Organic Syntheses via Metal Carbonyls

Volume 1

Edited by
IRVING WENDER
Pittsburgh Coal Research Center
Bureau of Mines
U.S. Department of the Interior
Pittsburgh, Pennsylvania

and
PIERO PINO
Istituto di Chimica Organica Industriale
Università di Pisa
Pisa, Italy

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Authors of Volume 1

F. CALDERAZZO
Cyanamid European Research Institute, Cologny, Geneva, Switzerland

R. ERCOLI
Istituto di Chimica Industriale, Università di Palermo, Palermo, Italy

R. F. HECK
Hercules Research Center, Wilmington, Delaware

C. HOOGZAND
Union Carbide European Research Associates, Brussels, Belgium

W. HÜBEL*
Union Carbide European Research Associates, Brussels, Belgium

G. NATTA
Istituto di Chimica Industriale del Politecnico, Milan, Italy

A. ROSENTHAL
University of British Columbia, Vancouver, Canada

I. WENDER
Pittsburgh Coal Research Center, Bureau of Mines, Pittsburgh, Pennsylvania

*Present address: Deutsches Patentamt, München, Germany.

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(Tentative)

Metal Carbonyls: Preparation, Structure, and Properties*

F. CALDERAZZO, *Cyanamid European Research Institute, Cologny, Geneva, Switzerland*

R. ERCOLI, *Istituto di Chimica Industriale, Facoltà di Ingegneria, Università di Palermo, Palermo, Italy*
and

G. NATTA, *Istituto di Chimica Industriale del Politecnico, Milan, Italy*

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* Since this chapter is long, its format differs somewhat from the other chapters. For the convenience of the reader, equations and structures in this chapter are numbered consecutively under each main heading; references are also placed after each main heading, except in Section V, where they are placed after each subheading. As with the other chapters, however, tables and figures are numbered consecutively throughout the chapter.

I. INTRODUCTION

A. Historical and General Considerations

Since tetracarbonylnickel was discovered in 1890 by Mond, Langer, and Quincke, the field of metal carbonyls has become extremely fertile and carbonyls of a large number of transition metals have been prepared. Those of manganese, $Mn_2(CO)_{10}$, vanadium, $V(CO)_6$, and technetium, $Tc_2(CO)_{10}$, were the last to be discovered in 1949, 1959, and 1961, respectively. A good knowledge of carbonyls of the first row transition elements has been achieved and their x-ray structures have been fully established.

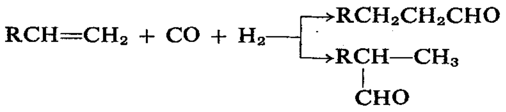
A large part of the material contained in the following sections deals with carbonyls of the first row transition metals, because these have been studied considerably more than the carbonyls of the second and third row elements. Care has been taken, however, to include material dealing with carbonyls of the second and third row elements also, since this is an area of increasing expansion. Apparently one of the main reasons for the smaller interest in carbonyls of the second and third row has been the high cost of the metals, especially for the group VIII elements. One can readily predict that the amount of work aimed at a deeper knowledge of ruthenium, iridium, and osmium carbonyls, for example, will gradually increase in the near future.

Most of the group VIII carbonyls of the second and third row elements are inadequately known. Even the existence of the reported $Rh_2(CO)_8$ and $Ir_2(CO)_8$ seems doubtful. Other substances, such as $Ru(CO)_5$ and $Os(CO)_5$ have been reported before the use of infrared spectrometry as a common laboratory technique. These two pentacarbonyls have been reported to be unstable at room temperature, with rapid conversion to the trimers $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ especially in the presence of light. It would be very interesting to establish the existence of the pentacarbonyls by infrared investigation of the freshly prepared products. The two pentacarbonyls should be easily characterized by their infrared spectra because only two structures are possible (C_{4v} and D_{3h}). If D_{3h} is the correct structure, the spectrum should be practically identical with that of $Fe(CO)_5$, apart from a slight wavenumbers shift. (See Note 1 on page 271.)

Mononuclear carbonyls of the second and third row metals of group VIII are usually unstable with respect to their polynuclear analogs. This is shown by the previously mentioned behavior of ruthenium and osmium pentacarbonyls converting to the corresponding trinuclear compounds and also by the high stability of the polynuclear rhodium and iridium carbonyls, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, and $Ir_4(CO)_{12}$. Interestingly, bridging CO groups in polynuclear carbonyls of group VIII tend to disappear with increasing atomic number of the central metal atom. This is probably due to the larger size of the metal orbitals which favors the formation of direct metal–metal bonds, as discussed by Coffey, Lewis, and Nyholm (1). This great tendency to metal–metal bond formation is probably also responsible for the nonexistence of the mononuclear nickel analogs, $Pd(CO)_4$ and $Pt(CO)_4$. This view is substantiated by the recent isolation of a polymeric carbonyl of platinum, $Pt_n(CO)_{2n}$ by Chatt and co-workers (2).

This chapter also contains several sections dealing with some special subjects, as hydrido metal carbonyls, nitrosyl metal carbonyls, halogeno metal carbonyls, etc. This subdivision has been required by the fact that each one of these classes of compounds has its own properties sometimes largely different from those of the main type.

Metal carbonyls are very important as catalysts for several organic syntheses. Perhaps the best known example is the hydroformylation of olefins (the oxo process), catalyzed by octacarbonyldicobalt:



$$RCH{=}CH_2 + CO + H_2 \longrightarrow \begin{cases} RCH_2CH_2CHO \\ RCH(CHO){-}CH_3 \end{cases} \qquad (1)$$

The same reaction, conducted with alcohols instead of hydrogen, yields esters; whereas with water, carboxylic acids are obtained. Acetylene can be converted into succinic acid by the reaction of water and carbon monoxide in the presence of $Co_2(CO)_8$ in the proper solvent. Acetylene can also be converted into acrylates with carbon monoxide and alcohols in the presence of tetracarbonylnickel. When pentacarbonyliron is used as a catalyst, hydroquinone is also obtained in addition to acrylates. Trimerizations of acetylenes to aromatic compounds take place in the presence of metal carbonyls and their derivatives.

All these reactions and others will be reviewed in the following chapters, some appearing in this volume and others in a later volume. It appeared, therefore, essential to have an introductory chapter on metal carbonyls, since the investigation of their properties is an essential prerequisite to the understanding of the mechanism of these catalytic reactions.

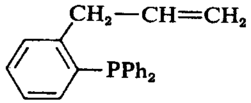
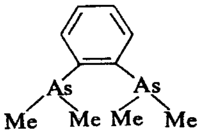
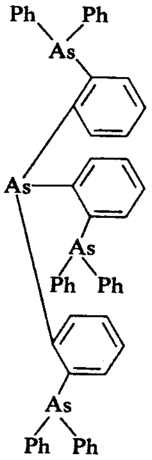
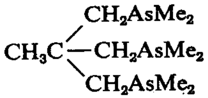
In this connection, one of the most interesting features of metal carbonyls is that of stabilizing organic systems which are unstable under normal conditions. This is the case, for example, of metal carbonyl derivatives containing substituted cyclobutadienes as organic ligands. Several compounds of this type have been prepared and fully established. Recently, the unsubstituted cyclobutadienetricarbonyliron, $C_4H_4Fe(CO)_3$, has been isolated (3). Carbene systems can also be trapped in stable combinations with metal carbonyls; for example, the complexes $M(CO)_5C(OCH_3)(C_6H_5)$ ($M = Cr$ or W) have been isolated as orange-red crystalline solids (4). Finally, σ bonds between alkyl groups and transition metals, which are usually unstable, become stable when carbon monoxide groups are also bonded to the central metal atom. This made possible the isolation of compounds such as $CH_3Co(CO)_4$ and $CH_3Mn(CO)_5$. Alkylcobalttetracarbonyls are probably intermediates in the hydroformylation reaction (Eq. 1).

In conclusion, the catalytic properties of metal carbonyls can be correlated with their capacity of stabilizing usually highly energetic organic systems. The synthesis of complex organic systems from simple ones has to be related to the possibility of the catalyst forming intermediates of relatively low energy and kinetically labile with respect to the end products.

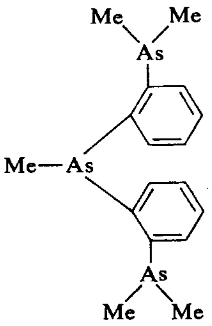
The present chapter covers what the authors have considered to be important developments in the field of metal carbonyls up to December 1965. Regular publications such as *Chemical Abstracts* and *Current Chemical Papers* as well as the systematic personal reading of the chemical journals were used for this purpose. New relevant material was also added in the course of 1966 and 1967 during the correction of galley proofs and page proofs. Within the limits of the permitted length, this chapter has been made as complete as possible by the use of the tables containing lists of compounds according to classes and lower divisions. The reader should, however, be aware of the fact that this chapter has been conceived to be instructive rather than encyclopedic.

B. List of Abbreviations

Throughout the text and the tables the following abbreviations have been used.

Allylphos	*o*-Allylphenyldiphenylphosphine	
Bu	*n*-Butyl	
Cp	Cyclopentadienyl	C_5H_5
Den	Diethylenetriamine	
Diars	*o*-Phenylenebis(dimethylarsine)	
Diglyme	2,2′-Dimethoxydiethyl ether	$MeO(CH_2)_2O(CH_2)_2OMe$
Diphos	1,2-Bis(diphenylphosphino)ethane	$Ph_2PCH_2CH_2PPh_2$
Dipy	2,2′-Dipyridyl	
Dithian	1,4-Dithian	
DMF	Dimethylformamide	
En	Ethylenediamine	
Et	Ethyl	
Me	Methyl	
Ph	Phenyl	
Phen	1,10-Phenanthroline	
Pr	*n*-Propyl	
Py	Pyridine	
QAS	Tris(*o*-diphenylarsinophenyl)arsine	
Terpy	2,2′,2″-Terpyridyl	
THF	Tetrahydrofuran	
v-Triars	Tris-1,1,1-(dimethylarsinomethyl)ethane	 $CH_3C(CH_2AsMe_2)_3$

TTAS Bis(*o*-dimethylarsinophenyl)methylarsine



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1. C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, **1964**, 1741.
2. G. Booth, J. Chatt, and P. Chini, *Chem. Commun.* (*British*), **1965**, 639.
3. G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).
4. E. O. Fischer and A. Maasböl, *Angew. Chem.*, **76**, 645 (1964); O. S. Mills and A. D. Redhouse, *Angew. Chem.*, **77**, 1142 (1965).

II. PREPARATION OF METAL CARBONYLS

A. Introduction

Since tetracarbonylnickel was isolated in 1890 by Mond, Langer, and Quincke (1) from nickel metal and carbon monoxide at atmospheric pressure, many other metal carbonyls have been prepared but not always in such a simple way. Nickel and iron are the only metals easily converted into the corresponding carbonyls. Small amounts of $Fe(CO)_5$ can be detected in carbon monoxide kept in iron cylinders at high pressure even at room temperature. Most other transition metals, even as finely divided powders, are unreactive, or practically so, toward carbon monoxide.

The next step was to use compounds of the metals as starting materials; the main problem being, therefore, reduction of the metal to the zerovalent state. From this point of view, all carbonylations of metal compounds to form the corresponding metal carbonyls have always been reductions because the oxidation number of the central metal atom in metal carbonyls is lower than in any of the readily available metal compounds. This prevailed even before the term "reductive carbonylation"

was introduced (2) to denote a certain type of reaction in the presence of carbon monoxide aimed at preparing $Mn_2(CO)_{10}$ and the hexacarbonyls of group VI. A reducing system is obviously necessary to produce carbonylation of the metal if it is in a higher valence state. It would be, however, erroneous to think that the function of the reducing agent is that of forming some highly active metal, which then would react in the nascent state with carbon monoxide. Simple energetic considerations rule out this possibility. Although mechanistic studies on the formation of metal carbonyls are lacking, it seems reasonable to regard a carbonylation process as one occurring through gradual reduction of the oxidation number of the metal with simultaneous coordination of carbon monoxide groups.

The main difficulty in planning new carbonylation methods is the choice of the reducing agent. The simplest one is carbon monoxide itself; this compound is converted into carbon dioxide or phosgene analogs, COX_2, depending on whether the starting material is a metal oxide or a metal halide.

The syntheses of $Os(CO)_5$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$ from the corresponding low-melting and volatile oxides OsO_4 (mp ~ 40°C), Te_2O_7 (mp 290°C), and Re_2O_7 (mp 220°C) exemplify this type of reaction. When the starting material is a metal halide the addition of a halogen acceptor (usually copper) is necessary to drive the reaction toward the formation of the metal carbonyl and to avoid contamination with intermediate halogeno metal carbonyls.

The 1:1 mixture of carbon monoxide and hydrogen is a very convenient source of both the reducing agent and the ligand. Unfortunately, only a few of the metals of group VIII (cobalt and ruthenium in particular) can be converted into the corresponding carbonyls simply by treatment of a metal salt with carbon monoxide and hydrogen in the proper solvent. The salts of the manganese, chromium, and vanadium subgroups are unaffected by such a carbonylation system. The metals of these three subgroups have required the use of sophisticated systems to make the synthesis of the carbonyls possible.

Strongly electropositive metals (Na, Mg) have been used as reducing agents to prepare $Mn_2(CO)_{10}$, $Cr(CO)_6$, and $V(CO)_6$. However, with the exception of $Cr(CO)_6$, the final products of the reaction are not the carbonyls themselves, but their reduced forms, namely $[Mn(CO)_5]^-$ and $[V(CO)_6]^-$. Carbonylations of metal compounds in the presence of strongly electropositive metals as reducing agents can be divided into two main categories: (*1*) those in which the reducing system consists of the metal suspended in a liquid medium, usually an ether; and (*2*) those in which a third component (pyridine, naphthalene, benzophenone) is present in addition to the electropositive metal and the solvent. In the former case the electron transfer process from the electropositive metal to the transition element probably occurs because of the solubility (3), although very small, of some group IA and IIA metals in different ethers. The well-known capability of certain ethers, such as tetrahydrofuran, of facilitating reductions of some organometallic compounds by alkali metals probably can be correlated with the ability of these solvents to transport electrons to the substance to be reduced. This amounts to saying that, kinetically, the first act of the reduction is an attack on the substance to be reduced by the solvent. The second group of reducing systems mentioned above contains substances which are known or are likely to give radical anions in the presence of alkali metals or electropositive metals in general. In this case the radical anion, or a solvated form of it, should be regarded as directly responsible for the reduction. In other words, electron transfer occurs between the radical anion and the transition metal.

For example, sodium benzophenone ketyl has been employed for the synthesis of both $Cr(CO)_6$ and $Mn_2(CO)_{10}$ (see Sec. II-E, F for references). An important difference exists, however, between the chromium and the manganese syntheses. Hexacarbonylchromium as such is apparently obtained at the end of the reaction, whereas manganese is present in the final reaction mixture as the $[Mn(CO)_5]^-$ anion. Since the reduced form of chromium, $[Cr(CO)_5]^{2-}$, is known (obtained by sodium reduction of $Cr(CO)_6$ in liquid ammonia) the question arises as to why the sodium benzophenone system gives only the zerovalent species. Both thermodynamic and kinetic factors are probably involved in explaining the difference, the former being connected with the reduction potentials of the carbonyl, and the latter with the mechanism of reduction of the carbonyl by the sodium benzophenone system.

If the description of the electron transfer processes given above is correct, a carbon monoxide replacement by the benzophenone radical anion or by the solvent is the first step in the further reduction of the hexacarbonyl:

$$Cr(CO)_6 + \text{Solvent} \longrightarrow [Cr(CO)_5\text{Solvent}] + CO \qquad (1)$$

Dissolved carbon monoxide would presumably counteract the reaction (1) by inhibiting the reduction processes.

The situation is different with $Mn_2(CO)_{10}$. The corresponding anion has the same number of carbon monoxide groups as each of the two units constituting the dimer and the only limiting factor here is the metal–metal bond dissociation energy.

The material presented in the following sections is divided into subgroups of metals, starting from nickel down to the metals of the titanium subgroup. No experimental details for preparing metal carbonyls are given in the following sections. The reader can obtain this information from specialized publications (4–6). The authors hope that the following sections will provide information and guidance for improving the known methods of synthesis.

A final remark concerns the way the subject matter is divided in the sections that follow. Methods of preparing metal carbonyls have been divided essentially into two main classes: (*1*) dry methods: reactions occurring in the absence of added liquid, and (*2*) wet methods: reactions in the presence of liquids. Nothing, however, is implied about how the substances come into contact. Although most of the heterogeneous reactions are found among the dry methods, this is not always the case. Examples of dry method reactions that are almost certainly homogeneous are the syntheses of $Os(CO)_5$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$ from OsO_4, Tc_2O_7, and Re_2O_7, respectively, and carbon monoxide. Owing to the low melting point and high volatility of the oxides, these carbonylations take place, at least initially, in the gas phase and this partially explains the smoothness of the reactions and the high conversions obtained. It is interesting to note in this connection that a volatile carbonyl oxide of osmium, $Os_4O_4(CO)_{12}$, has recently been isolated from the reaction of OsO_4 with carbon monoxide (*6a*). On the other hand, in some of the wet methods, reactions take place with at least one of the reagents insoluble in the reaction medium.

B. Tetracarbonylnickel

In this subgroup the only neutral carbonyl known is tetracarbonylnickel, $Ni(CO)_4$. It was discovered in 1890 by Mond, Langer, and Quincke (1). A dicarbonyl of platinum of unknown structure, $Pt_n(CO)_{2n}$, has been described by Booth, Chatt, and Chini (*6b*).

1. Dry Methods from the Metal

Although some finely divided metals (e.g., Fe, Co, Re) are known to be slowly converted into the corresponding metal carbonyls under drastic conditions, active nickel is unique in its ability to be easily transformed into the carbonyl by simple contact with carbon monoxide at room temperature and atmospheric pressure. Mond and others prepared $Ni(CO)_4$ by passing carbon monoxide at 30°C over nickel that was obtained by reducing nickel oxide with hydrogen at 400°C.

Since then, the contact method has been the basis of the well-known Mond process for producing pure nickel and many patents on the preparation of this metal carbonyl have appeared. A technical publication issued in 1955 by the International Nickel Company (7) lists 55 patents on the production of $Ni(CO)_4$, most of them dealing with dry contact methods. The reduction of ores, oxides, or salts, followed by reaction with carbon monoxide under a variety of conditions (temperature below 150°C and pressures of 1–130 atm) is the most common procedure.

Several papers also have appeared on the synthesis of $Ni(CO)_4$. Most of them deal with various methods for preparing highly active nickel, since it seems to be the crucial point of the synthesis.

Tassilly, Pénau, and Roux (8) obtained $Ni(CO)_4$ in 24% yield by reducing a mixture of NiO and vulcanic ash with hydrogen at 400°C and by treating the resulting material with carbon monoxide at 30 mm Hg at 45°C. Good yields of $Ni(CO)_4$ were reported by Laird (9) and by Van Duin (10), who used nickel obtained by hydrogenative reduction of either ignited $NiCO_3$ at 250°C or the oxalate at 290°C. The carbonylation was carried out at about 90°C with carbon monoxide at atmospheric pressure.

Mayer and Wibaut (11) reduced nickel oxalate supported on infusorial earth with a stream of carbon monoxide at 450°C. Carbonylation was then obtained by rapidly lowering the temperature to 100°C.

Gilliland and Blanchard (12) reported that good yields of $Ni(CO)_4$ were obtained when nickel formate was pyrolyzed, some mercury was added to the resultant nickel metal, and carbon monoxide was passed over this mixture at room temperature.

2. *Dry Methods from Nickel Salts*

During the preparation of halogenocarbonyls of rhenium, $ReX(CO)_5$, from active rhenium metal and NiX_2, Hieber and co-workers (13) observed the formation of $Ni(CO)_4$ from nickel halides by the following reaction:

$$2Re + NiX_2 + 14CO \longrightarrow 2Re(CO)_5X + Ni(CO)_4 \tag{2}$$

With X = Cl, Br, and I, and reaction conditions of 250°C and 220 atm for 16 hr under the yields of $Ni(CO)_4$ were 60, 95, and 98% respectively.

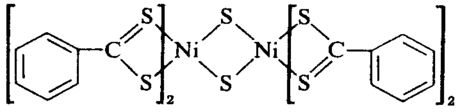
A systematic study (14) showed that under the standard conditions used (Cu or Ag as reducing agents, 10 hr at 250°C and 200 atm) the conversion of NiX_2 into the carbonyl was 2, 1, and 100% when X was Cl, Br, and I, respectively.

3. *Wet Methods in Aqueous Solutions*

The reaction of carbon monoxide at atmospheric pressure with aqueous alkaline nickel sulfate in the presence of ethyl mercaptan gives $Ni(CO)_4$ in good yields (15).

Later, Windsor and Blanchard (16) investigated the synthesis of $Ni(CO)_4$ from NiS formed *in situ* from $NiSO_4$ and Na_2S in aqueous alkaline solutions. The best yields were obtained by using an approximately 1*N* solution of NaOH. If Na_2S is replaced by Na_2Se, the yields are considerably reduced.

Synthesis at atmospheric pressure has been studied by Hieber and Brück (17), who observed that formation of $Ni(CO)_4$ in the presence of sodium hydrogen sulfide from nickel(II) dithiobenzoate is accompanied by the formation of compounds of type **1**. The maximum yield of $Ni(CO)_4$ observed was 50%. The yield could be increased beyond this limit only if complex **1** were unstable and could be converted again into the original Ni(II) salt by the action of carbon monoxide in alkaline medium. According to these authors the synthesis of $Ni(CO)_4$ is prevented if conditions suitable for the formation of **1** are absent.



(1)

However, Behrens and Eisenmann (18) later showed that, in absence of oxygen and when conditions are provided for the removal of soluble nickel and cobalt products, the sulfides of these metals are quantitatively transformed into $Ni(CO)_4$ and $[Co(CO)_4]^-$, according to the equations:

$$NiS + 5CO + 4OH^- \longrightarrow Ni(CO)_4 + CO_3^{2-} + S^{2-} + 2H_2O \tag{3}$$

$$2CoS + 11CO + 12OH^- \longrightarrow 2[Co(CO)_4]^- + 3CO_3^{2-} + 2S^{2-} + 6H_2O \tag{4}$$

These authors assumed that the formation of $Ni(CO)_4$ is due to an equilibrium involving carbon monoxide, the metal sulfide, and sulfur

$$NiS + 4CO \rightleftharpoons Ni(CO)_4 + S \tag{5}$$

which is continuously shifted to the right by the reaction

$$S + CO + 4OH^- \longrightarrow S^{2-} + CO_3^{2-} + 2H_2O \tag{6}$$

Hieber and co-workers (19–21) also showed that, by using sodium dithionite or formamidinesulfinic acid as reducing agents, practically quantitative yields of $Ni(CO)_4$ could be obtained from nickel(II) salts in aqueous solution at atmospheric pressure. (See Note 2 on page 272.)

A patent (22) describes the use of metallic iron as the reducing agent in the synthesis of $Ni(CO)_4$ in aqueous solution. Almost quantitative yields of $Ni(CO)_4$ are reported (22) to be obtained by treating aqueous solutions of $NiCl_2$ with carbon monoxide at room temperature and atmospheric pressure. Iron powder is used as the reducing agent and small amounts of Na_2S and $Na_2S_2O_3$ are added as promoters. The concurrent formation of $Fe(CO)_5$ was reported to be negligible. The reaction time is greatly reduced if carbon monoxide is used at a slightly higher pressure (15 atm).

Reppe (23) reported the preparation of $Ni(CO)_4$ in practically quantitative yields from nickel chloride in strongly ammoniacal aqueous solution at 120°C and with carbon monoxide at 50 atm.

4. Wet Methods in Nonaqueous Solvents

The reaction between finely divided nickel and carbon monoxide in the presence of a liquid capable of dissolving the formed carbonyl does not appear to have been reported as yet, although there is little doubt that it should give satisfactory results, at least at high carbon monoxide pressures.

Nickel salts of organic acids such as the acetate, propionate, and naphthenate, dissolved or suspended in organic solvents, give high yields of $Ni(CO)_4$ by treatment with carbon monoxide and hydrogen at 100–300°C and 50–300 atm (24).

C. Cobalt, Rhodium, and Iridium Carbonyls

1. Historical

The first detailed report on $Co_2(CO)_8$ and $Co_4(CO)_{12}$ appeared in 1910 (25). $Co_6(CO)_{16}$ has been reported just recently (P. Chini, *Chem. Commun.(British)*, **1967**, 440).

The carbonyls of rhodium, $Rh_2(CO)_8$ and $[Rh(CO)_3]_x$, were first reported by Lagally (26) in 1943. He also reported a tetranuclear $Rh_4(CO)_{11}$, which was later correctly reformulated as $Rh_6(CO)_{16}$ (27). The tricarbonyl of rhodium has been reported to be tetrameric according to a preliminary x-ray investigation (27*a*).

The iridium carbonyls $[Ir(CO)_4]_m$ and $[Ir(CO)_3]_n$ were first prepared in 1940 by Hieber and Lagally (28). The tricarbonyl is a tetramer, $Ir_4(CO)_{12}$, according to preliminary x-ray data (27*a*).

2. Dry Methods from the Metals

$Co_2(CO)_8$. The reaction of carbon monoxide at 30–40 atm and 150°C with finely divided cobalt was first used to prepare octacarbonyldicobalt (25). The cobalt metal was prepared by reduction of cobalt oxalate with hydrogen (5 atm) at 300°C.

Since then, several patents have appeared dealing with the synthesis of $Co_2(CO)_8$ from cobalt metal and carbon monoxide under pressure at high temperatures. Thus, I. G. Farbenindustrie (29,30) claims that 99% of the cobalt is converted into $Co_2(CO)_8$ with carbon monoxide free of oxygen, carbon dioxide, and other impurities. Formation of the carbonyl is strongly inhibited by oxygen; with an oxygen content of 0.3%, the conversion falls to 2%.

Cobalt may also be used on supports; thus (31), a sulfur-containing cobalt carbonate supported on infusorial earth was reduced at 400°C with hydrogen and then heated at 120°C with carbon monoxide at 100 atm for 2 hr. Yields as high as 92% have been claimed.

A systematic study of the influence of operating conditions such as temperature and pressure apparently has not been made. However, very high pressures of carbon monoxide are sometimes recommended. For example, a pelleted, reduced cobalt oxide (32) was converted into $Co_2(CO)_8$ in high yields by operating at 170°C and 700–1000 atm of carbon monoxide. Others state that addition of iodine (14) or sulfur (33) results in better yields of $Co_2(CO)_8$ from finely divided cobalt.

When zinc, cadmium, tin, indium, or thallium powders are added to finely divided cobalt (34), the corresponding mixed cobalt carbonyls are obtained:

$$M + nCo + 4nCO \longrightarrow M[Co(CO)_4]_n \tag{7}$$

with $n = 1, 2$, or 3 depending on the metal employed (see Sec. XI). $Co_2(CO)_8$ can be recovered from these compounds by oxidation with the stoichiometric amount of iodine in benzene.

$Rh_2(CO)_8$. Lagally (26) reported the isolation of $Rh_2(CO)_8$, with the dry synthesis from the metal being the preferred method of preparation. The rhodium metal was obtained by reducing Na_3RhCl_6 with hydrogen at temperatures below 150°C and then it was reacted at 200°C with carbon monoxide (450 atm) for 15 hr. The carbonyl was claimed to be isolated from the resulting material by crystallization from hydrocarbons. It is worth mentioning here that no other significant reports about this carbonyl have appeared in the literature.

3. Dry Methods from Metal Salts

$Co_2(CO)_8$. The dry synthesis from cobalt halides and sulfides in the

presence of reducing metals has been extensively studied by Hieber and co-workers (35). The reactions

$$2CoS + 8CO + 4Cu \longrightarrow Co_2(CO)_8 + 2Cu_2S \qquad (8)$$

$$2CoI_2 + 8CO + 4Cu \longrightarrow Co_2(CO)_8 + 4CuI \qquad (9)$$

give quantitative yields of the carbonyl when carried out at 160–190°C and 150–250 atm of carbon monoxide for 12 hr.

Systematic work (36) on the reactivity of the four cobalt halides showed that 100% of CoI_2 is transformed into $Co_2(CO)_8$ at 150°C, whereas CoF_2, $CoCl_2$, and $CoBr_2$ respectively give, at 200°C, yields of 0, 2.5, and 4.5%. In the case of CoI_2, an intermediate iodocarbonyl, $CoI_2(CO)$, was isolated from the reaction mixture. With reducing metals, the yields decrease in the order: Cu > Ag > Pt > Au.

With Zn or Cd powders, formation of mixed cobalt carbonyls, $M[Co(CO)_4]_2$, occurs (M = Zn, Cd) (see Sec. XI).

$Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$. Both these carbonyls can be obtained from anhydrous $RhCl_3$ (26) and carbon monoxide at 200 atm for 15 hr in the presence of copper (or Ag, Cd, Zn). Temperature appears to have an important effect on the nature of the final products. At 50–80°C the brick-red tetramer is formed, whereas in the range 80–230°C the reaction products contain only $Rh_6(CO)_{16}$. Under these conditions, no $Rh_2(CO)_8$ was obtained. Small amounts of impure $Rh_2(CO)_8$ were reported, together with the main products, $[RhX(CO)_2]_n$, when anhydrous rhodium halides RhX_3 (X = Cl, Br, I) were reacted with carbon monoxide at about 180°C, without any added reducing metal. $Rh_2(CO)_8$ was apparently obtained only when finely divided rhodium metal (prepared from Na_3RhCl_6 and hydrogen at temperatures not higher than 150°C) was reacted with carbon monoxide at 280 atm and 200°C (see above). There is doubt about the existence of $Rh_2(CO)_8$.

$Ir_4(CO)_{12}$ and $[Ir(CO)_4]_n$. These carbonyls were first reported by Hieber and Lagally (28), who prepared them from the halides IrX_3 or from the haloiridiates M_2IrX_6 or M_3IrX_6 ($M = NH_4$, Na, K; X = Cl, Br, I). The halides were carbonylated for 24 to 48 hr with carbon monoxide at 350 atm. Temperatures of 140, 120 and 100°C were required for the chloride, the bromide, and the iodide. The copper lining of the autoclave acted as a halogen acceptor. The haloiridiates required a temperature of 170–200°C and the addition of an excess of copper or silver for carbonylation.

A mixture of the two carbonyls was always obtained. Separation was based on the relatively significant solubility of $[Ir(CO)_4]_n$ in ether and carbon tetrachloride compared with the very limited solubility of the tricarbonyl in these solvents.

Some $Ir_4(CO)_{12}$ is also formed (37*a*) when a stream of carbon monoxide at atmospheric pressure is reacted with $IrX_3 \cdot H_2O$ at 150°C. The main products of this reaction are the halogenocarbonyls $IrX(CO)_3$ and $IrX_2(CO)_2$.

It is worth mentioning that, after the original paper by Hieber and Lagally (28), no other reports have appeared on the preparation and properties of the tetracarbonyl of iridium $[Ir(CO)_4]_n$. Noack (37*b*), in an attempt to study its infrared spectrum, found no definite evidence for its formation under various operating conditions.

$Co_4(CO)_{12}$ from $Co_2(CO)_8$. When $Co_2(CO)_8$ is heated to 60°C in an inert atmosphere (25) carbon monoxide is evolved slowly with formation of the tetramer $Co_4(CO)_{12}$. After 20 hr the reaction is complete.

$$2Co_2(CO)_8 \longrightarrow Co_4(CO)_{12} + 4CO \qquad (10)$$

The carbonyl is recovered by crystallization from benzene.

4. *Wet Methods in Aqueous Solutions*

$Co_2(CO)_8$. Among the metal carbonyls of this subgroup, only $Co_2(CO)_8$ has been prepared in aqueous solution. Actually the synthesis in aqueous medium leads to the formation of the tetracarbonylcobaltate anion $[Co(CO)_4]^-$ or of the hydridocarbonyl $CoH(CO)_4$, which require further oxidation for transformation into $Co_2(CO)_8$.

Manchot and co-workers (15,38,39) and Reihlen and co-workers (40) were the first to observe that alkaline solutions of Fe(II), Co(II), and Ni(II), in the presence of sulfur-containing promoters, are capable of absorbing carbon monoxide at room temperature and atmospheric pressure. Schubert (41) then studied the reaction between cobalt(II) cysteinate and carbon monoxide in alkaline solutions. He succeeded in preparing the tetracarbonylcobaltate anion by this method. Since cobalt(III) cysteinate was found in the reaction mixtures, Schubert explained his results by the disproportionation, $4Co(II) \rightarrow 3Co(III) + Co(I-)$, followed by reduction of cobalt (III) by carbon monoxide, the latter being oxidized to carbonate.

Later, Blanchard and co-workers (42,43) recognized that in strong alkaline solution the formation of $[Co(CO)_4]^-$ may be represented by the equation:

$$2CoCl_2 + 12KOH + 11CO \longrightarrow 2KCo(CO)_4 + 3K_2CO_3 + 4KCl + 6H_2O \qquad (11)$$

Blanchard and Gilmont (44) also reported that equimolecular quantities of $CoCl_2$ and KCN in 4*N* KOH absorbed more than 4 moles of carbon monoxide per atom of cobalt, suggesting that carbon monoxide was also consumed to form carbonate.

More recently, carbonylation in the presence of KCN was accurately investigated by Hieber and Bartenstein (45). They showed that when the ratio CN^-/Co^{2+} is between 1 and 2, cobalt is quantitatively transformed into $[Co(CO)_4]^-$. For a ratio of 5, $[Co(CO)(CN)_3]^{2-}$ is formed and for a value of 6 no carbon monoxide is absorbed. Moreover, they excluded the disproportionation to cobalt(III) in this system. They proposed the occurrence of the following reactions:

$$6Co^{2+} + 3CO + 12OH^- \longrightarrow 6Co^+ + 3CO_3^{2-} + 6H_2O \qquad (12)$$

$$6Co^+ + 12CO + 12CN^- \longrightarrow 6[Co(CN)_2(CO)_2]^- \qquad (13)$$

$$6[Co(CN)_2(CO)_2]^- \longrightarrow 2[Co(CO)_4]^- + 4Co^{2+} + 12CN^- + 4CO \qquad (14)$$

According to this scheme, cobalt(II) would be reduced to cobalt(I), followed by disproportionation to cobalt(II) and cobalt(I−). In conclusion, although it is difficult to propose a unified mechanism for these carbonylations of cobalt in aqueous alkaline solutions, they do appear to depend on the reducing properties of carbon monoxide.

The function of promoters (sulfur-containing compounds, cysteine, cyanide ion) probably is to form complexes with the cobalt ion, the net result being a modification of the oxidation-reduction potential of cobalt.

For preparative purposes, better results were obtained when reducing agents were deliberately added to the system. Thus, some methods have been described (20,21) in which $Na_2S_2O_4$ or formamidinesulfinic acid were employed for the reduction. With the former reducing agent, the yield of $[Co(CO)_4]^-$ is practically quantitative. From the solution, 90% of $Hg[Co(CO)_4]_2$ can be isolated by addition of $HgCl_2$, or 40% of $Co_2(CO)_8$ can be obtained by oxidation with silver(I).

At high carbon monoxide pressures, aqueous solution of cobalt salts are easily carbonylated. By treating $CoSO_4$ or $CoCl_2$ in aqueous ammonia solution with carbon monoxide (95–110 atm) at 120–140°C for 16–18 hr, Reppe (23) obtained 66 and 56% of $Co_2(CO)_8$. The carbonyl could be isolated from the reaction mixtures by acidification with HCl or H_3PO_4, and subsequent spontaneous loss of hydrogen from the intermediate $CoH(CO)_4$.

5. *Wet Methods in Nonaqueous Solvents*

The carbonyls of cobalt are more frequently prepared in non-aqueous solvents.

$Co_2(CO)_8$. In some instances the dry methods of synthesis described above may be carried out in the presence of anhydrous solvents. Thus Adkins and Krsek (46) prepared solutions of $Co_2(CO)_8$ by reacting Raney cobalt suspended in diethyl ether with carbon monoxide at about 250 atm and 150°C. In the experience of the authors of this chapter, analogous results can be obtained by using hydrocarbons as solvents and Raney cobalt or cobalt supported on Al_2O_3–SiO_2, but the yields are erratic and frequently poor.

According to a Japanese patent (47), Co_2O_3 suspended in benzene is transformed into the carbonyl by reaction with carbon monoxide and hydrogen at 200 atm and 110°C in the presence of some pyridine and preformed $Co_2(CO)_8$.

The best way to synthesize octacarbonyldicobalt is to use the high pressure method with anhydrous cobalt salts of organic or inorganic acids dissolved or suspended in nonaqueous media. Hydrogen is used as the reducing agent. The one-step synthesis from cobalt salts in the presence of hydrogen was first reported in some American patents issued in 1949 (24,48). Salts such as the carbonate, butyrate, 2-ethylhexanoate and naphthenate in solvents such as alcohols, ketones, or hydrocarbons were carbonylated at 140–300°C under 100–200 atm with carbon monoxide and hydrogen. The reactions may be regarded as:

$$2(RCOO)_2Co + 2H_2 + 8CO \longrightarrow Co_2(CO)_8 + 4RCOOH \qquad (15)$$

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2CoH(CO)_4 \qquad (16)$$

It was soon realized (49,50) that the reaction is accelerated by preformed $Co_2(CO)_8$. In this case the reaction temperature can be lowered to 80°C.

Wender and co-workers reported the synthesis of $Co_2(CO)_8$ in 53% yield from cobalt carbonate (51,52). A preparative procedure which does not require the predrying of the cobalt(II) salt was given by Szabó, Markó, and Bor (53). Commercially available cobalt acetate (the tetrahydrate) suspended in acetic anhydride was treated with carbon monoxide and hydrogen at 160–180°C. A detailed description of this method of preparation is given by King (5). Szabó and Markó (54) have reported also that hexane solutions of cobalt stearate are converted into $Co_2(CO)_8$ (together with $Co_4(CO)_{12}$ and tetracarbonylacylcobalt derivatives) when treated with triethylaluminum at room temperature and 1 atm of carbon monoxide.

A systematic investigation of the synthesis of $Co_2(CO)_8$ from cobalt salts in organic solvents using hydrogen as the reducing agent was reported by Chini (55,56). At 95°C, with cobalt 2-ethylhexanoate dissolved in toluene, in the presence of preformed $Co_2(CO)_8$ and at superatmospheric pressure of carbon monoxide and hydrogen, the reaction is first order with respect to both dissolved hydrogen and $Co_2(CO)_8$. As the amount of the latter increases with time, the reaction shows a very characteristic autocatalytic behavior. Above 15 atm, carbon monoxide has a retarding effect on the formation of $Co_2(CO)_8$. Finally, the cobalt(II) concentration appears to have no kinetic effect.

When organic Lewis bases are employed as solvents, a very smooth reaction is frequently observed and 80–95% yields of $Co_2(CO)_8$ are obtained at 30°C with 100 atm hydrogen and 80 atm carbon monoxide. The Lewis bases used were: C_6–C_7 aliphatic ketones, 1-butanol, tetrahydrofuran, diethylene glycol diethyl ether, ethyl and cyclohexyl acetate, and methyl benzoate. The reaction time varies from 2 to 48 hr, depending on the base employed. Under the same conditions, acetone, *tert*-butanol, diethyl ether, and dimethylaniline give $Co_2(CO)_8$ and large amounts of the carbonylcobaltate, $[CoB_6][Co(CO)_4]_2$, whereas no reaction takes place with benzophenone, C_6–C_8 aliphatic ethers, diphenyl ether, dioxane, triethylamine, and dimethylformamide. The occurrence of the carbonylation at such a low temperature (30°C) was explained by the ability of the Lewis base to create conditions for the simultaneous presence in the system of $Co_2(CO)_8$ and $[Co(B_6)][Co(CO)_4]_2$.

$Co_4(CO)_{12}$. A method for a direct synthesis of $Co_4(CO)_{12}$ from cobalt salts and carbon monoxide has not yet been developed. The previously mentioned Mond's method (25) has been improved by the use of hydrocarbons as solvents (57,58).

Ercoli and co-workers (59) have reported a method for the preparation of $Co_4(CO)_{12}$ from cobalt(II) ethylhexanoate or cobalt(II) and cobalt(III) acetylacetonates. These are reacted with hydrogen at 30–50 atm, and with $Co_2(CO)_8$ in amounts corresponding to the following stoichiometry:

$$2(RCOO)_2Co + 3Co_2(CO)_8 + 2H_2 \longrightarrow 2Co_4(CO)_{12} + 4RCOOH \tag{17}$$

The yields are better than 90%. It is noteworthy that a transfer of carbon monoxide from $Co_2(CO)_8$ to cobalt(II) is involved in this reaction.

D. Iron, Ruthenium, and Osmium Carbonyls

1. Historical

Pentacarbonyliron, $Fe(CO)_5$, was discovered independently by Berthelot (60) and by Mond and Quincke (61) in 1891.

Enneacarbonyldiiron, $Fe_2(CO)_9$, was described by Dewar and Jones in 1905 (62) and they reported dodecacarbonyltriiron (as polymeric $Fe(CO)_4$) in 1907 (63).

The ruthenium carbonyls $Ru(CO)_5$ and $[Ru(CO)_x]_n$ were discovered by Manchot and Manchot (64), who also described an enneacarbonyldiruthenium that was later reformulated by Corey and Dahl (65) as dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$.

Pentacarbonylosmium, $Os(CO)_5$, was first described and characterized by Hieber and Stallmann in 1943 (66); they isolated also an enneacarbonyldiosmium, later reformulated by Corey and Dahl (65) as dodecacarbonyltriosmium, $Os_3(CO)_{12}$.

2. Dry Methods from the Metals

$Fe(CO)_5$. In the original preparations by Berthelot (60) and by Mond and Quincke (61), $Fe(CO)_5$ was obtained by reacting carbon monoxide at atmospheric pressure with active iron metal prepared from oxides or salts.

Mittasch (67) reported that good yields of $Fe(CO)_5$ are obtained at about 200°C and 50–200 atm, especially if oxygen is completely absent from the gas. Small amounts of sulfur or selenium have a favorable effect. The effects of S, Se, and Te have been investigated in a systematic way (68). Finely divided iron with an average particle diameter of 10^{-4} cm was submitted to a carbon monoxide pressure of 200 atm and then heated for 15 hr at 200°C. The conversion was 26.4%, whereas when 0.3 at. % of sulfur was added, 94.5% of $Fe(CO)_5$ was obtained. Selenium and tellurium in amounts of 0.9 and 1 at. % gave a conversion of 93.0 and 88.6%. With larger amounts of these elements a progressive drop in conversion was observed. It was suggested that these elements act as catalysts via intermediate formation of complexes, e.g., $Fe_3S_2(CO)_9$, which would then be split by carbon monoxide into $Fe(CO)_5$ and sulfur.

$Ru(CO)_5$. Poor yields of this carbonyl were obtained (64) from ruthenium powder and carbon monoxide under pressure. After 14 days of reaction at 300°C and 400 atm the conversion was only 10%. The strong adsorption of $Ru(CO)_5$ on the metal was regarded as preventing the reaction from proceeding further.

$Os(CO)_5$. Only traces of this carbonyl were observed (66) when osmium powder was reacted with carbon monoxide (350 atm) for 15 hr at 250°C.

Polynuclear carbonyls. There are no reports on the preparation of polynuclear carbonyls of the iron subgroup from the metals by dry methods.

3. *Dry Methods from Metal Salts and Oxides*

Fe(CO)$_5$. In a systematic study (14) of the formation of this carbonyl from anhydrous FeX_2 (X = Cl, Br, I) in copper-lined autoclaves, Hieber and co-workers showed that, in 15 hr at 200°C and 200 atm of carbon monoxide, no carbonyl was formed when X was Cl or Br, whereas a yield of 50–75% was obtained with the iodide. The iodocarbonyl $FeI_2(CO)_4$ also is formed in 25–50% yield. By addition of copper or silver powder the yield from FeI_2 increased to 98%. At 250°C with a large excess of Cu, $FeCl_2$, and $FeBr_2$ gave $Fe(CO)_5$ in 1.3 and 19.5% yields.

Ru(CO)$_5$ and Ru$_3$(CO)$_{12}$. Both these carbonyls were formed when RuI_3, mixed with a large excess of silver powder, was kept at 170°C for 24 hr under carbon monoxide at about 450 atm in a rotating autoclave (64). The volatile $Ru(CO)_5$ then was recovered from the vented gases by trapping it at low temperature; $Ru_3(CO)_{12}$ was extracted from the residue with benzene. Analogous results were obtained from the halogenocarbonyl, $RuI_2(CO)_2$. This compound gave $Ru(CO)_5$ only, when warmed with copper or silver powder at 170°C in a stream of carbon monoxide.

Os(CO)$_5$ and Os$_3$(CO)$_{12}$. As with Ru, these carbonyls were formed when the halides ($OsCl_3$ and Os_2Br_9) and an "oxyiodide," mixed with powdered copper or silver, were reacted with carbon monoxide at high pressure and temperature (200–300 atm, 150–300°C) (66). However, the best method for preparing $Os(CO)_5$ seems to be dry reduction of the tetraoxide by carbon monoxide itself:

$$OsO_4 + 9CO \longrightarrow Os(CO)_5 + 4CO_2 \qquad (18)$$

This reaction was carried out at 300°C and 300 atm and gave quantitative yields of the carbonyl. Formation of the carbonyl was also observed under less drastic conditions (100°C and 50 atm). The yields, however, were erratic and seemed dependent on the amounts of starting materials employed.

4. *Wet Methods in Aqueous Solution*

Fe(CO)$_5$. Because of the very satisfactory results obtained by the dry methods described above, limited efforts have been made to find new synthetic methods.

Reppe (23) described the high pressure synthesis of iron, cobalt, and nickel carbonyls. Pentacarbonyliron was obtained in 40–50% yields by treating an ammoniacal solution of Mohr's salt with carbon monoxide (115 atm) at 80°C for 16 hr.

Fe$_3$(CO)$_{12}$. Although this carbonyl was first obtained by heating nonaqueous solutions of $Fe_2(CO)_9$ (63), it is now prepared almost exclusively by starting from alkaline solutions containing carbonylferrate anions. This method is due to Freundlich and Cuy (69), who observed that $Fe(CO)_5$ reacted at room temperature with aqueous alkali to give brown solutions which then were treated with $(NH_4)_2SO_4$ and extracted with diethyl ether. Oxidation of the ether layer with copper(II) sulfate gave crystals of dodecacarbonyltriiron. More directly, the carbonyl was obtained by air oxidation of the alkaline solutions. It is worth mentioning that the freezing point depression observed (63) during attempts to determine the molecular weight of $Fe_3(CO)_{12}$ was very small and it corresponded approximately to a polymer $[Fe(CO)_4]_{20}$. Later attempts (70*a*) to determine the molecular weight by different methods also failed and only tetrameric or perhaps higher structures were indicated by those measurements. At a later date, Hieber and Becker (70*b*) reported that the tetracarbonyl is a trimer according to molecular weight determinations in pentacarbonyliron as solvent.

Methods for preparing $Fe_3(CO)_{12}$ were later improved somewhat (71). Hieber and Brendel (72) reported quantitative yields of this compound by oxidizing alkaline solutions containing carbonylferrates with MnO_2, followed by removal of excess MnO_2, acidification, and extraction of the carbonyl with petroleum ether.

A 90% yield of $Fe_3(CO)_{12}$ was reported in a patent (73) disclosing a method for treating $Fe(CO)_5$ with aqueous triethylamine to form a compound formulated as $NR_3H_2Fe_3(CO)_{11}$, which was acidified with formic acid. The resulting $Fe_3(CO)_{12}$ was then extracted with petroleum ether. The acidification with formic acid was reported to occur according to the following stoichiometry:

$$4NR_3H_2Fe_3(CO)_{11} + 2H^+ \longrightarrow \tfrac{11}{3}\,Fe_3(CO)_{12} + Fe^{2+} + 5H_2 + 4NR_3 \qquad (19)$$

The compound $NR_3H_2Fe_3(CO)_{11}$ reported in this patent (73) is the alkylammonium salt $[NR_3H][Fe_3H(CO)_{11}]$. Case and Whiting (74) reported the absorption spectra in the visible region of the $[Fe_3H(CO)_{11}]^-$ anion, prepared according to this patent.

5. *Wet Methods in Nonaqueous Solvents*

Syntheses in nonaqueous solvents are reported for $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$.

Fe$_2$(CO)$_9$. This carbonyl is obtained by the action of light on $Fe(CO)_5$. An accurate description of the operations involved is given by Speyer and Wolf (75). They obtained moderate yields of $Fe_2(CO)_9$ by exposing to sunlight concentrated solutions of $Fe(CO)_5$ in glacial acetic acid or in acetic anhydride. The reaction was carried out *in vacuo* or in a hydrogen atmosphere, with periodic venting of the gases.

Eyber (76) showed that the quantum yield of this reaction is 2 and he accordingly proposed the following mechanism:

$$Fe(CO)_5 \longrightarrow {}^*Fe(CO)_5 \tag{20}$$

$$Fe(CO)_5 + {}^*Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO \tag{21}$$

He also observed an inhibiting effect on the reaction by hydrogen whereas carbon monoxide, argon, and carbon dioxide had no significant effect.

$Ru_3(CO)_{12}$. This carbonyl is formed when solutions of $Ru(CO)_5$ in hydrocarbons or alcohols are warmed for a short time, more suitably in the presence of light (64). Liquid $Ru(CO)_5$ loses carbon monoxide at 50°C to form some $Ru_3(CO)_{12}$.

During the thermal and photochemical decompositions of $Ru(CO)_5$, Manchot and Manchot (64) observed the formation of a red-green dichroic carbonyl, tentatively formulated as $[Ru(CO)_3]_x$.

Pino and co-workers (77,78) described a direct method for preparing $Ru_3(CO)_{12}$ from ruthenium(III) acetylacetonate, carbon monoxide, and hydrogen (3:1) under pressure (150–200 atm) and at 140–160°C. Acetone, benzene, and methanol were used as solvents for the reaction; yields as high as 82% were obtained in methanol. Interestingly, when an aliphatic or aromatic alcohol is used as solvent, $Ru_3(CO)_{12}$ is obtained even in the absence of hydrogen. Thus, in benzyl alcohol, a 35% yield is obtained under a carbon monoxide pressure of 160 atm. Subsequently a British patent (79) described a similar method of preparing $Ru_3(CO)_{12}$ from ruthenium(III) salts with carbon monoxide and hydrogen under pressure.

The possibility of carbonylating ruthenium in the absence of hydrogen when an alcohol is present suggests that reduction of ruthenium(III) can be carried out by the alcohol. Benzaldehyde, benzene, and toluene were identified among the products of the carbonylation of ruthenium(III) in benzyl alcohol (78).

E. Manganese, Technetium, and Rhenium Carbonyls

1. Historical

Decacarbonyldirhenium was first prepared in 1941 by Hieber and Fuchs (80).

In 1949 a carbonyl of manganese was reported by Hurd and co-workers (81), who isolated very small quantities of sublimed crystals. Although the amounts isolated were insufficient for characterization, its properties seemed to correspond to those of $Mn_2(CO)_{10}$.

Decacarbonyldimanganese was prepared and fully characterized in 1954 by Brimm and co-workers (82).

Decacarbonylditechnetium was described independently, in 1961, by Hileman, Huggins, and Kaesz (83) and by Hieber and co-workers (84,85).

Polynuclear carbonyls $[M(CO)_4]_n$ of technetium (86) and rhenium (87) also have been described. However, the alternative formulation of these two compounds as hydridocarbonyls cannot yet be excluded, considering the experimental data now available. On the other hand, the rhenium compound is less likely to be a hydridocarbonyl since it is prepared in a hydrogen-free system.

2. Dry Methods from Metal Oxides and Salts

None of the carbonyls of this group could be obtained by direct action of carbon monoxide on the metals. Negative results were reported for manganese (25) and for rhenium (80).

$Tc_2(CO)_{10}$. This carbonyl was prepared (83–85) by the action of carbon monoxide at 350–250 atm on the oxide, Tc_2O_7, at 220–275°C for 20–12 hr. ^{99}Tc is a β emitter, and certain precautions must be taken to avoid radioactive contamination. Hieber and co-workers (85) have described equipment in which the manipulations of the volatile technetium compounds Tc_2O_7 (mp 290°C) and $Tc_2(CO)_{10}$ can be carried out safely. A detailed description of the synthesis of $Tc_2(CO)_{10}$ has been given by Hileman (88).

$Re_2(CO)_{10}$. Hieber and Fuchs (80) reported that no carbonyl could be obtained from the interaction of rhenium halides and carbon monoxide in the presence of metals as reducing agents. They found, however, that Re_2O_7 is reduced by carbon monoxide at high temperature and pressure with simultaneous formation of the carbonyl:

$$Re_2O_7 + 17CO \longrightarrow Re_2(CO)_{10} + 7CO_2 \tag{22}$$

Quantitative yields were reported at 250°C for 16 hr at 350 atm. Good results were obtained also from ReO_3, ReO_2, and Re_2S_7, but poor yields were obtained from $KReO_4$.

Osborne and Stiddard (87) prepared a polynuclear tetracarbonylrhenium $[Re(CO)_4]_n$ by reacting Re_2S_7 with carbon monoxide (85 atm) at 200°C in the presence of copper powder. This carbonyl is a colorless crystalline compound which can be sublimed *in vacuo* (100°/0.1 mm Hg); it is insoluble in common organic solvents and it shows two infrared bands in the C—O stretching region at 2055 and 1995 cm^{-1}.

3. *Wet Methods in Nonaqueous Solvents*

$Mn_2(CO)_{10}$. Brimm and co-workers (82) obtained this carbonyl (1% yield) when carbon monoxide at 200 atm was reacted at room temperature for 15–17 hr with a mixture of magnesium powder, manganese iodide, copper, and copper iodide suspended in ether. The manganese iodide had been prepared by heating manganese powder and cuprous iodide at 450°C.

In a later patent (89) the action of phenylmagnesium bromide or chloride and carbon monoxide at 30 atm on anhydrous $MnCl_2$ in ether, preferably at temperatures between −20 and +30°C, is claimed to give $Mn_2(CO)_{10}$ in about 10% yield.

Closson and co-workers (90) later reported the use of sodium benzophenone ketyl as the reducing agent for synthesis of $Mn_2(CO)_{10}$ from manganese(II) salts. The preparation of the carbonyl was carried out in three steps:

(a) Reaction of anhydrous manganese(II) chloride with the ketyl in tetrahydrofuran.

(b) Carbonylation of the resulting mixture with carbon monoxide at 200–700 atm and 65–200°C.

(c) Hydrolysis and steam distillation of the $Mn_2(CO)_{10}$ from the resulting mixture.

The highest yield of $Mn_2(CO)_{10}$ obtained by this method was 32%.

Step (c), hydrolysis and steam distillation, is necessary because the manganese occurs in the final reaction mixture as $[Mn(CO)_5]^-$. During this operation $[Mn(CO)_5]^-$ is hydrolyzed to $MnH(CO)_5$, which is then oxidized to $Mn_2(CO)_{10}$.

Carbonylation in the presence of aluminum alkyls, first introduced by Russian workers (91) for the synthesis of carbonyls of group VI, was extended to manganese by Podall and co-workers (92). They obtained decacarbonyldimanganese in about 60% yield under their best conditions. The method is based on reduction of an anhydrous manganese(II) salt with a trialkylaluminum compound dissolved in an ether or in benzene, in the presence of carbon monoxide under pressure.

In the systematic study of the reaction (92) a number of factors were considered and the following conclusions were drawn.

(a) Yields depend on the manganese compound, increasing in the order: chloride, iodide, formate, acetylacetonate, isopropoxide, acetate = benzoate.

(b) Yields depend on the solvent, increasing in the order: pyridine, diethylene glycol dimethyl ether, tetrahydrofuran, benzene, diethyl ether, anisole, and diisopropyl ether.

(c) Yields depend on the molar ratio $AlR_3/Mn(II)$, increasing from 10% for a ratio 0.9, to 55 and 79%, for ratios of 7.2 and 9. For higher ratios, the yields decrease.

The observed dependence of yields on the alkylaluminum compound, the temperature, and pressure was as follows.

With benzene as reaction medium, the best results were obtained with triisobutylaluminum, triethylaluminum, and sodium tetraethylaluminate. In ether, however, the latter gave poor yields. Over 170 atm, no variation of yields with pressure was observed. The optimum temperature depended on the nature of the solvent; 165°C with benzene and 145°C with anisole or isopropyl ether.

The procedure reported by Podall and co-workers is, however, rather tedious. They pretreated the manganese compound with a trialkylaluminum at 0°C before reacting the resulting mixture with carbon monoxide. At the end of the reaction, they added methanol to the contents of the autoclave and the carbonyl was then steam distilled.

Calderazzo (93) has indicated a way to simplify Podall's procedure. Manganese(II) acetate, diisopropyl ether and triisobutylaluminum, in that order, were dissolved in diisopropyl ether and placed in an autoclave; then carbon monoxide was introduced at room temperature. The mixture then was heated gradually to 60°C; at about this temperature, gas absorption took place. The temperature was raised to 140°C and maintained at this level for 20 hr. At the end of the reaction, the contents of the autoclave were cooled to room temperature and collected under nitrogen. After cooling to about −50°C, the carbonyl separated out. After filtering, it was sublimed at 50°C in high vacuum. Pure $Mn_2(CO)_{10}$ was obtained in 48% yield. This procedure does not require the use of large volumes of liquids, and it permits the preparation of 20 g of $Mn_2(CO)_{10}$ in a single run using a one-liter autoclave.

Finally a method was described (94) for preparing $Mn_2(CO)_{10}$ from anhydrous $MnCl_2$, magnesium, and carbon monoxide in dimethylformamide; yields of 14% were reported. From the experience of the authors of this chapter, this method gives unsatisfactory results.

$Re_2(CO)_{10}$. Davison, McCleverty, and Wilkinson (95) have reported a method for preparing $Re_2(CO)_{10}$ from anhydrous $ReCl_5$ or $ReCl_3$ by using sodium in tetrahydrofuran as reducing agent. By operating at 130°C and

compounds of the type $CrPh_3 \cdot [(C_2H_5)_2O]_n$ are probably intermediates in the formation of $Cr(CO)_6$. Zeiss (107) proposed the following reaction sequence:

$$CrPh_3(ether)_3 \xrightarrow{CO} Cr(CO)_3Ph_3 \xrightarrow{CO} \underset{(1)}{\overset{+}{Cr}(CO)_6\overset{-}{Ph}} \tag{23}$$

$$\overset{+}{Cr}(CO)_6\overset{-}{Ph} \xrightarrow{H_2O} Cr(CO)_6 + \tfrac{1}{2}H_2 + PhOH \tag{24}$$

This reaction scheme involving successive internal oxidation-reductions of chromium(III) is reasonable, except for the last step in Eq. 23 in which the cationic carbonyl species **1** is formed. Step 24, i.e., formation of phenol from **1** is also not obvious. In our opinion, the cationic species **1** would not be stable in the presence of carbon monoxide, or it would rearrange easily to $Cr(CO)_6$ and biphenyl. Furthermore, it does not seem necessary that a proposed mechanism has to account for the formation of both $Cr(CO)_6$ and phenol. Phenol was found to be present only in trace amounts and its stoichiometry with respect to the formed $Cr(CO)_6$ was therefore not established. Perhaps a more reasonable mechanism for the formation of $Cr(CO)_6$ is that the replacement of phenyl groups by carbon monoxide continues until $Cr(CO)_6$ is formed. This would then react with the excess PhMgBr present to form $MgBr^+[Cr(CO)_5—C(=O)—Ph]^-$ (**2**), which then would revert to $Cr(CO)_6$ in the presence of water. Compounds similar to **2** are now known.

Fischer and Maasböl (111) reported the preparation of the anion $[W(CO)_5—C(=O)—Ph]^-$ (**3**) by treatment of $W(CO)_6$ with LiPh in diethyl ether. Attempts to isolate the corresponding hydrido compound by acidification of **3** yielded $W(CO)_6$ and benzaldehyde.

Nesmeyanov and co-workers (112) preferred to regard the Grignard reagent in the Job-Cassal synthesis merely as a reducing agent. Probably while searching for a more readily available reducing agent, they obtained $W(CO)_6$ and $Mo(CO)_6$ in 14 and 10% yields when they used zinc or iron powders. The reaction was carried out in ether-benzene with carbon monoxide at atmospheric pressure and at 0–10°C. From a similar system operating at about 100 atm (113), $W(CO)_6$ and $Mo(CO)_6$ were obtained in yields of 70 and 46%.

Similar carbonylations of molybdenum and tungsten are reported in some American patents (114,115) describing the preparation of $Mo(CO)_6$ and $W(CO)_6$ in excellent yields (60–90%). Halides or oxyhalides as the starting materials were suspended in ether and reacted with aluminum or aluminum alloys and carbon monoxide at 70 atm and 20–100°C for 3–16 hr; sometimes $Fe(CO)_5$ or $Ni(CO)_4$ was used as a promoter.

An interesting reaction is that between $MoCl_5$ and $Fe(CO)_5$ in the presence of hydrogen chloride and carbon monoxide under pressure to give $Mo(CO)_6$ in 28% yield (116). The reaction of WCl_6 with $Fe(CO)_5$ in the presence of hydrogen under pressure gave yields of $W(CO)_6$ as high as 85% in diethyl ether (117).

Apparently molybdenum and tungsten undergo carbonylation quite easily. Chromium salts, on the other hand, are less prone to be converted into $Cr(CO)_6$; indeed until recently a practical method for preparing this carbonyl in large quantities was unavailable. The Grignard method has the disadvantage of requiring difficultly available materials as well as giving poorly reproducible yields.

In 1957, Natta and co-workers (118) published a method for preparing $Cr(CO)_6$ by using a metal–pyridine system as the reducing agent. Anhydrous pyridine, magnesium powder, and small amounts of iodine or organic halogenated compounds were used to carbonylate chromium(III) and chromium(II) salts at 130–180°C and 100–300 atm for 4–12 hr.

Yields higher than 80% were obtained in the carbonylation of chromium(III) acetylacetonate, although anhydrous chromium(III) acetate, chromium(III) 2-ethylhexanoate, and several other chromium(III) and chromium(II) salts, could also be converted into $Cr(CO)_6$ (119).

The intermediacy of $Cr(CO)_5$ (pyridine) during the synthesis was suggested by the isolation of this compound from the reaction mixture. The essential feature of this method is the reducing power of the metal–pyridine system; indeed, no carbonylation of chromium(III) salts could be obtained when pyridine was absent.

Magnesium and pyridine were shown to give blue solutions extremely sensitive to air. These blue solutions probably contain the pyridine radical anion $C_5H_5N^-$, which is presumably the actual electron-transfer agent.

The metal–pyridine system for the synthesis of $Cr(CO)_6$ was later used also by Nesmeyanov and co-workers (120). They obtained $Cr(CO)_6$ in 37% yield by carbonylation of anhydrous $CrCl_3$ with lithium or sodium at room temperature.

Other compounds known to give radical anions in the presence of alkali metals are benzophenone and aromatic condensed hydrocarbons, such as naphthalene. Interestingly, both these systems were later used in carbonylation reactions to synthesize $Mn_2(CO)_{10}$ and $Cr(CO)_6$. The manganese carbonyl case has already been discussed. Shapiro and Podall (121) reported the use of sodium naphthalene for preparing $Cr(CO)_6$ from anhydrous $CrCl_3$ and carbon monoxide under pressure (250 atm) in tetrahydrofuran at 25°C. The yield, however, was rather poor (about 10%).

Nesmeyanov and co-workers (122) reported a 65% yield of $Cr(CO)_6$ from carbonylation at 65°C of $CrCl_3$ in ethyl ether with carbon monoxide at 100 atm; lithium aluminum hydride was used as the reducing agent.

Finally, two additional methods of preparing $Cr(CO)_6$ are the $Al–AlCl_3$–benzene system and reductive carbonylation with trialkylaluminum compounds. By the former method, Fischer and co-workers (123) obtained $Cr(CO)_6$ in 84% yield by treating anhydrous $CrCl_3$ at 140–150°C with a benzene suspension of $AlCl_3$ and aluminum powder and carbon monoxide under pressure. The bis(benzene)chromium(I) cation, $[Cr(C_6H_6)_2]^+$, was regarded as a reaction intermediate. The main evidence for this view was the inability to obtain $Cr(CO)_6$ when the reaction was carried out in heptane.

The trialkylaluminum method has been used (92) to prepare $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in yields of 92, 76, and 92%. Several aspects of this method of preparation have been discussed previously (see synthesis of $Mn_2(CO)_{10}$).

Podall and co-workers (123*a*) have also reported the preparation of Group VI metal carbonyls. In particular they obtained $Cr(CO)_6$ by treating $CrCl_2$ or $CrCl_3$ or chromium(III) acetylacetonate with sodium in diglyme as solvent. The best yields (30%) were obtained in 0–25°C. This reductive carbonylation seems to give $Na_2Cr(CO)_5$ as the final reaction product, from which $Cr(CO)_6$ is obtained in a hydrolytic step.

G. Hexacarbonylvanadium, Hexacarbonylniobate(I−), and Hexacarbonyltantalate(I−)

1. *Historical*

In this group only vanadium is known to give a neutral carbonyl, $V(CO)_6$, whereas niobium and tantalum form the corresponding carbonylmetallates $[M(CO)_6]^-$. Hexacarbonylvanadium was discovered in 1959 by Natta, Ercoli, Calderazzo, and co-workers (124). The existence of a diamagnetic dodecacarbonyldivanadium, later reported by Pruett and Wyman (125), was not confirmed (see Sec. IV).

The carbonylmetallates of niobium and tantalum were described in 1961 by Werner and Podall (126), who isolated the sodium salts of the $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ anions.

2. *Methods of Preparation*

No methods are known for preparing $V(CO)_6$, $[Nb(CO)_6]^-$, or $[Ta(CO)_6]^-$ in dry or aqueous systems.

Hexacarbonylvanadium was prepared (127,128) by reduction and carbonylation of VCl_3, $VOCl_3$, or vanadium(III) acetylacetonate with carbon monoxide at 150–300 atm and 120–150°C. The reducing system consisted of a mixture of magnesium and zinc powders suspended in anhydrous pyridine. The reaction does not give hexacarbonylvanadium directly; the $[V(CO)_6]^-$ anion of the magnesium salt is the final product of the reaction.

After evaporation of the pyridine and addition of water to the crude reaction mixture, a yellow-orange solution of magnesium hexacarbonylvanadate is obtained.

To isolate hexacarbonylvanadium the following steps are necessary: acidification, extraction with ethyl ether, evaporation of the ether solution, drying of the crude solid $V(CO)_6$, followed by sublimation of the carbonyl. The reactions occurring during these operations are:

$$[Mg(py)_n][V(CO)_6] \xrightarrow[(C_2H_5)_2O]{HCl} [pyH][V(CO)_6)] + \cdots \tag{25}$$

$$[pyH][V(CO)_6] \xrightarrow[(C_2H_5)_2O]{HCl(excess)} [(C_2H_5)_2OH][V(CO)_6] + \cdots \tag{26}$$

$$[(C_2H_5)_2OH][V(CO)_6] \xrightarrow{evaporation} \tfrac{1}{2}H_2 + V(CO)_6 + (C_2H_5)_2O \tag{27}$$

The yields in the carbonylation step are above 90%, but the sequence of operations required for isolating the hexacarbonyl causes severe losses. However, by careful manipulations, 50–60% yields of $V(CO)_6$ are normally obtained.

Werner and Podall (126) achieved the reductive carbonylation of VCl_3, $NbCl_5$, and $TaCl_5$ with sodium dispersion and using diglyme as solvent at 90–120°C under 200–350 atm of carbon monoxide. The carbonylation step by this method seems to give less satisfactory results. The reported yields of the salts $Na(diglyme)_2[M(CO)_6]$ (**1**) ($M = V, Ta$) are 62 and 32%. Acidification of **1** is also required to obtain $V(CO)_6$. The yields in the acidification step were reported to be quantitative, but no experimental details have been given.

Two patents (129,130) report the reduction of VX_3 ($X = Cl, Br$) with sodium dispersion and aromatic polycyclic hydrocarbons as "promoters," and the simultaneous carbonylation of these mixtures at 25–125°C by carbon monoxide at 30–170 atm. "Dodecarbonyldivanadium" was reported to be obtained in 20–22% yields.

Bis(toluene)vanadium and other similar bis(arene)vanadium(0) compounds can be converted into $V(CO)_6$ by reacting their hydrocarbon solutions with carbon monoxide at 35–70 atm and 70–80°C (125,131). The reported yields were low. In addition, it was not specified whether $V(CO)_6$ or its reduced form, $[V(CO)_6]^-$, was present at the end of reaction. The latter seems more probable. Calderazzo and Cini have shown (132) that the reaction of bis(mesitylene)vanadium with carbon monoxide (100 atm) at 35°C gives bis(mesitylene)vanadium(I)-hexacarbonylvanadate(I−), $[V(C_6H_3Me_3)_2][V(CO)_6]$. This was explained by the transitory formation of $V(CO)_6$, followed by a fast oxidation-reduction with the unreacted $V(C_6H_3Me_3)_2$ still present in solution.

H. Transition Metals of Group IV

Two American patents (133,134) dealing with a method for refining titanium, zirconium, and hafnium, claim that carbonyls of formula $M(CO)_7$ (M = Ti, Zr, Hf) are produced during the process. According to these patents, the raw metals were treated with carbon monoxide at 4–8 atm and at 300–400°C, whereby conversion of the metals to the heptacarbonyls was obtained. No carbonyls of these three metals have been reported in the scientific literature.

A substituted carbonyl of titanium, however, has been isolated and fully characterized. This is the cyclopentadienyl derivative, $Ti(C_5H_5)_2(CO)_2$, prepared by treating $TiCl_2(C_5H_5)_2$ with sodium cyclopentadienide and carbon monoxide under pressure (135). The cyclopentadienylcarbonyl is a red-brown solid melting with decomposition at about 90°C. It is volatile and can be sublimed *in vacuo* with some decomposition.

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III. PHYSICAL AND THERMODYNAMIC DATA OF METAL CARBONYLS

A. Introduction

Some physical properties of the metal carbonyls are presented in Table 1. The vapor pressure values are also tabulated in Table 2, since a similar compilation has never appeared before. Knowledge of the vapor pressures of the metal carbonyls at different temperatures has important practical utility for safety reasons and for operations involving distillation and sublimation. Moreover, the vapor pressure measurements represent the first step toward the determination of important thermodynamic properties.

