THE VOLATILE METAL CARBONYLS[1]

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The metal carbonyls constitute not only a most interesting but also a most unusual series of compounds. In fact, there is no other type of compound which has any close resemblance to the metal carbonyls. One of the most outstanding characteristics of the metal carbonyls, the reversibility of their formation, is possessed also by hydrates, ammoniates, and similar complexes, but it is only in the carbonyls that the central atom of the complex has the oxidation and reduction valence of zero.

Nickel carbonyl is, perhaps, the most typical of the carbonyls. If finely divided metallic nickel is prepared by heating nickel formate at the lowest possible temperature (below 200°C.), this active nickel will at room temperature and atmospheric pressure take up carbon monoxide as rapidly as it can be supplied, with the formation of nickel carbonyl, $Ni(CO)_4$. This is a colorless, very mobile liquid with a vapor pressure of one-third of an atmosphere at room temperature. When it is slowly heated, nickel carbonyl begins to decompose at about 60°C. into nickel (usually deposited on the walls as a brilliant mirror) and carbon monoxide; at higher temperature the decomposition is complete. These mirrors, if they are uncontaminated by traces of oxygen, will frequently disappear again in a stream of cold carbon monoxide. When it is heated suddenly, nickel carbonyl decomposes irreversibly with a rather mild detonation.

$$Ni(CO)_4 \rightarrow Ni + 2C + 2CO_2$$

If the central atom of the metal carbonyl is regarded as zero valent, then the carbonyl group is also zero valent. Thus, this group in the metal carbonyls is of a totally different character from the carbonyl group in other carbon compounds, such as acetone and phosgene, where two primary valence bonds attach the carbonyl group to other parts of the molecule. Furthermore, carbonyl compounds of the latter type cannot be reversibly formed from carbon monoxide.

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Many of the metal carbonyls possess the surprising property of a high degree of volatility, as is shown in table 1.

Nitric oxide has a property similar to that of carbon monoxide of combining reversibly with metals, although this reversibility is often partly concealed, in that decomposition of the nitrosyls leads to a disproportionation of the liberated nitric oxide and a consequent formation of nitrate or nitrite of the metal. Very volatile hydrogen compounds of metal carbonyls have been prepared by indirect reactions; although these have not been synthesized directly, they break down very easily into hydrogen and non-volatile carbonyls. Volatile nitrosyl and hydrogen compounds are listed in table 2.

TABLE 1

Volatile carbonyls

CARBONYL	MELTING POINT	VAPOR PRESSURE	TEMPERATURE AT WHICH IT BEGINS TO DECOMPOSE
	°C.	*mm.*	*°C.*
$Ni(CO)_4$	−25	261 (at 15°C.)	60
$Fe(CO)_5$	−21	15 (at 25°C.)	150
$Ru(CO)_5$	−22	Very volatile	−15
$Cr(CO)_6$	Sinters at 90	1 (at 48°C.)	130
$Mo(CO)_6$	Sinters at 120	2.3 (at 55°C.)	150
$W(CO)_6$	Sinters at 125	1.2 (at 67°C.)	150
$[Co(CO)_4]_2$	50	0.07 (at 15°C.)	53

TABLE 2

Volatile nitrosyl carbonyls and carbonyl hydrides

COMPOUND	MELTING POINT	VAPOR PRESSURE
	°C.	*mm.*
$Co(CO)_3NO$	−11	56 (at 16°C.)
$Fe(CO)_2(NO)_2$	+18	4.5 (at 0°C.)
$Co(CO)_4H$	−33	High
$Fe(CO)_4H_2$	−70	11 (at −10°C.)

