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The Chemistry of Manganese Carbonyl

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I. INTRODUCTION

There is now a vast review literature on the chemistry of the carbonyls of chromium, molybdenum, tungsten, iron, cobalt, and nickel[1-4]. However, although more than two hundred papers and patents have been published since 1954 on the chemistry of manganese carbonyl, no review of this subject has appeared. Our paper represents an attempt to fill this gap.

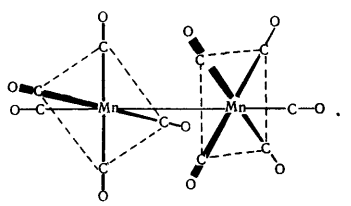
Manganese carbonyl and its derivatives possess several interesting properties, so that they attract wide attention from research workers in various specialised fields.

The present review deals with the structural peculiarities, methods of preparation, chemical properties, and chief fields of practical application of manganese carbonyl and its derivatives other than π-cyclopentadienylmanganese tricarbonyl, the chemistry of which will be discussed in a special paper. The literature published up to the beginning of 1966 is covered in the review.

II. STRUCTURE OF MANGANESE CARBONYL

Decacarbonyldimanganese $Mn_2(CO)_{10}$, like other carbonyls of transition metals, conforms to Sidgwick's rule, according to which the manganese atom must acquire a further eleven electrons. By interacting with five molecules of carbon monoxide the manganese atom gains ten electrons. The electron shell is completed by the formation of a bond between two atoms of the metal.

The decacarbonyldimanganese molecule can be represented by two octahedral groups, the centre of each being occupied by a manganese atom, while five corners are occupied by carbonyl groups, and the sixth by the adjacent metal atom:



A bond is formed between the manganese atom and a carbonyl group by coordination of the free d^2sp^3 orbitals of the manganese atom with the $(s-p_x)^2$ electrons of the carbon atom. It follows from the principle of maximum overlap of atomic orbitals that all the Mn–C–O groups are linear[5-7]. This should not involve any considerable change in the distribution of the electron cloud between the carbon and oxygen atoms, so that, as in free carbon monoxide, the carbon–oxygen bond should be somewhat in the nature of a triple bond. It has in fact been found that the carbon–oxygen distance in the $Mn_2(CO)_{10}$ molecule is 1.16 Å, which is intermediate between the values of 1.128 Å for the triple bond C≡O in carbon monoxide and 1.225 Å for the double bond C=O in formaldehyde.

Electrical neutrality of the manganese atom is probably established by some displacement of its d-electrons towards the carbon atom, as a result of which the manganese–carbon bond is partly double-bonded in character. It has been found experimentally[9] that the length of the manganese–carbon bond is ~ 1.83 Å, which is considerably less than the sum of the covalent radii.

The character of the manganese–manganese bond has not yet been elucidated. Its length in the $Mn_2(CO)_{10}$ molecule is 2.93 Å, whereas the sum of the covalent radii should be only 2.74 Å. The anomalous character of the manganese–manganese bond is confirmed also by the relatively low bond energy of 34 ± 13 kcal mole^{-1}.[10]

It has been found[12-14] that the axial carbonyl group is somewhat more firmly bound to the manganese atom than are the equatorial groups, although the difference in bond energy is not large. This can probably be explained by a breakdown in the symmetry of the electron cloud owing to the presence of different substituents around the manganese atom.

The structure given for the manganese carbonyl molecule agrees well with X-ray data[8].

III. METHODS OF PREPARATION AND PROPERTIES

In contrast to the carbonyls of nickel, chromium, and iron, decacarbonyldimanganese is not formed by the direct interaction of powdered metallic manganese and carbon monoxide. All the methods at present known for its preparation involve reducing a salt or an oxide of manganese to the metal and reaction of the latter *in situ* with carbon monoxide[15].

The existence of a manganese carbonyl was first reported in 1949 by Hurd et al.[16], who obtained mass-spectrometric evidence of its formation during the reduction of manganese iodide by a Grignard reagent in the presence of carbon monoxide. In 1954 Brimm et al.[17,18] obtained a 1% yield of decacarbonyldimanganese by the reaction

$$2\,MnI_2 + 2\,Mg + 10\,CO \rightarrow Mn_2(CO)_{10} + 2\,MgI_2.$$

The method of preparing manganese carbonyl by means of Grignard reagents has since been considerably improved[19-23].

Metallic sodium[24], sodium hydride, and lithium tetrahydroaluminate[25,26] can be employed as reducing agents. In the last case hydrogen pentacarbonylmanganate is formed, and this then decomposes with the evolution of hydrogen:

$$2\,HMn(CO)_5 \rightarrow Mn_2(CO)_{10} + H_2.$$

It is of interest to obtain manganese carbonyl by means of certain radical-anions, e.g. benzophenone ketyl[27,28]. The manganese salt resulting from the double decomposition

$$2\,(C_6H_5)_2C^{\cdot}{-}ONa + MnCl_2 \rightarrow \begin{matrix}(C_6H_5)_2C{-}O & & (C_6H_5)_2\dot{C}{-}O \\ \quad\quad\backslash\quad / & \rightleftarrows & \quad\quad\backslash \\ \quad\quad Mn & & \quad\quad Mn \\ (C_6H_5)_2C{-}O\quad\quad & & (C_6H_5)_2\dot{C}{-}O\quad\quad\end{matrix}$$

readily decomposes on heating, with the separation of metallic manganese:

$$[(C_6H_5)_2\dot{C}{-}O]_2Mn \rightarrow 2\,(C_6H_5)_2C{=}O + Mn.$$

This reacts with carbon monoxide under pressure, to form manganese carbonyl:

$$2\,Mn + 10\,CO \rightarrow Mn_2(CO)_{10}.$$

A disadvantage of this method is the difficulty of separating the manganese carbonyl from benzophenone. Other radical-anions, e.g. naphthalene–sodium[29], can be used instead of ketyls.

The best yields (up to 54%) of decacarbonyldimanganese are obtained by using as reductants diethylzinc[30], a trialkylaluminium[31,32], or metallic aluminium activated by an organoaluminium compound[33].

Finally, decacarbonyldimanganese can be prepared from derivatives of cyclopentadienylmanganese tricarbonyl by the action of metallic sodium in the presence of diglyme[34,35] or an amine[36].

Decacarbonyldimanganese consists of golden-yellow crystals melting at 154–155°C. It readily sublimes in a vacuum, the heat of sublimation being 15 kcal mole^{-1}.[37] In the air at room temperature it is stable for several months. When heated in air above 110°C it decomposes with the formation of a metallic mirror and carbon monoxide. In an atmosphere of carbon monoxide it is stable up to 250°C.

Manganese carbonyl is soluble in most organic solvents, but is insoluble in water. In air the solutions decompose rapidly at room temperature.

The infrared absorption spectrum of decacarbonyldimanganese is characterised by strong bands at 2063, 2028, and 1997 cm^{-1} which are assigned to the carbonyl groups, and two bands in the region of 640 cm^{-1} attributable to the manganese–carbon bond[11,37]. For the nuclear magnetic resonance (n.m.r.) spectra of manganese carbonyl see Ref. 38.

IV. HYDROGEN CARBONYLMANGANATES AND ALLIED COMPOUNDS

1. Preparation and Properties of Hydrogen Carbonylmanganates

Two hydrogen carbonylmanganates—$HMn(CO)_5$ and $H_2Mn_2(CO)_9$—are formed by the reduction of decacarbonyldimanganese with hydrogen, lithium, tetrahydroaluminate[39], or a hydroborate[40] in an inert solvent. Metals (magnesium, aluminium, amalgams) and other reducing agents can also be used[41].

Hydrogen pentacarbonylmanganate $HMn(CO)_5$ is a colourless liquid (m.p. = −24.6°C, $d^{20} = 1.465$, $n_D^{20} = 1.518$, and dipole moment = 0.70 D), which decomposes at 100°C.[42,43] The infrared absorption spectra of this compound and its deuterio-analogue are characterised by carbonyl bands in the range 2150–1950 cm^{-1}, bands at 1782, 735, 664, 615, and 458 cm^{-1} assigned to the hydrogen–manganese bond, and bands at 1287 and 676 cm^{-1} ascribed to the manganese–deuterium bond[11,44–46].

