CO)_6$ (M = Cr, Mo, or W), and $M_2(CO)_{10}$ (M = Mn or Re) generate the $RCCl_3$ radicals on interaction with trichloromethyl compounds. $Fe(CO)_5$, $Mo(CO)_6$, and $Mn_2(CO)_{10}$ combined with hydrogen donors hydrogenate trichloromethyl compounds to dichloromethyl derivatives. It has been found that $Cr(CO)_6$ and $W(CO)_6$ are ineffective in this reaction. A new radical-chain method has been developed for the reduction of a wide variety of trichloromethyl compounds (ααα-tri, αααβ-tetra-, αααγ-tetra, and αααω-tetra-chloroalkanes, DDT and its analogues, and trichloromethyl compounds containing functional groups).

IV. THE MECHANISM OF THE REDUCTION REACTION. STUDY BY THE EPR METHOD

There exists much chemical evidence for the formation of the $R\dot{C}Cl_2$ radicals in accordance with Scheme 3. Thus it has been found that the chain transfer constants in the telomerisation of CCl_4 with propene initiated by $Cr(CO)_6$ [51] and $Mn_2(CO)_{10}$ [52] agree with the values obtained for the same reaction initiated by peroxides.

The formation of the $\dot{C}Cl_3$ radicals on treatment of CCl_4 with $Mo_2(CO)_6(\eta\text{-}C_5H_5)_3$ has been demonstrated.[53] The reaction of CCl_4 with $Fe(CO)_5$ in the absence of hydrogen donors and unsaturated compounds leads to the formation of CCl_3CCl_3,[54] which can be regarded as proof of the intermediate formation of the $\dot{C}Cl_3$ radical. The presence of the $\dot{C}Cl_3$ and $R\dot{C}Cl_2$ radicals obtained by treating trichloromethyl derivatives with metal carbonyls combined with a nucleophile has been frequently revealed by the addition to olefins and other unsaturated compounds.[5,55]

The radical character of the reduction of the CCl_3 group to $CHCl_2$ under consideration has been unambiguously established by EPR in an investigation of a photochemical interaction of polychloroalkanes containing the CCl_3 group with metal carbonyls and also of the reactions of certain hydrogen donors with metal carbonyls.

1. Reactions of Polychlorohydrocarbons with Metal Carbonyls

Certain data obtained using EPR in conjunction with the spin trapping method are presented in Table 17. In all cases it is possible to identify the nitroxy-radicals $RCCl_2N(\dot{O})R'$—the spin-adducts of the $R\dot{C}Cl_2$ radicals and the R'NO spin trapping agent (experiments 1–4, 6, 8–10, and 13–16), whose formation is described by Eqns (1)–(3) of Scheme 3:

Scheme 3

$$M(CO)_n \rightleftharpoons M(CO)_{n-1} + CO, \quad (1)$$

$$M(CO)_{n-1} + RCCl_3 \rightarrow ClM(CO)_{n-1} + R\dot{C}Cl_2, \quad (2)$$

$$R\dot{C}Cl_2 + R'NO \rightarrow RCCl_2N(\dot{O})R', \quad (3)$$

$$ClM(CO)_{n-1} + R'NO \rightarrow ClM(CO)_{n-1}N(\dot{O})R'. \quad (4)$$

Table 16. The reduction of polychloromethanes $RCCl_3$ by transition metal complexes (TMC) in combination with hydrogen donors (HA).

No.	TMC	HA	R	[$RCCl_3$] : [HA] : [TMC]	T, °C	τ	F, %	Yield, %	Refs.
1	$H_2PtCl_6 \cdot 6H_2O$	Cl_3SiH	$Cl(CH_2)_2$	1 : 1.3 : 0.0001	140	4.5	100	73	[2, 35]
2	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	$Cl(CH_2)_4$	1 : 1.3 : 0.0001	145	3	100	92	[2]
3*	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	$CHClC_3H_7$	1 : 1 : 0.0075	145	5	72	40	[27]
4	$RuCl_2[P(C_6H_5)_3]_3$	iso-C_3H_7OH	n-C_4H_9	1 : 9 : 0.002	150	3	98	quant.	[50]
5**	$RuCl_2[P(C_6H_5)_3]_3$	iso-C_3H_7OH	n-C_6H_{13}	1 : 9 : 0.002	150	3	98	quant.	[50]
6**	$RuCl_2[P(C_6H_5)_3]_3$	iso-C_3H_7OH	n-C_8H_{17}	1 : 9 : 0.002	150	3	98	quant.	[50]

*$CCl_2 = CHC_3H_7$ is also formed in 15% yield.
**Benzyl alcohol and cyclohexanol are also effective in this reaction.

Table 17. EPR spectroscopic parameters of the radicals obtained by the photochemical interaction of polychloroalkanes with metal carbonyls in the presence of spin trapping agents.

