

THE ROLE OF ORGANOMETALLIC COMPOUNDS IN THE DEVELOPMENT OF COORDINATION CHEMISTRY

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This paper describes and discusses a particular class of coordination compound, namely that type of metal complex where one or more carbons are the ligand atoms. Since the complexes have metal-carbon bonds, they are also known as organometallic compounds.

It is now well-established that many organometallic compounds are also coordination compounds. However, this fact was far less evident before the reports^{1, 2} of the discovery of ferrocene, in 1951 and 1952, than it is today. As with many areas of scientific endeavour, two fields of study have converged to the mutual benefit of both. Before describing some of the specific organometallic compounds which have advanced our knowledge of coordination chemistry, it is of interest to trace briefly the convergence of these two fields.

The history of organometallic compounds is commonly supposed to have begun with the researches of Bunsen on cacodyl (tetramethyldiarsine) in 1841³. In the ensuing thirty years organo-derivatives of mercury, zinc, cadmium, tin and lead were reported. However, from the point of view of the close relationship between organometallic chemistry and coordination chemistry a more significant discovery was the earlier work of the Danish chemist Zeise who, in 1831, reported the compound $\text{KCl} \cdot \text{PtCl}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{H}_2\text{O}$, known as Zeise's salt, as a product of the reduction of platinum(IV) chloride with alcohol⁴. Zeise's salt was the first metal-olefin complex to be discovered, and for many years the structures and mode of bonding of the carbon atoms to the metal in this and similar compounds were matters of considerable dispute⁵. It was not until 1951 that a satisfactory theory was put forward by Dewar to account for the existence of metal-olefin complexes⁶. It was proposed that in a mono-olefin complex the two carbon atoms of the double bond would be equivalently bound to the metal. Overlap of the π -bonding orbital of the olefin with a vacant σ -type orbital of the metal furnishes a dative bond of essentially σ -type. To this is added a π -type bond originating from overlap of a filled d orbital of the metal with an empty π -antibonding orbital of the double bond^{6, 7}. The stereo-chemical implications of this description of the bonding were confirmed by X-ray crystallographic studies⁸⁻¹⁰†.

† Recent n.m.r. studies [R. Cramer, *J. Am. Chem. Soc.* **86**, 217 (1964)] have shown that in some rhodium-olefin complexes in solution the olefin may rotate with the σ -bond as axis. If this occurs d_{xy} as well as d_{xz} metal orbitals are involved in the π -type bond. However, rotation does not require that the π -bond be broken (*loc. cit.*).

What later proved to be a landmark both for coordination chemistry and for organometallic chemistry was the discovery of nickel tetracarbonyl by Mond and his co-workers in 1890¹¹, and of iron pentacarbonyl in 1891^{12, 13}. The metal carbonyls¹⁴ have always been the subject of intensive study.

Following the development of the concept of electron pair donor bonds, the carbonyls were quickly recognized as coordination compounds of special novelty because of the low oxidation state of the metal. However, the fact that they were also organometallic compounds was ignored, since there seemed to be little connection between them and substances such as tetraethyllead and the Grignard reagents. This arbitrary distinction was only removed after the comparatively recent discovery of substances like methylmanganese pentacarbonyl (*Figure 1*) which contain in the same molecule two different types of metal-carbon bond.

For many years the constitution of the metal carbonyls posed a problem. However, considerable progress was made through the realization that the so-called "effective atomic number rule" (E.A.N.) was obeyed¹⁵; that is, if carbon monoxide groups were regarded as electron pair donors, then in simple carbonyls $M(CO)_y$ with one metallic atom in the molecule the effective atomic number of M (atomic number of $M + 2y$) was invariably a rare gas number. Exceptions to the E.A.N. rule are now known but in the early days the formalism served the useful purpose of classifying the metal

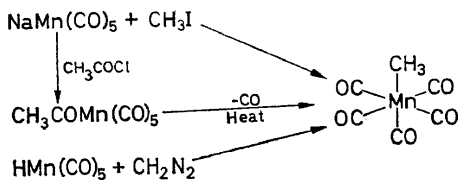


Figure 1. Methylmanganese pentacarbonyl *see* Closson, Kozikowski and Coffield. *J. Org. Chem.* **22**, 598 (1957) and Hieber and Wagner. *Z. Naturforsch.* **12b**, 478 (1957)

carbonyls as inner orbital complexes and this in turn led to the valence bond concept of hybridization being used to account for and even predict possible structures¹⁶. Thus nickel in nickel tetracarbonyl must use sp^3 hybrid orbitals, and hence be tetrahedral in agreement with the known structure¹⁷.