The $HMn(CO)_5$ molecule has the shape of a distorted octahedron, the length of the hydrogen–manganese bond being 1.5–1.6 Å.[47,48]

The second hydrogen carbonylmanganate $H_2Mn_2(CO)_9$ is unknown in the pure form, but several of its derivatives have been obtained.

Hydrogen carbonylmanganates are weak acids, the dissociation constant of $HMn(CO)_5$ being 0.8×10^{-7}. In aqueous alkalis the hydrogen atom is replaced by an alkali-metal cation[49]:

$$HMn(CO)_5 + KOH \rightarrow KMn(CO)_5 + H_2O.$$

The same salts can be obtained by reducing decacarbonyldimanganese with the alkali metals or their amalgams[50,51].

Hydrogen carbonylmanganates react with Lewis bases to form saltlike complexes[40]. With pyridine, for example, the reaction is

$$6\,HMn(CO)_5 + 12\,C_5H_5N \rightarrow 2\,[Mn(C_5H_5N)_6][Mn(CO)_5]_2 + 10\,CO + 3H_2.$$

Hydrogen carbonylmanganates are strong reducing agents. According to Hieber and Wagner[42], the reduction potential of hydrogen pentacarbonylmanganate in aqueous alkali at 20°C is −0.68 V. In inert solvents this compound reduces halogens:

$$2\,HMn(CO)_5 + I_2 \rightarrow Mn_2(CO)_{10} + 2\,HI.$$

These hydrogen derivatives are able to react also with halogenated hydrocarbons. On ultraviolet irradiation in chloroform or carbon tetrachloride they are converted into the halogenocarbonylmanganese derivatives—$MnCl(CO)_5$ and $[MnCl(CO)_4]_2$.

Hydrogen pentacarbonylmanganate serves as starting material for the preparation of various organic derivatives of manganese carbonyl. With diazomethane, for example, it forms pentacarbonylmethylmanganese[52]:

$$HMn(CO)_5 + CH_2N_2 \rightarrow MnCH_3(CO)_5 + N_2.$$

Hydrogen pentacarbonylmanganate has found an interesting application in the preparation of fluoroalkyl derivatives of manganese carbonyl[43]:

$$HMn(CO)_5 + CF_2{=}CF_2 \rightarrow HCF_2{-}CF_2{-}Mn(CO)_5.$$

2. Ionic Complexes of Manganese Carbonyl

Besides the alkali-metal salts of the hydrogen carbonylmanganates, several compounds are known which are formed by the pentacarbonylmanganate ion with complex cations. In contrast to the analogous complexes of iron and cobalt, they can be obtained only in alkaline solution, owing to the acidic character of hydrogen pentacarbonylmanganate. Hieber and Schropp[53] isolated complex salts formed with the tri-*o*-phenanthroline-nickel(II) and -iron(II), dibenzenechromium(I), and dicyclopentadienylcobalt(I) cations. It is interesting that the dibenzenechromium salt is readily decomposed even at room temperature:

$$2\,[Cr(C_6H_6)_2][Mn(CO)_5] \rightarrow Mn_2^0(CO)_{10} + 2\,Cr^0(C_6H_6)_2$$

whereas the other complexes are considerably more stable. Salts of analogous structure are formed also by the interaction of decacarbonyldimanganese with pyridine[54] and with 1,10-phenanthroline[55].

Complexes are known also in which the carbonylmanganese group is the cation. Such compounds were first obtained by Fischer and his coworkers[56,57] by the reaction

$$ClMn(CO)_5 + AlCl_3 + CO \rightarrow [Mn(CO)_6]^+AlCl_4^-.$$

Instead of a carbon monoxide molecule, an ethylene molecule can be introduced into the cation:

$$ClMn(CO)_5 + AlCl_3 + C_2H_4 \rightarrow [Mn(CO)_5C_2H_4]^+AlCl_4^-.$$

Several complex salts have been obtained by the interaction of such carbonylmanganese cations with various anions[58–61]. All these compounds are usually stable in an inert atmosphere for several days, but they decompose rapidly in air in the presence of moisture.

3. Polymetallic Derivatives

Several compounds are known in which the manganese atom is attached by a covalent bond to atoms of other metals.

Hieber and Schropp[53] obtained mercury derivatives of manganese carbonyl:

$$2KMn(CO)_5 + Hg(CN)_2 \rightarrow [Mn(CO)_5]_2Hg + 2KCN.$$

The same compound was isolated by King[58] from the reaction between sodium pentacarbonylmanganate and sodium amalgam in the presence of 1,4-dibromobutane. Bis-pentacarbonylmanganesemercury readily reacts with mer-

cury halides to form complexes which are practically undissociated:

$$[Mn(CO)_5]_2Hg + HgCl_2 \rightarrow [Mn(CO)_5]_2Hg \cdot HgCl_2 \text{ or } (CO)_5MnHgCl.$$

In the reaction of potassium pentacarbonylmanganate with alkylmercury compounds, the mixed organomercury compounds which are probably formed as intermediates disproportionate with separation of the dialkylmercury:

$$RHgOH + KMn(CO)_5 \rightarrow [RHg—Mn(CO)_5] \rightarrow R_2Hg + [Mn(CO)_5]_2Hg.$$

This reaction may find application for the synthesis of fully organic mercury compounds.

Compounds containing a manganese–metal bond have been obtained by treating sodium pentacarbonylmanganate with chlorine derivatives of various metals[62]:

$$L_nMCl_m + m\,NaMn(CO)_5 \rightarrow L_nM[Mn(CO)_5]_m + m\,NaCl$$

where L = alkyl, aryl, aralkyl, alkaryl, or a radical containing phosphorus, arsenic, or antimony and M = Sn, Si, Ge, Ag, Au, Cu, etc.[64–67]

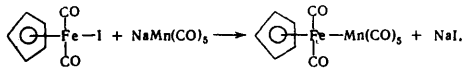
Trichlorogermanylmanganese pentacarbonyl was synthesised by a somewhat different method[63]:

$$Cl_3GeH + ClMn(CO)_5 \rightarrow Cl_3Ge—Mn(CO)_5 + HCl.$$

Stable bispentacarbonylmanganesegermane was prepared by Stone and his coworkers[64] by the reaction of hydrogen pentacarbonylmanganate with germane:

$$GeH_4 + 2HMn(CO)_5 \rightarrow H_2Ge[Mn(CO)_5]_2 + 2H_2.$$

The so called "mixed" carbonyls—i.e. compounds containing carbonyl groups of other metals as well as the pentacarbonylmanganese group—belong to this same type of compounds. The first such compound was cyclopentadienyldicarbonyliron–pentacarbonylmanganese, obtained in 40% yield by King et al.[78] by the reaction



Analogous methods were used to prepare "mixed" carbonyls of manganese and rhenium[79]:

$$(CO)_5ReCl + NaMn(CO)_5 \rightarrow (CO)_5Re—Mn(CO)_5 + NaCl$$

$$(CO)_5ReNa + ClMn(CO)_5 \rightarrow (CO)_5Re—Mn(CO)_5 + NaCl$$

as well as cobalt[80], molybdenum, and tungsten[81].

V. DERIVATIVES OF MANGANESE CARBONYL CONTAINING A CARBON–MANGANESE σ-BOND

1. Alkyl- and Acyl-manganese Pentacarbonyls

Like acids, hydrogen carbonylmanganates are able to react with various alkylating agents to form compounds in which the carbon atom is attached directly to the metal atom. The relatively high stability of these compounds can be explained by the influence of the carbonyl groups on the organic substituents[82].

The simplest organic derivative of manganese carbonyl, pentacarbonylmethylmanganese, can be obtained by the action of diazomethane on hydrogen carbonylmanganate[52,83]:

$$CH_2N_2 + HMn(CO)_5 \rightarrow CH_3Mn(CO)_5 + N_2.$$

Other methylating agents, e.g. dimethyl sulphate[84], can be used besides diazomethane.