TABLE 1

Selected Physical Data of Metal Carbonyls

			Solubility at room temperature	
Compound	Color	Mp (°C)	Hydrocarbons	THF
$Ni(CO)_4$	Colorless	−19.3 (bp 42.1)	Very good	Very good
$Fe(CO)_5$	Yellow	−20.5 (bp 103–104)[a]	Very good	Very good
$Fe_2(CO)_9$	Orange	100 dec.	Extremely low	Reacts
$Fe_3(CO)_{12}$	Black-green	140–150 dec.	Moderate	—
$Ru(CO)_5$[b]	Colorless	−22	Good	—
$Ru_3(CO)_{12}$	Orange-red	150 dec. (in air)	Moderate	—
$[Ru(CO)_x]_n$[b]	Green	—	Extremely low	—
$Os(CO)_5$[b]	Colorless	−15 ~	—	—
$Os_3(CO)_{12}$	Yellow-orange	224	Good	—
$Co_2(CO)_8$	Orange	51–52 dec.	Good	Reacts
$Co_4(CO)_{12}$	Black	—	Very low	Reacts
$Co_6(CO)_{16}$[b]	Black	100–110 dec.	Very low	—
$Rh_2(CO)_8$[b]	Orange	76 dec.	—	—
$Rh_4(CO)_{12}$	Brick red	150 dec.	—	—
$Rh_6(CO)_{16}$	Black	> 220 dec.	Low	—
$[Ir(CO)_4]_n$[b]	Yellow-green	—	—	—
$Ir_4(CO)_{12}$	Canary yellow	210 dec.	Very poor	Poor
$Mn_2(CO)_{10}$	Golden yellow	154–155	Moderate	Good
$Tc_2(CO)_{10}$	Colorless	159–160	≥ 5%	—
$Re_2(CO)_{10}$	Colorless	177	—	—
$[Re(CO)_4]_n$[b]	Colorless	Subl. 100°/0.1 mm	Very low	Very low
$Cr(CO)_6$	Colorless	130 dec.	Very low	Low
$Mo(CO)_6$	Colorless	—	Very low	Low
$W(CO)_6$	Colorless	—	Very low	Low
$V(CO)_6$	Black-green	~ 70 dec.	~ 2% (w/v)[c]	Reacts

[a] Extrapolated.

[b] No other reports known apart from that of the discoverers.

[c] Reacts very slowly with aromatic hydrocarbons.

B. Vapor Pressures and Heats of Vaporization

The vapor pressures in mm Hg at different temperatures were calculated using the empirical equations numbered below.

TABLE 2

Vapor Pressures of Some Metal Carbonyls

Compound	Vapor pressure (mm Hg)													
	10°C	15°C	20°C	30°C	40°C	50°C	60°C	70°C	100°C	110°C	120°C	130°C	140°C	150°C
$Ni(CO)_4$	211.8	262.7	322.9	478.8	692.0									
$Fe(CO)_5$	11.8	15.7	20.8	35.4	58.2	92.7	143.7	217.1	655.9					
$Ru(CO)_5$			~ 50											
$Os(CO)_5$			~ 4.5											
$Co_2(CO)_8$		0.07												
$Mn_2(CO)_{10}$									3.0^a	5.1	8.5	13.6	21.3	32.8^a
$Re_2(CO)_{10}$								0.04^a	0.36	0.7	1.3	2.4	4.3	7.4
$Cr(CO)_6$				0.28^a	0.69^a	1.63	3.64	7.76	58.9	107.9	191.5	330.4		
$Mo(CO)_6$				0.27^a	0.63^a	1.43	3.06	6.26	42.8	75.9	130.9	219.3	358.9	
$W(CO)_6$				0.06^a	0.14^a	0.35	1.25	1.74	14.1	26.2	47.4	83.2	142.0	236.6

[a] Extrapolated.

For $Ni(CO)_4$, valid from −35 to 45°C (1):

$$\log p = 7.690 - 1519/T \tag{1}$$

Another equation has been reported (2):

$$\log p = 7.878 - 1574.49/T$$

For $Fe(CO)_5$, the following equation has been found (3):

$$\log p = 8.3098 - 2050.7/T \tag{2}$$

The equation proposed by Dewar and Jones (4), $\log p = 7.349 - 1681/T$, gives too high values of the vapor pressures and too low values of the heat of vaporization. The most probable value of the heat of vaporization is 8.9 kcal/mole, as suggested in a publication of the U.S. Bureau of Standards (5). Trautz and Badstübner's data (3) give a molar entropy of vaporization of 23.7 eu compared with that of 20.4 eu given by Dewar and Jones. The accepted value (5) of the entropy of vaporization of $Fe(CO)_5$ is 23.5 cal deg^{-1} $mole^{-1}$. These entropy change values suggest that $Fe(CO)_5$ behaves approximately as a Troutonian liquid.

The variation of vapor pressures with temperature for a number of other metal carbonyls is given below.

For $Mn_2(CO)_{10}$ between 102 and 146°C (6):

$$\log p = 9.225 - 3262.6/T \tag{3}$$

For $Re_2(CO)_{10}$ between 78 and 135.5°C (7):

$$\log p = 10.68 - 4152/T \tag{4}$$

For $Cr(CO)_6$ between 50 and 140°C (8):

$$\log p = 11.832 - 3755.2/T \tag{5}$$

For $Mo(CO)_6$ between 55 and 145°C (8):

$$\log p = 11.174 - 3561.3/T \tag{6}$$

For $W(CO)_6$ between 55 and 145°C (8):

$$\log p = 11.523 - 3872.0/T \tag{7}$$

The vapor pressures of the hexacarbonyls of the sixth group have also been determined by Rezukhina and Shvyrev (9). The relations given by these authors are:

$Cr(CO)_6$: $\log p = 11.475 - 3622.9/T$; between 46.1 and 138.4°C
$Mo(CO)_6$: $\log p = 11.727 - 3788.3/T$; between 50.5 and 129.6°C
$W(CO)_6$: $\log p = 10.947 - 3640.4/T$; between 65.6 and 137°C

The three latter equations give vapor pressures normally lower than those reported by Hieber and Romberg. The largest discrepancy between the two sets of values is found for $Mo(CO)_6$. The heats of sublimation (see Table 3) increase in the order $Mo(CO)_6 < Cr(CO)_6 < W(CO)_6$ according to Hieber and Romberg (8) and in the order $Cr(CO)_6 < W(CO)_6 < Mo(CO)_6$ according to other workers (9).

TABLE 3

Heats of Vaporization of Some Metal Carbonyls

Compound	Heat of vaporization, ΔH_v (kcal/mole)	Reference
$Ni(CO)_4$	7.20	2
	6.92	1
	6.50	19
	7.0	5
$Fe(CO)_5$	8.9	5
	9.38	3
	7.71[a]	—
$Mn_2(CO)_{10}$	15.0	6
$Re_2(CO)_{10}$	19.0	7
$Cr(CO)_6$	17.18	8
	16.57	9
	18.2	10
$Mo(CO)_6$	16.29	8
	17.33	9
	17.39	20
	16.66	21
$W(CO)_6$	17.71	8
	16.66	9

[a] Calculated from the vapor pressure data given in ref. 4.

Vapor pressures of $Cr(CO)_6$ between 27.6 and 42.3°C have been measured by Cordes and Schneider (10) using the Knudsen effusion method. The relation $\log p = 12.7 - 3980/T$ was found by these authors, who also give a heat of vaporization of 18.2 kcal/mole. The vapor pressures of $Cr(CO)_6$ at different temperatures given by Windsor and Blanchard (11) are too high, and therefore probably not properly corrected for the carbon monoxide pressure formed by the decomposition of the carbonyl; this reaches 10 mm Hg at temperatures around 130°C (9).

A redetermination of the vapor pressure of $Cr(CO)_6$ between 0 and 37.5°C has appeared (9*a*). The value of the heat of sublimation was found to be 17.09 kcal/mole, in good agreement with that reported by Hieber and Romberg (8).

C. Heats of Combustion and Formation

In spite of the numerous experimental difficulties, the heats of formation of some metal carbonyls have been determined.

Some selected values of heats of formation of metal carbonyls are given by Skinner (12).

Some of the older values obtained for $Ni(CO)_4$ and $Fe(CO)_5$ have also been critically reviewed (13,14).

For $Ni(CO)_4$, $Fe(CO)_5$, and the hexacarbonyls of group VI, the more recent values of Cotton, Fischer, and Wilkinson are reported in Table 4.

TABLE 4

Heats of Combustion and Formation of Some Metal Carbonyls
(Reference numbers in parentheses)

Compound	Heat of combustion (kcal/mole)	Heat of formation[a] (kcal/mole)	Mean dissociation energies[b] of M—C bond
$Ni(CO)_4$	−282.2 (13)[c]	−148.7 (24)	35.2 (14)
		−151.6 (13)	
		−151.0 (25)	
$Fe(CO)_5$	−386.9 (14)[c]	−182.6 (14)	27.7 (14)
		−187.8 (5)	
$Mn_2(CO)_{10}$	−777.0 (22)[d]	−400.9 (22)	15.7
$Cr(CO)_6$	−443.1 (23)[c]	−257.5 (23)	27.1 (14)
$Mo(CO)_6$	−507.5 (23)[c]	−234.8 (23)	35.9 (14)
$W(CO)_6$	−537.8 (23)[c]	−227.2 (23)	42.1 (14)

[a] Heats of formation of the metal carbonyl in the liquid state ($Ni(CO)_4$ and $Fe(CO)_5$) or the solid state (all the others) from the solid metal, graphite, and oxygen gas.

[b] For the equation $M_{(g)} + nCO_{(g)} = M(CO)n_g$. The value for $Mn_2(CO)_{10}$ was calculated from the heat of formation in the literature, the heat of vaporization of the metal, the heat of vaporization of the metal carbonyl, and the metal–metal bond energy given in ref. 6 (34 ± 13 kcal/mole). The metal–metal bond dissociation energy was found to be 18.9 kcal/mole by mass spectrometric methods (26).

[c] For the combustion to metal oxides with oxygen.

[d] For the reaction: $Mn_2(CO)_{10} + 4HNO_3$ (in $16H_2O$) $+ 6O_{2(g)} = 2Mn(NO_3)_2$ (in $10.309H_2O$) $+ 10CO_{2(g)} + 2H_2O$ (liq.).

In order to get a rough estimate of the relative metal–carbon bond strength in metal carbonyls the above-mentioned authors have calculated the enthalpy change of the following processes:

$$\frac{1}{n}\,\mathrm{M(CO)}_{n(g)} = \frac{1}{n}\,\mathrm{M}_{(g)} + \mathrm{CO}_{(g)} \quad (\Delta H) \tag{8}$$

which gives the values in the last column of Table 4. The latter are in good agreement with the average bond dissociation energies obtained from the results of electron impact measurements (27).

The mean metal–CO dissociation energies for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ (35.2, 27.7, and 27.1 kcal/mole, respectively) are, however, inconsistent with the usually higher reactivity of $Ni(CO)_4$ and $Fe(CO)_5$ compared with $Cr(CO)_6$ and with the fact that $Ni(CO)_4$ was found to exchange its carbonyl groups (15) with ^{14}CO at a much faster rate than $Fe(CO)_5$ (16) and $Cr(CO)_6$ (17). It has been pointed out (14) that a more realistic evaluation of bond energies is obtained by taking into account the promotion energies of the metal and ligands to their corresponding valence states, i.e.,

$$\frac{1}{n}\,\mathrm{M(CO)}_{n(g)} = \frac{1}{n}\,\mathrm{M}^{*}_{(g)} + \mathrm{CO}^{*}_{(g)} \quad (\Delta H^{*}) \tag{9}$$

This calculation has been carried out for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ and values for ΔH^* of 87, 89, and 77 kcal/mole, respectively, have been found.

It is interesting to note that although, according to the heats of formations calculated with Eq. 8, $Fe(CO)_5$ appears to be less stable than $Ni(CO)_4$, the opposite order of stability is found for the two metal carbonyls when the promotion energies as defined above are also taken into account. From the data of Table 4, it would also appear that stability increases regularly from $Cr(CO)_6$ to $W(CO)_6$.

The thermodynamic equilibrium constants for the reactions:

$$\mathrm{Ni}_{(s)} + 4\mathrm{CO}_{(g)} = \mathrm{Ni(CO)}_{4(g)} \tag{10}$$

$$\mathrm{Fe}_{(s)} + 5\mathrm{CO}_{(g)} = \mathrm{Fe(CO)}_{5(g)} \tag{11}$$

have been calculated by using the known standard heats of reaction and the entropies deduced from spectroscopic data (18). The equations relating equilibrium constants to temperature are, for $Ni(CO)_4$ and $Fe(CO)_5$, respectively:

$$\log K = 8546/T - 21.64 \tag{12}$$

$$\log K = 8940/T - 30.09 \tag{13}$$

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IV. STRUCTURE OF METAL CARBONYLS

A. Introduction

The structures of several metal carbonyls have been elucidated in recent years, especially by Dahl and his co-workers, by x-ray diffraction studies. In the course of the present discussion, reference will also be given to other physical data (infrared measurements, dipole moments, Mössbauer resonance spectra, nuclear magnetic resonance spectra, magnetic susceptibility measurements, etc.) capable of giving useful information about the various structures.

The subject will be divided into the two natural classes: mononuclear metal carbonyls and polynuclear metal carbonyls.

It is worth mentioning that additional calculations in the course of the determinations of the x-ray structures of $Ni(CO)_4$ (1) and $Fe(CO)_5$ (2) have established conclusively that carbon monoxide is bonded to the metal through the carbon atom.

B. Mononuclear Metal Carbonyls

Of the known metal carbonyls, the structures of $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have been reported.

$Ni(CO)_4$. By an electron diffraction study in the vapor phase (3), the carbonyl groups have been found to be tetrahedrally arranged around the nickel. A later x-ray diffraction study (1) on the solid carbonyl at −55 ± 5° has shown the molecule to be a regular tetrahedron with the interatomic distances reported in Table 5. Agreement between the two structure determinations is excellent.

$Fe(CO)_5$. An early electron diffraction study on the vapor by Ewens and Lister (4) had shown $Fe(CO)_5$ to be a trigonal bipyramid. A later x-ray study (5) of this carbonyl in the solid state between −70 and −110° has virtually confirmed these results, but the molecule was found to be slightly distorted. More specifically the oxygen atoms have been reported to be 0.12–0.13 Å displaced from the positions of an ideal trigonal bipyramid. However, a further refinement (2) of the structure has led to the conclusion that "within the experimental error the molecule in the *C*2/*c* space group is a trigonal bipyramid." The previously reported deviations from the theoretical positions have not been considered significant.

A further structural investigation by electron diffraction methods on the vapor (6) has established a difference in lengths for the axial and trigonal iron–carbon bonds. The axial iron–carbon bonds were found to be significantly shorter than the trigonal ones, as shown in Fig. 1. Donohue and Caron (6*a*) have, however, suggested that the x-ray results cannot be taken to indicate any significant difference in lengths between axial and trigonal iron–carbon bonds.

The Mössbauer resonance spectra of $Fe(CO)_5$ taken at 78°K, i.e., below

TABLE 5

Interatomic Distances of Mononuclear Metal Carbonyls

(Reference numbers in parentheses).

Compound	Interatomic distances (Å)	
	M—C	C—O
$Ni(CO)_4$	1.84 ± 0.03 (1)	1.15 ± 0.03 (1)
$Fe(CO)_5$	1.82 ± 0.02 (5) 1.84 ± 0.03 (4) 1.79 ± 0.02 (2)	1.14 ± 0.02 (5) 1.15 ± 0.04 (4) 1.12 ± 0.02 (2)
	Axial 1.797 ± 0.015 Trigonal 1.842 ± 0.015 (6)	1.136 ± 0.003 (6)
$Cr(CO)_6$	1.92 ± 0.04 (9) 1.80 (8)	1.16 ± 0.05 (9) 1.15 (8)
$Mo(CO)_6$	2.08 ± 0.04 (9) 2.13 (8)	1.15 ± 0.05 (9) 1.15 (8)
$W(CO)_6$	2.06 ± 0.04 (9) ≤ 2.3 (8)	1.13 ± 0.05 (9)

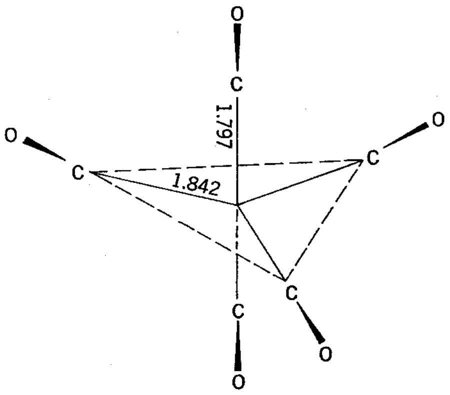


FIG. 1. Molecular configuration of $Fe(CO)_5$, showing the difference in length between axial and trigonal metal–carbon bonds (6).

the freezing point of the carbonyl, are in agreement (7) with a dsp^3 hybridization implied by the trigonal bipyramid structure.

The *hexacarbonyls of the group VI metals* have been studied by x-ray (8) and electron diffraction (9) methods. The conclusion was that the three molecules are regular octahedra, but apparently the interatomic distances have not been determined with sufficient precision, at least for $W(CO)_6$. The octahedral arrangement of the ligands is well established and other data, particularly infrared measurements in the CO stretching region, have confirmed the results of the x-ray and electron diffraction studies.

Hexacarbonylvanadium was first reported by Natta, Ercoli, Calderazzo, and co-workers in 1959 (10). Some months later the same carbonyl was reported by Pruett and Wyman (11) who erroneously attributed a dimeric formula to it, mainly on the basis of electron spin resonance and nuclear magnetic resonance measurements.

The monomeric nature of this carbonyl, both in the solid state and in solution, has been established by x-ray measurements on a single crystal (10), by magnetic susceptibility measurements in the solid state (10) and in solution (12), and by infrared measurements in the CO stretching region (13,14). The x-ray measurements show that $V(CO)_6$ has unit cell dimensions similar to those of the hexacarbonyls of the group VI metals. The presence of one unpaired electron can only be explained by a monomeric formula, which is also suggested by the high volatility of the carbonyl. The infrared spectrum of $V(CO)_6$ in hydrocarbons shows only one band at 1975 cm^{-1}, which suggests an approximately octahedral arrangement of the CO groups around the metal. Therefore, the molecule has to be a monomer in solution. The absence of electron spin resonance signals at room temperature either in the solid state or in heptane solution has been confirmed (14). This is not by any means conclusive evidence for diamagnetism. The spin-lattice relaxation time of benzene solutions of $V(CO)_6$ was measured by nuclear magnetic resonance techniques (15); the approximate magnetic moment calculated from the relaxation time was found to agree well with that calculated from the magnetic susceptibility data in solution (12). Nyholm and co-workers have measured the magnetic susceptibility of hexacarbonylvanadium in the temperature range 90–300°K. The temperature dependence of the susceptibility is that of a normal paramagnetic substance, with a value of Θ practically equal to zero (15*a*).

Infrared spectra and other measurements. The infrared spectra of the mononuclear metal carbonyls in the gas phase correlate well with the x-ray and electron diffraction data. The selection rules for the tetrahedral and octahedral symmetry groups predict one C—O stretching vibration and one metal–carbon stretching vibration, both active in the infrared. For a trigonal bipyramid (point group D_{3h}), two C—O and two metal–carbon infrared active stretching vibrations are expected. The infrared spectra of mononuclear carbonyls meet these expectations, as shown in Table 6.

TABLE 6

Infrared C–O and M–C Stretching Vibrations[a] and Dipole Moments of Some Mononuclear Metal Carbonyls

(Reference numbers in parentheses)

Compound	ν_{C-O} (cm^{-1})	ν_{M-C} (cm^{-1})	Dipole moment $\mu \times 10^{18}$ esu
$Ni(CO)_4$	2057.6 (22)	422 (16)	0.3[b] (23)
$Fe(CO)_5$	2013.5 2034.4 } (22)	474 432 } (17)	0.63[c] (24)
$Cr(CO)_6$	2000.1 (22)	441 (18)	—
$Mo(CO)_6$	2002.6 (22)	368 (18)	—
$W(CO)_6$	1997.5 (22)	374 (18)	—

[a] In the gas phase.
[b] At 0° in CCl_4.
[c] In benzene at 25°.

The infrared spectra of the mononuclear carbonyls of the first row transition metals, with the exception of $V(CO)_6$, have been studied extensively. Since only the most recent and complete vibrational assignments for $Ni(CO)_4$ (16), $Fe(CO)_5$ (17), and the three hexacarbonyls (18) are mentioned here, it is recommended that the reader use the references given in these papers as a literature source for a more detailed study of the subject.

The infrared spectrum of solid $Ni(CO)_4$ has been published (19) and found to correlate well with the published x-ray structure obtained at low temperature.

As mentioned before, the vibrational spectrum of $Fe(CO)_5$ is in satisfactory agreement with a D_{3h} symmetry. However, some minor details of the assignment of the bands are still unresolved (20). There is a report (21) of an interesting case of breakdown of the selection rules for concentrated solutions of $Fe(CO)_5$ in heptane and for the pure liquid, in the CO stretching region around 2000 cm^{-1}. Only for 0.5% solutions or less does the infrared spectrum of $Fe(CO)_5$ show the two well-resolved bands expected for D_{3h} symmetry.

C. Polynuclear Metal Carbonyls

$Co_2(CO)_8$. The complete x-ray structure of $Co_2(CO)_8$ has been published (25) and the molecule has been shown to consist of dimeric units with the two cobalt atoms bonded together through the two bridging CO groups. The cobalt–cobalt distance is 2.52 Å, the mean terminal carbon–oxygen distance is 1.17 Å. The main feature of the molecule is that the two cobalt atoms and the two bridging CO groups are not in the same plane, which is in disagreement with early proposals based on infrared spectra (26,27), but in agreement with a suggestion made by Mills and Robinson (28). The molecule has C_s symmetry, i.e., it contains a plane of symmetry perpendicular to the cobalt–cobalt bond (see Fig. 2).

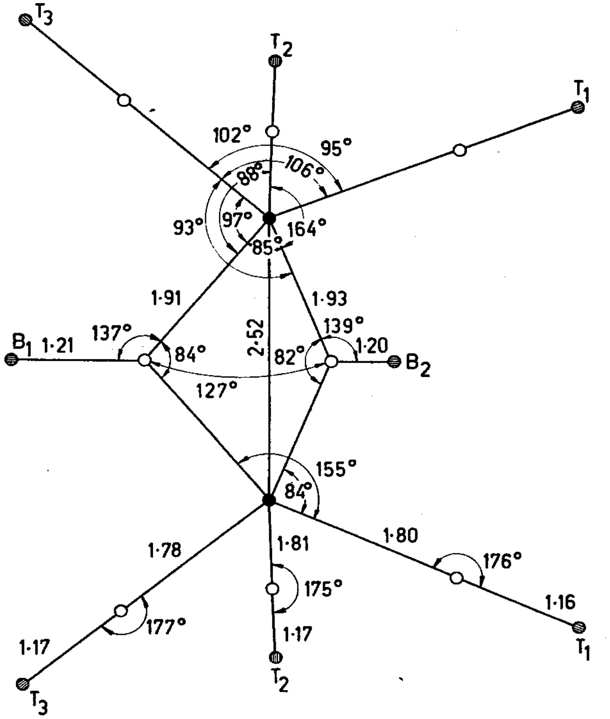
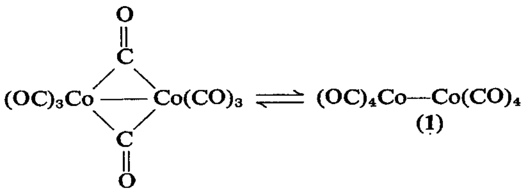


FIG. 2. The molecular structure of $Co_2(CO)_8$ (Sumner, Klug, and Alexander, *Acta Cryst.*, **17**, 732 (1964)).

In solution, $Co_2(CO)_8$ has a dipole moment of 1.29 D (29). Several papers on the infrared spectra of $Co_2(CO)_8$ have been published. Two papers (30,31) had independently pointed out that the solution spectrum of $Co_2(CO)_8$ was richer in bands than previously thought on the basis of measurements carried out using optics with lower resolution (26,27).

Later, Bor (32) assigned the band at highest frequency in the carbonyl region as the totally symmetrical vibration which is infrared active in those metal carbonyls belonging to the point groups C_n, C_{nv}, C_s, or S_4. At the same time the presence of two isomeric forms of $Co_2(CO)_8$ in solution was suggested. This hypothesis has now been definitely established by Noack (33) and by Bor (34) himself. Both authors agree that there are two forms of $Co_2(CO)_8$ in solution: one corresponding to that of the crystalline substance; the other having no bridging CO groups, but with the two cobalt atoms held together only by a metal–metal bond (**1**). Noack has shown that the two forms are related by a temperature dependent equilibrium and that at room temperature a pentane solution of $Co_2(CO)_8$ contains about 43% of the CO-bridged isomer and 53% of the other one. At −104° the percentages are 84 and 16, respectively. The enthalpy of reaction 1 is +1.30 kcal/mole and the entropy change is +5 eu. The driving force of the forward reaction 1 is, therefore, given by the entropy factor (34*a*).



$$(\mathrm{OC})_3\mathrm{Co}\overset{\overset{\mathrm{O}}{\|}\,\mathrm{C}}{\underset{\underset{\|}{\mathrm{C}}\,\mathrm{O}}{\text{———}}}\mathrm{Co(CO)_3} \rightleftharpoons \underset{(\mathbf{1})}{(\mathrm{OC})_4\mathrm{Co{—}Co(CO)_4}} \qquad (1)$$

The conclusions drawn by Bor and by Noack are substantially the same as far as the existence of the two isomers in solution is concerned, but no complete agreement appears to have been reached yet about the possible structure of the high temperature nonbridged form (**1**). The cobalt atoms can, in fact, be considered to be in a trigonal bipyramidal or in a tetragonal pyramidal arrangement. Further, each of these arrangements can be staggered or eclipsed. An additional possibility is an arrangement of lower symmetry (C_2). A decision among these possibilities is still to be made. Bor favors a C_{2v} symmetry structure (34), but Noack (35) gives arguments favoring the trigonal bipyramidal arrangement (D_{3d}). Keller and Wawersik (35*a*) have reported that monomeric $Co(CO)_4$ is formed when $Co_2(CO)_8$ is sublimed at room temperature and the cold finger is maintained at liquid nitrogen temperature. The monomer is stable only at low temperature and was detected by electron paramagnetic resonance measurements at liquid nitrogen temperature.

$Co_4(CO)_{12}$. An early two-dimensional x-ray diffraction study (36) and two later three-dimensional studies (36*a*,37) have established the structure shown in Fig. 3a for the compound in the solid state. The four cobalt atoms occupy the positions of a regular tetrahedron. Three of them, bridged by CO groups, carry two terminal carbon monoxide groups, whereas the fourth cobalt atom is bonded only to the three other cobalt atoms and to three terminal CO groups. This structure contains nine terminal and three bridging CO groups. Cotton and Monchamp (30) have questioned that such a structure (of C_{3v} symmetry) should give rise to six stretching vibrations for the terminal CO groups and two vibrations for the bridging CO groups. However, the infrared spectrum of $Co_4(CO)_{12}$ was simpler, especially in the CO bridging region where only one main band was observed. Since then, five bands have been recognized in the terminal CO stretching region as due to fundamental vibrations and also the second vibration associated with the bridging CO groups has been localized (32,38) at 1898 cm^{-1}. This latter band which was assigned (32) to the A_1 mode, is extremely weak, but a recent analysis (39) of the CO stretching modes of $Co_4(CO)_{12}$ has pointed out that the totally symmetrical vibration associated with the bridging CO groups should in fact be expected to have a very low intensity.

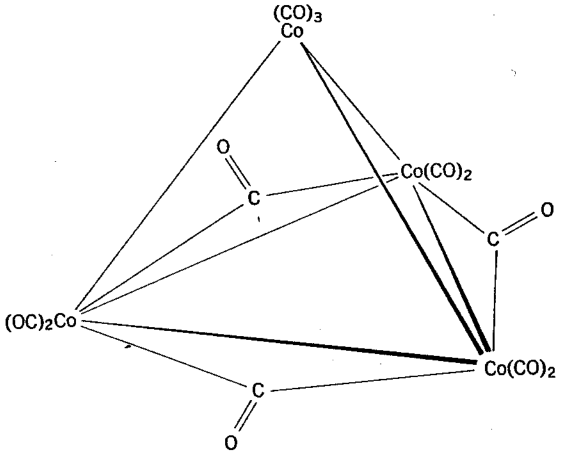


FIG. 3a. Molecular configuration of $Co_4(CO)_{12}$ (36,36*a*,37).

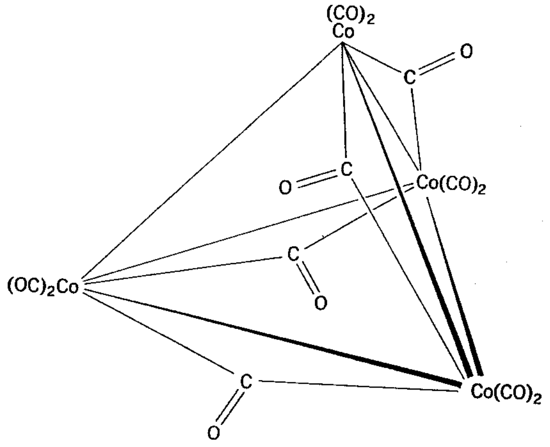


FIG. 3b. The structure proposed by Smith (40) for $Co_4(CO)_{12}$ in solution.

The debate about the infrared spectrum of $Co_4(CO)_{12}$ or, in other words, of its structure in solution, has not come to an end. Smith (40) has proposed another structure for the carbonyl which would not conflict with the infrared data. The proposed structure is shown in Fig. 3b. This has symmetry D_{2d} and contains eight terminal and four bridging CO groups. It should give rise to a total number of five CO stretching vibrations, one of them being associated with the bridging carbon monoxide groups. Cotton (40*a*) has considered the possibility that $Co_4(CO)_{12}$ can exist in solution in forms having structures different from that established for the crystal. In particular he envisaged that $Co_4(CO)_{12}$ could be in equilibrium with the form proposed by Smith and also with a third one not containing bridging CO groups, of T_d symmetry. Since both Smith's structure and that of T_d symmetry contain four equivalent cobalt atoms, only one ^{59}Co nmr resonance should be observed. However, two resonances were observed (40*b*,40*c*) in solutions of $Co_4(CO)_{12}$ in a ratio of approximately 3:1. This seems to confirm that the solid state structure persists in solution.

$Rh_2(CO)_8$. No x-ray determinations or infrared measurements have yet been reported.

$Rh_4(CO)_{12}$. A tetrameric formula was suggested by Beck and Lottes (40*d*) for the red tricarbonylrhodium described by Lagally (41) on the basis of its volatility (it sublimes at 65° in high vacuum), its infrared spectrum, and by its similarity with the cobalt analog. The infrared spectrum of this metal carbonyl in petroleum ether shows a band at 1885 cm^{-1}, indicative

of bridging CO groups. Mention has been made (36*a*) that $Rh_4(CO)_{12}$ has lattice parameter data similar to those of $Co_4(CO)_{12}$.

$Rh_6(CO)_{16}$. The previously reported (41) black $Rh_4(CO)_{11}$ has been shown by x-ray methods (42) to have the molecular formula $Rh_6(CO)_{16}$. This compound, which is the first known example of a hexanuclear metal carbonyl, represents a particularly interesting case of molecular arrangement; one, however, that is not completely unknown in inorganic chemistry. The six rhodium atoms are at the corners of an octahedron. Each rhodium atom carries two terminal CO groups. Each of the four remaining CO groups bridges three rhodium atoms. The interatomic distances are:

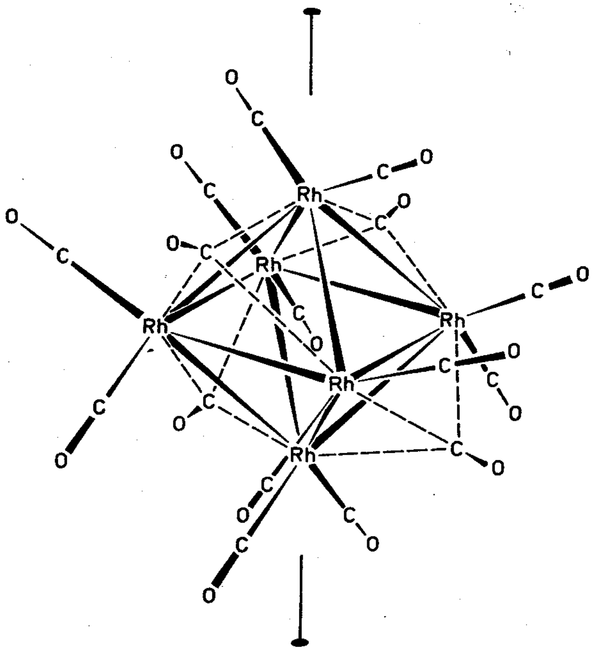


FIG. 4. Molecular structure of $Rh_6(CO)_{16}$ (E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963)). Reproduced by permission.

Rh—C (terminal CO groups)	1.864 ± 0.015 Å
C—O (terminal CO groups)	1.155 ± 0.015 Å
Rh—C (bridging CO groups)	2.168 ± 0.012 Å
C—O (bridging CO groups)	1.201 ± 0.022 Å

$[Ir(CO)_4]_n$. No infrared studies or x-ray structural determinations have been reported yet. It has been mentioned (43) that this carbonyl differs from $Co_2(CO)_8$ in containing only a metal–metal bond and no bridging CO groups in the solid. This suggestion seems very reasonable in view of the fact that a nonbridged form of $Co_2(CO)_8$ is now known in solution and that the tendency to form direct metal–metal bonds increases when descending a vertical triad of transition elements. It should, however, be pointed out that not very much is known about this carbonyl and that even its molecular complexity is unknown. Hieber and Lagally who first reported the carbonyl (44) were unable to determine its molecular weight, which was assumed to correspond to twice its simple formula by analogy with octacarbonyldicobalt.

$Ir_4(CO)_{12}$. This carbonyl has been reported (36*a*) to be a tetramer with the iridium atoms occupying the positions of a tetrahedron with no bridging carbon monoxide groups. An investigation of the infrared spectrum (45) has indicated that the compound has no absorptions attributable to bridging CO groups.

$Fe_2(CO)_9$. By means of Patterson and Fourier analyses, the molecular formula of this orange-gold iron carbonyl was found to be $Fe_2(CO)_9$ (46). The structure was described as that of two iron atoms joined together by three bridging CO groups; three terminal CO groups are also bonded to the iron atoms (Fig. 5). The *six* bonds are slightly distorted from a regular octahedral configuration. The interatomic distances are: Fe—Fe 2.46; $\mathrm{Fe{-}C(C{\equiv}O)}$ 1.9; $\mathrm{Fe{-}C(C{=}O)}$ 1.8; $\mathrm{C{\equiv}O}$ 1.15; and $\mathrm{C{=}O}$ 1.3 Å.

Because of the almost complete insolubility of the compound in inert solvents, the infrared spectrum of $Fe_2(CO)_9$ could only be taken in the solid state (47), which is unfortunate since the comparison between the experimental and theoretical number of bands expected for the structure shown in Fig. 5 is less conclusive because of crystal effects. Sheline and Pitzer assigned a band at 1828 cm^{-1} to the bridging CO groups. Since then,

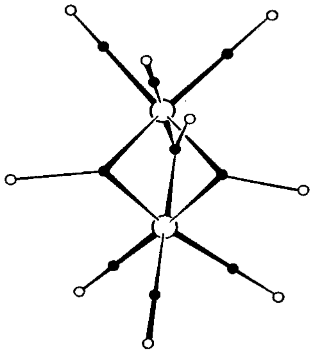


FIG. 5. View of the $Fe_2(CO)_9$ molecule, according to Powell and Ewens (46).

this assignment has been largely confirmed in several other cases of metal carbonyls containing bridging CO groups.

However, several facts about $Fe_2(CO)_9$ are far from being clearly understood. Although the structure of $Fe_2(CO)_9$ appears similar to that of $Co_2(CO)_8$ (with one bridging CO group more), several chemical properties of enneacarbonyldiiron differ greatly from the related cobalt carbonyl. The compound is insoluble in aliphatic hydrocarbons and reacts readily with many other organic solvents to form mainly $Fe(CO)_5$. Previous reports regarding the nonvolatility of $Fe_2(CO)_9$ are incorrect: the compound can in fact be sublimed at about 35° under high vacuum (48), but at a rate considerably lower than that of $Co_2(CO)_8$. Further research is undoubtedly necessary to rationalize these peculiar experimental findings.

Mössbauer resonances (7,49,50) taken using $Fe_2(CO)_9$ as stationary absorber have suggested that, in agreement with the x-ray results, the two iron atoms are in an octahedral environment. However, the diamagnetism (51) of the compound and the fact that the iron atoms are only 2.46 Å apart would strongly suggest the presence of a completely formed metal–metal bond, which would give the iron atoms a coordination number of seven. Ewens himself states in a later paper, which appeared (52) some years after his x-ray investigation, that the existence of a covalent Fe—Fe bond in $Fe_2(CO)_9$ is likely on the basis of magnetic measurements and x-ray data.

$Fe_3(CO)_{12}$. An early x-ray study on $Fe_3(CO)_{12}$ had shown (53) this metal carbonyl to be monoclinic prismatic and had established the molecular formula. The structure of $Fe_3(CO)_{12}$ in the solid state has now been conclusively established by a three-dimensional x-ray study (36*a*) and is shown in Fig. 6*d*. Before commenting on this structure, it will be worthwhile to discuss some of the controversial reports which have preceded the elucidation of the structure. This will enable the reader to become acquainted with one of the most difficult problems encountered by workers in the field of metal carbonyls. Also, we shall comment on some of the previous data which were obtained mainly in solution (infrared data and isotopic carbon monoxide exchange). These solution data are perhaps still valid if one considers the possibility of structural modifications of $Fe_3(CO)_{12}$ when the carbonyl is brought into solution.

The compound is diamagnetic (54); although the diamagnetic susceptibility was found to be rather small, probably because of some paramagnetic impurities. Infrared measurements in the carbonyl region do not conclusively show the presence of bridging CO groups. The solution spectra of $Fe_3(CO)_{12}$ show, in addition to two terminal CO stretching vibrations, two weak bands in the bridging CO region at 1865 and 1834 cm^{-1} in tetrachloroethylene (1858, 1826 cm^{-1} according to other authors (55)), with a molar extinction coefficient of 250 and 310, respectively (38), in comparison with 18,000 for the strongest terminal band. Cotton and Wilkinson (55) have suggested that these two bands are not due to fundamental vibrations, in disagreement with a previous assignment by Sheline (56). Dahl and

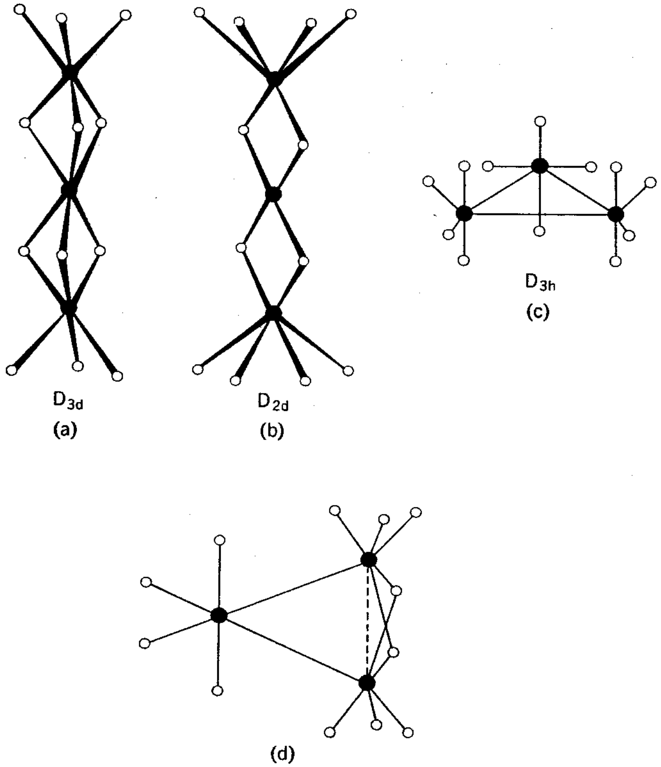


FIG. 6. Molecular arrangements of $Fe_3(CO)_{12}$ previously considered (*a*), (*b*), and (*c*). The structure established by three-dimensional x-ray investigation (36*a*) is (*d*). ● = Fe; ○ = CO.

Rundle (57) have observed a very strong band at 1875 cm^{-1} in a single crystal of $Fe_3(CO)_{12}$ under polarized infrared absorption. The structures of $Fe_3(CO)_{12}$ which were previously taken into consideration together with the now established structure (6*d*) are shown in Fig. 6. Structures (*a*), (*b*), and (*c*) (Fig. 6) for which both terminal and bridging CO stretching vibrations are expected, were favored by the infrared measurements. Dobson and Sheline (58) have also proposed that the two weak bands in the bridging CO region are due to fundamental vibrations.

Mössbauer spectra (7,49,50) show that two equivalent iron atoms, different from the third one, are present in the molecule. Structures (*a*), (*b*), and (*d*) (Fig. 6) are therefore in agreement with the results of Mössbauer resonance studies.

Structure (*a*) would be in agreement with the isotopic exchange reaction (59) with ^{14}CO, which suggests the presence of six CO groups different from the other six.

An early three-dimensional x-ray investigation (60) had indicated that the carbonyl has a triangular arrangement of the iron atoms. The positions of the lighter atoms were, however, not located because of disordering of the molecules in the crystal.

Incidentally, a structure similar to (*a*) in Fig. 6 was proposed by Mills on the basis of a preliminary x-ray investigation (61) showing the molecule of $Fe_3(CO)_{12}$ to be centrosymmetric.

Structure (*d*) in Fig. 6 was initially deduced indirectly from the x-ray structure of the $[Fe_3H(CO)_{11}]^-$ anion (62) and subsequently established by a direct three-dimensional x-ray investigation (36*a*). Structure (*d*) for $Fe_3(CO)_{12}$ is in agreement with the results of both the Mössbauer and infrared spectra, although the very low intensity of the bridging carbon monoxide stretching vibrations is not yet explained. The structure is also in close relationship with the structure of $Fe_2(CO)_9$, if one imagines one of the bridging CO groups of the enneacarbonyl being replaced by an $Fe(CO)_4$ unit.

$Ru_3(CO)_{12}$. This carbonyl, previously formulated (63) as $Ru_2(CO)_9$ has been found by x-ray methods (43) to be a trimer as is the osmium analog (see below), with which it is isomorphous. A report of the detailed structure of dodecacarbonyltriruthenium has not yet appeared.

$Os_3(CO)_{12}$. This carbonyl, previously formulated incorrectly (64) as $Os_2(CO)_9$ has been shown by x-ray analysis (65) to be a trimer and to have the structure shown in Fig. 7. The average Os–Os distance is 2.88 Å. In agreement with the arrangement of osmium atoms shown in Fig. 4.7, the infrared spectrum of $Os_3(CO)_{12}$ does not show bridging CO stretching vibrations (40). The compound shows the expected four bands in the terminal CO stretching region (66). A detailed study of the infrared spectrum of $Os_3(CO)_{12}$ has also appeared (66*a*).

$Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$. The isomorphous $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are monoclinic and a preliminary x-ray investigation (67) had shown the absence of CO bridging groups and an approximate D_{4d} symmetry. $Tc_2(CO)_{10}$ has also been shown (68) to be isomorphous with the other two compounds. The recently published (69) refined structure of $Mn_2(CO)_{10}$ is shown in Fig. 8.

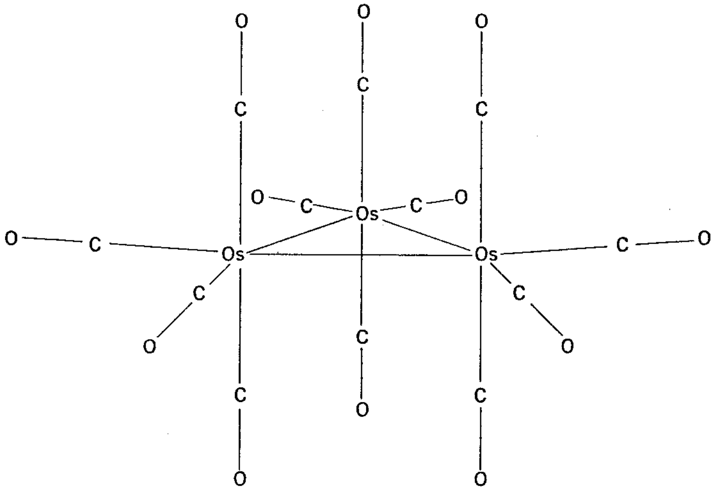


FIG. 7. View of the $Os_3(CO)_{12}$ molecule (65).

The $Mn_2(CO)_{10}$ molecule has approximately D_{4d} symmetry and no bridging CO groups. An interesting feature of the $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ structures is the large metal–metal distance, 2.923 and 3.02 Å, respectively. For $Mn_2(CO)_{10}$ this distance is about 0.5 Å larger than the Mn—Mn distance calculated from the sum of the covalent radii.

The structure of $Tc_2(CO)_{10}$ has also been published (70). As expected, the molecule symmetry is approximately D_{4d}. The Tc—Tc distance is 3.036 ± 0.006 Å.

The absence of bridging CO groups in $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$ has been confirmed by infrared measurements in the CO stretching region. High resolution spectra of the three metal carbonyls,

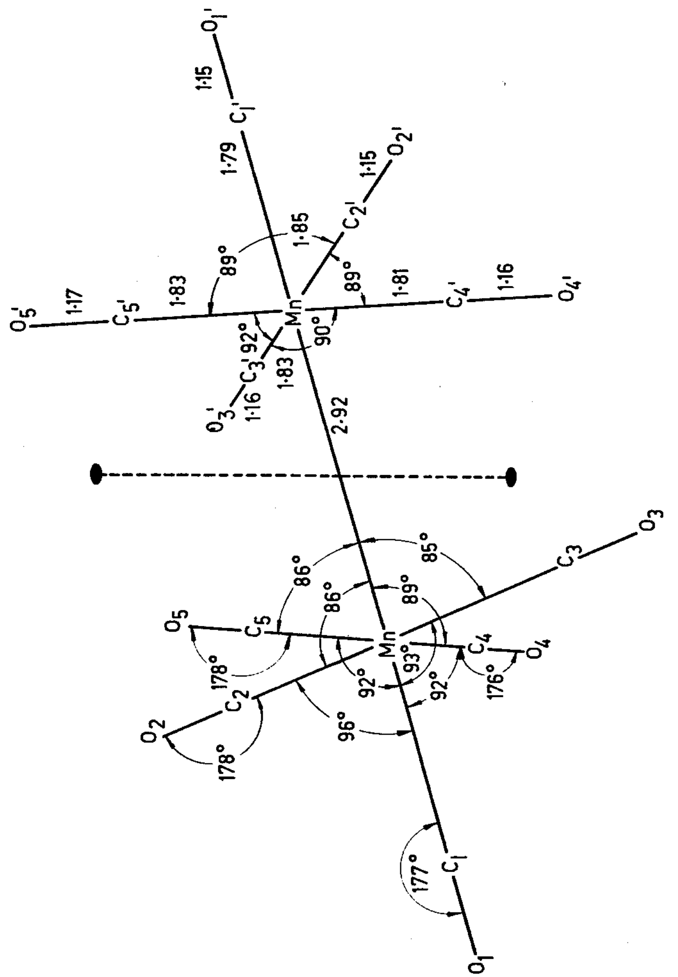


FIG. 8. Molecular configuration, bond distances, and bond angles of $Mn_2(CO)_{10}$. (L. F. Dahl and R. E. Rundle, *Acta Cryst.* **16**, 419 (1963).)

which were reported by Hileman, Huggins, and Kaesz (71), showed the absence of bands below 1974 cm^{-1}. In agreement with their crystal structures, the carbonyls have three CO stretching vibrations.

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V. CHEMICAL PROPERTIES OF METAL CARBONYLS

A. Introduction

In the following sections the reactions of the metal carbonyls will be discussed. The subject has been divided into subgroups of metals starting from nickel down to titanium. In addition, within each subgroup of metals the reactions have been divided into: (*a*) reactions involving change of the oxidation number, and (*b*) substitution reactions. In the first class are included all those reactions that lead to reduction or oxidation of the central metal atom, which in the original carbonyl has to be regarded as being in a zero oxidation state. Apart from the oxidations in the presence of mineral acids such as nitric and sulfuric, oxidations also can be caused by normally nonoxidizing acids such as carboxylic acids. For these, the oxidation can be regarded as a direct electron transfer from the metal carbonyl to the proton of the acid. Hydrogen evolution should therefore take place.

$$M(CO)_m + nH^+ \longrightarrow M^{n+} + \frac{n}{2} H_2 + mCO \qquad (1)$$

Since we consider here mainly reactions occurring in nonaqueous carboxylic acids, Eq. 1 does not imply anything about the final state of the metal in the $n+$ oxidation state. In most of the cases, the metal will not be ionized but rather complexed to the carboxylate anion. Reactions similar to Eq. 1 will occur in principle with any protic substance and therefore also with β-diketones and all those compounds for which enol forms are possible. Acetylacetonates of iron(II) and iron(III), of chromium(III) and molybdenum(III) have been prepared by using the corresponding metal carbonyls as starting materials. It is likely that the use of this type of reaction will become more and more important in preparative inorganic chemistry, compared with the usual methods consisting of treating a metal salt with the complexing agent in aqueous solutions or alcohol–water mixtures. The reasons for this are manifold. Many of the metal carbonyls are now commercially available; they are also usually much purer—with respect to their metal content—than the corresponding starting materials. When a metal carbonyl is used in the preparation of a metal chelate, no acid is evolved in the course of the reaction; it therefore goes to completion without the need for adding a neutralizing base. A base can compete for coordination positions on the metal and alter the stereochemistry of the final product in an undesired manner.

Reductions of metal carbonyls to carbonylmetallates are also included in the reactions of class (*a*). Alkali metals are normally used as reducing agents in various solvents. These reactions are interpreted straightforwardly as electron transfers from the electropositive metal to the metal carbonyls.

Two other reactions by which reduced carbonyl species are produced are: disproportionation reactions and reductions in aqueous or alcoholic solutions of alkali hydroxides. These disproportionation reactions which, from a rigorous point of view, are improperly so designated, are those reactions in which ionic compounds are obtained in the presence of Lewis bases from a neutral metal carbonyl. The following reaction of $Co_2(CO)_8$ with pyridine typifies this type of reaction:

$$3Co_2(CO)_8 + 12py \longrightarrow 2[Co\,py_6][Co(CO)_4]_2 + 8CO \qquad (2)$$

The cationic part of the salt does not contain bonded carbon monoxide groups, but there are reasons to believe that the first step of reaction 2 is the true disproportionation reaction:

$$Co_2(CO)_8 + B \longrightarrow [Co(CO)_4B]^+[Co(CO)_4]^- \qquad (3)$$

Reaction 3, in which B represents a Lewis base, has been shown to take place when B is an aliphatic alcohol (1). These intermediate products, containing cobalt(I), are usually not stable at room temperature; a further electron transfer takes place with evolution of carbon monoxide and formation of the final species containing cobalt(II) and cobalt(I−). However, in some special cases, the nature of the Lewis base is such that the intermediate cobalt(I) species becomes stable even at room temperature and can be isolated as such. This is true for triphenylphosphine which gives isolable ionic compounds of the type $[Co(CO)_3(Ph_3)_2][Co(CO)_4]$ (2).

Disproportionation reactions are most commonly encountered with $Co_2(CO)_8$ and they have been widely studied. Several other metal carbonyls give disproportionation reactions, namely the carbonyls of iron, hexacarbonylvanadium, and decacarbonyldimanganese. The two metal carbonyls which appear to react most rapidly with Lewis bases are $Co_2(CO)_8$ and $V(CO)_6$; these carbonyls react with ketones and nitrogen bases very quickly even at room temperature. With $V(CO)_6$, ionic compounds of formula $[V(B)_n][V(CO)_6]_2$ containing both vanadium(II) and vanadium(I−) are formed.

The mechanism of the reactions of $Co_2(CO)_8$ and $V(CO)_6$ with Lewis bases is not known but a reasonable one is the following. The reactions probably take place via a preliminary substitution of one carbon monoxide group of the metal carbonyl by the base. In the dimeric $Co_2(CO)_8$ the substitution product $Co_2(CO)_7B$ presumably undergoes a heterolytic cleavage of the metal–metal bond (the form of $Co_2(CO)_8$ not containing bridging CO groups can be considered to be the reactive one) with formation of the cobalt(I)–cobalt(I−) species shown in Eq. 3. In the case of the monomeric $V(CO)_6$, the substitution step to $V(CO)_5B$, for example, is presumably followed, in a much faster step, by an electron transfer to unreacted $V(CO)_6$, with formation of $[V(CO)_5B][V(CO)_6]$. This intermediate ionic compound can further reduce unreacted $V(CO)_6$ with carbon monoxide evolution and formation of the final $[V(B)_n][V(CO)_6]_2$.

A further reduction of metal carbonyls can take place, as mentioned previously, with solutions of alkali metal hydroxides. The mechanism of the reaction is not well understood. Experimentally one finds that the metal carbonyl is reduced to a carbonylmetallate anion with simultaneous formation of carbonate ions. With $Fe(CO)_5$, for example, the reaction can be visualized to occur according to the following stoichiometry:

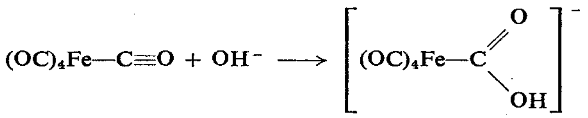
$$Fe(CO)_5 + 4OH^- \longrightarrow [Fe(CO)_4]^{2-} + CO_3^{2-} + 2H_2O \qquad (4)$$

The reaction is actually much more complicated because polynuclear carbonylmetallates of iron are also obtained depending on the conditions, and the hydridotetracarbonylferrate $[FeH(CO)_4]^-$ is also a product of the reaction unless the medium is strongly alkaline. These complicating facts are, however, irrelevant to the following discussion. By analogy with a mechanism discussed earlier by Hieber and co-workers (3) for the case of $Co_2(CO)_8$, one should consider first the displacement of one carbon monoxide group of $Fe(CO)_5$ by OH^-. This should be followed by an electron transfer to iron and formation of CO_2:

$$(OC)_5Fe + OH^- \longrightarrow [(OC)_4FeOH]^- + CO \qquad (5)$$

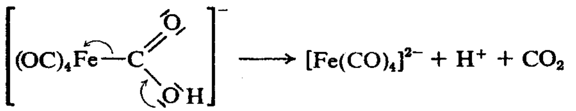
$$[(OC)_4FeOH]^- + CO \longrightarrow CO_2 + H^+ + [Fe(CO)_4]^{2-} \qquad (6)$$

A slightly different reaction mechanism has been proposed by Kruck and co-workers (4). They suggest that step 5 does not occur with loss of carbon monoxide, but that CO is actually retained in the coordination sphere of the metal with formation of a carboxylferrate anion. The formation of this anion should be regarded as occurring by attack on the central metal atom by the hydroxyl anion, followed by migration of OH to an adjacent carbon monoxide group.



$$(OC)_4Fe{-}C{\equiv}O + OH^- \longrightarrow \left[(OC)_4Fe{-}C\begin{matrix}{/\!\!/}O\\ \diagdown OH\end{matrix}\right]^- \qquad (7)$$

The electron transfer to iron with formation of CO_2 would then occur on the carboxylferrate anion itself.



$$\left[(OC)_4Fe{-}C\begin{matrix}{/\!\!/}O\\ \diagdown OH\end{matrix}\right]^- \longrightarrow [Fe(CO)_4]^{2-} + H^+ + CO_2 \qquad (8)$$

Reactions of class (*b*), i.e., substitution reactions, do not require special comment. Substitution reactions are those in which one or more carbon monoxide groups of the metal carbonyl are replaced by other ligands, as olefins, acetylenic compounds, nitrogen bases, trialkyl- and triarylphosphines, etc. A special type of substitution is the isotopic carbon monoxide exchange reaction:

$$M(CO)_m + {}^{14}CO \longrightarrow M({}^{14}CO)_m + CO \qquad (9)$$

These reactions have been studied by Keeley and Johnson (5), Basolo and Wojcicki (6), Pajaro, Calderazzo, and Ercoli (7) and by Cetini and Gambino (8,9)

The exchange reactions of $Ni(CO)_4$ (6) and $Co_2(CO)_8$ (6) are fast and the order with respect to carbon monoxide concentration is zero. All the carbon monoxide groups of $Co_2(CO)_8$ exchange at the same rate. It has been suggested (10) that the carbon monoxide exchange reaction of $Co_2(CO)_8$ occurs through a mechanism involving that form of octacarbonyldicobalt, $(OC)_4Co{-}Co(CO)_4$, which does not contain bridging CO groups and is present in solution in considerable concentration at room temperature (see Sec. IV). This hypothesis is supported by the experimental finding that $HgCo_2(CO)_8$, which also has only metal–metal bonds, exchanges its carbon monoxide groups rapidly and at a rate independent of carbon monoxide concentration (10). Pentacarbonyliron exchanges its carbon monoxide groups very slowly (5), the reported half-time being > 4 yr at room temperature. The isotopic exchange of $Fe(CO)_5$ becomes, however, reasonably fast in the presence of acids (11). Hexacarbonylchromium (7) and the corresponding molybdenum (8) and tungsten (9) carbonyls exchange their carbon monoxide groups with ^{14}CO at a rate which is independent of carbon monoxide concentration.

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B. Carbonyls of the Nickel Subgroup Metals

1. *Reactions Involving Changes in Oxidation Number*

a. Oxidations. Tetracarbonylnickel is oxidized by atmospheric oxygen in the gas phase (1). Solutions of $Ni(CO)_4$ in organic solvents also are attacked by oxygen with formation of a green gelatinous mass, considered to be basic nickel carbonate (2). In organic solvents, halogens, cyanogen, and sulfur decompose $Ni(CO)_4$ with formation of the corresponding nickel(II) salts (3). Other acids, such as H_2S and HCl, decompose it slowly with hydrogen and carbon monoxide evolution.

The reaction between tetracarbonylnickel and carbon disulfide in the gas phase has been studied in detail by Dewar and Jones (4). They showed that this reaction is so strongly inhibited by carbon monoxide that it cannot be carried out in the liquid phase.

In the gas phase, especially at reduced pressure, the reaction takes place according to the equation:

$$2Ni(CO)_4 + CS_2 \longrightarrow 2NiS + C + 8CO \qquad (10)$$

and produces a mirror on the glass container.

With COS the reaction takes place very slowly and incompletely. Other sulfur compounds, such as allyl sulfide, thiophene, and thiourea are partially desulfurized with formation of brown deposits.

A black crystalline nickel phosphide, NiP, was obtained by the reaction at 50°C between $Ni(CO)_4$ and phosphorus or PH_3 vapors in a carbon monoxide stream. In liquid phase this reaction yielded an amorphous material (5).

The action of nitrogen oxides was studied by Frazer and Trout (6), who showed that nitrogen dioxide gives rise to the formation of a mixture of $Ni(NO_2)_2$ and $Ni(NO_3)_2$. Anderson (7) and Reihlen (8) independently reported that the reactions of $Ni(CO)_4$ with nitrogen oxide in methanol and ethanol gave a green product $[Ni(NO)(OH)(OMe)]\cdot CH_3OH$, and a blue product, $Ni(NO)(OH)(OEt)$. The product obtained from the gas phase reaction of $Ni(CO)_4$ with nitrogen oxide in the presence of traces of water corresponded to the formula $Ni(NO)(OH)(H_2O)_{1.5-2}$, according to Anderson. Griffith, Lewis, and Wilkinson (9) suggested that the products obtained from the methanol and the vapor phase reactions could be $Ni(NO)(OH)(OMe)_2$ and $Ni(NO)(OH)_3$.

Feltham and Cariel (10) reinvestigated the reaction of $Ni(CO)_4$ with nitrogen oxide under pressure either in an inert solvent or in alcohols. The product obtained from the inert solvent reaction had the formula $Ni(NO)(NO_2)$. According to these authors the solvent does not play a role in the reaction, which was proposed as occurring by the following stoichiometry:

$$Ni(CO)_4 + 4NO \longrightarrow Ni(NO)(NO_2) + 4CO + N_2O \qquad (11)$$

Only solvation could account for the different compositions obtained by substituting cyclohexane for alcohols (10).

Tetracarbonylnickel reacts with many halogenated organic compounds, giving nickel halides. For example, ultraviolet irradiation of acetyl chloride (11) at 55°C gave biacetyl, carbon monoxide, and $NiCl_2$. In a reaction between $Ni(CO)_4$ and allylic chlorides (12) coupling of two allyl radicals, with formation of the corresponding dienes was observed. Grignard compounds also react with tetracarbonylnickel (13) giving nickel metal, nickel chloride, and organic compounds containing carbonyl groups. Thus, RMgBr ($R = C_6H_5$, n-C_3H_7, iso-C_3H_7, n-C_4H_9), in ether with excess $Ni(CO)_4$ at about 0°C gave keto alcohols, RCOCHOHR (14), in yields ranging from 70% ($R = C_6H_5$) to 35% ($R =$ iso-C_3H_7). Organometallic compounds of nickel have been postulated as possible unstable intermediates in these reactions.

b. Reductions. The following carbonylnickelate anions have been reported:

$$[Ni_2(CO)_6]^{2-},\ [Ni_3(CO)_8]^{2-},\ [Ni_4(CO)_9]^{2-},\ [Ni_5(CO)_9]^{2-},$$
$$[Ni_4H(CO)_9]^{-},\ [Ni_5H(CO)_9]^{-}$$

Reduction of tetracarbonylnickel with sodium metal was carried out in liquid ammonia (15). Unlike other metal carbonyls, tetracarbonylnickel, under these conditions, gives a neutral species rather than a salt. The hydrido complex $[NiH(CO)_3]_2$ is the product of this reaction:

$$2Ni(CO)_4 + 2Na + 2NH_3 \longrightarrow [NiH(CO)_3]_2 + 2CO + 2NaNH_2 \qquad (12)$$

This compound was isolated from the reaction mixture as the cinnabar red tetraammoniate $[NiH(CO)_3]_2\cdot 4NH_3$.

In later investigations, Behrens and co-workers (16,17) showed that the formation of $[NiH(CO)_3]_2$ takes place also with potassium and lithium. They suggested that the hexacarbonyldinickelates $M_2[Ni_2(CO)_6]$ are labile intermediates, which immediately undergo a total ammonolysis as follows:

$$Na_2[Ni_2(CO)_6] + 6NH_3 \longrightarrow [NiH(CO)_3]_2\cdot 4NH_3 + 2NaNH_2 \qquad (13)$$

At temperatures above −30°C, $[NiH(CO)_3]_2\cdot 4NH_3$ decomposes to $Ni(CO)_4$ and ammonia. Hydrogen could be identified with some difficulty among the decomposition products. Reaction of the tetraammoniate with water gave the enneacarbonyltetranickelate $[Ni_4(CO)_9]^{2-}$ and the hydridoenneacarbonyltetranickelate $[Ni_4H(CO)_9]^{-}$ anions.

Reduction of tetracarbonylnickel has also been carried out with sodium amalgam in tetrahydrofuran (18). In this case the reaction takes place according to the equation:

$$4Ni(CO)_4 + 2Na \longrightarrow [Ni_4(CO)_9]^{2-} + 2Na^{+} + 7CO \qquad (14)$$

Later (19), it was shown that the amalgams of Na, K, and Mg in tetrahydrofuran act in the same manner, whereas lithium amalgam, which is a stronger reducing agent, leads to the formation of the octacarbonyltrinickelate anion $[Ni_3(CO)_8]^{2-}$, whose existence had been reported previously (20).

The Na, K, and Mg salts of the $[Ni_4(CO)_9]^{2-}$ anion are extremely air sensitive. With the exception of the cadmium salt, all crystallize with 1.5–10 molecules of tetrahydrofuran or acetone.

It is a well-established fact that many metal carbonyls of the other groups are reduced to carbonylmetallate ions by reaction with alkali or alkoxide solutions. At the same time some of the bonded carbon monoxide is oxidized to carbonate ions.

Tetracarbonylnickel was for a long time considered stable to alkali (21). Later (20) it was shown, however, that in saturated methanol solutions of NaOH, not less than 57% of the $Ni(CO)_4$ is transformed into the anion

$[Ni_3(CO)_8]^{2-}$ after 80 hr. Conceivably, this formation of the octacarbonyltrinickelate anion is accompanied by oxidation of carbon monoxide to carbonate ion.

c. Disproportionation reactions. The reactions of tetracarbonylnickel with nitrogen Lewis bases, namely pyridine and phenanthroline, were originally interpreted (22) as substitutions of some of the carbon monoxide groups. Actually the chemistry of these reactions is more complicated.

It has been established (23) that liquid ammonia replaces one or more carbon monoxide groups, with formation of substitution products of the type $Ni(CO)_{4-x}(NH_3)_x$. On the other hand, it has been reported (18) that other Lewis bases, such as pyridine, ethylenediamine, and piperidine give disproportionation reactions with formation of nickel(II) and carbonylnickelate anions, $[Ni_2(CO)_6]^{2-}$, $[Ni_4(CO)_9]^{2-}$ and $[Ni_4H(CO)_9]^-$.

A systematic study by Hieber and co-workers (24) has clarified many aspects of these reactions. They suggested that, with relatively weak bases such as pyridine, tetracarbonylnickel forms the substitution products $Ni(CO)_3py$ and $Ni(CO)_2py_2$, unstable under the reaction conditions. This was followed by the formation of the following ionic complexes:

$$3Ni(CO)_3py + 3py \rightleftharpoons [Nipy_6][Ni_2(CO)_6] + 3CO \tag{15}$$

$$3Ni(CO)_2py_2 \rightleftharpoons [Nipy_6][Ni_2(CO)_6] \tag{16}$$

Successive addition of $Ni(CO)_3py$ and loss of pyridine result in polynuclear carbonylnickelates, namely $[Ni_3(CO)_8]^{2-}$, $[Ni_4(CO)_9]^{2-}$ and $[Ni_5(CO)_9]^{2-}$. Interestingly, the deep red salt $[Nipy_6][Ni_5(CO)_9]$ is transformed into tetracarbonylnickel when a stream of carbon monoxide is bubbled through a pyridine solution at room temperature. This reaction is reversible.

Piperidine, morpholine, and γ-picoline behave like pyridine, whereas the stronger base ethylenediamine stabilizes the $[Ni_4(CO)_9]^{2-}$ anion.

If the basicity of the system is still greater, as in the presence of KOH, the ions $[Ni_3(CO)_8]^{2-}$ and $[Ni_2(CO)_6]^{2-}$ are formed.

The $[Ni_2(CO)_6]^{2-}$ anion is a strong reducing agent. It can reduce the cations $[Ni\ phen_3]^{2+}$ and $[Fe\ phen_3]^{2+}$ with formation of the substitution compounds:

$$[Ni\ phen_3]^{2+} + [Ni_2(CO)_6]^{2-} \longrightarrow 3Ni(CO)_2phen \tag{17}$$

$$[Fe\ phen_3]^{2+} + [Ni_2(CO)_6]^{2-} \longrightarrow 2Ni(CO)_2phen + Fe + 2CO + phen \tag{18}$$

This high reducing power makes it difficult to isolate complex salts from the binuclear and trinuclear carbonylnickelates.

Additional difficulties in the study of these reactions arise from the fact that the enneacarbonylpentanickelate anion slowly loses nickel according to the equation:

$$[Ni_5(CO)_9]^{2-} \longrightarrow [Ni_4(CO)_9]^{2-} + Ni \tag{19}$$

Moreover, the doubly charged anions easily undergo protonation with formation of the anions $[Ni_5H(CO)_9]^-$ and $[Ni_4H(CO)_9]$.

2. Substitution Reactions

a. Compounds containing carbon–carbon unsaturated bonds. Several substitution reactions of $Ni(CO)_4$ with different ligands have been reviewed by Schrauzer (24*a*).

By reaction of $Ni(CO)_4$ with allyl iodide in benzene at 70–80°C, the π-allyl complex $(NiC_3H_5I)_2$ is obtained as a deep red volatile solid (25). By treatment with NaC_5H_5, this gives the mixed π-allylcyclopentadienyl complex $Ni(C_3H_5)C_5H_5$. The bromo analog of the dimeric π-allyl compound also has been reported (26). Both the halo complexes have relatively small dipole moments (1.62 and 1.3 D, respectively), and a halogen-bridged structure has been proposed for these complexes.

An interesting complex with the formula $NiC_8H_{12}Cl_2$ (**1**) was obtained by the reaction of $Ni(CO)_4$ with tetramethyldichlorocyclobutene. Nuclear magnetic resonance and chemical data indicated that this compound is the nickel(II) chloride complex of the unknown tetramethylcyclobutadiene (27). The presence of the cyclobutadiene ring in **1** has been confirmed by Dunitz, Mills, and co-workers (28) who investigated the structure of the benzene adduct of **1** by x-ray and found the molecular formula $(NiCl_2C_8H_{12})_2 \cdot C_6H_6$. The tetramethylcyclobutadiene complex of nickel, as it exists in the solvate, is a dimer. It has two chlorine atoms bridging the two nickel atoms, and the cyclobutadiene ring is approximately planar and square. The unit $Ni_2Cl_4[C_4(CH_3)_4]_2$ of the benzene adduct is represented in Fig. 9. A cyclobutadiene complex similar to **1** was obtained (29) by a

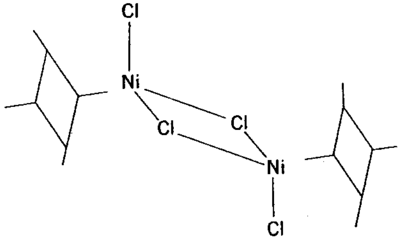
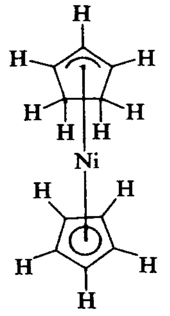


FIG. 9. View of the $Ni_2Cl_4[C_4(CH_3)_4]_2$ unit in the benzene adduct $Ni_2Cl_4[C_4(CH_3)_4]_2 \cdot C_6H_6$.

ligand transfer reaction between tetraphenylcyclobutadienepalladium bromide and $Ni(CO)_4$. This complex is dibromotetraphenylcyclobutadienenickel. The reaction of $Ni(CO)_4$ with triphenylcyclopropenyl bromide (30) gave $NiBr(CO)C_3(C_6H_5)_3$, which is believed to be a π-cyclopropenyl complex of nickel. A dimeric halogen-bridged structure has been suggested for this compound. The reaction of diphenylcyclopropenone with $Ni(CO)_4$ was reported (31) to give a pale green solid (mp 188–189°) with the composition Ni(CO) (diphenylcyclopropenone)$_3$.

Surprisingly, the vapor phase reaction of $Ni(CO)_4$ with cyclopentadiene (32) gave only small amounts of nickelocene, $Ni(C_5H_5)_2$. However, the reaction of $Ni(CO)_4$ with cyclopentadiene in *n*-hexane at 70° (32) gave $NiC_{10}H_{12}$ to which the cyclopentadienyl–cyclopentenylnickel(II) type of structure (**2**) has been assigned on the basis of its proton resonance spectrum and chemical data (33–35). In this molecule one of the rings is a normal cyclopentadienyl anion $C_5H_5^-$, the other is a $C_5H_7^-$ anion to which the central metal atom, formally in the oxidation state 2+, is bonded through a π-allyl arrangement involving three carbon atoms.



(2)

From the reaction of $Ni(CO)_4$ with $Ni(C_5H_5)_2$, two mixed carbonylcyclopentadienyl compounds have been reported (36): the red diamagnetic dimeric $[NiC_5H_5(CO)_2]_2$ and the green paramagnetic (37) $Ni_3(C_5H_5)_3(CO)_2$ with one unpaired electron. The x-ray structure of the latter has been determined (38), showing that the three nickel atoms occupy the positions of an equilateral triangle with the two carbon monoxide groups symmetrically arranged above and below the plane containing the nickel atoms. Each of the two carbon monoxide groups should be regarded as bridging three nickel atoms.