In the metal carbonyls the overlap of the orbital on the carbon atom containing the lone pair with a vacant metal orbital may be regarded as forming a metal-carbon σ -bond. In view of the low basicity of carbon monoxide, however, this is not in itself regarded as sufficient to explain the stability of the carbonyls, and a further source of bonding is invoked. In all of the metal carbonyls there are filled non-bonding d -orbitals of the metal which are of the correct symmetry to overlap with fairly low lying π -antibonding orbitals of carbon monoxide. Formation of this additional π -bond by transference of charge from the metal can be seen to be, not only a supplementary bond, but also the means of strengthening the original σ -bond by removal of the charge separation induced by it. Improved σ -bonding allows more extensive metal-to-ligand π -bonding. This produces what has been described¹⁸ as a "synergic" interaction between the two types of bonding. This scheme has been particularly successful in inter-

preparing the infra-red spectra of carbonyls and their derivatives, and this subject will be enlarged upon later.

In a modern view, then, metal-carbon bonds both in metal carbonyls and in metal-olefin complexes have σ and π components[†]. This concept has also been useful in understanding the nature of the metal-carbon bonds in the numerous types of complex formed between metals and groups of unsaturated carbon atoms, which have been isolated since the discovery of ferrocene. These include the cyclopentadienyl, arene, cyclobutadiene, and π -allyl metal compounds, whose discovery has opened up a whole new area, common both to coordination chemistry and to organometallic chemistry.

In the development of modern coordination chemistry the role played by the metal carbonyls and their derivatives has been especially significant. Thus the zero oxidation state of the metal in these compounds stimulated the synthesis of other compounds having transition metals in unusually low oxidation states. Moreover, the metal carbonyls proved to be the parent substances of other species such as the metal carbonyl anions, the metal carbonyl nitrosyls, the metal carbonyl hydrides and the metal carbonyl halides. These four classes of carbonyl derivatives have been increasingly studied, and are currently providing new structural, spectroscopic and preparative information of significance to the whole field of coordination chemistry. The study of metal carbonyl chemistry has also provided the stimulus for a current interest in the synthesis of compounds containing metal-metal bonds.

With this introduction let us consider some studies in metal carbonyl chemistry which are pertinent to the subjects just mentioned. Discussion is based primarily on results obtained by employing just four carbonyl species as starting materials for the synthesis of new compounds, and also on additional work suggested by the initial studies. The four metal carbonyl complexes were π -C₅H₅V(CO)₄, Fe(CO)₅, HMn(CO)₅, and [Mn(CO)₅]⁻.

First to be reviewed are results obtained by exploring the chemistry of π -cyclopentadienylvanadium tetracarbonyl. Some seven years after ferrocene was discovered the field of hydrocarbon-metal complexes had expanded

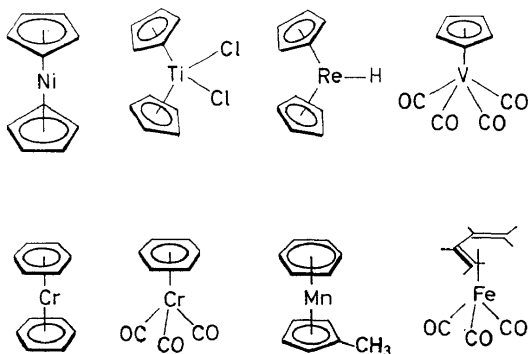


Figure 2

[†] In classic studies on the chemical behaviour of Zeise's salt, and related olefin-metal compounds, Anderson¹⁹ in 1934 pointed out that carbon monoxide and ethylene appeared to play similar roles in their respective metal complexes.

to include compounds such as those summarized in *Figure 2*. A variety of metal sandwich complexes had been described wherein cyclopentadienyl, benzene, and diene groups act as ligands to metals. It was obvious that the next step in this expanding field should be the synthesis of complexes in which seven carbon atoms are equivalently bonded to a metal. The first such neutral tropylium compound was obtained²⁰ by heating π -cyclopentadienylvanadium tetracarbonyl with cycloheptatriene†. It was conceivable that this reaction could have afforded either of the compounds shown in *Figure 3*. Since these two possible products differ in composition