No.	Initiators	Polychloroalkane	Spin trapping agent	Radical*	a_N, G	a_{Cl}, G	a_H, G	Refs.
1	$Fe(CO)_5$, $Cr(CO)_6$ $Mo(CO)_6$, $W(CO)_6$ $Mn_2(CO)_{10}$	CCl_4	PBN	$CCl_3CH(C_6H_5)N(\dot{O})C(CH_3)_3$ (XXI)	13.4	—	1.3	[56, 57]
2	$Cr(CO)_6$, $W(CO)_6$ $Mn_2(CO)_{10}$	CCl_4	ND	$CCl_3N(\dot{O})Ar$ (XXII)	10.7	1.3	—	[57]
3	$[(C_2H_5)_3Sn]_2$	CCl_4	ND	(XXII)	10.7	1.3	—	[58]
4	$[(CH_3)_3CO]_2$	CCl_4	ND	(XXII)	10.7	1.3	—	[58]
5	$Fe(CO)_5$	CCl_4	MNP	$ClFe(CO)_4N(\dot{O})C(CH_3)_3$ (XXIII)	15.9	0.9	—	[56]
6	$Cr(CO)_6$	CCl_4	ND	(XXII) $ClCr(CO)_5N(\dot{O})Ar$ (XXIV) $Cl\dot{C}r(CO)_4(ArNO)$ $Cl^{53}\dot{C}r(CO)_4(ArNO)$ **	10.7 13.7 8.3 8.3	1.3 — — —	— — — —	[58] [59]
7	$Cr(CO)_6$	CCl_4	NB	$ClCr(CO)_5O\dot{N}Ar^1$ (XXV) $Cl\dot{C}r(CO)_4(ONAr^1)$	8.0 6.2	— —	*** —	[59]
8	$Cr(CO)_6$	CCl_4	MNP	$Cl^{53}\dot{C}r(CO_4[(CH_3)_3CNO]$ ** (XXVI) $CCl_3N(\dot{O})C(CH_3)_3$ (XXVII)	7.3 12.5	— 2.2	— —	[59]
9	$Fe(CO)_5$	$HCCl_3$	PBN	$CHCl_2CH(C_6H_5)N(\dot{O})C(CH_3)_3$ (XXI)	14.2	—	2.2	[56]
10	$(Me_3CO)_2$	$HCCl_3$	PBN	(XXI)	13.4	—	1.3	[56]
11	$Fe(CO)_5$	$HCCl_3$	MNP	(XXIII)	16.0	0.9	—	[56]
12	$Fe(CO)_5$	$C_6H_5CH_2Cl$	MNP	(XXIII) $C_6H_5CH_2N(\dot{O})C(CH_3)_3$	15.9 14.2	0.9 —	— 7.2	[61]
13	$Fe(CO)_5$	$ClCH_2CH_2CCl_3$	PBN	$Cl(CH_2)_2CCl_2CH(C_6H_5)N(\dot{O})C(CH_3)_3$	13.8	—	1.7	[62]
14	$(Me_3CO)_2$	$HCCl_2CH_2CCl_2H$	PBN	$HCCl_2CH_2CCl_2CH(C_6H_5)N(\dot{O})C(CH_3)_3$	13.8	—	1.7	[63, 64, 65]
15	$Mn_2(CO)_{10}$	$HCCl_2CCl_3$	MNP	$HCCl_2CCl_2N(\dot{O})C(CH_3)_3$ (XXVIII)	12.8	4.5 and 1.0	—	[57]
16	$(C_6H_5CO_2)_2$	$HCCl_2CCl_2H$	MNP	(XXVIII)	12.8	4.5 and 1.0	—	[57]

*Ar = 2,3,5,6-$(CH_3)_4C_6H$, Ar^1 = 2,4,6-$[(CH_3)_2C]_3C_6H_2$.
**$a_{^{53}Cr}$ = 18.6 G.
***a_H for the *meta*-position.

In a number of instances it has been possible to identify the spin-adducts of the metal carbonyl metal-centred radicals with the spin trapping agent (experiments 5, 6–8, 11, and 12) [Eqns.(2) and (4) of Scheme 3].

The reliability of the assignment of the signals in the spectrum has been confirmed by the literature data and also by the specific synthesis of the test radicals and of their spin adducts by known methods (Table 17, experiments 3, 4, 10, 14, and 16). Thus the radicals obtained on treatment with mononuclear Fe, Cr, Mo, and W carbonyls as well as the dinuclear Mn and Re carbonyls give rise to nitroxy-radicals on reaction with the spin trapping agents α-phenyl-t-butyl-nitrone (PBN),[56,57,60] nitrosodurene (ND),[57,59,60] and 2-methyl-2-nitrosopropane (MNP)[60] (Table 17) (experiments 1, 2, 6, and 8). The parameters of the spectra of these radicals agreed with the literature data.[58,64] In addition it has been shown that the parameters of the spectra of the nitroxy-radicals obtained by the reaction of metal carbonyls with CCl_4 in the presence of ND agree with the parameters of the radicals obtained by a specific synthesis involving the

photochemical interaction of hexaethyldistannane (experiment 3) or t-butyl peroxide (TBP)[58] (experiment 4) with CCl_4 in the presence of ND.

In conformity with the known rules, $\dot{C}Cl_3$ radicals have been obtained by the reaction of $CHCl_3$ with TBP (experiment 10), while the reaction with $Fe(CO)_5$ yielded $\dot{C}HCl_2$ radicals (experiment 9). Their spin adducts with PBN gave rise to different spectra.[56] The treatment of CCl_4 and $CHCl_3$ with $Fe(CO)_5$ in the presence of MNP gave rise to the same spectrum, namely that of the spin-adducts of the iron-containing radical (XXIII) (experiment 5, 11, and 12).