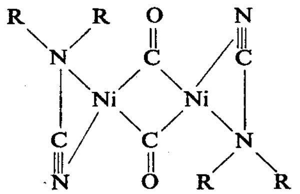
$[Ni(CO)C_5H_5]_2$ very likely contains bridging CO groups, C—O stretching vibrations at 1879 and 1838 cm^{-1}, that are not coplanar with the two nickel atoms (39). The reactions of this dimeric carbonylcyclopentadienyl compound with acetylenes (39,40), tetraalkyldiphosphines (40*a*) and diarsines (40*a*), have been reported. In each case the two carbon monoxide groups are replaced and dimeric compounds containing carbon, phosphorus, and arsenic bridges are obtained. Similar sulfur-bridged compounds also have been prepared indirectly (41).

Direct reaction of $Ni(CO)_4$ with acrylonitrile (42), duroquinone (43), and acrylaldehyde (44) gave compounds of the type NiL_2 in which L indicates the unsaturated compound. An addition compound with triphenylphosphine, $Ni(CH_2{=}CHCN)_2(PPh_3)_2$, also has been reported (45). Further, mixed duroquinone–olefin complexes of zerovalent nickel of the general type Ni(duroquinone)(olefin) have been reported, with the olefin being either cyclooctatetraene (46), 1,5-cyclooctadiene, bicyclo(2,2,1)heptadiene, or dicyclopentadiene (47). The electronic structures, absorption spectra, and magnetic susceptibility measurements of this type of compound have been reported (48).

By infrared spectrometry, it has been established that the nitrile group of $Ni(CH_2{=}CHCN)_2$ is not directly involved in the bond and that the metal is bonded to the ligand through the π electrons of the C=C bond. The acrylonitrile complex is slightly paramagnetic (44) ($\mu_{eff} = 0.66$ B.M.). Complexes, 1:1, with arylsubstituted 1,1-dicyano- and 1,1,2-tricyanoethylene, such as $Ni(CN)_2C{=}CHC_6H_5$ and $Ni(CN)_2C{=}CC_6H_5(CN)$ also have been described (49). The latter are radical-type compounds, showing magnetic moments from 0.75 to 2.1 B.M. as well as EPR signals. X-ray investigation of the compound nickel(1,5-cyclooctadieneduroquinone) (50) has shown that the arrangement of the four double bonds around the nickel atom is tetrahedral. The acrylonitrile complex and its analogs dimerize norbornadiene catalytically (51). Acetylene has been reported (42) to give cyclooctatetraene in the presence of $Ni(CH_2{=}CHCN)_2$. In the presence of $Ni(CH_2{=}CHCN)_2$, diphenylacetylene gives hexaphenylbenzene and 2,3,4,5-tetraphenylbenzonitrile; 2-butyne gives hexamethylbenzene; and acetylene gives benzene, some styrene, and cyclooctatetraene. This latter compound was not obtained with $Ni(CH_2{=}CHCN)_2 \cdot P(C_6H_5)_3$, which gave exclusively benzene and styrene. Overall, the catalytic activity of these nickel complexes does not seem to be high, judging by the yield of products obtained per gram of catalyst (52).

b. Isonitriles. $Ni(CO)_4$ reacts with phenyl isonitrile (53,54) to give the completely substituted $Ni(CNPh)_4$. The mono-, bi-, and trisubstitution products of $Ni(CO)_4$ with phenyl isonitrile have not been isolated in a pure state; they have been identified only by spectroscopy (55). With methyl isonitrile only three carbon monoxide groups are replaced and $Ni(CO)(CNMe)_3$ is obtained (54,56). Later (57) the substitution products $Ni(CO)_{4-n}(CNR)_n$ ($n = 1,2,3$ for R = Me, Et, and Bu; $n = 4$ for R = Me) have been prepared by varying the reaction conditions; the vibrational spectra of the products were measured.

c. Nitrogen bases. A monosubstitution product $Ni(CO)_3py$ has been proposed (58) as the primary product of the reaction of $Ni(CO)_4$ with pyridine. Infrared spectrometry strongly indicated its existence but the product was too unstable for isolation. Infrared evidence for the existence of an unstable disubstitution product with phenanthroline (58) has also been presented. Other substitution products which can be classified here with the nitrogen bases are the compounds prepared by reacting $Ni(CO)_4$ with dialkylcyanamids (59,60). The complexes obtained from these reactions correspond to the formula $Ni_2(NCNR_2)_2(CO)_2$ and have C—O stretching vibrations at 1788–1795 cm^{-1}, suggesting the presence of bridging CO groups. The bonding to the central metal atom in these diamagnetic compounds (3) is believed to be through the lone pair on the nitrogen of the amine group and the π electrons of the nitrile group.



(3)

d. P, As, and Sb-containing ligands. The first substitution product of $Ni(CO)_4$ with a phosphorus-containing ligand was prepared by Reppe and Schweckendiek (61). Irvine and Wilkinson (62) prepared $Ni(PCl_3)_4$ from $Ni(CO)_4$ and PCl_3; treatment of this chloro compound with PBr_3 (63) gave $Ni(PBr_3)_4$. The interesting compound $Ni(PF_3)_4$ was obtained (63) by reacting $Ni(PCl_3)_4$ or $Ni(PBr_3)_4$ with PF_3. This fluoro compound is a colorless, volatile liquid, bp 70.7°/760 mm, d = 1.800 at 25°, and it is soluble in hydrocarbons. It has been suggested that $Ni(PF_3)_4$ is very similar in structure to $Ni(CO)_4$, the strongly electronegative fluorine atoms making a suitable orbital on the phosphorus available for π-bonding with the metal.

Several phosphorus-, arsenic-, and antimony-containing substitution products of $Ni(CO)_4$ have been prepared; representative examples are given in Table 7. These compounds are obtained generally by replacement of CO groups in $Ni(CO)_4$ by the ligand. Trisubstitution products containing only one residual carbon monoxide group are difficult to obtain; a few examples of this type are known. Chatt and Hart (64) obtained trisubstitution products by using tridentate tertiary phosphines.

Completely substituted nickel(0) complexes can easily be prepared without using the highly toxic $Ni(CO)_4$ as starting material. Thus, $Ni(diphos)_2$ complexes can be prepared by treating the bidentate ligand directly with Raney nickel (65). Similarly, $Ni(PF_3)_4$ can be prepared by treating nickel powder with PF_3 at high temperature and pressure:

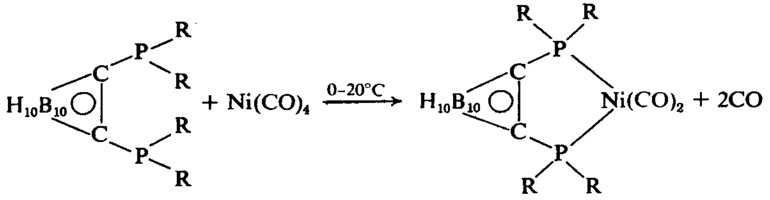
$$Ni + 4PF_3 \xrightarrow[100°]{350\ atm} Ni(PF_3)_4 \tag{20}$$

Quantitative yields were obtained from nickel that had been prepared by decomposition of nickel oxalate in a hydrogen atmosphere (66).

Nickelocene has been reported to react with trialkyl- and triarylphosphites to give good yields of $Ni[P(OR)_3]_4$ (67).

The reactions of $Ni(CO)_4$ with diphosphines of the type $R_2P–PR_2$ give binuclear complexes $Ni_2(CO)_6P_2R_4$ in which the phosphorus–phosphorus bond of the ligand is intact (68). The preparation of a complex of this type with R = Ph had been reported previously in a patent by Schweckendiek (69).

Substitution products of $Ni(CO)_4$ with a phosphine-substituted carborane have been reported (70).



(21)

Meriwether and Fiene (71) have studied spectroscopically the exchange reaction of several dicarbonylnickelbis(trialkylphospine) complexes with tertiary phosphines. The reactions are first order with respect to the

$$Ni(CO)_2(PR_3)_2 + PR'_3 \rightleftharpoons Ni(CO)_2(PR)_3(PR'_3) + PR_3 \tag{22}$$

$$Ni(CO)_2(PR_3)(PR'_3) + PR'_3 \rightleftharpoons Ni(CO)(PR'_3)_2 + PR_3 \tag{23}$$

TABLE 7

Carbonyl Compounds of Zerovalent Nickel, Palladium, and Platinum with P-, As-, and Sb-Containing Ligands

Compound	Mp °C	Color	Reference
$Ni(CO)_3PPh_3$	126	Colorless	61,71
$Ni(CO)_3P(OC_6H_4Cl\text{-}p)_3$	70–71	Colorless	82
$Ni(CO)_3AsPh_3$	105	Colorless	61
$Ni(CO)_3SbPh_3$	96–100	—	61
$Ni(CO)_3SbCl_3$	—	Pale buff	83
$[Ni(CO)_3P(CF_3)_2]_2$	105	Red-black	84
$Ni(CO)_3PF_3$	—	Colorless	85
$Ni(CO)_3P(CF_3)_3$	−71	Colorless	86
$Ni_2(CO)_6P_2Ph_4$	190–200 dec.	Yellow	68,69
$Ni_2(CO)_6P_2Me_4$	140	Grey	90
$Ni(CO)_2(PPh_3)_2$	212 dec.	Pale yellow	61,71,75
$Ni(CO)_2(PBu_3)_2$	Liquid	—	61
$Ni(CO)_2(P(CF_3)_3)_2$	−31	Colorless	84,86
$Ni(CO)_2(P(OPh)_3)_2$	95	Colorless	71,76
$Ni(CO)_2(P(OC_6H_4Cl\text{-}p)_3)_2$	132	—	82
$Ni(CO)_2(P(OC_6H_4NO_2\text{-}p)_3)_2$	135	Yellow	82
$Ni(CO)_2$Diphos	13	Colorless	87
$Ni(CO)_2(o\text{-}C_6H_4(PMe_2)_2)$	121–125	Colorless	65
$Ni(CO)_2(o\text{-}C_6H_4(PEt_2)_2)$	65	Colorless	87
$Ni(CO)_2(P(NMe_2)_3)_2$	86–87	Colorless	88,89
$Ni(CO)_2(P(CH_2CH_2CN)_3)_2$	140 dec.	Colorless	71
$Ni(CO)_2(o\text{-}C_6H_4(AsMe_2)_2)$	125	Colorless	91
$Ni(CO)_2(o\text{-}C_6H_4(AsPh_2)_2)$	182–190	Colorless	65
$Ni(CO)_2(PF_3)_2$	−93	Colorless	85
$Ni(CO)(P(OEt)_3)_3$	0	Colorless	71,82
$Ni(CO)(P(OPh)_3)_3$	98.5	Colorless	82
$Ni(CO)(PF_3)_3$	−93	Colorless	85
$Ni(CO)(PhP(o\text{-}C_6H_4PEt_2)_2)$	189–191.5	Orange	64
$Ni(CO)(H_3CC(CH_2PPh_2)_3)$	317 dec.	Yellow	64
$Ni(PF_3)_4$	b_{760} 70.7	Colorless	63,66
$Ni(PCl_2C_6H_5)_4$	86.5	Yellow	82
$Ni(PCl_3)_4$	120 dec.	Light yellow	62
$Ni(PBr_3)_4$	80 dec.	Red-orange	63
$Ni(PF_2Me)_4$	—	—	92
$Ni(PF_2Ph)_4$	—	—	92
$Pd(PF_3)_4$	−20 dec.	Colorless	79,93
$Pt(CO)_2(PPh_3)_2$	118 dec.	Colorless	77,78
$Pt(CO)(PPh_3)_3$	95 dec.	Orange	77,78
$Pt_3(CO)_4(PPh_3)_3$	177–179 dec.	Black	77
$Pt_3(CO)_3(PPh_3)_4$	179–182 dec.	Bright red	77
$Pt(PF_3)_4$	−15, b_{730} 86	Colorless	79

complex and zero order in the ligand; a dissociative mechanism involving a tricoordinated nickel was therefore suggested.

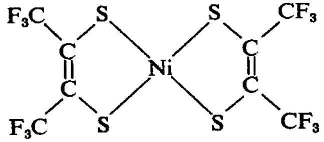
Bigorgne (72–74) has systematically studied the infrared spectra of carbonyl nickel derivatives of the general type $(Ni(CO)_{4-n}(ER_3)_n$, with $n = 1,2,3$ and E = P, As, Sb, Bi, with particular regard to the assignment of the CO stretching vibrations and the calculation of force constants.

The catalytic properties of phosphine derivatives of $Ni(CO)_4$ were first described by Reppe and Schweckendiek (61). $Ni(CO)_2(PPh_3)_2$ catalyzes the trimerization of propargyl alcohol to a mixture of 1,2,4- and 1,3,5-tri-(hydroxymethyl)benzene. Later (75) the trimerizations of phenylacetylene to 1,2,4-triphenylbenzene and of phenylethynylcarbinol to 1,3,5-tri(α-hydroxybenzyl)benzene were reported. Reed (76) has reported the dimerization of butadiene to cycloocta-1,5-diene catalyzed by $Ni(CO)_2(PPh_3)_2$ and similar compounds of trimethyl- and triphenylphosphite.

The palladium and platinum analogs of $Ni(CO)_4$ are not known. On the other hand, a not well-defined dicarbonyl of platinum, $Pt_n(CO)_{2n}$, has been described by Booth, Chatt, and Chini (77) who obtained it by treating the chlorocarbonyl $PtCl_2(CO)_2$ with water in the presence of carbon monoxide. This carbonyl showed infrared bands at 2068 and 1891 cm^{-1} that are not due to metal–hydrogen stretching vibrations but rather to C—O stretching vibrations. The same infrared pattern was in fact observed when the compound was prepared in deuterated water.

Other compounds of palladium(0) and platinum(0) that can be formally considered as substitution products of the unknown tetracarbonyls have been prepared. Tertiary phosphine derivatives of the type $Pt(CO)_{4-n}(PR_3)_n$ were first obtained by Malatesta and Cariello (78). These were prepared by treating $Pt(PR_3)_4$ with carbon monoxide under pressure. The orange $Pt(CO)(PPh_3)_3$ decomposes at 95°. The same compound was described later by the previously mentioned authors (77), who also reported the preparation of trinuclear phosphine-substituted carbonyls of platinum of formulas $Pt_3(CO)_3(PPh_3)_4$ and $Pt_3(CO)_4(PPh_3)_3$. Malatesta and Cariello (78) earlier reported $Pt(PPh_3)_4$. Tetrakis(trifluorophosphine) compounds of palladium(0) and platinum(0), $M(PF_3)_4$, have been reported by Kruck and Baur (79). These two compounds were prepared by reacting the metal(II) chlorides with PF_3 under pressure at 100° in the presence of copper powder.

e. S-, Se-, and Te-containing ligands. Relatively few reactions of $Ni(CO)_4$ with ligands of this type have been reported. King (80) described a reaction of $Ni(CO)_4$ with bis(trifluoromethyl)dithietene that yielded a black sublimable $NiC_4F_6S_2$, in an amount insufficient for detailed study. The same reaction was reported independently by Holm and co-workers (81) who showed that it gave a volatile and diamagnetic black compound corresponding to the formula $NiC_4(CF_3)_4S_4$ (4).



(4)

Bouquet and Bigorgne (72) claim to have prepared the sulfur derivative $Ni(CO)_3S(C_2H_5)_2$ showing infrared bands at 2072, 1991, and 1986 cm⁻¹, but the method of preparation was not reported.

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C. Carbonyls of the Cobalt Subgroup Metals

1. Reactions Involving Changes in Oxidation Number

a. Oxidations. Both $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are air sensitive. However, in our experience, large crystals of $Co_2(CO)_8$ or $Co_4(CO)_{12}$, as obtained by vacuum sublimation at room temperature or slightly higher, may be handled in air for a short time without appreciable decomposition. The presence of cobalt metal or some other impurities in the solid may catalyze violent oxidation. Formation of a bluish carbonate is observed when crystals of both carbonyls are slowly contacted with air over a prolonged time. Solutions of the carbonyls are rapidly decomposed by air. Octacarbonyldicobalt in benzene gives a dark precipitate and evolves carbon monoxide and carbon dioxide in a 4:1 ratio (1).

By reaction with halogens, both carbonyls are quantitatively decomposed to the corresponding cobalt(II) halides and carbon monoxide. The reaction of $Co_2(CO)_8$ with bromine has been reported by Hieber and co-workers (2).

Oxidizing acids completely transform the carbonyl into cobalt(II) salts. Nonoxidizing acids were reported as reacting with more difficulty and only partially (2). Conceivably, a sequence of reactions comprising dismutation, acidification, and spontaneous oxidation of the hydridocarbonyl could effect a complete oxidation of $Co_2(CO)_8$ to cobalt(II) with evolution of the corresponding amount of hydrogen:

$$3Co_2(CO)_8 + 12H_2O \longrightarrow 2[Co(H_2O)_6][Co(CO)_4]_2 + 8CO \tag{24}$$

$$[Co(H_2O)_6][Co(CO)_4]_2 + 2HCl \longrightarrow [Co(H_2O)_6]Cl_2 + 2CoH(CO)_4 \tag{25}$$

$$2CoH(CO)_4 \longrightarrow H_2 + Co_2(CO)_8 \tag{26}$$

By various routes the carbonyls of cobalt can be oxidized, by partial replacement of the original carbon monoxide groups, to complexes in which the central metal atom is in an oxidation state of 1+ (see Sec. VIII on cationic metal carbonyls).

b. Reductions. Chemical reduction of cobalt carbonyls gives the tetracarbonylcobaltate anion $[Co(CO)_4]^-$. In contrast with iron and nickel which form several polynuclear carbonylmetallates, cobalt gives only the mononuclear anion. This behavior undoubtedly results from the high stability of the mononuclear anion compared with anions of higher molecular complexity.

The $[Co(CO)_4]^-$ anion in pyridine shows essentially only one C—O stretching vibration in the infrared at 1883 cm^{-1} (3). In diglyme and tetrahydrofuran solutions of unspecified concentrations the band was observed at 1886 cm^{-1} (4).

Edgell and co-workers (5) reported that the infrared C—O stretching of $NaCo(CO)_4$ shows a remarkable solvent shift and, moreover, that extra bands were observed in pure tetrahydrofuran. In water and DMF, again one single band is observed. Apart from these second order effects—probably ion pair formation—the presence of a single band in pyridine solutions of $[Co(py)_n][Co(CO)_4]_2$ (3) and in solutions of $NaCo(CO)_4$ in solvents of high dielectric constant, suggests that the $[Co(CO)_4]^-$ anion has a tetrahedral structure.

The reduction potential (6) and the polarographic half-wave potential (7) of $Co_2(CO)_8$ were found to be -0.40 and -0.35 V, respectively, in reference to the calomel electrode.

At room temperature, $Co_2(CO)_8$ dissolved in inert solvents can be quantitatively reduced by sodium amalgam to $NaCo(CO)_4$ (8). Later it was shown that this reaction occurs through the intermediate formation of $Hg[Co(CO)_4]_2$ (9,10).

Both $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are reduced by alkali metals dissolved in liquid ammonia.

Behrens and Weber (11,12) reported that the following reductions take place below −75°C.

$$Co_2(CO)_8 + 2Na \longrightarrow 2NaCo(CO)_4 \qquad (27)$$

$$Co_4(CO)_{12} + 3Na \longrightarrow 3NaCo(CO)_4 + Co \qquad (28)$$

At higher temperatures, ammonia acts as a Lewis base causing the disproportionation of the carbonyls with formation of $[Co(NH_3)_6][Co(CO)_4]_2$.

Reduction of $Co_2(CO)_8$ to $[Co(CO)_4]^-$ occurs largely when the carbonyl is treated with strongly alkaline solutions. In early work, it was reported (13) that in strong alkali, the hydridocarbonyl and dodecacarbonyltetracobalt are formed according to the equation:

$$3Co_2(CO)_8 + 4OH^- \longrightarrow 4CoH(CO)_4 + \tfrac{1}{2}Co_4(CO)_{12} + 2CO_3^{2-} \qquad (29)$$

In weakly alkaline solution, formation of hydridocarbonyl and cobalt hydroxide was postulated:

$$3Co_2(CO)_8 + 4H_2O \longrightarrow 4CoH(CO)_4 + 2Co(OH)_2 + 8CO \qquad (30)$$

The presence of $Co_4(CO)_{12}$ in strongly alkaline solution was not confirmed by Wender, Sternberg, and Orchin (8), who explained also that the reaction occurring in weakly alkaline medium resulted from disproportionation of $Co_2(CO)_8$ by the Lewis base, water. Benzene solutions of $Co_2(CO)_8$ were slowly transformed by water into the water-soluble $[Co(H_2O)_6][Co(CO)_4]_2$, from which $Co(OH)_2$ was precipitated by alkali.

$$3Co_2(CO)_8 + 12H_2O \longrightarrow 2[Co(H_2O)_6][Co(CO)_4]_2 + 8CO \qquad (31)$$

Hieber and co-workers (14) later reinvestigated the same reaction in strongly alkaline solution and concluded that disproportionation of $Co_2(CO)_8$ by water is accompanied by oxidation of the resulting carbon monoxide and reduction of $Co_2(CO)_8$ to carbonylcobaltate:

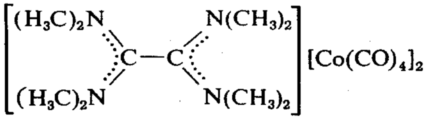
$$8Co_2(CO)_8 + 8CO + 32OH^- \longrightarrow 16[Co(CO)_4]^- + 8CO_3^{2-} + 16H_2O \qquad (32)$$

The overall reaction was represented as the sum of eqs. 31 and 32,

$$11Co_2(CO)_8 + 32OH^- \longrightarrow 2Co^{2+} + 20[Co(CO)_4]^- + 8CO_3^{2-} + 16H_2O \qquad (33)$$

91% of the cobalt is so reduced to tetracarbonylcobaltate.

King (15) described the reduction of $Co_2(CO)_8$ to $[Co(CO)_4]^-$ by tetrakis(dimethylamino)ethylene in hydrocarbons, with formation of the salt:



c. Disproportionation reactions. By action of different ligands, oxidation-reduction reactions occur with $Co_2(CO)_8$ and $Co_4(CO)_{12}$. Depending on the nature of the ligand used, these reactions may occur according to either of the following stoichiometries:

$$2Co(0) \longrightarrow Co(I) + Co(I-) \qquad (34)$$

$$3Co(0) \longrightarrow Co(II) + 2Co(I-) \qquad (35)$$

Cobalt(I−) in eqs. 34 and 35 represents the tetracarbonylcobaltate anion $[Co(CO)_4]^-$; the cationic cobalt is in general penta- or hexacoordinate. Reaction 34 take place with isocyanides, phosphines, arsines, and stibines, whereas nitrogen- and oxygen-containing ligands promote the second type of reactions.

Disproportionations to Co(I) and Co(I−). By these reactions, low-spin pentacoordinate complexes of cobalt(I) are obtained. The reaction of octacarbonyldicobalt with isocyanides leads to formation of yellow-brown crystalline compounds, fairly stable in air despite the unusual oxidation states of cobalt in both the cation and anion (16).

$$Co_2(CO)_8 + 5RNC \longrightarrow [Co(CNR)_5][Co(CO)_4] + 4CO \qquad (36)$$

It had been originally proposed (17) that isocyanides would form substitution compounds of the type $[Co(CO)(\text{isocyanide})_3]_2$ or $Co_2(CO)_3(\text{isocyanide})_5$. It is now established beyond doubt that isocyanides, such as methyl isocyanide (16,18) and phenyl isocyanide (18), react in the same way and lead always to the formation of the pentacoordinate cobalt(I) cation. The salt-like character of the reaction products was demonstrated by conductivity measurements and by successful replacement of the $[Co(CO)_4]^-$ anion with other complex anions by metathetical reactions.

Tertiary phosphines, arsines, and stibines produced ionic tetracarbonylcobaltates,

$$Co_2(CO)_8 + 2L \longrightarrow [Co(CO)_3L_2][Co(CO)_4] + CO \qquad (37)$$

as well as substitution products $[Co(CO)_3L]_2$ (19–23). A more detailed account of these reactions with tertiary phosphines, arsines, and stibines will be given later in the discussion of the substitution reactions of cobalt carbonyls.

Disproportionations to cobalt(II) and cobalt(I−). The reactions of nitrogen- and oxygen-containing Lewis bases with octacarbonyldicobalt was reported several years ago by Hieber and co-workers, who interpreted them as substitution reactions (2).

Later, Hieber and Schulten (13) observed that reaction of aqueous ammonia solutions with $Co_2(CO)_8$ generates the tetracarbonylcobaltate anion.

Wender, Sternberg, and Orchin (8) showed that, independent of the alkalinity, the reaction between $Co_2(CO)_8$ and many Lewis bases, B, gives rise to disproportionations of the type:

$$3Co_2(CO)_8 + 2nB \longrightarrow 2[Co(B)_n][Co(CO)_4]_2 + 8CO \qquad (38)$$

here n is 6, 3, 2 for monodentate, bidentate, and tridentate ligands, respectively. These authors suggested that the first stage of this reaction was disproportionation to Co(I) and Co(I−):

$$Co_2(CO)_8 + B \longrightarrow [Co(CO)_4B]^+[Co(CO)_4]^- \qquad (39)$$

Recently their suggestion was confirmed (24) by a study of the reaction between $Co_2(CO)_8$ and alcohols or water. By use of ion exchange and radioisotope techniques strong evidence was gathered for formation of the cationic species $[Co(CO)_4ROH]^+$ during the reaction of $Co_2(CO)_8$ with alcohols. The alcohol complex is stable only below 0°C.

Table 8 lists the reactions of $Co_2(CO)_8$ with many nitrogen and oxygen bases according to eq. 38. Sometimes the number of ligands coordinated to cobalt(II) in these compounds varies and differs from what is expected. This is true with benzonitrile and with several oxygen ligands, such as methanol, acetophenone, benzophenone, and dioxane. Most of the compounds described in Table 8 were isolated, although they are unstable because of their tendency to partially lose the ligands coordinated to the cation and their sensitivity to atmospheric oxygen. The products with ethylenediamine and phenanthroline, however, are remarkably stable in air.

Reaction of aliphatic and alicyclic primary and secondary amines with $Co_2(CO)_8$ brings about carbonylation of the amine and formation of the corresponding formamides (25,27,29) has been observed.

With some Lewis bases, such as *tert*-butanol (8), aniline, and benzidine (29), octacarbonyldicobalt reacts slowly, losing carbon monoxide and finally yielding dodecacarbonyltetracobalt. Here, the disproportionation

TABLE 8

Lewis Bases that React with $Co_2(CO)_8$ According to the Scheme:
$3Co_2(CO)_8 + 2nB \rightarrow 2[Co(B)_n][Co(CO)_4]_2 + 8CO$

Lewis base (B)	No. of B coord. to Co(II)	Color	Properties	Ref.
Ammonia	6	Orange-red	Air sensitive	13
Methylamine	6	Light pink	Air sensitive	27
Dimethylamine	6	—	—	25,27
Ethylenediamine	3	Pink	Air stable	14
Diethylenetriamine	2	Orange-red	—	29
o-Phenylenediamine	3	Red	Air sensitive	29
p-Phenylenediamine	6	Brick red	Air sensitive	29
Acetonitrile	6	Red	Dec. at −10°C	27
Benzonitrile	6 and 1.9	Black	Air sensitive	30
Pyridine	6	Ochre yellow	Air sensitive	8,26,27,28
α-Picoline	6	Brown-black	Air sensitive	29
γ-Picoline	6	Pink	Air sensitive	29
Quinoline	6	Violet	Air sensitive	29
o-Phenanthroline	3	Yellow	Fairly air stable	8,13,14
Ethyleneimine	6	Pink	Air sensitive	29
Pyrrolidine	6	Red-violet	Air sensitive	29
Morpholine	6	Pink-red	—	29
Formamide	6	Pink	Air sensitive	29
Dimethylformamide	6	—	—	25,31
Ethanolamine	3	Pink	Air sensitive	29
Diethanolamine	2	Light pink	Air sensitive	29
Triethanolamine	2	Pink	Air sensitive	29
Water	6	Pink	Not isolated	8,14
Methanol	6 and 1.87	Black	Not isolated; pyrophoric with n = 1.87	8,14
Ethanol	6 and 1.87	—	Not isolated; pyrophoric with n = 1.87	8
Acetophenone	0.5	Brown-black	Air sensitive	30
Benzophenone	0.25	Brown-black	Air sensitive	30
Dioxane	0.5	Black	Air sensitive	30

reaction is regarded (29) as an intermediate step, followed by the spontaneous decomposition of tetracarbonylcobaltate into dodecacarbonyltetracobalt and cobalt metal:

$$3[Co(C_6H_5NH_2)_n][Co(CO)_4]_2 \longrightarrow 2Co_4(CO)_{12} + Co + 3nC_6H_5NH_2 \qquad (40)$$

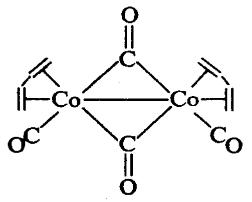
Dodecacarbonyltetracobalt reacts with pyridine (27) according to the equation:

$$3Co_4(CO)_{12} + 24C_5H_5N \longrightarrow 4[Co(C_5H_5N)_6][Co(CO)_4]_2 + 4CO \qquad (41)$$

2. *Substitution Reactions*

a. Compounds containing carbon–carbon unsaturated bonds. Although compounds of formula $Co_2(CO)_7CH_2{=}CHR$ have been postulated (32) as intermediates in the hydroformylation reaction, no compounds of this type have been isolated so far. It has been pointed out (33) that $Co_2(CO)_8$ does not react at room temperature with 1-dodecene. $Co_2(CO)_8$ has been reported (34) to react with tetrafluoroethylene to give an orange crystalline compound (mp 70°) of formula $(CO)_4CoCF_2CF_2Co(CO)_4$, which is a σ-type complex (35).

Fischer and co-workers (36) described the reaction of butadiene with $Co_2(CO)_8$ in the presence of ultraviolet irradiation to give $[Co(CO)_2C_4H_6]_2$. This compound has a dipole moment of 3.02 D, its infrared spectrum shows a band at 1822 cm^{-1} attributed to bridging CO groups, and, on this basis, the "*cis*" structure **5** was assigned to it. However, since the two cobalt atoms and the two bridging CO groups are probably not coplanar (see structure of $Co_2(CO)_8$ which shows a finite dipole moment in solution (37)), the presence of a small dipole moment does not appear sufficiently good evidence for assigning a "*cis*" structure. Other cobalt carbonyl compounds derived from conjugated diolefins and norbornadiene have been obtained without use of ultraviolet irradiation. Binuclear compounds of the type $Co_2(CO)_6$ (diolefin) (**7**) and $Co_2(CO)_4$(diolefin)$_2$ (**5** or **6**) have been synthesized (38). The butadiene and isoprene derivatives were not obtained in a pure state. No evidence for the presence of isomers was found and no conclusions were drawn about possible structural arrangements.



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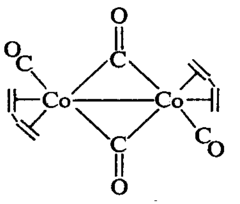

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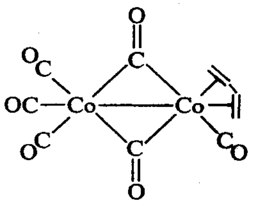


(7)

Reactions of $Co_2(CO)_8$ with conjugated perfluorodiolefins have been reported. Octacarbonyldicobalt reacts (39,40) with octafluorocyclohexa-1,3-diene with fluorine abstraction and formation of the red complex $(OC)_3CoC_6F_6Co(CO)_3$ (mp 47–48°). This compound has been shown by x-ray analysis to contain a perfluorocyclohex-1-yn-3-ene group (an isomer of perfluorobenzene), with the two cobalt atoms coordinated to the triple bond of the unsaturated cyclic system. The molecular configuration (39) of this compound is shown in Fig. 10.

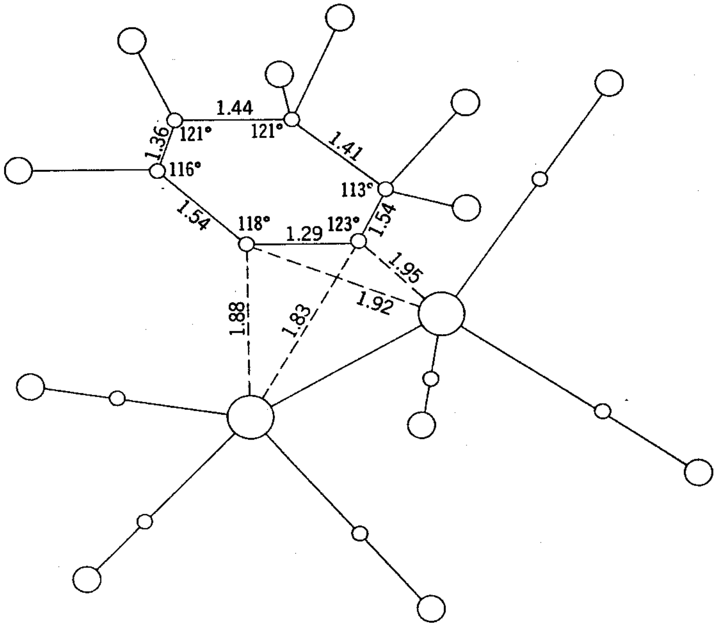
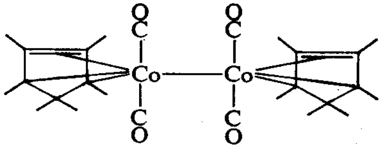


FIG. 10. Molecular configuration of $(OC)_3CoC_6F_6Co(CO)_3$. (N. A. Bailey, M. R. Churchill, R. Hunt, R. Mason, and G. Wilkinson, *Proc. Chem. Soc.*, **1964**, 401.) Published by permission.

Perfluorocyclopentadiene and $Co_2(CO)_8$ react at room temperature (41) to give a 65% yield of a dimeric orange compound having the formula

$Co_2(CO)_4(C_5F_6)_2$; the proposed structure **8** of the compound is shown here without the fluorine atoms.



(**8**)

$Co_2(CO)_8$ has been reported to react with cycloheptatriene in the presence of ultraviolet irradiation to give $Co(CO)_3C_7H_7$ in low yields (42). In this compound the cycloheptatrienyl ring is probably bonded to the metal through only three carbon atoms in an arrangement of the allyl type.

It was reported (38) that $Co_2(CO)_8$ does not react with cyclooctatetraene, bicyclo[2,2,2]-octa-2,5-diene, cycloocta-1,5-diene, and *p*-benzoquinone. A cobalt carbonyl complex containing an eight-membered unsaturated ring was described by Fischer and Palm (43). A mixture of 1,3,5- and 1,3,6-cyclooctatrienes gave the yellow crystalline $[Co(CO)_2C_8H_{10}]_2$, diamagnetic and stable in air. Cyclooctatriene is present in the complex in the 1,3,6 form. This compound shows (36) infrared bands in the carbonyl region at 2032, 2008, and 1815 cm^{-1}, the latter being attributed to bridging CO groups. It appears, therefore, that polyolefins, conjugated or not, react with $Co_2(CO)_8$ to give substitution products containing bridging CO groups.

In contrast, the substitution products obtained from acetylenic compounds contain only terminal carbon monoxide groups. Since $Co_2(CO)_8$ is present in solution in two isomeric forms, one of which does not contain bridging CO groups, the question arises whether the different types of substitution products obtained with polyolefins and with acetylenic compounds are due to a preferential attack on one form or to rearrangement after reaction with the more reactive form.

Some years ago Wender and co-workers described (44,45) the reaction of acetylenic compounds with $Co_2(CO)_8$. The stoichiometry of the reaction is:

$$RC{\equiv}CR' + Co_2(CO)_8 \longrightarrow Co_2(CO)_6RC_2R' + 2CO \qquad (42)$$

The reaction is quantitative and fast even at room temperature, giving red-orange to deep red solid or liquid products, depending on the nature of R and R′. The infrared spectra of the acetylenic complexes did not show bridging CO groups. This was later confirmed (46) by an x-ray study of the diphenylacetylene derivative $Co_2(CO)_6PhC_2Ph$. In this compound each cobalt is in a distorted octahedral configuration, the acetylenic carbon–carbon bond is nearly perpendicular to the cobalt–cobalt bond and the two cobalt atoms and the two atoms of the acetylenic group are almost tetrahedrally arranged.

Reaction 42 was studied kinetically (47) by measuring the carbon monoxide evolved. The results suggest a reaction mechanism in which $Co_2(CO)_8$ reacts in an intermediate step with a molecule of an acetylene with evolution of one molecule of carbon monoxide and formation of $Co_2(CO)_7$. Later (48) the same authors studied the influence of the groups R and R′ on the kinetics of reaction 42. It was possible to establish an order of reactivity for several acetylenic compounds with respect to 1-hexyne as standard, but the experimental data in most cases could not be rationalized in terms of electronic or steric effects. It would be interesting to re-examine these kinetic data taking into account the existence in solution of a nonbridged form of $Co_2(CO)_8$.

Perfluoro-2-butyne reacts (49) with $Co_2(CO)_8$ to give a red, volatile complex $Co_2(CO)_6C_4F_6$ which does not show infrared bands attributable to bridging CO groups and for which it is reasonable to assume a structure similar to that found for the other acetylene compounds.

Compounds with disubstituted acetylenes react (50) with carbon monoxide under pressure at 70°C giving rise to a new type of complex:

$$Co_2(CO)_6RC_2R' + 3CO \longrightarrow Co_2(CO)_9RC_2R' \qquad (43)$$

Only $\frac{7}{9}$ of the carbon monoxide contained in these substances can be obtained by decomposition with iodine in pyridine; the same proportion of carbon monoxide exchanges with gaseous ^{14}CO at room temperature. On the basis of chemical and spectroscopic data a structure containing a lactone type ring was postulated. This was later confirmed by an x-ray analysis by Mills and Robinson (51) on the acetylene compound $Co_2(CO)_9C_2H_2$. In this structure each cobalt atom is surrounded by five carbon atoms in a square pyramid configuration (see Fig. 11). By joining the two square "pyramids along the basal edge and folding the whole along the join," the structure shown in Fig. 11 is obtained. The two cobalt atoms and the bridging carbon atoms are not coplanar. The authors suggested that such a folded structure could also occur in $Co_2(CO)_8$ in which it had been considered that the two cobalt atoms and the two bridging CO groups were coplanar. This suggestion has been confirmed (52).

High resolution infrared spectra of compounds $Co_2(CO)_6RC_2R$ and the lactone-type compounds $Co_2(CO)_9RC_2R$ have been published (53). The number of CO stretching bands was found to correspond to that predictable on the basis of the known structures in the solid state.

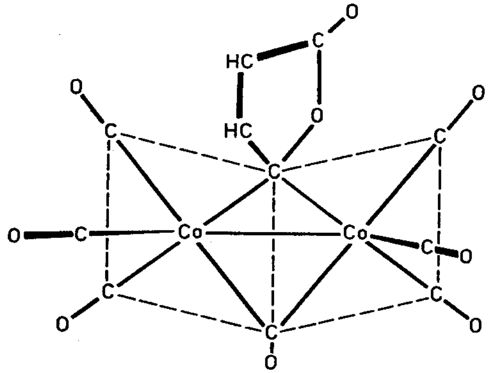
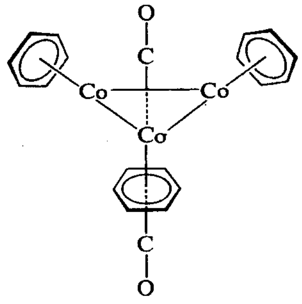


FIG. 11. View of the $Co_2(CO)_9C_2H_2$ molecule (O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, **1959**, 156). Published by permission.

Although well-defined compounds have not been isolated, there is some evidence that $Co_2(CO)_8$ reacts (33) with allene and substituted allenes (having at least one hydrogen atom bonded to an allenic carbon). $Co_2(CO)_8$ does not react thermally with aromatic hydrocarbons (54) to form π-arene complexes. However, when benzene or toluene solutions of $Co_2(CO)_8$ are treated at 80° with $AlBr_3$, carbon monoxide is evolved and the cation $[Co_3(CO)_2\ arene_3]^+$ is formed. This has been obtained (54) in a pure state as the iodide, tetraphenylborate, and reineckate by metathetical reactions in water–acetone solution. The intermediate product in the formation of the cation $[Co_3(CO)_2arene_3]^+$ is the adduct $Co_2(CO)_8 \cdot AlBr_3$ that has been isolated by addition of $AlBr_3$ to a heptane solution of $Co_2(CO)_8$, the latter acting here as a Lewis base. By heating the aluminum bromide adduct in benzene or in toluene, the complex cation can be obtained as the bromide $[Co_3(CO)_2arene_3]Br$. The most probable structure for the cation, which shows an infrared band at 1675 cm^{-1}, is shown in **9**.

This is by analogy with the closely related compound $Ni_3(C_5H_5)_3(CO)_2$ for which a triangular arrangement of the nickel atoms has been found by x-ray diffraction studies (55). It is noteworthy that in both these structures the CO groups form bridges over three metal atoms. Fischer and coworkers have also described (56) the arene–cobalt cationic species **9**.

$Co_2(CO)_8$ reacts readily with cyclopentadiene (57) to give the mixed cyclopentadienyl carbonyl $CoC_5H_5(CO)_2$, a dark red oil, bp 75°/22 mm. Friedel-Crafts acylations, which work successfully with $MnC_5H_5(CO)_3$ and $VC_5H_5(CO)_4$, failed (58) with $CoC_5H_5(CO)_2$. However, this should not be taken as evidence against the aromatic character of the cyclopentadienyl anion in the compound, because the conditions used for the reaction could have caused decomposition of the relatively unstable material. In the course of the reaction between C_5H_6 and $Co_2(CO)_8$ hydrogen is not evolved

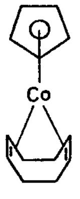


(9)

$$Co_2(CO)_8 + 2C_5H_6 \longrightarrow 2CoC_5H_5(CO)_2 + 4CO + H_2 \qquad (44)$$

but is consumed by the excess of cyclopentadiene, forming (59) cyclopentene and cyclopentane. Dicarbonylcyclopentadienylcobalt reacts with halogens to give the halogeno complexes $CoX_2(C_5H_5)(CO)_2$ (60).

Several reactions of $CoC_5H_5(CO)_2$ with unsaturated compounds have been reported (61–63). In every case carbon monoxide was completely displaced and the complexes **10** from 1,5-cyclooctadiene (63), **11** from 1,3-cyclohexadiene (63), **12** and **13** from a mixture of 1,3,5- and 1,3,6-cyclooctatrienes (61,63), and **14** from duroquinone (62) have been described. $CoC_5H_5(CO)_2$ and cyclooctatetraene give (64) the brown crystalline $CoC_5H_5(C_8H_8)$, mp 81–82°. The cyclooctatetraene ligand can be hydrogenated in the presence of Raney nickel and even brominated, without destroying the complex. This behavior contrasts with that of the



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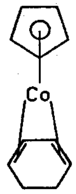

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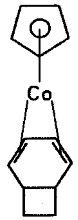

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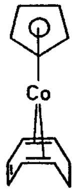

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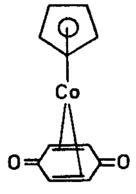
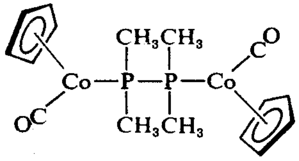


(14)

iron complex $Fe(CO)_3C_8H_8$. Fritz and Keller (65) found that two CoC_5H_5 units can be bonded to the same C_8H_8 ring; in fact, they isolated the complex $[Co(C_5H_5)]_2C_8H_8$ from the reaction of $CoC_5H_5(CO)_2$ with cyclooctatetraene.

The reactions of $CoC_5H_5(CO)_2$ with bidentate phosphines have been described (66). $P_2(CH_3)_4$ gives the black crystalline $[CoC_5H_5(CO)_2]_2P_2Me_4$, for which structure **15** has been proposed.



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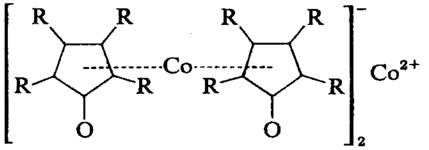
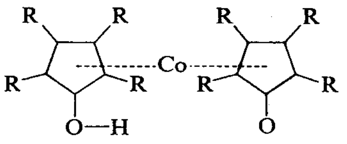


(16)

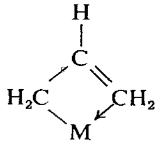
$Co_2(CO)_8$ reacts with tetracyclone (67) (tetraphenylcyclopentadienone) at 130–160° giving the thermally very stable (dec. about 400°) deep violet compound of formula Co_3(tetracyclone)$_4$ (**16**). This should be regarded as Co[Co(tetracyclone$_2$]$_2$, i.e., as a cobalt(II) salt containing the anion [Co(tetracyclone)$_2$]$^-$. By treatment of (**16**) with dry HCl, the diamagnetic compound CoH(tetracyclone)$_2$ (**17**) was obtained; the latter with acetic anhydride yielded the acetyl derivative Co(tetracyclone)$_2COCH_3$. When the reaction of $Co_2(CO)_8$ with tetracyclone was carried out at lower temperatures (~ 60°), substitution products of $Co_2(CO)_8$ were obtained but they could not be isolated in a pure state.

b. π-Allylcarbonyl complexes of cobalt. Because π-allylcarbonyl compounds of cobalt were the first π-allylcarbonyl derivatives to be reported, they will be discussed here, although briefly. Other π-allylcarbonyl complexes of transition metals have been reported since then. The reader interested in this subject can find further references in a review by Green and Nagy (68).

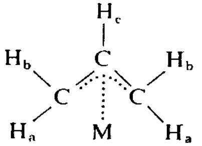
With the preparation (69–71) of $[PdClC_3H_5]_2$ it was realized a few years ago that the allyl radical C_3H_5 can form complexes acting as a three-electron donor to the metal. Of the two possible structures **18** and **19**, the symmetrical **19** was considered the most likely one, owing to nuclear magnetic resonance and infrared spectroscopy studies on the palladium compound (72) and on π-allyltricarbonylcobalt (73). The latter compound was obtained from reaction of $NaCo(CO)_4$ with allyl bromide.



(17)

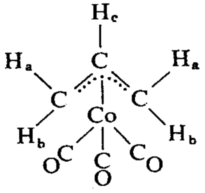


(18)



(19)

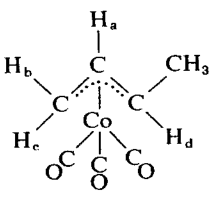
$$NaCo(CO)_4 + C_3H_5Br \longrightarrow CO + CoC_3H_5(CO)_3 + NaBr \qquad (45)$$



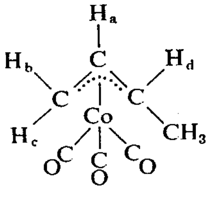
(20)

The proton resonance spectrum of **20** shows three peaks whose intensities are in the ratio 2:2:1. In fact, although the two methylene groups are equivalent, the two hydrogen atoms on each methylene group are different because they are in different orientations with respect to the cobalt atom.

Another π-allyl type complex arises from the reaction of $CoH(CO)_4$ with butadiene (74); a red liquid (b_1 33–35°) is obtained. Later (75) the correct formula of the complex was established as $Co(CO)_3C_4H_7$. It was then found (76) that the complex exists in two isomeric forms. Nuclear magnetic resonance measurements (77) made it possible to elucidate the structures of the two isomeric forms; **21** is the more stable isomer. If the π-allyl group is terminally substituted, the possibility of *syn* and *anti* isomers arises, because of the restricted rotation around the carbon–carbon bond. The *syn* isomer is **21** (related to the middle hydrogen atom). The reaction of 1,4-pentadiene with $CoH(CO)_4$ was reported (78) to give the *syn* and *anti* isomers of 1-ethylallyltricarbonylcobalt together with 5-hexenal and 2-methylcyclopentanone.



(21)



(22)

Crystallographic data on $[PdClC_3H_5]_2$ (79,80) confirm the conclusion drawn from proton resonance measurements on the stereochemistry of π-allyl systems. X-ray structural analysis of $[PdClC_3H_5]_2$ has shown the equivalence of the methylene carbons.

The infrared spectra of some π-allyl systems not containing carbon monoxide as additional ligand have been measured (81).

c. P-, As-, and Sb-containing compounds. Several publications have appeared on the reaction of $Co_2(CO)_8$ with compounds containing phosphorus, arsenic, and antimony, particularly triaryl- and trialkylphosphines (82–85). It is now established that, with trialkyl- and triarylphosphines, ionic compounds (**23**) are obtained together with substitution products (**24**):

$$\underset{(23)}{[Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-} \qquad \underset{(24)}{[Co(CO)_3PR_3]_2}$$

The relative amounts of **23** and **24** may change depending on the conditions used, especially on the temperature. Between 30 and 40°, formation of the substitution products is favored. For example, by heating in benzene at reflux temperature for 10 min, $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ is converted almost quantitatively into the dimer $[Co(CO)_3PPh_3]_2$ (86*a*).

The ionic compounds from triphenylarsine and triphenylstibine $[Co(CO)_3(AsPh_3)_2][Co(CO)_4]$ and $[Co(CO)_3(SbPh_3)_2][Co(CO)_4]$ are very unstable and at 0° the substitution products are formed according to the equation:

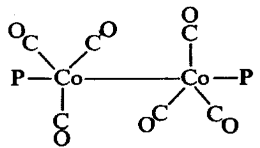
$$[Co(CO)_3L_2][Co(CO)_4] \longrightarrow [Co(CO)_3L]_2 + CO \qquad (46)$$

Triphenylphosphite invariably forms the substitution product (83,86*b*).

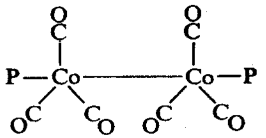
The infrared spectra of $[Co(CO)_3PPh_3]_2$ and $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ have been studied (87). The substitution product does not show any infrared stretching mode attributable to bridging carbon monoxide; the molecule should therefore be joined only by a cobalt–cobalt bond as in **25**. A decision between a staggered form of symmetry D_{3d} (**25**) and an eclipsed form D_{3h} (**26**) is not possible because the two forms give rise to the same number of infrared active CO stretching vibrations. For the cation $[Co(CO)_3(PPh_3)_2]^+$, the structure **27** has been suggested.

The reaction of $Co_2(CO)_8$ with triphenylphosphine in nujol as solvent gives the substitution product $Co_2(CO)_7PPh_3$ (88). Structure **28** has been suggested for this compound on the basis of infrared data. The reaction of $Co_2(CO)_8$ with tris(dimethylamino)phosphine (89) (Tdp) gives the ionic product $[Co(CO)_3Tdp_2][Co(CO)_4]$ mainly and only traces of the substitution compound $[Co(CO)_3Tdp]_2$.

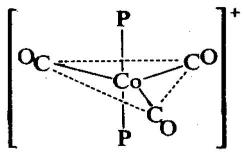
The reactions of $Co_2(CO)_8$ with bidentate phosphines and arsines have been reported. 1,2-bis(diphenylphosphino)ethane (90) at room temperature gives the ionic $[Co_2(CO)_4Diphos_3][Co(CO)_4]_2$. Because the dimeric cation does not show bands attributable to CO-bridging groups, it is concluded that the two cobalt atoms are joined by diphosphine bridges.



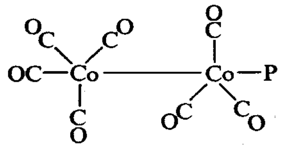
(**25**)



(**26**)

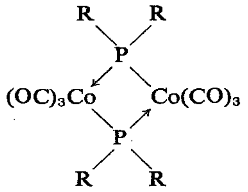


(**27**)

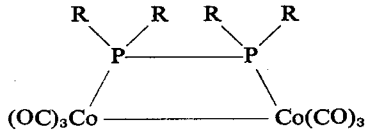


(**28**)

Tetraphenyldiphosphine $Ph_2P–PPh_2$ reacts with $Co_2(CO)_8$ giving a dimeric substitution product to which structures **29** or **30** have been assigned. The same product is obtained (91,92) by the reaction of $NaCo(CO)_4$ with $P(C_6H_5)_2Cl$.



(**29**)



(**30**)

The cobalt–cobalt bond in the dimeric substitution products can be split by the action of sodium amalgam in tetrahydrofuran (93):

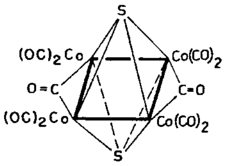
$$[Co(CO)_3PR_3]_2 \xrightarrow[THF]{2Na(Hg)} 2Na[Co(CO)_3PR_3] \qquad (47)$$

The tricarbonyl of iridium $[Ir(CO)_3]_n$ reacts with trialkyl- and triarylphosphites to give apparently dimeric substitution products of formula

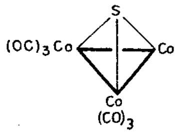
$[Ir(CO)_2P(OR)_3]_2$. These compounds appear to have bridging CO groups, as suggested by the infrared data in the C—O stretching region (94).

d. Sulfur-containing compounds. The reactions of ethyl mercaptan and thiophenol with $Co_2(CO)_8$ had been reported (95) by Hieber and Spacu. Products formulated as $[Co(CO)_3SR]_n$, with R = C_2H_5, C_6H_5, and *n* probably equal 2, were isolated as crystalline air-stable solids. Their solubility in nonpolar organic solvents suggested that they were substitution products of $Co_2(CO)_8$. Klumpp, Markó, and Bor have reported (96), however, that the reaction of $Co_2(CO)_8$ with ethyl mercaptan at 0° without solvent (the conditions used by Hieber and Spacu) results in a mixture of $Co_4(CO)_5(C_2H_5S)_7$ and some unidentified products. $Co_4(CO)_5(C_2H_5S)_7$ (**31**) was isolated in a pure state from the reaction of $Co_2(CO)_8$ with ethyl mercaptan or diethyl disulfide in hexane. This is a black crystalline substance, very slightly soluble in benzene. By using lower ratios of sulfur compound to $Co_2(CO)_8$, the black crystalline $Co_4(CO)_7(C_2H_5S)_3$ (**32**) was also isolated from the reaction. From benzyl mercaptan the black crystalline $Co_3(CO)_6(S)(SCH_2C_6H_5)$ (**33**) was obtained. While **31** and **32** show infrared bands at low wavenumbers suggestive of bridging CO groups, only terminal carbon monoxide groups are evident in the infrared spectrum of **33**.

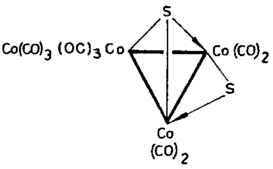
$Co_2(CO)_8$ reacts with sulfur in hydrocarbon solution at room temperature to give sulfur-substituted cobalt carbonyl derivatives (97–99). The products isolated are: $[Co_2(CO)_5S]_n$ (**34**) (*n* being probably 2), $Co_3(CO)_9S$ (**35**), and $Co_3(CO)_7S_2$ (**36**); on the basis of the infrared data the following structures have been suggested:



(34)



(35)



(36)

$Co_2(CO)_8$ reacts also with CS_2 (100) giving various products; by chromatography it was possible to isolate in very small yields a compound corresponding to the formula $[Co_4(CO)_{10}]CS_2$. No bridging CO groups are present in its infrared spectrum and a "butterfly" structure similar to that found by Dahl and Smith (101) for the acetylenic derivative $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ has been suggested.

A tetrameric carbonyl derivative of formula $Co_4(CO)_4(SC_2H_5)_8$ was obtained in 17% yield by reacting cobalt(II) ethylmercaptide with carbon monoxide at atmospheric pressure in methanol at room temperature. No bridging C—O stretching vibrations were observed in the infrared spectrum (102).

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D. Carbonyls of the Iron Subgroup Metals

1. Reactions Involving Changes in Oxidation Number

a. Oxidations. The reactions of $Fe(CO)_5$ with aqueous chlorine and bromine under uncontrolled conditions lead to the quantitative formation of iron(II) halides (1). Under controlled conditions, halogeno metal carbonyls, $FeX_2(CO)_4$, are formed.

The action of aqueous acids on $Fe(CO)_5$ is very slow; in ether or carbon tetrachloride solutions, however, smooth reactions are observed with hydrogen and carbon monoxide evolution and formation of iron(II) salts.

Concentrated H_2SO_4 and HNO_3 react with pentacarbonyliron with formation of iron(II) and iron(III) salts, respectively (1).

The reaction of $Fe(CO)_5$ with acetylacetone in the presence of ultraviolet irradiation leads to the formation of iron(III) acetylacetonate in 45% yield (2).

The formation of iron(III) acetylacetonate from $Fe(CO)_5$ and acetylacetone has been confirmed (3). However, Fitch and Lagowski (4) later reported that when the reaction and the subsequent manipulations were carried out under complete exclusion of air, only iron(II) acetylacetonate was produced.

Pentacarbonyliron is completely oxidized by copper(II) chloride in acetone (5), according to the equation:

$$Fe(CO)_5 + 2CuCl_2 \longrightarrow Cu_2Cl_2 + FeCl_2 + 5CO \qquad (48)$$

By reaction with CCl_4, $Fe(CO)_5$ gives, among other compounds, $FeCl_2$, carbon monoxide, $COCl_2$, and hexachloroethane (6).

The reactions of pentacarbonyliron with some organic halides, such as dichlorodiphenylmethane and carbon tetrabromide, have been reported (7). With dichlorodiphenylmethane, the reaction takes place according to the equation:

$$2Fe(CO)_5 + 2(C_6H_5)_2CCl_2 \longrightarrow 10CO + 2FeCl_2 + (C_6H_5)_2C{=}C(C_6H_5)_2 \qquad (49)$$

b. Reductions. The following carbonylferrate binegative anions and the corresponding mononegative anions are known.

$$[Fe(CO)_4]^{2-};\quad [Fe_2(CO)_8]^{2-};\quad [Fe_3(CO)_{11}]^{2-};\quad [Fe_4(CO)_{13}]^{2-}$$

$$[FeH(CO_4]^-;\quad [Fe_2H(CO)_8]^-;\quad [Fe_3H(CO)_{11}]^-;\quad Fe_4H(CO)_{13}]^-$$

The trinuclear and tetranuclear anions are usually very deeply colored, red or dark red; the others are orange-red or very slightly colored, depending on the molecular complexity. The absorption spectra of several carbonylferrates have been reported (8–10). The trinuclear and tetranuclear species have characteristic absorption band maxima in the visible region (8). Contrary to a previous report (9), the $[Fe(CO)_4]^{2-}$ anion shows only a continuous absorption in the visible region with no shoulders or maxima. According to Hieber and Schubert (8), the $[Fe_2(CO)_8]^{2-}$ anion has an absorption maximum at 347 mμ, whereas, according to Case and Whiting (10), this species and the corresponding mononegative anion $[Fe_2H(CO)_8]^-$ absorb at 480 mμ. The former assignment appears to be the correct one. Since the spectroscopic data have been used as criteria for identifying the species formed in the reactions of iron carbonyls with alkali, it appears worthwhile to present the absorption data for some of the anions in tabular form, together with the infrared C—O stretching frequencies (Table 9).

TABLE 9

Ultraviolet-Visible and Infrared Absorption Band Maxima of Some Carbonylferrate Anions

Anion	λ_{max} (mμ)	Log ε	Ref.	ν_{CO} (cm^{-1})	Ref.
$[Fe(CO)_4]^{2-}$	< 300		9	1730	11
$[Fe_2(CO)_8]^{2-}$	347	3.95	9	1916m 1866s 1842w	11
$[Fe_3H(CO)_{11}]^-$	527	3.50	8	2070vw 2004s	11
	540	3.01	10	1980m 1950w	
$[Fe_3(CO)_{11}]^{2-}$	485	3.50	9	1941s 1913m 1884w	11
$[Fe_4(CO)_{13}]^{2-}$	500	3.65	9	2030vw 1967s 1950m 1829vw	11

The $[Fe(CO)_4]^{2-}$ anion in dimethylformamide has a single band in the infrared C—O stretching region at 1730 cm^{-1} (11). This suggests a tetrahedral structure. Raman spectra of $[Fe(CO)_4]^{2-}$ (as $Na_2Fe(CO)_4$), showing a band at 1788 cm^{-1} in aqueous solution (12) for the totally symmetrical stretching vibration, are also consistent with a tetrahedral structure. (Spectroscopic and structural data for the mononegative anions are given in Sec. VI.)

The reduction of iron carbonyls leads to the formation of mono- or polynuclear anions, depending on the reaction conditions and in some instances on the degree of complexity of the metal carbonyl employed.

Alkali metals in liquid ammonia (13,14) invariably reduce iron(0) to iron(II−), according to the equations:

$$Fe(CO)_5 + 2Na \longrightarrow Na_2Fe(CO)_4 + CO \qquad (50)$$

$$Fe_2(CO)_9 + 4Na \longrightarrow 2Na_2Fe(CO)_4 + CO \qquad (51)$$

$$Fe_3(CO)_{12} + 6Na \longrightarrow 3Na_2Fe(CO)_4 \qquad (52)$$

Sodium amalgam acts in a similar manner when tetrahydrofuran is used as solvent (15,16). By these reactions, the tetracarbonylferrate anion is obtained in a pure state.

It has been reported (17) that pentacarbonyliron is reduced by bis(biphenyl)chromium to the tetranuclear tridecacarbonyltetraferrate anion in benzene solution at 90°C, thus:

$$2Cr(C_6H_5{-}C_6H_5)_2 + 4Fe(CO)_5 \longrightarrow [Cr(C_6H_5{-}C_6H_5)_2]_2[Fe_4(CO)_{13}] + 7CO \qquad (53)$$

Although it has been known for many years that $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ in strongly alkaline solutions are transformed into water-soluble products (18,19), only recently have these reactions been clarified.

The existence of the $[Fe(CO)_4]^{2-}$ anion in the alkaline solutions obtained from pentacarbonyliron was first reported by Hock and Stuhlmann (5) and then confirmed by Feigl and Krumholz (20).

In spite of the fact that the acid properties of $FeH_2(CO)_4$ in aqueous solutions were not immediately recognized (21), Feigl and Krumholz (22) succeeded in isolating complex salts of $[Fe(CO)_4]^{2-}$ and $[FeH(CO)_4]^-$ by treating $Fe(CO)_5$ with aqueous ammoniacal solutions of $[Cd(NH_3)_2]^{2+}$ and $[Ni(NH_3)_6]^{2+}$. Later, the potentiometric titration of $K_2Fe(CO)_4$ and $Ba[FeH(CO)_4]_2$ solutions with HCl was reported (23).

Iron carbonyls are reduced by hydroxides or alkoxides, while at the same time some of the carbon monoxide groups are converted into carbonate ions. Hock and Stuhlmann (24) recognized this for pentacarbonyliron; they formulated the reaction as

$$Fe(CO)_5 + 2NaOC_2H_5 \longrightarrow Na_2Fe(CO)_4 + CO(OC_2H_5)_2 \qquad (54)$$

which represents the oxidation of carbon monoxide to diethyl carbonate.

Hieber and co-workers have reported the reactions of $Fe(CO)_5$ (21), $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ (25) with solutions of alkali. All these reductions can be represented by the general scheme:

$$Fe_n(CO)_m + 4OH^- \longrightarrow [Fe_n(CO)_{m-1}]^{2-} + CO_3^{2-} + 2H_2O \qquad (55)$$

with n being 1, 2, 3, and m being 5, 9, and 12, respectively.

Thus, the primary products of the reaction have the same molecular complexity as the starting carbonyls. However, the carbonylferrates so formed are unstable and structural changes soon take place.

For example, the $[Fe(CO)_4]^{2-}$ anion was reported (26,27) to be easily hydrolyzed to $[FeH(CO)_4]^-$, which slowly dimerizes and loses hydrogen:

$$2[FeH(CO)_4]^- \longrightarrow [Fe_2H_2(CO)_8]^{2-} \longrightarrow [Fe_2(CO)_8]^{2-} + H_2 \qquad (56)$$

Although the intermediate formation of the dimer was considered doubtful (19), the spontaneous conversion of $[FeH(CO)_4]^-$ into $[Fe_2(CO)_8]^{2-}$ is a well-established fact.

Either in alkaline methanol (9) or aqueous solutions (8) and especially under irradiation with high-frequency light, the octacarbonyldiferrate anion is not stable and decomposes according to the following equations:

$$2[Fe_2(CO)_8]^{2-} \longrightarrow [Fe(CO)_4]^{2-} + [Fe_3(CO)_{11}]^{2-} + CO \qquad (57)$$

$$2[Fe_2(CO)_8]^{2-} + H_2O \longrightarrow [FeH(CO)_4]^- + [Fe_3(CO)_{11}]^{2-} + OH^- + CO \qquad (58)$$

The $[Fe_2(CO)_8]^{2-}$ anion is characterized by an absorption band at 347 mμ, whereas the trinuclear carbonylferrate anion has a maximum at 485 mμ. According to Hieber and Beutner (9), the occurrence of reaction 58 is responsible for the wrong assignment by Case and Whiting (10) of a band at 480 mμ to the $[Fe_2(CO)_8]^{2-}$ anion.

The undecacarbonyltriferrate $[Fe_3(CO)_{11}]^{2-}$ decomposes slowly at room temperature with formation of $[Fe(CO)_4]^{2-}$.

It is interesting to note that reduction of iron carbonyls was reported to occur also in liquid ammonia. Behrens and Wakamatsu (28) reported that in liquid ammonia at 20°C, $Fe(CO)_5$ and $Fe_2(CO)_9$ react as follows:

$$Fe(CO)_5 + 4NH_3 \xrightarrow{\text{14 days}} (NH_4)_2[Fe(CO)_4] + NH_2CONH_2 \qquad (59)$$

$$Fe_2(CO)_9 + 4NH_3 \xrightarrow{\text{40 hr}} (NH_4)_2[Fe_2(CO)_8] + NH_2CONH_2 \qquad (60)$$

The formation of $CO(NH_2)_2$ in ammonia is strictly equivalent to the formation of CO_3^{2-} in aqueous solutions.

c. Disproportionation reactions. A variety of Lewis bases having nitrogen or oxygen as donor atoms react with iron carbonyls giving mono- or polynuclear carbonylferrates while one iron atom is oxidized to the ferrous cation. The reaction can be schematically represented as:

$$mFe + nB \longrightarrow [Fe(B)_n]^{2+}[Fe_{m-1}]^{2-} \qquad (61)$$

with m being ≥2.

The compounds isolated in reactions of this type were previously considered as substitution products containing zerovalent iron (29–31). Later, Hieber and his co-workers carried out a detailed revision of their former work and recognized the saltlike nature of the reaction products. This work is discussed in the next section.

Pentacarbonyliron in the presence of nitrogen bases. Pentacarbonyliron reacts with nitrogen bases forming mono- or polynuclear carbonylferrates, depending on the nature of the base and on the reaction conditions.

Polynuclear anions are the most frequently encountered products of these reactions. The reaction with pyridine at 85°C in the presence of ultraviolet irradiation (32,33) takes place according to the equation:

$$5Fe(CO)_5 + 6C_5H_5N \longrightarrow [Fe(C_5H_5N)_6][Fe_4(CO)_{13}] + 12CO \qquad (62)$$

The tridecacarbonyltetraferrate anion, which cannot be prepared from iron carbonyls, either by direct reduction or by reaction with strong alkaline solution, is obtained by reaction 62.

By reaction with phenanthroline, pentacarbonyliron gives the octacarbonyldiferrate anion:

$$3Fe(CO)_5 + 3phen \longrightarrow [Fe\ phen_3][Fe_2(CO)_8] + 7CO \qquad (63)$$

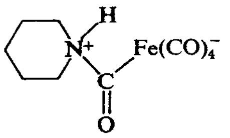
The results obtained by Hieber and co-workers with various nitrogen bases are summarized in Table 10.

In a few cases, a certain amount of the expected carbon monoxide is not evolved since it is fixed in the amine. Thus, for instance, Hieber and co-workers (29) reported that in the reaction between hydrazine hydrate and pentacarbonyliron, semicarbazide is formed.

$$H_2N{-}NH_2 \xrightarrow[H_2O]{Fe(CO)_5} NH_2NHCONH_2 \qquad (64)$$

The mechanism of the reactions between $Fe(CO)_5$ and amines has attracted considerable interest, and therefore many efforts were devoted to the detection of the primary reaction products. Hieber and co-workers (34,35) suggested that addition compounds $Fe(CO)_5 \cdot$amine (with amine being piperidine, morpholine, and phenanthroline) are the precursors to carbonylferrates. These addition compounds are usually unstable and decompose rapidly to give carbonylferrates. In the case of 2-pyridinealdehyde anil a product of composition $[Fe(CO)_5]_2$ PhN=CH—C_5H_4N was isolated (36). This was obtained by heating $Fe(CO)_5$ with the anil in benzene at 80°C. No carbon monoxide evolution was observed during this reaction and the red-brown compound so obtained did not show any conductivity in acetone; it was very soluble in nonpolar solvents, such as benzene and petroleum ether, and its infrared C—O stretching vibrations were all above 1950 cm^{-1}. All this suggested a nonionic formulation for this compound. Also from the reaction of $Fe(CO)_5$ with piperidine, a product of composition $Fe(CO)_5$(piperidine)$_3$ was isolated (35), which was stable only below 0°C. Later, Edgell and co-workers (11) published a detailed spectroscopic investigation of the reactions of $Fe(CO)_5$ with *n*-butylamine and piperidine at room temperature. The results previously published by Hieber and co-workers (34–36) were substantially confirmed and the nature of the formed products defined in a more precise manner.

Three different products were identified spectroscopically. The first one was a species formulated as $Fe(CO)_5$(piperidine)$_3$, then the $[FeH(CO)_4]^-$ anion appeared, and finally a third species, suggested to be $Fe(CO)_4$(piperidine) became evident in the infrared spectrum. The first species was suggested to contain the grouping as shown in Scheme I.



(Scheme I)

Previous results (37) suggesting the disproportionation of $Fe(CO)_5$ in the presence of piperidine were not confirmed:

$$2Fe(CO)_5 \rightleftharpoons [Fe(CO)_6]^{2+}[Fe(CO)_4]^{2-} \qquad (65)$$

The $[Fe(CO)_4]^{2-}$ anion absorbs at 1730 cm^{-1} according to Edgell and co-workers (11); whereas on mixing $Fe(CO)_5$ with piperidine, the lowest frequency band observed (37) in the infrared spectrum was at 1898 cm^{-1}.

Pentacarbonyliron in the presence of oxygen bases. Pentacarbonyliron is not attacked by oxygen Lewis bases, such as methanol. This can be deduced from the fact that pentacarbonyliron is one of the final products of the reaction between methanol and dodecacarbonyltriiron at 70°C (25). On the other hand, pyridine oxide is reduced by $Fe(CO)_5$. With dimethyl sulfoxide (DMSO), triphenylphosphine oxide, and triphenylarsine oxide, at 80°C for several hours in the presence of ultraviolet irradiation, the compounds $[Fe(DMSO)_6][Fe_4(CO)_{13}]$, $[Fe(OPPh_3)_2][Fe_2(CO)_8]$, and $[Fe(OAsPh_3)_3][Fe_2(CO)_8]$ are formed (38).

Enneacarbonyldiiron. No disproportionation reactions of enneacarbonyldiiron in the presence of nitrogen or oxygen Lewis bases have been reported.