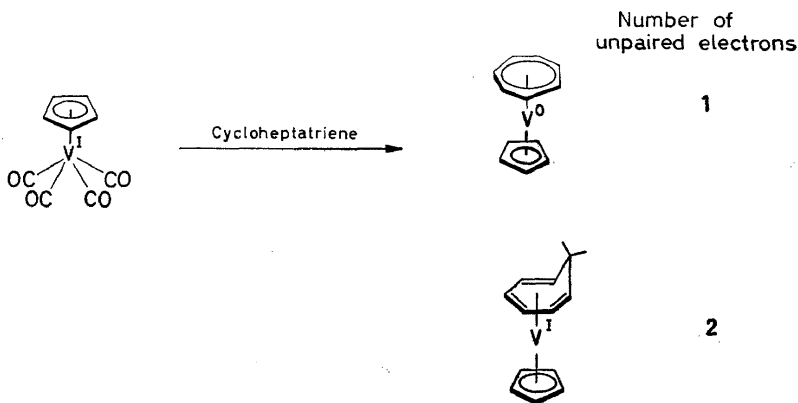


Figure 3

only by one hydrogen atom, elemental analysis cannot be used to distinguish between them. However, the cycloheptatriene complex has the vanadium atom in oxidation state I, if the normal convention of assigning a minus one charge to the cyclopentadienyl ring is adopted. In this structure the paramagnetism of the complex should correspond to two unpaired electrons. In a π -cycloheptatrienyl- π -cyclopentadienylvanadium complex, however, paramagnetism equivalent to one unpaired electron should be observed, since the vanadium atom can formally be regarded as being in oxidation state zero. The magnetism of 1.69 β observed for the product was convincing evidence of formation of a true C_7H_7 sandwich complex. This compound naturally aroused considerable interest, and even some scepticism, but last year, shortly before his untimely death, Rundle²² confirmed the structure by an X-ray crystallographic study (*Figure 4*). The apparent oxidation state of zero for vanadium, stabilized in this complex‡, is

† The first tropylium-metal complex to be reported²¹ was $[C_7H_7Mo(CO)_3]BF_4$. This complex, unlike $C_5H_5VC_7H_7$, is not a neutral molecule. Since the discovery of these two complexes other C_7H_7 metal compounds have been reported. For a review see reference 23.

‡ In $C_7H_7VC_5H_5$ the vanadium atom could be assigned a formal oxidation state of two if the cycloheptatrienyl anion is assumed to be present $[C_7H_7^-V^{II}C_5H_5^-]$. This seems less likely, however, because of the discovery of the hexacarbonyl and other complexes in which vanadium must be in oxidation state zero, and the well-known stability of the tropylium ion.

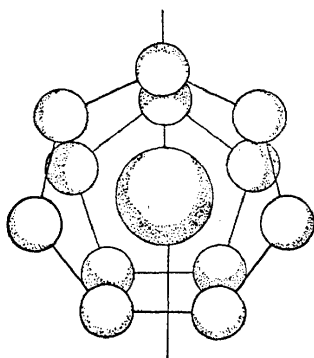


Figure 4. π -Cyclopentadienyl π -cycloheptatrienyl vanadium. Projection of molecule perpendicular to the molecular axes. See Rundle and Engebretson. *J. Am. Chem. Soc.* **85**, 481 (1963)

of course rather uncommon for this metal, but is also found in dibenzenevanadium, in vanadium hexacarbonyl, and in the phosphine complexes $V[C_2H_4(PMe_2)_2]_3$ and $(Ph_3P)_2V(CO)_4$.

Another interesting coordination compound obtainable from π -cyclopentadienylvanadium tetracarbonyl is the sulphur bridged complex $[\pi-C_5H_5V(SMe)_2]_2$ ²⁴. Complexes in which organosulphur groups bridge two metal atoms have long been known (Figure 5). Hieber and co-workers²⁵, for example, first isolated several iron compounds by reacting iron pentacarbonyl with sulphur compounds. More recently many other sulphur bridged complexes have been described. All the compounds were found to be diamagnetic. To account for this in some of the structures, it was necessary to postulate electron pairing in metal-metal bonds. An X-ray analysis of $[EtSFe(CO)_3]_2$ was especially significant since the observed molecular geometry was in accord with the presence of a bent metal-metal bond²⁶.

Examination of the magnetic properties of the sulphur bridged vanadium complex (Figure 6), however, showed it to be weakly paramagnetic (Table I). Regardless of the oxidation state assigned to vanadium, each of the vanadium atoms will have two electrons fewer than the krypton configuration if each

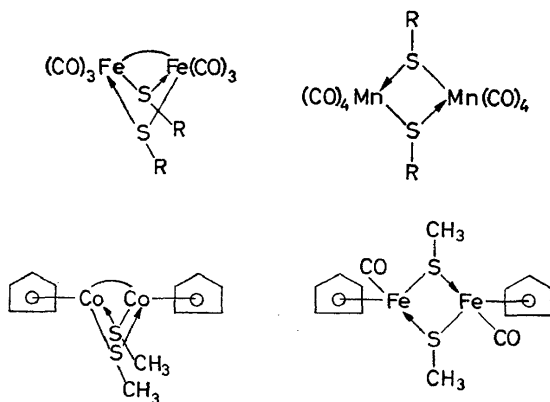


Figure 5

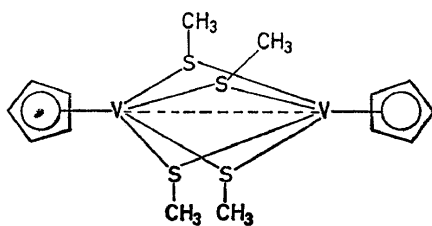


Figure 6.