The radicals $ClCH_2CH_2\dot{C}Cl_2$ have been obtained by two procedures: by treating $ClCH_2CH_2CCl_3$ with $Fe(CO)_5$ and by the reaction of benzoyl peroxide with $ClCH_2CH_2CHCl_2$. The EPR spectroscopic parameters of the spin-adducts of these radicals with PBN are identical (experiments 13 and 14).

The reaction of CCl_3CHCl_2 with $MN_2(CO)_{10}$ in the presence of MNP yielded additional information, namely, in conformity with the general rule,[63-65] the two β-chloroatoms in the nitroxy-radical (XXVIII) are non-equivalent (experiment 15). The same nitroxy-radical has been obtained by a specific synthesis—by abstracting hydrogen from $HCCl_2CCl_2H$ by phenyl radicals in the presence of MNP.[63,65] The hyperfine interaction constants (HIC) for the nitroxy-radicals obtained by the two procedures have the same values (experiments 15 and 16).

Much information has been obtained[59] as a result of the study of the radicals formed on treatment of CCl_4 with $Cr(CO)_6$ in the presence of ND (experiment 6), 2,4,6-tris-(t-butyl)nitrosobenzene (NB) (experiment 7), and MNP (experiment 8). Not only the spin adducts of the $\dot{C}Cl_2$ radicals with the spin trapping agent (experiments 6 and 8) but also the spin-adducts of the chromium-containing radicals (XXIV) and (XXV) (experiments 6 and 7) were identified in these experiments. In addition, the chromium-centred radicals $Cl\dot{C}r(CO)_4(ArNO)$ and $Cl^{53}\dot{C}r(CO)_4(ArNO)$ (experiment 6), $ClCr(CO)_4(ONAr')$ (experiment 7), and the radical (XXVI) (experiment 8) were identified. The richness of the information in this instance arises because in the experiments a sufficient concentration of the chromium-centred radicals had been obtained (experiments 6 and 8), it was possible to identify in the EPR spectrum a quartet of triplets due to ^{53}Cr having $I = 3/2$ (the content of this isotope in natural chromium is 9.5%).[66] It is noteworthy that, when $Cr(CO)_6$ is allowed to react with CCl_4, the resulting $Cl\dot{C}r(CO)_5$ radicals add to ND at the nitrogen atom with formation of the spin-adducts (XXIV) (experiment 6) and to NB via the oxygen atom with formation of the radical (XXV) (experiment 7). The signals in the spectrum were assigned to the radical (XXV) taking into account the data quoted by Terabe and Konaka.[67]

2. Photochemical and Thermal Interactions of Metal Carbonyls with Hydrogen Donors

The interactions of mononuclear and dinuclear metal carbonyls with silicon hydrides, isopropyl alcohol, hexamethylphosphoramide (HMP), and DMF have been investigated. Under certain conditions (ultraviolet irradiation), these hydrogen donors do not constitute an inert medium for metal carbonyls. It has been established by EPR that, under ultraviolet irradiation, the reaction of hydrogen donors with metal carbonyls can proceed via at least two pathways. It has been shown for a series of hydrogen donors that the latter are incorporated in the coordination sphere of the metal carbonyl, substituting a CO group. It has been shown[59] that the reaction of $Cr(CO)_6$ with CCl_4 in the presence of MNP and HMP (Table 18, experiment 1) produces, together with the radicals (XXVII) and (XXVI) identified in the absence of HMP (Table 17, experiment 8), also the radicals (XXIX) obtained as a result of the substitution of the CO groups in the metal carbonyl by HMP and MNP molecules. The spin-adducts of the radicals $OP[N(CH_3)_2]_3\dot{M}n(CO)_4$ were identified in the reaction of $Mn_2(CO)_{10}$ with HMP in the presence of MNP and ND (experiment 12).

On the other hand, certain hydrogen donors react with metal carbonyls to form metal carbonyl hydrides.[78] The radicals $(C_2H_5)_3\dot{S}i$ [67,68] $(CH_3)_2\dot{C}OH$, and $OP[(N(CH_3)_2]_2\cdot\dot{N}(CH_3)CH_2$,[69] identified in the form of the spin-adducts with the NB, ND, and MNP spin trapping agents, have been obtained by abstracting hydrogen from $(C_2H_5)_3SiH$ (Table 18, experiments 2, 5, and 6),[67,68] iso-C_3H_7OH (experiments 7–9), and HMP (experiments 10 and 11). The formation of radicals with an unpaired electron on the silicon atom in the reactions of $M(CO)_n$ with $(C_2H_5)_3SiH$ has been confirmed by the hyperfine structure (HFS) of the EPR spectra resulting from the splitting by the nuclei of the ^{29}Si isotope, having a magnetic moment $I = 1/2$ (the content of the ^{29}Si isotope in the natural element is 4.7%).[66]

The reaction of DMF with metal carbonyls results in the formation of complex mixtures of radicals (experiments 13–17), including a radical obtained by the abstraction of hydrogen from the methyl group of DMF and identified in the form of a spin-adduct with MNP (XLI) (experiment 15). In addition spin-adducts of radicals to which the structures $(CH_3)_2\dot{N}$ and $(CH_3)_2\dot{N}(O^-)CH$ have been attributed, were identified (experiment 13). The intermediate formation of metal carbonyl hydrides, which were not identified, has been postulated for the reactions of the metal carbonyls with iso-C_3H_7OH, HMP, and DMF; these hydrides apparently ultimately transfer hydrogen to a molecule of the spin trapping agent.[69] Indeed, the spin-adducts of MNP with hydrogen (XXXIII) (experiments 7, 9, 10, 14, and 17) and the spin-adducts of ND with hydrogen (XXXIV) (experiments 8, 11, and 16) have been identified. The formation of transition metal hydrides on interaction of transition metal complexes with alcohols have been described in some communications.[70,71]

The effectiveness of the transition metal hydride complexes as reductants has been demonstrated in a number of reports [see, for example, the reduction of CCl_4 by $HMn(CO)_4\cdot P(C_6H_5)_3$ or $MoH_2(\eta\text{-}C_5H_5)_2$ (in Section III of the present review)]. The authors present evidence in support of the radical character of these reactions.