TABLE 10

Reactions of Pentacarbonyliron with Nitrogen Bases

Nitrogen base	Reaction conditions				Carbonylferrate anion	Coordination number of Fe^{2+}	Ref.
	Temp. (°C)	Solvent	Time (hr)	Radiation			
Morpholine	Room				$[Fe(CO)_4]^{2-}$	6[a]	33,35
Benzidine	120	Toluene	14			2	41
Phenanthroline	65	Acetone	14		$[Fe_2(CO)_8]^{2-}$	6	34
Ammonia		py				6	39
2-Picoline	80	—	10	UV		2	41
4-Picoline	80	—	10			4	41
2-Aminopyridine	85	Benzene	30			4–6	41
Diethylenetriamine	90	—	14			6	41
2-Formylpyridine	80	Benzene	24	UV		6	36
2-(Methyliminomethyl) pyridine	80	Benzene	20	UV		6	36
2-(Ethyliminomethyl) pyridine	80	Benzene	48	UV		6	36
o-Phenylenediamine	90	Benzene	30		$[Fe_3(CO)_{11}]^{2-}$	6	36
2,2′-Dipyridyl	80	Benzene	24			6	36
Pyridine	85		60	UV	$[Fe_4(CO)_{13}]^{2-}$	6	32
2,4-Dimethylpyridine	85		60			4	35
Piperidine	85	Benzene				6[a]	35
N-Formylpiperidine	95	—	96			6	35
Morpholine	100	—	30			6	35
Morpholine	Room	—	80			6[a]	35
N-Formylmorpholine	80	—	48			6	35
Pyrrolidine	80	Benzene	30	UV		6	35
Dimethylformamide	100	—	12			6	35
Diethylformamide	85	Benzene	60			6	35
Isoquinoline	85	Benzene	20	UV		6	36
Pyrrolidone	80	Benzene	50	UV		6	36
N-Methylpyrrolidone	85	Benzene	48	UV		4	36

[a] The base coordinated to the ferrous ion is the compound arising from the carbonylation of the amine.

Dodecacarbonyltriiron in the presence of nitrogen bases. The reactivity of dodecacarbonyltriiron towards Lewis bases is higher than that of pentacarbonyliron.

The disproportionation reaction may lead to the formation of a mixture of carbonylferrates, whose relative amounts depend on the reaction conditions. Thus, for instance, with liquid ammonia the compound $[Fe(NH_3)_6][Fe_3(CO)_{11}]$ is formed initially (39). In view of the instability of the $[Fe_3(CO)_{11}]^{2-}$ anion, this was suggested (39) to undergo conversion to the anions $[Fe_2(CO)_8]^{2-}$ and $[Fe_4(CO)_{13}]^{2-}$. However, on the basis of additional spectroscopic data this was later recognized to be inexact (33). The initially formed undecacarbonyltriferrate anion is actually converted to the dinuclear anion $[Fe_2(CO)_8]^{2-}$ according to the equation:

$$3[Fe(NH_3)_6][Fe_3(CO)_{11}] + 6NH_3 \longrightarrow 4[Fe(NH_3)_6][Fe_2(CO)_8] + CO \qquad (66)$$

On the basis of the spectroscopic data, no evidence was found for the formation of the $[Fe_4(CO)_{13}]^{2-}$ in the course of this reaction.

The reaction of $Fe_3(CO)_{12}$ with ammonia at room temperature has been studied by Behrens and Wakamatsu (28). After 14 days at room temperature, the anions $[Fe_2(CO)_8]^{2-}$ and $[Fe(CO)_4]^{2-}$ are produced according to the equation:

$$4Fe_3(CO)_{12} + 30NH_3 \longrightarrow 3[Fe(NH_3)_6][Fe_2(CO)_8] + 3(NH_4)_2Fe(CO)_4 + 3CO(NH_2)_2 + 9CO \qquad (67)$$

The reaction with ethylenediamine (en) has been extensively studied by Hieber and co-workers (40). At high temperature $[Fe(CO)_4]^{2-}$ is the main product, whereas $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$ are obtained at milder conditions:

$$Fe_3(CO)_{12} \xrightarrow[40^\circ C]{en} [Fe\,en_3][Fe_3(CO)_{11}] \xrightarrow{90^\circ C} [Fe\,en_3][Fe_2(CO)_8] \xrightarrow[145^\circ C]{} [Fe\,en_3][Fe(CO)_4] \qquad (68)$$

In refluxing acetone or benzene, phenanthroline (34) gives the reaction:

$$Fe_3(CO)_{12} + 3phen \longrightarrow [Fe\,phen_3][Fe_2(CO)_8] + 4CO \qquad (69)$$

Hieber and co-workers (36,41) have also investigated the reaction of dodecacarbonyltriiron with the following bases: 2-methylpyridine, 2-(methyliminomethyl)pyridine, and 2-pyridinealdehyde anil. The reaction products were iron(II) derivatives of the $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$ anions.

Dodecacarbonyltriiron in the presence of oxygen bases. Unlike pentacarbonyliron, dodecacarbonyltriiron reacts with methanol even at room temperature (25). Under reaction conditions varying from 10 days at 20°C to 2 hr at 70°C, the products are pentacarbonyliron (~55%), ferrous methylate (6–11%), and undecacarbonyltriferrate anion, which can be present as the ferrous salt or as the free $Fe_3H_2(CO)_{11}$, depending on the reaction time.

The similar reaction with ethyl alcohol has been shown to occur according to the following stoichiometry:

$$6Fe_3(CO)_{12} \xrightarrow{nROH} [Fe(ROH)_{n-2}][Fe_3H(CO)_{11}]_2 + 10Fe(CO)_5 + Fe(OR)_2 \qquad (70)$$

With pyridine oxide and with dimethyl sulfoxide (38), dodecacarbonyltriiron disproportionates to give the tridecacarbonyltetraferrate anion, whereas with triphenylphosphine and triphenylarsine oxides the corresponding salts containing the octacarbonyldiferrate anion are obtained.

2. *Substitution Reactions*

a. Compounds containing carbon–carbon unsaturated bonds. Many carbonyl olefin π complexes of iron have been described; a number of them are reported in Table 11. Only some of the most interesting aspects of their chemistry and some of the structural problems connected with their formation will be discussed.

The compound $Fe(CO)_3C_4H_6$, obtained from the reaction of $Fe(CO)_5$ with butadiene (42,43), has the structure shown in Fig. 12, as determined

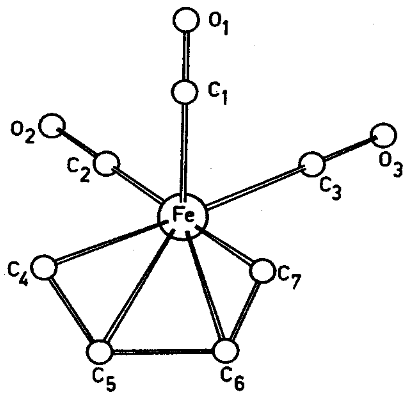


FIG. 12. Structure of the $Fe(CO)_3C_4H_6$ molecule (O. S. Mills and G. Robinson, *Acta Cryst.*, **16**, 758 (1963)).

TABLE 11

Iron Carbonyls with Ligands Having Unsaturated Carbon–Carbon Bonds

Compound	Color	Mp (°C)	ν_{CO} (cm^{-1})	Ref.
(Butadiene)Fe(CO)$_3$	Pale yellow	19	2053, 1985, 1975	42,43,150
(Octafluorocyclohexa-1,3-diene)Fe(CO)$_3$	Pale yellow	45	2108, 2054, 2018	151
(1,1′-Bicyclohexenyl)Fe(CO)$_3$	Orange	33	2034, 1967, 1952	152
(Cycloheptatriene)Fe(CO)$_3$	Yellow	$b_{0.4}$70	2050, 1989, 1975	68–70
(Cyclooctatetraene)Fe(CO)$_3$	Red	92–93.5	2061, 1993, 1976, 1942, 1895, 1845	72–74,81,153
([2,2,1]-Bicycloheptadiene)Fe(CO)$_3$	Orange-red	$b_{0.2}$60.5	—	154
(8,9-Dihydroindene)Fe(CO)$_3$	Yellow	Liquid	—	155
(Hexatriene)$_2$Fe(CO)$_3$	Orange-red	Liquid	2045, 1970	156
(Tetraphenylallene)Fe(CO)$_3$	Red	102–103	2060, 1999, 1985	49,50
(1-Methylallyl)FeCl(CO)$_3$	Yellow	58 dec.	2089, 2042, 2003	95,150,157
(Allyl)FeCl(CO)$_3$	Yellow	88–89 dec.	2096, 2051, 2012	95,150,158
(2-Methylallyl)FeI(CO)$_3$	Dark brown	100	2075, 2029, 2003	159
(Cinnamaldehyde)Fe(CO)$_3$	Red	75–82 dec.	2073, 2015, 1994	92
(Cinnamaldehyde)Fe(CO)$_4$	Yellow	87–92	2096, 2032, 2014, 1980	87
(Acrylonitrile)Fe(CO)$_4$	Yellow	47–48	—	85
(Maleic anhydride)Fe(CO)$_4$	Light yellow	147–148 dec.	2118, 2059, 2047, 2029	86–88
(Methyl methacrylate)Fe(CO)$_4$	—	—	—	89
(Butadiene)Fe(CO)$_4$	Orange	Liquid	2084, 2004, 1981	84,150
(Ethylene)Fe(CO)$_4$	Yellow-orange	b_{12} 34	2088, 2007, 2013, 1986	83
(Vinylcycloheptatriene)Fe$_2$(CO)$_6$	Yellow	126–127	2051, 2037, 1979, 1966	160
(Hexatriene)Fe$_2$(CO)$_8$	Yellow	82.5–83	2085, 2075, 2014, 1994, 1965, 1950	83
(Cyclooctatetraene)Fe$_2$(CO)$_6$	Yellow-orange	~190 dec.	—	72–74,153
(Acenaphthylene)Fe$_2$(CO)$_6$	Red-purple	158	2047,1985	155
(*m*-Divinylbenzene)Fe$_2$(CO)$_6$	Orange	135–136	2045, 1985	65
(*p*-Divinylbenzene)Fe$_2$(CO)$_6$	Yellow	—	—	65
(Azulene)Fe$_2$(CO)$_5$	Dark red	> 100 dec.	2046, 1996, 1976	94
Bis(cyclopentadienyl)Fe$_2$(CO)$_4$	Dark purple	192–194	2005, 1961, 1794.5	56,57,61

by x-ray diffraction studies in the solid state at −40° (44). The butadiene residue has the cisoid arrangement. The C—C distances of the butadiene group (1.45 and 1.46 Å) are identical within experimental error. A plane of symmetry passes through O_1—C_1—Fe and bisects the bond C_5—C_6. The carbon atoms of the butadiene group are coplanar but the trigonal axis of the carbonyl groups makes an angle of 61° with this plane. In this structure the iron is bonded through the π electrons of the two double bonds of the butadiene residue since the iron atom was found to be "closer to the centers of the double bonds than to the carbons themselves." However, Churchill and Mason (45) who have determined the x-ray structure of the similar complex $Fe(CO)_3$(octafluorocyclohexa-1,3-diene), found that the iron atom is in a pseudooctahedral environment and bonded to the planar C_4 unit through one π and two σ bonds. The same authors suggested that a similar arrangement could also exist in butadiene iron tricarbonyl where the π electron density, therefore, would not be completely delocalized, as previously suggested. The structure of the octafluorocyclohexadiene complex is shown in Fig. 13.

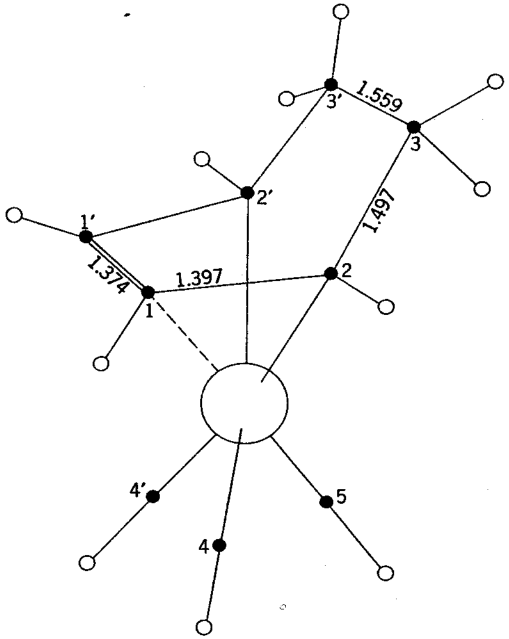
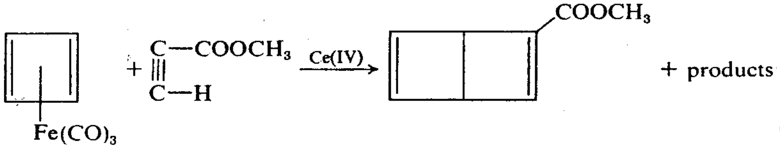


FIG. 13. Molecular configuration of tricarbonyloctafluorocyclohexa-1,3-dieneiron (M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, **1964**, 226. Published by permission).

Iron tricarbonyl complexes of conjugated dienes were isolated from the thermal reactions of $Fe(CO)_5$ with methyl linoleate (46,47). Frankel and co-workers (47) have shown that the (methyl octadecadienoate)tricarbonyliron so obtained is a mixture of isomeric iron tricarbonyl complexes. They also showed that these complexes are soluble hydrogenation catalysts. Gutowski and Jonáš (48) have studied the proton magnetic resonance spectrum of the methyl linoleate iron tricarbonyl compound.

The reactions of iron carbonyls with cumulenes have been reported (49, 50). Tetraphenylallene reacts with $Fe(CO)_5$ in isooctane at reflux temperature to give the red crystalline $Fe(CO)_3C_3Ph_4$. Although both double bonds of the allene system were believed to be involved in the bonding to the metal, a participation of the aromatic unsaturation could not be excluded. The reaction of allene itself with $Fe_3(CO)_{12}$ resulted in the formation of two insufficiently characterized products, namely $[Fe(CO)_3C_3H_4]_2$ and $[Fe(CO)_3C_6H_8]_{1-2}$. An iron carbonyl compound containing an unsubstituted cumulene system was indirectly obtained by reacting $Fe_3(CO)_{12}$ with 1,4-dibromo-2-butyne. In the course of the reaction, dehalogenation of the acetylene compound occurred with formation of the red crystalline $Fe_2(CO)_5C_4H_4$. Possible structures have been considered for this binuclear complex, which shows a doublet in the proton resonance spectrum that suggests the presence of two nonequivalent methylene groups.

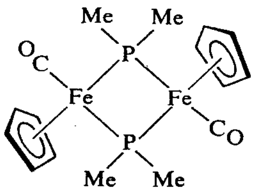
The prediction by Longuet-Higgins and Orgel (51) that cyclobutadiene might be stabilized through complex formation with transition metals has been confirmed by isolation of some metal complexes containing the *substituted* cyclic system. However, no complexes had been known in which cyclobutadiene itself was present. Pettit and co-workers (52) first prepared such a compound, namely tricarbonylcyclobutadieneiron by dehalogenation of *cis*-3,4-dichlorocyclobutene in the presence of $Fe_2(CO)_9$. The complex is a yellow crystalline solid (mp 26°, bp_3 68–70°). The decomposition of the cyclobutadiene complex with ceric ions in the presence of acetylenic compounds results in the formation of Dewar benzene derivatives, which are to be expected from the addition of the acetylenic compound to cyclobutadiene (53). Tricarbonylcyclobutadieneiron represents a new type of aromatic system (54): several electrophilic substitutions, such



(71)

as Friedel-Crafts acylations, have been successfully carried out on this system to obtain new substituted cyclobutadiene iron tricarbonyl complexes.

It is known that the reaction of $Fe(CO)_5$ with cyclopentadiene (55) gives ferrocene, $Fe(C_5H_5)_2$. The first product of the reaction, however, is $Fe_2(C_5H_5)_2(CO)_4$. The latter compound can be better prepared by refluxing $Fe(CO)_5$ with dicyclopentadiene (56,57). The x-ray structure of $Fe_2(C_5H_5)_2(CO)_4$ shows that the molecule is centrosymmetric and contains two bridging and two terminal CO groups (58,59). The Fe—Fe distance (2.94 ± 0.02 Å) indicates the existence of a metal–metal bond. It has since been shown (60) that the infrared spectrum of the compound in solution is not in agreement with the centrosymmetric structure, thus suggesting that the molecule in solution could have a structure different from that of the solid. Noack (61) has shown that some of the bands reported for $CHCl_3$ solutions of the material were due to reaction of $Fe(C_5H_5)_2(CO)_4$ with the solvent. The spectrum in heptane shows two bands due to terminal CO groups and one due to bridging CO groups. It was proposed that $Fe(C_5H_5)_2(CO)_4$ in solution is no longer centrosymmetric with a nonplanar arrangement of the two iron atoms and the two bridging CO groups. In agreement with this, $Fe_2(C_5H_5)_2(CO)_4$ has been found to have a dipole moment of 3.1 D in benzene solution (62). The existence of two isomeric forms of $Fe(C_5H_5)_2(CO)_4$ was excluded by measuring the intensity of the bands at different temperatures. Very interestingly, the reaction of $Fe_2(C_5H_5)_2(CO)_4$ with P_2Me_4 has been shown (63) to give both the *trans* and the *cis* isomers.



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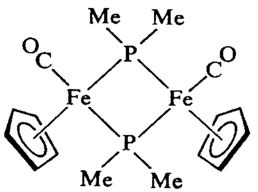
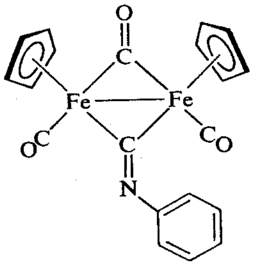


(38)

An isocyanide-substituted tetracarbonylbis(cyclopentadienyl)diiron has been described (64). This complex has the interesting feature of containing a bridging isocyanide group; the two cyclopentadienyl rings and the two terminal CO groups are in *cis* positions, as shown schematically in **39**.

Unlike the group VI metal carbonyls, the carbonyls of iron do not react directly with aromatic hydrocarbons to give carbonyliron-π-arene complexes (65). However, it has been reported that $Fe_3(CO)_{12}$ reacts with *m*- and *p*-divinylbenzenes to give the corresponding binuclear compounds $Fe_2(CO)_6(CH_2{=}CH)_2C_6H_4$, in which the π electrons of the aromatic ring most probably participate in bonding of the ligand to the iron. In contrast, 1,4-diphenylbutadiene reacts with $Fe_3(CO)_{12}$ to give a tricarbonyliron compound in which, on the basis of nuclear magnetic resonance data, the aromatic ring is not involved in the bonding (65).



(39)

Manuel (66) and Harper (67) succeeded in preparing a carbonyl compound of iron with an aromatic hydrocarbon not containing an unsaturated side chain. By treating $Fe_3(CO)_{12}$ with anthracene, the orange $Fe(CO)_3C_{14}H_{10}$ was obtained in very low yields. In this compound, however, only two of the double bonds of anthracene in a terminal ring are believed to be involved in the bonding to iron. As far as the type of bonding is concerned, this compound should resemble $Fe(CO)_3$butadiene rather than $Cr(CO)_3C_6H_6$.

Cycloheptatriene (68) reacts with $Fe(CO)_5$ and $Fe_3(CO)_{12}$ to give the tricarbonyl compound $Fe(CO)_3C_7H_8$ (69,70). The reaction gives also the diene complex $Fe(CO)_3C_7H_{10}$.

A cationic tricarbonyliron derivative containing the tropylium cation was prepared from the reaction of tricarbonyl(methyl tropyl ether)iron with fluoboric acid. The resulting $[Fe(CO)_3C_7H_7]^+$ has one double bond of the unsaturated ligand not involved in the bond to the central metal atom, as indicated by infrared data in the C—H stretching region (71).

Cyclooctatetraene (72–74) reacts with $Fe(CO)_5$ and $Fe_3(CO)_{12}$ to give a mononuclear complex $Fe(CO)_3C_8H_8$ and two binuclear complexes $Fe_2(CO)_6C_8H_8$ and $Fe_2(CO)_7C_8H_8$. $Fe(CO)_3C_8H_8$ shows some peculiar features: it does not absorb hydrogen in the presence of platinum, or add bromine; its nuclear magnetic resonance spectrum shows only one proton resonance peak. Davison, McFarlane, and Wilkinson (75) have observed that $Fe(CO)_3C_8H_8$, after conversion to the protonated complex, can be reduced by $NaBH_4$ in tetrahydrofuran to $Fe(CO)_3C_8H_{10}$, yellow, mp 36.5°C.

The x-ray structures of $Fe(CO)_3C_8H_8$ and $Fe_2(CO)_6C_8H_8$ (76–78) are shown in Fig. 14. In both complexes, the cyclooctatetraene rings are not planar. The $Fe(CO)_3$ groups are associated with four nearly planar carbon atoms in an arrangement very similar to that found for the butadiene compound $Fe(CO)_3C_4H_6$.

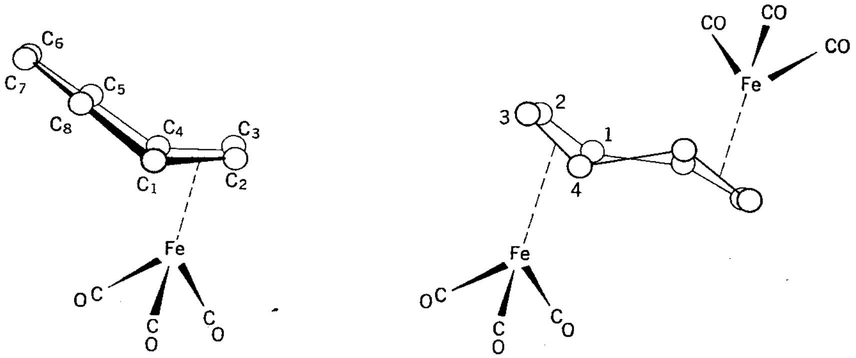
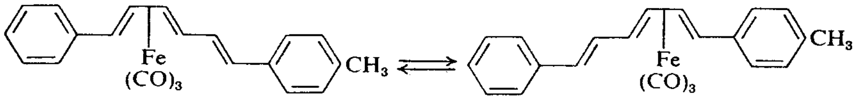


FIG. 14. View of the $Fe(CO)_3C_8H_8$ and $Fe_2(CO)_6C_8H_8$ molecules. (Adapted from B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 and 489 (1961).)

The presence of only one single proton resonance peak in the solution spectrum of $Fe(CO)_3C_8H_8$ was difficult to reconcile with the x-ray structure.

It has been suggested that in solution, the $Fe(CO)_3$ group can rapidly shift around the cyclooctatetraene ring in such a way that the nuclear magnetic resonance signal observed is only a time-averaged representation of the actual situation. A confirmation of this suggestion came from the experimentally observed isomerization of a tricarbonyliron compound containing a conjugated triene system (79,80) as shown in Scheme II.

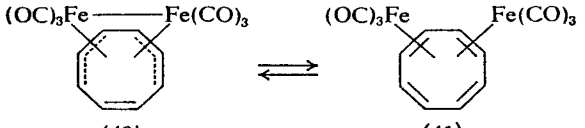


(Scheme II)

In a cyclic and completely conjugated system such as $Fe(CO)_3C_8H_8$, the $Fe(CO)_3$ shift will be favored compared with either an open chain system or with a cyclic system, such as $Fe(CO)_3$(cycloheptatriene), in which the unsaturation is not fully conjugated, although the arrangements are all *cisoid.*

The infrared spectra of $Fe(CO)_3C_8H_8$ were measured (81). The symmetry of the molecule is low (C_s) and is the same either in the solid state or in solution. This eliminates the possibility that the single proton resonance observed is due to a change in structure from the solid state to the solution and confirms that a dynamic effect of the type just mentioned is responsible for the "anomalous" proton resonance spectrum.

It has also been reported (82) that the reaction of cyclooctatetraene with $Fe_2(CO)_9$ gives, in addition to the two complexes already known, two other compounds of formula $Fe_2(CO)_6C_8H_8$, **40** and **41**. Both these complexes were envisaged as having the two $Fe(CO)_3$ groups on the same side of the cyclooctatetraene ring, in contrast with the binuclear isomer of known structure. Furthermore, **40** would be a bis(π-allyl) type of complex, whereas **41** was suggested to be a normal bis-diene compound with the two tricarbonyliron groups *cis* to each other. As indicated by the nuclear magnetic resonance spectra, **40** and **41** are in equilibrium.



(40) **(41)**

Tetracarbonyliron complexes of ethylene (83) and butadiene (84) of general formula $Fe(CO)_4$(olefin) can be obtained by the direct reaction of $Fe_2(CO)_9$ with the olefinic compounds. Tetracarbonyl derivatives of acrylonitrile (85), maleic anhydride (86–88), methyl methacrylate (89), and other olefins with electron-withdrawing substituents have been prepared by the reaction of the unsaturated ligand with $Fe_2(CO)_9$ or with $Fe(CO)_5$ under ultraviolet (89) or γ-ray (88) irradiation. The ligand is probably bonded to the metal through the carbon–carbon double bond. This was originally suggested by Kettle and Orgel (85) for the acrylonitrile compound on the basis of infrared data and it has been recently confirmed by x-ray work (90). The molecule $Fe(CO)_4(CH_2{=}CHCN)$ is virtually a trigonal bipyramid (cf. $Fe(CO)_5$) in which one of the equatorial positions is occupied by the center of the carbon–carbon double bond. The distances from the iron atom to the two vinyl carbon atoms are 2.09 and 2.10 Å.

The existence of optical isomers in tetracarbonyliron complexes of this type becomes possible when the symmetry of the olefin ligand is low. Tetracarbonyl(fumaric acid)iron has actually been resolved into the two enantiomers by fractional crystallization of the monobrucine salt (91).

With cinnamaldehyde, in addition to the yellow tetracarbonyl compound, a red tricarbonyl derivative $Fe(CO)_3(PhCH{=}CHCHO)$ has also been reported (92) in which the carbonyl group of the aldehyde function is involved in bonding to the metal.

Iron carbonyl compounds with substituted fulvenes have also been reported (93). The azulene complex $Fe_2(CO)_5C_{10}H_8$ was reported some years ago (68). Several substituted azulene derivatives of the same type have been described (94) and a new type of isomerism has been postulated to explain some peculiar features of these compounds.

Enneacarbonyldiiron has been reported (95) to react with allyl halides to give π-allyl complexes of formula $Fe(C_3H_5)(CO)_3X$, with X being Cl, Br, and I. In these compounds, the iron atom was considered to be symmetrically bonded to the three carbon atoms of the allyl group, similarly to the analogous cobalt complex $Co(C_3H_5)(CO)_3$ (see Sec. V—C—2). By reductive dehalogenation with $Na[FeC_5H_5(CO)_3]$ or $NaMn(CO)_5$, or by treatment with deactivated alumina, the halogenoallyl derivatives can be converted to the dimeric $[Fe(C_3H_5)(CO)_3]_2$ (96). Electron spin resonance measurements have enabled the detection of the monomeric paramagnetic species in equilibrium with the dimer:

$$[Fe(C_3H_5)(CO)_3]_2 \rightleftharpoons 2Fe(C_3H_5)(CO)_3 \tag{72}$$

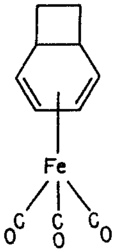
Rearrangement and isomerization of olefinic compounds have been shown to occur in the presence of carbonyls of iron. Nonconjugated dienes isomerize to the corresponding conjugated compounds (97); for example, 1,5-cyclooctadiene is quantitatively converted to 1,3-cyclooctadiene. Terminal olefins are converted to internal olefins when heated with $Fe(CO)_5$ (98,99). If ultraviolet irradiation is also present, isomerization occurs under milder conditions (50°C for 1-undecene) (100). Apparently the effect of radiation is not simply that of converting $Fe(CO)_5$ into $Fe_2(CO)_9$, which then would be solely responsible for the isomerization. Enneacarbonyldiiron alone is, in fact, capable of isomerizing 1-undecene but to a smaller extent under comparable conditions. Isomerization of olefins under ultraviolet irradiation has been considered as taking place via the intermediate formation of an iron tetracarbonyl olefin complex (101):

$$Fe(CO)_5 \rightleftharpoons \{Fe(CO)_4\} + CO \tag{73}$$

$$\{Fe(CO)_4\} + \text{olefin} \longrightarrow Fe(CO)_4\,(\text{olefin}) \tag{74}$$

The inhibiting effect of carbon monoxide and Lewis bases, such as diethylamine and triphenylphosphine, has been interpreted as a competition effect by the added base on the intermediate coordinately unsaturated species.

Rearrangements have also been reported to occur during the coordination of the olefin to the metal. For example, a mixture of 1,3,5- and 1,3,6-cyclooctatriene reacts with $Fe_3(CO)_{12}$ or $Fe(CO)_5$ to give (bicyclo[4,2,0]-octa-2,4-diene)$Fe(CO)_3$ **(42)** and (1,3,5-cyclooctatriene)$Fe(CO)_3$ **(43)** (102,103). The previous report (104) concerning the preparation of (1,3,6-cyclooctatriene)$Fe(CO)_3$ from the same isomeric mixture and $Fe_2(CO)_9$ was not confirmed. In the course of the reactions of $Fe(CO)_5$ with noncyclic diolefins, iron tricarbonyl complexes are formed in which the bonded diene is structurally different from the starting diolefins (105). For example, both *cis*-1,3-pentadiene and 1,4-pentadiene yield $Fe(CO)_3$-(*trans*-1,3-pentadiene) (see diagram 75).



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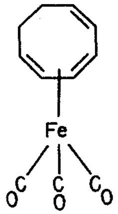

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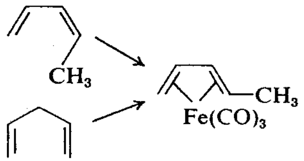
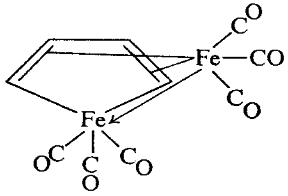


(75)

Once the system becomes conjugated, the subsequent main requirement seems to be that of providing the least steric crowding in order to form a stable iron tricarbonyl complex.

Mössbauer resonance studies of several olefin complexes of iron carbonyls have appeared (106–108). Many other interesting reactions of unsaturated compounds with iron carbonyls have been reported and will be briefly mentioned here, although strictly speaking, they do not belong in the category of substitution reactions. Some of them, however, are worth mentioning. Thiophene reacts (68) with $Fe(CO)_5$ or, better, with $Fe_3(CO)_{12}$ with replacement of sulfur by iron and formation of compound **44** (109). This has an infrared spectrum identical with that of the product obtained from $Fe_3(CO)_{12}$ and acetylene (110). The reaction of $Fe_3(CO)_{12}$ with tetrafluoroethylene (111) gives a stable, sublimable compound (mp 77°) to which structure **45** has been assigned (112,113).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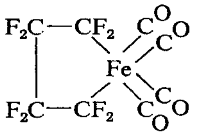

(45)

b. With P-, As-, and Sb-containing ligands. Several years ago Hieber and Wirsching (114) described the reaction of $Fe(CO)_5$ with $SbCl_5$ at −20° in CCl_4: no gas was evolved in this reaction and a yellow precipitate was obtained. At −5°, a vigorous evolution of carbon monoxide occurred and brown-orange crystals having the composition $Fe(CO)_4SbCl_5$ were found. This compound is soluble in benzene and is probably dissociated in solution to $Fe(CO)_4Cl_2 + SbCl_3$.

The compound $Fe(CO)_3(SbCl_3)_2$ has been obtained (115) by the room temperature reaction of $Fe(CO)_5$ with $SbCl_3$; this compound is an amorphous powder insoluble in common organic solvents (Table 12).

Substitution products with triarylphosphines, $Fe(CO)_4PPh_3$, $Fe(CO)_3(PPh_3)_2$, and the mixed $Fe(CO)_3(PPh_3)(SbPh_3)$, were first reported by Reppe and Schweckendiek (116). Cotton and Parish (117), on the basis of infrared spectral measurements, have suggested that compounds $Fe(CO)_4L$ and $Fe(CO)_3L_2$ ($L = PPh_3$) have a trigonal bipyramidal configuration. Further, the disubstitution products probably have the *trans* configuration (**46**). This has later been confirmed by Reckziegel and Bigorgne (118*a*). Pentacarbonyliron reacts thermally with tertiary phosphines and phosphites to give monosubstitution and bisubstitution products, the latter having the *trans* configuration. In an attempt to prepare the still

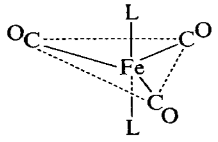
TABLE 12

Iron Carbonyls with Phosphorus-, Arsenic-, and Antimony-Containing Ligands

Compound	Color	Mp (°C)	ν_{CO}(cm^{-1})	Ref.
$Fe(CO)_4PPh_3$	Pale yellow	201–203	2055, 1978, 1943	116,117,161
$Fe(CO)_4P(NMe_2)_3$	Yellow	46–85	2041, 1969, 1930	162
$Fe(CO)_4PF_3$	Yellow	Liquid	2101, 2094, 2021, 2004, 1996, 1970, 1960	120
$Fe(CO)_3(PPh_3)_2$	Yellow	272	1884.8	116,117,161
$Fe(CO)_3(P(NMe_2)_3)_2$	Colorless	200–203	1871	162
$[Fe(CO)_3IP(CF_3)]_2$	Red	—	2127, 2088	125
$Fe(CO)_3$ Diphos[a]	Yellow	144–145	1984, 1912, 1890	121,122
$Fe(CO)_3(PPh_3)(SbPh_3)$	—	242	—	116
$Fe_2(CO)_8$ Diphos	—	170–172	2053, 1980, 1938	119,122
$Fe_2(CO)_8P_2Me_4$	Orange	146–148 dec.	2059, 2049, 1982, 1947	123,163
$Fe_2(CO)_6P_2Me_4$	Yellow	170 dec.	2047, 2009, 1976, 1963	123
$Fe_2(CO)_6P_2Et_4$	Orange	143–145	2045, 2007, 1972, 1962	123
$Fe(CO)_4AsPh_3$	Yellow	178	2053.7, 1977.1, 1945.3	161
$Fe(CO)_3(AsPh_3)_2$	Yellow	193–195	1884.3	161
$Fe(CO)_3Diars$	Golden yellow	131	1996, 1916, 1877	119,164
$Fe(CO)Diars_2$	Dull yellow	150 dec.	1953	164,165
$Fe_2(CO)_6As_2Me_4$	Orange	> 350 dec.	2037, 2024, 1998, 1965, 1958	123
$Fe(CO)_4SbPh_3$	Yellowish brown	136	2048.0, 1975.3, 1942.3	161
$Fe(CO)_3(SbPh_3)_2$	Brown	196	1882.0	161
$Fe(CO)_3(SbCl_3)_2$	Pale yellow	—	—	115

[a] Obtained by ligand exchange from $Fe(CO)_3C_8H_8$.

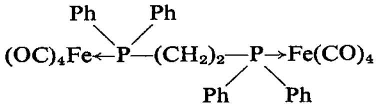
elusive *cis* isomers, the above-mentioned authors (118*a*) heated tricarbonylbutadieneiron and tricarbonylcycloheptatrieneiron with a phosphorus-containing ligand. However, one of the CO groups rather than the hydrocarbon ligand was displaced from the complex and compounds of the type $Fe(CO)_2(C_4H_6)L$ were obtained. The carbon monoxide displacement reaction from tricarbonylbutadieneiron by tertiary phosphines and phosphites had been previously reported by Nesmeyanov and co-workers (118*b*).



(46)

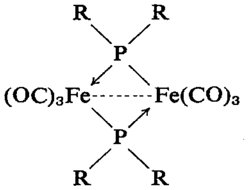
Several other phosphine- arsine-, and stibine-substituted derivatives of iron carbonyl have been described. The preparation of the complexes is usually carried out by heating the carbonyl of iron with the ligand in the presence of a solvent. The ultraviolet-initiated preparation of some arsine- and phosphine derivatives of iron has been reported (119). Compounds of the type $Fe(CO)_{5-x}(PF_3)_x$, with x ranging from 1 to 5, have been prepared by direct interaction of $Fe(CO)_5$ with PF_3 at elevated temperatures and pressures (120).

Particularly interesting are the products obtained with bidentate phosphines, such as bis(diphenylphosphino)ethane. The disubstitution product $Fe(CO)_3C_2H_4(PPh_2)_2$ was obtained (121,122) by ligand exchange from $Fe(CO)_3C_8H_8$. The direct reaction of $Fe(CO)_5$ with the same phosphine gives, however, the bridged complex **47**. With diphosphines and diarsines such as $R_2P{-}PR_2$, tricarbonyl and tetracarbonyl derivatives of the type **48** and **49** have been obtained (123). Dodecacarbonyltriiron and tetramethyldiphosphine in benzene at reflux temperature give (124) a tetracarbonyl complex of type **49**.



$$(OC)_4Fe \leftarrow \overset{Ph\ \ Ph}{\underset{Ph\ \ Ph}{P}}{-}(CH_2)_2{-}P \rightarrow Fe(CO)_4$$

(47)



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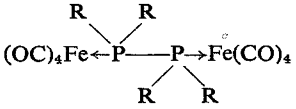


$$(OC)_4Fe \leftarrow \overset{R\ \ R}{P}{-}\underset{R\ \ R}{P} \rightarrow Fe(CO)_4$$

(49)

An interesting reaction of $Fe(CO)_5$ with bis(trifluoromethyl)iodophosphine $(CF_3)_2PI$ has been described (125). A complex $[Fe(CO)_3P(CF_3)_2I]_2$ that does not appear to have CO bridges has been obtained. Clearly, the phosphine molecule has been split as shown in **48** and iodine or phosphorous bridges were formed.

$Fe(CO)_4EPh_3$ and $Fe(CO_3(EPh_3)_2$, E = P, As, give stable yellow solutions in 98% sulfuric acid (126) and each of their nuclear magnetic resonance spectra shows a high field proton resonance line at about 18 τ. It is believed that the species present are of the type $[FeH(CO)_{4-x}(EPh_3)_{1+x}]^+$, the protonation occurring at a lone pair on the iron. It has also been shown that the isotopic ^{14}CO exchange reaction in phosphine-substituted carbonyls of iron, normally very slow, is accelerated in the presence of acids, such as trifluoroacetic and sulfuric (127). Only three of the CO groups in $Fe(CO)_4P(C_6H_5)_3$ exchange, after a certain induction time.

c. S-, Se-, and Te-containing ligands. According to Dewar and Jones (128), $Fe(CO)_5$ does not react with sulfur in the cold in carbon tetrachloride and xylene solutions. The compounds $Fe_2(CO)_6S_2$ and $Fe_3(CO)_9X_2$ (X = S, Se, Te), which can be considered as substitution products of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, have been obtained by the indirect reaction (129) of tetracarbonylferrate with sodium polysulfide and XO_3^{2-}, respectively. The x-ray structures of $Fe_3(CO)_9Se_2$ (130), $Fe_3(CO)_9S_2$ (131), and $Fe_2(CO)_6S_2$ (132) have been published; also see Table 13 for other data.

The configurations of the three molecules are represented in **50**, **51**, and **52**. In $Fe_3(CO)_9Se_2$, two iron atoms (3.51 Å apart) are held together by selenium bridges; the third iron atom is bonded to these iron atoms as well as to the two selenium atoms. The coordination number of the third iron atom therefore is probably seven. As it is known from its x-ray structure, **52** represents the first example of a transition metal complex containing two bridging sulfur atoms. The two sulfur atoms in this complex are at a bonding distance of 2.01 Å. King (133) reported that the reaction of $Fe_3(CO)_{12}$ with cyclohexene episulfide gives a purple-red $Fe_3(CO)_9S_2$ which appeared different by color, melting point, and infrared spectrum from the $Fe_3(CO)_9S_2$ previously reported by Hieber and Gruber (129). Later it was shown that the product isolated by King was a 1:1 mixture of $Fe_3(CO)_9S_2$ and $Fe_2(CO)_6S_2$ (131). The reaction conditions and the

TABLE 13

Iron Carbonyls with Sulfur-, Selenium-, and Tellurium-Containing Ligands, Isocyanides, and Ammonia

Compound	Color	Mp (°C)	ν_{CO}(cm^{-1})	Ref.
$Fe_2(CO)_6S_2$	Ruby red	—	2081, 2042, 2005	129
$Fe_3(CO)_9S_2$	Deep red	—	2062, 2045, 2024 1985	129
$Fe_3(CO)_9Se_2$	Black-violet	—	2058, 2040, 2018, 1985	129
$Fe_3(CO)_9Te_2$	Black	—	2074, 2045, 2026, 2004, 1976, 1959	129
$Fe_2(CO)_8SO_2$	Yellow	120–125 dec.	2137, 2092, 2070, 2058, 2024	141
anti-$[Fe(CO)_3SMe]_2$	Red	65–67.5	2085, 2050, 2000	136–138
syn-$[Fe(CO)_3SMe]_2$	Orange	101.5–103.5	2075, 2040, 2000	137,138
$[Fe(CO)_3SEt]_2$	—	75	2075, 2038, 2003, 1992, 1956	2,140,166
$[Fe(CO)_3SPh]_2$	Brick red	140	2073, 2038, 2003, 1957	135,136, 140
$[Fe(CO)_3Te(p\text{-}MeOC_6H_4)]_2$	Red-brown	—	2062, 2026, 1996, 1988	143
$Fe(CO)_4TePh_2$	Brown	—	2096, 2030, 2000, 1968	143
$Fe(CO)_4$(dimethyl sulfoxide)	Yellow	60–62	—	142
$Fe(CO)_4$ (tetramethylene sulfoxide)	Yellow	82–84	—	142
$[Fe(CO)_3CH_2S]_2$[a]	Red	76–77	2080, 2045, 2000	167
$Fe_2(CO)_6C_4F_6S_2$[b]	Red-black	80.5–81.5	2120, 2080, 2030	167
$Fe_2(CO)_6C_2F_4S_2$[c]	Dark red	70–72	2110, 2070, 2030	167
$Fe_2(CO)_6(CH_3SCH{=}CH_2)$[d]	Orange	—	2073, 2038, 2002, 1995	168
$Fe(CO)_4(CNMe)$	Light yellow	31.5	2072, 1996, 1967	117,144
$Fe(CO)_3(CNMe)_2$	Yellow-orange	100–130	2009vw, 1925s	117,114
$Fe(CO)_3(CNMe)(CNEt)$	Yellow	60	—	169
$Fe(CO)_4(CNSiMe_3)$	Yellow	47–48	2050, 1996, 1972	117,170
$Fe(CO)_4(CNGeMe_3)$	Yellow	69–70	2057, 1997, 1968	117,170
$Fe(CO)_4(CNCMe_3)$	Pale yellow	53.5–54.5	2066, 1997, 1966	117
$Fe(CO)_3(CNCMe_3)_2$	Yellow	98–98.5	2006vw, 1923s	117
$Fe(CO)_4NH_3$	Yellow	—	2047, 1988, 1931	146,147
$[Fe(CO)_3NH]_2$	Orange	81.5	2074, 2032, 1987	147

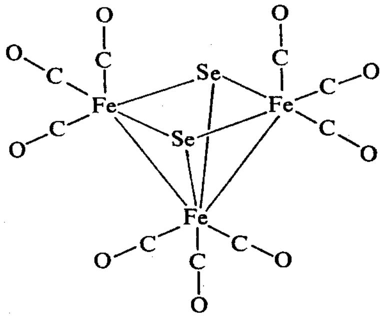
[a] From $Fe(CO)_5$ and 1,2-ethanedithiol.

[b] From $Fe(CO)_5$ and bis(trifluoromethyl)dithietene.

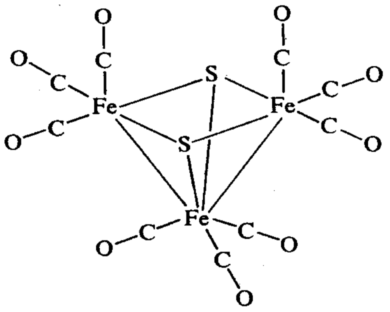
[c] From $Fe_3(CO)_{12}$ and $(CF_2)_2S_4$.

[d] From $Fe_3(CO)_{12}$ and methyl vinyl sulfide.

isolation procedure are probably very critical. Havlin and Knox (134) have in fact shown that $Fe_2(CO)_6S_2$ is a minor component of the reaction and that the main product is $Fe_3(CO)_9S_2$, identical with the compound previously described by Hieber and Gruber.



(50)



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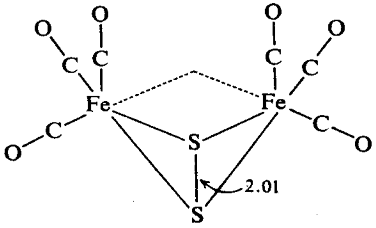


(52)

Compounds of the general type $[Fe(CO)_3SR]_2$ ($R = CH_3, C_2H_5, C_6H_5$) have been prepared by reacting $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with alkyl mercaptans or dialkyl disulfide. The dimeric nature of this type of compound was first recognized by Kettle and Orgel (135).

$[Fe(CO)_3SCH_3]_2$, originally prepared from $Fe_3(CO)_{12}$ and dimethyl sulfide (136), has been obtained from $Fe_3(CO)_{12}$ and dimethyl disulfide (137) and shown by chromatography on alumina to consist of a mixture of two isomers. It was suggested that the two isomers differ in the relative orientation of the two methyl groups; they were designated *syn* and *anti* isomers (138). By an improved method, $[Fe(CO)_3SCH_3]_2$ can be prepared in 60% yields from $Fe(CO)_5$ and dimethyl disulfide in the presence of carbon monoxide under pressure (138).

The crystal structure (139) of the ethyl derivative $[Fe(CO)_3SC_2H_5]_2$ consists of two sulfur-bridged iron atoms, each bonded to three CO groups (see Fig. 15). The iron atoms are in a distorted tetragonal pyramidal arrangement. The ideal C_{2v} symmetry of the molecule is destroyed by the orientation of the ethyl groups. The distances (Å) are: $Fe_1—Fe_2$ 2.537 ± 0.01, $Fe_1—S_3$ 2.266 ± 0.013, $Fe_1—S_4$ 2.221 ± 0.014, $Fe_2—S_3$ 2.284 ± 0.012, $Fe_2—S_4$ 2.264 ± 0.011. The previous suggestion (140), mainly based on dipole moment measurements, that compounds of the type $[Fe(CO)_3X]_2$ (with X = S, Se, SC_2H_5, SC_6H_5) should have a nonplanar arrangement of the

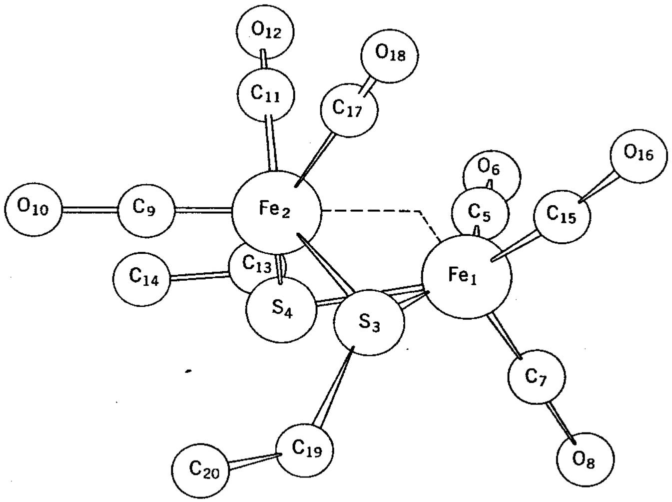
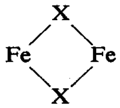


FIG. 15. The molecular configuration of $[Fe(CO)_3SC_2H_5]_2$ (L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963)). Published by permission.



group, is completely confirmed.

A dimeric substituted iron carbonyl has been obtained by reacting $Fe_2(CO)_9$ with liquid sulfur dioxide. This compound, of formula $Fe_2(CO)_8SO_2$, was regarded as having a structure with an SO_2 bridge between the two iron atoms (141).

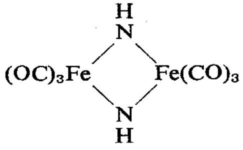
By using irradiation techniques, Strohmeier and co-workers (142) succeeded in preparing iron tetracarbonyl derivatives of the type $Fe(CO)_4L$, with L being tetramethylene sulfoxide and dimethyl sulfoxide. In these two compounds, the ligand was considered to be bonded to the metal through the sulfur atom.

Bis(*p*-methoxyphenyl)ditelluride reacts with $Fe_3(CO)_{12}$ to give a derivative of the general type $[Fe(CO)_3X]_2$. Diphenyltellurium, however, reacts differently and the mononuclear $Fe(CO)_4TePh_2$ is obtained (143).

d. Isonitriles and isocyanates. Mono- and disubstitution products $Fe(CO)_4CNR$ and $Fe(CO)_3(CNR)_2$ can be obtained (117,144) by reacting $Fe(CO)_5$ with isocyanides (R = Me, Et, *p*-$MeOC_6H_4$, CMe_3). Even under drastic conditions, only two CO groups can be replaced in $Fe(CO)_5$. Similarly, disubstitution products could be obtained from $Fe_3(CO)_{12}$. As for the phosphine-substituted compounds, Cotton and Parish (117) have found that the isonitrile derivatives most probably have a trigonal bipyramid configuration, with one or two of the axial positions occupied by the isonitrile groups.

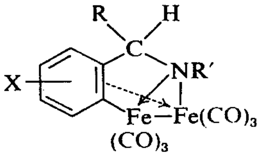
Manuel (145) has reported the isolation of an isocyanato complex of formula $[Fe(CO)_3(PhNCO)]_2$, for which an isocyanato-bridged structure was suggested. The formula $[Fe(CO)_4(PhNCO)]_2$ could not be excluded, although it was considered less probable.

e. Nitrogen-containing ligands. Because of the great tendency of carbonyl derivatives of iron to give valence disproportionation with N-bases, no examples are known of direct replacement of CO groups from any carbonyl of iron by aliphatic or aromatic amines. However, $Fe(CO)_4NH_3$, which has been considered formally as a true substitution product of $Fe(CO)_5$, has been prepared in an indirect way by the reaction of $[FeH(CO)_4]^-$ with hydroxylamine-*O*-sulfonic acid (146). By reaction of $[Fe(CO)_4]^{2-}$ with NO_2^- or NH_2OH, the volatile orange $[Fe(CO)_3NH]_2$ was obtained. For this compound the nitrogen-bridged structure **53** has been proposed (147).



(53)

Pauson and co-workers (148) have described the reaction of $Fe_2(CO)_9$ with Schiff bases derived from aromatic aldehydes and ketones and that of $Fe(CO)_5$ with azobenzenes in the presence of ultraviolet irradiation. For the compounds obtained, the formulations **54** and **55** were proposed. A dimeric nitrosobenzene complex of iron has been prepared by the reaction of $Fe(CO)_5$ with nitrobenzene in the presence of ultraviolet irradiation (149). To this complex, the NO-bridged structure **56** has been assigned.



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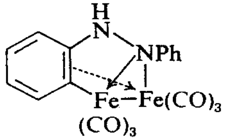

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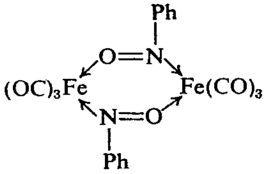

(56)

A detailed discussion of the reactions of nitrogen compounds with metal carbonyls will be found in the chapter by Rosenthal and Wender.

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E. Carbonyls of Group VII Transition Metals

1. Reactions Involving Changes in Oxidation Number

a. Oxidations. The carbonyls of this group are air stable in the solid state and are slowly oxidized in solution. Dilute acids and also often concentrated acids do not attack $Re_2(CO)_{10}$ (1).

These carbonyls are not decomposed by chlorine, bromine, and iodine, but rather are converted into the corresponding halogenopentacarbonyls, $MX(CO)_5$ (see Sec. IX).

Attempts to obtain fluorocarbonylrhenium derivatives by reaction of fluorine with decacarbonyldirhenium (2) were unsuccessful because no reaction occurred at 25°C, whereas at higher temperatures extensive

oxidation occurred with formation of ReF_6. It is of great interest that, when ReF_6 was reacted with $Re_2(CO)_{10}$, blue crystals of the oxytetrafluoride $ReOF_4$ were isolated. Formation of this compound requires a splitting of the carbon–oxygen bond of carbon monoxide. Analogous results were obtained by reacting ReF_6 with the hexacarbonyls of molybdenum and tungsten.

The pseudohalogeno derivative, $Mn(CO)_5SCN$, was prepared by reacting $Mn_2(CO)_{10}$ with thiocyanogen (3). By the action of N_2O_4 at 0°C on $Mn_2(CO)_{10}$, the compound $Mn(CO)_5NO_3$ was obtained (4). In both these compounds, manganese can be formally considered to be in an oxidation state of $1+$.

b. Reductions. Compounds containing the anions $[M(CO)_5]^-$, with $M = Mn$, Tc, and Re, are known, but only the anion $[Mn(CO)_5]^-$ is sufficiently stable in alkaline aqueous solution; the other anions are readily hydrolyzed.

The simplest method for the preparation of the pentacarbonyl-metallates of this group is treatment of the carbonyls with sodium amalgam, sodium, or other electropositive metals. Tetrahydrofuran is the most commonly used solvent; the reduction is carried out at room temperature. In the case of sodium, the reduction occurs according to the following stoichiometry:

$$M_2(CO)_{10} + 2Na \longrightarrow 2NaM(CO)_5 \qquad (76)$$

The formation of $[Mn(CO)_5]^-$ under these conditions has been first reported by Brimm and co-workers (5) and later described in detail by Hieber and Wagner (6,7).

A detailed description of the experimental procedure for the preparation of $NaMn(CO)_5$ is given by King and Stone (8).

It has been reported that, by reduction of $Re_2(CO)_{10}$ in dimethyl ether with sodium amalgam in a sealed tube (9), the corresponding sodium pentacarbonylrhenate can be isolated in the pure state, whereas when tetrahydrofuran is used as solvent, the solvated salt $NaRe(CO)_5 \cdot 0.5\text{–}2C_4H_8O$ is obtained. This latter can be obtained free from solvent by heating in high vacuum, although some decomposition occurs during this operation.

With lithium amalgam in diethyl ether, $LiRe(CO)_5$ is obtained. In the case of decacarbonylditechnetium (10) the reaction took place with appreciable evolution of carbon monoxide. From the acidified product was isolated a polynuclear technetium carbonyl, formulated as $Tc_3(CO)_{12}$ (possibly $Tc_3H_3(CO)_{12}$), in addition to the expected $TcH(CO)_5$.

The reaction of $Mn_2(CO)_{10}$ with $NaBH_4$, followed by acidification with

H_3PO_4, was reported to produce the polynuclear hydridocarbonyls, $Mn_2H_2(CO)_9$ (11), $Mn_3H_n(CO)_{12}$ (12), and $Mn_3H(CO)_{10}(BH_3)_2$ (13). These compounds will be discussed more fully in Sec. VI. Similarly, the yellow-orange color observed (9) when $Re_2(CO)_{10}$ is reduced with lithium in tetrahydrofuran was attributed to the presence of polynuclear carbonylrhenates.

Decacarbonyldimanganese is not affected by aqueous sodium hydroxide (5). Alcoholic alkalies, however, attack it rapidly at room temperature (6,7) with partial oxidation of CO to CO_3^{2-} and reduction of manganese(0) to manganese(I−). The reaction takes place according to the following overall equation:

$$13Mn_2(CO)_{10} + 40OH^- \longrightarrow 2Mn^{2+} + 24[Mn(CO)_5]^- + 10CO_3^{2-} + 20H_2O \quad (77)$$

Unless the solution is strongly alkaline, the pentacarbonylmanganate anion is hydrolyzed by water. In alkaline solution it can be titrated by iodine, according to the equation:

$$2[Mn(CO)_5]^- + I_2 \longrightarrow Mn_2(CO)_{10} + 2I^- \quad (78)$$

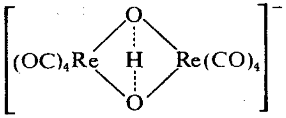
The complex salts with [Ni phen$_3$]$^{2+}$, [Fe phen$_3$]$^{2+}$, $[Cr(C_6H_6)_2]^+$, $[Co(C_5H_5)_2]^+$, and the mercury salts $Hg[Mn(CO)_5]_2$ and $Hg[Mn(CO)_5]_2 \cdot HgX_2$ (X = Cl, Br, I) have been described (14).

It is to be noted that the complex salt containing the dibenzenechromium(I) cation decomposes *in vacuo* at 20–60°C, according to the following oxidation-reduction equation:

$$2[Cr(C_6H_6)_2][Mn(CO)_5] \longrightarrow 2Cr(C_6H_6)_2 + Mn_2(CO)_{10} \quad (79)$$

On the other hand, the cobalticinium complex $[Co(C_5H_5)_2][Mn(CO)_5]$ is so stable that it can be sublimed without decomposition at 160–180°C under high vacuum.

Decacarbonyldirhenium reacts differently with alkali (15). During the reaction, hydrogen evolution occurs and a binuclear anion is obtained, to which structure **57** has been assigned.



(57)

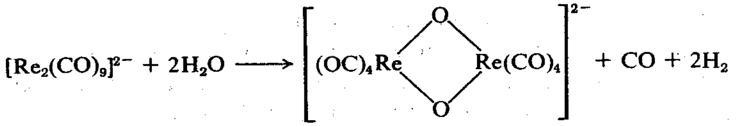
The reaction occurs according to the equation:

$$Re_2(CO)_{10} + 3KOH + H_2O \longrightarrow K[Re_2(CO)_8O_2H] + K_2CO_3 + CO + 2H_2 \quad (80)$$

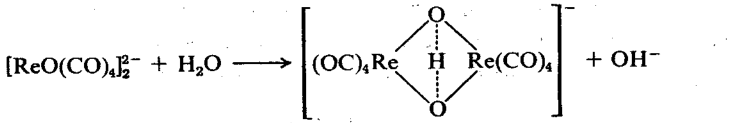
In this reaction one mole of carbon monoxide is oxidized to carbonate ion and the second mole is converted to formate.

The formation of $[Re_2(CO)_8O_2H]^-$ was considered (9) to result from the following reactions:

$$Re_2(CO)_{10} + 4OH^- \longrightarrow [Re_2(CO)_9]^{2-} + CO_3^{2-} + 2H_2O \quad (81)$$



(82)



(83)

Equation 81 represents the usual reduction of the carbonyl with oxidation of the equivalent amount of carbon monoxide to carbonate ion.

c. Disproportionation reactions. Decacarbonyldirhenium was reported to react slowly with nitrogen Lewis basis and only carbon monoxide substitution was observed (16).

With pyridine at 240°C and phenanthroline at 120°C, the compounds $Re(CO)_3py_2$ and $Re(CO)_3$phen were reported. Whether these compounds are monomeric or dimeric does not seem to have been investigated as yet. Decacarbonyldimanganese reacts by substitution or by disproportionation, depending on the nature of the Lewis base employed. Hieber and coworkers report (11,17) that with tertiary phosphines and phosphites or with weak nitrogen bases, such as aniline and *o*-phenylenediamine, substitution products are formed exclusively. With stronger bases, such as pyridine, γ-picoline, diethanolamine, morpholine, ethylenediamine, diethylenetriamine, and piperidine, the following disproportionation reaction occurs:

$$3Mn_2(CO)_{10} + 2nB \longrightarrow 2[Mn(B)_n][Mn(CO)_5]_2 + 10CO \quad (84)$$

In Eq. 84, B is the nitrogen compound, and *n* is 6, 3, and 2 with mono-, bi-, and tridentate ligands, respectively. The reaction is strictly similar to that of octacarbonyldicobalt, but it takes place under more drastic conditions; temperatures of 50–120°C are frequently required. *p*-Methoxyphenyl isocyanide reacts at 100°C in the same way.

It seems reasonable to assume that reaction 84 occurs through the initial cleavage of the metal–metal bond followed by formation of a salt in which the amine is coordinated to the cationic part as $[Mn(CO)_5(amine)]^+$.

Infrared evidence (11) suggests that the intermediate salt is formed in the course of the reaction of $Mn_2(CO)_{10}$ with *n*-butylamine at room temperature:

$$Mn_2(CO)_{10} + C_4H_9NH_2 \longrightarrow [Mn(CO)_5(C_4H_9NH_2)][Mn(CO)_5] \qquad (85)$$

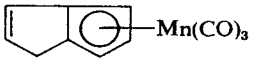
The reaction is reversible and the original carbonyl can be recovered upon evaporation of the reaction mixture *in vacuo.*

Bidentate nitrogen bases, such as phenanthroline, react with $Mn_2(CO)_{10}$ in the dark in nonpolar solvents (17) to yield a symmetrical diamagnetic substitution product, $Mn(CO)_3phen–Mn(CO)_5$. This, on irradiation with visible light, splits into $[Mn(CO)_3phen]_2$ and $Mn_2(CO)_{10}$. However, in polar solvents the reaction with 2,2′-dipyridyl takes place according to the disproportionation reaction (84).

2. *Substitution Reactions*

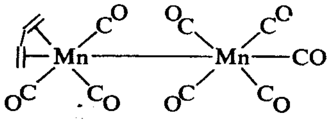
a. Compounds containing carbon–carbon unsaturated bonds. Comparatively few reactions of decacarbonyldimanganese and technetium and rhenium analogs with unsaturated hydrocarbons are known. Both the lower reactivity and the relatively recent isolation of these carbonyls (as compared with iron and cobalt carbonyls) are responsible for the still limited number of complexes of this type reported so far.

Unlike $Co_2(CO)_8$, acetylenes do not give substitution products with $Mn_2(CO)_{10}$. Decacarbonyldimanganese and acetylene at 150°C give (18) a 40% yield of a yellow viscous oil, $b_{18}144°$, which was shown to be tricarbonyldihydropentalenylmanganese (**58**). This can be, therefore, better classified as a "ligand-synthesis" reaction.



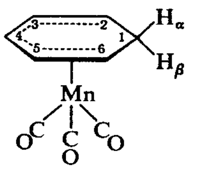
(**58**)

Decacarbonyldimanganese reacts slowly with butadiene in the presence of ultraviolet irradiation forming a butadiene-substituted compound of formula $Mn_2(CO)_8C_4H_6$ (19). Three configurations are possible for this compound; **59** is favored on the basis of infrared evidence.



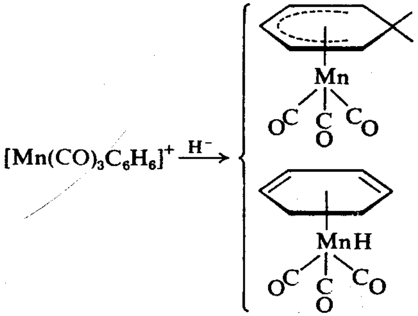
(**59**)

$Mn_2(CO)_{10}$ reacts at 145°C with cyclohexa-1,3-diene (20) and gives low yields of tricarbonylcyclohexadienylmanganese (**60**), $Mn(CO)_3C_6H_7$. The



(**60**)

reaction is accompanied by hydrogen abstraction from the diene. The proton resonance spectrum is in agreement with the proposed structure **60**. $Mn(CO)_3C_6H_7$ has also been obtained by reduction of the cation $[Mn(CO)_3C_6H_6]^+$ with $LiAlH_4$ or $NaBH_4$.



(**60**)

(**61**)

Since then, however, it has been recognized (21) that this reduction also leads to the formation of the hydrido derivative **61**. The 1-methyl-substituted cyclohexadienyl compound was obtained by reacting the $[Mn(CO)_3C_6H_6]^+$ cation with methyllithium (22). The methyl group was suggested to be in the *exo* position.

The hexamethyl-substituted cyclohexadienyl compound of rhenium has been prepared by reduction of the $[Re(CO)_3C_6(CH_3)_6]^+$ in diethyl ether (23).

It would appear that the direct reaction of $Mn_2(CO)_{10}$ with cyclopentadiene has not yet been tried. However, the mixed cyclopentadienyl, $MnC_5H_5(CO)_3$, has been prepared by several indirect methods; for example, from $Mn(C_5H_5)_2$ and carbon monoxide under pressure (24,25), from the dry reaction (26) of $Mn_2(CO)_{10}$ with $Mn(C_5H_5)_2$ at 100–300°, or by the reaction of $Mn(pyridine)_2Cl_2$ with carbon monoxide and cyclopentadiene in dimethylformamide with magnesium as a reducing agent (27).

The yellow, liquid methylcyclopentadienyltricarbonylmanganese (28) $Mn(C_5H_4CH_3)(CO)_3$ (b_{10} 112°), ethylcyclopentadienyltricarbonylmanganese (29) $Mn(C_5H_4C_2H_5)(CO)_3$ ($b_{0.015}$ 20°), and *tert*-butylcyclopentadienyltricarbonylmanganese (30) $Mn(C_5H_4C(CH_3)_3)(CO)_3$ (b_{1-2} 97–98°), have also been described. The two latter compounds were obtained by Friedel-Crafts alkylation of $MnC_5H_5(CO)_3$.

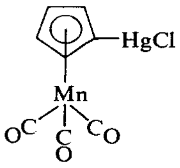
$TcC_5H_5(CO)_3$ is prepared in small quantities by neutron irradiation (31) of $[MoC_5H_5(CO)_3]_2$. The colorless $ReC_5H_5(CO)_3$, mp 112°, can be prepared from $Re_2(CO)_{10}$ and dicyclopentadiene (32), and from the halogenocarbonyl (33,34) $ReCl(CO)_5$ with NaC_5H_5:

$$ReCl(CO)_5 + NaC_5H_5 \longrightarrow ReC_5H_5(CO)_3 + NaCl + 2CO \qquad (86)$$

An alternative method of preparation is the treatment of rhenium halide and sodium cyclopentadienide (35) with carbon monoxide under pressure at 225°.

The cyclopentadienyl ring in $MnC_5H_5(CO)_3$ behaves chemically as an aromatic system. It has been shown to undergo several substitution reactions, such as Friedel-Crafts acylation with acetyl chloride or acid anhydrides (36–38), and alkylations with isobutylene or cyclohexyl chloride (38), methyl chloride (29), and *tert*-butyl chloride (30). Methylcyclopentadienyltricarbonylmanganese undergoes similar electrophilic substitutions (39). Friedel-Crafts alkylations of $Mn(C_5H_4CH_3)(CO)_3$ with ethyl bromide in the presence of $AlCl_3$ have also been described. For further information about substitutions and other organic reactions of $MnC_5H_5(CO)_3$, see the comprehensive review by Plesske (40).

$MnC_5H_5(CO)_3$ has been shown to undergo mercuration (41) with mercuric acetate in the presence of $CaCl_2$ to give the yellow chloromercuric derivative **62** (42). Apart from electrophilic substitutions at ring positions,



(62)

$MnC_5H_5(CO)_3$ has been shown to undergo a series of reactions involving functional groups on a side chain. For a survey of the numerous reactions of the latter type which can be carried out on derivatives of $MnC_5H_5(CO)_3$, see the paper by Cais and Narkis (43), in which references to some previous work on this subject can also be found.

$ReC_5H_5(CO)_3$ can be acylated (33,44) with C_6H_5COCl and CH_3COCl in the presence of $AlCl_3$. A similar Friedel-Crafts acylation by C_6H_5COCl has been shown (33) to occur also with $TcC_5H_5(CO)_3$.

Cyclopentadienyltricarbonylmanganese can also undergo replacement reactions of the carbon monoxide groups, usually in the presence of ultraviolet irradiation (see Scheme III).

$MnC_5H_5(CO)_3 + \xrightarrow{UV}$

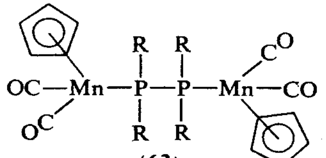
		Ref.
R_2S	$\longrightarrow MnC_5H_5(CO)_2SR_2$	45
ethylene	$\longrightarrow MnC_5H_5(CO)_2C_2H_4$	46
butadiene	$\longrightarrow MnC_5H_5(CO)C_4H_6$	47
cyclohexadiene	$\longrightarrow [MnC_5H_5(CO)_2]_2C_6H_8$	48
pyridine	$\longrightarrow MnC_5H_5(CO)_2py$	49
$PhC{\equiv}CPh$	$\longrightarrow MnC_5H_5(CO)_2(PhC_2Ph)$	50
PPh_3	$\longrightarrow MnC_5H_5(CO)_2PPh_3$	51
$F_3CC{\equiv}CCF_3$	$\longrightarrow MnC_5H_5(CO)_2(F_3CC_2CF_3)$	52

$$Mn(C_5H_4CH_3)(CO)_3 \xrightarrow[UV]{\text{piperidine}} Mn(C_5H_4CH_3)(CO)_2(NC_5H_{11}) \qquad 53$$

Scheme III

Irradiation with ultraviolet light seems to be important in these substitutions. $MnC_5H_5(CO)_3$ can in fact be recovered unchanged after prolonged heating at 200° with triphenylphosphine, while ready substitution takes place at room temperature under irradiation. It has also been found (52) that hexafluorobut-2-yne does not react with $MnC_5H_5(CO)_3$ merely on heating. Other thermal and photochemical substitution reactions of $MnC_5H_5(CO)_3$ with phosphorus- and arsenic-containing ligands have been described (54,55). With monodentate ligands, the products obtained are of the type $MnC_5H_5(CO)_2L$ while with the bidentate ligand 1,2-bis(diphenylphosphino)ethane, Diphos, two types of compounds are obtained, viz., $MnC_5H_5(CO)(Diphos)$ and $[MnC_5H_5(CO)_2]_2(Diphos)$.

Complexes with diphosphines of the type P_2R_4 have also been prepared in the presence of ultraviolet irradiation (56). Here, a dimeric product, for which structure **63** was proposed, was also obtained.



(63)

Because the infrared spectrum (57) of $MnC_5H_5(CO)_3$ shows only two bands in the carbonyl stretching region, it was suggested that the compound has a triangular pyramidal structure with the cyclopentadienyl ring perpendicular to the threefold axis of symmetry. This view has been substantiated by an x-ray study (58) which shows that, although the molecule as a whole has no symmetry, there is a common axis through the cyclopentadienyl ring and in the middle of the three carbon monoxide groups. Looking at the molecule through this axis, the carbon atom C_1 (Fig. 16) is almost opposite to C_7 on the ring, and C_3 and C_2 are almost eclipsed by the C_8 and C_6 of the ring. The molecule, therefore, has nearly a vertical mirror plane. The results of a microwave spectrum study of $MnC_5H_5(CO)_3$ (59) are in agreement with the x-ray structure.

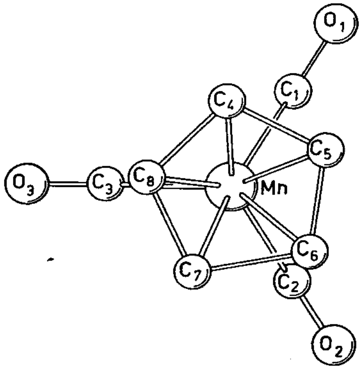
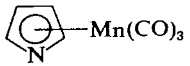


FIG. 16. The $MnC_5H_5(CO)_3$ molecule viewed along its pseudo axis (A. F. Berndt and R. E. Marsh, *Acta Cryst.*, **16**, 118 (1963)).