Table 1. Magnetic data for $[\text{C}_5\text{H}_5\text{V}(\text{CH}_3\text{S})_2]_2^\dagger$

T ($^\circ\text{K}$)	$10^6 \chi \text{ cor}^M$	μ_{eff} (β)
195.1	308	0.70
280.1	340	0.88
298.3	351	0.92
313.3	366	0.96
328.3	379	1.00
344.5	390	1.04

† Solid measured by the Gouy method, with results expressed per vanadium atom.

sulphur retains one unshared electron pair. Each metal atom then possesses two electrons not directly involved in metal-ligand bonding. If these electrons are unpaired, and do not interact appreciably with a similar set on the other vanadium, a magnetic moment of 2.8β per vanadium is expected. However, if these electrons are locally paired, or by means of metal-metal interaction have their spins completely quenched through exchange forces, diamagnetism should result.

The magnetic moments, calculated from the Curie law, are considerably less than that expected for even one unpaired electron. The results suggest strong exchange interaction between the metal atoms whereby a ground state singlet is produced. The multiplicity of the lowest paramagnetic state is presumably triplet, but the data are insufficiently extensive to allow evaluation of the exchange energy. A molecular triplet state could arise by formation of a strong vanadium-vanadium bond, leaving a single electron on each metal which could then couple through a weaker exchange mechanism. The latter effect is now well established in binuclear complexes such as copper(II) acetate monohydrate^{27-29†}.

The vanadium complex $[\pi\text{-C}_5\text{H}_5\text{V}(\text{SMe})_2]_2$ appears to represent the first example of a binuclear organometallic compound in which a paramagnetic state is within thermal range. In binuclear metal carbonyls having bridging carbonyl groups, like $\text{Fe}_2(\text{CO})_9$ (Figure 7), the singlet-triplet separation is much greater than kT , with virtual complete occupation of the singlet level at room temperature. It is perhaps worth mentioning that at the time of its discovery the vanadium compound was the first

† Recently an alternative explanation for spin-spin coupling in binuclear complexes has been given in terms of a super exchange mechanism operating through the bridging groups [W. E. Hatfield and J. S. Paschal, *J. Am. Chem. Soc.* **86**, 3888 (1964)].

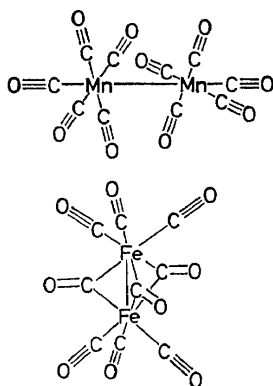
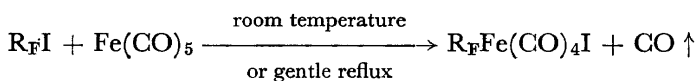


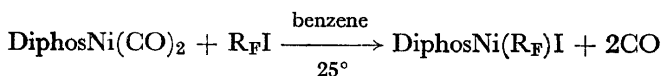
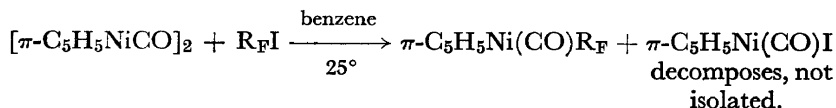
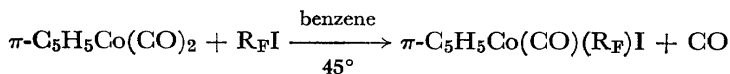
Figure 7

example of a binuclear complex with four bridging groups. Recently, however, King³⁰ has reported other compounds obtained from reactions between cyclopentadienylmetal carbonyls and bis(trifluoromethyl)-dithietene. The vanadium complex from this disulphide also has a low magnetic moment [0.6 β at 298°K], suggesting vanadium–vanadium double bond character.

Although the chemistry of iron pentacarbonyl has been under continuous study since its discovery, this organometallic compound continues to provide a starting point for the preparation of unusual coordination compounds. Thus it was primarily the discovery³¹ of the smooth reaction of iron pentacarbonyl with perfluoroalkyl iodides according to the equation:



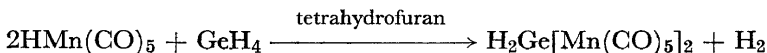
which led us to develop the chemistry of the fluorocarbon derivatives of the transition metals in which the fluorocarbon groups are σ -bonded to the metals³². It has long been known that iodine reacts with iron pentacarbonyl to afford iron tetracarbonyl di-iodide. The similarity between the latter reaction and the reaction involving the perfluoroalkyl iodides suggested that these iodides should react with all those metal carbonyls or metal carbonyl derivatives known to react with iodine. This has proved to be true, and for example perfluoroalkyl-iodo-derivatives of cobalt and nickel have thereby been obtained^{33–35}.



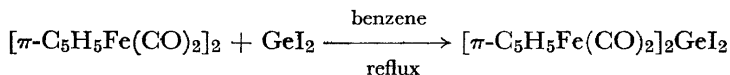
Coordination compounds of the transition metals having fluorocarbon groups as ligands will be mentioned again later, but continuing now to discuss novel reactions of iron pentacarbonyl it is interesting to recall some work involving tetraorganotin compounds.