Vapor density measurements have shown all of the volatile carbonyls of tables 1 and 2, except cobalt tetracarbonyl, to be monomeric. The cobalt tetracarbonyl is dimeric. It is placed in table 1 to show the transition between the volatile and non-volatile carbonyls. Actually, it can be sublimed in a vacuum or, better, in a current of carbon monoxide. Several of the carbonyls listed in table 3 as non-volatile can be sublimed with nearly the same ease as cobalt tetracarbonyl. The pure nitrosyls in this list appear to be completely non-volatile, and their degree of polymerization is not known. They do, however, decompose and give fumes with moist air. The molecular weights of these non-volatile carbonyls, with the exception of ruthenium tetracarbonyl, have been determined by the freezing-point method in indifferent solvents, and the degree of polymerization shown in the formulas has been found. Ruthenium tetracarbonyl may be expected to have the same polymerization as the trimeric iron tetracarbonyl.

TABLE 3

Non-volatile carbonyls and nitrosyls

NON-VOLATILE CARBONYLS			NON-VOLATILE NITROSYLS	
$Fe_2(CO)_9$	$[Co(CO)_4]_2$	$Ru_2(CO)_9$		
$[Fe(CO)_4]_3$	$[Co(CO)_3]_4$	$[Ru(CO)_4]_n$	$Fe(NO)_4$	$Ru(NO)_{4-5}$

TABLE 4

Other non-volatile carbonyls

CARBONYLS OF METAL HALIDES	CARBONYLS CONTAINING PYRIDINE, ETHYLENEDIAMINE, OR *o*-PHENANTHROLINE	COMPOUNDS IN WHICH HYDROGEN OF CARBONYL HYDRIDES HAS BEEN REPLACED BY A METAL
$PtCl_2(CO)$	$Fe_2(CO)_4py_3$*	$Fe(CO)_4Hg$
$PtCl_2(CO)_2$	$Fe(CO)_2(CN)_2py$	$Fe(CO)_4Hg_2Cl_2$
$(PtCl_2)_2(CO)_3$	$Fe(CO)_4en_2I_2$	$[Co(CO)_4]_2Hg$
$RuI_2(CO)_2$	$Fe(CO)_2py_2I_2$	$Co(CO)_4Ag$
$RhCl_2.RhO(CO)_3$	$Fe(CO)_2(o\text{-phthr})_2I_2$	$KCo(CO)_4$
$IrCl_2(CO)_2$	$Fe(CO)_2(o\text{-phthr})I_2$	$K_2Fe(CO)_4$
$PdCl_2CO$	$Fe(CO)py_2I_2$	$K_3[Fe(CN)_5CO]$
$OsCl_2(CO)_3$	$W(CO)_4(o\text{-phthr})$	
$Fe(CO)_4I_2$	$Cr(CO)_4py_2$	
$Fe(CO)_5I_2$	$Cr_2(CO)_7py_5$	
	$Cr(CO)_3py_3$	
	$Co_2(CO)_5py_4$	
	$Co(CO)_3(o\text{-phthr})$	
	$Ni_2(CO)_4py$	
	$Ni(CO)_2py$	
	$Ni_2(CO)_3py_2$	
	$Ni(CO)_2(o\text{-phthr})$	

* py = pyridine; en = ethylenediamine; *o*-phthr = *o*-phenanthroline.

In addition to the volatile metal carbonyls,—and under this title let us include always the volatile nitrosyl carbonyls and carbonyl hydrides,—there have been prepared a bewildering number of non-volatile complexes which contain carbonyl or nitrosyl groups or both. In table 4 is shown a typical, but far from complete, list of such compounds.

In the first column of table 4 appear carbonyls of metal halides. One of the carbonyls of platinous chloride is so stable that it can be sublimed like cobalt tetracarbonyl. The iodides $Fe(CO)_4I_2$ and $Fe(CO)_5I_2$ are obtained only at low temperatures by the addition of iodine to anhydrous iron carbonyl. Addition of water causes immediate decomposition into ferrous iodide and carbon monoxide.

When the carbonyls and nitrosyl carbonyls are treated with such complex-forming substances as ammonia, pyridine (py), ethylenediamine (en), *o*-phenanthroline (*o*-phthr), etc., there is usually a rapid evolution of carbon monoxide. The formulas given in the second column show the composition of some of the substances that can be crystallized at various temperatures. It is particularly noteworthy that in no case has there been a complete displacement of the carbonyl groups to give a zero valent complex of the metal.