The dipole moments of $MnC_5H_5(CO)_3$ and the cyclohexadienyl derivative $Mn(CO)_3C_6H_7$ in heptane, benzene, and dioxane have been measured (60) and compared with that of $Cr(CO)_3C_6H_6$ in dioxane.

Pyrrole, which is similar in many respects to cyclopentadiene, reacts (61) with $Mn_2(CO)_{10}$ to give an orange crystalline product, tricarbonyl-π-pyrrolylmanganese (**64**). This compound, which was also obtained by reacting $MnBr(CO)_5$ with KC_4H_4N (62), is believed to be a half-sandwich complex, very similar to $MnC_5H_5(CO)_3$, as far as bonding is concerned.



(**64**)

b. Nitrogen-, phosphorus-, antimony-, and arsenic-containing ligands. $Mn_2(CO)_9NH_3$, an NH_3 substitution product of $Mn_2(CO)_{10}$ is obtained (63) by treating a solution of pentacarbonylmanganate with hydroxylamine-*O*-sulfonic acid:

$$2[Mn(CO)_5]^- + H_2O \longrightarrow [Mn_2(CO)_9H]^- + OH^- + CO \qquad (87)$$

$$[Mn_2(CO)_9H]^- + NH_2OSO_3^- \longrightarrow Mn_2(CO)_9NH_3 + SO_4^{2-} \qquad (88)$$

Enneacarbonylamminedimanganese is an orange-red solid, insoluble in water, and slightly soluble in benzene.

Monosubstituted compounds of the type $Mn_2(CO)_9L$ (with L being acetonitrile, propionitrile, acrylonitrile, benzonitrile, and pyridine) have been prepared directly by ultraviolet irradiation of $Mn_2(CO)_{10}$ in the presence of the appropriate ligand. The infrared data in the CO stretching region indicate that the ligand replaces one of the axial carbon monoxide groups of $Mn_2(CO)_{10}$(19).

The reactions of $Mn_2(CO)_{10}$ with P, As, and Sb-containing ligands have been studied extensively (64–68).

Nyholm and Rao (65) have found that *o*-phenylenebis(dimethylarsine), Diars, reacts at 160° with $Mn_2(CO)_{10}$ to give the substitution product $Mn(CO)_3$Diars, which is monomeric and paramagnetic ($\mu_{eff} = 1.76$ B.M.) but at lower temperature (130°) the dimeric diamagnetic $[Mn(CO)_3Diars]_2$ is formed. The dimer can be converted into the monomer by heating above the melting point.

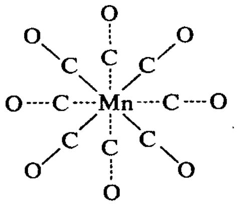
Hieber and Freyer (66,68) investigated the reactions of $Mn_2(CO)_{10}$ with trialkyl- and triarylphosphines. The reactions were carried out by heating the carbonyl with the tertiary phosphine in the presence of a solvent. These authors found that the substitution products so obtained had variable molecular complexity and magnetic properties depending on the nature of R. When R was Ph or Et, monomeric, paramagnetic derivatives, $Mn(CO)_4PR_3$ (**65**), were obtained, but when R was C_6H_{11} or with triphenylphosphite, diamagnetic and dimeric substitution products **66** and **67** were formed. However, the yellow solutions of the latter compounds become deep red at temperatures around 100°. Correspondingly, small magnetic moments were measured for these solutions. A temperature dependent equilibrium in solution between monomer and dimer has therefore been suggested:

$[Mn(CO)_4P(C_6H_{11})_3]_2$ (**66**)

$[Mn(CO)_4P(OPh)_3]_2$ (**67**)

$$[Mn(CO)_4PR_3]_2 \rightleftharpoons 2Mn(CO)_4PR_3 \qquad (89)$$

Osborne and Stiddard (69) reported the photochemical reactions of decacarbonyldimanganese with PR_3 (with R being Ph, Et, OPh, and $p\text{-}FC_6H_4$) and with $AsPh_3$. In all cases tetracarbonyl dimeric products, such as $[Mn(CO)_4PPh_3]_2$ were obtained. Some of the compounds were, however, weakly paramagnetic. This was explained by assuming a dimer $\rightleftharpoons$ monomer equilibrium of the type postulated by Hieber and Freyer. Osborne and Stiddard also showed that the thermal reaction of $Mn_2(CO)_{10}$ with PPh_3 *without solvent* gives a dimeric substance identical with that prepared from the photochemical reaction. In conclusion, it seems that the nature of the products obtained from the reaction of $Mn_2(CO)_{10}$ with tertiary phosphines and arsines depends strongly on the reaction conditions. Ultraviolet irradiation seems, however, to cause the least degree of alteration of the $Mn_2(CO)_{10}$ backbone. Products of monosubstitution of the type $Mn(CO)_9L$ are probably intermediates in the photochemical reaction. Sheline and co-workers (19) have isolated $Mn_2(CO)_9PPh_3$ from the reaction of the carbonyl with triphenylphosphine. From an investigation (69) of the infrared spectra in the CO stretching region, the dimeric compounds $[Mn(CO)_4L]_2$ (with L being PR_3 or AsR_3) seem to contain the L substituents *trans* with respect to the metal–metal bond; the carbon monoxide groups are probably in a staggered configuration. In **68** is shown a view of the $[Mn(CO)_4L]_2$ molecule along the metal–metal bond axis.

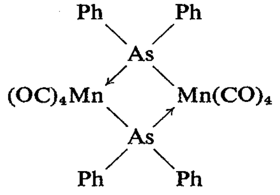


(68)

The compound $[Mn(CO)_4PF_3]_2$ has also been prepared (70) and a three-dimensional x-ray analysis of this molecule confirms that the PF_3 ligands are *trans* with respect to the metal–metal bond.

Decacarbonyldirhenium reacts with tertiary phosphines to give substitution products. Hieber and Freyer (66) have reported the dimeric diamagnetic $[Re(CO)_4PPh_3]_2$ obtained by treating $Re_2(CO)_{10}$ with triphenylphosphine in boiling xylene for 48 hr. Nyman (71), however, later reported that the product obtained under these conditions was the paramagnetic $Re(CO)_3(PPh_3)_2$. The Hieber and Freyer compound could be obtained only by reducing the reaction time to 10 hr or, better, by ultraviolet irradiation of a solution of the carbonyl in the presence of the ligand.

The thermal reaction of $Mn_2(CO)_{10}$ with triphenylarsine has been reported to give the substitution product $Mn(CO)_4AsPh_3$, which is monomeric and paramagnetic (66). However, Lambert (67) later reported that the same reaction (perhaps carried out at somewhat higher temperature) gives rise to the diamagnetic, dimeric $[Mn(CO)_4AsPh_2]_2$, for which structure **69** was suggested. Arsenic-bridged compounds of the type **69**, with R being CH_3 and CF_3, have been obtained by reacting $Mn_2(CO)_{10}$ with cacodyl (72) and with the corresponding perfluoro derivative $(CF_3)_2As\text{–}As(CF_3)_2$ (73). A complex of formula $Mn_2(CO)_8P(CF_3)_2I$, probably containing both iodine and $P(CF_3)_2$ as bridges between the two manganese atoms, is obtained by the reaction of $Mn_2(CO)_{10}$ with $(CF_3)_2PI$ (74). In agreement with the proposed structure, the compound shows C—O stretching vibrations at 2101, 2045, and 1985 cm^{-1} due to terminal carbon monoxide groups. The reaction was shown (75) to be quite general and to occur according to the following equations:



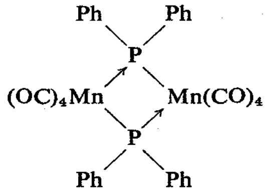
(69)

$$Mn_2(CO)_{10} + (CF_3)_2PX \longrightarrow Mn_2(CO)_8P(CF_3)_2X + 2CO \qquad (90)$$

$$Mn_2(CO)_{10} + (CF_3)_2AsI \longrightarrow Mn_2(CO)_8As(CF_3)_2I + 2CO \qquad (91)$$

with X = Cl, Br, I, $SeCF_3$, or $P(CF_3)_2$.

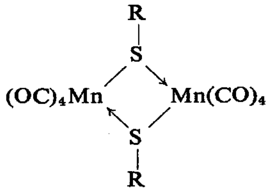
A phosphorus-bridged manganese carbonyl has been obtained (76) from the reaction of Ph_2PCl with $NaMn(CO)_5$ (**70**). The same compound, **70**, can be obtained by direct reaction of $Mn_2(CO)_{10}$ with tetraphenylbiphosphine (72). Hieber and Freyer (68) have briefly mentioned



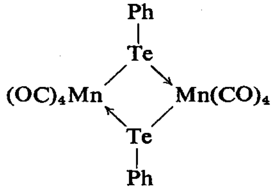
(70)

that heating of $Mn_2(CO)_{10}$ with the bidentate phosphine, Diphos, gives the dimeric $Mn_2(CO)_8$Diphos.

c. Sulfur-, selenium-, and tellurium-containing ligands. Substitution products of $Mn_2(CO)_{10}$ are obtained by the reaction of the carbonyl with diphenyltellurium (77) and, indirectly, by the reaction of $MnH(CO)_5$ with diethyl and dibutyl disulfide (78). These compounds, which are dimeric and diamagnetic and do not show infrared bands at low wavenumbers suggestive of bridging CO groups, probably have the tellurium- and sulfur-bridged structures **71** and **72**.



(71)



(72)

The series of these binuclear complexes has been completed by Welcman and Rot (79) who described the analogous selenium-bridged compounds obtained by reacting $MnH(CO)_5$ with dialkyl diselenides, RSeSeR. Alkylthio derivatives of technetium, probably having structures similar to those of the parent manganese compounds, have been described (80). In this case the preparation requires treating $TcCl(CO)_5$ with mercaptans:

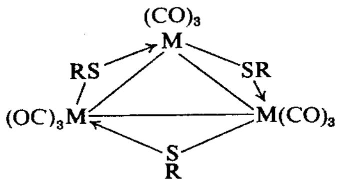
$$2TcCl(CO)_5 + 2RSH \xrightarrow[\text{methanol}]{50^\circ} [Tc(CO)_4SR]_2 + 2CO + 2HCl \tag{92}$$

By reacting $ReCl(CO)_5$ with thiophenol, Hieber and Schuster (15) obtained a dimeric, sulfur-bridged compound having the formula $[Re(CO)_4SPh]_2$, thus:

$$2Re(CO)_5Cl + 2C_6H_5SH \longrightarrow [Re(CO)_4SC_6H_5]_2 + 2HCl + 2CO \tag{93}$$

This result was confirmed by Osborne and Stone (81) who also found that under more drastic conditions a trimer, $[Re(CO)_3SPh]_3$, was formed. The same compound and some other alkyl analogs were reported independently by Abel and co-workers (82). They prepared the ethyl derivatives $[M(CO)_3SEt]_3$ (with M being Mn or Re) by treating $Mn(CO)_5Br$ or $Re(CO)_5Cl$ with bis(methylthio)dimethyltin. The intermediate compound so obtained underwent a spontaneous cleavage and finally gave the trimer.

The structure represented in **73** has been proposed for the trimeric manganese and rhenium compounds.



(73)

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F. Carbonyls of Group VI Transition Metals

1. Reactions Involving Changes in Oxidation Number

a. Oxidations. The carbonyls of this group are very stable toward air oxidation. Even in solution they are altered by atmospheric oxygen only very slowly.

Hexacarbonylchromium is not affected by concentrated HCl; it is slowly attacked by H_2SO_4 at room temperature but it is readily decomposed by nitric acid. Chlorine oxidizes it to $CrCl_3$ with evolution of carbon monoxide and phosgene. It shows a striking resistance to attack by bromine and iodine at room temperature (1).

Molybdenum and tungsten carbonyls, on the contrary, react readily with bromine. With the molybdenum carbonyl the reaction leads to the formation of $MoBr_4$. At low temperature (−78°C), however, hexacarbonylmolybdenum and liquid chlorine give $MoCl_2(CO)_4$. The latter is a yellow, thermally unstable solid (*1a*).

Reactions of the hexacarbonyls with iodine at elevated temperature have been reported (2). In sealed tubes at 150°C, $Mo(CO)_6$ and $W(CO)_6$ yield the triiodides MI_3, whereas $Cr(CO)_6$ gives products of uncertain composition.

The reaction of hexacarbonylmolybdenum with fluorine has been studied in detail (3). At −75°C, the (occasionally explosive) reaction yields CO, MoF_5, and MoF_4. At temperatures above 50°C, the reaction yields MoF_6 and MoO_2, with evolution of COF_2.

The exceptional resistance of hexacarbonylchromium in comparison with the reactivity of hexacarbonylmolybdenum is also shown by the differences in behavior with sulfur trioxide (4). $Cr(CO)_6$ is unaffected by SO_3 even at 160°C, whereas $Mo(CO)_6$ suspended in liquid SO_3 is oxidized at −10°C, with formation of the tetracarbonylpyrosulfate $MoO(CO)_4(SO_3)_2$.

Carboxylic acids and β-diketones readily oxidize all the carbonyls of this group. The solvent and donor properties of these reagents explain the occurrence of the oxidations, for which an initial carbon monoxide displacement can be postulated.

Hexacarbonylmolybdenum reacts quantitatively with benzoic acid at 160°C, yielding a yellow molybdenum(II) benzoate, sublimable without decomposition at 420°C in high vacuum (5). With boiling acetic or propionic acids, the corresponding molybdenum(II) salts are obtained (*6a*).

Several other molybdenum(II) carboxylates have been prepared (*6b*). Osmometric molecular weight determinations of the perfluorobutyrate and of the salicylate showed that they are dimeric (66). Structures with two bridging and two chelating carboxylate groups were proposed.

The preparation of molybdenum(III) acetylacetonate from hexacarbonylmolybdenum has been described (7); the reactions of chromium and molybdenum carbonyl with acetylacetone and with trifluoroacetylacetone have been investigated (8). These reactions can be formally visualized as electron transfer processes from the zerovalent metal to the active proton of the β-diketone, for example:

$$M(CO)_6 + 3(CH_3CO)_2CH_2 \longrightarrow \tfrac{3}{2}H_2 + M[(CH_3CO)_2CH]_3 + 6CO \qquad (94)$$

It has been reported, however, that the amount of gas evolved was less than that required by the stoichiometry of reaction 94 and that very little or no hydrogen was observed in the gas evolved during the reaction.

Temperatures around 120°C are required for converting chromium and molybdenum hexacarbonyls to the corresponding β-diketonates.

In the presence of ultraviolet irradiation, reactions of the same type were observed with chromium, molybdenum, and tungsten hexacarbonyls at lower temperatures (80°C). With hexafluoroacetone and acetylacetone in benzene or carbon tetrachloride (9), all the carbon monoxide and hydrogen required by the stoichiometry of reaction 94 is evolved.

Upon thermal decomposition, the carbonyls of this group generally form adherent coatings of the corresponding metal. However, hexacarbonylchromium pyrolyzed at 500°C gives a chromium oxide in which the O/Cr ratio is 0.86 (10).

b. Reductions. The following carbonylmetallate anions of Cr, Mo, and W have been reported:

$$[M(CO)_5]^{2-},\quad [M_2(CO)_{10}]^{2-},\quad [MH(CO)_5]^{-},\quad [M_2H(CO)_{10}]^{-},$$
$$[Cr_3(CO)_{14}]^{2-},\quad \text{and}\quad [Mo_3(CO)_{14}]^{2-}$$

Some bi- and trinuclear anions containing hydroxo or methoxo groups are also known. The anion $[Cr_2(CO)_6(OH)_3H]^{2-}$ is such an example.

Reduction of the hexacarbonylmetals has been performed satisfactorily by the action of sodium or other alkali metals and by alkali earth metals in liquid ammonia (11). The reduction can be represented by the general equation:

$$M(CO)_6 + 2Na \longrightarrow Na_2M(CO)_5 + CO \qquad (95)$$

However, only 5–10% of the required amount of carbon monoxide was detected. The rest was reported to form "NaCO" with the excess of the metal. The exact nature of this reaction by-product was not investigated (12). During the reduction of $Cr(CO)_6$ and $Mo(CO)_6$ an appreciable amount of hydrogen is produced, due to the formation of sodium amide.

The yellow disodium pentacarbonylchromate is stable in anhydrous ammonia, pyridine, and acetone. It is oxidized by water according to the equation:

$$2[Cr(CO)_5]^{2-} + 3H_2O \longrightarrow [Cr_2H(CO)_{10}]^{-} + H_2 + 3OH^{-} \qquad (96)$$

This reaction was studied in detail by Behrens and Klek (13). They also showed that the ammonium ion in aqueous solution does not form ammonium salts, but behaves like a Brönsted acid to form the yellow volatile $Cr(CO)_5NH_3$. The same behavior has been demonstrated for the pentacarbonylmolybdate anion (14).

The reduction of the hexacarbonyls with sodium tetrahydridoborate was first carried out in liquid ammonia at 40–60°C, in sealed tubes for long reaction times (14,15). Under these conditions, the decacarbonyldimetallates $Na_2[M_2(CO)_{10}]$ (with M = Cr, Mo, W) were obtained. The reaction, which takes place with hydrogen evolution, is represented in the case of hexacarbonylchromium by the following overall scheme:

$$2Cr(CO)_6 + 2NaBH_4 + 6NH_3 \longrightarrow Na_2[Cr_2(CO)_{10}] + 2B(NH_2)_3 + 2CO + 7H_2 \qquad (97)$$

With hexacarbonylmolybdenum, particularly long reaction times (two months) are required for the formation of the $[Mo_2(CO)_{10}]^{2-}$ anion. It has been suggested that this reaction takes place through the intermediate formation of tri- and pentanuclear carbonylmetallates. The trinuclear anions $[Cr_3(CO)_{14}]^{2-}$ and $[Mo_3(CO)_{14}]^{2-}$ have been actually isolated (16) from the reaction of the hexacarbonyls with sodium tetrahydridoborate in boiling tetrahydrofuran:

$$3M(CO)_6 + 2NaBH_4 \longrightarrow Na_2[M_3(CO)_{14}] + 4CO + H_2 + B_2H_6 \qquad (98)$$

Both salts, black-green and black-violet, respectively, are converted into the $[M(CO)_5]^{2-}$ anions and the corresponding hexacarbonyls by the action of carbon monoxide under pressure in sealed tubes at 150°C.

Carbonate ion formation was observed during the reaction of $Cr(CO)_6$ with alkali (1). Later (17), it was reported that the reaction between hexacarbonylchromium and alcoholic potassium hydroxide produces a yellow, not well-defined product, which, upon acidification, gives a volatile substance tentatively formulated as $CrH_2(CO)_5$. The existence of this hydrido compound has never been confirmed.

Further systematic investigations by Hieber and co-workers (18–21) showed that on warming with alcoholic KOH, $Cr(CO)_6$, and $Mo(CO)_6$ give only binuclear carbonylmetallates containing hydroxo- or methoxo bridges.

With $Mo(CO)_6$, no hydrogen evolution or carbonate ion formation is observed; the reaction therefore is to be regarded as a substitution:

$$2Mo(CO)_6 + 9OH^- \longrightarrow [Mo_2(OH)_3(CO)_6]^{3-} + 6HCOO^- \qquad (99)$$

For $Cr(CO)_6$, the reaction was interpreted as involving the intermediate conversion of $Cr(CO)_6$ to $[CrH(CO)_5]^-$ ion, which is then oxidized by water:

$$2Cr(CO)_6 + 6OH^- \longrightarrow 2[CrH(CO)_5]^- + 2CO_3^{2-} + 2H_2O \qquad (100)$$

$$2[CrH(CO)_5]^- + 4OH^- + 3H_2O \longrightarrow [Cr_2(OH)_3H(CO)_6]^{2-} + 2H_2 + 4HCOO^- \qquad (101)$$

The salt $K[Cr_2H(CO)_{10}]$ has been isolated in good yields from the direct reaction of $Cr(CO)_6$ with potassium hydroxide (22).

With $W(CO)_6$, the course of the reaction is more complicated. At 80–100°C a part of the carbonyl reacts according to a substitution reaction of type (99), whereas another part undergoes reduction:

$$2W(CO)_6 + 12KOH \xrightarrow{2CH_3OH} K_4[W_2(OH)_2(CO)_6(CH_3OH)_2] + 2K_2CO_3 + 4HCOOK + 2H_2O + H_2 \qquad (102)$$

At 130°C in methanol, a trinuclear carbonylmetallate, formulated as $[W_3(OH)(OCH_3)H(CO)_9(CH_3OH)]^{3-}$ was also obtained.

It is peculiar to all these reactions that in methanol as solvent, carbonylmetallate anions containing methoxo and/or methanol groups are obtained, whereas in ethanol solutions anions containing only hydroxo groups are obtained.

It should also be mentioned that acidification of the hydroxohydridocarbonyltungstates with mineral acids gave (23) the hydroxohydridocarbonyl $W_2(OH)_3H_3(CO)_6$ and hydroxoaquohydridocarbonyl $W_3(OH)_2H_4(CO)_9 \cdot H_2O$ (**74**).

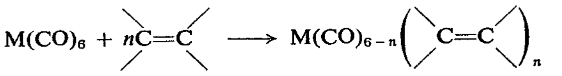
Heating compound **74** in aqueous solution and then adding ammonia gives $W(CO)_3(NH_3)_3$. This is not the only product of the reaction. After removing $W(CO)_3NH_3$ by filtration and acidifying the filtrate, the tetramer $W_4(CO)_{12}(H_2O)_4H_4 \cdot 4H_2O$ is obtained. The dehydrated compound $W_4(CO)_{12}(H_2O)_4H_4$ can bind 1 mole of benzene per 2 tungsten atoms rather tightly.

For a further discussion of some anionic hydridocarbonylmetals, see Sec. VI.

c. Disproportionation reactions. No disproportionation reactions for the carbonyls of group VI metals in the presence of Lewis bases have been reported as yet.

2. *Substitution Reactions*

a. Compounds containing nonaromatic carbon–carbon unsaturation. Heating or irradiating the carbonyls in the presence of compounds with olefinic unsaturation usually gives substituted metal carbonyls according to the general equation:



(103)

For a detailed compilation of the complexes prepared by this type of reaction, see certain review articles (24–26) and particularly the comprehensive monograph by Fischer and Werner (27).

Only some interesting aspects of the reactions of olefinic systems with the hexacarbonyls of group VI metals and the more recent developments in this field will be discussed. Reaction 103 has been carried out in most cases with olefins containing a fully conjugated system, such as butadiene (28); here the yellow crystalline $Mo(CO)_2(C_4H_6)_2$ is obtained by use of ultraviolet irradiation in the presence of mercury. With cyclohexa-1,3-diene, the complex $Mo(CO)_2(C_6H_8)_2$ has been obtained (29). With a mixture of 1,3,5- and 1,3,6-cyclooctatrienes (30), compounds of types

$M(CO)_3(1,3,5\text{-}C_8H_{10})$ and $M(CO)_2(1,3,6\text{-}C_8H_{10})_2$ are formed. For the latter, only two conjugated double bonds are used for coordination to the metal.

Complex formation is also possible when the double bonds of an olefin, even if not conjugated, can assume the correct orientation with respect to the metal. This is true for cycloocta-1,5-diene (31–34) and bicyclo[2,2,1]-heptadiene (35) from which were obtained the compounds $Cr(CO)_4C_8H_{12}$ (golden yellow, dec. 70°), $Mo(CO)_4C_8H_{12}$ (yellow, 129–131° dec.), $W(CO)_4C_8H_{12}$ (yellow, 141–142° dec.), and $Mo(CO)_4C_7H_8$ (pale yellow, mp 76–77°).

Leigh and Fischer (34) have shown that the reactions of cyclooctadienes with the hexacarbonyls of the group VI metals are complicated by isomerization of the diolefin. The isomerization is solvent dependent. Cycloocta-1,5-diene is converted into *o*-xylene in the presence of $Cr(CO)_6$. When heated with $Mo(CO)_6$ and $W(CO)_6$, cycloocta-1,3-diene undergoes isomerization and complex formation to give compounds $M(CO)_4(1,5\text{-}C_8H_{12})$, with M being molybdenum or tungsten.

Olefin complexes of dimethyldivinylsilane (36) $(CH_3)_2Si(CH{=}CH_2)_2$ and bicyclo[4,3,0]nonatriene (37) have also been described.

$Cr(CO)_6$ and tetracyclone react at 180° to give black crystals of a material which has no CO groups bonded to the metal; the nature of this compound has not been further investigated. $Mo(CO)_6$, however, reacts at 160° with tetracyclone to give the complex $Mo(CO)_2$(tetracyclone) (38).

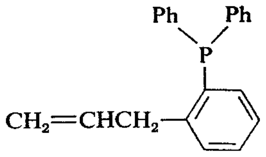
A very interesting ligand exchange reaction occurs (39) when tetraphenylcyclobutadienepalladium iodide is treated with $Mo(CO)_6$ at 80° in benzene. The brown complex $[Mo(CO)_3(C_4Ph_4)I]_2$ (dec. 290°) is obtained. This is believed to be a tetraphenylcyclobutadiene carbonyl complex of molybdenum. A similar reaction also occurs with $W(CO)_6$.

All the compounds just mentioned contain olefins with two or three double bonds. Complexes in which the unsaturated ligand contains only one carbon–carbon double bond are more rare. We shall discuss some of the known examples.

Dicarbonylbis(acrolein)molybdenum was obtained by Tate and coworkers (40) by treating $Mo(CO)_3(\text{acetonitrile})_3$ with the ligand. For the resulting $Mo(CO)_2(\text{acrolein})_2$, a polymeric structure involving bonding of the metal to both the C=C and the C=O bonds of acrolein was suggested. Coordination of the aldehydic group through an oxygen electron pair was considered less probable.

The preparation of monoolefin complexes of group VI metal carbonyls has also been accomplished by ultraviolet irradiation of $Mo(CO)_6$ and $W(CO)_6$ in the presence of the olefin (41). Complexes of types $M(CO)_5$(olefin) and $M(CO)_4(\text{olefin})_2$ have been obtained (with M = Mo, W) but, owing to their instability, only $Mo(CO)_5$(propylene) could be isolated and analyzed. Other compounds (with olefin = ethylene, *trans*-2-butene, *cis*-2-butene) were characterized by their infrared spectra.

Stable monoolefin complexes of chromium, molybdenum, and tungsten were later prepared by using *o*-allylphenyldiphenylphosphine (allylphos) (**75**) as a chelating agent (42). Compounds of formula $M(CO)_4$(ligand) with



(75)

M being Cr, Mo, and W, were isolated by ligand exchange reaction from $M(CO)_4$(norbornadiene). Isomerization of the ligand to *o*-propenylphenyldiphenylphosphine occurred under the reaction conditions. For molybdenum, the complex could be obtained, although in lower yield, by direct reaction of the hexacarbonyl with the chelating ligand. In these compounds, two coordination positions of the central metal atom are occupied by the olefinic double bond and by the lone pair on the phosphorus.

The ultraviolet induced reactions of $Mo(CO)_6$ or $W(CO)_6$ with acetylene derivatives have been reported (41) to give pentacarbonyl derivatives of tungsten, $W(CO)_5R'C_2R''$ ($R' = R'' = H$; $R' = CH_3$, $R'' = H$; $R' = R'' = Et$) and the tetracarbonyl derivative $W(CO)_4(C_2H_2)_2$, whereas $Mo(CO)_6$ appears to yield only the corresponding pentacarbonyl derivatives $Mo(CO)_5R'C_2R''$. However, the compounds were not isolated; their formulas were inferred from the infrared spectra. The tetracarbonyl derivative $W(CO)_4(C_2H_2)_2$ is believed to have a *trans* configuration because it shows one single band at 1939 cm^{-1} in the carbonyl stretching region.

It is most interesting to note that the *thermal* reaction of $Mo(CO)_6$ or $W(CO)_6$ with diphenylacetylene follows a completely different course (43). By this method, products are obtained which contain tetraphenylcyclobutadiene as ligand; this clearly arises from the dimerization of the acetylene.

The diethylacetylene derivative $W(CO)(EtC_2Et)_3$ has been obtained from the reaction of $W(CO)_3(NCMe)_3$ with diethylacetylene (44). This compound shows only a single CO stretching vibration at 2035 cm^{-1}. A tetrahedral arrangement of the ligands around the metal has been suggested for it. The reaction was later extended (45) to other disubstituted acetylenes and the methyl and phenyl derivatives were obtained. Monosubstituted acetylenes were reported to give unidentified products under the same conditions. The diphenylacetylene derivative $W(CO)(PhC_2Ph)_3$ was also obtained (46) by simply irradiating $W(CO)_6$ in the presence of the ligand.

The ligand replacement reaction between $W(CO)_3$(acetonitrile)$_3$ and bis-(trifluoromethyl)acetylene does not give the expected $W(CO)(F_3CC_2CF_3)_3$ but rather $W(F_3CC_2CF_3)_3$(acetonitrile) (47).

Acetylene derivatives of formally zerovalent molybdenum and tungsten, $K_3[Mo(CO)_3(C_2H_2)_3]$ and $K_3[W(CO)_3(C_2H_2)_3]$, have been prepared by reacting $M(CO)_3(NH_3)_3$ with potassium acetylide in liquid ammonia (48). These complexes are air and moisture sensitive.

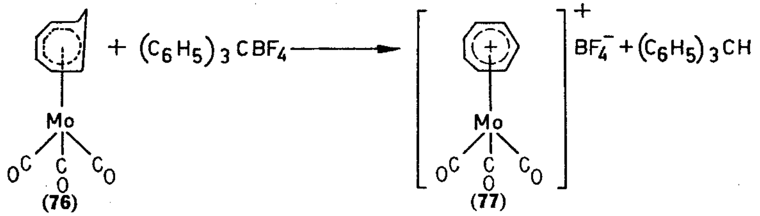
b. Cycloheptatriene-, cycloheptatrienyl-, and cyclooctatetraene derivatives. The cycloheptatrienyl cation $C_7H_7^+$, having the same number of π electrons as the cyclopentadienyl anion $C_5H_5^-$ and C_6H_6, is in principle capable of forming π complexes with transition metals. However, when $Mo(CO)_6$ was treated with cycloheptatriene, the expected cycloheptatrienyl (or tropylium) complex was not formed; instead, cycloheptatriene-molybdenum tricarbonyl, $Mo(CO)_3C_7H_8$, was isolated (49). Later tricarbonylcycloheptatriene chromium and ring-substituted analogs were also described (50), and finally $W(CO)_3C_7H_8$ was reported (51). The physical properties and infrared C—O stretching frequencies of these compounds are given in Table 14.

TABLE 14

Cycloheptatriene Tricarbonyls of Cr, Mo, and W

Compound	Color	Mp (°C)	ν_{CO} (cm^{-1})	Ref.
$Cr(CO)_3C_7H_8$	Red	128–130 dec.	1991, 1921, 1893	50
$Mo(CO)_3C_7H_8$	Red	110	2000, 1929, 1895	50
$W(CO)_3C_7H_8$	Red	117–118	—	51

Strohmeier (52) has reported an improved method for the preparation of $Mo(CO)_3C_7H_8$. The first tropylium complex was prepared by Dauben and Honnen (53) who carried out the hydrogen abstraction from $Mo(CO)_3C_7H_8$ (76) by using trityl fluoroborate. In agreement with the proposed structure for 77, only one proton resonance peak and two infrared C—O stretching vibrations have been observed.



(104)

The perchlorate and the tetrafluoroborate of tricarbonylcycloheptatrienylchromium were later prepared by Munro and Pauson (54) who also studied the reactions of these complexes with several nucleophilic reagents:

$$[Cr(CO)_3C_7H_7]^+ + X^- \longrightarrow Cr(CO)_3C_7H_7X \qquad (105)$$

This reaction gave substituted tricarbonylcycloheptatrienechromium compounds, which were later (55) shown to be in the *exo* configuration. Reaction of the $[Cr(CO)_3(C_7H_7)]^+$ cation as its perchlorate with NaC_5H_5 brings about ring contraction (56) and formation of $Cr(CO)_3C_6H_6$. A possible mechanism for this reaction has been discussed. The cycloheptatriene rings in $Mo(CO)_3C_7H_8$ and $Cr(CO)_3C_7H_8$ are rather labile; they can easily be replaced by an aromatic compound such as mesitylene (54), by amines (57), by phosphines (57), by isonitriles (58), and by alkyl sulfides (59,60).

Although the cycloheptatrienyl cation contains a delocalized system of six π electrons extended over a seven-membered planar ring, the six π-electron system in C_7H_8 and in $M(CO)_3C_7H_8$ is extended over six carbon atoms and bypasses the CH_2 group (49).

The x-ray investigation of $Mo(CO)_3C_7H_8$ (61) has completely confirmed the previous structural hypotheses (50). The molecule has approximately a plane of symmetry passing through the molybdenum atom, the methylene group and one of the three CO groups. The cycloheptatriene ring behaves as a triene system, as is clearly shown by the alternating C—C distances. The CH_2 group deviates from the plane of the other six carbon atoms (Fig. 17).

Tricarbonylcyclooctatetraenemolybdenum has been prepared (62) by reacting tricarbonyldiglymemolybdenum with C_8H_8 in hexane at 50°.

c. Cyclopentadienyl carbonyl derivatives. The group VI metal carbonyls react with cyclopentadiene in the vapor phase with replacement of carbon monoxide by the cyclopentadienyl anion (63). While $Cr(CO)_6$ gives bis(cyclopentadienyl)chromium directly, $Mo(CO)_6$ and $W(CO)_6$ give the mixed cyclopentadienyl complexes $[MoC_5H_5(CO)_3]_2$ and $[WC_5H_5(CO)_3]_2$ (64).

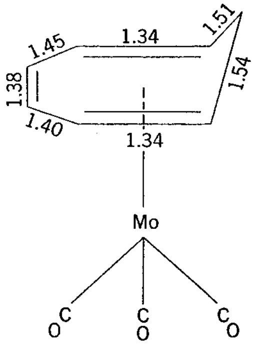


FIG. 17. View and C—C distances of $Mo(CO)_3C_7H_8$.

The mixed cyclopentadienylcarbonyl complexes of Cr, Mo, and W can also be obtained by the reaction of the metal carbonyls with alkali metal cyclopentadienides in tetrahydrofuran (64) or in dimethylformamide (65):

$$M(CO)_6 + Na(Li, K)C_5H_5 \longrightarrow Na(Li, K)[MC_5H_5(CO)_3] + 3CO \qquad (106)$$

with M = Cr, Mo, W.

The alkali metal salts are soluble in water, and on acidification with acetic acid the corresponding hydrido compounds $MH(C_5H_5)(CO)_3$ are formed. They are unstable and lose hydrogen with formation of the corresponding dimeric cyclopentadienyl carbonyls:

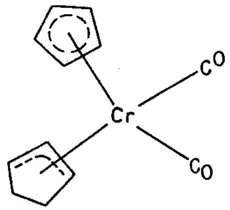
$$2MH(C_5H_5)(CO)_3 \longrightarrow [MC_5H_5(CO)_3]_2 + H_2 \qquad (107)$$

In the case of chromium, reaction 107 was found to be reversible. The three hydrido complexes are yellow crystalline solids, and show increasing stability from Cr to W. Alkyl cyclopentadienyl metal tricarbonyls have also been obtained by the following reactions:

$$Na[MoC_5H_5(CO)_3] + CH_3I \longrightarrow NaI + CH_3MoC_5H_5(CO)_3 \qquad (108)$$

$$WH(C_5H_5)(CO)_3 + CH_2N_2 \xrightarrow{Et_2O} N_2 + CH_3WC_5H_5(CO)_3 \qquad (109)$$

$[CrC_5H_5(CO)_3]_2$ can also be obtained (66) by the direct reaction of $Cr(C_5H_5)_2$ with carbon monoxide under pressure at high temperature; if hydrogen is present, $CrH(C_5H_5)(CO)_3$ is also formed. In the reaction of $Cr(C_5H_5)_2$ with carbon monoxide and hydrogen, another product that does not show any acidic property is formed (67). On the basis of infrared and NMR spectra, this compound has been formulated as cyclopentadienylcyclopentenyldicarbonylchromium(II), $Cr(CO)_2(C_5H_5)(C_5H_7)$ (**78**).



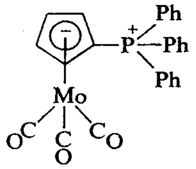
(**78**)

A three-dimensional x-ray diffraction study (68) has established the molecular structure of $[MoC_5H_5(CO)_3]_2$. In agreement with its infrared spectrum, the compound does not contain bridging CO groups but only a metal–metal bond.

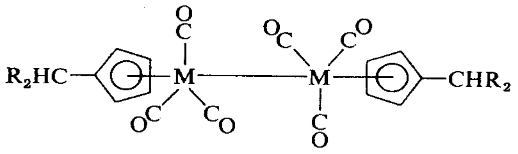
The proton resonance spectrum of $[MoC_5H_5(CO)_3]_2$ has been measured as a function of temperature (69). At 100°K a transition in line width has been attributed to an onset of ring reorientation. The potential barrier of the rotation about the metal–ring bond has been estimated to be about 3.9 kcal/mole.

The dimeric tricarbonylindenylmolybdenum, $[MoC_9H_7(CO)_3]_2$ (mp 185–188°) was first prepared by King and Stone (70). An improved method of preparing this compound, consisting of treating $Mo(CO)_6$ with indene in ethylcyclohexane at reflux temperature, was published later (71).

Treating $Mo(CO)_6$ with triphenylphosphonium cyclopentadienide gave the complex (**79**), in which the central metal atom is believed to be bonded to the cyclopentadienyl system (72). Cyclopentadienyl derivatives are usually obtained by reacting the hexacarbonyls with fulvenes. Alkyl-substituted compounds (**80**) were isolated from the reaction of $Mo(CO)_6$



(**79**)



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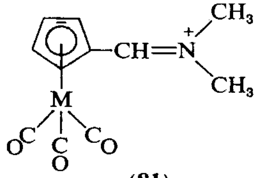


(81)

and $W(CO)_6$ with dialkylfulvenes. Here abstraction of hydrogen from the solvent or from the excess dialkylfulvene must have occurred (73). From $Cr(CO)_6$ and $Mo(CO)_6$ in the presence of 6-dimethylaminofulvene, compounds of structure **81** were obtained. The positive charge on the nitrogen is stabilized by the methyl groups (74).

d. Arenecarbonyl derivatives. Three independent research groups (75–77) found that $Cr(CO)_6$ reacts with aromatic compounds to give π-arene chromium tricarbonyls:

$$Cr(CO)_6 + \text{arene} \rightleftharpoons Cr(CO)_3\text{arene} + 3CO \tag{110}$$

The same reaction occurs with $Mo(CO)_6$ and $W(CO)_6$.

A large number of tricarbonylarene compounds, including some containing functional groups on the aromatic ring, have been prepared by reaction 110 (method A in Table 15).

For a detailed compilation of tricarbonylarenemetal complexes, see the excellent review by Zeiss (78). Since that review was written, many other compounds of this type have been described. Some of the new compounds prepared since then are reported in Table 15.

The mechanism of reaction 110 is of a great interest and it will be discussed in a later section dealing with mechanistic studies.

As a consequence of the observation that $Cr(CO)_6$, but not $Cr(\text{arene})_2$, can eventually be obtained from $Cr(CO)_3$arene:

$$Cr(CO)_6 \underset{}{\overset{\text{arene}}{\rightleftharpoons}} Cr(CO)_3\text{arene} \underset{}{\overset{\text{arene}}{\rightleftharpoons}} Cr(\text{arene})_2 \tag{111}$$

TABLE 15. Arene Chromium-, Molybdenum-, and Tungsten Tricarbonyls

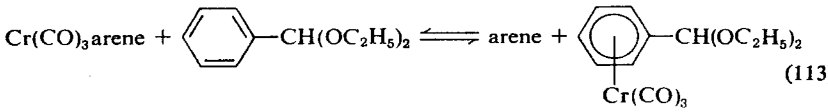
Compound	Color	Mp (°C)	Method of preparation[a]	Ref.
(*p*-$C_6H_4Cl_2$)$Cr(CO)_3$	Deep yellow	88	A	124
(*p*-$C_6H_4F_2$)$Cr(CO)_3$	Deep yellow	111	A	124
(Me_3SiPh)$Cr(CO)_3$	Yellow	72–73	A	125
(Me_3GePh)$Cr(CO)_3$	Yellow	79.5–80	A	125
(Me_3SnPh)$Cr(CO)_3$	Yellow	78.5–79	A	125
(Indene)$Cr(CO)_3$	Yellow	97	A	126
(Fluorene)$Cr(CO)_3$	Yellow	138–139	A	126
(Phenanthrene)$Cr(CO)_3$	Orange	158–160	A	70,127
(Pyrene)$Cr(CO)_3$	Red	—	A	70
(Thianaphthene)$Cr(CO)_3$	Yellow	115 dec.	A	70
(Acenaphthylene)$Cr(CO)_3$	Purple-black	~175 dec.	A	70
(Anthracene)$Cr(CO)_3$	Violet-black	189–192	A	127,128,129
(6,6-Diphenylfulvene)$Cr(CO)_3$	Black-brown	203–209 dec.		130
(Paracyclophane)$Cr(CO)_3$[b]	—	—	A	131
Diphenyl$[Cr(CO)_3]_2$	Orange	215–216 dec.	B	132
1,2-Diphenylethane$[Cr(CO)_3]_2$	Yellow-orange	236–238 dec.	B	132
Stilbene$[Cr(CO)_3]_2$	Red	243–245 dec.	B	132
Diphenylmethane$[Cr(CO)_3]_2$	Yellow-orange	216–217 dec.	B	132
trans-(Stilbene)$Cr(CO)_3$	Red	135–136	A, B	84,132,133
cis-(Stilbene)$Cr(CO)_3$	Yellow	109–111.5	—[c]	84
(Diphenylmethane)$Cr(CO)_3$	Yellow	97–98	A	131,133
(1,2-Diphenylethane)$Cr(CO)_3$	Yellow	98–100	—[d]	132
(1,1-Diphenylethane)$Cr(CO)_3$	—	70–71	A	131
trans-(2-Hydroxyindane)$Cr(CO)_3$	—	132–133	—[e]	134
cis-(2-Hydroxyindane)$Cr(CO)_3$	—	96–97	—[e]	134
(Indanone)$Cr(CO)_3$	—	124	A	135
(α-Tetralone)$Cr(CO)_3$	—	128	A	135
(1,2-$(MeO)_2C_6H_4$)$Cr(CO)_3$	Bright yellow	116	A	111
(1,3,5-$(MeO)_3C_6H_3$)$Cr(CO)_3$	Yellow	157	A	111
(Benzophenone)$Cr(CO)_3$	Orange	88–89	A	92,135
(Benzyl chloride)$Cr(CO)_3$	Yellow	63–64	—[f]	92
(1,3-$(MeOOC)(MeO)C_6H_4$)$Cr(CO)_3$	Red	57–58	A	123
(Benzoylacetone)$Cr(CO)_3$	Red	115–117	—[g]	83
(Benzaldehyde)$Cr(CO)_3$	Red	46.5–47.5	B	80
(1,4-$(MeOOC)_2C_6H_4$)$Cr(CO)_3$	Red	128	A	136
(Fluorobenzene)$Mo(CO)_3$	Yellow	—	A	137
(Toluene)$Mo(CO)_3$	Yellow	127–128	A	137
(*p*-Xylene)$Mo(CO)_3$	Yellow	139–140	A	137
(Toluene)$W(CO)_3$	Yellow	140–142	A	138
(*p*-Xylene)$W(CO)_3$	Yellow	143–145 dec.	A	138

[a] Method A = from $Cr(CO)_6$ + aromatic compound (Eq. 110); method B = by the exchange reaction 112. [b] Several compounds of this type are described in Ref. 131. [c] Prepared by Wittig reaction from (Benzaldehyde)$Cr(CO)_3$ and triphenylbenzylphosphonium chloride. [d] By hydrogenation of (Stilbene)$Cr(CO)_3$. [e] By hydrolysis of the corresponding acetoxyindane derivative. [f] By treatment of ($PhCH_2OH$)-$Cr(CO)_3$ with conc. HCl. [g] By Claisen condensation of acetone on (methyl benzoate) $Cr(CO)_3$.

it was thought that in the tricarbonylarenechromium complexes the metal–CO bond is relatively strong compared with the metal–ring bond. This view was substantiated by the successful displacement of the aromatic ligand by another aromatic compound (79) according to the reaction:

$$Cr(CO)_3\text{arene} + \text{arene}' \rightleftharpoons Cr(CO)_3\text{arene}' + \text{arene} \qquad (112)$$

Apart from its theoretical interest, reaction 112 is very useful in the preparation of chromiumtricarbonylarenes containing functional groups on the aromatic ring (method B in Table 15). These complexes sometimes can be obtained only with great difficulty by the direct reaction 110. Thus, tricarbonylbenzaldehydechromium can be obtained (80) by exchange of $Cr(CO)_3$(toluene) or $Cr(CO)_3$(benzene) with the diethyl acetal of benzaldehyde followed by hydrolysis of the resulting product: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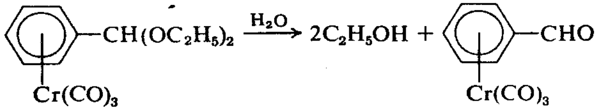
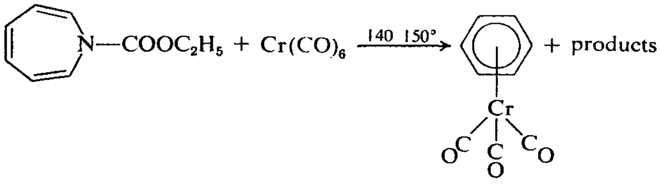
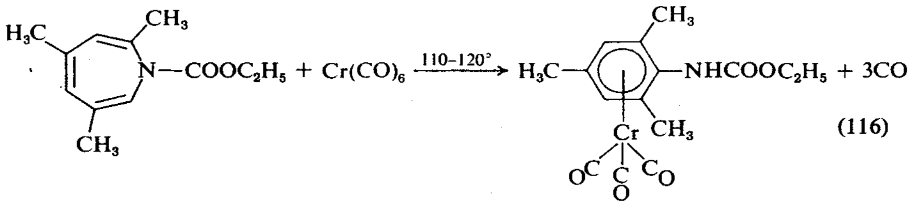

(114)

The exchange reaction 112 was also successfully employed for the synthesis of bis(chromiumtricarbonyl)diphenyl and related compounds by treating the aromatic compounds with a large excess of benzene- or toluenetricarbonylchromium.

Tricarbonylarenechromium derivatives were obtained by reacting $Cr(CO)_6$ with carbethoxyazepines (81) (Eqs. 115, 116).


(115)

Treatment of $Cr(CO)_6$ with 1-methoxycyclohexa-1,3-diene in refluxing nonane formed $Cr(CO)_3C_6H_6$ in 82% yield (82). Other methoxy-substituted cyclic dienes were shown to undergo this methanol elimination and aromatization reaction.


(116)

Chromium tricarbonylarene complexes are usually thermally stable ($Cr(CO)_3C_6H_6$, mp 177.5–178° and $Cr(CO)_3C_6H_3(CH_3)_3$, mp 161.5–163°); in the solid state they are ordinarily stable to air.

Tricarbonylarenechromium complexes and the molybdenum analogs have been extensively investigated in order to establish the degree of reactivity of the aromatic portion of the molecule. The main interest here is to compare to reactivity of the aromatic system bonded to the $M(CO)_3$ group with the corresponding uncomplexed aromatic compound. The reactions that have been reported to occur with tricarbonylarenemetal derivatives are of two different types: (a) reactions on a functional group, and (b) substitution reactions on ring positions. Esterifications (79), Claisen condensations (83), Cannizzaro reactions (80), and Wittig reactions (84) are possible for $Cr(CO)_3C_6H_6$ and analogs. Of course, substitution reactions are of paramount interest. Friedel-Crafts acylations, isotopic hydrogen exchange, and replacement of chlorine by OCH_3^- in $Cr(CO)_3C_6H_5Cl$ have been reported:

$$Cr(CO)_3C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} Cr(CO)_3C_6H_5COCH_3 + HCl \qquad (117)$$

$$Cr(CO)_3C_6H_5Cl + CH_3O^- \longrightarrow Cr(CO)_3C_6H_5OCH_3 + Cl^- \qquad (118)$$

Particularly interesting are the Friedel-Crafts acylations. The benzene- (85,86), toluene- (85,87,88), *p*-xylene- (87), and 1,3,5-trimethylbenzene (87) derivatives undergo acetylation with CH_3COCl in the presence of $AlCl_3$. It was found that acetylation of tricarbonyltoluenechromium (87) gives *ortho*- and *para*(methylacetophenone)$Cr(CO)_3$ in a 1:1.5 ratio, with very small amounts of the *meta* isomer. An *ortho*:*meta*:*para* ratio of 1:0.38:1.18 for the same reaction was reported by Herberich and Fischer (88). These results should be compared with the acetylation of toluene, which under analogous conditions gives the *para* isomer predominantly. There is no obvious explanation for this as yet.

Brown (89) has attempted to treat the problem of the change in reactivity of an aromatic system bonded to a $Cr(CO)_3$ group, compared with the uncomplexed system. He applied a molecular orbital treatment to a transition state of the Wheland type, in which the conjugation is extended over five carbon atoms of the benzene ring. He predicted that nucleophilic substitutions should occur much faster in tricarbonylbenzenechromium than in benzene. On the other hand, only tentative conclusions could be drawn for the corresponding electrophilic and radical-type reactions. He concluded that the corresponding reaction rates, however, should not vary significantly from those observed in uncomplexed aromatic systems. These predictions were found to be substantially correct. The pseudo-first order rate constant for reaction 118 was found (90) to be 5.03×10^{-5} sec^{-1} at 65° in comparison with the immeasurably slow reaction of chlorobenzene itself. Qualitative results of the same type had been previously obtained by Nicholls and Whiting (77). Valuable quantitative data on the reactivity of tricarbonylbenzenechromium have been obtained also by Anisimov and co-workers (91). They found that $Cr(CO)_3C_6H_6$ gives isotopic hydrogen exchange with C_2H_5OD in the presence of C_2H_5ONa. The rate constant of the reaction is about 1.0×10^{-5} at 100° (about 50% exchange after 20 hr), whereas under analogous conditions benzene itself does not give any exchange. Provided the mechanism of this reaction is such that it can be classified as an electrophilic substitution, this result, combined with the previous one, would suggest that both the electrophilic and the nucleophilic reactivities of $Cr(CO)_3$arene complexes are considerably enhanced compared with the corresponding uncomplexed aromatic compounds.

Pettit and co-workers (92) have taken a different theoretical approach to the problem of chemical reactivity in tricarbonylarenemetal systems. They first consider that the bonding in $M(CO)_3$arene compounds arises from two main contributions: donation of electrons from the ligand to the metal and back-donation from filled *d* orbitals of the metal to antibonding orbitals of the ligand. The effect of the $M(CO)_3$ group on the reactivity of the aromatic ligand will depend on the relative importance of each of these two mechanisms. The enhanced reactivity in nucleophilic reactions of the tricarbonylarenechromium compounds having been already well established, Pettit and co-workers tried to collect kinetic and equilibrium data to show that back-donation predominates in certain cases. (See Note 3 on page 272.)

Isotopic exchange reactions of tricarbonylarenechromium derivatives have also been studied. While isotopic exchange with labeled ^{14}CO

$$Cr(CO)_3\text{arene} + {}^{14}CO \rightleftharpoons Cr({}^{14}CO)_3\text{arene} + CO \qquad (119)$$

does not occur (93) at 110°, $Cr(CO)_3C_6H_6$ and $Cr(CO)_3C_{10}H_8$ do exchange (94,95) their aromatic ligands at 120° with the corresponding ^{14}C-labeled aromatic compounds:

$$ArCr(CO)_3 + {}^*Ar \rightleftharpoons {}^*ArCr(CO)_3 + Ar \qquad (120)$$

The rate of exchange increases with the dielectric constant of the solvent (96).

Although the arene ligand is thermally the most labile part of the $M(CO)_3$arene molecule, the CO groups are preferably labilized in the presence of ultraviolet irradiation. For example, reaction 119 has been shown to occur in the presence of ultraviolet irradiation (97). Also the photochemical treatment of $Cr(CO)_3$arene compounds with PPh_3, pyridine, dimethyl sulfoxide, and olefins causes the displacement of one of the CO groups and compounds of the type $Cr(CO)_2$(arene)L are obtained, in which L is one of the above-mentioned ligands (98–102, 28). The infrared spectra of these substitution products have been measured by Strohmeier and co-workers (98–101). Substitution products have also been described for the type $Cr(CO)_2$(arene)L with L being an acetylenic compound. The deep violet hexamethylbenzene derivative $Cr(CO)_2(C_6Me_6)(PhC_2Ph)$ is stable in air and decomposes at 110° (101).

The infrared spectra of π-arene chromium tricarbonyls in the carbonyl region have been measured (103,104). In Table 16 some infrared data in the C—O stretching region are reported.

It has been shown (85,104) that the presence of a $Cr(CO)_3$ group has a strong influence on the C—H stretching vibrations, on the skeletal C—C stretching, and on the C—H out-of-plane bands: the first is decreased in intensity, the second is shifted towards lower frequencies, and the third disappears. The two main features of solution spectra of tricarbonylarenechromium complexes are as follows.

(a) The presence of usually only two C—O stretching frequencies even for the analogs of benzene, which suggests that the number of bands is dictated by the local symmetry of the carbonyl moiety (C_{3v}) rather than by the overall symmetry of the molecule.

(b) The shift toward higher or lower frequencies of the C—O stretching vibrations caused by electron-withdrawing or electron-releasing groups on the benzene ring. The latter effect is probably related to the degree of d_π-p_π bonding from the metal to the CO group. The shift depends on the number of substituents on the ring, and very little on their relative position. This effect is clearly evident from the infrared data in Table 16 for the series of anisole derivatives.

Intensity measurements of the infrared C—O stretching bands in

$Cr(CO)_3(C_6Et_6)$ and $Cr(CO)_3C_6H_6$ have been reported (105). The far-infrared spectra of some tricarbonylarenechromium complexes have been measured (106).

Tricarbonylarenechromium compounds have dipole moments (107–109) ranging from 4 to 6 D, depending on the nature and the number of the substituents R on the arene groups. The dipole moments are solvent dependent (109). Since the moments increase with the electron-releasing ability of the substituent R, it has been suggested that the aromatic ring is the site of the partial positive charge.

TABLE 16

C—O Stretching Frequencies of Some Tricarbonylarenechromium Compounds

$Cr(CO)_3$ compound	ν_{CO} (cm^{-1})	Ref.
Methyl benzoate	1997, 1930[a]	103
Fluorobenzene	1996, 1930[a]	103
Acetophenone	1992, 1923[b]	85
Benzene	1987, 1917[a]	103
p-Xylene	1979, 1908[a]	103
Mesitylene	1975, 1905[a]	103
Hexamethylbenzene	1962, 1888[a]	103
Hexaethylbenzene	1959, 1886[a]	103
$MeOC_6H_5$	1975, 1903[b]	111
$1,2\text{-}(MeO)_2C_6H_4$	1969, 1894[b]	111
$1,3\text{-}(MeO)_2C_6H_4$	1970, 1895[b]	111
$1,4\text{-}(MeO)_2C_6H_4$	1971, 1898[b]	111
$1,2,3\text{-}(MeO)_3C_6H_3$	1965, 1888[b]	111
$1,2,4\text{-}(MeO)_3C_6H_3$	1966, 1889[b]	111
$1,3,5\text{-}(MeO)_3C_6H_3$	1965, 1888[b]	111

[a] Cyclohexane solution.

[b] CCl_4 solution.

Surprisingly, the proton resonance spectra of tricarbonylarenemetal derivatives have not been studied very extensively. A preliminary report (110) disclosed that the phenyl protons of $Cr(CO)_3C_6H_6$ and some of its methyl derivatives are shifted to high fields by 1.5–2.0 ppm, compared with the corresponding uncomplexed aromatic hydrocarbons. Similar results were obtained for some methoxy-substituted tricarbonylarenechromium compounds (111).

(See Note 4 on page 272.)

Two-dimensional and three-dimensional x-ray diffraction studies of some tricarbonylarenechromium compounds have been reported. The molecular configuration of the compounds of this class is therefore fully established. X-ray structures have been reported for tricarbonylbenzenechromium (112–114), bis(chromiumtricarbonyl)diphenyl (115), tricarbonylhexamethylbenzenechromium (116), and tricarbonylphenanthrenechromium (117).

An early two-dimensional study (112,113) of $Cr(CO)_3C_6H_6$ had shown that the plane containing the three CO groups is parallel to the benzene ring. The average C—C distance in the benzene ring was found to be 1.40 Å, without indication of any significant difference in the six pairs of carbon atoms. The carbon and oxygen atoms of each CO group are colinear with the metal; a common threefold symmetry axis goes through the ring, the metal atom and the three CO groups. A later three-dimensional study (114) of the same molecule has completely confirmed these results. In particular this has shown unambiguously that no significant distortion of the benzene ring from D_{6h} symmetry occurs, and that all the carbon–carbon distances are equal, within the experimental error. The molecule of $Cr(CO)_3C_6H_6$ together with some average interatomic distances is represented in Fig. 18.

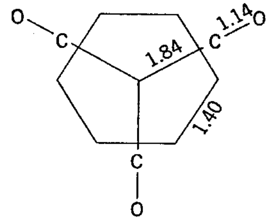


FIG. 18. Molecular configuration of $Cr(CO)_3C_6H_6$ viewed from above the threefold symmetry axis.

The foregoing results of the x-ray studies seem to exclude the existence of alternate carbon–carbon distances in the benzene ring of the tricarbonylarene derivatives of chromium and molybdenum, contrary to what was suggested initially by Fritz and Manchot (118,119). These authors studied the infrared solution spectra of $Cr(CO)_3C_6H_6$ and $Mo(CO)_3C_6H_6$ and the corresponding deuterated compounds; they concluded that a model with a threefold axis for the benzene ring was best suited to explain the data. The same problem existed for dibenzenechromium, $Cr(C_6H_6)_2$, which was found by x-ray studies to have equal (120) and alternating (121) carbon–carbon distances. A later electron diffraction study of this molecule in the gas phase (122) excludes any significant distortion of the benzene ring from a sixfold symmetry.

The x-ray structure of tricarbonylhexamethylbenzenechromium (116) shows that this molecule does not present any special feature compared with $Cr(CO)_3C_6H_6$, apart from an interesting twofold distortion of the aromatic ring. There are two sets of carbon–carbon distances, two short bonds of 1.37 Å and four longer bonds of 1.44 Å. This result, however, was not considered to be indicative of any special bonding situation in the complex, because hexamethylbenzene itself may present a similar distortion at ordinary temperature.

By proper substitution of the ring positions of $Cr(CO)_3C_6H_6$, the symmetry elements of this molecule can be destroyed and optical isomers become possible. This has been confirmed by the isolation of the two enantiomers of the chromiumtricarbonyl derivative of *m*-methoxybenzoic acid (123).

e. Metal carbonyl derivatives of heterocyclic unsaturated systems. Hexacarbonylchromium and thiophene react to give $Cr(CO)_3C_4H_4S$, a red crystalline solid (139). The x-ray structure of this compound has been published (140).

An attempt to prepare a sandwich derivative of pyridine by protecting the lone pair on the nitrogen was made by Wilkinson and co-workers (141) who reacted $Mo(CO)_6$ with methylpyridinium iodide. This attempt was unsuccessful because the undesired reaction of iodide ion with the hexacarbonyl occurred and formed the complex anion $[MoI(CO)_5]^-$ (142*a*). However, the chromium salt, $[C_5H_5NCH_3][CrI(CO)_5]$, was converted by heating at 130–150° into a tricarbonyl compound of formula $Cr(CO)_3(CH_3C_5H_4N)$, which was found (142*b*) to be *N*-methyldihydropyridinetricarbonylchromium.

f. Oxygen- and sulfur-containing ligands. Relatively few examples of substitution products with oxygen- and sulfur-containing ligands are known for the three hexacarbonyls of the group VI metals. No thermal reaction was reported (143) to occur between diphenyltellurium and $Cr(CO)_6$.

Table 17 describes the most representative examples of compounds of this class prepared to date. The thiourea, thioacetamide, and dimethylformamide complexes have been included in the table in keeping with the generally accepted view that these ligands are sulfur and oxygen donors, respectively. Since these ligands can also potentially act as nitrogen donors a definitive investigation of the bonding seems desirable.

All the pentacarbonyl derivatives and some of the other compounds listed in Table 17 were obtained by irradiation of the hexacarbonyls in the presence of the ligand.

g. Nitrogen-containing ligands. Several amine-substituted carbonyl compounds of Cr, Mo, and W have been described and most of the known examples are listed in Table 18. Their preparation involves treating the hexacarbonyl with the ligand while heating or irradiating with ultraviolet light. By the thermal method, mixtures of mono-, bi-, and trisubstitution products are obtained, whereas the ultraviolet irradiation method apparently is better for preparing the monosubstituted derivatives, $M(CO)_5L$.

Both the thermal and photochemical processes give *cis* bi-, and trisubstitution products. $Mo(CO)_4py_2$ prepared by ultraviolet irradiation was found to have a dipole moment of 9.3 D (151), suggesting the *cis* isomer. This interpretation is supported by the findings of Kraihanzel and Cotton (152), who reported four bands in the C—O stretching region for $Mo(CO)_4py_2$ prepared by the thermal method.

Acrylonitrile complexes of the type $Mo(CO)_{6-n}(\text{acrylonitrile})_n$, with n being 1, 2 and 3, were prepared by ligand displacement from the corresponding acetonitrile complexes (153). On the basis of infrared and nuclear magnetic resonance data, it was concluded that when n is 1 and 2, the attachment of acrylonitrile is through the lone pair of electrons on nitrogen, whereas when n is 3 the coordination of acrylonitrile to molybdenum is through the olefinic double bond. It is noteworthy that direct reaction of $Mo(CO)_6$ with a large excess of acrylonitrile at reflux temperature gave a compound of formula $Mo(CO)_2(\text{acrylonitrile})_2$ (154). A polymeric structure was suggested for this compound.

The infrared spectra of several amine-substituted group VI carbonyls of the type $M(CO)_{6-n}L_n$ have been recorded by Kraihanzel and Cotton; assignments of bands and calculation of force constants were reported (152).

Cotton and Wing (155) have determined the x-ray structure of *cis*-tricarbonyldiethylenetriaminemolybdenum and found that the coordination around the molybdenum is that of a distorted octahedron.

By reaction of $Na[MoC_5H_5(CO)_3]$ with *p*-anisyldiazonium tetrafluoroborate, the first known example of an arylazo derivative of a transition

TABLE 17

Carbonyl Compounds of Chromium, Molybdenum, and Tungsten with Oxygen- and Sulfur-Containing Ligands

Compound	Mp (°C)	Color	ν_{CO} (cm^{-1})	Ref.
$Mo(CO)_5(DMF)$[a]	—	—	2068, 1924, 1847	144
$Mo(CO)_5$(isopropyl ether)[a]	—	—	2079, 1940, 1893	144
$Mo(CO)_4(OPPh_3)_2$	215 dec.	Yellow	2008, 1880, 1848, 1797	145
$Mo(CO)_3(DMF)_3$	145–148 dec.	Yellow	1960, 1922, 1851	146
$Mo(CO)_3$(diglyme)	156–160 dec.	Yellow	1904, 1834	147
$Mo(CO)_3(OPPh_3)_3$	221 dec.	Yellow	1900, 1775, 1735	145
$W(CO)_5$(ethanol)[a]	—	—	2078, 1929, 1885	144
$W(CO)_4(DMF)_2$[a]	—	—	1997, 1858, 1832, 1791	144
$W(CO)_4(OPPh_3)_2$	200	Orange	2000, 1860, 1839, 1790	145
$W(CO)_5$(acetone)[a]	—	—	2067, 1920, 1847	144
$Cr(CO)_5SO_2$[b]	—	—	—	148
$Cr(CO)_5$(dimethyl sulfoxide)[c]	102 dec.	Light yellow	—	148
$Cr(CO)_5$(tetrahydrothiophene)	27	Yellow	—	148
$Cr(CO)_4$(2,5-dithiahexane)	130 dec.	Bright yellow	2020, 1914, 1898, 1869	149
$Cr(CO)_3$(3,6,9-trithiaundecane)	130 dec.	Yellow	1932, 1818	149
$Mo(CO)_4$(2,5-dithiahexane)	148 dec.	Yellow	2030, 1919, 1905, 1868	149
$Mo(CO)_3(CH_3CSNH_2)_3$[d]	122	Green-yellow	1909, 1798, 1783	60
$Mo(CO)_3$(3,6,9-trithiaundecane)	145 dec.	Off white	1932, 1812	149
$Mo(CO)_3$(tetrahydrothiophene)$_3$	—	Pale yellow	1925, 1821	60
$Mo(CO)_3$(dimethyl sulfide)$_3$[d]	—	Pale yellow	1925, 1799	60
$Mo(CO)_3$(diethyl sulfide)$_3$[d]	90 dec.	Gray-yellow	1930, 1826	60
$Mo_2(CO)_6(EtS(CH_2)_2SEt)_3$[d]	154–157	Yellow	1926, 1811	150
$Mo_2(CO)_6(MeS(CH_2)_2SMe)_3$[d]	148–150	Pale yellow	1930, 1814	150
$W(CO)_5$(dimethyl sulfoxide)[c]	96	Yellow-green	—	148
$W(CO)_5SO_2$[b]	—	—	—	148
$W(CO)_5$(tetrahydrothiophene)	36	Green-yellow	—	148
$W(CO)_4$(2,5-dithiahexane)	160 dec.	Dark orange	2023, 1910, 1896, 1867	149

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[a] Identified by infrared spectrum only.

[b] Not isolated, indirect evidence only.

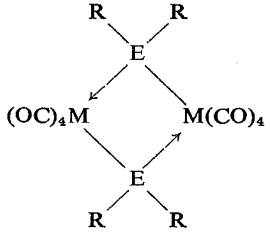
[c] Complexes of this type were suggested to contain a sulfur–metal bond, rather than an oxygen–metal bond.

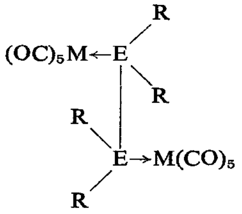
[d] Prepared by ligand exchange from $Mo(CO)_3$(cycloheptatriene).

metal was obtained (156). The product obtained from the reaction has the formula $MoC_5H_5(CO)_2(N_2C_6H_4OCH_3)$; it is a red-orange crystalline solid, soluble in the common organic solvents and insoluble in water.

h. Phosphorus-, arsenic-, and antimony-containing ligands. Representative examples of complexes obtained from reactions of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ with this type of ligand are presented in Table 19. The reactions normally involve treating the hexacarbonyl with the ligand in the presence of a solvent. It has been reported (178), however, that ultraviolet irradiation is required to obtain the tetrasubstitution products of $Cr(CO)_6$ and $Mo(CO)_6$ with Venanzi's tetradentate ligand (179) tris(*o*-diphenylarsinophenyl)arsine, As[*o*-$C_6H_4AsPh_2$]$_3$, whereas in the absence of ultraviolet light only three positions of the arsine are made available for the metal.

Interestingly, although the organic alkyl and aryl diarsines and diphosphines of the type $R_2E–ER_2$ (E = P, As; R = Et, Me, Ph) give, according to Chatt and co-workers (180,181), E-bridged complexes of the two types **82** and **83**, $(CF_3)_2AsAs(CF_3)_2$ has been reported (182) to give no crystalline complexes with $Cr(CO)_6$. Compounds of the type **82** and **83** have also been reported by Hayter (183).


(82)


(83)

The disubstitution products, $M(CO)_4L_2$, can exist in the *cis* and *trans* forms. The same is obviously true for the tri- and tetrasubstituted compounds. The two isomers of $Mo(CO)_4(PEt_3)_2$ were separated for the first time by Poilblanc and Bigorgne (184), who also report that isomerization occurs in solution. The separation of *cis* and *trans* isomers of $Mo(CO)_4(PPh_3)_2$ proved more difficult (185). The *trans* isomer crystallizes first while the *cis* isomer can be obtained from the mother liquors. This probably explains why Hieber and Peterhans (186) had previously obtained only the *trans* isomers of $M(CO)_4(PPh_3)_2$ with M = Cr, Mo, and W. After four days at 45°C, hydrocarbon solutions of initially pure *cis*- and *trans*-$Mo(CO)_4(PPh_3)_2$ give identical mixtures of the two isomers, thus demonstrating the interconversion of one isomer to the other (185). The existence

TABLE 18

Carbonyl Compounds of Chromium, Molybdenum, and Tungsten with Nitrogen-Containing Ligands

Compound	Mp (°C)	Color	ν_{CO} (cm^{-1})	Ref.
$Cr(CO)_5NH_3$	—	Yellow	—	157,158
$Cr(CO)_5$py	96	Yellow	2073, 1986, 1938, 1905	152,157,159
$Cr(CO)_5$cyclohexylamine	107 dec.	Yellow	2067, 1980, 1935, 1890	152
$Cr(CO)_5NEt_3$	5	Lemon-yellow	—	160
$Cr(CO)_5$piperidine[a]	69.5	Yellow	—	160
$Cr(CO)_5$morpholine	—	Yellow	2080, 1992, 1945, 1920	161
$Cr(CO)_5NCMe$	71	Yellow	—	162
$Cr(CO)_4py_2$	172 dec.	Yellow-orange	2020, 1899, 1878, 1837	152,163
$Cr(CO)_4$en	> 280 dec.	Yellow	2004, 1873, 1855, 1810	152
$Cr(CO)_3(NH_3)_3$	—	Yellow	—	158,164
$Cr(CO)_3py_3$	—	Red	—	163,164
$Cr(CO)_4$phen	—	Deep red	—	163,164
$Cr(CO)_4$dipy	—	Deep orange	2010, 1908, 1888, 1833	165
$Cr(CO)_3$(dipy)(NH_3)	—	Black	1873, 1765	158
$Cr(CO)_3$den	> 230 dec.	Pale brown	1881, 1735	57
$Cr(CO)_3$(1,3,5-trimethylhexahydrotriazine)[c]	—	Yellow	$\sim$1900, $\sim$1785, $\sim$1770	166
$Mo(CO)_5NH_3$	—	Yellow	—	167
$Mo(CO)_5$py	—	—	2079, 1987, 1944, 1890	152,168
$Mo(CO)_5$cyclohexylamine	102 dec.	Yellow	2072, 1983, 1938, 1895	152
$Mo(CO)_5$piperidine[a]	75–76	Yellow	—	160
$Mo(CO)_5$morpholine	105–108	Pale yellow	2074, 1988, 1943, 1915	161
$Mo(CO)_5$pyrrolidine	53–55	Pale yellow	2072, 1982, 1940, 1910	161
$[Mo(CO)_5]_2$piperazine	—	Pale yellow	2079, 1980, 1940, 1901	161
$Mo(CO)_4py_2$	115 dec.	Yellow-orange	2025, 1907, 1881, 1839	152,168
$Mo(CO)_4$dipy	150–170 dec.	Red	2022,1906, 1877, 1826	57,165
$Mo(CO)_4$phen	—	Ruby red	—	163
$Mo(CO)_4(NCMe)_2$	90 dec.	Yellow	—	169
$Mo(CO)_4(PhCH{=}CPhCN)$[c]	102–103 dec.	Red	—	170
$Mo(CO)_3(NH_3)_3$	—	—	—	167
$Mo(CO)_3py_3$	—	Yellow-brown	1888, 1850, 1818, 1746	57,163
$Mo(CO)_3$(dipy)(PPh_3)	—	Purple	1913, 1820, 1792	171
$Mo(CO)_3$terpy[d]	—	Light red	1901, 1815, 1765	172
$Mo(CO)_3$den	> 230 dec.	Pale yellow	1883, 1723	57
$Mo(CO)_2phen_2$	—	Blue-black	1782, 1720	173
$W(CO)_5NH_3$	—	Light yellow	—	167
$W(CO)_5$py	114	Light yellow	2076, 1980, 1933, 1895	152,167,174
$W(CO)_5$cyclohexylamine	—	Yellow	2071, 1974, 1929, 1894	152
$W(CO)_5$aniline	115–117 dec.	Yellow	—	174
$W(CO)_5$piperidine[a]	97	Yellow	—	160
$W(CO)_5$morpholine	139–141	Pale yellow	2070, 1979, 1935, 1915	161
$W(CO)_5NCMe$	85	Yellow	2083, 1948, 1931	144,153,169
$W(CO)_5$acrylonitrile	74–75	Pale yellow	2079, 1949, 1934	153,175
$W(CO)_4py_2$	$\sim$120 dec.	Orange	2012, 1888, 1869, 1828	152,167, 174,176
$W(CO)_4$phen	—	Red	—	176
$W(CO)_4$dipy	—	Deep red	2008, 1900, 1880, 1829	165,176
$W(CO)_4(NCMe)_2$	100 dec.	Yellow	2021, 1913, 1874, 1825	144,169
$W(CO)_4$(acrylonitrile)$_2$	—	—	2011, 1939, 1918, 1848	153
$W(CO)_3$terpy[d]	—	—	—	172
$W(CO)_3$den	> 230 dec.	Dark yellow	1873, 1718	57
$W(CO)_3(NCMe)_3$	—	Yellow	1892, 1776	144,177
$W(CO)_3$(acrylonitrile)$_3$	—	—	2012, 1980, 1911, 1842	153
$W(CO)_2phen_2$	—	Dark blue	1766, 1736	173

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[a] Disubstitution products also described.