This work is mentioned for two reasons. Firstly it is relevant to the current interest in complexes containing covalent metal-metal bonds. Secondly, it is not uncommon in organometallic chemistry to obtain as a reaction product a compound of unexpected nature. In 1960 there was considerable interest in diene-iron tricarbonyl complexes. We attempted to make a compound of this kind by heating dibutyldivinyltin with iron pentacarbonyl in ethylcyclohexane³⁶. The yellow crystalline product proved to have an unexpected composition. The molecular composition was in fact double that of the empirical composition of a compound previously obtained by Hieber and Breu³⁷ by treating dibutyltin dichloride with the potassium salt of iron carbonyl. The two compounds were shown to be identical. To account for the properties, the most satisfactory structure involves iron-tin-iron bridges. By treating other tetraorganotin compounds with iron pentacarbonyl other dialkyltin-iron tetracarbonyl dimers, $[\text{R}_2\text{SnFe}(\text{CO})_4]_2$, were prepared. During the last two years this area of study has been considerably extended by the synthesis of compounds in which Group IV metals are bound to transition metals. Most of the complexes have been prepared by treating organo-germanium, -tin and -lead halides with alkali metal salts of metal carbonyls^{38a}. For a novel extension of this approach see Graham and Patil^{38b}.

While discussing complexes of this kind, having Group IV element-transition metal bonds, it is appropriate to refer to the reaction between pentacarbonylmanganese hydride and germane³⁹:



Bis(pentacarbonylmanganese)germane is a pale-yellow, air stable, volatile solid. Its stability suggests that it should be possible to prepare a number of transition metal complexes containing GeX_2 ($\text{X} = \text{H}$, halogen, alkyl *etc.*) groups. In agreement with this, we have recently obtained⁴⁰ an iron compound, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{GeI}_2$:

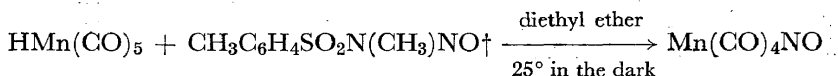


The formal similarity between $[(\text{CO})_5\text{Mn}]_2\text{GeH}_2$ and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{-GeI}_2^\dagger$ is perhaps not surprising in view of similarities in the chemistry of the two carbonyls $\text{Mn}_2(\text{CO})_{10}$ and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ ⁴¹.

It is of interest that the structure of pentacarbonylmanganese hydride has only recently been elucidated⁴³ although the hydridocarbonyl has played a key role in several important developments. For example, the hydride has been used to prepare tetracarbonylnitrosylmanganese, a representative of a new class of metal carbonyl nitrosyl, and to prepare several fluoroalkyl manganese pentacarbonyls.

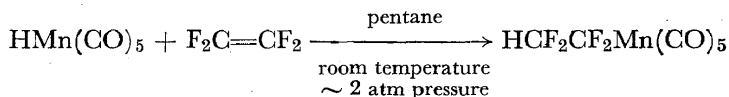
† A tin compound $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$, analogous to $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{GeI}_2$, has recently been reported⁴².

The compounds $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$ have long been recognized as an interesting isoelectronic and isosteric series⁴⁴. Recently this series was significantly extended by the preparation of trinitrosyl-carbonylmanganese by Barraclough and Lewis⁴⁵. In this complex the manganese atom can be regarded as attaining the effective atomic number of krypton by sharing nine electrons with the three nitrosyl groups, and two electrons with the carbonyl group. There is, however, an alternative combination of nitrosyl and carbonyl groups which can contribute eleven electrons to the valence shell of a manganese atom. This combination would consist of four carbonyl and one nitrosyl groups in the complex $\text{Mn}(\text{CO})_4\text{NO}$. This nitrosyl was obtained by the reaction⁴⁶:

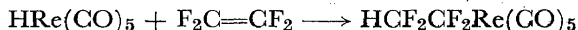
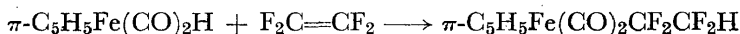
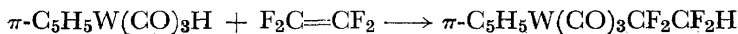


Tetracarbonylnitrosylmanganese (0) is a deep-red air-sensitive diamagnetic liquid, forming reddish-brown vapours resembling bromine in appearance. The number of CO and NO stretching modes observed in the infra-red spectrum of the nitrosyl compound is in accord with a trigonal bipyramidal structure having the NO group at the apex on a threefold axis. In possessing a trigonal bipyramidal structure tetracarbonylnitrosylmanganese is similar to iron pentacarbonyl. Thus, this nitrosyl may be regarded as the first member of a new isoelectronic and isosteric series based on iron pentacarbonyl.

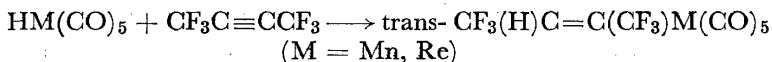
In 1960, Treichel discovered⁴⁷ that manganese pentacarbonyl hydride would add readily across the double bond of tetrafluoroethylene:



This reaction was subsequently shown to be fairly general, and has proved very useful in the synthesis of many fluoroalkyl transition metal complexes. Several hydrido-metal carbonyls have been found to react with tetrafluoroethylene under mild conditions of temperature and pressure⁴⁹⁻⁵¹.