On the basis of the data presented above, it is possible to consider the mechanism of the reduction reaction as a whole, when the reacting system contains a trichloromethyl derivative, a metal carbonyl, and a hydrogen donor.

The radical-chain mechanism of the above reactions has been unambiguously established. This means that the mechanism involves, as usual, three stages: chain initiation, propagation, and termination.

In broad outline, without considering the reactions of the hydrogen donor, which will be done below, the initiation consists in the dissociation of the mononuclear metal carbonyl with formation of the coordination-unsaturated species $M(CO)_{n-1}(B)$ and CO [reaction (1), Schemes 3 and 4]. The species (B) abstract chlorine from $RCCl_3$ with formation of the radical $\dot{R}CCl_2$ [stage (2), Schemes 3 and 4]. In the presence of dinuclear Mn and Re carbonyls the initial initiation stage involves dissociation in accordance with the scheme

$$(CO)_5M—M(CO)_5 \rightleftarrows 2\dot{M}(CO)_5. \quad (C)$$

The radicals (C) abstract chlorine from $RCCl_3$.

Table 18. EPR spectroscopic parameters of the radicals obtained by the photochemical or thermal interaction of metal carbonyls (MC) with hydrogen donors (HA).

No.	MC	HA	Spin trapping agent*	Radical[2*]	a_N, G	Other HFI constants		Refs.
						X	a_X, G	
1	$Cr(CO)_6$	$OP[N(CH_3)_2]_3+CCl_4$	MNP	(XXVII)	12.5	Cl	2.2	[59]
				(XXVI)	7.3	^{53}Cr	18.6	
				$ClCr(CO)_3[ONC(CH_3)_3]\{OP[N(CH_3)_2]_3\}$ (XXIX)	7.3	P	3.3	
2	$Fe(CO)_5$	$(C_2H_5)_3SiH$	NB	$(C_2H_5)_3SiON\dot{A}r^1$ (XXX)	10.3	H-м	1.9	
				$(C_2H_5)_3{}^{29}SiON\dot{A}r^1$ (XXXI)	10.3 —	H-м ^{29}Si	1.9 5.3	[67,68]
3	$Fe(CO)_5$	$(C_2H_5)_3SiH+CCl_4$	ND	(XXII)	10.7	Cl	1.3	[67]
4	$Cr(CO)_6$	$(C_2H_5)_3SiH+CCl_3CCl_2H$	MNP	(XXVIII)[5*]	12.5	Cl(1)	4.3	
				$ClCr(CO)_4[ONC(CH_3)_3]$[6*]	— 7.3	Cl(2)	1.1	[67]
				$XCr(CO)_4[ONC(CH_3)_3]$[7*]	6.3	—	—	
5	$M(CO)_6$ (M=Cr, Mo, W)	$(C_2H_5)_3SiH$	NB	(XXX)+(XXXI)	10.3 —	H-м ^{29}Si	1.9 5.3	[67]
6	$M_2(CO)_{10}$, (M=Mn, Re)	$(C_2H_5)_3SiH$	NB	(XXX)+(XXXI)	10.3 —	H-м ^{29}Si	1.9 5.3	[67]
7	$Fe(CO)_5$	*изо*-C_3H_7OH	ND	$(CH_3)_2C(OH)N(\dot{O})Ar$ (XXXII)	14.0	—	—	[69]
			MNP	$HN(\dot{O})C(CH_3)_3$ (XXXIII)	13.3	H	11.8	
8	$Mn_2(CO)_{10}$	*изо*-C_3H_7OH	ND	$Mn(CO)_5N(\dot{O})Ar$ (XXXII)	16.1 14.0	Mn —	8.9 —	[69]
				$HN(\dot{O})Ar$ (XXXIV)	12.8	H	12.0	
9	$M(CO)_6$ (M=Cr, Mo, W)	*изо*-C_3H_7OH	MNP ND	(XXXIII) (XXXII)	13.3 14.0	H —	11.8 —	[69]
10	$M(CO)_6$ (M=Cr, Mo, W) $M_2(CO)_{10}$ (M=Mn, Re)	$OP[N(CH_3)_2]_3$	MNP	$OP[N(CH_3)_2]$ $N(CH_3)CH_2N(\dot{O})C(CH_3)_3$ (XXXV)	14.5 —	N H	3.1 7.8	[69]
				(XXXIII)	— 13.3	P H	0.8 11.8	
11	$M(CO)_6$ (M=Cr, Mo, W) $M_2(CO)_{10}$ (M=Mn, Re)	$OP[N(CH_3)_2]_3$	ND	$OP[N(CH_3)_2]_2$ $N(CH_3)CH_2N(\dot{O})Ar$ (XXXVI)	13.5 —	N H(1)	2.0 10.6	[69]
				(XXXIV)	— 12.8	H(2) H	8.3 12.0	
12	$Mn_2(CO)_{10}$	$OP[N(CH_3)_2]_3$	MNP	$OP[N(CH_3)_2]_3$ $Mn(CO)_4N(\dot{O})C(CH_3)_3$ (XXXVII)	16.6	Mn	11.7	[69]
			ND	$OP[N(CH_3)_2]_3Mn(CO)_4N(\dot{O})Ar$ (XXXVIII)	17.3 —	Mn P	12.7 2.1	
13	$M(CO)_6$ (M=Cr, Mo, W)	$HC(O)N(CH_3)_2$	ND	$(CH_3)_2N(O^-)CH(\dot{O})NAr$ (XXXIX)	13.7	H	7.9	[69]
				$(CH_3)_2N(\dot{O})NAr$ (XL)	13.7	N	3.7	
14	$Cr(CO)_6$	$HC(O)N(CH_3)_2$	MNP	(XXXIII)	13.3	H	11.8	[69]
15	$Mo(CO)_6$	$HC(O)N(CH_3)_2$	MNP	$HC(O)N(CH_3)CH_2N(\dot{O})C(CH_3)_3$ (XLI)	15.3 — —	N H(1) H(2)	2.4 10.2 9.1	[69]
16	$Mn_2(CO)_{10}$	$HC(O)N(CH_3)_2$	ND	$(CO)_5MnOC(H)N(CH_3)_2$ | $N(\dot{O})Ar$ (XLII)	13.7	H	7.9	[69]
				(XXXIV)	12.8	H	12.0	
17	$Mn_2(CO)_{10}$	$HC(O)N(CH_3)_2$	MNP	$(CO)_5MnC(H)N(CH_3)_2$ | $ON(\dot{O})Ar$ (XLIII)	23.3	—	—	[69]
				(XXXIII)	13.3	H	11.8	