[b] Several other alkylhexahydrotriazine complexes of Cr, Mo, and W reported.

[c] Attachment through the carbon–carbon double bond is believed (170) to occur in this case, but for further discussion of this, see Ref. 153.

[d] Infrared evidence only; not isolated.

TABLE 19

Carbonyl Compounds of Chromium, Molybdenum, and Tungsten with Phosphorus-, Arsenic-, and Antimony-Containing Ligands

Compound	Mp (°C)	Color	ν_{CO} (cm^{-1})	Ref.
$\mathrm{Cr(CO)_5PPh_3}$	127–128	Pale yellow	2066, 1988, 1942	187,194
$\mathrm{Cr(CO)_5P(OPh)_3}$	59.5–60	Colorless	2080, 2000, 1960	187,194
$\mathrm{Cr(CO)_5P(CH_2CH_2CN)_3}$	136–137	Colorless	2063, 1988, 1938	187,194
$\mathrm{Cr(CO)_5P(NMe_2)_3}$	145 dec.	Yellow	2055, 1978, 1932	195
$\mathrm{Cr(CO)_5AsPh_3}$	135–135.5	Yellow	2066, 1988, 1942	187,194
trans-$\mathrm{Cr(CO)_4(PPh_3)_2}$	251–252 dec.	Yellow	2012w, 1949w, 1897vs	186,187
$\mathrm{Cr(CO)_4(P(OPh)_3)_2}$	148–149	Colorless	2038w, 1976w, 1930vs	187,194
$\mathrm{Cr(CO)_4(P(OBu)_3)_2}$	$\mathrm{b_1}$ 230	Pale green	2024w, 1960w, 1906vs	187,194
$\mathrm{Cr(CO)_4Diphos}$[a]	201 dec.	Yellow	2012, 1901, 1877	188,197
$\mathrm{Cr(CO)_4[CH_2(PPh_2)_2]}$[a]	170.5–171.5	Yellow	2006, 1915, 1897, 1875	188
$\mathrm{Cr(CO)_4[\mathit{o}\text{-}C_6H_4(PPh_2)_2]}$[a]	162–164.5	Colorless	2001, 1906, 1884	188
$\mathrm{Cr(CO)_4[C_2H_4(AsPh_2)_2]}$	173	Yellow	2008, 1893, 1869	198
$\mathrm{Cr(CO)_4Diars}$	170	Pale yellow	2012, 1922, 1898	199,200
$\mathrm{Cr(CO)_3(P(OPh)_3)_3}$	126–126.5	Colorless	2028, 1961, 1908, 1876	187
$\mathrm{Cr(CO)_3(PF_3)_3}$	—	Colorless	2062, 2010, 1998	196
$\mathrm{Cr(CO)_3(\mathit{v}\text{-}triars)}$	—	Yellow	1923, 1825	201
$\mathrm{Cr(CO)_3QAS}$[a]	279–281	Yellow	1934, 1838	178
cis-$\mathrm{Cr(CO)_2Diphos_2}$	280–280.5	Pale orange	1848, 1708	188
trans-$\mathrm{Cr(CO)_2Diphos_2}$	279–280	Vermilion-red	—	188
cis-$\mathrm{Cr(CO)_2[\mathit{o}\text{-}C_6H_4(PPh_2)_2]_2}$	263.5–266.5	Orange	1826, 1760	188
trans-$\mathrm{Cr(CO)_2[\mathit{o}\text{-}C_6H_4(PPh_2)_2]_2}$	Not isolated	—	1844	188
$\mathrm{Cr(CO)_2[C_2H_4(AsPh_2)_2]_2}$[a]	230–233	Yellow	1834, 1769	198
$\mathrm{Cr(CO)_2QAS}$[b]	304–305	Orange	1841, 1788	178
$\mathrm{Cr(CO)_2Diars_2}$	226 dec.	Yellow	1845, 1771	199,200
$\mathrm{Cr_2(CO)_6Diphos_3}$[a,c]	263 dec.	Yellow	1923, 1834	197
$\mathrm{Cr_2(CO)_8(PEt_2)_2}$[a]	> 350	Maroon	2003, 1942	180
$\mathrm{Mo(CO)_5PPh_3}$	138–139	Colorless	2074, 1988, 1946	187,194
$\mathrm{Mo(CO)_5P(NMe_2)_3}$	152–154 dec.	Colorless	2066, 1983, 1938	195
cis-$\mathrm{Mo(CO)_4(PPh_3)_2}$	—	—	2020, 1926, 1908, 1893	184
trans-$\mathrm{Mo(CO)_4(PPh_3)_2}$	273–275 dec.	Yellow	1902	186

(continued)

TABLE 19 (continued)

Compound	Mp(°C)	Color	ν_{CO} (cm^{-1})	Ref.
cis-$\mathrm{Mo(CO)_4(PEt_3)_2}$	73	Colorless	2014, 1915, 1900.5, 1890	184,185
trans-$\mathrm{Mo(CO)_4(PEt_3)_2}$	58	Yellow	1887	184,185
trans-$\mathrm{Mo(CO)_4(P(OPh)_3)_2}$	110–111	Colorless	2055w, 1990m, 1941vs	187
$\mathrm{Mo(CO)_4Diars}$	158	Colorless	2026, 1938, 1923, 1914	199,200
$\mathrm{Mo(CO)_4[C_2H_4(AsPh_2)_2]}$	176	Colorless	2020, 1908, 1879	198
$\mathrm{Mo(CO)_3(PPh_3)_3}$[c]	160 dec.	Yellow	1949, 1908, 1891, 1835	57
cis-$\mathrm{Mo(CO)_3(P(OPh)_3)_3}$	—	Yellow	1898, 1757, 1733	203
$\mathrm{Mo(CO)_3(PF_3)_3}$	89	Colorless	2074, 2026, 1994	202
$\mathrm{Mo(CO)_3(PCl_3)_3}$[c]	85 dec.	Yellow	2041, 1989, 1960	57
$\mathrm{Mo(CO)_3(AsPh_3)_3}$	170 dec.	Yellow	1957, 1910, 1889, 1847	57
$\mathrm{Mo(CO)_3(SbPh_3)_3}$	220 dec.	Yellow	1972, 1945, 1875, 1850	57
$\mathrm{Mo(CO)_2Diars_2}$	231	Pale yellow	1859, 1786	199, 200
$\mathrm{Mo_2(CO)_{10}P_2Me_4}$	141–142	Colorless	2079, 2069, 1990, 1954	180
$\mathrm{Mo_2(CO)_{10}As_2Me_4}$	116.5–117.5	Yellow	2077, 2069, 1992, 1954	180
$\mathrm{Mo_2(CO)_8(AsMe_2)_2}$	310–315 dec.	—	2026, 1960	180
$\mathrm{W(CO)_5PPh_3}$	146–147	Pale yellow	2075, 1980, 1939	187,194
trans-$\mathrm{W(CO)_4(PPh_3)_2}$	292–294 dec.	Yellow	1894	186
$\mathrm{W(CO)_4(P(NMe_2)_3)_2}$	153	Yellow	1870	195
$\mathrm{W(CO)_4Diars}$	168	Pale yellow	2016, 1923, 1905, 1885	199,200
$\mathrm{W(CO)_3(\mathit{v}\text{-}Triars)}$	—	—	1930, 1835	201
$\mathrm{W(CO)_2Diars_2}$	237 dec.	Bright yellow	1850, 1774	199,200
$\mathrm{W_2(CO)_{10}P_2Me_4}$	162–163	Colorless	2079, 2068, 1981, 1946	180
$\mathrm{W_2(CO)_{10}As_2Me_4}$	144–146	Yellow	2079, 2070, 1985, 1947	180
$\mathrm{W_2(CO)_8(AsMe_2)_2}$	> 350	—	2018, 1946	180

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[a] Molybdenum and tungsten analogs also described.

[b] Molybdenum analog also described.

[c] Obtained by ligand exchange from $\mathrm{Cr(CO)_3}$(cycloheptatriene).

of isomers has also been established by Poilblanc and Bigorgne for the trisubstituted phosphine derivatives $Mo(CO)_3L_3$.

The infrared spectra of some disubstituted compounds (187) in general contain two weak bands at higher frequency in addition to the single band expected for the D_{4h} symmetry of the *trans* isomer. This suggests *trans* ⇌ *cis* rearrangement in solution. Chatt and Watson (188) also report evidence for such a rearrangement for substitution products of $Cr(CO)_6$ with bidentate phosphines.

Cotton and Kraihanzel (189) have analyzed the infrared spectra of phosphine-substituted carbonyls of group VI metals in the C—O stretching region.

Substitution compounds of chromium, molybdenum, and tungsten with dialkylphosphide anions, PR_2^-, have been reported (190). Their formation occurs by ligand displacement from $M(CO)_3(NH_3)_3$:

$$M(CO)_3(NH_3)_3 + 3KPPh_2 \longrightarrow K_3[M(CO)_3(PPh_2)_3] + 3NH_3 \qquad (121)$$

In these compounds the oxidation number of the metal is formally zero.

i. Isonitriles. $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ show a relatively low reactivity towards alkyl isonitriles (191). $Cr(CO)_6$ does not react with CH_3NC on heating at 100° for several days. With an aromatic isonitrile the monosubstitution products $M(CO)_5$ (p-$CNC_6H_4OCH_3$), with M being Cr, Mo, W, have been isolated by heating the hexacarbonyls at 130°C for 2–3 hr. The trisubstitution product, $Cr(CO)_3(CNR)_3$, can be obtained by ligand exchange from $Cr(CO)_3(NH_3)_3$ (164). By the same ligand exchange reaction but using $Mo(CO)_3C_7H_8$ and $Cr(CO)_3C_7H_8$ as starting materials, other alkyl and aryl isonitrile complexes have been obtained (58).

Bigorgne (192) has reacted $Mo(CO)_6$ with phenyl isonitrile and found that also the bi- and trisubstitution products can be obtained by the direct thermal reaction. Only mixtures of the three compounds were, however, obtained and no isolation of the products was apparently attempted.

Murdoch and Henzi have reported (193) that mono-, bi-, and trisubstitution products of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ with phenyl- and cyclohexyl isonitriles can be obtained by the reaction of the halogenopentacarbonylmetal anions $[MX(CO)_5]^-$ (X = Cl, Br, I) with the ligand.

j. Mechanistic studies. As discussed in the previous sections, the hexacarbonyls of chromium, molybdenum, and tungsten react with several Lewis bases to give substitution reactions of the type:

$$M(CO)_6 + nL \rightleftharpoons M(CO)_{6-n}L_n + nCO \qquad (122)$$

Reactions of this type have been carried out either thermally or photochemically with different nucleophiles, such as amines, tertiary phosphines, aromatic hydrocarbons, and so on. The isotopic exchange reaction

$$M(CO)_6 + {}^{14}CO \rightleftharpoons M({}^{14}CO)_6 + CO \qquad (123)$$

falls in the same category.

Kinetic data on reaction 123 are available in the literature for $Cr(CO)_6$ (93), $Mo(CO)_6$ (204), and $W(CO)_6$ (205). These three reactions have been found to be first order in $M(CO)_6$ concentration and to be independent of carbon monoxide concentration. A dissociative reaction pathway was therefore suggested for the isotopic carbon monoxide exchange:

$$M(CO)_6 \xrightarrow{\text{slow}} \{M(CO)_5\} + CO \qquad (124)$$

$$\{M(CO)_5\} + {}^{14}CO \xrightarrow{\text{rapid}} M({}^{14}CO)_6 \qquad (125)$$

The activation energies for the exchange reactions are (in kcal/mole): 39 ($Cr(CO)_6$), 30.8 ($Mo(CO)_6$), and 40.4 ($W(CO)_6$). These results are consistent with the generally accepted idea that octahedral complexes prefer to react via dissociative mechanisms and suggest that reactions of the type represented in Eq. 122 would occur similarly through a coordinately unsaturated pentacarbonyl species. This was confirmed by kinetic studies on the reactions of $Mo(CO)_6$ with phosphines (206), amines (206), and aromatic hydrocarbons (207,207*a*). Zero order kinetics with respect to the nucleophile concentration were found in all the experiments; when activation parameters were determined, these were found to be in excellent agreement with those previously obtained for the carbon monoxide exchange reactions. The activation energy for the reaction of $Mo(CO)_6$ with 1,2-bis(diphenylphosphino)ethane was found (206) to be 30.1 kcal/mole, compared with 30.8 kcal/mole for the system $Mo(CO)_6/{}^{14}CO$.

The reaction of group VI hexacarbonyls with aromatic compounds deserves some comment.

$$M(CO)_6 + \text{arene} \longrightarrow M(CO)_3\text{arene} + 3CO \qquad (126)$$

Strohmeier (137) found that the rate of formation of $Mo(CO)_3C_6H_{6-n}R_n$ (with R being F, H, Me for $n = 1$ and Me for $n = 2$), was only slightly influenced by the nature of the substituent R.

The same author investigated the kinetics of the reaction of $Mo(CO)_6$ with p-xylene to give $Mo(CO)_3C_6H_4Me_2$. He reported (208) that the rate of evolution of carbon monoxide obeyed the following kinetic expression:

$$\frac{d[CO]}{dt} = k\sqrt{[Mo(CO)_6]}\cdot\sqrt[3]{[p\text{-xylene}]} \qquad (127)$$

This result suggested that the formation of the molybdenum complex takes place by a mechanism more complicated than the one previously postulated by Fischer and co-workers (76). These authors had postulated the simultaneous displacement of three carbon monoxide groups from the hexacarbonyl by the aromatic hydrocarbon.

Later, Brown (207) and Werner (207*a*) and their co-workers studied the reactions of $Mo(CO)_6$ with aromatic hydrocarbons and obtained some additional kinetic data. Brown operated under pseudo-first order conditions, i.e., with a large excess of the aromatic compound. He found the reaction to be first order with respect to $Mo(CO)_6$ concentration but obviously he could not determine the order with respect to the aromatic hydrocarbon. Werner showed the reaction to be first order with respect to $Mo(CO)_6$ concentration and independent of arene concentration. Accordingly, he proposed the following reaction mechanism:

$$Mo(CO)_6 \xrightleftharpoons{\text{slow}} \{Mo(CO)_5\} \xrightleftharpoons{+\,L(\text{rapid})} Mo(CO)_5L \qquad (128)$$

$$Mo(CO)_5L \xrightleftharpoons{-CO} Mo(CO)_4L \xrightleftharpoons{-CO} Mo(CO)_3L \qquad (129)$$

Hexacarbonylmolybdenum therefore reacts by a dissociative mechanism as was the case for the isotopic exchange reaction with ^{14}CO, which was also found to be independent of carbon monoxide concentration (204).

Both Strohmeier (208) and Werner (207*a*) probably did not provide for sufficiently prompt elimination of carbon monoxide from the reaction mixture. Equilibrium effects can possibly be responsible for both Strohmeier's kinetic expression (Eq. 127) and Werner's dependence of rate constants on initial $Mo(CO)_6$ concentration and on the aromatic hydrocarbon used.

In connection with these mechanistic studies on the formation of tricarbonylarenemetal compounds, it is pertinent that Sheline and coworkers (209) found some infrared evidence for the existence of labile compounds of the type $W(CO)_5L$, with L being benzene, substituted benzenes, or condensed aromatic hydrocarbons such as naphthalene or anthracene. These species were produced by irradiation of hydrocarbon solutions of $W(CO)_6$ and the aromatic compound at room temperature or lower (−80 or −180°).

Although kinetic data for photochemical reactions of the type as shown in Eq. 122 are not yet available, Strohmeier and Gerlach suggested (210, 211) that dissociative mechanisms should also be operative in these cases. In other words, an unstable pentacarbonyl species should be formed as intermediate in the rate determining step, followed by a rapid reaction with the nucleophile

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_6^* \longrightarrow \{M(CO)_5\} + CO \qquad (130)$$

This reaction mechanism is supported by the observations (212,213) that the infrared spectra of the hexacarbonyls change drastically under ultraviolet irradiation. For hydrocarbon solutions of $W(CO)_6$, three bands at 2075, 1936, and 1912 cm^{-1} were detected in the infrared spectrum, suggestive of pentacarbonyl species. At room temperature the half-life of the newly formed species is about 2 min. When hydrocarbon solutions of the hexacarbonyls were cooled below the freezing point of the solvent and irradiated directly in an infrared cell, a more rapid examination of the produced species was made possible. From observations of changes in the spectra with temperature, it was concluded that probably the pentacarbonyl species in the frozen-glass state has a square pyramidal configuration, whereas in the fluid state it is a trigonal bipyramid.

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G. Carbonyls of Groups V and IV Transition Metals

The number of carbonyl derivatives of groups V and IV transition metals is limited. The only known example of a carbonyl compound from the group IV metals is $Ti(C_5H_5)_2(CO)_2$. A list of the known compounds is given in Table 20.

Chemistry of hexacarbonylvanadium. $V(CO)_6$ is the only metal carbonyl in which the central metal atom does not attain the electronic configuration of the next inert gas. It is paramagnetic, the effective atomic number of the central metal atom being 35. The tendency of $V(CO)_6$ to complete the shell of 36 electrons and hence form the diamagnetic $[V(CO)_6]^-$ anion is evidenced by its chemical reactivity. Hexacarbonylvanadium undergoes disproportionation in the presence of Lewis bases, such as diethyl ether, dioxane, pyridine, aliphatic amines, ketones, aldehydes, alcohols, and esters (1,2):

$$3V(CO)_6 + nB \longrightarrow [V(B)_n][V(CO)_6]_2 + 6CO \tag{131}$$

These reactions are usually fast. The salts $[V(B)_n][V(CO)_6]_2$ can be isolated and analyzed, although they are extremely sensitive to air. In the infrared they show one very intense band at 1861–1859 cm^{-1} and another weak one at 1894–1895 cm^{-1}. Although the cause of this second band is not yet clear, this is characteristic of the infrared pattern of the $[V(CO)_6]^-$ anion (see Table 21). Only a single C—O stretching vibration should in fact be observed in the infrared spectrum of the $[V(CO)_6]^-$ anion if this had O_h symmetry. The extra band at higher wavenumbers observed in tetrahydrofuran could result from a proximity effect by the cation with a consequent distortion of the octahedron. This, in substance, is how Edgell and coworkers (4) explained the presence of extra bands in the infrared spectrum of $NaCo(CO)_4$.

TABLE 20
Carbonyl Derivatives of groups V and IV Transition Metals

Compound	Color	Mp (°C)	Ref.
$V(CO)_6$	Black-green	70 dec.	1,29,30
$[V(CO)_6]^-$	Yellow	—	1,2
$[V(CO)_5PPh_3]^-$	Orange	—	2,7
$V(CO)_4(PPh_3)_2$	Yellow	142 dec.	7
$VC_5H_5(CO)_4$	Orange	138	10
$VC_5H_5(CO)_2$(butadiene)	Red	135–140 dec.	22
$[VC_5H_5(CO)_3]^{2-}$	Yellow	—	11
$V(CO)_3C_7H_7$	Dark green	134–137 dec.	23
$[Nb(CO)_6]^-$	—	—	31
$NbC_5H_5(CO)_4$	Orange-red	144–146	32,33
$[Ta(CO)_6]^-$	Yellow	—	31
$TaC_5H_5(CO)_4$	Red	171–173	33
$Ti(C_5H_5)_2(CO)_2$	Red-brown	> 90 dec.	34

The value of n in Eq. 131 can vary from 4 to 6, but it is usually 6 with oxygen-containing Lewis bases (3) such as acetaldehyde, acetone, methanol, and dimethylformamide.

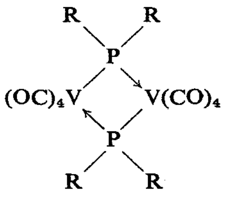
The tendency of $V(CO)_6$ to form the more stable anion is also evidenced by the oxidative properties exhibited by hexacarbonylvanadium toward vanadium π complexes, such as $V(C_5H_5)_2$ (5) and $V(C_6H_3Me_3)_2$ (6). (See Sec. VIII.)

Very few substitution reactions of $V(CO)_6$ have been described so far. The reaction with PPh_3 gives *trans*-$V(CO)_4(PPh_3)_2$ (7). The reactions of $V(CO)_6$ with several phosphines of the types PR_3, PR_2H, and PRH_2 have been reported (8). Tertiary phosphines give derivatives of type **(84)** or **(85)** depending on the nature of R.

$V(CO)_4(PR_3)_2$ **(84)** $R = Ph, Et, Pr$

$[V(CO)_4(PR_3)_2]_2$ **(85)** $R = C_6H_{11}$

The reactions of $V(CO)_6$ with PH_3, $PHPh_2$ (8) and P_2Ph_4 (9) give dimeric diamagnetic compounds $[V(CO)_4PR_2]_2$ for which PR_2-bridged structures **(86)** have been proposed.

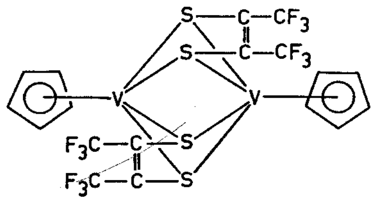


(86)

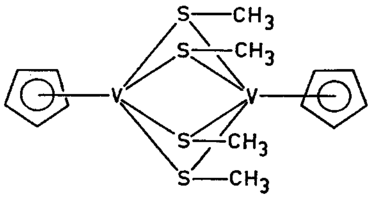
R = H, Ph

Another substitution reaction is the treatment of $V(CO)_6$ with NO, where the nitrosyl $V(CO)_5NO$ was reported (2) to be formed. This compound, however, is very unstable; it could not be isolated and only infrared measurements of its solution have been carried out.

$VC_5H_5(CO)_4$ was first prepared by the reaction of $V(C_5H_5)_2$ with carbon monoxide (10) or, better, with carbon monoxide and hydrogen under pressure (11). Nevertheless, the cyclopentadienyl compound can also be obtained (12) in good yield by the direct reaction of $V(CO)_6$ with cyclopentadiene at about 40°. The reactions of $VC_5H_5(CO)_4$ with tris(dimethylamino)phosphine, Tdp, (13), bis(trifluoromethyl)dithietene (14), and dimethyl disulfide (15) have been described. In the first case the monosubstitution product $VC_5H_5(CO)_3Tdp$ is obtained. Bis(trifluoromethyl)dithietene and dimethyl disulfide cause the displacement of all the carbon monoxide groups from $VC_5H_5(CO)_4$ and the formation of dimeric, probably sulfur-bridged, compounds **(87)** and **(88)**.



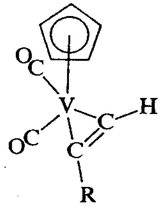
(87)



(88)

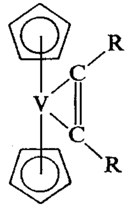
By reaction with cycloheptatriene, $VC_5H_5(CO)_4$ is converted into the mixed complex $V(C_5H_5)(C_7H_7)$, paramagnetic for one electron; therefore the central vanadium atom should be regarded as in a zero oxidation state (16).

The reactions of $VC_5H_5(CO)_4$ with acetylene (17), with monosubstituted acetylenes (17) and with disubstituted acetylenes (18) have been described. Compounds of the type $VC_5H_5(CO)_2(RC_2H)$ **(89)**, with R being H, Pr, Bu and *t*-Bu, were isolated. With disubstituted acetylenes, such as the dimethyl ester of 2-butynedioic acid and bis(trifluoromethyl)acetylene, complexes of composition $V(C_5H_5)_2(RC_2R)$ **(90)**, were obtained.



(89)

R = H, Pr, Bu, *t*-Bu



(90)

R = COOMe, CF_3

Tetracarbonylcyclopentadienylvanadium can be acetylated on the five-membered ring with acetyl chloride in the presence of $AlCl_3$ (19–21).

Reactions with aliphatic and cyclic dienes in the presence of ultraviolet irradiation give compounds of formula $VC_5H_5(CO)_2$(diene) (22).

$V(CO)_3C_7H_7$ has been obtained (23) directly from $V(CO)_6$ and C_7H_8, without evolution of hydrogen. Here, as in the previous case of C_5H_6, the hydrogen is probably absorbed by the excess of unsaturated compound employed. Calderazzo and Calvi have shown (24) that the reaction between $V(CO)_6$ and C_7H_8 gives not only $V(CO)_3(C_7H_7)$ but also a red-brown microcrystalline product of formula $[V(C_7H_8)(C_7H_7)][V(CO)_6]$. In this ionic compound, the positive charge is on the cycloheptatrienyl ring, and the vanadium atom is in a zero oxidation state. In agreement with this interpretation, the compound has a μ_{eff} of 1.84 B.M., corresponding approximately to one unpaired electron.

It has been shown (25) that aromatic compounds react with $V(CO)_6$ at about 35° to give the ionic red crystalline $[V(CO)_4\text{arene}][V(CO)_6]$.

$$2V(CO)_6 + \text{arene} \longrightarrow [V(CO)_4\text{arene}][V(CO)_6] + 2CO \qquad (132)$$

Later (26*a*), reaction 132 was shown to be of a completely general character and several other methyl-substituted compounds of the same type were prepared and characterized. The only limitation is the presence of basic groups on the aromatic molecule. In such a case the competing disproportionation reaction 131 becomes predominant. Despite that, the anisole derivative $[V(CO)_4(PhOMe)][V(CO)_6]$ could be isolated, although in very small yields. From the infrared spectra in the C—O stretching region, a square pyramidal configuration for the $[V(CO)_4\text{arene}]^+$ cation was suggested.

TABLE 21

Infrared Carbonyl Stretching Frequencies in Derivatives of Groups V and IV Transition Metals

Compound	ν_{CO} (cm^{-1})	Medium	Ref.
$V(CO)_6$	1976	Cyclohexane	2
$[V(CO)_6]^-$	1895 w, 1859 vs	THF	6
$VC_5H_5(CO)_4$	2019, 1919	Chloroform	35
$[VC_5H_5(CO)_3]^{2-}$	1748, 1645	Nujol	36
$V(CO)_3C_7H_7$	1975, 1915	Heptane	23
$NbC_5H_5(CO)_4$	2000, 1901	CS_2	33
$[Ta(CO)_6]^-$	1850	—	31
$TaC_5H_5(CO)_4$	2020, 1900	CS_2	33
$Ti(C_5H_5)_2(CO)_2$	1964, 1883	Benzene	34
	1975, 1897	Heptane	26*b*

Attempts have been made to use the $[V(CO)_4\text{arene}]^+$ cations as starting material for the synthesis of the still unknown $V(CO)_3$arene complexes. However, all attempts to prepare these complexes from the tetracarbonylarenevanadium (I) compounds were unsuccessful. On the other hand, by

treatment of $[V(CO)_4C_6H_{6-n}R_n]^+$ with sodium tetrahydridoborate, the cyclohexadienyl compounds $V(CO)_4C_6H_{7-n}R_n$ were obtained (27).

$$[V(CO)_4C_6H_{6-n}R_n]^+ + BH_4^- \longrightarrow V(CO)_4C_6H_{7-n}R_n + \tfrac{1}{2}B_2H_6 \qquad (133)$$

Similar reactions with $NaBD_4$ yielded the corresponding deuterated compounds. The nuclear magnetic resonance spectra suggested that the addition of hydrogen occurs at unsubstituted positions of the aromatic ring.

No extensive x-ray structural work has yet been done on vanadium carbonyl derivatives. A preliminary communication on the x-ray structure of $V(CO)_3C_7H_7$ has appeared (28). The compound appears to have a "piano-stool" configuration with the planar C_7 ring approximately parallel to the plane containing the three carbon monoxide groups.

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VI. HYDRIDO METAL CARBONYLS AND RELATED COMPOUNDS

Transition metals do not give definite hydrides of the type MH_n, but rather have a tendency to give hydrides of the interstitial type (Ti, V) or other hydrides of more definite composition but indefinite nature (Ni, Co, Fe, and Cr).

However, when other ligands such as carbon monoxide, *tert*-phosphines, or the cyclopentadienyl anion are bonded to a transition metal, definite hydrides (although of usually low stability both to air and heat) are obtained. Some of the hydrido carbonyls and substituted hydrido carbonyls of transition metals that have been reported are listed in Table 22. The isolation and handling of the unsubstituted hydrido metal carbonyls is usually very difficult because of their volatility and thermal instability; many of them are unstable even at room temperature.

Hydrido metal carbonyls exist either as neutral species, such as $MnH(CO)_5$, or as negatively charged species, such as $[FeH(CO)_4]^-$. It is perhaps worth pointing out that in the latter example, the metal should be formulated as in a zero oxidation state, if the negative charge is regarded as being carried by the hydrido ligand.

Some of the hydrido carbonyls behave in aqueous solution as strong acids, as is the case for $CoH(CO)_4$. However, it would be unwise to use this experimental fact and draw conclusions about the polarity of the metal–hydrogen bond in the gas phase or in solutions of nonpolar organic solvents.

For a review on the general subject of hydrido complexes of transition metals, see Ref. 1.

TABLE 22

Hydrido Metal Carbonyls and Related Compounds

Compound	Mp (°C)	Color	Ref.
$CrH_2(CO)_5$[a]	—	—	49
$Cr(C_5H_5)H(CO)_3$	57–58 dec.	Yellow	50–52
$[Cr_2H(CO)_{10}]^-$	—	Yellow	14,15,53
$Mo(C_5H_5)H(CO)_3$	50–52 dec.	Yellow	50–52
$Mo(C_5H_5)_2H(CO)_4$-$\mu$$[PMe_2]$	215	Red-orange	22,23
$[Mo_2H(CO)_{10}]^-$	—	—	14,15,54
$W(C_5H_5)H(CO)_3$	65.5–67	Yellow	50–52
$[W_2H(CO)_{10}]^-$	—	—	14,15
$MnH(CO)_5$	−24.6 bp ~100[b]	Colorless	4,5
$Mn_2H_2(CO)_9$	—	Red	16
$Mn_3H(CO)_{10}(BH_3)_2$	—	Dark red	18
$Mn_2H(CO)_8$-$\mu$$[PPh_2]$	154–155	Yellow	55
$Mn_2H(CO)_8$-$\mu$$[P(CF_3)_2]$	—	Yellow	56
$MnH(CO)_4PPh_3$	137–5	Yellow	57
$TcH(CO)_5$[c]	—	—	58
$ReH(CO)_5$	12.5	Colorless	59,60
$Re_3H_3(CO)_{12}$	—	Colorless	20
$FeH_2(CO)_4$	*ca.* −70	Light yellow	61
$[FeH(CO)_4]^-$	—	Light pink or colorless	62,63
$Fe_3H_2(CO)_{11}$[a]	—	—	64,65
$[Fe_3H(CO)_{11}]^-$	—	Dark red	13,64
$Fe_4H_2(CO)_{13}$	—	Black-brown	21
$[Fe_4H(CO)_{13}]^-$	—	Deep brown	21,66
$Fe(C_5H_5)H(CO)_2$	−5	Yellow	67
$OsH_2(CO)_4$[a]	—	—	68
$CoH(CO)_4$	−26	Yellow	69–71
$CoH(CO)_3P(OPh)_3$	~0 dec.	—	72
$CoH(CO)_2(P(OPh)_3)_2$	88	Colorless	73
$CoH(CO)_3PPh_3$	~20 dec.	Light yellow	72
$CoH(CO)(PF_3)_3$	−67	Light yellow	3
$FeCo_3H(CO)_{12}$	~100 dec.	Black-violet	74
$RhH(CO)_4$	*ca.* −11	Pale yellow	75
$RhH(CO)(PPh_3)_3$	—	—	38
$IrH(CO)_4$[a]	—	—	76
$IrH(CO)(PPh_3)_3$	—	—	38
$Ni_2H_2(CO)_6$[d]	—	—	77–80
$Ni_4H_2(CO)_9$[e]	—	Black-violet	81

[a] Not isolated in a pure state or of doubtful existence.
[b] Extrapolated.
[c] Isolated in traces and identified only by infrared spectrum.
[d] Isolated as vermilion-red $Ni_2H_2(CO)_6 \cdot 4NH_3$.
[e] Nickel analysis only.

A. Mononuclear Compounds

The preparation of hydrido metal carbonyls involves the use of vacuum techniques because the hydrido compound formed on acidification of a carbonylmetallate according to reaction 1 must be separated as soon as possible from the reaction mixture and collected in a cold trap in order to limit its spontaneous decomposition.

$$[M(CO)_n]^- + H^+ \longrightarrow MH(CO)_n \tag{1}$$

$CoH(CO)_4$ is best prepared (2) by acidification, with dilute H_2SO_4, of the solution of tetracarbonylcobaltate(I−) obtained from $Co_2(CO)_8$ by a disproportionation reaction in the presence of pyridine:

$$3Co_2(CO)_8 + 12py \longrightarrow 2\,[Copy_6][Co(CO)_4]_2 + 8CO \tag{2}$$

$$[Copy_6][Co(CO)_4]_2 \xrightarrow{2H^+} 2CoH(CO)_4 + 6py + Co^{2+} \tag{3}$$

Kruck and Lang (3) have obtained tris(trifluorophosphine)carbonylhydridocobalt, $CoH(CO)(PF_3)_3$, in excellent yields by treating $Co_2(CO)_8$ either with PF_3 and HF or with PF_3 and hydrogen in the presence of platinum.

$$\tfrac{3}{2}Co_2(CO)_8 + 6PF_3 + 2HF \xrightarrow[70^\circ]{400\ \text{atm}} 2CoH(CO)(PF_3)_3 + CoF_2 + 10CO \tag{4}$$

$$Co_2(CO)_8 + 6PF_3 + H_2 \xrightarrow[70^\circ,\ 5\ \text{days}]{240\ \text{atm}} 2CoH(CO)(PF_3)_3 + 6CO \tag{5}$$

The compound shows a remarkable thermal stability: it can be distilled at 80.5° at normal pressure without appreciable decomposition and it is oxidized by atmospheric oxygen only very slowly.

$MnH(CO)_5$ was prepared (4,5) by acidification of an aqueous solution of $NaMn(CO)_5$ with dilute H_3PO_4. When the compound must be free of water or of any hydrogen-containing substance, the following procedure is recommended (6). The complex, $NaMn(CO)_5 \cdot n$THF, obtained from $Mn_2(CO)_{10}$ and Na sand in tetrahydrofuran, is heated at about 60° *in vacuo* for several hours to eliminate the tetrahydrofuran of crystallization. The sodium pentacarbonylmanganate(I−) is then treated with dry hydrogen chloride at about −10° and the hydride is collected under vacuum in a container cooled to liquid nitrogen temperature.

The preparation of $MnH(CO)_5$ and $Mo(C_5H_5)H(CO)_3$ has been described in detail (7,8). The uncharged mononuclear compounds listed in Table 22 are very volatile. Those with phosphorus-containing substituents are less volatile and show a relatively high thermal stability. The thermal

stability of $MnH(CO)_5$ is much higher than that of $CoH(CO)_4$ and $FeH_2(CO)_4$. The latter compounds decompose at room temperature with evolution of hydrogen and formation of $Co_2(CO)_8$ and $Fe_2(CO)_{12}$. For the cobalt compound this is a reversible process:

$$2CoH(CO)_4 \rightleftharpoons H_2 + Co_2(CO)_8 \tag{6}$$

The rate of decomposition of $CoH(CO)_4$ is proportional to the square of its concentration (9,9*a*). This explains why $CoH(CO)_4$ is relatively stable in dilute solutions or when diluted with an inert gas (CO, H_2, or He—there is no specific action by any one of these gases). The hydrido compounds of Co, Fe, and Mn behave as acids in aqueous solution. $CoH(CO)_4$ is soluble in either hydrocarbons or water; in aqueous solution, it is as strong an acid as HCl (9).

The first dissociation constant (10) of $FeH_2(CO)_4$ ($K_1 = 3.6 \times 10^{-5}$) is comparable with that of acetic acid. $MnH(CO)_5$ is, however, a very weak acid ($K = 0.8 \times 10^{-7}$) in aqueous solution (5). Aqueous solutions of the pentacarbonylmanganates are hydrolyzed according to the following equation:

$$[Mn(CO)_5]^- + H_2O \longrightarrow MnH(CO)_5 + OH^- \tag{7}$$

In decreasing order, the solubilities in H_2O (5) are as follows: for $CoH(CO)_4$, $\sim 3 \times 10^{-2}$ mole/l at 18°; for $FeH_2(CO)_4$, 1.1×10^{-3} at 0°; and for $MnH(CO)_5$, 1.25×10^{-4} at 20°.

$VH(CO)_6$ has not yet been isolated as such. Acidification of aqueous solutions of alkali metal hexacarbonylvanadates gives $V(CO)_6$ rather than $VH(CO)_6$. However, when acidification is carried out in the presence of diethyl ether (11), the hydrido carbonyl can be extracted as the oxonium salt $[(C_2H_5)_2OH]^+\ [V(CO)_6]^-$. The hypothetical $VH(CO)_6$ is probably a strong acid, since its alkali metal salts are stable toward hydrolysis and it forms the oxonium salt. Although probably complicated by experimental uncertainties, the potentiometric titration (12) of aqueous solutions of $VH(CO)_6$ supports the view that this compound behaves as a strong acid.

B. Polynuclear Compounds

Several hydrido polynuclear compounds are known. These are anionic or neutral species.

Examples of the anionic type are: $[Fe_3H(CO)_{11}]^-$, $[Fe_4H(CO)_{13}]^-$, and $[M_2H(CO)_{10}]^-$, with M being Cr, Mo, and W (see Table 22).

The most readily available of these compounds is $[Fe_3H(CO)_{11}]^-$. Its preparation was reported in detail by Case and Whiting (13) and consists of treating $Fe(CO)_5$ with aqueous triethylamine at 80° for 10 hr. Almost quantitative yields of $[NEt_3H][Fe_3H(CO)_{11}]$ are obtained as dark red prisms.

Sodium or tetraalkylammonium salts of the $[M_2H(CO)_{10}]^-$ anions ($M = Cr, Mo, W$) can be prepared by the direct reaction of the hexacarbonyls with $NaBH_4$ or NEt_4BH_4 (14,15). For other indirect methods of preparing these binuclear species, see Section V-F.

Examples of uncharged polynuclear hydrido complexes are: $Mn_2H_2(CO)_9$ (16), $Mn_3H_n(CO)_{12}$ (17), $Mn_3H(CO)_{10}(BH_3)_2$ (18), $Tc_3H_3(CO)_{12}$ (or $Tc_3(CO)_{12}$?) (19), $Re_3H_3(CO)_{12}$ (20), $Fe_4H_2(CO)_{13}$ (21), and $Mo_2(C_5H_5)_2H(CO)_4$-$\mu[PMe_2]$ (22,23).

It is worth noting that $Mn_2H_2(CO)_9$, $Mn_3H_n(CO)_{12}$, and $Mn_3H(CO)_{10}(BH_3)_2$ have been reported to be obtained by treating $Mn_2(CO)_{10}$ with $NaBH_4$ in tetrahydrofuran, followed by acidification with H_3PO_4. Considering that $MnH(CO)_5$ is also a product of this reaction, it is soon realized how complex is the chemical behavior of decacarbonyldimanganese with respect to $NaBH_4$.

From the reaction of $Tc_2(CO)_{10}$ with sodium amalgam, followed by acidification with H_3PO_4, extraction with cyclohexane and evaporation of the solvent, a trinuclear carbonyl compound was isolated (19). To account for its observed diamagnetism, the compound was regarded as the hydrido $Tc_3H_3(CO)_{12}$, although the hydrogen could not be detected either by analysis or by nuclear magnetic resonance measurements. Formulation of the technetium compound as hydrido is, however, strongly supported by the isolation of $Re_3H_3(CO)_{12}$ (20). This compound was obtained by reacting $Re_2(CO)_{10}$ with $NaBH_4$ and then acidifying. The presence of hydrogen was established by direct elemental analysis. On the other hand, the infrared evidence for the presence of hydrogen in the compound was rather ambiguous; also no proton peaks could be observed in the nuclear magnetic resonance spectrum. Later infrared and Raman spectra investigations (24) of this rhenium complex were only partially successful in resolving the problem. A very weak band at 1100 cm^{-1} was observed which on deuteration shifted to 787 cm^{-1}. This band was assigned to a rhenium–hydrogen stretching vibration. The unusually low wavenumber for a metal–hydrogen stretching was correlated with the particular bonding situation of hydrogen, which probably bridges two rhenium atoms.

C. Bonding and Structures

Although the nature of bonding in hydrido metal carbonyls has been the subject of many papers, it was only recently that the problem seems to have been clarified.

$CoH(CO)_4$, $FeH_2(CO)_4$, and $MnH(CO)_5$ have been extensively investigated, especially by infrared and NMR methods. Of particular value from structural and diagnostic points of view are the NMR measurements, since hydrido metal carbonyls are characterized by proton resonances at high field, as shown in Table 23.

TABLE 23

Proton Resonance and Infrared Spectra of Hydrido Metal Carbonyls and Related Compounds

Compound	Chemical shift τ^a from TMS^b	ν_{M-H} (cm^{-1})	Ref.
$Cr(C_5H_5)H(CO)_3$	15.95	—	52
$Mo(C_5H_5)H(CO)_3$	15.65	—	52
$Mo_2(C_5H_5)_2H(CO)_4$-$\mu[PMe_2]$	21.73 (Doublet)	—	22
$[Cr_2H(CO)_{10}]^-$	29.17	—	14,15
$[Mo_2H(CO)_{10}]^-$	22.15	—	14,15
$[W_2H(CO)_{10}]^-$	22.52	—	14,15
$W(C_5H_5)H(CO)_3$	17.55	—	52
$MnH(CO)_5$	17.5	1782–3	33,34
$Mn_2H(CO)_8$-$\mu[PPh_2]$	26.8 (Doublet)	—	55
$Mn_2H(CO)_8$-$\mu[P(CF_3)_2]$	29.07	—	56
$ReH(CO)_5$	—	1832	60
$FeH_2(CO)_4$	21.1	—	29
$CoH(CO)_4$	20.7	1934	32,82
$CoH(CO)(PF_3)_3$	21.4	—	3
$RhH(CO)(PPh_3)_3$	19.9	—	38
$IrH(CO)(PPh_3)_3$	21.2	—	38
$IrHCl_2(CO)(PEtPh_2)_2$	19.0	2008	83

[a] $\tau = 10 - \delta$.

[b] TMS = tetramethylsilane.

$CoH(CO)_4$, which has been most extensively studied because of the interest in it as catalyst for the hydroformylation reaction (25,26), will be discussed more fully. The bonding considerations derived will be generally applicable to the other hydrido metal carbonyls.

Some pertinent experimental findings about $CoH(CO)_4$ are: (a) the compound shows a large proton chemical shift to high field similar to other hydrido carbonyls of transition metals (27); (b) the compound does not show infrared bands attributable to O—H stretching vibrations (27–29); and (c) the compound behaves as a strong acid in aqueous solution, although its solubility in water is rather low. On the basis of these findings, it was possible to rule out the first structural hypothesis (30,31) in which the hydrogen atom was considered as being bonded to the lone pair of electrons of the oxygen atom. It is now generally agreed that the hydrogen atom is bonded to the cobalt. Bands involving Co—H vibration modes have been identified in the infrared spectrum of $CoH(CO)_4$ (28,29,32). The Co—H stretching vibration has been located (32) at 1934 cm^{-1} in the gas phase, whereas a band at 703 cm^{-1} is attributable to a Co—H bending motion. In $MnH(CO)_5$ the Mn—H stretching vibration is at about 1782 cm^{-1} (33,34). From spectroscopic data (32) it appears that the metal–hydrogen force constant is higher in $CoH(CO)_4$ than in $MnH(CO)_5$.

Electron diffraction (30) and infrared studies suggest, but do not prove, that the CO groups are approximately tetrahedrally arranged about the cobalt atom.

On the basis of theoretical considerations two structures were proposed. In one of the structures, the bond is formed by interaction between the d_{z^2} orbital of the metal and the 1s orbital of the hydrogen, the hydrogen being placed on a C_3 axis of the $[Co(CO)_4]$ tetrahedron. The Co—H distance was calculated (35) to be about 1.2 Å (= 2.3 au). In another structure postulated by Liehr (36), a tetrahedral arrangement of the CO groups was again assumed and it was proposed that the hydrogen was bonded to the cobalt atom through the d_{z^2} (or $d_{x^2-y^2}$) orbital, the hydrogen atom being located on the fourfold rotation-reflection axis of the tetrahedron. Although no Co—H distance was deduced, the large chemical shift was interpreted as due to the shielding of the proton by the high electron density on the metal.

It appears now, however, that the large proton chemical shift in $CoH(CO)_4$ does not necessarily imply an exceedingly short Co—H distance. The NMR data of the hydrido metal carbonyls have been theoretically explained (37) on the basis of a normal Co—H distance, i.e., between 2.5 and 2.9 au (the sum of the covalent radii for Co—H being 2.8 au). Support for this theory has been given by the recent preparation of two substituted carbonyl hydrides of iridium and rhodium, $IrHCO(PPh_3)_3$ and $RhHCO(PPh_3)_3$, which show a large chemical shift to high field (38), comparable with that of $CoH(CO)_4$ (see Table 23). The location of hydrogen in the rhodium complex was shown by an x-ray investigation (39) in which the metal–hydrogen distance was found to be 1.72 ± 0.15 Å. Preliminary x-ray data (40) on $MnH(CO)_5$ have shown that the molecule has approximately C_{4v} symmetry. The position of the hydrogen ligand was not established precisely, but if certain assumptions are valid, the manganese–hydrogen distance should be in the range 1.4–1.6 Å. A further report on the x-ray structure of $MnH(CO)_5$ (41) has substantially confirmed the preliminary data. Although the hydrogen position was still not located, further evidence was gathered that the hydrogen atom should occupy a definite position around the metal, which is in an approximately octahedral environment. On the other hand, an Mn—H distance of 1.28 Å was calculated from the second moment that was obtained in a broad-line proton nuclear magnetic resonance investigation of a polycrystalline sample of $MnH(CO)_5$ at $-165°$ (42).

The view that hydrogen probably occupies a definite position in the coordination sphere of the metal in all the hydrido carbonyl compounds is also supported by the Raman spectrum of $[FeH(CO)_4]^-$, isoelectronic with $CoH(CO)_4$ (43). This spectroscopic investigation definitely excludes a tetrahedral arrangement of the CO groups and the number of vibration modes observed suggests a C_{3v} symmetry of the molecule. It will be noticed that a trigonal bipyramidal model with three CO groups in the equatorial positions belongs to this symmetry group.

The high resolution spectrum of $MnH(CO)_5$ in the CO stretching region has been reported (44).

Sometimes, the metal–hydrogen stretching vibrations are not easily observed in the infrared spectrum. This is true for the hydrido compound of rhenium, $ReH(CO)_2(PPh_3)_2$, reported by Freni and co-workers (45).

The structures of polynuclear hydrido metal carbonyls present several interesting aspects. Although not directly located, the hydrogen atom of $Mo_2(C_5H_5)_2H(CO)_4$-$\mu[PMe_2]$ was suggested to occupy a symmetrical position between the two metal atoms (23). A molybdenum–hydrogen–molybdenum three-center bond would account for the observed diamagnetism of the compound, the presence of a direct metal–metal bond being therefore not strictly required.

A similar metal–hydrogen–metal bond has also been suggested to exist in the compound $Mn_3H(CO)_{10}(BH_3)_2$ (18). A representation of this molecule is shown in Fig. 19.

The anionic hydrido species of group VI transition metals $[M_2H(CO)_{10}]^-$ have also been suggested to contain the hydrido ligand symmetrically and equally bonded to both metal atoms (14). This view has been verified by an x-ray investigation of $[Cr_2H(CO)_{10}]^-$ as its tetra-

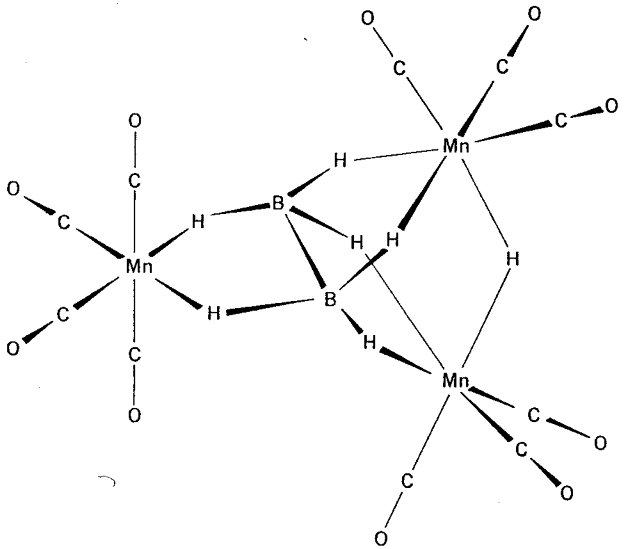
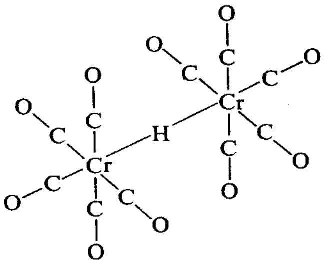


FIG. 19. Molecular configuration of $Mn_3H(CO)_{10}(BH_3)_2$ (H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965)). Published by permission.

ethylammonium salt (46). It was suggested that the hydrogen, although not directly located, had to be collinear with the two chromium atoms in order to preserve the D_{4h} symmetry of the molecule. A representation of the $[Cr_2H(CO)_{10}]^-$ anion as the D_{4h} model is shown by **1**.



(**1**)

Finally, the x-ray structure of $[Fe_3H(CO)_{11}]^-$ is of considerable interest because of the structural analogies which have been proposed to exist between this anionic hydrido complex and $Fe_3(CO)_{12}$ (47). As Fig. 20 shows, the anion has been found to have a triangular arrangement of the iron atoms. Two of the iron atoms have three terminal CO groups. One unique CO group is in the molecule and this bridges the two equivalent iron atoms. The hydrogen atom, although not directly located, was assumed to be symmetrically arranged with respect to the two equivalent iron atoms and to constitute with them a delocalized three-center metal–hydrogen–metal bond. The three-center bond would then enable the two equivalent iron atoms to reach the closed shell configuration; therefore a direct metal–metal bond between them is not strictly required. In conclusion, the molecular configuration of $[Fe_3H(CO)_{11}]^-$ consists of two equivalent iron atoms and a third one with a different environment. The Mössbauer spectra of the anion (48) are consistent with the established x-ray structure.

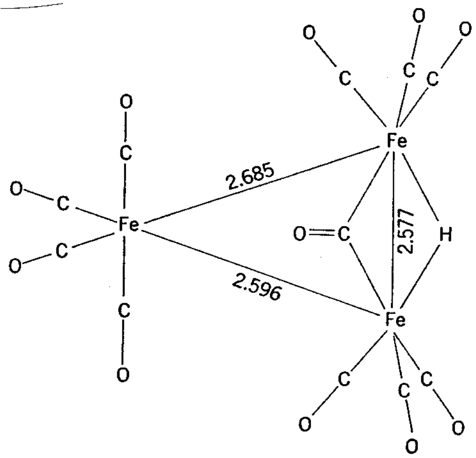


FIG. 20. A schematic representation of the $[Fe_3H(CO)_{11}]^-$ anion.

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VII. NITROSYL METAL CARBONYLS AND RELATED COMPOUNDS

Nitrosyl metal carbonyls are those compounds in which both carbon monoxide and nitrogen oxide are bonded to a transition metal.

The list in Table 24 is not limited to nitrosyl metal carbonyls as defined above but it is extended to some substituted compounds. Even some compounds which do not contain carbon monoxide have been included. This is done to provide a broader view of the chemistry of nitrogen oxide complexes. The discussion, however, will be limited mainly to unsubstituted nitrosyl metal carbonyls.

An excellent review of the coordination chemistry of nitrogen oxide has appeared (1). Nitrosyl metal carbonyls, however, have been treated only briefly. Also previous reviews on metal carbonyls have treated nitrosyl derivatives in a somewhat casual way. It seems therefore justified to have a separate section dealing with this subject.

Nitrogen oxide can be bonded to metals as NO^-, NO, or NO^+. For metal carbonyl nitrosyls it is generally accepted that nitrogen oxide is bonded to the transition metal as NO^+. The bonding can be visualized as involving a decrease of one unit in the oxidation state of the metal, followed by the donation of an electron pair from the nitrosyl cation NO^+ to the metal through the nitrogen atom.

It is to be noted that nitrosyl metal carbonyls as defined above contain the central metal atom in a 1− oxidation state or lower, depending on the number of NO groups present and on the charge of the compound.

Since NO^+ is isoelectronic with carbon monoxide, Seel (1*a*) proposed the word "nitrosyl" for those compounds in which nitrogen oxide acts as a three-electron donor. Two series of diamagnetic metal carbonyl nitrosyls are known; i.e., the "pseudotetracarbonylnickel" and the "pseudopentacarbonyliron" series:

$$\begin{array}{llll} Ni(CO)_4 & Co(NO)(CO)_3 & Fe(NO)_2(CO)_2 & Mn(NO)_3CO \\ Fe(CO)_5 & & & Mn(NO)(CO)_4 \end{array}$$

A. Methods of Preparation

$Co(NO)(CO)_3$. The reaction by which Mond and Wallis (2) first pre-

TABLE 24

Nitrosyl Metal Carbonyls and Related Compounds

Compound	Color	Mp or bp (°C)	Ref.
$[NiBr(NO)]_n$[a]	Blue-black	—	30
$[NiI(NO)]_n$[a]	Blue-black	—	30
$NiC_5H_5(NO)$	Red-brown	b_{15} 47–48	9[b],31,32
		mp −41	
$Ni(NO_2)(NO)$	Light blue	—	9[c]
cis-$[NiI(NO)PPh_3]_2$	Blue-black	185–190 dec.	33
$NiI(NO)(PPh_3)_2$	Blue-black	180–185 dec.	33
$Ni(NO)_2(PPh_3)_2$	Dark purple	—	34
$[PdCl(NO)]_n$	Deep brown	—	35
$PdCl_2(NO)_2$	Black-brown	—	35–37
$PtC_5H_5(NO)$	Orange	mp 64	38
$Co(NO)(CO)_3$	Deep red	b_{760} 77.8[d]	39
		78.6	2
		mp −1.05	2
		−11	40
$Co(NO)(PF_3)_3$	Red-brown	mp −92	41
$Co(NO)(CO)(PPh_3)_2$	Red	mp 130	13
$CF_3Co(NO)_2P(OPh)_3$	Red-brown	mp 58	42
$C_2F_5Co(NO)_2PPh_3$	Violet-brown	mp 65	43
$[CoCl(NO)_2]_2$	Black	—	44,45
$[CoBr(NO)_2]_2$	Black	—	44,45
$[CoI(NO)_2]_2$	Black	—	44,45
$K[CoCN(NO)(CO)_2]$	Red-brown	—	46
$[RhCl(NO)_2]_n$	Black	—	36,47
$[RhBr(NO)_2]_n$	Black	—	47
$[RhI(NO)_2]_n$	Black	—	47
$Rh(NO)(PPh_3)_3$	Deep red	175 dec.	48
$Ir(NO)(PPh_3)_3$	Orange	mp 155–156	49
$Fe(NO)_2(CO)_2$	Deep red	50 dec.	
		mp 18.5	4,5
		18.1	
		d_4 1.568	
$Fe(NO)_2(PF_3)_2$	Red-brown	Liquid	41
$Fe(NO)(CO)_2(\pi\text{-allyl})$	Deep red	Liquid	50
$[FeNO(CO)_3]^-$	Deep yellow	—	51
$Fe_2Hg(NO)_2(CO)_6$	Deep red	Sublimes	52

(*continued*)

TABLE 24 (*continued*)

Compound	Color	Mp or bp (°C)	Ref.
$Fe(NO)_2(CO)SbPh_3$	Red-orange	105–115 dec.	13
$CF_3COFe(NO)(CO)(PPh_3)_2$	Deep red	—	53
$[FeBr(NO)_2]_2$	Black	—	30,45
$[FeI(NO)_2]_2$	Black	—	30,45
$[Fe(NO)_3]Cl$	Black	—	54
$[Fe(NO)_3]Br$	Black	—	54
$[Fe(NO)_3]I$	Black	—	54
$[Fe(NO)_3]NO$	Black-brown	0 dec.	22,55
$Ru(NO)_5$ (?)	Red	—	24
$Mn(NO)(CO)_4$	Deep red	mp −1.5 ÷ 0	8
$Mn(NO)_3CO$	Green	mp 27	7,56
$Mn(NO)_3PPh_3$	Deep green	119 dec.	7,57
$Mn(NO)(CO)_3PPh_3$	Red	185–190 dec.	58,59
$Mn(NO)(CO)_2(PPh_3)_2$	Orange	205–210 dec.	59
$[MnC_5H_5(NO)(CO)_2]^+$	—	—	31
$[MnC_5H_5(NO)(CO)]_2$	Violet	> 200 dec.	27
$CH_3OOCMnC_5H_5(NO)(CO)$	Orange	mp 56–58	60
$Mn_2(NO)_2(CO)_7$	Deep red	~ 140 dec.	8
$Mn_2(C_5H_5)_3(NO)_3$	Dark purple	100 dec.	26
$CrC_5H_5(NO)(CO)_2$	Red-orange	mp 67–68	32
$[CrC_5H_5(NO)_2]_2$	Dark violet	mp 158–159	27
$[CrC_5H_5(NO)_2]Cl$	Greenish yellow	~ 140 dec.	26
$CH_3CrC_5H_5(NO)_2$	Green	mp 83	61
$[CrC_5H_5(NO)_2(CO)]PF_6$	Olive	143–144 dec.	62
$MoC_5H_5(NO)(CO)_2$	Orange-red	mp 85	32
$WC_5H_5(NO)(CO)_2$	Orange-red	mp 105–107	32
$V(NO)(CO)PPh_3$	Orange	88–90 dec.	63
$VNO(CO)_5$[e]	Red-violet	—	64

[a] Probably $n = 4$.

[b] Obtained from $Ni(CO)_4$ and NO in the presence of cyclopentadiene.

[c] Obtained from $Ni(CO)_4$ and NO at room temperature in cyclohexane.

[d] Extrapolated.

[e] Not isolated, infrared spectrum only.

pared the compound in 1922 is still probably the best method for its preparation.

$$Co_2(CO)_8 + 2NO \longrightarrow 2Co(NO)(CO)_3 + 2CO \tag{1}$$

The reaction is fast and quantitative at 40°.

Other methods of preparation involve the oxidation of the $[Co(CO)_4]^-$ anion by nitrogen oxide (3) or by $NaNO_2$ (4). If high pressure reaction vessels are not available for the preparation of $Co_2(CO)_8$, an alkaline solution of $[Co(CO)_4]^-$ can be obtained by treating an alkaline solution of Co^{2+}, containing small amounts of CN^-, with carbon monoxide at atmospheric pressure. The subsequent treatment with nitrogen oxide gives $Co(NO)(CO)_3$, which can be separated from the reaction mixture by evaporation under vacuum into a trap at Dry Ice temperature (4*a*) (58% yield).

Fe(NO)₂(CO)₂. This is prepared by the reaction (5) of nitrogen oxide and $Fe(CO)_5$ at 95°. $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ also give the nitrosyl carbonyl, but by some complex reactions during which $Fe(CO)_5$ is also formed. $Fe(NO)_2(CO)_2$ can be prepared in about 40% yield by treatment of an aqueous alkaline solution of $Na[FeH(CO)_4]$, obtained from $Fe(CO)_5$ and aqueous sodium hydroxide, with $NaNO_2$ and acetic acid (4). $Fe(NO)_2(CO)_2$ has more recently been prepared from NOCl and $Fe(CO)_5$; however, the yields were not high (6).

Mn(NO)₃(CO). This compound was prepared (7) by the action of NO on $MnI(CO)_5$ at about 100°. The stability of this compound toward oxidation is lower than that of the cobalt and iron nitrosyl carbonyls mentioned above.

Mn(NO)(CO)₄. This was prepared (8) in a rather unexpected way by the reaction of $MnH(CO)_5$ with *N*-nitroso-*N*-methyl-*p*-tolylsulfonamide. This is the first member of the "pseudopentacarbonyliron series" to have been prepared.

The simple unsubstituted metal carbonyl nitrosyls are all highly colored substances that are liquid at temperatures around 30°; the highest melting point is that of $Mn(NO)_3CO$, (27°). They are all very volatile: the extrapolated boiling point of $CoNO(CO)_3$ is 77.8° at ordinary pressure. Their covalent character is also evidenced by their large solubilities in organic solvents and their insolubility in water.

Compounds of a rather different nature are obtained from the reaction of $Ni(CO)_4$ with nitrogen oxide. The blue, air and water sensitive solid obtained from this reaction has been formulated (9) as $Ni(NO_2)NO$. When the reaction is carried out in the presence of cyclopentadiene and an amine, the cyclopentadienyl compound $Ni(C_5H_5)NO$ is obtained.

No unsubstituted nitrosyl carbonyls of the group VI transition metals are known as yet. Treatment of $Mo(CO)_6$ with NO and HCl in ethyl alcohol gives the nitrosyl derivative $Mo(NO)_2(C_2H_5OH)_2Cl_2$ (9*a*). By ligand exchange, $Mo(NO)_2(PPh_3)_2Cl_2$ can be prepared from it.

B. Chemical Properties

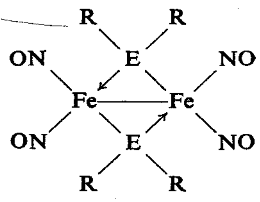
Nitrogen oxide and carbon monoxide groups in $Co(NO)(CO)_3$ are quantitatively displaced by reaction with bromine (10). Of particular interest are the reactions of the nitrosylcarbonyls of cobalt and iron with different ligands. The early work by Hieber and Anderson (11) on the reaction of $Co(NO)(CO)_3$ with pyridine has been recognized (12) to be partly incorrect. The reaction of $Co(NO)(CO)_3$ with pyridine gives initially the substitution product $Co(NO)(CO)py_2$, which could not be isolated and was identified only spectroscopically. Then the system reacts further to give ionic compounds, probably $[Co(py)_n][Co(CO)_4]_2$. True substitution products of $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$ have been obtained, however, with 1,10-phenanthroline (12), 2,2′-dipyridyl (12), triarylphosphines (13), triarylarsines (12,13), triarylstibines (12,13), alkyl and aryl isonitriles (14), PCl_3, PCl_2Ph, and $PClPh_2$ (15).

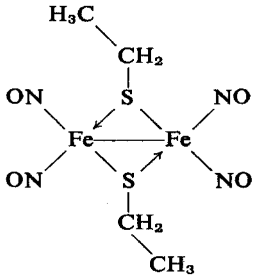
Malatesta and Araneo (13) made the observation that carbon monoxide groups, but not nitrogen oxide groups, can be replaced in nitrosyl metal carbonyls. The products obtained from the substitution reactions therefore, are of the type: $Co(NO)(CO)_2L$, $Co(NO)(CO)L_2$, $Fe(NO)_2(CO)L$, and $Fe(NO)_2L_2$. The trisubstitution products of $Co(NO)(CO)_3$ are not obtainable directly, even under drastic conditions (12). Similarly, carbon monoxide, but not nitrogen oxide, is displaced from $Mn(NO)_3CO$; $Mn(NO)_3P(C_6H_5)_3$ is obtained (7) by treating the nitrosylcarbonyl with triphenylphosphine. The reactions of $Fe(NO)_2(CO)_2$ with alkyl and aryl diphosphines and diarsines have been investigated (16,17) and found to give phosphorus- and arsenic-bridged complexes of the type **1**. The analogy between these compounds and Roussin's red ethyl ester (**2**) (18) is evident.

The reactions of $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$ with aqueous and methanolic alkaline solutions have been investigated by Hieber and his coworkers. $Co(NO)(CO)_3$ reacts with methanolic KOH to give the tetracarbonylcobaltate ion. The following equation has been proposed (19) to represent the reaction:

$$3Co(NO)(CO)_3 + 9OH^- \longrightarrow 2Co(OH)_2 + [Co(CO)_4]^- + 2HCO_2^- + 3CO_3^{2-} + N_2 + NH_3 \quad (2)$$

From $Fe(NO)_2(CO)_2$ and various alkaline systems (20), the nitrosylcarbonylferrate anion $[Fe(NO)(CO)_3]^-$ is formed. The same anion is obtained from the system $Fe(NO)_2(CO)_2$, Na amalgam, and THF.





E = P, As; R = Me, Ph, CF_3

(**1**) (**2**)

The reaction of the mercury derivative $Hg[FeNO(CO)_3]_2$ with triphenylphosphine has been shown (21) to give the substitution product $Fe_2Hg(NO)_2(CO)_4(PPh_3)_2$. The similar reaction with $P(N(CH_3)_2)_3$, Tdp, gives $Fe(NO)_2(Tdp)_2$ and the ionic $[FeNO(CO)_2(Tdp)_2][FeNO(CO)_3]$, depending on the reaction conditions.

C. Bonding and Structures

With few exceptions the compounds in Table 24 contain nitrogen oxide acting as a three-electron donor to the transition metals; i.e., being bonded as nitrosonium ion NO^+. The compound $Fe(NO)_4$ is a striking example of a molecule in which both types of NO (as NO^+ and as NO^-) are present. It has been suggested (22) that this compound should probably be regarded as $[Fe(NO)_3]^+NO^-$. It has also been proposed (23) that the compound previously reported (24) as $Ru(NO)_5$ is possibly $Ru(NO)_4$ and has a structure similar to that of the iron compound. The main evidence for these new formulations is the infrared spectrum. As shown in Table 25, NO ligands absorb in the region between 1700 and 1850 cm^{-1}, depending on the degree and nature of substitution. The compound $Fe(NO)_4$ shows a band at about 1140 cm^{-1} which has been attributed to the NO^- group.

An alternative suggestion has been made (24*a*) concerning the structure of $Fe(NO)_4$. This was regarded as a dimer, $(NO)_3FeN_2O_4Fe(NO)_3$, with a *trans*-hyponitrite group bridging two $Fe(NO)_3$ units. The same was tentatively suggested to hold for the ruthenium analog.

TABLE 25

Infrared Stretching Vibrations in Nitrosyl Metal Carbonyls and Related Compounds

Compound	ν_{NO} (cm^{-1})	ν_{CO} (cm^{-1})	Ref.
$Ni(C_5H_5)NO$	1833	—	31
$[Ni(NO)]NO_2$	1845	—	9
$PdC_5H_5(NO)$	1789	—	38
$PdCl_2(NO)_2$	1833, 1818	—	36
$PtC_5H_5(NO)$	1739	—	38
$CoNO(CO)_3$	1822	2108, 2047	65
$Co(NO)(CO)(PPh_3)_2$	1717	1956.7	15
$Co(NO)(PF_3)_3$	1844	—	41
$[CoCl(NO)_2]_2$	1859, 1790	—	66
$[CoBr(NO)_2]_2$	1858, 1795	—	66
$[CoI(NO)_2]_2$	1846, 1792	—	66
$[RhCl(NO)_2]_n$	1703, 1605	—	36
	1721, 1575	—	47
$[RhBr(NO)_2]_n$	1718, 1568	—	47
$[RhI(NO)_2]_n$	1710, 1559	—	47
$FeNO(CO)_2C_3H_5$	1761	2038, 1983	50
$Fe(NO)_2(CO)_2$	1810, 1766	2083, 2034	7
$Fe_2Hg(NO)_2(CO)_6$	1771, 1744	2070, 2051, 2007, 1973, 1950	67
$[Fe(CO)_3NO]^-$	1651	1984, 1881	68
$CF_3COFe(NO)(CO)(PPh_3)_2$	1710	1931	53
$Fe(NO)_2(CO)PPh_3$	1764, 1722	2009	6
$Fe(NO)_2(PF_3)_2$	1838, 1788	—	41
$[FeI(NO)_2]_2$	1818, 1771	—	66
$[Fe(NO)_3]Cl$	1826, 1763	—	66
$[Fe(NO)_3]Br$	1821, 1764	—	66
$[Fe(NO)_3]I$	1809, 1763	—	66
$[Fe(NO)_3]NO$	1810, 1730, 1140	—	22
$Mn(NO)(CO)_4$	1759	2095, 2019, 1972	8
$Mn(NO)_3(CO)$	1823, 1734	2088	7
$Mn(NO)_3PPh_3$	1780, 1697	—	57
$Mn_2(C_5H_5)_3(NO)_3$	1732, 1510, 1495~	—	26
$[CrC_5H_5(NO)_2]Cl$	1823, 1715	—	26
$[CrC_5H_5(NO)_2(CO)]^+$	1873, 1779	2137	62
$V(NO)(CO)_5$	1700	2108, 2064 1992	64

The frequency shift of the infrared N—O stretching vibration, depending on whether the nitrosyl group is bonded as NO^+ or NO^-, is explained in terms of valence bond theory by the following two bonding forms:

$$\overset{(-)}{M}-\overset{(+)}{N}\equiv O \qquad \overset{(+)}{M}-\overset{(-)}{N}=O$$

(3) (4)

Infrared data are valuable because they can help in distinguishing between limiting forms of bonding, such as **3** and **4**. Besides that, when the predominant bonding form is **3**, the central metal atom has a certain excess of negative charge that can be relieved by virtue of an additional bond between a filled d orbital on the metal and the correctly oriented p orbital on nitrogen. Nitrogen oxide in fact has been recognized (15) to be as good a π acceptor as carbon monoxide or slightly better. The infrared N—O stretching frequencies are very sensitive to relatively small changes in bonding. The infrared data of Table 25 illustrate the situation quite clearly. From what was said before, it is, for example, readily understood why the NO stretching frequency of $[Fe(NO)(CO)_3]^-$ is lowered to 1651 cm^{-1} relative to $Fe(NO)_2(CO)_2$, and why substitution of one or two carbon monoxide groups in $Co(NO)(CO)_3$ with a weaker π-electron acceptor such as PR_3, will cause an analogous decrease of the N—O bond order and, consequently, a decrease of the N—O stretching frequencies.