Higher alkylmanganese pentacarbonyls can be obtained by the reaction of hydrogen pentacarbonylmanganate with alkenes[85]:

$$CH_2—CH=CH_2 + HMn(CO)_5 \rightarrow CH_3CH_2CH_2—Mn(CO)_5.$$

A method which has found some application for the preparation of alkyl derivatives of manganese carbonyl involves the use of organic derivatives of the alkali metals or of Grignard reagents[52]:

$$C_4H_9Li + BrMn(CO)_5 \rightarrow C_4H_9—Mn(CO)_5 + LiBr.$$

A method based on the reaction of alkali-metal pentacarbonylmanganates with organic halides[83,86]

$$R—X + NaMn(CO)_5 \rightarrow R—Mn(CO)_5 + NaX$$

is most often used. It is possible to obtain only the simplest carbonylalkylmanganese compounds by means of this reaction, since beginning with the isopropyl halides the reaction leads to the formation of halogenopentacarbonylmanganese derivatives, e.g. [50]

$$2\,C_4H_9Br + 2NaMn(CO)_5 \rightarrow 2BrMn(CO)_5 + 2NaBr + C_8H_{18}.$$

However, this method is widely used to obtain alkenyl derivatives of manganese carbonyl[91,92], and also for the synthesis of pentacarbonylacylmanganese derivatives[87]:

$$R—\overset{\overset{O}{\|}}{C}—Cl + NaMn(CO)_5 \rightarrow R—\overset{\overset{O}{\|}}{C}—Mn(CO)_5 + NaCl$$

which when heated to 100–120°C are readily converted into pentacarbonylalkylmanganese compounds:

$$R—CO—Mn(CO)_5 \rightarrow R—Mn(CO)_5 + CO.$$

Numerous alkyl and acyl derivatives of manganese carbonyl have been prepared by all the above methods. Aromatic[93] and heteroaromatic[88,94–96] derivatives can also be obtained by such methods:

$$C_6H_5Cl + NaMn(CO)_5 \rightarrow C_6H_5—Mn(CO)_5 + NaCl$$

as well as compounds containing two pentacarbonylmanganese groups separated by a chain of carbon atoms[89,90]:

$$Cl—(CH_2)_8—Cl + 2NaMn(CO)_5 \rightarrow (CO)_5Mn—(CH_2)_8—Mn(CO)_5 + 2NaCl$$

$$R(COCl)_2 + 2NaMn(CO)_5 \xrightarrow[-2NaCl]{} R—[CO—Mn(CO)_5]_2 \xrightarrow[-2CO]{} R[Mn(CO)_5]_2.$$

Organic derivatives of manganese carbonyl containing a carbon–manganese σ-bond are usually stable towards oxygen and moisture, but on prolonged storage they slowly decompose with the evolution of carbon monoxide. On treatment with halogens the organic radical is replaced by a halogen atom:

$$R—Mn(CO)_5 + Br_2 \rightarrow RBr + BrMn(CO)_5.$$

Concentrated hydrohalic acids act similarly.

Calderazzo and Noack[97] investigated the reaction between lithium iodide and pentacarbonylmethylmanganese, in which one carbonyl group is replaced by an iodine atom, and is then incorporated between the methyl group and the manganese atom:

$$CH_3—Mn(CO)_5 + LiI \rightarrow Li[CH_3CO—Mn(CO)_4I].$$

This reaction is a particular case of the addition to organomanganese pentacarbonyls of ligands which possess a lone pair of electrons, e.g. carbon monoxide, triphenylphosphine,, amines, etc. The ligand displaces one carbonyl group, which is incorporated between the alkyl group and the metal atom:

$$R—Mn(CO)_5 + L \rightarrow RCO—Mn(CO)_4L.$$

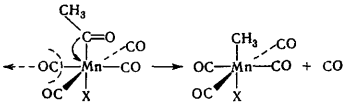
The addition of carbon monoxide (carbonylation) and that of triphenylphosphine have been studied in the greatest detail.

The carbonylation reaction

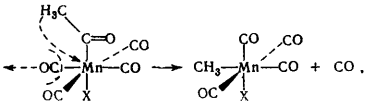
$$R-Mn(CO)_5+CO\rightleftarrows R-CO-Mn(CO)_5,$$

discovered by Coffield et al.[87] in 1957, is reversible: acylmanganese carbonyls when heated to 100°C are converted into the corresponding alkyl derivatives. It was shown with labelled carbon monoxide[98] that in the carbonylation the free carbon monoxide molecule is not immediately incorporated between the alkyl radical and the manganese atom, and in the reverse reaction the liberated carbonyl group also was not initially linked with the alkyl radical.

Mawby et al.[99] point out two alternative mechanisms for the decarbonylation of acyl derivatives of manganese carbonyl—(*a*) carbonyl insertion



or (*b*) migration of the alkyl group



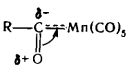
It has not yet proved possible to establish precisely which of these two mechanisms is correct. However, in the carbonylation of complexes of the type $RMn(CO)_4X$, where X is some ligand other than carbonyl, these mechanisms yield different products. If the reaction involves alkyl migration, the product should have a *cis*-configuration; in the contrary case a *trans*-isomer should be formed.

From a study of the decarbonylation of *trans*-tetracarbonyltriphenylphosphineacetylmanganese Mawby et al.[90] concluded that an alkyl migration mechanism (*b*) is to be preferred. Addition to alkylmanganese pentacarbonyls of phosphines and secondary amines[100,101] and other reactions involving incorporation of a carbonyl group between a manganese atom and an alkyl radical probably occur by the same mechanism.

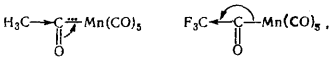
The rate of carbonylation of a pentacarbonylalkylmanganese depends on the nature of the organic radical. Calderazzo and Cotton showed that the rate of carbonylation decreases in the sequence[102]

$$n\text{-}C_3H_7\gtrsim C_2H_5>C_6H_5>CH_3\gg C_6H_5CH_2\simeq CF_3.$$

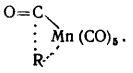
The ease of conversion of alkyl derivatives of manganese carbonyl into the corresponding acyl derivatives and of the reverse reaction indicates that the acyl carbonyl group has a special character. Although the infrared spectra of the acyl derivatives contain an absorption band in the range 1590–1640 cm^{-1}, corresponding to the carbonyl absorption band in aldehydes and ketones, the acyl carbonyl exhibits none of the chemical properties characteristic of a ketonic or an aldehydic carbonyl group. Its specific character is probably due to an increase in electron density on the carbon atom resulting from the positive inductive effect of the pentacarbonylmanganese group. Some levelling out of all the manganese–carbon bonds in the pentacarbonylacylmanganese molecules, owing to the formation of a dative π-bond between the manganese and the acyl carbon atom



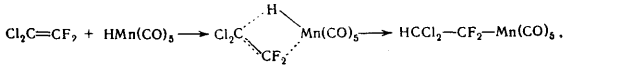
may also be assumed. The presence of strong electron-acceptor groups in the organic radical will prevent an increase in the multiplicity of the Mn=C bond, and thereby tend to strengthen the C–R bond and impede decarbonylation:



It may further be supposed that pentacarbonylacylmanganese molecules will contain a seven-coordinated manganese atom



Complexes of this type have recently been prepared[103]. The hypothesis of seven-coordinated manganese complexes provides an explanation not only for the mechanism of the decarbonylation of acyl derivatives of manganese carbonyl but also for the addition of unsymmetrical halogenated alkenes to hydrogen carbonylmanganate, which under normal conditions involves the formation of only one isomer:



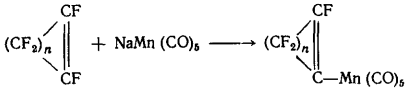
2. Perfluoro-derivatives

A large number of papers have recently been published on perfluoroalkylmanganese pentacarbonyls. The interest taken in these compounds is due to their great stability in comparison with their hydrocarbon analogues, this being an effect of the electronegative fluorine atoms.