*For the significance of the abbreviations used for the spin trapping agents, see text.

[2]*For the designation of Ar and Ar^1, see the footnotes to Table 17.

[3]*g = 1.9983.

[4]*g = 1.9981.

[5]*Concerning the non-equivalence of the two hydrogen atoms in compound (XXVIII) (see Gasanov and Freidlina[65]).

[6]*g = 1.9993.

[7]*g = 1.9982.

Chain termination can proceed, as usual, via many pathways. One of the possible chain termination pathways has been established experimentally. It has been found that some of the $R\dot{C}Cl_2$ radicals recombine during the reduction process with formation of RCl_2CCl_2R, which is dechlorinated to RCCl = CClR whose formation as a side product has been demonstrated in many instances [stage (5) of Scheme 4]. The most complex component of the scheme is the chain propagation stages in which the principal reaction products are generated. These stages apparently depend on the nature of all the components of the reaction and its conditions. At least three types of chain propagation may be noted:

Scheme 4

$$M(CO)_n \rightleftarrows M(CO)_{n-1} + CO, \quad (1)$$
$$M(CO)_{n-1} + RCCl_3 \rightarrow ClM(CO)_{n-1} + R\dot{C}Cl_2, \quad (2)$$
(initiation)

$$R\dot{C}Cl_2 + HA \rightarrow RCl_2H + A^{\cdot}, \quad (3)$$
$$A^{\cdot} + ClM(CO)_{n-1} \rightarrow ACl + M(CO)_{n-1}, \quad (4)$$
$$HA + M(CO)_{n-1} \rightarrow HM(CO)_{n-1} + A^{\cdot}, \quad (3a)$$
$$RCCl_3 + A^{\cdot} \rightarrow R\dot{C}Cl_2 + ACl, \quad (3b)$$
$$R\dot{C}Cl_2 + HM(CO)_{n-1} \rightarrow RCl_2H + M(CO)_{n-1}, \quad (3c)$$
$$ClM(CO)_{n-1} + HA \rightarrow A^{\cdot} + HCl + M(CO)_{n-1}, \quad (4a)$$
(chain propagation (three variants))

$$2R\dot{C}Cl_2 \rightarrow RCl_2CCl_2R \rightarrow RCCl{=}CClR\} \text{ chain termination}. \quad (5)$$

Firstly, the $R\dot{C}Cl_2$ radicals can abstract hydrogen directly from the hydrogen donor [stage (3)]; the reaction chain is propagated by the $M(CO)_{n-1}$ species [stage (4)]. Secondly, the $R\dot{C}Cl_2$ radicals can abstract hydrogen from the metal carbonyl hydride and not from the hydrogen donor [stage (3c)]; the chain is again propagated by the same $M(CO)_{n-1}$ species. Stage (4a) differs from stages (3), (4), and (3a)–(3c) by the fact that $ClM(CO)_{n-1}$ reacts with the hydrogen donor to form the chain-propagating $M(CO)_{n-1}$ species.