Fairey and Irving (25) have shown that the infrared frequencies of the N—O stretching vibrations are considerably solvent dependent, an effect normally observed also in the case of the C—O stretching vibrations. Polar solvents shift the NO stretching vibrations to higher wavenumbers in compounds of the type $RuX_3(NO)L_2$, where X is a halogen atom and L different ligands, such as tertiary phosphines, arsines, and stibines. In view of this, comparison of infrared solution data are significant only if the solvent is the same.

Slightly stronger π-acceptor properties of nitrogen oxide compared with carbon monoxide would be consistent with the previously mentioned observation that, in $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$, only the carbon monoxide groups can be displaced by triarylphosphines or other ligands. In fact, an increased d_π–p_π bond from the metal to the NO ligand will strengthen the metal–nitrogen bond with respect to the metal–carbon bond.

Rather few examples of polynuclear nitrosyl compounds are known. For $Mn_2(C_5H_5)_3(NO)_3$ and $[Cr(C_5H_5)(NO)_2]_2$, structures containing NO bridges have been proposed (26,27). Also the dimeric $[MnC_5H_5(CO)(NO)]_2$ has been suggested to have NO bridges (28). These suggestions have been made on the basis of infrared bands attributed to N—O stretching modes and occurring at unusually low frequencies. X-ray structural work to elucidate this point would be desirable.

No x-ray studies have been published for any of the known nitrosyl metal carbonyls. An early electron diffraction investigation (29) of $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ has, however, been reported. This indicated that in both compounds the nitrogen oxide and carbon monoxide ligands are in a tetrahedral arrangement around the central metal atom. The following distances have been found, and are compared with those in $Ni(CO)_4$ obtained by the same method.

Compound	Distances (Å)			
	M—C	C—O	M—N	N—O
$Fe(NO)_2(CO)_2$	1.84 ± 0.02	1.15 ± 0.03	1.77 ± 0.02	1.12 ± 0.03
$Co(NO)(CO)_3$	1.83 ± 0.02	1.14 ± 0.03	1.76 ± 0.03	1.10 ± 0.04
$Ni(CO)_4$	1.82 ± 0.02	1.15 ± 0.03	—	—

It is interesting to note that, while in metal carbonyls the C—O distance (mean value about 1.16 Å) is higher than in the free carbon monoxide molecule (1.128 Å), the N—O distance in $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ is somewhat lower than in nitrogen oxide (1.15 Å).

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VIII. CATIONIC METAL CARBONYLS AND RELATED COMPOUNDS

The existence of cationic metal carbonyl species has been postulated for some years. The dramatic change in the infrared spectrum of pentacarbonyliron upon addition of organic nitrogen bases was attributed by Wender and co-workers (1) to the presence of the hexacarbonyliron cation formed according to the disproportionation:

$$2\mathrm{Fe(CO)_5} \xrightarrow{N\text{-base}} [\mathrm{Fe(CO)_6}]^{2+}[\mathrm{Fe(CO)_4}]^{2-} \qquad (1)$$

Although the occurrence of disproportionation (1) is debatable in view of a later investigation by Edgell and co-workers (2), the original paper by Wender and co-workers has the merit of having drawn attention to the possible existence of cationic metal carbonyls. Further, it was also suggested that enneacarbonyldicobalt, $Co_2(CO)_9$, was formed when $Co_2(CO)_8$ was treated with carbon monoxide at high temperature and pressure. The ionic structure $[Co(CO)_5]^+[Co(CO)_4]^-$ was then considered. Unfortunately, the instability under normal conditions of pressure and temperature of this new carbonyl precluded the study of its properties (3). However, the assignment of an ionic structure to $Co_2(CO)_9$ has been indirectly confirmed by the closely related reaction (4,5) of $Co_2(CO)_8$ with triaryl- and trialkylphosphines. Ionic compounds have been isolated from this reaction:

$$\mathrm{Co_2(CO)_8} + 2\mathrm{PR_3} \longrightarrow [\mathrm{Co(CO)_3(PR_3)_2}]^+[\mathrm{Co(CO)_4}]^- + \mathrm{CO} \qquad (2)$$

The cation formed is in fact the phosphine-substituted analog of $[Co(CO)_5]^+$.

Evidence for the existence of the thermally unstable species $[Co(CO)_4ROH]^+$ has been obtained. The cation is formed when $Co_2(CO)_8$ is treated with alcohols (6).

However, unsubstituted cationic metal carbonyls have been isolated and characterized only lately. One of the most common methods of preparation requires the use of (a) a halogeno metal carbonyl, (b) a Lewis acid capable of abstracting a halide anion from it, and (c) a ligand in order to saturate the coordination number of the metal. The preparation of $[Mn(CO)_6]^+$ (7–9) from $MnCl(CO)_5$, carbon monoxide under pressure, and $AlCl_3$ typifies this:

$$\mathrm{MnCl(CO)_5} + \mathrm{CO} + \mathrm{AlCl_3} \longrightarrow [\mathrm{Mn(CO)_6}]^+[\mathrm{AlCl_4}]^- \qquad (3)$$

The cation $[Re(CO)_6]^+$, isoelectronic with $[V(CO)_6]^-$ and $[Ta(CO)_6]^-$ was prepared by Hieber and Kruck (9) by a similar method from the dry reaction of $Re(CO)_5Cl$ with carbon monoxide at 85–95° and 300–500 atm. The $[Tc(CO)_6]^+$ cation was obtained similarly (10).

From preliminary experiments (9) it seems that the cationic species $[Fe(CO)_6]^{2+}$ and $[Os(CO)_6]^{2+}$ can also be obtained from the halogenocarbonyls $FeCl_2(CO)_4$ and $OsCl_2(CO)_4$. The tetrachloroaluminate of $[Re(CO)_6]^+$ is stable to 205° and dissolves in water without decomposition. In contrast, the manganese complex, $[Mn(CO)_6]^+$ is rapidly reduced to $[Mn(CO)_5]^-$, which is in turn hydrolyzed to $MnH(CO)_5$, according to the overall reaction:

$$[\mathrm{Mn(CO)_6}]^+ + \mathrm{H_2O} \longrightarrow \mathrm{MnH(CO)_5} + \mathrm{H^+} + \mathrm{CO_2} \qquad (4)$$

In addition to the unsubstituted cationic species many other complex cations containing both carbon monoxide and other ligands have been prepared. A cationic substituted metal carbonyl has been obtained (11) by the reaction of $MnBr(CO)_5$ with refluxing mesitylene in the presence of $AlCl_3$. This reaction, which gives the cation $[Mn(CO)_3C_6H_3Me_3]^+$, has been extended (12) to the preparation of the benzene, toluene, hexamethylbenzene, and naphthalene analogs.

Cyclopentadienyl-substituted cationic metal carbonyls can be prepared in several different ways. $[FeC_5H_5(CO)_3]^+$ and $[FeC_5H_5(CO)_2C_2H_4]^+$ have been obtained (13) by the reaction of the cyclopentadienylhalogeno metal carbonyl with carbon monoxide (or ethylene) in the presence of $AlBr_3$ as halogen acceptor:

$$\mathrm{FeBr(C_5H_5)(CO)_2} + \mathrm{AlBr_3} + \mathrm{CO} \longrightarrow [\mathrm{FeC_5H_5(CO)_3}]\mathrm{AlBr_4} \qquad (5)$$

$$\mathrm{FeBr(C_5H_5)(CO)_2} + \mathrm{AlBr_3} + \mathrm{C_2H_4} \longrightarrow [\mathrm{FeC_5H_5(CO)_2C_2H_4}]\mathrm{AlBr_4} \qquad (6)$$

$[MoC_5H_5(CO)_4]^+$ and $[WC_5H_5(CO)_4]^+$ have been synthesized similarly (8,13). $[FeC_5H_5(CO)_3]^+$ can also be prepared under carbon monoxide pressure from $FeI(C_5H_5)(CO)_2$ in aqueous HPF_6 (14) or by treatment (15) of $FeCl(C_5H_5)(CO)_2$ with $NaBPh_4$, thus:

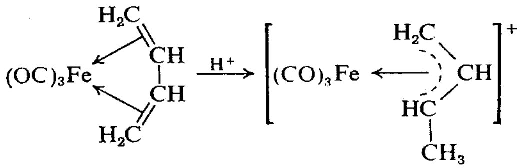
$$FeCl(C_5H_5)(CO)_2 + NaBPh_4 \xrightarrow{CO} NaCl + [FeC_5H_5(CO)_3]^+BPh_4^- \qquad (7)$$

In a more complicated system $[CrC_5H_5(CO)_4]Br_4$ was obtained (16) from $Cr(C_5H_5)H(CO)_3$, carbon monoxide, and boron trifluoride etherate.

Hydrocarbon-substituted cationic species are also obtained by either hydride abstraction from or protonation of π-olefin metal carbonyl compounds. A few examples of these types of reactions will be given here. The cycloheptatrienyl complex $[Mo(CO)_3C_7H_7]^+$ was obtained (17) from the following reaction:

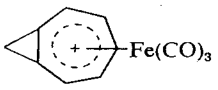
$$Mo(CO)_3C_7H_8 + (C_6H_5)_3CBF_4 \longrightarrow [Mo(CO)_3C_7H_7]^+BF_4^- + (C_6H_5)_3CH \qquad (8)$$

The same hydride abstraction reaction applied to tricarbonylcyclohexa-1,3-dieneiron gives the tricarbonylcyclohexadienyliron cation (18). Protonation of neutral diolefin complexes (19,19*a*) gives π-allyl systems:



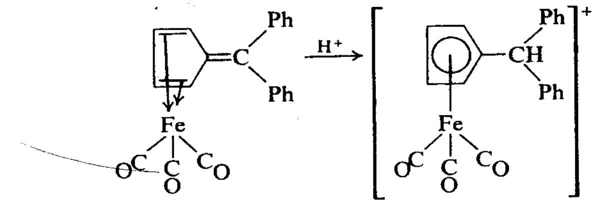
(9)

Similarly the treatment of the cyclooctatetraene complex $Fe(CO)_3C_8H_8$ with HBF_4 (20) gives the cation $[Fe(CO)_3C_8H_9]^+$, which has been shown (21) to have a bicyclic structure: tricarbonylbicyclo[5,1,0]octadieniumiron cation (**1**).



(1)

A substituted methylcyclopentadienyliron cation is obtained (22) by protonation of a tricarbonylfulveneiron derivative:



(10)

Finally, cationic carbonyl complexes of vanadium can be obtained by using $V(CO)_6$ as an oxidizing agent. The cation $[V(C_5H_5)_2(CO)_2]^+$, has been prepared (23) by the reaction of $V(CO)_6$ with $V(C_5H_5)_2$ and carbon monoxide at atmospheric pressure and room temperature:

$$V(C_5H_5)_2 + V(CO)_6 + 2CO \longrightarrow [V(C_5H_5)_2(CO)_2][V(CO)_6] \qquad (11)$$

The reaction of $V(CO)_6$ with aromatic hydrocarbons (24) has also been shown to give cationic tetracarbonylarenevanadium(I) complexes:

$$2V(CO)_6 + \text{arene} \longrightarrow [V(CO)_4\text{arene}]^+[V(CO)_6]^- + 2CO \qquad (12)$$

The mechanism of formation of these arenevanadium compounds probably involves the intermediate formation of unchanged substitution products of $V(CO)_6$, which are then oxidized to the final products by a second molecule of hexacarbonylvanadium:

$$V(CO)_6 + \text{arene} \underset{+CO}{\overset{-CO}{\rightleftharpoons}} [V(CO)_5\text{arene}] \underset{+CO}{\overset{-CO}{\rightleftharpoons}} [V(CO)_4\text{arene}] \qquad (13)$$

$$[V(CO)_4\text{arene}] + V(CO)_6 \longrightarrow [V(CO)_4\text{arene}]^+[V(CO)_6]^- \qquad (14)$$

Physical Measurements. The two colorless cations $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ are diamagnetic and, in accordance with a probable octahedral arrangement of substituents, have only one C—O stretching frequency, at 2101 and 2083 cm⁻¹, respectively.

TABLE 26

Carbonyl Stretching Frequencies and Intensity Measurements in Isoelectronic Hexacoordinate Metal Carbonyls

Compound	ν_{C-O} (cm^{-1})	I × 10^{-7} (cm × mol^{-1} × 1)	Solvent
$[Mn(CO)_6]^+$	2090	34.8	THF
$[Cr(CO)_6]$	1896	70.7	CCl_4
$[V(CO)_6]^-$	1859	130.8	THF

TABLE 27

Substituted Cationic Metal Carbonyls and Infrared Data in the Carbonyl Stretching Region

Cation	ν_{CO} (cm^{-1})	Ref.
$[Co(CO)_3(PPh_3)_2]^+$	—	4,5
$[Co_2(CO)_4\text{Diphos}]^{2+}$	2000, 1950	27
$[F_5C_2CoC_5H_5(CO)_2]^+$	2140, 2080	27*a*
$[F_5C_2CoC_5H_5(CO)(PPh_3)]^+$	2080	27*a*
$[FeC_5H_5(CO)_3]^+$	2132, 2079, 1996	8,13–15,28
$[FeC_5H_5(CO)_2(\text{ethylene})]^+$	2083, 2049	13
$[FeC_5H_5(CO)_2(\text{propylene})]^+$	—	29
$[FeC_5H_5(CO)_2(\text{butadiene})]^+$	—	29[a]
$[FeC_5H_5(CO)_2(\text{cyclohexene})]^+$	—	29
$[FeC_5H_5(CO)_2C_3H_4]^+$	2131, 2079	30[b]
$[Fe(CO)_3(\text{cyclohexadienyl})]^+$	—	18
$[Fe(CO)_3(\text{1-methyl-}\pi\text{-allyl})]^+$	2150, 2085	19
$[Fe(CO)_3(\text{pentadienyl})]^+$	2120, 2072	31
$[Fe(CO)_3(\text{1,5-dimethylpentadienyl})]^+$	2111, 2060	31
$[Fe_2(CO)_4(C_5H_5)_2PMe_2]^+$	2038, 2026, 2015, 1992, 1970, 1942	32
$[Mn(CO)_5(\text{ethylene})]^+$	2165, 2083, 2062	7
$[Mn(CO)_5PPh_3]^+$	2138, 2086, 2046	33,34
$[Mn(CO)_4(PPh_3)_2]^+$	2003	33,34
$[Mn(CO)_4(TePh_2)_2]^+$	—	35
$[Mn(CO)_3C_6H_6]^+$	2083, 2024	12
$[Mn(CO)_3C_6H_3Me_3]^+$	2070, 2016	11,12
$[Mn(CO)_2\text{Diphos}_2]^+$	1897	27,36
$[CrC_5H_5(CO)_4]^+$	2114, 2037	16
$[MoC_5H_5(CO)_4]^+$	2128, 2041, 1980	8
$[Mo(C_5H_5)CO(C_6H_6)]^+$	2013	37
$[MoC_5H_5(CO)_3(\text{ethylene})]^+$	2105, 2053, 2006	13
$[MoC_5H_5(CO)_3NH_3]^+$	2070, 2008, 1980[c]	38
$[Mo(CO)_3(\text{cycloheptatrienyl})]^+$	2028, 1987, 1949	17
$[WC_5H_5(CO)_4]^+$	2128, 2028, 1965	8
$[WC_5H_5(CO)C_6H_6]^+$	2009	37
$[W(CO)_3(C_6Me_6)Cl]^+$	2080, 2020, 2005[c]	39
$[WC_5H_5(CO)_3(\text{ethylene})]^+$	2105, 2053, 2004	13
$[WC_5H_5(CO)_3NH_3]^+$	2058, 1976, 1953[c]	38
$[V(C_5H_5)_2(CO)_2]^+$	2050, 2010	23
$[V(CO)_4C_6H_6]^+$	2068, 2018, 1986	24

[a] Only one double bond of buta-1,3-diene is coordinated to the central atom.

[b] Obtained by addition of dry HCl to the σ-propargyl compound $FeC_5H_5(CO)_2CH_2C_2H$.

[c] For the tetraphenylborate.

Comparison of infrared spectra (25) in the isoelectronic series $[Mn(CO)_6]^+$, $Cr(CO)_6$, $[V(CO)_6]^-$ shows a regular decrease in the C—O stretching frequency and a regular increase in the intensity along the series (see Table 26). The frequency shift is in agreement with the corresponding increase of negative charge on the metal.

$[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ as the tetrachloroaluminates in acetic anhydride and water respectively, do not exchange with ^{14}CO (26). All the cations listed in Table 27 are diamagnetic and most are not stable in water, $[FeC_5H_5(CO)_2(C_2H_4)]^+$ being one of the exceptions.

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IX. HALOGENO METAL CARBONYLS AND RELATED COMPOUNDS

A. Introduction

The known halogeno metal carbonyls are listed in Table 28. The substituted analogs have been excluded from the list, with the exception of those of cobalt, for which unsubstituted compounds are not known or at least not well established. The discussion will be limited to halogenocarbonyls of the transition metals with the exclusion of the group IB metals, from copper to gold. Halogenocarbonyls containing hydrocarbon ligands, such as $FeBr(C_5H_5)(CO)_2$ or $FeBr(C_3H_5)(CO)_3$ will not be discussed.

The preparation of halogeno metal carbonyls can be carried out, especially with the second and third row of group VIII metals, by treating the metal halides with carbon monoxide at high temperature with or without the use of a halogen acceptor. Carbon monoxide itself can act as a halogen acceptor, forming phosgene and phosgene analogs, COX_2. Halogenocarbonyls of iron and group VII transition metals are, however, better prepared by treatment of the corresponding metal carbonyls with halogens.

Halogeno metal carbonyls can be considered formally as coordination compounds of metals whose oxidation state is equal (for the uncharged compounds) to the number of halogen atoms attached to it. Oxidation states of 1+ and 2+ are often encountered in this class of compounds. Zero oxidation states are found in some negatively charged compounds, such as $[CrCl(CO)_5]^-$.

Infrared data on halogeno metal carbonyls are very helpful for structural

TABLE 28

Halogeno Metal Carbonyls and Related Compounds

Compound	Color	Mp (°C)	Ref.
$[Pd_2Cl(CO)_2]_n$	Yellow	150 dec.	5
$[PdCl_2CO]_n$	Yellow	—	4
$PtCl_2(CO)_2$	Colorless	103	8,11,101
$PtBr_2(CO)_2$	Colorless	75 sublimes	11
$PtI_2(CO)_2$	Cherry red	40 sublimes	11
$[PtCl_2(CO)]_2$	Brick red	195	8,11
$[PtBr_2(CO)]_2$	Red	187	11,15,102
$[PtI_2(CO)]_2$	Violet	140	11,15
$Pt_2Cl_4(CO)_3$	Orange	123	8,11
$Pt_2Br_4(CO)_3$	Brick red	142	11
$[PtCl_3(CO)]^-$	Yellow	220[a]	11,15,19
$[PtBr_3(CO)]^-$	Golden yellow	245[a]	11,15
$[PtI_3(CO)]^-$	Orange-red	230[a]	11,15
$PtF_8(CO)_2$	Pale yellow	Sublimes	9
$[CoI_2(CO)]_n$	Black-brown	—	21
$CoI(CO)_3(PPh_3)$	Dark brown	185 dec.	22
$CoBr(CO)_2(PPh_3)_2$[b]	Brown	107–108 dec.	22,23
$CoI(CO)_2(PPh_3)_2$[b]	Brown	97–100 dec.	22,23
$[RhCl(CO)_2]_n$	Ruby red	125.5	2,25,26
$[RhBr(CO)_2]_n$	Brown	118	25,26
$[RhI(CO)_2]_n$	Orange	114	25
$[Rh(CN)(CO)_2]_n$	Blue	—	103
$[RhF_3(CO)_2]_2$	Orange-red	—	9
$[RhCl_2(CO)_2]^-$	Pale yellow	81 dec.[c]	33
$[RhBr_2(CO)_2]^-$	Pale yellow	86 dec.[c]	33
$[RhI_2(CO)_2]^-$	Mustard yellow	78 dec.[c]	33
$[Rh_2Br_4(CO)_2]^{2-}$	Orange-red	174 dec.[c]	33
$IrCl_2(CO)_2$	Colorless	140 dec.	32,36
$IrBr_2(CO)_2$	Pale yellow	—	36
$IrI_2(CO)_2$	Light yellow	—	36
$IrCl(CO)_3$	Light brown	—	36
$IrBr(CO)_3$	Brown	—	36
$IrI(CO)_3$	Deep brown	—	36
$IrI_3(CO)_3$	Deep red	—	37
$[IrI_3(CO)_2]_2$	Brown-red	—	37
$Ir_2I_6(CO)_3$	Dark red	—	37

(*continued*)

TABLE 28 (continued)

Compound	Color	Mp (°C)	Ref.
$[IrBr_4(CO)_2]^-$	Yellow	190 dec.^{a}	40
$[IrI_4(CO)_2]^-$	Red	210^a	37,40
$[IrBr_5CO]^-$	Pink	293^a	37
$[IrI_5(CO)]^-$	Brown-red	308^a	37
$[Ir_2Cl_4(CO)_4]^-$	Brown	225 dec.^{a}	40
$[Ir_2Br_4(CO)_4]^-$	Dark brown	250^a	40
$[IrI_4(CO)]^-$	Red	273^a	37,104
$[Ir_2I_6(CO)_4]^-$	Brown	260^a	40
$[Ir_2I_6(CO)_4]^{2-}$	Light red	284^a	37
$[IrI_3CO]^-$	Brown	256^a	37
$[IrI_2(CO)_2]^-$	Green-yellow	158^a	37
$FeI_2(CO)_5$	—	—	53,54
$FeCl_2(CO)_4$	Yellow	—	47
$FeBr_2(CO)_4$	Brown-red	—	47,48
$FeI_2(CO)_4$	Red	—	47
$Fe_2I_2(CO)_8$	White	−5	56
$FeICl(CO)_4$	Deep yellow	—	105
$FeIBr(CO)_4$	Red-brown	—	105
$[FeCl_2(CO)_2]_n$	Deep brown	—	105
$[FeI_2(CO)_2]_n$	Deep brown	—	106
$[FeI(CO)_2]_n$	—	—	106
$RuI_2(CO)_4$	Golden yellow	> 140 dec.	1,68
$[RuCl_2(CO)_2]_n$	Lemon-yellow	—	63
$[RuBr_2(CO)_2]_n$	Light orange	—	63
$[RuI_2(CO)_2]_n$	Ochre	—	63,64
$[RuBr(CO)]_n$	Colorless	—	67
$OsCl_2(CO)_4$	Colorless	—	69
$OsBr_2(CO)_4$	Colorless and light yellow	—	69
$OsI_2(CO)_4$	Yellow and deep yellow	—	69
$[OsBr(CO)_4]_2$	Yellow	—	69
$[OsI(CO)_4]_2$	Yellow-orange	—	69
$OsCl_2(CO)_3$	Colorless	269–273	70
$OsBr_2(CO)_3$	Yellow	—	69
$OsI_2(CO)_3$	Deep yellow	—	69

(continued)

TABLE 28 (continued)

Compound	Color	Mp (°C)	Ref.
$[OsBr_2(CO)_2]_n$	Yellowish	—	69
$[OsI_2(CO)_2]_n$	Light yellow	—	69
$MnCl(CO)_5$	Pale yellow	—	75
$MnBr(CO)_5$	Yellow	—	75
$MnI(CO)_5$	Orange	—	75,76
$Mn(SCN)(CO)_5$	Golden yellow	—	107,108
$[MnCl(CO)_4]_2$	Orange	—	75
$[MnBr(CO)_4]_2$	Brown	—	75
$[MnI(CO)_4]_2$	Dark brown	—	75
$[MnCl_2(CO)_4]^-$	Pale yellow	—	74,95
$[MnBr_2(CO)_4]^-$	—	—	74,95
$[MnI_2(CO)_4]^-$	Deep red	—	74,95
$[Mn_2Cl_2(CO)_8]^{2-}$	Yellow	—	74
$[Mn_2Br_2(CO)_8]^{2-}$	—	—	74
$[Mn_2I_2(CO)_8]^{2-}$	Red	—	74
$TcCl(CO)_5{}^d$	Colorless	—	87,109
$TcBr(CO)_5$	—	—	87,109
$TcI(CO)_5{}^d$	—	—	87,109
$[TcCl(CO)_4]_2{}^d$	—	—	87,110
$[TcBr(CO)_4]_2{}^d$	—	—	87,110
$[TcI(CO)_4]_2{}^d$	—	—	87,110
$ReCl(CO)_5$	Colorless	—	77,78,111
$ReBr(CO)_5$	Colorless	—	77,78
$ReI(CO)_5$	Colorless	—	76–78
$[ReCl(CO)_4]_2$	Colorless	—	112
$[ReBr(CO)_4]_2$	Colorless	—	112
$[ReI(CO)_4]_2$	Yellow	—	112
$[ReBr_2(CO)_4]^-$	Pale cream	—	113
$[ReI_2(CO)_4]^-$	Pale yellow	—	113
$[ReI_3(CO)_3]^{2-}$	Colorless	—	113
$[Re_2Br_3(CO)_7]^-$	Colorless	—	113
$[Re_2I_2(CO)_8]^{2-}$	Colorless	—	113
$CrI(CO)_5$	Deep blue	—	96
$Cr_2I(CO)_{10}$	Red	—	97
$[CrCl(CO)_5]^{-\,d}$	Yellow	—	100

(continued)

TABLE 28 (continued)

Compound	Color	Mp (°C)	Ref.
$[CrBr(CO)_5]^-$	Yellow	—	100
$[CrI(CO)_5]^-$	Yellow	—	98,100
$MoCl_2(CO)_4$	Yellow	—	97*a*
$[MoCl(CO)_5]^-$	Yellow	—	100
$[MoBr(CO)_5]^-$	Yellow	—	100
$[MoI(CO)_5]^-$	Yellow	—	98–100
$[WCl(CO)_5]^-$	Yellow	—	100
$[WBr(CO)_5]^-$	Yellow	—	100
$[WI(CO)_5]^-$	Yellow	—	98,100

[a] For the tetraphenylarsonium salt.
[b] According to Ref. 22 the compound crystallizes with one mole of benzene.
[c] For the tetraethylammonium salt.
[d] Identified by infrared spectrum only.

considerations. This class of compounds is characterized by C—O stretching vibrations at very high wavenumbers, sometimes as high as that for CO in the gas phase (see Table 29). This can be attributed to the inductive effect of the strongly electronegative halogen groups.

The halogeno metal carbonyls for which complete x-ray structures are known are $RuI_2(CO)_4$ (1), $[RhCl(CO)_2]_n$ (2), and $[MnBr(CO)_4]_2$ (3); for the latter two, halogen-bridged structures have been found. Moreover, from the infrared data available for binuclear or polynuclear compounds, no C—O stretching vibrations at relatively low wavenumbers are observed. The conclusion, therefore, is that CO bridges are not common in this class of compounds and that the links between the monomeric units are the results of metal–metal bonds (as probably in $[Mn_2X_2(CO)_8]^{2-}$) or of halogen bridges (as, for example, in $[MnBr(CO)_4]_2$).

B. The Nickel Subgroup

While halogeno metal carbonyls of nickel are not known, several compounds of palladium and platinum have been reported.

A compound of formula $PdCl_2(CO)$ was obtained by Manchot and König (4) by the action of carbon monoxide on an ethanol suspension of palladium(II) chloride at 0°. The compound is readily decomposed by water. Although its molecular weight is not known, it is probably a dimer similar to the analogous platinum compound (see below).

TABLE 29

Infrared Carbonyl Stretching Vibrations of Some Halogeno Metal Carbonyls

Compound	ν_{CO} (cm^{-1})	Medium	Ref.
$PtCl_2(CO)_2$	2200, 2162	CCl_4 (nujol)	7
$PtBr_2(CO)_2$	2178, 2132	—	11
$PtI_2(CO)_2$	2132, 2144	—	11
$[PtCl_2(CO)]_2$	2152	Nujol	16
$[PtBr_2(CO)]_2$	2130	Nujol	16
$[PtI_2(CO)]_2$	2112	Nujol	16
$Pt_2Cl_4(CO)_3$	2114, 2079	—	11
$Pt_2Br_4(CO)_3$	2096, 2061	—	11
$[PtCl_3CO]^-$	2083	—	11
$[PtBr_3CO]^-$	2070	—	11
$[PtI_3CO]^-$	2061	—	11
$CoI(CO)_3(PPh_3)$	2060, 1966	THF	22,114
$CoBr(CO)_2(PPh_3)_2$	1972, 1910	Nujol	23
$CoI(CO)_2(PPh_3)_2$	1972, 1910	Nujol	23
$[RhCl(CO)_2]_n$	2107, 2095, 2043, 2016	Gas	26
$[RhBr(CO)_2]_n$	2107, 2092, 2042, 2018	Gas	26
$IrI_3(CO)_3$	2178, 2114	Nujol	37
$[IrI_3(CO)_2]_2$	2123, 2087	Nujol	37
$Ir_2I_6(CO)_3$	2118, 2074, 2041sh	Nujol	37
$[IrI_2(CO)_2]^{-}$ [a]	2020, 1941	Nujol	37
$[Ir_2I_6(CO)_4]^{2-}$ [a]	2100, 2070	Nujol	37
$[IrI_4(CO)_2]^{2-}$ [a]	2109, 2074	Nujol	37
$FeCl_2(CO)_4$	2164, 2124, 2108, 2084	C_2Cl_4	51
$FeBr_2(CO)_4$	2150, 2108, 2098.5, 2074	C_6H_{14}	51,115
$FeI_2(CO)_4$	2131(m–s), 2086(vs), 2062(s), 2047(vw)	C_6H_{14}	51
$RuI_2(CO)_4$	2068(s), 2097(s), 2106(vs), 2119(w), 2161(m)	CCl_4	68
$[RuI_2(CO)_2]_n$	2050, 1995	—	64
$MnCl(CO)_5$	2138w, 2054s, 2022w, 1999m	CCl_4	109
$MnBr(CO)_5$	2133w, 2050w, 2019w, 2001m	CCl_4	109
$MnI(CO)_5$	2125w, 2044s, 2016w, 2003m	CCl_4	109
$[MnCl(CO)_4]_2$	2104w, 2045s, 2012m, 1977m	CCl_4	110
$[MnBr(CO)_4]_2$	2099w, 2042s, 2011m, 1975m	CCl_4	110
$[MnI(CO)_4]_2$	2087w, 2033s, 2009m, 1976m	CCl_4	110
$[MnCl_2(CO)_4]^{-}$ [b]	2098vw, 2026s, 1986w, 1936s	$C_2H_4Cl_2$	95
$[MnBr_2(CO)_4]^{-}$ [b]	2098w, 2026s, 1990m, 1939s	$C_2H_4Cl_2$	95

(continued)

TABLE 29 (continued)

Compound	ν_{CO} (cm^{-1})	Medium	Ref.
$[MnI_2(CO)_4]^{-\,b}$	2082m, 2006s, 1986s, 1939s	$C_2H_4Cl_2$	95
$[Mn_2Cl_2(CO)_8]^{2-\,b}$	2022s, 1931s	$CHCl_3$	74
$[Mn_2Br_2(CO)_8]^{2-\,b}$	2022s, 1922s	$CHCl_3$	74
$[Mn_2I_2(CO)_8]^{2-\,b}$	2020s, 1910s	$CHCl_3$	74
$TcCl(CO)_5$	2153w, 2057s, 2028w, 1991m	CCl_4	109
$TcBr(CO)_5$	2150w, 2056s, 2027w, 1995m	CCl_4	109
$TcI(CO)_5$	2146w, 2055s, 2024w, 2000m	CCl_4	109
$[TcCl(CO)_4]_2$	2119w, 2048s, 2011m, 1972m	CCl_4	110
$[TcBr(CO)_4]_2$	2116w, 2046s, 2012m, 1973m	CCl_4	110
$[TcI(CO)_4]_2$	2108w, 2042s, 2012m, 1975m	CCl_4	110
$ReCl(CO)_5$	2156w, 2045s, 2016w, 1982m	CCl_4	109
$ReBr(CO)_5$	2150w, 2045s, 2016w, 1984m	CCl_4	109
$ReI(CO)_5$	2145w, 2042s, 2013w, 1987m	CCl_4	109
$[ReCl(CO)_4]_2$	2114w, 2032s, 2000m, 1959m	CCl_4	110
$[ReBr(CO)_4]_2$	2113w, 2031s, 2000m, 1964m	CCl_4	110
$[ReI(CO)_4]_2$	2106w, 2029s, 2001m, 1965m	CCl_4	110
$[CrCl(CO)_5]^{-\,b}$	2056w, 1912s, 1875m	KBr	100
$[CrBr(CO)_5]^{-\,b}$	2058w, 1906s, 1875m	KBr	100
$[CrI(CO)_5]^{-\,b}$	2055w, 1930sh, 1914s, 1853m	KBr	100
$Cr_2I(CO)_{10}$	2021, 1998.5, 1986	C_6H_{12}	97
$[MoCl(CO)_5]^{-\,b}$	2064w, 1913s, 1871m	KBr	100
$[MoBr(CO)_5]^{-\,b}$	2064w, 1914s, 1875m	KBr	100
$[MoI(CO)_5]^{-\,b}$	2061w, 1974sh, 1925s, 1860m	KBr	100
$[MoI_3(CO)_4]^{-\,c}$	2065, 2003, 1994, 1961, 1941	Halocarbon	116
$[WCl(CO)_5]^{-\,b}$	2061w, 1904s, 1869m	KBr	100
$[WBr(CO)_5]^{-\,b}$	2064w, 1904s, 1868m	KBr	100
$[WI(CO)_5]^{-\,b}$	2058w, 1926sh, 1911s, 1840m	KBr	100
$[WI_3(CO)_4]^{-\,c}$	2067, 1995–1983, 1949, 1930	Halocarbon	116

[a] For the tetraphenylarsonium salt.
[b] For the tetraalkylammonium salt.
[c] For the methylpyridinium salt.

A chlorocarbonyl of formula $[Pd_2Cl(CO)_2]_n$ has been obtained by Fischer and Vogler (5) by treatment of $PdCl_2(PhCN)_2$ with carbon monoxide. The molecular weight of this diamagnetic compound is unknown.

The anion $[Pd_2Cl_4(CO)_2]^{2-}$ was reported by Hel'man and Meĭlakh (6) as the ammonium salt and a structure with CO bridges was assigned to it. The presence of CO bridges, however, appears to be unlikely in this type of compound and, moreover, the existence of that binegative anion is not certain. Irving and Magnusson (7) have, in fact, reported that the anion isolated by the Russian workers was actually $[PdCl_3(CO)]^-$.

Three types of halogenocarbonyls of platinum, $PtX_2(CO)_2$, $[PtX_2(CO)]_2$, and $Pt_2X_4(CO)_3$ are known from the studies of Schützenberger (8) who prepared the chloro derivatives by passing carbon monoxide and chlorine over platinum sponge at 250°. In addition, the anion $[PtX_3(CO)]^-$ has been described. All the uncharged halogenocarbonyls of platinum are volatile and soluble in the common organic solvents. Resistance to hydrolysis decreases in the order $[PtX_3(CO)]^- > [PtX_2(CO)]_2 > Pt_2X_4(CO)_3 > PtX_2(CO)_2$; stability to heat usually increases from the iodo to the chloro derivatives.

It is worth mentioning that a compound of formula $PtF_8(CO)_2$ has been prepared by Sharp (9) by reacting PtF_4 with carbon monoxide under pressure. If this compound had to be considered a true fluorocarbonyl, platinum would be ten-coordinate and would thus have the oxidation state of +8, which is rather unusual. Jørgenson (10) has suggested an ionic formulation for the compound, namely $(COF)_2^+(PtF_6)^{2-}$. A more extended investigation of the platinum fluoro derivative and of the rhodium compound $[RhF_3(CO)_2]_2$, also prepared by Sharp (9), seems desirable, because of the great theoretical interest in such compounds. These two compounds are, in fact, the only known examples of "fluorocarbonyls."

$PtX_2(CO)_2$. In this series, besides the chloro, the bromo and iodo derivatives are also known. The latter two were prepared by Malatesta and Naldini (11) by the action of carbon monoxide under pressure (180–210 atm) at about 105° on H_2PtBr_6 and PtI_2. The chloro and bromo derivatives are stable. The iodo compound is less stable and is easily converted even at room temperature into $[PtI_2CO]_2$, with evolution of carbon monoxide. The chloro derivative also loses carbon monoxide at high temperature; it melts at 103° but then solidifies again, the next melting point being 195°. This is due to the following reaction:

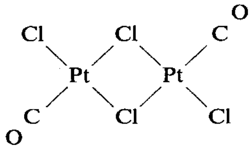
$$2PtX_2(CO)_2 \longrightarrow 2CO + [PtX_2CO]_2 \qquad (1)$$

$PtCl_2(CO)_2$ is diamagnetic (12). Chatt and Williams (13) have measured its dipole moment (4.65 ± 0.5 D) and concluded that the compound has a square planar *cis* configuration.

Compounds of the type *cis*-$PtX_2(CO)(PR_3)$ with X being Cl, Br, and I, and R being Et, Pr, and Bu, have been isolated from the reaction of the dimeric halogen-bridged $[PtX_2(PR_3)]_2$ compounds with carbon monoxide (14).

$[PtX_2CO]_2$. The bromo and iodo derivatives have been obtained from

the corresponding chloro derivative by treatment with HBr or HI (15). These compounds can also be prepared by reaction 1. Although they were initially assumed to be dimeric, the molecular complexity as $[PtBr_2CO]_2$ was later established by Irving and Magnusson (16). Since there are no stretching vibrations in the infrared spectrum which can be attributed to bridging CO groups, these authors concluded that $[PtCl_2CO]_2$ has the symmetric *trans* configuration (1):



(1)

$[PtCl_2(CO)]_2$ exchanges its carbon monoxide with ^{14}CO instantaneously at 25° in benzene (17). The $[PtX_2(CO)]_2$ compounds react with monodendate (L = NH_3, pyridine, *p*-toluidine) or bidentate (LL = 2,2′-dipyridyl) ligands to give $PtX_2(CO)L$ and $[PtX(CO)LL]^+[PtX_3(CO)]^-$ (18), respectively.

$[PtX_3(CO)]^-$. The $[PtX_3(CO)]^-$ anions, with X = Cl, Br, I, have been described by Mylius and Foerster (15). The first one was obtained by reacting $[PtCl_2(CO)]_2$ with HCl; the two others from $[PtCl_3(CO)]^-$ by exchange with HBr and HI. Malatesta and Naldini (11) have shown that the reactions of dry H_2PtCl_6, K_2PtCl_4, H_2PtBr_6, and H_2PtI_6 with carbon monoxide give, among other products, the $[PtX_3(CO)]^-$ anions. The anion $[PtCl_3(CO)]^-$ has also been obtained from an aqueous acid solution of $[PtCl_6]^{2-}$ and carbon monoxide (19). By successive addition of pyridine the anion was separated as the pyridinium salt, $[C_5H_5NH][PtCl_3(CO)]$.

$Pt_2X_4(CO)_3$. The iodo derivative of this class has not yet been reported. The chloro and bromo derivatives have been obtained (11) in a pure state by controlled decomposition at room temperature of solutions of the corresponding $PtX_2(CO)_2$ compounds in anhydrous benzene. Not much is known about the structure of these compounds. However, since the infrared spectrum does not show bands attributable to bridging CO stretching vibrations, the compounds should contain halogen bridges rather than CO bridges as originally proposed (20).

C. The Cobalt Subgroup

No stable unsubstituted halogenocarbonyls of cobalt are known. Some years ago a compound, unstable at room temperature and having the composition $CoI_2(CO)$, was obtained by the reaction of CoI_2 with carbon monoxide under pressure at room temperature (21).

The halogenation of $[Co(CO)_3PPh_3]^-$ with CF_3I gives the triphenylphosphine-substituted iodocarbonyl $CoI(CO)_3PPh_3$ (22). The analogous $CoX(CO)_2(PPh_3)_2$ compounds have been prepared and their infrared spectra and dipole moments measured (22,23). They are nonpolar compounds, very soluble in tetrahydrofuran.

A substance reported as having the composition $Rh_2Cl_2O \cdot 3CO$ was obtained (24) from $RhCl_3 \cdot H_2O$ and carbon monoxide at 140°; this is probably identical with the $[RhCl(CO)_2]_n$ product later prepared by Lagally (25). This is a ruby red, volatile substance, soluble in organic solvents. Its infrared spectrum, in the gas phase, and its dipole moment (1.64 ± 0.3 D) have been measured (26). From cryoscopic measurements in benzene, the compound was found to be dimeric in solution. The x-ray structure published by Dahl and co-workers (2) has, however, shown that the compound is a polymer *in the solid state*. The structure presents several interesting features (see Fig. 21). Two planar $[RhCl(CO)_2]$ units are bonded together through chlorine bridges to form an angle markedly different from 180°. The dimeric units are then joined together by metal–metal bonds. The rhodium atoms are essentially in an octahedral environment. The volatility of the compound and the molecular weight measurements can be explained by assuming that the metal–metal bonds are easily broken in solution. In the reactions discussed later, the chlorocarbonyl of rhodium is considered to react as a dimer in solution.

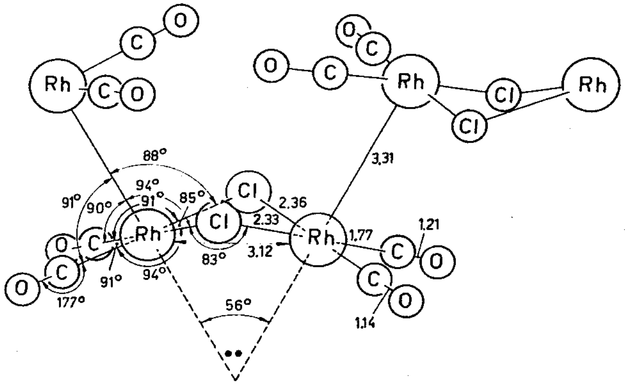


FIG. 21. Molecular configuration of $[RhCl(CO)_2]_n$ (L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961)). Published by permission.

The reactions of the chlorocarbonyl of rhodium with nitrogen bases (27), with alkyl- and arylphosphines, arsines and stibines (27,28), and with triarylphosphites (29) have been described. With L = arylphosphines, arylarsines, or arylstibines, the following reaction occurs:

$$[RhCl(CO)_2]_2 + 4L \longrightarrow 2CO + \underset{(\mathbf{2})}{2RhCl(CO)L_2} \tag{2}$$

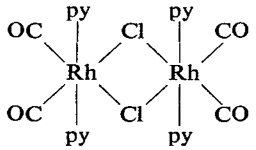
For arylstibines, however, Hieber and co-workers (27) have reported that the addition compound $RhCl(CO)_2L_3$ is obtained. The experimental conditions apparently are the same as those reported by Vallarino (28). Later work (29*a*) would imply that the product of the reaction between $[RhX(CO)_2]_2$ (X = Cl, Br) and $SbPh_3$ does contain hexacoordinate rhodium and should be formulated as $RhCl(CO)(SbPh_3)_4$.

The tetracoordinate substitution products (**2**) obtained by reaction 2 should be *trans* square planar since they are diamagnetic and show a low dipole moment (between 2.5 and 3.6 D). Tetracoordinate rhodium complexes of the type **2** (with L = PPh_3) have also been obtained by an interesting reaction consisting of boiling $RhCl_3$ with the ligand in solutions of 2-methoxyethanol (30). The CO group in the complex arises from the solvent.

Finally, when L = pyridine, two moles of ligand are added per rhodium atom in the complex, according to the reaction:

$$[RhCl(CO)_2]_2 + 4C_5H_5N \longrightarrow 2RhCl(CO)_2(C_5H_5N)_2 \tag{3}$$

No reaction occurs with the bidentate 1,10-phenanthroline. This led Hieber and co-workers to suggest that the compound obtained from reaction 3 is a halogen-bridged dimer in which the two pyridine groups in each unit are *trans* to each other.



(**3**)

The ^{14}CO isotopic exchange reactions of

$$[RhCl(CO)_2]_2,\ RhCl(CO)(PPh_3)_2,\ \text{and}\ RhCl_3(CO)(PPh_3)_2$$

have been investigated. The unsubstituted halogenocarbonyl (17) and $RhCl(CO)(PPh_3)_2$ (17,31) were found to exchange their CO instantaneously with ^{14}CO even at low temperature (0 and −20°, respectively).

The analogous reaction with $RhCl_3(CO)(PPh_3)_2$ was found (32) to be slower and independent of carbon monoxide concentration. The following dissociative S_N1 mechanism was therefore suggested for the latter reaction:

$$RhCl_3(CO)(PPh_3)_2 \rightleftharpoons RhCl_3(PPh_3)_2 + CO \tag{4}$$

Vallarino (33) has described the preparation of halogenocarbonylrhodates by addition of halide ions to $[RhX(CO)_2]_2$. The products of this reaction are the $[RhX_2(CO)_2]^-$ anions, with X being Cl, Br, and I:

$$[RhX(CO)_2]_2 + X^- \longrightarrow [RhX_2(CO)_2]^- \tag{5}$$

Bonati and Wilkinson (34) have described a mixed acetylacetonatocarbonyl complex of rhodium obtained by reacting a solution of $[RhCl(CO)_2]_2$ with acetylacetone:

$$[RhCl(CO)_2]_2 + 2C_5H_8O_2 \longrightarrow 2Rh(C_5H_7O_2)(CO)_2 + 2HCl \tag{6}$$

The halogenocarbonyl compounds of iridium were first described by Manchot and Hieber and their co-workers (35,36). Their chemistry was then extensively studied by Malatesta and his co-workers (37–40) and several new types of compounds were discovered. A wide range of halogenocarbonyls of iridium are now known, including some anionic species. The dihalogenodicarbonyl compounds, $IrX_2(CO)_2$, and the tricarbonyls, $IrX(CO)_3$, were prepared by the reaction of IrX_3 with carbon monoxide at atmospheric pressure at about 150°. $IrX_2(CO)_2$ and $IrX(CO)_3$ are decomposed rapidly by water. Iodocarbonyl compounds of iridium, $IrI_3(CO)_3$, $[IrI_3(CO)_2]_2$, and $Ir_2I_6(CO)_3$ have been obtained (37) by the reaction of iridium tri- and tetraiodides with carbon monoxide at high temperature and pressure.

Anionic halogenocarbonyls of iridium were first obtained by Malatesta and Sandroni (38) by reacting mixtures of IrI_3 and KI with carbon monoxide under pressure at 80–250°. The salts $K[IrI_4(CO)_2]$ and $K_2[IrI_5(CO)]$ were obtained in the same manner. The relative amounts of the two salts depend on the IrI_3:KI ratio employed (39); the addition of a halogen acceptor such as copper has no effect on the reaction. The presence of copper has, however, a marked influence on the reaction of potassium hexabromoiridate with carbon monoxide, $K_2[Ir_2Br_5(CO)_4]$ being formed (40). $K_3[IrBr_6]$, $K_2[IrBr_5(CO)]$, and $K[IrBr_4(CO)_2]$ are intermediate products of the reaction and were actually isolated from the reaction of K_2IrBr_6 with carbon monoxide at 220° and 220 atm, in the absence of copper (40). The infrared spectrum of $K_2[Ir_2Br_5(CO)_4]$ in which the two iridium atoms are in an average oxidation state +1.5, does not show bridging CO stretching vibrations. This suggests the presence of chlorine bridges joining the two iridium atoms.

Many phosphine-, arsine-, and stibine-substituted halogenocarbonyls of monovalent, bivalent, and trivalent iridium have been reported (39, 41–43). In Ref. 43 the preparations of $Ir_2H_2Cl_4(CO)_2(PEt_3)_2$ and $IrHCl_2(CO)(PEt_2Ph)_2$ are reported.

Of particular interest is the monovalent iridium complex $IrCl(CO)(PPh_3)_2$ obtained by the reaction of $IrCl_3 \cdot nH_2O$ with triphenylphosphine in the presence of alcohols (44). This complex has been reported (45) to absorb 1 mole of oxygen at room temperature in benzene solution. The oxygen adduct has the formula $IrCl(O_2)(CO)(PPh_3)_2$ and its x-ray structure has been reported (46). The most interesting feature of the structure is the position of the oxygen atoms relative to the iridium atom. They are equidistant from the Ir and 1.30 Å from each other; that is, at a distance greater than in molecular oxygen (1.20 Å) but shorter than in a normal peroxide (1.48 Å).

D. The Iron Subgroup

The three dihalogeno tetracarbonyls of iron, $FeX_2(CO)_4$, have been prepared by the action of halogens on $Fe(CO)_5$ (47,48). These compounds are somewhat soluble in organic solvents. The resistance to heat and hydrolysis increases from the chloro to the iodo derivative. $FeCl_2(CO)_4$ and $FeBr_2(CO)_4$ are decomposed immediately by water, whereas $FeI_2(CO)_4$ is hydrolyzed only upon heating. $FeI_2(CO)_4$ is diamagnetic (12,49) and should therefore be considered as a d^2sp^3 complex of iron(II). Weiss (50) suggested an octahedral *cis* configuration for $FeI_2(CO)_4$, on the basis of dipole moment measurements (3.69 D). The infrared spectrum is in agreement with this suggestion. Four C—O stretching vibrations (51) and two metal–halogen stretching vibrations (52) at 217 and 238 cm^{-1} (for $FeBr_2(CO)_4$) are in fact observed. Infrared evidence has been obtained for the existence of *trans*-$FeI_2(CO)_4$, which was prepared by exposure of the other isomer to light (52*a*).

Hieber (53) suggested that the reaction leading to the formation of $FeI_2(CO)_4$ goes through an intermediate "adduct," $FeI(CO)_5$, which is stable only at very low temperature. $FeI_2(CO)_5$ was also mentioned in the abstract of a paper by Wojcicki and Farona (54). $FeI_2(CO)_4$ was found (17) to exchange all four carbon monoxide groups with ^{14}CO rather rapidly at 31.8°, the exchange being dependent on the carbon monoxide concentration. Later (55) it was made known, however, that the exchange between $FeX_2(CO)_4$ (X = Br, I) and ^{14}CO is inhibited by addition of free halogen and is promoted by light and that the previously observed dependence on CO concentration was an artifact due to these secondary effects.

It has also been reported (56) that by reacting $Fe_3(CO)_{12}$ with iodine in tetrahydrofuran, $Fe_2I_2(CO)_8$ is obtained as a colorless solid below its melting point (−5°).

Halogenocarbonyls of iron with a lower content of carbon monoxide, $FeX_2(CO)_2$, and $FeX(CO)_2$, have also been synthesized (see Table 28).

Hieber and Muschi (57) have reported that $FeBr_2(CO)_4$ is reduced by sodium amalgam according to the following equation:

$$FeBr_2(CO)_4 + 4Na \longrightarrow Na_2[Fe(CO)_4] + 2NaBr \qquad (7)$$

The resulting sodium tetracarbonylferrate, however, reacts with the unconverted $FeBr_2(CO)_4$; the net result is decomposition to iron metal:

$$FeBr_2(CO)_4 + Na_2[Fe(CO)_4] \longrightarrow 2NaBr + 2Fe + 8CO \qquad (8)$$

The substitution reactions of $FeX_2(CO)_4$ with triphenylphosphine, triphenylarsine, and triphenylstibine have been described (58). The carbon monoxide evolved and the disubstitution products, $FeX_2(CO)_2L_2$, were isolated. In the reaction of $FeI_2(CO)_4$ with $SbPh_3$, the monosubstitution derivative $FeI_2(CO)_3$ $(SbPh_3)$ is obtained. Similarly, the monosubstitution derivatives $FeX_2(CO)_3(TePh_2)$ are obtained from $FeBr_2(CO)_4$ or $FeI(CO)_4$ and diphenyltellurium (59). Phosphine disubstituted compounds are more easily obtained (60) by direct carbonylation of $FeX_2(PR_3)_2$, as for example:

$$FeCl_2(P(C_2H_5)_3)_2 + 2CO \xrightarrow[15°,\ 6\ days]{1\ atm} FeCl_2(CO)_2(P(C_2H_5)_3)_2 \qquad (9)$$

Mono-, bi-, and trisubstitution products can be obtained by reacting $FeX_2(CO)_4$ (X = Br, I) with alkyl or aryl isonitriles (61,62), for example:

$$FeI_2(CO)_4 + 3p\text{-}CH_3C_6H_4NC \longrightarrow 3CO + FeI_2(CO)(p\text{-}CH_3C_6H_4NC)_3 \qquad (10)$$

The infrared spectra of the isonitrile derivatives have been measured (62) and the conclusion was reached that CO groups are better π acceptors than isonitriles.

The halogenocarbonyls of ruthenium $[RuX_2(CO)_2]_n$ were obtained by Manchot and König (63) by the action of a stream of carbon monoxide on anhydrous ruthenium trihalides at 210–290°. These compounds show a remarkable resistance to hydrolysis; the iodo derivative is attacked only with difficulty by dilute sulfuric and hydrochloric acids. Irving (64) has studied the chemical and physical properties of the diamagnetic iodo derivative (65), assigning to it a halogen-bridged polymeric structure.

$[RuI_2(CO)_2]_n$ reacts with nitrogen bases (64) such as pyridine, 2,2′-dipyridyl, acetonitrile, aniline, and ammonia and with triphenylphosphine, triphenylarsine, and triphenylstibine (66) to give diamagnetic addition compounds of the type $RuI_2(CO)_2L_2$.

A halogenocarbonyl of ruthenium with a lower content of carbon monoxide, $[RuBr(CO)]_n$, has also been obtained (67) by treatment of $RuBr_3$ with carbon monoxide under pressure at about 185° for 8 hr.

No halogenocarbonyls of the type $RuX_2(CO)_4$ had been reported until Dahl and his co-workers (68) prepared the iodo derivative, $RuI_2(CO)_4$, by treating RuI_3 with carbon monoxide under pressure at 170° in the presence of copper for 24 hr. X-ray analysis of $RuI_2(CO)_4$ showed that the ruthenium atom is in an essentially octahedral arrangement and that the two iodine atoms are *cis* to each other (1). This indirectly confirms the conclusions about the structure of $FeI_2(CO)_4$.

Halogenocarbonyls of osmium, $OsX_2(CO)_4$, $OsX_2(CO)_3$, $[OsX_2(CO)_2]_n$, and $[OsX(CO)_4]_2$, have been described by Hieber (69) and by Manchot (70) and their co-workers. It is interesting to note that in the series $OsX_2(CO)_4$, the bromo and iodo derivatives have been described as existing in two forms having different colors (69). This is probably due to the existence of *cis* and *trans* isomers but this point requires further investigation.

Halogenohydridocarbonyls of bivalent ruthenium and osmium of formula $MHX(CO)(PR_3)_3$ are obtained by treating the metal halide or a complex metal halide with a tertiary phosphine in an alcohol solvent (2-methoxyethanol or ethylene glycol) (30). These reactions are usually carried out in the presence of sodium or potassium hydroxide. For example, $OsHCl(CO)(PEt_2Ph)_3$ is obtained by boiling $OsCl_3(PEt_2Ph)_3$ with KOH in ethyl alcohol (30). The presence of sodium or potassium hydroxide, however, does not seem to be indispensable. Compounds of formula $MHX(CO)(PPh_3)_3$ were in fact obtained simply by heating $(NH_4)_2OsX_6$ or $RuCl_3$ with the tertiary phosphine in an alcohol solvent (71). Substituted nonhydridic halogenocarbonyls of ruthenium, $RuCl_2(CO)_2(PR_3)_2$, in both *cis* and *trans* forms, were obtained (30,72) by boiling the complex salt $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ with potassium hydroxide in allyl alcohol. The very interesting question of the origin of the hydrido and carbon monoxide groups in these complexes has been partially answered. Vaska and DiLuzio (73) found by deuteration methods that, in the course of the reaction between K_2IrCl_6 and PPh_3 in ethyl alcohol, the hydrido group in the final product, $IrHCl_2(PPh_3)_2$, originated from the α hydrogens of the alcohol. Chatt, Shaw, and Field (72) studied the reaction of $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ with ethyl alcohol in the presence of alkali and noticed that methane was formed. They suggested that the reaction takes place according to the following stoichiometry:

$$[Ru_2Cl_3(PEt_2Ph)_6]Cl + 2KOH + 2C_2H_5OH \longrightarrow 2RuHCl(CO)(PEt_2Ph)_3 + 2CH_4 + 2KCl + 2H_2O \quad (11)$$

It was postulated that the formation of the final hydridocarbonyl compound takes place via an initial ruthenium–ethoxide complex, followed by hydrogen transfer to ruthenium. Methane elimination and carbonyl group formation would then occur in a second step.

E. The Manganese Subgroup

Halogenocarbonyls of manganese, technetium, and rhenium of the series $MX(CO)_5$ and $[MX(CO)_4]_2$ have been reported. As for manganese, the anionic species $[MnX_2(CO)_4]^{2-}$ and $[Mn_2X_2(CO)_6]^{2-}$ are also known (74). In this series, resistance to heat and hydrolysis increases from chlorine to iodine.

The monomeric $MX(CO)_5$ compounds are obtained by treatment of the corresponding metal pentacarbonyls with halogens (75–77):

$$[M(CO)_5]_2 + X_2 \longrightarrow 2MX(CO)_5 \quad (12)$$

However, the three rhenium derivatives $ReX(CO)_5$ were originally prepared directly by the carbonylation of $ReCl_5$, $ReBr_3$, and K_2ReI_6 at 200–230° and 200 atm, in the presence of copper as halogen acceptor (78). $MnI(CO)_5$ was first isolated from the products of the carbonylation of MnI_2 under pressure (76).

The infrared spectrum of $MnX(CO)_5$ in the carbonyl stretching region is in agreement with an octahedral arrangement of ligands around the central metal atom (C_{4v} symmetry) for which three fundamental bands are expected (79). Four bands are actually found with high resolution optics; the fourth band is a weak band at about 2010 cm^{-1} that has been attributed to a $^{13}C—O$ stretching vibration mode (80).

The manganese $MnX(CO)_5$ compounds react with nitrogen bases (81) at 40–70°, with diphenyltellurium (59), with triphenylphosphine, triphenylarsine, and 2,2′-dipyridyl (75) at 120°, with 2,5-dithiahexane and 3,6,9-trithiaundecane (82), with *o*-phenylenebis(dimethylarsine) and 1,2-bis(diphenylphosphino)ethane (83), and with phenyl isocyanide in ethanol (84) at 60° for 3 hr, to give usually disubstitution products $MnX(CO)_3L_2$ or $MnX(CO)_3LL$ (where L is the monodentate and LL the bidentate ligand).

The reactions of $ReX(CO)_5$ with nitrogen bases had been described some years ago by Hieber and Fuchs (85). With pyridine (at 120–240°) or with 1,10-phenanthroline at about 80°, disubstitution products $ReX(CO)_3py_2$ and $ReX(CO)_3phen$ were obtained. The substitution products from the binuclear halogenocarbonyls $[MX(CO)_4]_2$ usually are the same as those from $MX(CO)_5$. It is interesting to note that the reactions of $ReX(CO)_5$ with liquid ammonia, *p*-tolyl isonitrile at 100°, and PPh_3 at 110° give saltlike compounds of the type $[Re(CO)_4L_2]^+X^-$ (86).

The halogenopentacarbonyls of technetium give substitution products of the type $TcX(CO)_3L_2$, with X being Cl, Br, and I, and L being PPh_3, py, and phen (87). The reactions were carried out at 50–70° and it was reported that the reaction conditions were not critical since only disubstitution products were obtained, regardless of temperature and ratio of reactants. However, for manganese, the nature of the substitution products and the degree of substitution depend considerably on the reaction conditions and on the nature of the ligand employed. With phenyl isonitrile, the trisubstitution product $MnBr(CO)_2(CNPh)_3$ was also obtained using diglyme as solvent (84). Monosubstitution is possible at room temperature.

Angelici and Basolo (88) have studied the kinetics of the reactions of $MnX(CO)_5$ with a variety of ligands at room temperature:

$$MnX(CO)_5 + L \longrightarrow CO + MnX(CO)_4L \qquad (13)$$

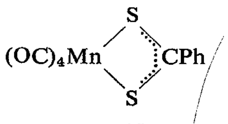
It was found that the reactions are independent of L and therefore a dissociative mechanism was postulated.

$$MnX(CO)_4L + L' \longrightarrow CO + MnX(CO)_3LL' \qquad (14)$$

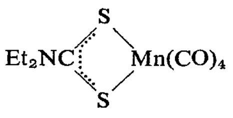
Reaction 14 has also been studied kinetically (89); its rate is independent of the nature and concentration of L′. The rate of reaction depends, however, on the nature of L and on the atomic number of X. This again suggests a dissociative mechanism.

Two of the three possible geometrical isomers of the species $MnX(CO)_3L_2$ have been identified (90). *Cis*- and *trans*-$MnBr(CO)_3(P(OPh)_3)_2$ have been isolated and characterized by infrared spectra and dipole moment measurements. The isomerization of the *cis* form has been found to be a first order process.

$MnBr(CO)_5$ is a valuable starting material for the preparation of new carbonyl complexes of manganese. For example, by treatment of $MnBr(CO)_5$ with dithiobenzoic acid (91) or with sodium diethyldithiocarbamate (92), the complexes (**4**) and (**5**) were obtained.



(**4**)



(**5**)

The isotopic CO exchange reaction

$$MnX(CO)_5 + {}^{14}CO \longrightarrow MnX({}^{14}CO)_5 + CO \qquad (15)$$

had been studied by Wojcicki and Basolo (17) and their results have been confirmed by Hieber and Wollman (93). The rate of exchange in toluene at 31.8° decreases from $MnCl(CO)_5$ to $MnI(CO)_5$ and one of the five carbon monoxide groups exchanges more slowly than the other four. (See Note 5 on page 272.) A possible explanation for the latter result is that the Mn—C bond *trans* to X is stronger than the Mn—C bond *trans* to CO. The exchange is dependent on $MnX(CO)_5$ concentration and independent of carbon monoxide concentration.

The x-ray structure of $[MnBr(CO)_4]_2$ has been published (3). In this molecule, the two manganese atoms are in an approximately octahedral configuration, with the bromines occupying bridging positions between the two $[Mn(CO)_4]$ units. The nonbonding distance between the two manganese atoms is 3.74 Å, considerably longer than the manganese–manganese distance (2.92 Å) in $Mn_2(CO)_{10}$ (94). Clearly there is no metal–metal interaction. It has been pointed out that the krypton configuration is reached if each manganese in an oxidation state +1 is regarded as receiving four electrons from the two bridging bromine atoms.

The anions $[MnX_2(CO)_4]^-$ and $[Mn_2Cl_2(CO)_8]^{2-}$ have been obtained by the action of tetraalkylammonium halides on $MnX(CO)_5$ and $Mn_2(CO)_{10}$ (74,95):

$$R_4NX + MnX(CO)_5 \longrightarrow R_4N[MnX_2(CO)_4] + CO \qquad (16)$$

$$2R_4NX + Mn_2(CO)_{10} \longrightarrow (R_4N)_2[Mn_2X_2(CO)_8] + 2CO \qquad (17)$$

Angelici (95) has reported that the $[MnX_2(CO)_4]^-$ anions probably have the *cis* configuration since they show four C—O stretching vibrations in the infrared spectrum.

F. The Chromium Subgroup

The only neutral halogenocarbonyls of this subgroup described until now are $CrI(CO)_5$, $Cr_2I(CO)_{10}$, and $MoCl_2(CO)_4$. The two iodo derivatives were both obtained by iodine oxidation of the $[CrI(CO)_5]^-$ anion (96,97).

$\mathrm{CrI(CO)_5}$ is a paramagnetic, deep blue substance, which is very sensitive to air and which readily decomposes at room temperature. $\mathrm{MoCl_2(CO)_4}$ is a yellow thermally unstable substance prepared from $\mathrm{Mo(CO)_6}$ and liquid chlorine at −78°C (*97a*).

The $\mathrm{[MI(CO)_5]^-}$ anions are obtained by reacting the hexacarbonyls with methylpyridinium iodide (98), and by the reaction of $\mathrm{Mo(CO)_6}$ with tetraalkylammonium halides or KI in diglyme (99). More recently (100), the complete series of the $\mathrm{[MX(CO)_5]^-}$ anions has been described; here M = Cr, Mo, and W, and X = Cl, Br, and I. The preparation again involves treatment of the hexacarbonyls with tetraalkylammonium halides:

$$\mathrm{NEt_4X + M(CO)_6 \longrightarrow NEt_4[MX(CO)_5] + CO} \qquad (18)$$

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X. ALKYL METAL CARBONYLS

A. Introduction

Transition metals as such are usually reluctant to form σ bonds to carbon atoms (1). The research of the last years has led, however, to the synthesis of many stable compounds containing alkyl groups σ-bonded to transition metals, such as $Mn(CO)_5Me$ (2), mp 94–95.5°, and $FeC_5H_5(CO)_2Me$ (3), mp 78–82°. It will be immediately noticed that these two compounds contain, in addition to the methyl group, a cyclopentadienyl ring and/or carbon monoxide as substituents, to which can be assigned the role of stabilizing the metal–carbon bond. It is worth mentioning that Lewis bases also can contribute to stabilization of metal–alkyl compounds; this is true for the complex $CrPh_3 \cdot 3THF$ described by Herwig and Zeiss (4). Trialkylphosphines enhance the stability of analogous compounds; for example, *trans*-bis(triethylphosphine)diphenylplatinum, mp 176–180°, which was synthesized by Chatt and Shaw (5).

Although the stabilization of metal–alkyl σ bonds can be attributed to the presence of additional substituents in the molecule, the reasons for the stabilization may not be the same in all the cases mentioned above. Chatt and Shaw (6) have discussed the stability of mixed alkyls of transition metals in terms of energy separation between the MO bonding orbitals and the MO nonbonding or antibonding orbitals. For a more detailed discussion of the metal–carbon bond in metal alkyls, see the review by Richardson (7).

The following discussion will be restricted mainly to pure alkyl metal carbonyls, i.e., those compounds containing, in addition to the alkyl group, carbon monoxide as the only ligand. However, some examples of phosphine-, arsine-, and stibine-substituted alkyl carbonyls, such as $Co(CO)_3(PPh_3)COMe$, will be discussed and are also reported in Table 30. Cyclopentadienylalkylcarbonyls, such as $FeC_5H_5(CO)_2Me$ and π-allyl metal compounds, are not included systematically in the table, but reference will be made to them whenever it seems necessary for a more comprehensive discussion of the general subject.