In the third column are shown compounds in which the hydrogen of the carbonyl hydrides has been replaced by a metal. The heavy metal compounds are insoluble in water but soluble in organic solvents. The alkali and alkaline-earth metal compounds are soluble in water and appear to bear the salt-to-acid relation to the corresponding hydrides.

The definitions of the terms "valence", "cohesion", and "chemical affinity" have never been very well standardized, but according to the most usual understanding of these concepts, they all arise from the same source, namely, the field of the atoms and molecules and, in fact, the field of the electrons and nuclei within the atoms. With the inert gases the field of the electrons and the field of the nucleus are mutually neutralized, and the lack of field external to the atom explains the lack of chemical affinity and the zero valence of the inert gases.

All other atoms possess external fields. Where definite groups of atoms can form in which the fields of the different atoms are mutually neutralized, there is little cohesion between the molecules and the compounds are volatile.

Through the position of the so-called valence electrons, the field between two atoms may be localized into what is regarded as a valence bond.

Although a study of the chemical composition of the volatile carbonyls may not furnish a definite decision as to the location of the chemical bonds, nevertheless the number of possible locations is limited. On the other hand, in non-volatile carbonyls in which the cohesion is continuous and not restricted within small groups of atoms, the problem of locating the position of the bonds becomes more complicated.

The importance and the theoretical significance of the large array of non-volatile mixed carbonyls should not be in any way minimized; nevertheless the present study concerns itself principally with the volatile carbonyls and the property of volatility. First, space does not allow the complete field to be covered, and second, the greater simplicity of the volatile compounds offers a greater possibility of understanding the nature and position of the valence bonds.

No attempt is made in this paper to discuss the significance of the magnetic and dielectric properties of the carbonyls or of the x-ray or electron diffraction, or the light absorption studies. Most interesting and important data have been obtained from these studies, and these must finally be coördinated before the nature of the carbonyls is completely understood.

We owe to Sidgwick (88, 82) the useful term "effective atomic number", which is applied to the central atom of complexes. This is the total number of electrons existing within the sphere of the atom in the complex, and embraces both those electrons originally belonging to the atom itself and also the electrons donated by the surrounding groups. The implication of this term is that the stability of the complex is dependent on the symmetry of the arrangement of the electron groups within the central atom, and particularly, that when the effective atomic number is equal to the atomic number of one of the inert gases, this will be reflected in the self-contained character of the central atom. If, furthermore, the field of the surrounding groups is self-contained except where it mutually neutralizes that of the central atom, then the whole complex will be self-contained, and if the net charge of the whole complex is zero, the complex will be volatile.

TABLE 5

Effective atomic number of central atom

VOLATILE CARBONYL	EFFECTIVE ATOMIC NUMBER OF CENTRAL ATOM	INERT GAS HAVING SAME ATOMIC NUMBER
$Ni(CO)_4$	$28 + 8 = 36$	Krypton
$Fe(CO)_5$	$26 + 10 = 36$	Krypton
$Ru(CO)_5$	$44 + 10 = 54$	Xenon
$Cr(CO)_6$	$24 + 12 = 36$	Krypton
$Mo(CO)_6$	$42 + 12 = 54$	Xenon
$W(CO)_6$	$74 + 12 = 86$	Radon

If it is postulated that each carbonyl group donates two electrons to the central atom it is seen in table 5 that the effective atomic number of the central atom in each of the volatile carbonyls is identical with the atomic number of an inert gas.

Since nickel carbonyl possesses the most self-contained field and of all the carbonyls is the least subject to rearrangement additions or substitutions, other than a complete dissociation into nickel and carbon monoxide, we may well first give our attention to its structure. There can be little doubt that nickel is the central atom of the complex, and that it is surrounded by four coördinately bound and symmetrically placed carbonyl groups. If we assume that each carbonyl group donates two electrons to the central atom, the effective atomic number of the nickel becomes $28 + (4 \times 2) = 36$, which is the atomic number of krypton.