Perfluoro-derivatives of manganese carbonyl can be obtained by all the general methods described above for the synthesis of alkyl and aryl derivatives[104]. Methods using organometallic compounds have acquired relatively greater value[105,106]:

$$BrMn(CO)_5+LiC_6F_5\rightarrow C_6F_5-Mn(CO)_5+LiBr$$
$$BrMn(CO)_5+C_6F_5MgBr\rightarrow C_6F_5-Mn(CO)_5+MgBr_2.$$

Certain methods for obtaining perfluoroalkyl derivatives of manganese carbonyl are specific. Thus when perfluorocycloalkenes react with the pentacarbonylmanganate anion, a fluorine atom adjacent to the double bond is replaced by $Mn(CO)_5$ [107,108]:



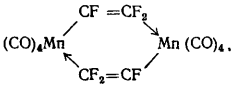
An extremely interesting reaction between perfluoroethylene and compounds containing a tin–manganese bond was accomplished by Clark and Tsai[109]. It involved incorporation of the tetrafluoroethylene molecule in the tin–manganese bond:

$$(CH_3)_3Sn-Mn(CO)_5+CF_2=CF_2\rightarrow(CH_3)_3Sn-CF_2-CF_2-Mn(CO)_5.$$

The resulting compound readily decomposed with the separation of an organomanganese dimer:

$$2[(CH_3)_3Sn-CF_2-CF_2-Mn(CO)_5]\rightarrow 2(CH_3)_3SnF+[CF_2=CF-Mn(CO)_4]_2+2CO$$

which, in the opinion of these workers, had the "bridge" structure



The infrared absorption spectra of these compounds have been studied in great detail[110-114]. There are also data on the ^{19}F n.m.r. spectra of several of these compounds[114-116].

The chemical properties of the perfluoroalkyl and perfluoroacyl derivatives of manganese pentacarbonyl do not in general differ from those of their hydrocarbon analogues[117-121].

VI. HALOGENO-CARBONYLS AND ALLIED COMPOUNDS

1. Halogeno-derivatives of Manganese Carbonyl

Decacarbonyldimanganese reacts with halogens to form halogenomanganese carbonyls[122]:

$$[Mn(CO)_5]_2 + Cl_2 \rightarrow 2ClMn(CO)_5,$$

Other methods for obtaining these compounds are the reactions of alkyl- and acyl-manganese pentacarbonyls with halogens[89]:

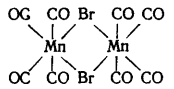
$$Mn(CO)_5R + Br_2 \rightarrow RBr + BrMn(CO)_5$$
$$RCO{-}Mn(CO)_5 + I_2 \rightarrow RCOI + IMn(CO)_5$$

and also heating decacarbonyldimanganese with carbon tetrachloride, chloroform, and other halogenated hydrocarbons under ultraviolet irradiation[42].

Halogenomanganese carbonyls are stable towards moisture and atmospheric oxygen at room temperature. On heating, carbon monoxide is gradually eliminated, with the formation of dimeric halogeno-carbonyls:

$$2Mn(CO)_5X \rightarrow [Mn(CO)_4X]_2 + 2CO.$$

These dimers have the bridge structure[123]



The Mn–Br distance is 2.526 ± 0.005 Å, and the Mn...Mn distance is 3.74 Å, which considerably exceeds the Mn–Mn distance in the decacarbonyldimanganese molecule.

A kinetic study has been made of isotope between exchange halogenomanganese pentacarbonyls and carbon monoxide[40,124]:

$$XMn(CO)_5 + C^*O \rightleftarrows XMn(CO)_4(C^*O) + CO.$$

The rate of exchange of carbon monoxide is found to depend on the atomic radius of the halogen: in the series—chlorine, bromine, iodine—the intensity of exchange diminishes in the proportions 200 : 8 : 1.[40]

The addition of a halogen atom to the pentacarbonylmanganese group makes the carbonyl group somewhat more mobile than in the original decacarbonyldimanganese. Halogenomanganese carbonyls interact with various ligands (L) possessing a lone pair of electrons, with replacement of one or two carbonyl groups:

$$XMn(CO)_5 + L \rightarrow LMn(CO)_4X + CO,$$
$$XMn(CO)_5 + 2L \rightarrow L_2Mn(CO)_3X + 2CO.$$

Besides the carbonyl group the halogen atom may also be replaced[125]:

$$BrMn(CO)_5 + 2KCN \rightarrow K[Mn(CO)_4(CN)_2] + CO + KBr.$$

The infrared spectra of halogenomanganese pentacarbonyls[126-128] support the hypothesis that the axial carbonyl in the pentacarbonylmanganese group is more firmly bound than are the equatorial groups to the manganese atom.

2. Nitrato- and Thiocyanato-compounds

Addison et al.[129,130] prepared stable nitratopentacarbonylmanganese by the reaction of decacarbonyldimanganese with dinitrogen tetroxide:

$$Mn_2(CO)_{10} + N_2O_4 \rightarrow Mn(CO)_5NO_3.$$

This compound consists of pale yellow crystals, and decomposes when heated in a vacuum above 55°C. It is soluble in polar solvents, but insoluble in carbon disulphide and aliphatic hydrocarbons. It is easily solvated in solution, with the formation of $[Mn(CO)_5Solv]^+NO_3^-$ complexes. The infrared spectrum of this compound confirms the presence of both carbonyl groups (ν_{CO} = 2060 and 2002 cm^{-1}) and a nitrato-group (ν_{NO_3} = 1486, 1284, 1010, and 805 cm^{-1}) attached to the manganese atom.

Farona and Wojcicki[131,132] prepared thiocyanatopentacarbonylmanganese by the reaction of sodium pentacarbonylmanganate with thiocyanogen chloride:

$$NaMn(CO)_5 + ClSCN \rightarrow Mn(CO)_5SCN + NaCl$$

obtaining golden-yellow crystals decomposing at 156°C and soluble in polar solvents. In air this compound is stable in the dark, but slowly decomposes in the light. It reacts with electron-donor ligands, e.g. triphenylphosphine or pyridine, with replacement of carbonyl groups:

$$Mn(CO)_5SCN + 2C_5H_5N \rightarrow Mn(CO)_3(C_5H_5N)_2SCN + 2CO.$$

It is noteworthy that the reaction between decacarbonyldimanganese and bithiocyanogen $(SCN)_2$ yields a polymeric compound instead of the expected thiocyanatopentacarbonylmanganese.

VII. PRODUCTS RESULTING FROM SUBSTITUTION OF CARBONYL GROUPS

Reactions involving the replacement of carbonyl groups are widespread in the chemistry of metal carbonyls. Carbon monoxide can easily be substituted by various ligands possessing electron-donor properties. Substitution of a carbonyl group in derivatives of manganese pentacarbonyl is not usually accompanied by change in the oxidation state of the metal atom. Complete replacement of all the carbonyl groups is rare, only one or two of them usually being replaced. This is probably due to the increase in stability of the manganese–carbon bond on introduction of an electron-donor ligand, consequent on an increase in the statistical weight of structures of the type[133,134]

$$L{-}M{=}C{=}O \longleftrightarrow L^+{-}M{\equiv}C{-}O^-.$$

1. Isocyanide and Nitrile Complexes

Isocyanides R.N : C are the closest analogues of carbon monoxide, and therefore they should readily displace the latter from metal carbonyls. However, complete replacement of carbonyl groups by alkyl isocyanide groups has been accomplished only with nickel tetracarbonyl[135]. In derivatives of manganese carbonyl only two carbonyl groups can be replaced[125]:

$$BrMn(CO)_5 + 2R{-}N{=}C \rightarrow BrMn(CO)_3(CNR)_2 + 2CO.$$

Further substitution of carbon monoxide is not prevented by instability of the isocyanide complexes, since

ionic isocyanide complexes of manganese are known[136] which do not contain carbonyl groups:

$$MnI_2 + 6R{-}N{=}C \rightarrow [Mn(CNR_6]I.$$

Furthermore, Pauson and Stubbs[137] obtained an isocyanide analogue of tricarbonylcyclopentadienylmanganese:

$$C_5H_5Mn(CO)_3 + 3\,C_6H_5NC \rightarrow C_6H_5Mn(CN{-}C_6H_5)_3 + 3CO$$

this being a stable crystalline substance melting at 97°C. Thus available data suggest that the difficulty of further replacement of carbonyl by isocyanide groups is associated with enhanced stability of the manganese–carbon bonds.