TABLE 30

Carbonyl Alkyl and Acyl Derivatives of Transition Metals

Compound	Color	Mp (°C)	Ref.
$NiC_5H_5(CO)CF_3$	Red	Liquid	67
$NiC_5H_5(CO)C_2F_5$	Red-purple	Liquid	67
$NiC_5H_5(CO)C_3F_7$	Red-purple	Liquid	67
$NiC_5H_5(PPh_3)Me$	Dark green	115–118 dec.	68
$Co(CO)_4Me$	Light yellow	−44	10
$Co(CO)_4COMe$	Yellow	−33	22
$Co(CO)_4CF_3$	Yellow	13	11,23
$Co(CO)_4C_2F_5$	Yellow-red	−30	11,13
$Co(CO)_4\textit{n}\text{-}C_3F_7$	Yellow-orange	Liquid (−33)	11,13
$Co(CO)_4CF_2CF_2H$	Yellow	Liquid	69
$Co(CO)_4C_7F_{15}$	Yellow-brown	30	13
$Co(CO)_4C_6F_5$	Pale yellow	38–39	69
$Co(CO)_4COCF_3$	Yellow	4	23
$Co(CO)_4COC_2F_5$	Deep yellow	−33	13
$Co(CO)_4COOCMe_3$	Yellow	Liquid	70
$Co(CO)_3(PPh_3)COMe$[a]	Yellow	123 dec.	20,21
$Co(CO)_2(P(OPh)_3)_2Me$	Pale yellow	~50	57
$Co(CO)_3(PPh_3)COCH_2CH_2OH$	Yellow-brown	95–100 dec.	71
$Co(CO)_3(PPh_3)CF_3$	Colorless	168	23
$Co(CO)_3(PPh_3)C_2F_5$	Yellow	145	13
$Co(CO)_3(AsPh_3)C_2F_5$	Deep yellow	134	13
$Co(CO)_3(SbPh_3)C_2F_5$	Brown-yellow	120	13
$Co(CO)_3(PPh_3)COC_2F_5$	Lemon yellow	138	13
$Co(CO)_3(PPh_3)COCF_3$	Yellow	172	23
$Co(CO)_4SiCl_3$	—	—	72
$Rh(C_5H_5)I(CO)CF_3$	Dark red	168–169	73
$Ir(CO)_2(PPh_3)_2COOMe$	Colorless	124	74
$Fe(CO)(NO)(PPh_3)_2COCF_3$	Deep red	—	75
$Fe(CO)_4(C_2F_4)_2$	Colorless	77	76
$Fe(CO)_4(C_2F_5)_2$	Pale yellow	62–63.5	77
$Fe(CO)_4(C_3F_7)_2$	Pale yellow	88–90	77
$FeC_5H_5(CO)_2Me$[b]	Caramel	78–82	3
$Fe(C_5H_5)(CO)_2COOMe$	Yellow-orange	34–36	18
$Fe(C_5H_5)(CO)_2CH_2SMe$	Yellow-brown	Liquid	78
$RuC_5H_5(CO)_2Me$	Colorless	39–40	79
$RuC_5H_5(CO)_2Et$	Colorless	−5	79
$Mn(CO)_5Me$	Colorless	94–94.5	2,80

(continued)

TABLE 30 (continued)

Compound	Color	Mp (°C)	Ref.
$Mn(CO)_5Et$	Pale yellow	Liquid	81
$Mn(CO)_5Ph$	Colorless	52	9
$Mn(CO)_5CH_2Ph$	Pale yellow	37.5–38.5	2
$Mn(CO)_5COMe$	Colorless	54–55	9
$Mn(CO)_5COPh$	Colorless	95–96	9
$Mn(CO)_5COEt$	Colorless	57–59	82
$Mn(CO)_5COPr$	Colorless	45–46.5	82
$Mn(CO)_5COCH_2Ph$	Colorless	91.5–93	82
$Mn(CO)_5COC_6H_4Me$	Yellow	98	24
$Mn(CO)_5CF_3$	Colorless	85	24,40
$Mn(CO)_5C_2F_5$	Colorless	15–17	12
$Mn(CO)_5(\text{iso-}C_3F_7)$	Colorless	2	11
$Mn(CO)_5(\textit{n}\text{-}C_3F_7)$	Colorless	Liquid	11,12
$Mn(CO_5)(CF_2)_4H$	Colorless	Liquid	11
$Mn(CO)_5(CF_2)_4Cl$	Pale yellow	Liquid	11
$Mn(CO)_5$(5-methyl-2-furoyl)	Yellow	87–89	83
$Mn(CO)_5CF_2CF_2H$	Colorless	30.5–31.5	84
$Mn(CO)_5CF_2CFClH$	Pale yellow	41–42	38,84
$Mn(CO)_5CFClCF_2H$	Colorless	51–52	38
$Mn(CO)_5COCH_2Cl$	Yellow	89–91	29
$Mn(CO)_5COCH_2CH_2Cl$	Yellow	56–58	29
$Mn(CO)_5C(CF_3){=}CHCF_3$	Yellow	Liquid	84
$Mn(CO)_5(\sigma\text{-allyl})$	Lemon yellow	Liquid	85,86
$Mn(CO)_5COCH_2F$	Colorless	67–69	29
$Mn(CO)_5COCHF_2$	Yellow	32–33	29
$Mn(CO)_5COCF_3$	Pale yellow	57	11,24,40
$Mn(CO)_5COC_2F_5$	Pale yellow	49–50	12
$Mn(CO)_5CO(\text{iso-}C_3F_7)$	Pale yellow	34–37	11
$Mn(CO)_5CO(\textit{n}\text{-}C_3F_7)$	Pale yellow	Liquid	11,12
$Mn(CO)_5CO(CF_2)_4Cl$	Pale yellow	39–40	11
$Mn(CO)_5CO(CF_2)_4H$	Pale yellow	22–23	11
$Mn(CO)_5CO(CF_2)_2H$	Colorless	46.5–47	84
$Mn(CO)_5COOEt$	Light yellow	59.5	87
$Mn(CO)_5CH_2CH_2COOMe$	Colorless	60.5	88
$Mn(CO)_5COC_6H_4COMn(CO)_5$	Colorless	—	88
$Mn(CO)_5COCH_2CH_2COOH$	—	97–98 dec.	88
$[Mn(CO)_5](CH_2)_3[Mn(CO)_5]$	Yellow	64–65	89
$[Mn(CO)_5]CO(CF_2)_3CO[Mn(CO)_5]$	Pale yellow	105–106	89
$[Mn(CO)_5](CF_2)_3[Mn(CO)_5]$	Colorless	161	89
$Mn(CO)_5C_6F_5$	Pale yellow	121–122	90,91
$Mn(CO)_5CF_2CF_2Me$	Colorless	41–42	37,38

(continued)

TABLE 30 (continued)

Compound	Color	Mp (°C)	Ref.
$Mn(CO)_5CF_2CF_2Ph$	Colorless	36–37	38
$Mn(CO)_4(C_6H_{11}NH_2)COMe$	Yellow	97–97.5	32
$Mn(CO)_4(P(C_6H_{11})_3)COMe$	Lemon yellow	103	92
$Mn(CO)_4(P(C_6H_{11})_3)COCF_3$	Lemon yellow	98	92
$Mn(CO)_4(PEt_3)Me$	Light yellow	1.5–2	92
$Mn(CO)_4(P(OPh)_3)Me$	Light yellow	72	92
$Mn(CO)_4(PPh_3)CH_3$	Yellow	102	92
$Mn(CO)_4(P(C_6H_{11})_3)Me$	Lemon yellow	122 dec.	92
trans-$Mn(CO)_4(PPh_3)CF_2CF_2CH_3$	Pale yellow	160 dec.	69
$Re(CO)_5Me$	Colorless	120	93
$Re(CO)_5Ph$	Colorless	46–47	94
$Re(CO)_5CH_2Ph$	Light yellow	33–34	94
$Re(CO)_5C_6F_5$	Colorless	152	15
$Re(CO)_5CF_2CF_2H$	Colorless	45–45.5	95
$Re(CO)_5CF_2CF_2CF_3$	Colorless	60–60.5	95
$Re(CO)_5COMe$	Pale yellow	80–81	94
$Re(CO)_5COPh$	Canary yellow	120 dec.	94
$Re(CO)_5C_2F_5$	Pale yellow	39–40	12
$Re(CO)_5C_3F_7$	Pale yellow	~27	12
$Re(CO)_5COC_2F_5$	Pale yellow	81–83	12
$Re(CO)_5COC_3F_7$	Pale yellow	54	12
$Re(CO)_5COC_6F_5$	Cream	114	15
$CrC_5H_5(CO)_3Me$	Yellow	—	3
$MoC_5H_5(CO)_3Me$[c]	Yellow	124 dec.	3
$MoC_5H_5(CO)_3Et$	Yellow	77.5–78.5	3
Mo(indenyl)$(CO)_3Me$	Yellow-orange	91–93 dec.	96
$MoC_5H_5(CO)_3(\sigma\text{-allyl})$	Pale yellow	Liquid	97
$Mo(C_5H_5)(CO)_3CH_2SMe$	Yellow	66–67	78
$WC_5H_5(CO)_3Me$[c]	Yellow	144.7–145.3	3,98
$WC_5H_5(CO)_3Et$	Yellow	93–93.5 dec.	3
$WC_5H_5(CO)_3(\sigma\text{-allyl})$	Pale yellow	24–26	99
$[W(CO)_5COC_6H_5]^-$	—	—	16

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[a] Other acyl cobalt tricarbonyl triphenylphosphines, $Co(CO)_3(PPh_3)COR$ are reported in Ref. 21 with mp and analyses.

[b] For many other carbonylalkyl- and carbonylacylcyclopentadienyliron complexes, see Refs. 14, 41, 90, and 100.

[c] For several other examples of carbonylalkyl- and carbonylacylcyclopentadienyl complexes of molybdenum and tungsten, see Refs. 41 and 99.

B. Methods of Preparation and Properties

The first example of a stable unsubstituted alkyl metal carbonyl was reported by Closson, Kozikowski, and Coffield (2), who obtained $Mn(CO)_5Me$ from $NaMn(CO)_5$ and dimethyl sulfate or methyl iodide in tetrahydrofuran.

$$NaMn(CO)_5 + CH_3X \longrightarrow Mn(CO)_5CH_3 + NaX \qquad (1)$$

Yields as high as 75% were later obtained (8) by operating at −40°C, using diethyl ether as solvent and a 50% excess of dimethyl sulfate as methylating agent. Coffield and co-workers (9) also reported the preparation of acylmanganese pentacarbonyls $Mn(CO)_5COR$, obtained by the reaction of acyl chlorides with $NaMn(CO)_5$ and further sublimation of the volatile acyl derivatives.

$$NaMn(CO)_5 + RCOCl \longrightarrow NaCl + Mn(CO)_5COR \qquad (2)$$

Shortly after the discovery of $Mn(CO)_5Me$, the compound $Co(CO)_4Me$, the first in the series of alkylcobalt tetracarbonyls, was prepared by Hieber and co-workers (10) by a reaction substantially similar to (1). The other members of the cobalt series and fluoroalkyl and fluoroacyl analogs were later prepared by three different groups: Hieber and co-workers in Germany, Heck and Breslow in the United States, and McClellan in the United States (see Table 30).

The perfluoroalkylmanganese, -rhenium, and -cobalt carbonyls cannot be prepared directly from the corresponding sodium or lithium carbonylmetallates and perfluoroalkyl halides, but they can be obtained by thermal decomposition of the corresponding perfluoroacyl metal carbonyls (11,12)

$$R_fCOCl + NaM(CO)_n \longrightarrow M(CO)_nCOR_f + NaCl \qquad (3)$$

$$M(CO)_nCOR_f \xrightarrow{\text{heat}} CO + M(CO)_nR_f$$

The tetracarbonylperfluoroacylcobalt compounds are more easily prepared by using the anhydrides of the perfluoroacids (13) as acylating agents, for example:

$$(C_2F_5CO)_2O + NaCo(CO)_4 \longrightarrow C_2F_5CO_2Na + Co(CO)_4COC_2F_5 \qquad (4)$$

King and Bisnette (14) and Stone and co-workers (15) found that perfluoroalkyl metal carbonyl derivatives can be readily obtained by reacting perfluoroolefins or perfluorobenzene with carbonylmetallates. For example, $[FeC_5H_5(CO)_2]^-$ and C_6F_6 give $FeC_5H_5(CO)_2C_6F_5$, and $[Re(CO)_5]^-$ gives $Re(CO)_5C_6F_5$.

Of particular interest is the preparation of the anions $[W(CO)_5COMe]^-$ and $[W(CO)_5COPh]^-$ obtained by reacting $W(CO)_6$ with the corresponding lithium alkyls. These compounds represent the first known example of metal–carbon bonds in an anionic metal carbonyl (16). An anionic acylmanganesepentacarbonyl, namely $[MnI(CO)_4COMe]^-$, was later prepared by Calderazzo and Noack by the direct reaction of $Mn(CO)_5Me$ with lithium iodide (17) (see Sec. X-C).

King has obtained a carbomethoxy compound of manganese formulated as $MnC_5H_5(CO)(NO)COOMe$. This compound is in principle separable into two optically active enantiomers since all its four ligands are different (18).

Mononuclear compounds containing cobalt–silicon bonds have been prepared by the reaction of octacarbonyldicobalt with silicon hydrides. So, for example, $Co_2(CO)_8$ and $SiHCl_3$ were mixed at liquid nitrogen temperature and on gradually warming to room temperature the reaction took place. The $Co(CO)_4SiCl_3$ so obtained is a volatile material that can be separated by distillation at room temperature (19).

Alkyl and acyl metal carbonyls are colorless or slightly colored volatile substances that are usually solid at room temperature. Care is necessary, however, in subliming acyl derivatives if high purity is required, since decarbonylation can occur to some extent in the gas phase. Crystallization at low temperature in an atmosphere of carbon monoxide has been used (8) to obtain very pure $Mn(CO)_5COCH_3$.

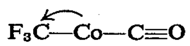
Although pentacarbonyl alkyl- and pentacarbonyl acyl compounds of manganese and rhenium are very stable towards oxidation and are reasonably stable thermally, the corresponding compounds of cobalt show a much lower stability and are usually stable only at temperatures below 0°. Few alkyl- and acyl cobalt tetracarbonyls have been isolated in a pure state; in many cases they have been converted into the more stable triphenylphosphine derivatives and isolated as such (20,21).

$$Co(CO)_4R + P(C_6H_5)_3 \longrightarrow Co(CO)_3P(C_6H_5)_3COR \tag{5}$$

$$Co(CO)_4COR + P(C_6H_5)_3 \longrightarrow CO + Co(CO)_3P(C_6H_5)_3COR \tag{6}$$

The thermal stability of the cobalt compounds can also be increased by substituting perfluoro groups for the acyl and alkyl groups. Thus, although $Co(CO)_4COMe$ starts to decompose (22) at −20° and decarbonylates to $Co(CO)_4Me$ even at lower temperatures, the corresponding perfluoro derivative, $Co(CO)_4CF_3$ is a liquid reasonably stable at room temperature (mp 13°) in an inert atmosphere. An increase in chain length in the perfluoroalkyl series also enhances the thermal stability: pentadecafluoroheptylcobalt tetracarbonyl, $Co(CO)_4C_7F_{15}$, is a yellow-brown solid (13) which melts at 30° and decomposes at 120°.

The thermal stability of perfluoroalkyl- and perfluoroacylcobalt tetracarbonyls has been attributed (23) to the inductive effect of the fluorine atoms, which withdraw negative charge from the cobalt atom:



$$F_3\overset{\curvearrowleft}{C}\text{—Co—C}\equiv O$$

This seems in agreement with the infrared spectra of alkyl and acyl metal carbonyls (24,25). It will be seen (Table 31) that perfluoroalkyls and perfluoroacyls show a considerable shift of the terminal CO stretching bands to higher frequencies. This shift is attributed to a decreased d_π–p_π bonding between the metal and the CO ligand as a consequence of the high electronegativity of the perfluoro group.

TABLE 31

Carbonyl Stretching Frequencies in Alkyl-, Perfluoroalkyl-, Acyl-, and Perfluoroacyl Metal Carbonyls

Compound	$\nu_{C\equiv O}$ (cm^{-1})	$\nu_{C=O}$ (cm^{-1})	Medium	Ref.
$Mn(CO)_5C_2F_5$	2130w, 2072w, 2038vs, 2023s, 2002w, 1983vw	—	C_2Cl_4	25
$Mn(CO)_5COC_2F_5$	2127m, 2069w, 2038vs, 2022s, 2002w, 1980vw	1659	C_2Cl_4	25
$Mn(CO)_5Me$	2108m, 2102w, 2010vs, 1989s, 1979w, 1949vw	—	C_2Cl_4	25
$Mn(CO)_5CF_3$	2144w-m, 2050vs, 2025s	—	C_6H_{12}	24
$Mn(CO)_5COMe$	2116w-m, 2053m(sh), 2009vs, 1994s	1640 1650	KBr CCl_4	24 82
$Mn(CO)_5COCF_3$	2139w-m, 2035vs, 2002m(sh)	1643	KBr	24
$Re(CO)_5COMe$	2131w-m, 2068m, 2061m, 2045m, 2018vs, 2001m-s, 1976w-m	1617m	CCl_4	94
$Co(CO)_4Me$	2111m-s, 2036vs	—	Gas	23
$Co(CO)_4COCF_3$	2127m-s, 2041vs	1685	Liquid	23

Acyl- and perfluoroacyl metal carbonyls are usually characterized by a strong band at 1640–1685 cm⁻¹, which has been attributed to the C—O stretching vibration of the acyl group. Usually, pentacarbonylalkyl- and pentacarbonylacyl derivatives of manganese and rhenium show three main bands in the carbonyl stretching region with the intensity sequence of medium–very strong–strong from about 2110 cm^{-1} to about 1990 cm^{-1} for the terminal carbon monoxide groups. This is in agreement with an octahedral arrangement of substituents, (C_{4v} symmetry). Some of the weak bands on the lower frequency side have been assigned to ^{13}C—O stretching vibrations (25). Orgel (26) has pointed out that extra bands, some of medium intensity, are present in the infrared data published by Hieber and co-workers for the pentacarbonylalkyl compounds of manganese and rhenium and the corresponding acyl derivatives. A possible explanation for these bands, in the case of the acyl derivatives, could be the presence of alkylmetal pentacarbonyls in equilibrium with the acyls, especially for solution spectra.

However, Orgel has also indicated the possibility that complexes of the type $Mn(CO)_5R$ could show up to a total number of five C—O stretching vibrations when the alkyl group R is not symmetrical with respect to the metal–carbon bond. This prediction has been recently confirmed experimentally for some pentacarbonylalkyls of manganese and rhenium, such as $Mn(CO)_5CF_2CFHCl$ (27).

It has since been pointed out that the symmetry of the organic residue attached to the metal is not solely important in determining the number of infrared active C—O stretching vibrations (of the terminal CO groups) in $M(CO)_5R$, with M being Mn or Re (28). The presence of a heavy halogen atom on the β carbon atom of the organic residue also seems to be an important factor. For example, $Mn(CO)_5CFClCF_2CH_3$ shows only three C—O stretching vibrations, whereas $Mn(CO)_5CF_2CFClH$ has five bands.

Calderazzo and Noack (29) have studied the ketonic C—O stretching vibration region at about 1650 cm^{-1} of some halogen-substituted acylmanganesepentacarbonyls of the type $Mn(CO)_5COCH_2X$ and $Mn(CO)_5COCHX_2$ with X being F and Cl. From the complex infrared pattern observed and from measurements at different temperatures down to −32°, it was concluded that rotational isomers existed in compounds of that type. It was suggested that different rotamers of compounds containing the grouping $CH_2X—C(=O)—Mn$ arise from restricted rotation about the carbon–carbon bond, and that this situation results in the appearance of more than one infrared band for the ketonic group.

Dipole moment data on several alkyl- and acylmanganesepentacarbonyls and similar derivatives of rhenium have been published (24). X-ray work on an alkyl metal carbonyl, $MoC_5H_5(CO)_3Et$, has been published (30).

C. Carbonylation Reactions

Particular interest has been recently shown in carbon monoxide insertion reactions. The interest in this field was originated by the important observation (9) that alkylmanganesepentacarbonyls under carbon monoxide pressure can be transformed into the corresponding acylmanganesepentacarbonyl derivatives:

$$\mathrm{Mn(CO)_5R + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn(CO)_5COR} \tag{7}$$

Later it was found (8) that reaction 7 can occur even at ordinary pressure, using solvents with reasonably high dielectric constants; this opened the way to obtain reliable kinetic and thermodynamic data for the reaction.

Coffield and co-workers (31) showed that by carrying out reaction 7 with labeled ^{14}CO, an acylmanganesepentacarbonyl with an unlabeled ketonic group was obtained. This experiment clearly indicated that the carbon monoxide inserted into the carbon–metal bond did not come directly from the gas phase. An indirect confirmation to this yet unpublished isotopic experiment came from the discovery that formation of acylmanganesecarbonyls from alkylmanganesepentacarbonyls could take place by using different nucleophiles, L, other than carbon monoxide, such as amines (32,33), triphenylphosphine (33,34) and tertiary phosphines in general (35):

$$\mathrm{Mn(CO)_5R + L \rightleftharpoons Mn(CO)_4(L)COR} \tag{8}$$

Calderazzo and Noack (17) have found that reaction 8 can also be carried out with charged nucleophiles, such as I^-:

$$\mathrm{Mn(CO)_5CH_3 + LiI \rightleftharpoons Li[MnI(CO)_4COCH_3]} \tag{9}$$

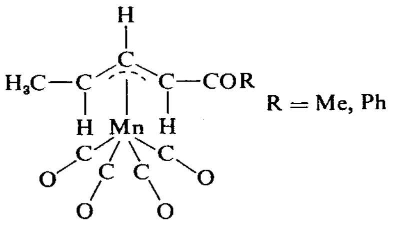
The lithium salt obtained by reaction 9 has been isolated in a pure state. It seems, therefore, that any reagent capable of forming a coordinative bond to manganese can potentially promote the carbonylation reaction. The main requirement seems to be that the alkylpentacarbonylmanganese has to be provided with a ligand which can saturate its coordination number once the alkyl group has been converted by some mechanism (see below) into the acyl group. There are, however, exceptions, because molecules which are capable of forming coordinative bonds do not always induce the carbonylation reaction. This prevails for phenyl isocyanide (36), which has been reported to react with $Mn(CO)_5Me$ to give the dimeric $Mn_2(CO)_9(CNPh)$ and $Mn_2(CO)_8(CNPh)_2$. The reaction conditions were, however, rather drastic (tetrahydrofuran at reflux temperature); it is not excluded that the primary product of the reaction is the still unknown $Mn(CO)_4(CNPh)COMe$. The behavior of $Mn(CO)_5Me$ with fluoroolefins is also somewhat peculiar. Stone and co-workers (37,38) have reported that $CF_2{=}CF_2$ reacts at 95° according to the equation:

$$Mn(CO)_5CH_3 + CF_2 = CF_2 \longrightarrow Mn(CO)_5CF_2CF_2CH_3 \qquad (10)$$

The expected $Mn(CO)_4(CF_2CF_2)COMe$ was not obtained.

The reactions of $Mn(CO)_5Me$ and $Mn(CO)_5Ph$ with butadiene (39) in which 1:1 adducts are formed are of considerable interest. Structure **1** has been assigned to the compounds obtained from these reactions. The initial step of the reaction has been suggested to be a coordination of the double bond of the diene to manganese with a consecutive or a simultaneous formation of the acyl group.

R = Me, Ph



(1)

Several alkyl metal carbonyls other than $Mn(CO)_5R$ have been reported to give carbonylation or decarbonylation reactions. Pentacarbonylperfluorobenzoylrhenium decarbonylates to pentacarbonylperfluorophenylrhenium (15):

$$Re(CO)_5COC_6H_5 \xrightarrow{130°} Re(CO)_5C_6H_5 + CO \qquad (11)$$

Carbonylation reactions have been reported to occur with tetracarbonylalkylcobalt compounds $Co(CO)_4R$ (22). Cyclopentadienylalkyls of iron, $FeC_5H_5(CO)_2R$, also undergo carbonylation (40). King and Bisnette (41) have reported that dicarbonylacylcyclopentadienyliron complexes can easily be decarbonylated to the corresponding alkyl derivatives under ultraviolet irradiation:

$$FeC_5H_5(CO)_2COR \xrightarrow{UV} CO + FeC_5H_5(CO)_2R \qquad (12)$$

McCleverty and Wilkinson (42) have, however, reported that the thermal carbonylation–decarbonylation reactions of carbonylalkylcyclopentadienyl compounds of the type $MC_5H_5(CO)_nR$ can sometimes be complicated by secondary reactions. Thus, heating $MoC_5H_5(CO)_3Et$ at 100° causes transfer of the ethyl group from the metal to the cyclopentadienyl ring, the main product being $[Mo(C_5H_4C_2H_5)(CO)_3]_2$.

A point of considerable interest is the mechanism of reaction 7 and of related reaction 8. Calderazzo and Cotton obtained kinetic and thermodynamic data for reaction 7, with R = CH_3. This was found (8) to be first order both in $Mn(CO)_5Me$ and carbon monoxide concentrations in 2,2′-diethoxydiethyl ether. The same authors found (43) that the rate of reaction 7 was largely influenced by the nature of the alkyl group R attached to the pentacarbonylalkylmanganese. Electron-withdrawing substituents such as CF_3 cause a remarkable decrease in the rate of formation of the acyl derivative, whereas electron-releasing groups such as Pr and Et have a favorable kinetic influence. Second order kinetics were also found (33) for the reaction of $Mn(CO)_5Me$ with cyclohexylamine in slightly polar solvents. An apparent change in the reaction mechanism was however observed for the reaction of $Mn(CO)_5Me$ with amines (33) and triphenylphosphine (34) in 2,2′-diethoxydiethyl ether. Both these reactions were found to be independent of the ligand concentration; the explanation proposed (34) is that a solvent-assisted mechanism was operating in these cases.

Reaction 9, i.e., the carbonylation of $Mn(CO)_5Me$ by iodide, was found to be dependent on iodide concentration, although also a pseudo-first order, solvent-assisted mechanism is probably operating simultaneously (44).

It appears therefore that the reactions of alkylmanganesepentacarbonyls with different nucleophiles usually follow second order kinetics. Pseudo-first order reactions can, however, occur in the case of solvation of the intermediate. Second order kinetics are consistent both with a mechanism of the type:

$$Mn(CO)_5R \overset{\text{rapid}}{\rightleftharpoons} Mn(CO)_4COR \overset{+\,L(\text{slow})}{\rightleftharpoons} Mn(CO)_4(L)COR \qquad (13)$$

or with the direct displacement reaction of the S_N2 type:

$$Mn(CO)_5R + L \xrightarrow{\text{slow}} Mn(CO)_4(L)COR \qquad (14)$$

whereas a dissociative mechanism of the S_N1 type:

$$Mn(CO)_5R + L \xrightarrow{\text{slow}} Mn(CO)_4COR \xrightarrow{+\,L(\text{fast})} Mn(CO)_4(L)COR \qquad (15)$$

appears not to be the prevailing one. Mechanism 14 or a similar one in which L is a solvent molecule is the preferred one.

The reactions of pentacarbonylacetylmanganese with different nucleophiles have also been studied (34,44):

$$\text{Mn(CO)}_5\text{COCH}_3 + \text{L} \rightleftharpoons \text{CO} + \text{Mn(CO)}_4\text{(L)COCH}_3 \qquad (16)$$

The products of the reaction are the same as those from reaction 8, the only difference being that carbon monoxide is evolved. The latter can be measured and therefore the kinetics can be studied gasometrically. Reaction 16 is independent of nucleophile concentration and more important, takes place with the same rate constant (k_{-1}) previously found (8) for the decarbonylation of $\text{Mn(CO)}_5\text{COMe}$ (reverse of reaction 7). This suggests that the reverse of reactions 7 (with $R = CH_3$) and 16 takes place by the same mechanism.

Incidentally, tetracarbonylacylcobalt compounds had also been found by Heck (45) to react with tertiary phosphines with evolution of carbon monoxide and formation of $\text{Co(CO)}_3\text{(PR}_3\text{)COR}$, the reaction being independent of the ligand concentration.

Two different reaction mechanisms can be postulated to explain why reaction 16 is independent of ligand concentration. They are represented below.

(A)

$$\text{Mn(CO)}_5\text{COCH}_3 \overset{\text{slow}}{\rightleftharpoons} \text{Mn(CO)}_4\text{COCH}_3 + \text{CO}$$

$$\text{Mn(CO)}_4\text{COCH}_3 + \text{L} \overset{\text{fast}}{\rightleftharpoons} \text{Mn(CO)}_4\text{(L)COCH}_3$$

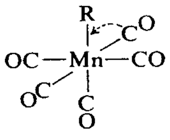
(B)

$$\text{Mn(CO)}_5\text{COCH}_3 \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} \text{Mn(CO)}_5\text{CH}_3 + \text{CO}$$

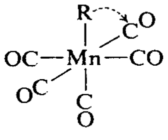
$$\text{Mn(CO)}_5\text{CH}_3 + \text{L} \underset{k'_{-B}}{\overset{k'_B}{\rightleftharpoons}} \text{Mn(CO)}_4\text{(L)COCH}_3$$

Only (A) can be considered as a true dissociative mechanism of the S_N1 type.

How the acetyl group is formed in the course of the carbonylation reaction 7 is another question. Several mechanisms are possible; all are reducible to two main types, namely the CO-insertion mechanism (**2**) and the methyl migration mechanism (**3**). This latter was the one proposed earlier (43) and for which Mawby, Basolo, and Pearson (46) have recently found some additional experimental evidence. These authors investigated the decarbonylation of *trans*-tetracarbonyltriphenylphosphineacetylmanganese and found that the corresponding *cis*-alkyl derivative was formed:



(2)



(3)

$$\textit{trans}\text{-Mn(CO)}_4\text{P(C}_6\text{H}_5)_3\text{COCH}_3 \rightleftharpoons \textit{cis}\text{-Mn(CO)}_4\text{P(C}_6\text{H}_5)_3\text{CH}_3 + \text{CO} \qquad (17)$$

This result can be best explained by assuming that the decarbonylation occurs by a mechanism of methyl migration. By the principle of microscopic reversibility, the same has to be true for the reverse process, i.e., for the carbonylation process.

Although the mechanism of methyl migration (**3**) appears most likely, some details are still to be investigated.

If one considers a carbonylation reaction induced by a nucleophile different from carbon monoxide, such as:

$$\text{Mn(CO)}_5\text{R} + \text{L} \rightleftharpoons \text{Mn(CO)}_4\text{(L)COR} \qquad (18)$$

an important question arises: In which position, with respect to the alkyl group, does the ligand attack the central metal atom to give the acylated product? Reactions of type 18 have been found (17) to give both *cis* and *trans* isomers. The answer to the question may come from investigating which geometrical isomer forms *first* in the course of reaction 18. There are indications in the literature (46,47) suggesting that the *trans* isomer is first formed.

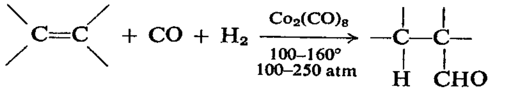
Finally, it is worth mentioning that $\text{FeC}_5\text{H}_5\text{(CO)}_2\text{Me}$ and its ethyl and phenyl analogs have been found to react with liquid SO_2 (48) to give a sulfonyl derivative, for example:

$$\text{FeC}_5\text{H}_5\text{(CO)}_2\text{CH}_3 + \text{SO}_2 \longrightarrow \text{FeC}_5\text{H}_5\text{(CO)}_2\text{(SO}_2\text{CH}_3) \qquad (19)$$

The infrared spectra rule out the presence of *acyl* derivatives.

D. Alkylcobalt Tetracarbonyls and the Hydroformylation (Oxo) Reaction

There is some chemical (49,50) and infrared (51) evidence that acylcobalt tetracarbonyls are formed during the oxo reaction (52); i.e., the reaction by which aldehydes are formed from olefins, carbon monoxide, and hydrogen in the presence of $Co_2(CO)_8$:



$$\text{>C=C<} + \text{CO} + \text{H}_2 \xrightarrow[\substack{100\text{–}160^\circ \\ 100\text{–}250\ \text{atm}}]{\text{Co}_2\text{(CO)}_8} -\underset{\text{H}}{\overset{|}{\underset{|}{\text{C}}}}-\underset{\text{CHO}}{\overset{|}{\underset{|}{\text{C}}}}- \qquad (20)$$

The main concern is to find an explanation for the inhibiting effect of carbon monoxide on the rate of formation of aldehydes (53–55). We will see that, despite the considerable efforts of the past years, the answer to this problem has not yet been found.

Breslow and Heck (22) have found that, as previously shown for alkyl manganese pentacarbonyls, $Co(CO)_4R$ adds carbon monoxide to form the corresponding acylcobalt tetracarbonyls. These had a characteristic infrared band at about 1720 cm^{-1} attributed to the C—O stretching of the acyl group:

$$Co(CO)_4R + CO \rightleftharpoons Co(CO)_4COR \qquad (21)$$

These authors also found that after preparing alkylcobalt tetracarbonyls from $NaCo(CO)_4$ and alkyl halides in diethyl ether, a band at 1720 cm^{-1} could be observed in the reaction mixture; this finding was presented as evidence for the existence of acylcobalt tricarbonyls in equilibrium with alkylcobalt tetracarbonyls, according to the equation:

$$Co(CO)_4R \rightleftharpoons Co(CO)_3COR \qquad (22)$$

The inhibiting effect of carbon monoxide was explained on the assumption that alkyl- and acyltricarbonyls are the active species in the hydroformylation (oxo) reaction, whereas the acyltetracarbonyls are inactive (56):

$$\begin{tikzcd} Co(CO)_4R \arrow[r, shift left] \arrow[d, shift left, "+CO"] & Co(CO)_3COR \arrow[l, shift left] \arrow[dl, "+CO"] \\ Co(CO)_4COR \arrow[u, shift left, "-CO"] & \end{tikzcd} \qquad (23)$$

The overall mechanism of the oxo reaction was presented as follows:

$$CoH(CO)_3 + RCH{=}CH_2 \longrightarrow Co(CO)_3CH_2CH_2R \xrightarrow{CO}$$
$$Co(CO)_3COCH_2CH_2R \xrightarrow{H_2} CoH(CO)_3 + RCH_2CH_2CHO \qquad (24)$$

Heck (57), however, has recognized that, although the band at about 1720 cm^{-1} may be suggestive of an equilibrium between the cobalt tricarbonyl and cobalt tetracarbonyl species (see Eq. 22), it must in fact be attributed to acylcobalt tetracarbonyls in equilibrium with alkylcobalt tetracarbonyls according to Eq. 21. This interpretation was based mainly on the spectroscopic work of Markó, Bor, and co-workers (51), who investigated the gas phase infrared spectrum of $Co(CO)_4Me$ and the solution spectra of several acylcobalt tetracarbonyl derivatives. The latter compounds show a band at about 1720 cm^{-1} attributed to the acyl group; the same band is observed in the spectrum of $Co(CO)_4Me$, the conclusion being that the extra acyl band in the spectrum of $Co(CO)_4Me$ is due to some $Co(CO)_4COMe$. The carbon monoxide necessary for this conversion probably ~~arises from~~ partial decomposition of the complex.

An alternative interpretation of the 1720 cm^{-1} band in the spectrum of $Co(CO)_4R$ has been given by Hieber and his co-workers (23) who believe the band is due to ketones formed according to the following equation:

$$2Co(CO)_4R \longrightarrow RCOR + \tfrac{1}{4}Co_4(CO)_{12} + \tfrac{1}{2}Co_2(CO)_8 \qquad (25)$$

The presence of ketones among the decomposition products of $Co(CO)_4Me$ and $Co(CO)_4Et$ has been confirmed (58). This may be a better explanation, since an inspection of the infrared data of Table 31 shows that the acyl band of $Co(CO)_4COR$ should be somewhere around 1680 cm^{-1} rather than at 1720 cm^{-1}

Whatever is the explanation for the band at 1720 cm^{-1}, it appears that the existence of acylcobalt *tricarbonyls* as chemically or physically detectable species in equilibrium (in appreciable concentration) with the corresponding tetracarbonyl derivatives is no longer tenable. Acylcobalt tricarbonyls can be, of course, intermediates (45) in some substitution reactions of $Co(CO)_4COR$, as in eq. 26:

$$Co(CO)_4COR + P(C_6H_5)_3 \longrightarrow CO + Co(CO)_3(P(C_6H_5)_3)COR \qquad (26)$$

but their role in the hydroformylation reaction in connection with the inhibiting effect of carbon monoxide is still not clear.

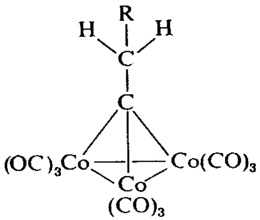
E. Enneacarbonyltricobalt Alkanes and Related Compounds

Since they formally belong to the class of alkyl metal carbonyls, the enneacarbonyltricobalt alkanes, corresponding to the general formula $Co_3(CO)_9CX$ will be discussed here briefly.

They were first prepared a few years ago (59) from the reaction of methanol solutions of the acetylenic complexes $Co_2(CO)_6RC_2H$ with dilute sulfuric acid. The dark purple diamagnetic solids were recognized as having a triangular arrangement of the cobalt atoms, but their structures were not completely elucidated until degradative chemical reactions were undertaken by Kruerke and Hübel (60). These authors were able to show that the compounds had to be considered as $Co_3(CO)_9C{-}CH_2R$ and they suggested structure **4** with a carbon atom joined to the three cobalt atoms. Since then, many other compounds of the same class have been prepared by new and improved methods of synthesis (61–63). By direct treatment of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ or solutions of the $[Co(CO)_4]^-$ anion with halogenated compounds, several derivatives have been prepared (see Table 32).

For example, $Co_2(CO)_8$ or the $[Co(CO)_4]^-$ anion reacts with CCl_4 to give the complex $Co_3(CO)_9CCl$.

The mechanism of formation of these compounds has not yet been clarified. Ercoli and co-workers (63) found that, in the reaction between $Co_2(CO)_8$ and CCl_4, yields of approximately 50% were obtained; they proposed the following stoichiometry:



(4)

$$5Co_2(CO)_8 + 3CCl_4 \longrightarrow 2Co_3(CO)_9CCl + 4CoCl_2 + 22CO + [CCl_2] \quad (27)$$

TABLE 32

Enneacarbonyltricobalt Alkanes and Related Compounds

Compound	Color	Mp (°C)	Ref.
$Co_3(CO)_9CH$	Dark purple	105–106	62,63
$Co_3(CO)_9CCH_3$	Dark purple	185 dec.	59,61,63
$Co_3(CO)_9CCH_2Ph$	Violet	68	60
$Co_3(CO)_9CBu$	Dark purple	—	59
$Co_3(CO)_9CF$	Dark purple	75–76	61,63
$Co_3(CO)_9CCl$	Black-violet	131–133	61–63
$Co_3(CO)_9CBr$	Black-violet	130–132	63
$Co_3(CO)_9CI$	Black-violet	96–98	63
$Co_3(CO)_9CCF_3$	Black-violet	—	61
$Co_3(CO)_9CPh$	Black-brown	—	61,62
$Co_3(CO)_9CCOOH$	Black-brown	—	61
$Co_3(CO)_9CCOOMe$	Deep violet	108–109	62,63
$Co_3(CO)_9CCOOEt$	—	44–45	61,63
$[Co_3(CO)_9C]_2$	Brown	—	62
$Co_3(CO)_9Si(CH{=}CH_2)$	Purple-black	—	101
$Co_3(CO)_9CCH{=}CHCOOH$	Red-violet	177 dec.	64
$Co_3(CO)_9CCH_2CH_2COOH$	Violet	136–137 dec.	64

The formation of the esters $Co_3(CO)_9CCOOR$ ($R = Me, Et$) by alcoholysis of $Co_3(CO)_9CBr$ is particularly interesting. The carbon monoxide insertion has been postulated to occur via an intermediate $Co_3(CO)_9CCo(CO)_4$.

Very interestingly, an enneacarbonyltricobalt derivative was isolated (64) from the carboxylation of acetylene in the presence of $Co_2(CO)_8$ as catalyst—a synthesis of succinic acid. This cobalt derivative contains a CH_2CH_2COOH organic residue bonded to the $Co_3(CO)_9C$ backbone.

All compounds of this class show analogous chemical and physical properties. Their infrared spectra have been measured (59,61,62,65); those in Ref. 62 and 65 seem to be particularly accurate. Four stretching frequencies in the region of terminal CO groups are observed; their position depends on the nature of the substituent X. The absorption bands are in the ranges 2116–2101(w–m), 2066–2054(vs), 2047–2038(m) and 2034–2018(w–m). There are no bands in the bridging carbonyl region, in agreement with the proposed structure **4**.

Cetini and co-workers (66) have studied the isotopic ^{14}CO exchange reaction of the compounds $Co_3(CO)_9CX$, with X being F, Cl, Br, H, and COOMe. The nine carbon monoxide groups are not kinetically equivalent; only three of them exchange at reasonable rates between 35 and 55°. The rate of exchange decreases in the sequence $F > Cl > Br > H$. In the case of the ester derivative, $Co_3(CO)_9CCOOMe$, only one carbon monoxide group seems to exchange and, moreover, this was shown not to be that of the ester group. These kinetic results appear difficult to explain on the basis of structure **4**.

Recent x-ray work (66*a*) has shown that the compound $Co_3(CO)_9CCH_3$ does have the structure shown in **4**.

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XI. MIXED METAL CARBONYLS

A. Introduction

The term "mixed metal carbonyls" requires definition. Strictly speaking these are compounds in which two or more different metals are present, each of them carrying some coordinated carbon monoxide groups. It follows from this definition that mixed compounds of this type are possible only with transition metals. However, several authors have departed from this definition and included any compound containing carbon monoxide and two or more different metals joined together by direct covalent metal–metal bonds in the category of mixed metal carbonyls. Thus, that all the metals in the compound should have carbon monoxide as a ligand is not strictly required.

We shall use the term "mixed metal carbonyls" in the broader sense, but we shall divide these carbonyls into two categories:

(A) Compounds containing only transition elements
(B) Compounds also containing nontransition elements

This classification is unambiguous except for compounds like $Ph_3PAu–Mn(CO)_5$. However, since a zero oxidation state is to be assigned to both metals, this compound should be classified as belonging to category B.

All mixed metal carbonyls have several properties in common. They are

usually soluble in organic solvents; some have sharp and definite melting points, others ~~can be~~ sublimed. In other words, the properties are essentially those of covalent compounds. If we consider a mixed metal carbonyl formed by two different transition metals (class A), each of them carrying some ligands of unspecified number and nature,

$$L_mM' - M''L_n$$

(1)

this unit exists as a separate entity in the crystal, in solution, or in the gas phase. The alternative interpretation of such a compound as a salt

$$[L_mM']^+[M''L_n]^-$$

(2)

is to be excluded in view of the properties mentioned above and because the ions are not detectable (conductivity measurements, infrared data in the C—O stretching region, failure of metathetical reactions, etc.).

In addition, formulation **2** would generally lead to a cation not attaining the next inert gas configuration. Infrared data are important in deciding rapidly and conclusively between formulations **1** and **2**. If, for example, an ionic formulation for the compound $C_5H_5(CO)_2FeMn(CO)_5$ is taken into consideration, carbonyl stretching vibrations of the anion $[Mn(CO)_5]^-$ at rather low wavenumbers should be observed, apart from second order effects. This is not the case.

As far as compounds of class B are concerned, the nontransition elements entering the combinations are contained in a region of the periodic table comprised between group IB (Cu, Ag, Au) and groups IVA and VA (Ge, Sn, Pb, and As, Sb, Bi) with values of electronegativities ranging from 1.44 (mercury) to 2.20 (arsenic) (see below).

In these compounds we find typical metallic elements like mercury, gold, tin, and lead or boundary elements (metalloids) such as germanium, arsenic, antimony, and bismuth. It will be noticed that combinations of the latter three elements in their trivalent state with metal carbonyls are not included in this section; they are discussed separately when treating the substitution reactions of the single metal carbonyls.

In the table in Scheme IV, the elements known to give mixed metal carbonyls of type B are reported, together with those which commonly give ionic carbonylmetallates. For each element the Allred and Rochow (*1a*) electronegativity values are reported. A special case is represented by beryllium for which largely covalent mixed metal carbonyls should be capable of existence, although none have yet been reported.

A final remark concerns the definition of the oxidation numbers of the coordinating elements in mixed metal carbonyls. For compounds of class A, no ambiguity is possible; unless anionic ligands (cyclopentadienyl, halogen) are present, the oxidation number of all the metals is zero.

Li	Be
0.97	1.47
Na	Mg
1.01	1.23
K	Ca
0.91	1.04
Rb	Sr
0.89	0.99
Cs	Ba
0.86	0.97

Cu	Zn	Ga	Ge	As
1.75	1.66	1.82	2.02	2.20
Ag	Cd	In	Sn	Sb
1.42	1.46	1.49	1.72	1.82
Au	Hg	Tl	Pb	Bi
1.42	1.44	1.44	1.55	1.67

——— Elements known or likely to give ionic carbonylmetallates;
--------- elements known or likely to give mixed metal carbonyls of type B.

Scheme IV

For example, $(CO)_5MnCo(CO)_4$, contains zerovalent manganese and cobalt with d^7 and d^9 configurations, respectively. The compound $(CO)_2C_5H_5FeMoC_5H_5(CO)_3$ contains, however, iron(I) (d^7) and molybdenum(I) (d^5).

For compounds of class B, the oxidation number is easily found according to the general rules and considering that metal–metal bonds should be regarded as perfectly homopolar. So, for example, in $Ph_3PAu-Mn(CO)_5$, the oxidation number of both gold and manganese is zero; in $(CO)_4Fe(SnR_2)_2Fe(CO)_2$, the oxidation number of iron is zero and that of tin is two.

A general discussion of compounds containing metal–metal bonds can be found in Ref. 1*c*.

B. Methods of Preparation

Compounds of type A, i.e., combinations between two or more transition elements, are prepared in a straightforward way by reacting a halogenocarbonylmetal with carbonylmetallates of alkali metals. The following reactions are examples of this method.

$$NaMn(CO)_5 + ReCl(CO)_5 \longrightarrow NaCl + (CO)_5MnRe(CO)_5 \quad (1)$$

$$NaCo(CO)_4 + MnBr(CO)_5 \longrightarrow NaBr + (CO)_4CoMn(CO)_5 \quad (2)$$

$$NaCo(CO)_4 + Fe(C_5H_5)(CO)_2I \longrightarrow NaI + (CO)_4CoFeC_5H_5(CO)_2 \quad (3)$$

$$NaRe(CO)_5 + Fe(C_5H_5)(CO)_2Cl \longrightarrow NaCl + (CO)_5ReFeC_5H_5(CO)_2 \quad (4)$$

Reactions of this type are usually carried out in an ether, such as tetrahydrofuran, and occur very rapidly. The extension of these reactions to metal carbonyls of other groups can face limitations due to the unavailability of the starting materials, such as neutral and stable halogenocarbonyls of group VI metals, for example. Other special methods which, however, could be generalized and used for the preparation of other compounds of the same type are given below.

The anion $[FeCo_3(CO)_{12}]^-$ was prepared (2) by reacting $Co_2(CO)_8$ with $Fe(CO)_5$ in the presence of acetone. The reaction is probably very complex and the anion is finally obtained as $[Co(acetone)_6][FeCo_3(CO)_{12}]_2$.

Ultraviolet irradiation of a hexane solution of $Fe(CO)_5$ and $Mn_2(CO)_{10}$ results in the formation of the mixed metal carbonyl (3):

$$Mn_2(CO)_{10} + Fe(CO)_5 \xrightarrow[\text{hexane}]{\text{UV}} [(CO)_5Mn]_2Fe(CO)_4 + CO \quad (5)$$

Kruck and Höfler (4) have found that, by warming a tetrahydrofuran solution of the salt $[Mn(CO)_6][Co(CO)_4]$ to room temperature, formation of the mixed metal carbonyl takes place:

$$[Mn(CO)_6][Co(CO)_4] \xrightarrow[\text{THF}]{20^\circ} (CO)_5MnCo(CO)_4 + CO \quad (6)$$

Similarly, hexacarbonylrhenium(I)-tetracarbonylcobaltate(−I), when heated at 60°, is converted into enneacarbonylrheniumcobalt (5).

The simplest method for preparing mixed metal carbonyls of class B is to treat an alkali metal carbonylmetallate with a halogeno, a cyano-, or a hydroxo-derivative of the nontransition element:

$$Ph_3SnCl + NaCo(CO)_4 \longrightarrow Ph_3SnCo(CO)_4 + NaCl \quad (7)$$

$$Ph_2PbBr_2 + 2NaCo(CO)_4 \longrightarrow Ph_2Pb[Co(CO)_4]_2 + 2NaBr \quad (8)$$

$$ZnBr_2 + 2NaCo(CO)_4 \longrightarrow Zn[Co(CO)_4]_2 + 2NaBr \quad (9)$$

$$(CO)_5MnSn(CH_3)_2Cl + Na[MoC_5H_5(CO)_3] \longrightarrow$$
$$NaCl + (CO)_5MnSn(CH_3)_2MoC_5H_5(CO)_3 \quad (10)$$

All the above reactions can be carried out in nonaqueous solvents (usually tetrahydrofuran) in which the mixed metal carbonyls are soluble and so can be separated easily from the insoluble alkali halide. Alternatively, the reactions can be done in aqueous solvents, so that the mixed metal carbonyls precipitate and can be recovered by filtration. This method has often been used to prepare mixed compounds of cobalt and iron from alkaline aqueous solutions of $[Co(CO)_4]^-$ or $[Fe(CO)_4]^{2-}$. For example:

$$3[Fe(CO)_4]^{2-} + 2[Pb(OH)_6]^{2-} + 12H^+ \longrightarrow PbFe_3(CO)_{12} + Pb^{2+} + 12H_2O \quad (11)$$

$$3[Fe(CO)_4]^{2-} + 2AsO_3^{3-} + 12H^+ \longrightarrow As_2Fe_3(CO)_{11} + CO + 6H_2O \quad (12)$$

$$2[Co(CO)_4]^- + HgCl_2 \longrightarrow HgCo_2(CO)_8 + 2Cl^- \quad (13)$$

The mercury derivatives of iron carbonyl, $HgFe(CO)_4$ (6) and $(HgCl)_2Fe(CO)_4$ (7), were prepared by treating aqueous solutions of mercuric sulfate and mercuric chloride with $Fe(CO)_5$ at room temperature.

If high pressure facilities are available, a convenient method of preparing mixed compounds of cobalt is the direct action of carbon monoxide under pressure on a cobalt(II) salt in the presence of the proper metal. By this method, Hieber and Teller (8) obtained cobalt carbonyl derivatives of three different types, namely $MCo_2(CO)_8$ ($M = Zn, Cd, Hg, Sn$), $MCo_3(CO)_{12}$ ($M = In, Tl$), and $MCo(CO)_4$ ($M = Tl$). In the case of the zinc compound, the reaction can be written as:

$$2CoBr_2 + 3Zn + 8CO \xrightarrow[\substack{350\ atm\\ 15\ hr}]{200^\circ} ZnCo_2(CO)_8 + 2ZnBr_2 \quad (14)$$

The best results are obtained with the bromide and the iodide. In the case of the mercury compound, $HgCo_2(CO)_8$, it is preferable to start from cobalt metal and a mercuric halide:

$$HgX_2 + 3Co + 8CO \xrightarrow[200\ atm]{150^\circ} HgCo_2(CO)_8 + CoX_2 \quad (15)$$

$$(X = Cl, Br, I)$$

Octacarbonylmercurydicobalt can also be prepared (9) in a more direct and simple way by treating $Co_2(CO)_8$ with mercury in hexane. Quantitative yields have been reported by this method.

$$Co_2(CO)_8 + Hg \xrightarrow{hexane} HgCo_2(CO)_8 \quad (16)$$

Hieber and Breu (10) were unable to obtain alkylmercurycarbonylcobalt derivatives by the reaction of $CoH(CO)_4$ with alkylmercury halides. Compounds of this type were later prepared by Kahn and Bigorgne (11) who described the compounds $Fe(CO)_4(HgR)_2$ ($R = Me, Et$). These were obtained by reacting $[Fe(CO)_4]^{2-}$ with RHgCl. Alkylmercury derivatives of tantalum have been reported by Keblys and Dubeck (12).

$$[Ta(CO)_6]^- + RHgCl \longrightarrow Ta(CO)_6HgR + Cl^- \quad (17)$$

Infrared data excluded the possibility that these compounds could be formulated either as $[RHg]^+[Ta(CO)_6]^-$ or as $RHgCOTa(CO)_5$. They must therefore be regarded as compounds of heptacoordinate tantalum.

C. Reactions of Mixed Metal Carbonyls

The reactions of mixed metal carbonyls have not been studied very extensively. These compounds are decomposed by iodine in pyridine, usually with quantitative evolution of carbon monoxide, unless a stable iodocarbonyl derivative is formed during the degradation process. This is the case with the compound $NiC_5H_5(CO)_3FeC_5H_5$ which, on reaction with iodine (13), evolves only part of the carbon monoxide, the rest remaining bonded to iron as $FeI(C_5H_5)(CO)_2$.

The most extensively studied reactions are the substitutions of carbon monoxide by other ligands, such as triphenylphosphine, amines, etc.

Hieber and Breu (10) have reported that $(C_4H_9)_3SnCo(CO)_4$ reacts with PPh_3 to give a monosubstitution product:

$$(C_4H_9)_3SnCo(CO)_4 + PPh_3 \longrightarrow CO + (C_4H_9)_3SnCo(CO)_3PPh_3 \quad (18)$$

Some reactions of $HgCo_2(CO)_8$ with different electron donors have been reported (14). Substitution products of $HgCo_2(CO)_8$ are obtained with PEt_3, PPh_3, $AsPh_3$, and $SbPh_3$.

$$HgCo_2(CO)_8 + 2L \longrightarrow HgCo_2(CO)_6L_2 + 2CO \quad (19)$$

With other ligands, $HgCo_2(CO)_8$ loses mercury as the metal, followed by the reaction characteristic of $Co_2(CO)_8$ with the particular ligand used; i.e., substitution (with $P(OR)_3$)

$$HgCo_2(CO)_8 + 2L \longrightarrow Hg + [Co(CO)_3L]_2 + 2CO \quad (20)$$

or valence disproportionation (with NH_3, py, or phen):

$$3HgCo_2(CO)_8 + 12L \longrightarrow 3Hg + 2[CoL_6][Co(CO)_4]_2 + 8CO \quad (21)$$

Nyholm and Vrieze (56) reported a case of metal–metal bond cleavage by molecular hydrogen. In benzene, the complex $ClHg\text{–}IrCl_2(CO)(PPh_3)_2$ reacts with hydrogen to give mercury metal, some mercurous chloride and the hydrido $IrCl_2H(CO)(PPh_3)_2$. Lewis and Wild (15) reported that bis-

(halomercury)tetracarbonyliron compounds such as $Fe(CO)_4(HgCl)_2$, react with amines to give disubstitution products. For example:

$$Fe(CO)_4(HgCl)_2 + 2py \longrightarrow Fe(CO)_2py_2(HgCl)_2 + 2CO \qquad (22)$$

The compound $(CO)(C_5H_5)Fe(CO)_2Ni(C_5H_5)$, to which a structure with two bridging CO groups was assigned (13), reacts with diphenylacetylene to give the two units, $[FeC_5H_5(CO)_2]_2$ and $Ni_2(C_5H_5)_2(PhC_2Ph)$.

Substitution reactions have also been reported (16*a*) for the complex $Ph_3PAuMn(CO)_5$. With triphenylphosphine, triphenylphosphite, triphenylarsine, and pyridine, monosubstitution products $Ph_3PAuMn(CO)_2L$ are obtained at 120°:

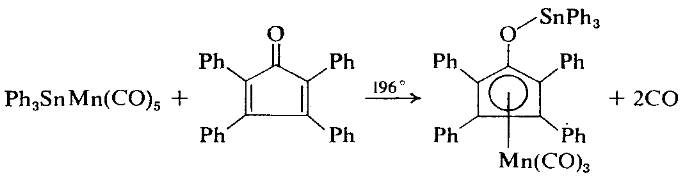
$$Ph_3PAuMn(CO)_5 + L \xrightarrow{120^\circ} Ph_3PAuMn(CO)_4L + CO \qquad (23)$$

The interesting point here is that *cis* compounds are obtained by this reaction, whereas $Mn_2(CO)_{10}$ gives tertiary phosphine substitution products containing the phosphine ligand *trans* with respect to the metal–metal bond (16*b*).

Gorsich (17) has described a substitution reaction of $Ph_3SnMn(CO)_5$ with triphenylphosphine:

$$Ph_3SnMn(CO)_5 + PPh_3 \xrightarrow{195^\circ} Ph_3SnMn(CO)_4PPh_3 + CO \qquad (24)$$

The same author (17) also reported the reaction of the mixed metal carbonyl with tetraphenylcyclopentadienone. The structure of the product has been elucidated by infrared measurements (18) and an x-ray diffraction study (19). Cleavage of the metal–metal bond occurs during this reaction with formation of a triphenylstannoxy derivative of tetraphenylcyclopentadienyltricarbonylmanganese:



(25)

A very interesting cleavage of a tin–manganese bond in $Me_3SnMn(CO)_5$ followed by insertion of tetrafluoroethylene in between the metal atoms of that bond has been reported by Clark and Tsai (20):

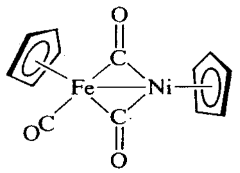
$$CF_2{=}CF_2 + Me_3SnMn(CO)_5 \xrightarrow[\text{UV, 6 hr}]{50^\circ} Me_3SnCF_2CF_2Mn(CO)_5 \qquad (26)$$

The reaction fails to occur in the absence of ultraviolet irradiation.

D. Bonding and Structures

In our classification of mixed metal carbonyls it is clear that class A compounds represent only a special case of binuclear metal carbonyls such as $Co_2(CO)_8$ and $Mn_2(CO)_{10}$. Since the formation of metal–metal bonds depends essentially on the size of the half-filled overlapping orbitals it is reasonable to assume that the metal–metal bond dissociation energy of $(CO)_5Mn{-}Re(CO)_5$ would be intermediate between those of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. When transition elements of the same vertical triad are known to give unmixed binuclear or trinuclear metal carbonyls, there is no reason to doubt the existence of the corresponding mixed carbonyls arising from all the possible combinations of the mononuclear units. So, for example, compounds such as $FeRu_2(CO)_{12}$ or $Fe_2Os(CO)_{12}$ should be stable and capable of existence, once the method for their preparation is found. However, a question arises here. The half-filled orbitals responsible for the formation of the metal–metal bonds increase in size on descending a vertical triad of transition metals. As a direct consequence, formation of polynuclear metal carbonyls occurs preferentially through direct metal–metal bonds rather than through bridging CO groups. In this connection, the structure of $Fe_3(CO)_{12}$ is to be compared with that of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. The question is then whether the yet unknown $FeRu_2(CO)_{12}$ would contain bridging CO groups. No x-ray structures have yet been reported for mixed metal carbonyls of the first class. Infrared data can, however, be used to assign tentatively some of the structures.

The compound $C_5H_5Ni(CO)_2Fe(CO)C_5H_5$ was found to have infrared C—O stretching vibrations at 1975, 1836, and 1806 cm^{-1} and it was concluded (13) that its structure should be one of the type shown below with both terminal and bridging CO groups (**3**). The tetranuclear $FeCo_3H(CO)_{12}$ has an infrared spectrum in the C—O stretching region very similar to that of $Co_4(CO)_{12}$ (2). In particular a band at 1890 cm^{-1} is present which can be attributed to bridging CO groups. That none of the



(3)

bands observed in this region is due to a metal–hydrogen stretching vibration is shown by the fact that a very similar pattern, although shifted to low wavenumbers, is present in the spectrum of the corresponding anion $[FeCo_3(CO)_{12}]^-$.

Another compound for which a CO-bridging structure has been proposed (21) is $(CO)_3Co(CO)_2FeC_5H_5(CO)$, again on the basis of infrared measurements. Most of the other mixed metal carbonyls do not show infrared C—O stretching vibrations at low wavenumbers and consequently were considered to contain only direct metal–metal bonds. In particular, it is noteworthy that both $(CO)_4CoMn(CO)_5$ (4,21) and $(CO)_4CoRe(CO)_5$ (5) seem to prefer an arrangement without CO bridges, at least in solution, whereas one of the parent carbonyls has a CO-bridged structure in the solid state.

Few structural data are available at present for mixed metal carbonyls of the second class, i.e., with nontransition elements. The x-ray structures of $Ph_3SnMn(CO)_4PPh_3$ (22), $Ph_2Sn[Mn(CO)_5]_2$ (23*a*) and (Triars)Cu–$Mn(CO)_5$ (23*b*) have been published only in a preliminary form. In the first molecule, a colinear arrangement of tin, manganese, and phosphorus was found, substantially with tin in a tetrahedral and manganese in an octahedral environment, as expected (see Fig. 22).

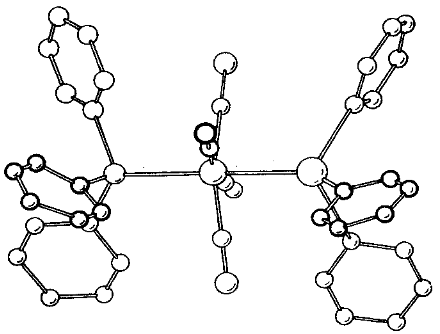


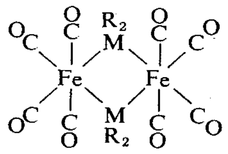
FIG. 22. View of the molecule $Ph_3PMn(CO)_4SnPh_3$ in the *b* axis projection. The central atoms are, from left to right, P, Mn, and Sn (R. F. Bryan, *Proc. Chem. Soc.*, **1964**, 232). Published by permission.

For $Ph_2Sn[Mn(CO)_5]_2$ the four bonds from the tin atom were found to form angles considerably different from those expected for a regular tetrahedron. The Mn–Sn–Mn angle was found to be 117° and it was suggested that the distortion arises from mutual repulsion of the two $Mn(CO)_5$ groups. Two series of mixed iron carbonyl derivatives of tin and lead are known (see Table 33 for specific references):

$(R_3Sn)_2Fe(CO)_4$ $[R_2SnFe(CO)_4]_2$

$(R_3Pb)_2Fe(CO)_4$ $[R_2PbFe(CO)_4]_2$

The dialkyllead and dialkyltin compounds, originally thought to be monomeric, were later recognized to be dimeric by Hein and Heuser (24) and by King and Stone (25), respectively. Tin- or lead-bridged structures of the type shown in structure **4** are probable for these compounds. Extensive spectroscopic studies of octacarbonylmercurydicobalt have been published. Infrared data in the C—O stretching region (26) indicate the absence of bridging CO groups. The Raman spectra of $CdCo_2(CO)_8$ and $HgCo_2(CO)_8$ (27) are consistent only with a linear arrangement of the three metal atoms Co–Hg–Co. The observed Raman spectrum of the cadmium derivative is in agreement with a D_{3d} symmetry of the molecule, as shown in Fig. 23. The Raman spectrum of $HgCo_2(CO)_8$ could not be observed in the complete range of frequencies but there was evidence that the conclusions drawn above were valid also for the mercury derivative.



(4)

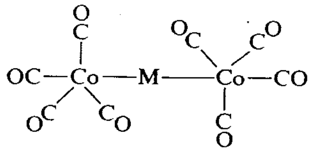


FIG. 23. The molecule, $MCo_2(CO)_8$ (M = Cd or Hg). D_{3d} model.

TABLE 33

Mixed Metal Carbonyls

Compound	Color	Mp (°C)	ν_{CO} (cm^{-1})	Ref.
Type A[a]				
$[FeCo_3(CO)_{12}]^-$	Black	—	—	2
$FeCo_3H(CO)_{12}$	Black-violet	> 100 dec.	2060, 2050, 1890	2
$(CO)_4Fe[Mn(CO)_5]_2$	Red	112	2067vs, 2019vs, 1987m	3
$(CO)C_5H_5Fe(CO)_2Co(CO)_3$	Dark red	52–53	2085, 2063, 2026, 1994, 1823	21
$(CO)_2C_5H_5FeRe(CO)_5$	Brown	72–74	—	28
$(CO)_2C_5H_5FeMoC_5H_5(CO)_3$	Red-violet	209	2040w, 2002w, 1959s, 1944sh, 1902m, 1887m	29
$(CO)C_5H_5Fe(CO)_2NiC_5H_5$	Chocolate brown	132 dec.	1975, 1836, 1806	13
$(CO)_2C_5H_5FeMn(CO)_5$	Dark red	76	2082s, 2056m, 2015m, 1992s, 1976s, 1945s	29
$FeCo_2(CO)_9S$	Dark violet	112 dec.	2104w, 2066vs, 2053vs, 2042s, 2029m, 2000w, 1984m, 1949vw	30
$(CO)_5MnCo(CO)_4$	Orange-red	45–46	2070, 2035, 2022, 2008, 1988	21,4
$Phen(CO)_3MnCo(CO)_4$	Deep red	100 dec.	2044s, 1998m, 1941s, 1885vs	4
$(CO)_5MnRe(CO)_5$	Yellow	167	2124w, 2054m, 2044w, 2031vw, 2017vs, 1998w, 1992vw, 1978m, 1945vw	31,32
$(CO)_5ReCo(CO)_4$	Orange-brown	66	2064, 2035, 1990	5
$Phen(CO)_3ReCo(CO)_4$	Deep red	—	2048s, 2039sm, 2010vs, 1931vs, 1892vs	5
$(CO)_3C_5H_5MoMn(CO)_5$	Red	80.5–81.5	2088, 2029, 1992, 1960, 1900, 1878	33
$C_7H_7(CO)_2MoMn(CO)_5$	Dark green	123 dec.	2058s, 1985s, 1960s, 1935–1908s	34
$(CO)_3C_5H_5MoRe(CO)_5$	Yellow-orange	100–100.5	2109, 2038, 2008, 1975, 1950, 1900, 1870	33
$(CO)_3C_5H_5WMn(CO)_5$	Dark red	90–91	—	33
$(CO)_3C_5H_5WRe(CO)_5$	Yellow	110–111.5	2110, 2038, 2009, 1986, 1978, 1955, 1948, 1895, 1865	33
$(CO)_3C_5H_5MoWC_5H_5(CO)_3$	Red	250	—	35
Type B[a]				
$ZnCo_2(CO)_8$	Yellow	—	—	8
$CdCo_2(CO)_8$	Canary yellow	80	—	8
$InCo_3(CO)_{12}$	Red	—	—	8
$TlCo(CO)_4$	Yellow	—	—	8
$TlCo_3(CO)_{12}$	Dark violet	—	—	8
$SnCo_2(CO)_8$	Canary yellow	—	—	8
$Ph_3PAuCo(CO)_4$	Pale brown	112–114	2054s, 1988s, 1957s	36
$HgCo_2(CO)_8$	Orange	81–82	2072s, 2022w, 2007vs, 1964vw	9,26,37–39
$(TTAS)Cu—Co(CO)_4$	Pale yellow	171	2033s, 1945sh, 1919s	57
$Hg[Co(CO)_2(P(OPh)_3)_2]_2$	Yellow	171	—	40
$(CO)_2C_5H_5FeHgCo(CO)_4$	Orange	93–94	—	41
$Me_2Sn[Co(CO)_4]_2$	Yellow-brown	—	—	10
$Me_2Sn[Co(CO)_3PPh_3]_2$	—	—	—	10
$(MeCOO)PbCo(CO)_4$	Yellow	—	—	42
$Ph_3PbCo(CO)_4$	Yellow	98 dec.	—	43
$Ph_2Pb[Co(CO)_4]_2$	Deep red	103–106 dec.	—	44
$ClHgIrCl_2(CO)(PPh_3)_2$	Colorless	270	2030	45,56
$Ph_3GeFeC_5H_5(CO)_2$	Pale yellow	160–161	1995, 1940	46

(*continued*)

TABLE 33 (*continued*)

Compound	Color	Mp (°C)	ν_{CO} (cm^{-1})	Ref.
$[(TTAS)Cu]_2Fe(CO)_4$	Yellow-brown	107	1942s, 1876sh, 1852vs	57
$[Me_2SnFe(CO)_4]_2$	Yellow	> 220 dec.	2064, 2045, 1998, 1987, 1975	11,25,58
$[Bu_2SnFe(CO)_4]_2$	Yellow	110–112	2060, 2041, 1993, 1981, 1969	10,11,25,58
$[Ph_2SnFe(CO)_4]_2$	Lemon yellow	—	—	44
$(Me_3Sn)_2Fe(CO)_4$	—	—	2057, 1998, 1987, 1968	11
$(Ph_3Sn)_2Fe(CO)_4$	Colorless	145–150 dec.	—	43,44
$Ph_3SnFeC_5H_5(CO)_2$	Orange	139–141	—	17
$Cl_2Sn[FeC_5H_5(CO)_2]_2$	Yellow	166–168	2040sh, 2025vs, 1993vs	47
$(Ph_3Pb)_2Fe(CO)_4$	Yellow	135–140 dec.	—	24,44
$(Et_3Pb)_2Fe(CO)_4$	—	—	2040, 1985, 1975, 1958	11
$(C_6H_{11})_3PbFe(CO)_4$	Yellow	140 dec.	—	24
$[Me_2PbFe(CO)_4]_2$	Red-brown	120–130 dec.	—	24
$[Et_2PbFe(CO)_4]_2$	Red	138 dec.	2049, 2031, 1985, 1975, 1962	11,24,48
$[Ph_2PbFe(CO)_4]_2$	Red	152 dec.	—	43,44
$(Ph_3PAu)_2Fe(CO)_4$	Pale yellow	150 dec.	2004m-s, 1934s, 1894s	36
$PbFe(CO)_4$	Black	—	—	42
$HgFe(CO)_4$	Lemon yellow	145–150 dec.	—	6,48,49
$Hg[FeC_5H_5(CO)_2]_2$	Orange	145–146	—	50,51
$(HgCl)_2Fe(CO)_4$	Pale yellow	—	2088sh, 2083s, 2023s, 2008s	6,7,15
$(HgCl)_2Fe(CO)_2py_2$	Bright yellow	> 340 dec.	2068, 2000 ($CHCl_3$)	15
$(MeHg)_2Fe(CO)_4$	—	—	2047, 1989, 1977, 1956	11
$Tl_2Fe_3(CO)_{12}$	Brown	—	—	52
$PbFe_3(CO)_{12}$	Black	—	—	52
$Sn_2Fe_5(CO)_{20}$	Deep red	—	—	52
$Bi_2Fe_5(CO)_{20}$	Black	—	—	52
$SbFe(CO)_4$	Deep red	—	—	52
$SbFe_2(CO)_8$	Black	—	—	52
$As_2Fe_3(CO)_{11}$	Black	—	—	52
$HgMn_2(CO)_{10}$	Pale yellow	~ 155 dec.	2067s, 2008s, 1975vs	51,53
$Ph_3GeMn(CO)_5$	Colorless	162–164	2100, 1995	23*b*,46
$Ph_3SnMn(CO)_5$	Colorless	148–150	—	17
$Me_2Sn[Mn(CO)_5]_2$	Pale yellow	102–104	—	17
$(TTAS)CuMn(CO)_5$	Light brown	140	2033s, 1919vs	23*b*,57
$Ph_2Sn[Mn(CO)_5]_2$	Colorless	137–139	—	17
$Et_3PbMn(CO)_5$	Yellow	Liquid	—	17
$Et_2Pb[Mn(CO)_5]_2$	Orange	77–79	—	17
$Ph_3AuMn(CO)_5$	Pale brown	151 dec.	2062m-s, 1961vs	23*b*,36
$(PhO)_3PAuMn(CO)_5$	Brown	68 dec.	2070m-s, 1990sh, 1965vs	16*a*
$(CO)_3C_5H_5MoSnMe_2Mn(CO)_5$	Yellow	95–96	2090, 2085, 2056, 2001, 1924, 1895	54
$[(CO)_5Re]_3SnSn[Re(CO)_5]_3$	Yellow	> 300	—	28
$Ph_3SnCrC_5H_5(CO)_3$	Colorless	220–222	—	55
$Ph_3SnMoC_5H_5(CO)_3$	—	212.5–213.5	1990, 1924–1905	55
$Cl_3SnMoC_5H_5(CO)_3$	Yellow	164 dec.	2060s, 1996sh, 1972s	47
$(HgCl)_2W(CO)_3bipy$	Orange	—	2000vs, 1924s, 1887s	59
$Cl_3SnWC_5H_5(CO)_3$	Yellow	187	2042s, 1972sh, 1950s 1924sh	47
$Ph_3SnWC_5H_5(CO)_3$	—	229–230.5	—	55
$Ph_2Sn[MoC_5H_5(CO)_3]_2$	—	190–191.5	1987, 1923, 1912, 1892	55
$Ph_2Sn[WC_5H_5(CO)_3]_2$	Yellow	207–209	—	55
$Ph_3PbMoC_5H_5(CO)_3$	Yellow	205	1988, 1930–1900	55
$Ph_3PbWC_5H_5(CO)_3$	Yellow	210–211.5	1978s, 1908s, 1892s, 1880s	55
$MeHgTa(CO)_6$	Dark red	50–60 dec.	2061, 1980, 1923	12

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[a] Type A: Compounds containing transition metals only; type B: compounds also containing nontransition elements.

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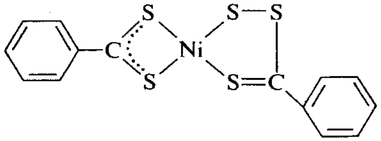
NOTES ADDED IN PROOF

1. Both $Ru(CO)_5$ and $Os(CO)_5$ have now been found to have the same number of infrared carbonyl stretching vibrations as $Fe(CO)_5$. A trigonal bipyramidal structure of D_{3h} symmetry was therefore suggested. (F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, in press.)

2. A recent investigation has suggested that compounds of type 1 containing tetravalent nickel in the original formulation, might be reformulated as nickel(II) derivatives. (J. P. Fackler and D. Coucouvanis, *J. Am. Chem. Soc.*, **89**, 1745 (1967).)



3. An investigation of the system $MnX(CO)_5/C^{18}O$ (X = Cl, Br) has, however, indicated no appreciable difference in exchange rates of equatorial and axial carbon monoxide groups. (B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *Chem. Commun.* (*British*), **1967**, 379.

4. Some papers dealing with this subject have recently appeared: B. Deubzer, H. P. Fritz, C. G. Kreiter, and K. Oefele, *J. Organometal. Chem.*, **7**, 289 (1967); D. A. Brown and J. R. Raju, *J. Chem. Soc.* (*A*), **1966**, 1617; H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **7**, 427 (1967).

5. Klopman and Calderazzo have investigated the kinetics of alkaline hydrolysis of a number of substituted (benzoic methyl esters) tricarbonylchromium compounds. The hydrolysis is faster in the complexes than in the corresponding uncomplexed aromatic esters. The ρ values for the two sets of reactions are 1.55 and 2.36, respectively, thus indicating a lower degree of sensitivity of the chromium complexes to electronic changes in the aromatic ring.

Organometallic Derivatives from Metal Carbonyls and Acetylenic Compounds

W. HÜBEL, *Union Carbide European Research Associates, Brussels**

During the last war, Reppe and co-workers (1) discovered that alkaline solutions of iron carbonyl hydride give hydroquinones when treated with acetylenes at moderate temperatures. Under certain conditions the formation of cyclopentadienone dimer and indanone has also been observed in these reactions. Since some organometallic complexes could be isolated when acetylene was used under pressure, the formation of cyclic products from acetylenes and carbon monoxide was thought to proceed via such organometallic intermediates. The elucidation of the nature of these complexes is only a recent development and, as will be shown, throws light on

* Present address: Deutsches Patentamt, 8 München 2.