Cobalt lacks one electron (82) and iron two electrons to give a structure of the same pattern. But the nitrosyl group has a structure similar to that of the carbonyl group and it possesses one more electron. Thus, in the nitrosyl carbonyls $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ we can have the effective atomic number of 36 for the central atom and the same electron pattern for the whole molecule. In the carbonyl hydrides $Co(CO)_4H$ and $Fe(CO)_4H_2$, the electrons necessary to complete the pattern are furnished by the hydrogen atoms.

If it is postulated that the nitrosyl group donates three electrons and each hydrogen one electron, we see in table 6 that in the volatile nitrosyl carbonyls and carbonyl hydrides the effective atomic number of the central atom is in each case equal to that of krypton.

TABLE 6

Effective atomic number of the central atom

CARBONYL	EFFECTIVE ATOMIC NUMBER OF CENTRAL ATOM
$Co(CO)_3NO$	$27 + 6 + 3 = 36$
$Co(CO)_4H$	$27 + 8 + 1 = 36$
$Fe(CO)_2(NO)_2$	$26 + 4 + 6 = 36$
$Fe(CO)_4H_2$	$26 + 8 + 2 = 36$

There can be little doubt then that the basic electron pattern of the highly volatile carbonyl hydrides and nitrosyl carbonyls is the same as that of nickel carbonyl. The center of the positive charges is not, however, coincident with the center of the electron pattern as in nickel carbonyl, and in consequence these modified tetracarbonyls display an electric moment.

The most favored electron pattern of carbon monoxide :C:::O: shows three electron pairs held in common. Two alternatives present themselves by which the nickel complex may be formed: (I) Without alteration of the triple bond between the carbon and oxygen atoms the lone pair of the carbon atom may enter the shell of the nickel atom:

$$Ni[:C:::O:]_4$$

(II) This lone pair may be donated to the nickel shell and at the same time the nickel may donate two electrons with a consequent shift of electrons to give the pattern

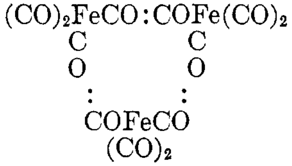
$$Ni[::C::O::]_4$$

If the structure of nitric oxide is identical with that of carbon monoxide except for an additional imprisoned electron, the extra electron would be transferred completely to the shell of the central atom in nitrosyl formation and the pattern would then be identical with that of the carbonyl.

$$\underset{\text{I}}{[:\mathrm{O}:::\mathrm{C}:]_3\mathrm{Co}[:\mathrm{N}:::\mathrm{O}:]} \qquad \underset{\text{II}}{[::\mathrm{O}::\mathrm{C}::]_3\mathrm{Co}[::\mathrm{N}::\mathrm{O}::]}$$

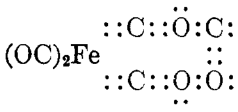
Evidently the coördination number is four in the cases already cited. There must be an inherent tendency among the carbonyls and nitrosyls to acquire the symmetry of this coördinate grouping. Indeed, it is probably the tendency to acquire this symmetry which is reflected in the prevalence of the tetracarbonyls among the non-volatile (or little volatile) carbonyls $[\mathrm{Co(CO)_4}]_2$, $[\mathrm{Fe(CO)_4}]_3$, and $[\mathrm{Ru(CO)_4}]_n$. If the polymerization is due to a linking of two carbonyl groups, each electron pair held in common will free two electrons to increase the effective atomic number of the central atoms.

$$\mathrm{(CO)_3CoCO:COCo(CO)_3}$$



$$\begin{array}{ccc} \mathrm{(CO)_2FeCO} & : & \mathrm{COFe(CO)_2} \\ \mathrm{C} & & \mathrm{C} \\ \mathrm{O} & & \mathrm{O} \\ \vdots & & \vdots \\ & \mathrm{COFeCO} & \\ & \mathrm{(CO)_2} & \end{array}$$