Products have also been obtained in which carbonyl groups in derivatives of manganese carbonyl have been replaced by cyano-groups[125]:

$$BrMn(CO)_5 + KCN \rightarrow K[Mn(CO)_4(CN)_2] + KBr.$$

2. Nitrosyl Derivatives of Manganese Carbonyl

Nitrosyl derivatives of manganese carbonyl can be obtained by the action of nitric oxide on the halogeno-carbonyls[138,139]:

$$Mn(CO)_5I + NO \rightarrow Mn(CO)_4NO + Mn(CO)(NO)_3.$$

Tetracarbonylnitrosylmanganese $Mn(CO)_4NO$ is a pale yellow liquid (m.p. between −1.5° and 0°C), while carbonyltrinitrosylmanganese $MnCO(NO)_3$ is a crystalline substance melting at 27°C. The infrared spectra of these compounds were studied by Beck and Lottes[140].

The carbonyl groups in the mixed carbonyl–nitrosyl complexes of manganese can be further replaced by various ligands:

$$Mn(NO)_3CO + P(C_6H_5)_3 \rightarrow Mn(NO)_3P(C_6H_5)_3 + CO.$$

Another method for obtaining products in which the carbonyl groups have been completely replaced is the action of nitric oxide on substituted derivatives of manganese carbonyl[141–143]:

$$LMn(CO)_4 + NO \rightarrow LMn(NO)_3 + LMn(CO)_3NO$$

where $L = (C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, etc.

A halogen derivative of manganese nitrosyl was obtained[144] by the reaction between iodotetracarbonyl(triphenyl phosphite)manganese and nitric oxide:

$$Mn(CO)_4P(OC_6H_5)_3I + NO \rightarrow Mn(NO)_2[P(OC_6H_5)_3]_2I + MnI_2 + CO.$$

3. Substitution of Carbonyl Groups by Nitrogen Compounds

Besides compounds containing multiple-bonded nitrogen, whose reactions with derivatives of manganese carbonyl have been described above, replacement of carbonyl groups can occur also with compounds in which the nitrogen atom possesses a lone pair of electrons, e.g. amines, pyridine, etc.

Ammonia reacts with bromopentacarbonylmanganese at 70°C and 35 atm to form $Mn(NH_3)_3(CO)_3Br$ (decomposing at ~ 190°C). The corresponding chloride and iodide have been obtained in analogous fashion, as well as the compounds $Mn(NH_3)_2(CO)_4Br$[125]† and $[Mn(NH_3)_3(CO)_3]^+[Mn(CO)_5]^-$.[146]

† This should probably be Ref. 145 (Ed. of Translation).

A similar reaction takes place with various amines[125,147–150]:

$$XMn(CO)_5 + R'NR''_2 \rightarrow Mn(CO)_3(NR'R''_2)_2X + CO.$$

Quaternary ammonium salts react with halogenomanganese pentacarbonyls forming crystalline salts[151]:

$$R_4N^+X^- + XMn(CO)_5 \rightarrow R_4N^+[Mn(CO)_4X_2]^- + CO.$$

The same products are obtained by the action of quaternary ammonium salts on dinuclear halogenomanganese carbonyls:

$$2\,R_4N^+X^- + [Mn(CO)_4X]_2 \rightarrow 2\,R_4N^+[Mn(CO)_4X_2]^-.$$

With decacarbonyldimanganese this reaction yields the complex $(R_4N)_2[MnX(CO)_4]_2$.

Angelici has recently reported[103] the preparation of products of the addition of primary amines to bromopentacarbonylmanganese:

$$3\,RNH_2 + BrMn(CO)_5 \rightarrow Mn(CO)_5(NHR)(NH_2R) + RNH_3^+Br^-$$

(where R = CH_3, iso-C_3H_7, n-C_4H_9, t-C_4H_9, cyclohexyl, or RNH_2 = ethylenediamine). Diamagnetic compounds have been isolated as a result of these reactions. If the structure proposed for the compounds is correct, they constitute the first example of stable complexes of manganese carbonyl having a coordination number of seven, in which the number of electrons around the manganese exceeds the number around the krypton atom.

4. Phosphorus, Arsenic, and Antimony Derivatives

The most thorough study has been made of products obtained by replacing carbonyl groups in derivatives of manganese carbonyl by various alkylated and arylated phosphines, arsines, and stibines. These compounds are readily formed by the direct interaction of decacarbonyldimanganese, or its derivatives, e.g. the halogeno-derivatives, with the ligands[125,152,153]:

$$XMn(CO)_5 + AR_3 \rightarrow Mn(CO)_4X \cdot AR_3 + CO$$

$$XMn(CO)_4X \cdot AR_3 + AR_3 \rightarrow Mn(CO)_3X(AR_3)_2 + CO$$

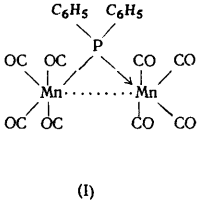
where X = Cl, Br, I; A = P, As, Sb; and R = Alk, Ar.

Angelici and Basolo established[154] the dependence of the rate of substitution of carbonyl groups on the nature of the ligand as $(C_6H_5)_3P > (C_6H_5)_3As \simeq (C_4H_9)_3P \simeq (C_6H_5)_2PCl > (C_6H_5O)_3P \simeq (C_6H_5)_3Sb > C_6H_5PCl_2 \simeq (C_4H_9O)_3P > CH_3C(CH_2O)_3P$.

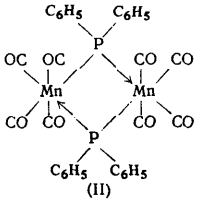
Exposure to ultraviolet radiation during replacement of the carbonyl groups results in the formation of dimeric products[155,156]:

$$Mn_2(CO)_{10} + 2AR_3 \xrightarrow{h\nu} [Mn(CO)_4AR_3]_2 + 2CO.$$

This reaction probably takes place in stages. Green and Moelwyn-Hughes[157] were able to isolate, from the reaction between diphenylphosphinous chloride and sodium pentacarbonylmanganate, two products of the stepwise replacement of carbon monoxide, to which they ascribed the structures

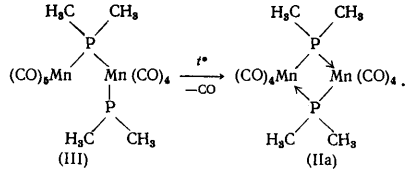


(I)



(II)

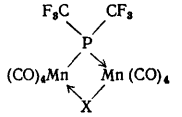
It was shown later[158] that the "doubly bridged" compound (IIa) is formed via the intermediate carbonyl complex (III), which contains only one "bridging" dimethylphosphino-group:



Dinuclear perfluoromethylated phosphine and arsine derivatives of manganese carbonyl have been prepared[159-161] by the reaction

$$[Mn(CO)_5]_2 + (CF_3)_2AX \rightarrow Mn_2(CO)_8A(CF_3)_2X + 2CO$$
(IV)

where A = P, As and X = Cl, Br, I, SCF_3, $SeCF_3$, $(CF_3)_2P$. Complexes of this type probably have the "doubly bridged" structure



In contrast to them, the compound $Mn_2(CO)_9P(CF_3)_2N(CH_3)_2$, obtained by the reaction between decacarbonyldimanganese and dimethylaminobistrifluoromethylphosphine[161], contains no "bridging" phosphine groups. It probably has the linear structure

$$(CO)_5Mn—Mn(CO)_4—P(CF_3)_2—N(CH_3)_2 .$$

Decacarbonyldimanganese reacts with *o*-phenylenebis-dimethylarsine at an elevated temperature[162,163] to form the diamagnetic dimeric product

$$\{Mn(CO)_3[(CH_3)_2As—C_6H_4—As(CH_3)_2]\}_2$$

which on further heating passes into a paramagnetic monomer:

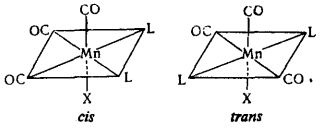
$$\{Mn(CO)_3[diars]\}_2 \rightarrow 2Mn(CO)_3[diars]$$
$$diars = o\text{-}(CH_3)_2AsC_6H_4As(CH_3)_2 .$$

The dimeric complex reacts in chloroform with free halogens:

$$\{Mn(CO)_3[diars]\}_2 + Cl_2 \rightarrow 2Mn(CO)_3[diars]Cl .$$

Excess of halogen produces a gradual replacement of carbonyl groups with the formation of $Mn(CO)_2[diars]Cl_2$ and $Mn[diars]Cl_3$. Analogous compounds have been obtained from decacarbonyldimanganese and ethylene-1,2-bisdiphenylphosphine[164-166].