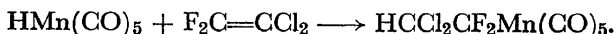
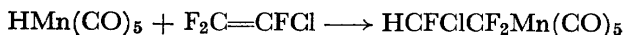


Moreover, related complexes have been prepared by treating hydrido-metal carbonyls with chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene and perfluorobut-2-yne. With the acetylene, and employing the usual mild conditions, reaction ceases after addition of one mole of hydride^{48, 51}:

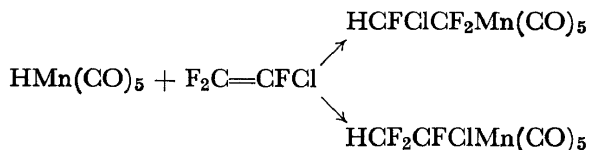


† *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide.

Reactions between hydridomanganese or hydridorhenium pentacarbonyl and chlorotrifluoro- or dichlorodifluoro-ethylene have been carefully studied, since the product might be a single isomer, or a mixture of isomers. When reactions are carried out between hydridomanganese pentacarbonyl and the chlorofluoroethylenes in a steel bomb so that an appreciable quantity of olefin is present in the liquid phase the hydromanganation products are mainly those isomers with CF₂ groups adjacent to the manganese atom⁵²:

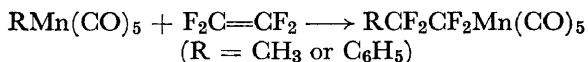


On the other hand, if the addition reactions are carried out under conditions whereby the chlorofluoroethylenes are present in lower concentration, a mixture of isomers is produced:



The relative proportions of the two isomers from chlorotrifluoroethylene can be changed by altering the ratio of the reactants. This is not the case with hydridorhenium pentacarbonyl. This hydride reacts with the chlorofluoroethylenes to afford the complexes $\text{HCCl}_2\text{CF}_2\text{Re}(\text{CO})_5$ and $\text{HCFC}_1\text{CF}_2\text{Re}(\text{CO})_5$ only, irrespective of the amount of the olefins taken for reaction. The contrasting behaviour of the two hydrido-metal carbonyls is but another example of differences in the chemistry of the organo-derivatives of manganese and rhenium†.

The discovery that hydridomanganese pentacarbonyl will add so readily to tetrafluoroethylene prompted an investigation to determine whether methyl- and phenyl-manganese pentacarbonyls would behave similarly. This proved to be the case, under appropriately chosen reaction conditions⁵².

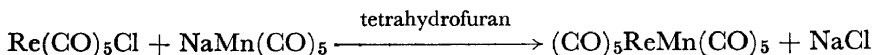
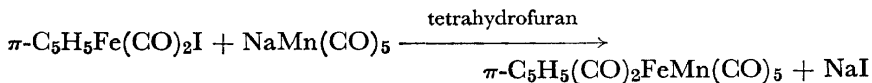


Even with excess of tetrafluoroethylene, methylmanganese pentacarbonyl affords $\text{CH}_3\text{CF}_2\text{CF}_2\text{Mn}(\text{CO})_5$, but with methylrhenium pentacarbonyl and excess of tetrafluoroethylene $\text{CH}_3(\text{CF}_2\text{CF}_2)_2\text{Re}(\text{CO})_5$ is obtained, albeit in very low yield, as well as the expected $\text{CH}_3\text{CF}_2\text{CF}_2\text{Re}(\text{CO})_5$ ⁵¹.

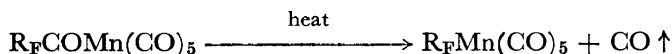
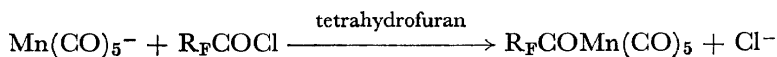
The pentacarbonylmanganese anion may be obtained by cleavage of the metal-metal bond in dimanganese decacarbonyl with an alkali metal amalgam, or an alkali metal. The presence of a metal-metal bond in dimanganese decacarbonyl (Figure 7) was shown by an X-ray crystallographic study of Dahl and Rundle⁵³. This crystallographic study was highly significant since among other things it demonstrated that metal atoms in polynuclear metal carbonyls need not necessarily be held together by

† Thus, for example, whereas manganese forms $[\text{C}_5\text{H}_5^-]_2\text{Mn}^{+2}$, rhenium forms $(\pi\text{-C}_5\text{H}_5)_2\text{ReH}$. Moreover, $\text{HRe}(\text{CO})_5$ does not react with germane to form $\text{H}_2\text{Ge}[\text{Re}(\text{CO})_5]_2$ under conditions where $\text{HMn}(\text{CO})_5$ yields $\text{H}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$.