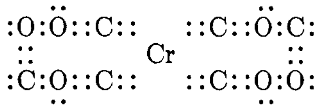
In iron pentacarbonyl if structure I is the correct carbonyl metal linkage the five carbonyl groups are bound directly to the central atom and the coördination number is five. If the carbonyl groups are bound in the pattern shown in II, only four would be bound to the central atom and the fifth would bridge across two of those directly bound:



$$\mathrm{(OC)_2Fe}\begin{array}{l} ::\mathrm{C}::\ddot{\mathrm{O}}:\mathrm{C}: \\ \qquad\qquad\;\; :: \\ ::\mathrm{C}::\underset{\cdot\cdot}{\mathrm{O}}:\mathrm{O}: \end{array}$$

The number of electrons saved by this bridge and thus passed along to bring the effective atomic number of the central atom up to 36 is two. If a similar bridge were formed according to pattern I the number of electrons saved for the central atom would be four, which would raise the effective atomic number to 38.

According to structure I chromium hexacarbonyl would contain six carbonyl groups directly bound to the central atom, and the coördination number would be six. According to structure II the electron pattern of nickel carbonyl with a coördination number of four would prevail and there would be two CO bridges:



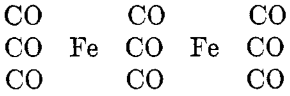
$$\begin{array}{lcl} :O:\overset{\cdot\cdot}{O}::C:: & & ::C::\overset{\cdot\cdot}{O}:C: \\ \ \begin{smallmatrix}\cdot\cdot\\\cdot\cdot\end{smallmatrix} & \mathrm{Cr} & \qquad\qquad\quad \begin{smallmatrix}\cdot\cdot\\\cdot\cdot\end{smallmatrix} \\ :C:\underset{\cdot\cdot}{O}::C:: & & ::C::\underset{\cdot\cdot}{O}:O: \end{array}$$

In the enneacarbonyls $Fe_2(CO)_9$ and $Ru_2(CO)_9$ there is obviously a CO bridge between the two metal atoms and the coördination number may be either four or five, according to whether the bridging CO joins two of the carbonyl groups or joins the two metal atoms directly.

$$(OC)_3FeCO:CO:COFe(CO)_3 \qquad (OC)_4Fe:CO:Fe(CO)_4$$

In either case structure I alone will allow the correct saving of electrons to bring the effective atomic number of iron to 36 or of ruthenium to 54.

In view of the low volatility, however, perhaps it is not necessary to make the effective atomic number of the iron equal to that of an inert gas. Hieber gives the probable structure as



$$\begin{array}{ccccc} CO & & CO & & CO \\ CO & Fe & CO & Fe & CO \\ CO & & CO & & CO \end{array}$$

with three CO bridges and the coördination number of six for the iron atoms. Such a structure he believes to be supported by the x-ray diffraction studies of the substance (Brill (7)).

PREPARATION OF CARBONYLS

1. All of the metal carbonyls, except that of chromium, have been prepared by direct combination of the metal with carbon monoxide. High pressures and somewhat elevated temperatures are often employed.
2. Carbonyls also are prepared from metal salts and carbon monoxide in the presence of quite a variety of combinations of reagents. Always, however, one essential function of the reagents is to effect the reduction of the metal. In the presence of strong alkalies the carbon monoxide may also, itself, act as the reducing agent, the fixation of the carbon dioxide by the alkali greatly enhancing the reducing power of the carbon monoxide.

NICKEL CARBONYL, $Ni(CO)_4$

Preparation of nickel carbonyl

Direct synthesis. Nickel carbonyl is undoubtedly most easily prepared by direct synthesis, although certain conditions have to be scrupulously observed to ensure the success of the process. Compact pieces of nickel that have been exposed to air are practically without action upon carbon monoxide. Finely divided, freshly reduced nickel combines readily with carbon monoxide at room temperature and atmospheric pressure. In the Mond process for the commercial production of nickel from its ores, the ore is converted to the oxide, the oxide is reduced with producer gas at an elevated temperature, the nickel is subjected to producer gas at a lower temperature, the nickel carbonyl vapor entrained in the producer gas is decomposed with deposition of nickel in a heated chamber, and the producer gas is again ready to repeat the cycle.