Mononuclear compounds of general formula $Mn(CO)_3L_2X$ can exist in the form of the stereoisomers[167-169]



cis *trans*

The relative proportions of *cis*- and *trans*-isomers formed as a result of the stepwise substitution of carbonyl groups depends on the nature of the added ligand. Thus the replacement of carbonyl groups by triphenylphosphine yields mainly the *trans*-isomer, whereas the pyridine complex exists solely in the *cis*-form[167,168]. The stability of a particular stereoisomer probably depends primarily on steric factors.

The chemical properties of the phosphine-substituted derivatives of manganese carbonyl and their arsine and stibine analogues are fundamentally similar to those of manganese carbonyl itself and its other derivatives[169,170]. These compounds react with sodium amalgam to form the corresponding salts:

$$Mn(CO)_4LX + 2Na \xrightarrow{Hg} NaMn(CO)_4L + NaX$$

$$Mn(CO)_3L_2X + 2Na \xrightarrow{Hg} NaMn(CO)_3L_2 + NaX$$

which can be used to prepare various alkyl and acyl derivatives:

$$NaMn(CO)_3L_2 + (RCO)_2O \rightarrow RCO—Mn(CO)_3L_2 + RCOONa .$$

On being heated, acyl derivatives are also capable of conversion into alkyl derivatives, with the loss of a molecule of carbon monoxide:

$$RCO—Mn(CO)_3L_2 \rightarrow R—Mn(CO)_3L_2 + CO .$$

Hydrolysis of sodium tetracarbonyltriphenylphosphine-manganate yields the corresponding hydrogen compound[170]:

$$NaMn(CO)_4P(C_6H_5O)_3 + H^+ \rightarrow HMn(CO)_4P(C_6H_5O)_3 .$$

The sodium salts can be used for the preparation of mercury derivatives of manganese carbonyl:

$$2NaMn(CO)_4PR_3 + Hg(CN)_2 \rightarrow [Mn(CO)_4PR_3]_2Hg + 2NaCN .$$

Analogous mercury derivatives were obtained also from manganese carbonyl compounds containing two ligand molecules:

$$2NaMn(CO)_3[P(C_6H_5)_3]_2 + Hg(CN)_2 \rightarrow \{Mn(CO)_3[P(C_6H_5)_3]_2\}_2Hg + 2NaCN .$$

5. Compounds containing Sulphur and Tellurium

The first derivative of manganese carbonyl containing a manganese–sulphur bond was prepared by Hieber and Schropp[125] by the reaction

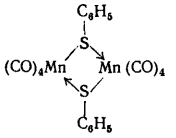
$$ClMn(CO)_5 + C_6H_5SH \rightarrow [Mn(CO)_4—S—C_6H_5]_2 .$$

This reaction was subsequently applied to decacarbonyldimanganese[171,172]:

$$R—SH + Mn_2(CO)_{10} \rightarrow 2RS—Mn(CO)_5$$

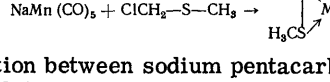
where R = C_2H_5, C_3H_7, C_6H_5, *p*-$CH_3C_6H_4$.

Reaction between manganese carbonyl and compounds containing two sulphur atoms (1,2-diphenylthioethane[164], dithian[173], etc.) has been used to synthesise dinuclear "bridged" compounds



resembling the dinuclear compounds containing phosphine or arsine.

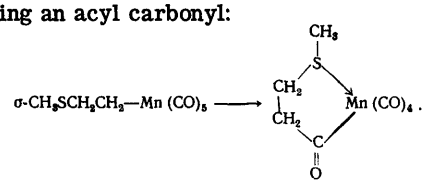
King and Bisnette[174] prepared compounds in which the sulphur atom was attached to the manganese atom by a π-bond:



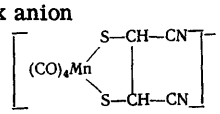
Interaction between sodium pentacarbonylmanganate and alkyl halides containing sulphur initially produces a compound containing a σ-bond:

$$NaMn(CO)_5 + ClCH_2CH_2—S—CH_3 \rightarrow \sigma\text{-}CH_2SCH_2CH_2—Mn(CO)_5 + NaCl$$

and this on ultraviolet irradiation passes into a π-derivative containing an acyl carbonyl:



Finally, the complex anion



in which the manganese atom is attached to two sulphur atoms, has been obtained[175] by the reaction between bromotetracarbonyltriphenylphosphinemanganese and sodium *cis*-1,2-dicyanoethane-1,2-dithiolate.

Derivatives of manganese pentacarbonyl containing the manganese–tellurium[176] and the manganese–selenium bonds can be prepared by similar methods.

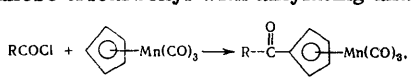
VIII. π-HYDROCARBON MANGANESE CARBONYL DERIVATIVES

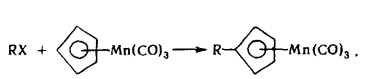
Besides the organic derivatives of manganese carbonyl described in Section V, in which the carbon atom is bound to the metal atom by a σ-bond, several compounds are known in which the π-electrons of carbon atoms effect the link between the manganese atom and a hydrocarbon group. As in other "sandwich" compounds, a π-bond between an organic group and a pentacarbonylmanganese group is possible only when the ligand has a coplanar configuration[177].

The most thoroughly studied π-complex of manganese carbonyl is cyclopentadienylmanganese tricarbonyl $C_5H_5Mn(CO)_3$. Several methods are now known for preparing it, one of the most convenient being the reaction between halogenomanganese pentacarbonyls and cyclopentadienyl-sodium[178] or -thallium[179]:

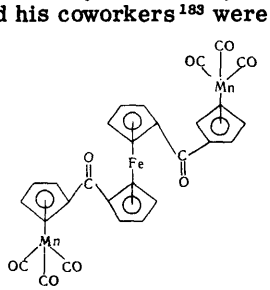
$$C_5H_5Na + BrMn(CO)_5 \rightarrow C_5H_5Mn(CO)_3 + 2CO + NaBr.$$

The chemistry of cyclopentadienylmanganese tricarbonyl and its derivatives has been described in detail[180,181], and therefore we shall mention only certain reactions of this compound. Various substituents can be introduced into the cyclopentadienyl ring by interaction of cyclopentadienylmanganese tricarbonyl with alkylating and acylating agents[182]:





The most diverse compounds containing a tricarbonylmanganese group have been synthesised by this method. For example, Cais and his coworkers[183] were able to obtain the compound



which contains a ferrocene "sandwich" besides tricarbonylmanganese groups.