bridging carbonyl groups. Moreover, the presence of a simple covalent metal-metal bond in dimanganese decacarbonyl suggested the possibility of preparing mixed metal carbonyls. For this the $[\text{Mn}(\text{CO})_5]^-$ anion has proved useful^{54, 55}:

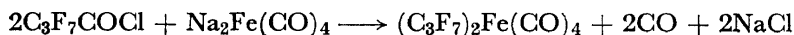
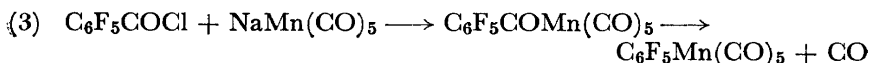
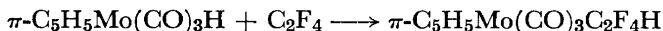
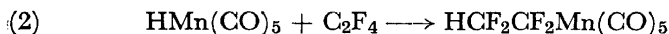
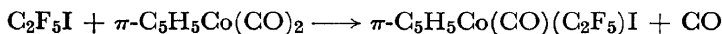
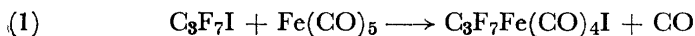


The pentacarbonylmanganese anion has also been employed in the synthesis of many organomanganese pentacarbonyls by treating the anion with appropriate organic halides⁵⁶. In this context the preparation of polyfluoro-organomanganese pentacarbonyls by the following reaction sequence can be mentioned³²:

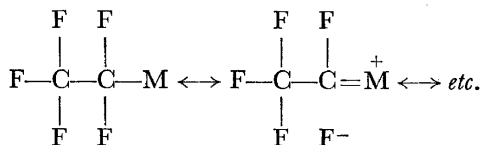


[R_F = perfluoroalkyl (*e.g.* C_2F_5), polyfluoroalkyl (*e.g.* $\text{H}(\text{CF}_2)_4$), perfluoroaryl (*e.g.* C_6F_5).]

As with the addition of pentacarbonylmanganese hydride to tetrafluoroethylene, these two reactions are also quite general. Many carbonyl metal anions will react with perfluoro-organo-acyl halides to afford a perfluoro-acylmetal carbonyl, which can be subsequently decarbonylated to yield a complex in which a fluorocarbon group is σ -bonded to a transition metal. During the course of this work³² seven different methods for preparing coordination compounds of this type have been employed. However, of these methods the three mentioned in this review namely, the reaction between a metal carbonyl and a perfluoroalkyl iodide, the addition of a metal carbonyl hydride to a fluoro-olefin, and the reaction between a carbonyl metal anion and a perfluoroacyl halide are the most important, since they have afforded the most compounds. For convenience, examples of these three methods are summarized:



Apart from their intrinsic interest as new species representing a convergence of fluorocarbon and transition metal chemistry these compounds have many interesting properties³². For example, they are chemically relatively robust for complexes having metal-carbon σ -bonds. Many of the compounds are indefinitely stable in the presence of air and moisture. Presumably the bond is stabilized by the high electronegativity of the fluorocarbon group which could lead to removal of negative charge from the metal, both by an inductive and by a mesomeric process, *e.g.*:



Such charge transfer would increase the ionic resonance energy of the carbon-metal bond. There is some evidence for the removal of negative charge from the metals from the infra-red spectra of the fluorocarbon compounds in the metal carbonyl region. The carbonyl frequencies are similar to those in analogous carbonyl halides⁵⁷. They occur at higher frequencies than corresponding absorptions in the parent carbonyls or in the alkylmetal carbonyls[†]. This is in accord with the idea that both in fluorocarbon-metal carbonyls and in metal carbonyl halides the fluorocarbon or halide substituents remove negative charge so that less $d\pi-p\pi$ bonding is possible between the metal and CO groups. Reduction in π -bonding between the metal and a carbonyl group will result in more triple bond character in the carbon-oxygen link so that it absorbs at higher frequency. In following frequency changes of this kind progressively the fluorocarbon-metal carbonyls are perhaps more useful than the carbonyl metal halides since the latter are limited to three kinds (Cl, Br or I).

In studies on the infra-red spectra of coordination compounds the number of observed absorptions of a particular kind has often provided important structural information. Thus, group theory predicts that complexes $\text{XM}(\text{CO})_5$ [$\text{M} = \text{Mn}, \text{Tc}, \text{Re}$; $\text{X} = \text{halogen}$] having octahedral symmetry should show three CO fundamental infra-red bands, classified as two A_1 and one E stretching modes⁵⁸. The generality of this prediction has been confirmed experimentally (*Table 2*)⁵⁹. Orgel⁵⁸, however, has pointed out that in addition to the normal frequencies, splitting of the intense E transition and appearance of a low intensity B_1 transition might be observed in complexes of this type if the ligand-metal group lacks axial symmetry. Preparation of a variety of fluorocarbon-metal pentacarbonyls permits a test of Orgel's suggestion since the various synthetic methods referred to earlier permit the preparation of compounds having varying degrees of asymmetry in the fluorocarbon group. Clearly, if X in an $\text{XM}(\text{CO})_5$ complex is a fluorocarbon group, it is capable of greater variation than if X