Chemical investigations have established that a hydrogen atom is split off from the hydrogen donor during the reaction with formation of the hydrogen donor oxidation products: acetone, chlorotriethylsilane, the disulphide RSSR, and di- and tri-amides from isopropyl alcohol, silicon hydrides, mercaptans, and dimethylaniline respectively. It has been demonstrated unambiguously by EPR that this splitting off process has a radical mechanism, since the $(CH_3)_2\dot{C}OH$,[69] $(C_2H_5)_3\dot{S}i$,[67,68] $OP[N(CH_3)_2]N(CH_3)\dot{C}H_2$,[69] and $HC(O)N.(CH_3)\dot{C}H_2$ [69] radicals, derived from isopropyl alcohol, triethylsilane, HMP, and DMF respectively, have been identified.

Taking into account the entire information contained in the EPR spectra obtained, the reaction schemes incorporating stages involving reactions of the hydrogen donors are considered below. Schemes 5 and 6, proposed by Gasanov,[69] are presented below in relation to the reactions of $Mn_2(CO)_{10}$ with HMP and the reactions of metal carbonyls with DMF:

Scheme 5

$$Mn_2(CO)_{10} \rightleftarrows 2\dot{M}n(CO)_5,$$
$$\dot{M}n(CO)_5 + OP[N(CH_3)_2]_3 \rightarrow HMn(CO)_5 + OP[N(CH_3)_2]_2N(CH_3)\dot{C}H_2, \quad (XLIV)$$
$$(XLIV) + RNO \rightarrow OP[N(CH_3)_2]_2N(CH_3)CH_2N(\dot{O})R, \quad (XXXV),\ (XXXVI)$$
$$HMn(CO)_5 \rightarrow HC(O)Mn(CO)_4,$$
$$HC(O)Mn(CO)_4 + OP[N(CH_3)_2]_3 \rightarrow HC(O)Mn(CO)_4\{OP[N(CH_3)_2]_3\},$$
$$HC(O)Mn(CO)_4\{OP[N(CH_3)_2]_3\} \rightarrow H\dot{C}O + OP[N(CH_3)_2]_2\dot{M}n(CO)_4,$$
$$H\dot{C}O + RNO \rightarrow HN(\dot{O})R, \quad (XXXIII),\ (XXXIV)$$
$$OP[N(CH_3)_2]_3\dot{M}n(CO)_4 + RNO \rightarrow OP[N(CH_3)_2]_3Mn(CO)_4N(\dot{O})R; \quad (XXXVII),\ (XXXVIII)$$
$$R = C(CH_3)_3;\ 2,\ 3,\ 5,\ 6\text{-}(CH_3)_4C_6H.$$

The radicals (XLIV) have been obtained by an independent procedure involving the treatment of HMP with TBP and have been identified by EPR using the same trapping agents[78] as in Scheme 3. The radicals (XXXIII)–(XXXVIII) have been identified by EPR.

Scheme 6

$$M(CO)_n + HC(O)N(CH_3)_2 \rightarrow [M(CO)_n]^{\ddagger} + H\dot{C}(O^-)N(CH_3)_2,$$
$$(XLV) \rightarrow H\dot{C}O + \bar{N}(CH_3)_2, \quad (XLV)$$
$$\bar{N}(CH_3)_2 + [M(CO)_n]^{\ddagger} \rightarrow \dot{N}(CH_3)_2 + M(CO)_n, \quad (XLVI)$$
$$H\dot{C}O + HC(O)N(CH_3)_2 \rightarrow H_2 + HC(O)N(CH_3)\dot{C}H_2 + CO, \quad (XLVII)$$
$$(XLVI) + HC(O)N(CH_3)_2 \rightarrow HN(CH_3)_2 + (XLVII).$$

In addition, the reaction of DMF with $Mn_2(CO)_{10}$ involves the formation of adducts by $Mn(CO)_5$ via the carbonyl group, namely $(CO)_5MnCH(\dot{O})NMe_2$ (XLVIII) and $(CO)_5MnO\dot{C}HN.(CH_3)_2$ (XVIX).

The radicals (XLV)–(XLIX) have been detected by EPR using MNP and MD as the spin trapping agents (Table 18, experiments 13–17).

It is noteworthy that the hypothesis that the formyl radicals $H\dot{C}O$, unidentified by Gasanov,[69] are formed in Schemes 5 and 6 has analogies in the literature. Thus it has been assumed[71,72] that the exchange of a carbonyl group in $HMn(CO)_5$ for ^{13}CO proceeds via the 1,2-migration of the CO group with its subsequent ejection from the rearranged molecule:

$$HMn(CO)_5 \xrightarrow{1,2\text{-}CO} HC(O)Mn(CO)_4 \xrightarrow{+{}^{13}CO} HC(O)Mn(CO)_4({}^{13}CO) \xrightarrow{-CO} HMn(CO)_4({}^{13}CO).$$

This is analogous to the formation of $HC(O)Mn(CO)_4$ in one of the stages of Scheme 3.

It has been postulated[73] that vinyl polymerisation initiated by $HMn(CO)_5$ can also involve the formation of $H\dot{C}O$ radicals as a result of the 1,2-migration of the CO group with subsequent elimination of the formyl radical.