The cyclopentadienyl ring in the cyclopentadienylmanganese tricarbonyl molecule exhibits all the properties characteristic of aromatic systems. At the same time the presence of carbonyl groups attached to the metal atom enables reactions typical of metal carbonyls to be carried out, e.g. the replacement of carbonyl groups by electron-donor ligands[184]:

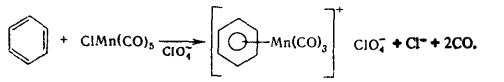
$$C_5H_5Mn(CO)_3 + (CH_3)_2NH \rightarrow C_5H_5Mn(CO)_2NH(CH_3)_2 + CO$$

$$C_5H_5Mn(CO)_3 + P(C_6H_5)_3 \rightarrow C_5H_5Mn(CO)_2P(C_6H_5)_3 + CO.$$

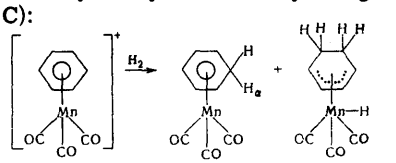
Strohmeier and von Hobe[185] replaced carbon monoxide in cyclopentadienyl tricarbonyl by diphenylacetylene:

$$C_5H_5Mn(CO)_3 + C_6H_5C{\equiv}CC_6H_5 \rightarrow C_5H_5Mn(CO)_2(C_6H_5C{\equiv}CC_6H_5) + CO.$$

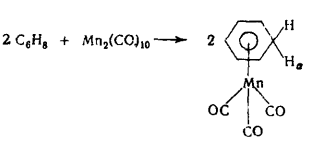
Aromatic systems other than the cyclopentadienyl ring are also able to form π-complexes with manganese carbonyl[185]. Hydrocarbons of the benzene series form either complexes of the type π-Ar–$Mn(CO)_4$ [186] or cations $[\pi\text{-Ar–}Mn(CO)_3]^+$. For example, benzene reacts with chloropentacarbonylmanganese in the presence of Friedel–Crafts catalysts according to the equation



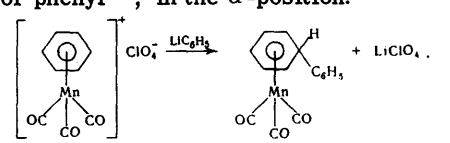
Reduction of this cation with sodium tetrahydroborate[188] or with hydrogen over Raney nickel yields π-cyclohexadienemanganese tricarbonyl (m.p. 78°C) and small amounts of hydrogen tricarbonyl-π-cyclohexadienylmanganate (decomposes at 95°C):



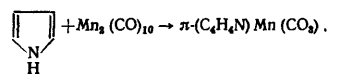
The first of these compounds can also be readily obtained by the interaction of decacarbonyldimanganese with cyclohexadiene[189]:



The benzenetricarbonylmanganese cation can be stabilised also by the addition of various substituents, e.g. methyl[190] or phenyl[191], in the α-position:

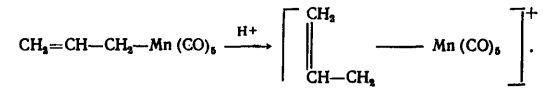


Joshi et al.[192,193] synthesised several derivatives of heterocyclic compounds and manganese carbonyl containing a π-bond:



Not only aromatic systems but also various unsaturated acyclic systems are able to form π-complexes with manganese carbonyl. It is supposed that the pentacarbonylethylenemanganese cation, which has already been discussed (Section IV, 2), formed by the reaction of ethylene with manganese carbonyl[56], and also by detachment of a

proton from ethylmanganese pentacarbonyl by the action of triphenylmethyl tetrafluoroborate[194], is a π-complex. It has been found[195] that an analogous cation is formed by the action of perchloric acid on σ-allylmanganese pentacarbonyl:



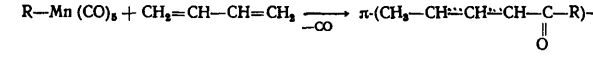
Stable π-allyl complexes of manganese carbonyl have been obtained by heating the corresponding σ-alkyl derivatives $R-Mn(CO)_5$ while exposed to ultraviolet radiation[85,92,196]. This reaction probably involves the intermediate formation of an unstable cation:

$$CH_2=CH-CH_2-Mn(CO)_5 \rightarrow [\pi\text{-}(CH_2\cdots CH\cdots CH_2)-Mn(CO)_5]^+$$

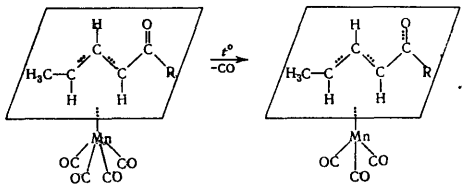
which is then stabilised by eliminating a molecule of carbon monoxide:

$$[\pi\text{-}(CH_2-CH-CH_2)-Mn(CO)_5]^+ \rightarrow \pi\text{-}(CH_2-CH-CH_2)-Mn(CO)_4 + CO.$$

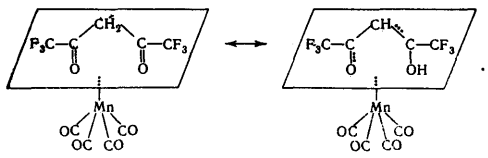
Analogous π-complexes have been obtained by interaction between dienes and alkyl or aryl derivatives of manganese pentacarbonyl[197]:



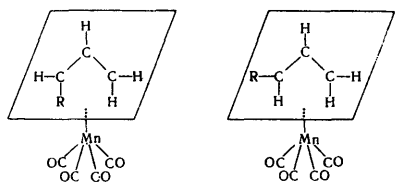
When such a compound (R = C_6H_5) is heated above 110°C, a molecule of carbon monoxide is split off, stabilisation of the resulting tricarbonyl complex probably being due to interaction of the π-orbitals of the ketonic carbonyl with *d*-electrons of the manganese atom:



Similar formation of a π-bond by π-electrons of an acyl carbonyl is probably observed also in tetracarbonylhexafluoropentane-2,4-dionemanganese, which was prepared by Kilner and Wojcicki[198]:



π-Allyl compounds of maganese carbonyl are distinguished from the corresponding σ-allyl complexes primarily by the coplanar arrangement of the carbon atoms in the organic portion of the molecule. Some workers postulate[192,193] that the higher homologues of π-allyl derivatives of manganese carbonyl may exist as different stereoisomers



anti-1-alkyl-π-allylmanganese tetracarbonyl

syn-1-alkyl-π-allylmanganese tetracarbonyl

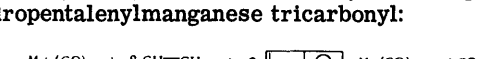
However, such a hypothesis is hardly justified, since such isomers are absent from the "sandwich" compounds, e.g. ferrocene and cyclopentadienylmanganese tricarbonyl, which are allied to the π-allyl complexes of manganese carbonyl[199].

The π-allyl complexes are rather more stable than the corresponding σ-allylmanganese pentacarbonyls. Their boiling (melting) points are usually higher than those of compounds containing a σ-bond. The infrared absorption spectra and the nuclear magnetic resonance spectra indicate that single and double bonds in the organic substituents are levelled out. The accompanying Table gives for comparison some physicochemical characteristics of σ- and π-allylmanganese carbonyls.

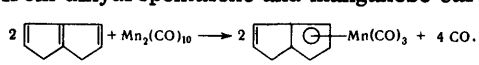
Physicochemical properties of σ- and π-allylmanganese carbonyls.

Property	σ-CH_2=$CHCH_2$Mn (CO)$_5$	π-(CH_2=$CHCH_2$)—Mn (CO)$_4$
State	Liquid	Crystals
Melting (boiling) point, °C	25/10^{-3}	55—56
Infrared absorption spectrum, cm^{-1}		
ν C=C	1620	1505
ν C=O	2110, 2079, 2024, 2004	2110, 2060, 2049, 1950
N.m.r. spectrum, τ, p.p.m.	6.14 (sextet)	4.80 (sextet)
	4.68 (triplet)	2.76 (doublet)
	1.81 (doublet)	1.77 (doublet)

Finally, we must deal with the very peculiar reaction between manganese carbonyl and acetylene[200-202], by means of which the most diverse derivatives of cyclopentadienylmanganese tricarbonyl can be obtained. At 150°C and 40–45 atm acetylene forms with decacarbonyldimanganese or with methylmanganese pentacarbonyl the compound π-dihydropentalenylmanganese tricarbonyl:

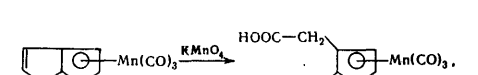


The same compound was obtained by Riemschneider[201] directly from dihydropentalene and manganese carbonyl:

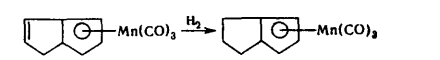


Analogous complexes have been obtained from azulene and indene[203-205].