[†] In $\text{Mn}(\text{CO})_5\text{Cl}$ carbonyl absorptions occur at 2138, 2054 and 1999 cm^{-1} ; in $\text{Mn}(\text{CO})_5\text{I}$ at 2125, 2044 and 2003 cm^{-1} ; and in $\text{CH}_3\text{CF}_2\text{CF}_2\text{Mn}(\text{CO})_5$ at 2134, 2041 and 2012 cm^{-1} . These values may be compared with those observed for $\text{Mn}_2(\text{CO})_{10}$ [2044, 2013, 1981 cm^{-1}] and $\text{CH}_3\text{Mn}(\text{CO})_5$ [2109, 2010 and 1989 cm^{-1}].

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 Table 2. Observed CO stretching frequencies for $\text{XMn}(\text{CO})_5$ molecules (cm^{-1})

X	A_1^{1b} (Weak)	E (V. Strong)	A_1^{1a} (Strong)	Solvent	Reference
Cl	2138	2054	1999	CCl_4	59
Br	2133	2050	2001	CCl_4	59
I	2125	2044	2003	CCl_4	59
CH_3	2109	2010	1989	C_6H_{12}	60
C_6H_5	2114	2021	1997	C_6H_{12}	60
C_2F_5	2130	2038	2023	C_2Cl_4	57

is a halogen atom Cl, Br, or I. The results summarized in Table 3 not only confirm the theoretical prediction of additional CO stretching frequencies in certain complexes but also show that the degree of splitting of the *E* band depends both on the nature of the metal and on the extent of asymmetry within the fluorocarbon-metal group⁶¹.

 Table 3. Observed carbonyl stretching modes for fluoro-organomanganese and fluoro-organorhenium pentacarbonyls [cm^{-1}]

Compound†	A_1^{1b}	B_1	<i>E</i>	δE	A_1^{1a}
$\text{C}_6\text{F}_5\text{COMn}(\text{CO})_5$	2125	2067	2042, 2030	12	2017
$\text{C}_2\text{F}_5\text{COMn}(\text{CO})_5$	2130	2069	2041, 2036	5	2023
$\text{HCCl}_2\text{CF}_2\text{Mn}(\text{CO})_5$	2131	2072	2043, 2037	6	2013
$\text{HCCl}_2\text{CF}_2\text{Re}(\text{CO})_5$	2148	2072	2038, 2035	3	2009
$\text{HCFClCF}_2\text{Mn}(\text{CO})_5$	2133	2072	2043, 2038	5	2014
$\text{HCF}_2\text{CFClMn}(\text{CO})_5$	2132	2075	2045, 2043	2	2014
$\text{CH}_3\text{CF}_2\text{CFClMn}(\text{CO})_5$	2133	—	2043	0	2011
$\text{CH}_3\text{CF}_2\text{CF}_2\text{Mn}(\text{CO})_5^\ddagger$	2134	—	2041	0	2012
$\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$	2130	—	2042	0	2011

† Cyclohexane solution. Spectra recorded with a grating spectrophotometer

‡ Gas phase spectrum shows $\delta E \sim 2 \text{ cm}^{-1}$.

If analogous manganese and rhenium complexes are compared [*e.g.* $\text{HCCl}_2\text{CF}_2\text{Mn}(\text{CO})_5$ and $\text{HCCl}_2\text{CF}_2\text{Re}(\text{CO})_5$] the degree of *E* band splitting and the intensity of the B_1 mode is greatest with manganese. This is to be expected, since with the larger rhenium atom the fluorocarbon group is further away from the four carbonyl groups occupying the equatorial positions in the octahedron. Consequently, any asymmetry in the fluorocarbon group will have less effect on the CO vibrations than with the smaller manganese atom.

Because of the stereochemistry of a saturated carbon atom in the complexes, the chlorofluoroalkyl side chains will be staggered in such a manner as to place chlorine, fluorine or hydrogen atoms preferentially closer to two out of the four equatorial CO groups, thus reducing the symmetry. Not surprisingly the appearance of additional bands is particularly marked with the acylmanganese pentacarbonyls. The stereochemical consequences of an acyl group would place its attached fluorocarbon group towards two of the four equatorial CO groups so that these four would no longer be equivalent, as they are in the axially symmetric pentafluorophenylmanganese pentacarbonyl which shows just three bands.

These studies show that the attachment of an organic group to the metal in a complex can lead to interesting spectroscopic results pertinent to the greater problem of the symmetry of coordination compounds as a whole.

It is to be hoped that this review has shown that the study of organo-metallic compounds can assist the general development of the wider field of coordination chemistry, and even how a sub-branch of organometallic chemistry, that concerned with fluorocarbon derivatives, can add to our knowledge of the behaviour of metal complexes.

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