The data obtained show that the interaction of metal carbonyls with hydrogen donors has a radical character. Its mechanism is extremely complex and depends both on the nature of the metal carbonyl and on the structure of the hydrogen donor. It is natural to suppose that, apart from the reactions indicated in Schemes 5 and 6, the radicals formed as intermediates in the trichloromethyl derivative + metal carbonyl + hydrogen donor system can also enter into other reactions. It has been shown that metal carbonyls in the systems investigated interact not only with the trichloromethyl derivatives but also with the hydrogen donors and thus participate both in the chain initiation stage and in the chain propagation stages. Whereas all the Fe, Cr, Mo, and W monocarbonyls and the dinuclear Mn and Re carbonyls investigated are capable of abstracting Cl from the CCl_3 group, i.e. of participating in the initiation stage, the successful reduction of CCl_3 to the $CHCl_2$ group can be achieved only with the aid of $Fe(CO)_5$, $Mo(CO)_6$, and $Mn_2(CO)_{10}$. Evidently this can be accounted for by the difficulties in other stages of the process. In particular there is a significant difference between the carbonylation capacities of the Mn and Re compounds; carbonylation by the Mn compounds proceeds much more readily[74–77] [cf Stage (4) in Scheme 3].

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Thus a fundamentally new radical-chain method for the reduction of trichloromethyl compounds to dichloromethyl derivatives by iron, molybdenum and manganese carbonyls

combined with hydrogen donors has been examined in the present review. The stages involved in a series of radical reactions in the $RCCl_3$ + MC + HA systems have been confirmed experimentally by EPR in conjunction with a spin trapping technique and also by chemical studies. It has been shown that iron, molybdenum, and manganese carbonyls participate not only in the initiation stage (with formation of $R\dot{C}Cl_2$) but also in the subsequent stages involving the formation of dichloromethyl compounds on interaction with trichloromethyl compounds in the presence of hydrogen donors. It has been found that the metal carbonyls interact not only with the trichloromethyl compounds but also with the hydrogen donors (alcohols, silicon hydrides, and DMF) via a radical mechanism.

The process schemes examined are important not only for the understanding and regulation of the reactions involving the reduction of CCl_3 to $CHCl_2$ but also for more complex systems. In particular, chain radical addition and telomerisation reactions in trichloromethyl compound + metal carbonyl + nucleophilic coinitiator + unsaturated compound systems must include a series of stages similar to those characterised in the present review.

REFERENCES

1. E.Ts.Chukovskaya, A.A.Kamyshova, and R.Kh.Freidlina, Zhur.Org.Khim., 1967, **3**, 1358.
2. E.Ts.Chukovskaya, N.A.Kuz'mina, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1967, **175**, 1301.
3. R.Kh. Freidlina and A.B.Belyavskii, Dokl.Akad.Nauk SSSR, 1959, **127**, 1027.
4. R.Kh.Freidlina and A.B.Belyavskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1961, 177.
5. E.Ts.Chukovskaya, R.G.Gasanov, I.I.Kandror, and R.Kh.Freidlina, Zhur.Vses.Khim.Obshch.im. Mendeleeva, 1979, **24**, 161.
6. M.Julia, G.Thuillier, and L.Saussine, J.Organomet. Chem., 1979, **177**, 211.
7. R.Kh.Freidlina, F.K.Velichko, E.Ts.Chukovaskaya, M.Ya.Khorlina, B.A.Krentsel', D.E.Il'ina, N.V.Kruglova, L.S.Mayants, and R.G.Gasanov, "Metody Elementoorganicheskoi Khimii. K Lor. Alifaticheskie Soedineniya" (Methods of Organoelemental Chemistry. Chlorine. Aliphatic Compounds), Izd.Nauka, Moscow, 1973, Chapters IV, V, and XI.
8. C.M.Starks, "Free Radical Telomerisation" Acad.Press, New York 1974.
9. A.N.Nesmeyanov, L.I.Zakharkin, and T.A.Kost, Izv. Akad.Nauk SSSR, Ser.Khim., 1955, 657.
10. B.P. 652768 (1951); Chem.Abs., 1952, **46**, 1577.
11. E.Ts.Chukovskaya, M.A.Rozhkova, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1973, **212**, 382.
12. E.Ts.Chukovskaya, M.A.Rozhkova, N.A.Kuz'mina, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 354.
13. E.C.Chukovskaya, R.Kh.Freidlina, and N.A.Kuzmina, Synthesis, 1983, 773.
14. E.Ts.Chukovskaya, N.A.Kuz'mina, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 2343.
15. R.Kh.Freidlina and A.B.Terent'ev, in "Advances in Free Radical Chemistry", London, Heyden, 1980, Vol.6, p.11.
16. N.A.Kuz'mina, E.Ts.Chukovskaya, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1980, **254**, 890.
17. T.T.Vasil'eva, N.V.Kruglova, and T.V.Tarasova, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1543.
18. N.V.Kruglova and T.N.Skokova, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 867.
19. T.T.Vasil'eva and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 2373.
20. N.A.Kuz'mina, N.P.Zhiryukhina, E.Ts.Chukovskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2090.
21. L.N.Kiseleva, N.A.Rybakova, N.A.Kuz'mina, T.T.Vasil'eva, and V.I.Dostovalova, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2095.
22. E.Ts.Chukovskaya, N.A.Kuz'mina, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1969, **188**, 1073.
23. E.Ts.Chukovskaya, N.A.Kuz'mina, M.A.Rozhkova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1345.
24. E.Ts.Chukovskaya, M.A.Rozhkova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1582.
25. T.T.Vasil'eva, L.N.Goncharova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 1182.
26. T.T.Vasil'eva, N.V.Kruglova, V.I.Dostovaiova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1856.
27. E.Ts.Chukovskaya and N.A.Kuz'mina, Izv.Akad.Nauk SSSR, Ser.Khim., 1969, 472.
28. N.A.Rybakova and L.N.Kiseleva, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1636.
29. M.G.Katz, A.Horowitz, and L.A.Rajbenbach, Trans. Faraday Soc., 1971, **67**, 2354.
30. M.Downie and J.B.Lee, Tetrahedron Letters, 1968, 4951.
31. T.Hirao, S.Kohno, Y.Ohahira, and T.Agawa, Bull. Chem.Soc.Japan, 1983, 56.
32. N.A.Kuz'mina, E.Ts.Chukovskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1206.
33. K.Rühlman, Z.Chem., 1956, 130.
34. N.V.Kruglova and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 388.
35. R.Kh.Freidlina, E.Ts.Chukovskaya, N.A.Kuz'mina, and A.A.Kamyshova, Izv.Akad.Nauk SSSR, Ser.Khim., 1968, 1319.
36. E.Ts.Chukovskaya, N.A.Kuz'mina, N.V.Blinova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 2061.
37. E.C.Ladd and H.Sargent, US P.2688043 (1954); Chem.Abs., 1955, **49**, 13287.
38. H.J.Prins, Rec.Trav.Chim., 1949, **69**, 419.
39. R.G.Petrova and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 1574.
40. R.G.Petrova and I.I.Kandror, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 2340.
41. R.G.Petrova, T.D.Churkina, I.A.Gokikova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 1816.
42. J.Braun and O.Kruber, Ber., 1913, **46**, 3952.
43. R.Kh.Freidlina and E.C.Chukovskaya, Synthesis, 1974, 484.