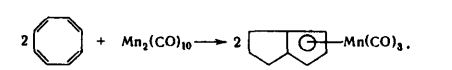
The oxidation of π-dihydropentalenylmanganese tricarbonyl yields cyclopentadienylmanganese tricarbonyl derivatives:



Reduction over Raney nickel results in a π-tetrahydropentalenyl derivative[206]:



which can be prepared also from manganese carbonyl and cyclo-octatetraene:



IX. COMPOUNDS CONTAINING A BORON ATOM

With most boron compounds manganese carbonyl can react only as a donor of electrons. Thus interaction of the borane–ether complex with sodium pentacarbonylmanganate gave[207] the unstable complex $[(C_2H_5)_4N]^+[H_3B{-}Mn(CO)_5]^-$, which decomposes with the evolution of diborane even at −25°C. A complex in which one carbonyl group had been replaced by triphenylphosphine

$$[H_3B{-}Mn(CO)_4P(C_6H_5)_3]^-[(C_2H_5)_4N]^+$$

was synthesised in an analogous fashion. Nöth and Schmidt[208] isolated several compounds containing a boron–manganese σ-bond, in which the boron atom was attached to a dimethylamino-group or a chlorine or bromine atom.

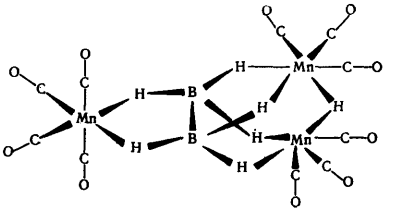
Reaction between diphenyl- or di-n-butyl-boron chloride and sodium pentacarbonylmanganate results in complete elimination of carbonyl groups with the formation of compounds of the type $(R_2B{-}Mn)_2$.

Ionic complexes of manganese carbonyl derivatives have also been obtained containing the tetrafluoroborate anion[194]:

$$C_2H_5Mn(CO)_5 + (C_6H_5)_3C^+BF_4^- \rightarrow [C_2H_4{-}Mn(CO)_5]^+BF_4^-$$

$$[C_2H_4{-}Mn(CO)_5]^+BF_4^- + P(C_6H_5)_3 \rightarrow [(C_6H_5)_3P]_2Mn(CO)_4]^+BF_4^- .$$

An interesting complex of a hydroboron with manganese carbonyl $B_2H_7Mn_3(CO)_{10}$ has recently been synthesised[209]. It is stable only in the absence of air. Electron diffraction has shown that the manganese and boron atoms are linked by hydrogen bonds:



The boron–manganese distances in this compound are 2.30 ± 0.02 Å, the boron–boron bond length is 1.76 ± 0.03 Å, and the manganese atoms are only 2.845 ± 0.003 Å apart. We may recall that the manganese–manganese bond length in the decacarbonyldimanganese molecule is 2.923 ± 0.003 Å.

An organoboron analogue of cyclopentadienylmanganese tricarbonyl has recently been synthesised[210]:

$$B_9C_2H_{11}Cs_2 + BrMn(CO_5) \xrightarrow{\text{rapid}} [B_9C_2H_{11}Mn(CO)_5]^- + 2\,CsBr$$

$$[B_9C_2H_{11}Mn(CO)_5]^- \xrightarrow{\text{slow}} [B_9C_2H_{11}Mn(CO)_3]^- + 2CO .$$

X. APPLICATIONS OF MANGANESE CARBONYL DERIVATIVES

Since manganese carbonyl derivatives have been relatively little studied, it is still early to speak of their widespread application. However, several prospects already exist for making use of these compounds.

During 1956–1957 the first papers appeared[211–214] on the use of methylcyclopentadienylmanganese tricarbonyl and its derivatives as anti-knock compounds. A great deal of work is now being done on the industrial application of cyclopentadienylmanganese tricarbonyl, which is almost twice as effective as tetraethyl-lead, at present widely employed for this purpose; furthermore, it is considerably less toxic[215]. Information is available[216,217] on the use for anti-knock purposes of other derivatives of manganese carbonyl, not containing a cyclopentadienyl ring, including decacarbonyldimanganese itself.

Derivatives of manganese carbonyl find some application as additives to lubricating oils[218].

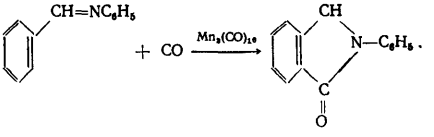
Furthermore, various compounds containing an M–CO bond are gradually finding increasingly wide use as catalysts for various processes. More than fifty types of reactions catalysed by metal carbonyls are known at the present time[199,219], many of them involving manganese carbonyl. The most important of these processes are given below.

(a) Carbonylation of Organic Compounds

Manganese carbonyl and its derivatives can act as a source of carbonyl groups for various processes of carbonylation. For example, dimethylformamide is formed by reaction between decacarbonyldimanganese and excess of dimethylamine[219,220]:

$$22\,(CH_3)_2NH + 3Mn_2(CO)_{10} \rightarrow 2\{Mn[(CH_3)_2NH]_6\}[Mn(CO)_5]_2 + 10HCON(CH_3)_2 .$$

Transfer of carbon monoxide can occur also catalytically in the presence of manganese carbonyl heated to 200–250°C under a high pressure of carbon monoxide. An example of such transfer is the carbonylation of *N*-phenylbenzylideneimine[221]:



Derivatives of metal carbonyls can be used to carbonylate other organic compounds besides amines, e.g. alkyl halides[222,223]:

$$CH_3Cl + NaMn(CO)_5 \rightarrow CH_3{-}Mn(CH)_5 \xrightarrow{CO} CH_3CO{-}Mn(CO)_5 \xrightarrow{Br_2} CH_3COBr + BrMn(CO)_5$$

(b) Hydrogenation

Various organic compounds can be hydrogenated in the presence of a hydrogen carbonylmanganate. With proton-acceptors present, hydrogen pentacarbonylmanganate decomposes forming decacarbonyldimanganese, while the hydrogen atom liberated is transferred to the acceptor:

$$2HMn(CO)_5 \rightarrow 2H^{\cdot} + Mn_2(CO)_{10}$$

$$CH_3COCH_3 + 2H^{\cdot} \rightarrow CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 .$$

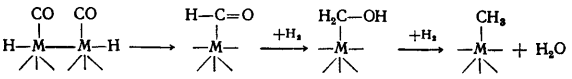
At elevated temperatures the hydrogenation may be autocatalytic[223,224].

(c) Transfer of Carbon Monoxide and Hydrogen (Fischer–Tropsch Synthesis)

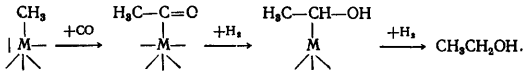
An example of the simultaneous transfer of carbon monoxide and hydrogen is provided by the synthesis of ethanol from methanol, carbon monoxide, and hydrogen in the presence of manganese carbonyl[225,226]:

$$CH_3OH + CO + H_2 \xrightarrow{Mn_2(CO)_{10}} CH_3CH_2OH .$$

The mechanism of this reaction can be represented by a scheme comprising (i) formation of methyl from carbon monoxide and hydrogen



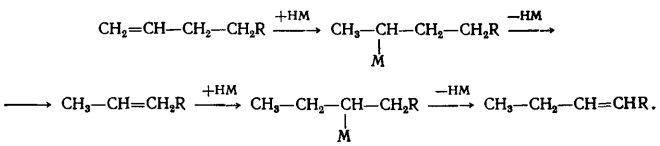
and (ii) chain growth



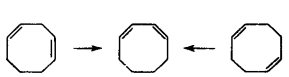
This reaction will probably provide a method of obtaining higher alcohols.

(*d*) Isomerisation of Alkenes

The isomerisation of alkenes involves the intermediate addition of the hydrocarbonylmetal complex (HM) at the double bond in the organic molecule, followed by its elimination according to the scheme



Wittenberg and Seibt[227] accomplished the isomerisation of cyclo-octa-1,4(and 1,5)-diene into cyclo-octa-1,3-diene in the presence of decacarbonyldimanganese:



(*e*) Polymerisation of Alkenes

Little work has yet been done on the possibility of using metal carbonyls as catalysts for the polymerisation of unsaturated compounds. Bamford and his coworkers[228,229] have accomplished the polymerisation of methyl methacrylate in the presence of manganese and rhenium carbonyls in polar solvents, and found them to exert a stereoregulating effect on processes of radical polymerisation.

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