44. T.Kunieda, T.Tamura, and T.Takizawa, Chem.Comm., 1972, 885.
45. T.Kunieda, T.Tamura, and T.Takizawa, Chem.Pharm. Bull., 1977, **25**, 1749.
46. Y.Nagai, H.Matsumoto, T.Yagihara, and K.Morishita, J.Chem.Soc.Japan, Ind.Sect., 1968, **71**, 1112; Chem. Abs., 1969, **70**, 4187.
47. Y.Sasson and G.L.Rempel, Tetrahedron Letters, 1974, 3221.
48. B.L.Booth and B.L.Shaw, J.Organomet.Chem., 1972, **43**, 369.
49. A.Nakamura, J.Organomet.Chem., 1979, **164**, 183.
50. Y.Sasson and G.L.Rempel, Synthesis, 1975, 448.
51. N.A.Grigor'ev, A.L.Tumanskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 199.
52. N.A.Grigor'ev, A.L.Tumanskaya, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1122.
53. R.Davis and J.F.Groves, J.Organometal.Chem., 1981, **215**, 23.
54. E.K.Gustorf, M.J.Jum, H.Huhn, and G.O.Schenck, Angew.Chem., 1963, **75**, 1120.
55. R.Kh.Freidlina, F.K.Velichko, and A.B.Terent'ev, Uspekhi Khim., 1984, 370 [Russ.Chem.Rev., 1984(3)].
56. R.G.Gasanov and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1977, **235**, 1309.
57. R.G.Gasanov and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1979, **246**, 111.
58. S.Terabe, K.Kuruma, and R.Konaka, J.Chem.Soc., Perkin Trans., II, 1973, 1252.
59. R.G.Gasanov and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1980, **254**, 113.
60. R.G.Gasanov, L.V.Ivanova, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1980, **255**, 1156.
61. T.T.Vasil'eva, R.G.Gasanov, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1290.
62. R.Kh.Freidlina, R.G.Gasanov, and N.A.Grigor'ev, Dokl.Akad.Nauk SSSR, 1978, **242**, 354.
63. G.A.Razuvaev, G.A.Abakumov, and V.K.Cherkasov, Dokl.Akad.Nauk SSSR, 1973, **212**, 374.
64. C.M.Camaggi, R.J.Holman, and M.J.Perkins, J.Chem. Soc., Perkin Trans. II, 1972, 501.
65. R.G.Gasanov and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2242.
66. J.E.Wertz and J.R.Bolton, "Electron Spin Resonance; Elementary Theory and Practical Applications" (Translated into Russian), Izd.Mir, Moscow, 1975, p.510.
67. S.Terabe and R.Konaka, J.Chem.Soc., Perkin Trans. II, 1973, 369.
68. R.G.Gasanov and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2178.
69. R.G.Gasanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, (in the Press).
70. J.Chatt, B.L.Shaw, and A.E.Field, J.Chem.Soc., 1964, 3466.
71. A.Berry and T.L.Brown, J.Organomet.Chem., 1971, **33**, 67.
72. A.Wojcicki, Adv.Organometal.Chem., 1973, **11**, 87.
73. C.H.Bamford and S.U.Mullic, J.Chem.Soc., Faraday Trans. I, 1978, **74**, 1634.
74. H.Berke and R.Hoffman, J.Amer.Chem.Soc., 1978, **100**, 7224.
75. B.H.Byers and T.L.Brown, J.Organomet.Chem., 1977, **127**, 181.
76. B.H.Byers and T.L.Brown, J.Amer.Chem.Soc., 1975, **97**, 947.
77. R.G.Gasanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1134.
78. P.Krusic, J.Amer.Chem.Soc., 1981, **103**, 2131.

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