For the laboratory preparation of nickel carbonyl the best results are obtained if commercial nickel formate is reduced in hydrogen at the lowest possible temperature, best below 200°C. After cooling, this reduced nickel absorbs carbon monoxide with great avidity, and if this gas is supplied rapidly a steady stream of liquid nickel carbonyl will flow from the outlet of the reaction vessel. The least trace of oxygen poisons the nickel so that it ceases to react readily, but strangely enough a few bubbles of hydrogen sulfide revivify the nickel (74).

Preparation from nickel salts. The formation of nickel carbonyl has been reported in several wet reactions with nickel salts, but none of these methods can compete with the dry synthesis as a method of preparation.

Manchot and Gall (67) observed that nickel carbonyl is formed when carbon monoxide is passed into a suspension of a nickel salt in caustic alkali and alkali sulfide.

Windsor and Blanchard (91) studied the mechanism of this process and reached the conclusion that in the presence of a sulfur-removing reagent the potential of the nickel in nickel sulfide could rise to the point of carbonyl formation.

$$\begin{aligned} 3Na_2S + 3NiCl_2 &\rightarrow 3NiS + 6NaCl \\ 3NiS &\rightarrow 3\,Ni + 3S \\ 3Ni + 12CO &\rightarrow 3Ni(CO)_4 \\ 3S + 6NaOH &\rightarrow 2Na_2S + Na_2SO_3 + 3H_2O \end{aligned}$$

$$3NiCl_2 + Na_2S + 12CO + 6NaOH \rightarrow 3Ni(CO)_4 + Na_2SO_3 + 6NaCl + 3H_2O$$

The summation in the last equation shows that nickel is reduced from +2 valence to zero valence at the expense of sulfur, which is oxidized from −2 to +4.

Blanchard, Rafter, and Adams (5) found that cyanide is fully as effective as sulfide in promoting carbonyl formation in an alkaline suspension of a nickel salt. They propose a mechanism analogous to that for the sulfide method, similar steps being summarized in the over-all equation:

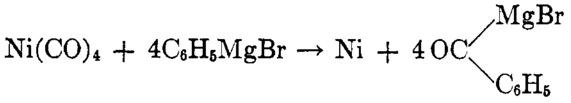
$$NiCl_2 + KCN + 2NaOH + 4CO \rightarrow Ni(CO)_4 + KCNO + 2NaCl + H_2O$$

It should be stated that in the cyanide method, as indeed in the sulfide method, it is extremely probable that the intermediate formation of complex ions containing the carbonyl group plays an important part in facilitating the over-all result indicated by the equations.

Job and Reich noted that such unsaturated compounds as ethylene (53) and carbon monoxide (52) alone failed to react with Grignard reagents, but that in the presence of certain metal salts a reaction took place. In the case of nickel chloride it was found that nickel carbonyl could be detected, but no considerable amount was ever obtained. The Grignard reagent reduces the nickel salt as follows:

$$\mathrm{NiCl_2 + 2RMgBr \rightarrow Ni + R \cdot R + 2MgBrCl}$$

The reduced nickel combines with carbon monoxide to give nickel carbonyl, but the latter is very reactive toward the Grignard reagent, the equation



$$\mathrm{Ni(CO)_4 + 4C_6H_5MgBr \rightarrow Ni + 4\,OC}\begin{matrix}\diagup\mathrm{MgBr}\\ \diagdown\mathrm{C_6H_5}\end{matrix}$$

probably indicating the first step of a train of reactions. The nickel thus set free again takes up carbon monoxide to form nickel carbonyl. Thus an equilibrium concentration of nickel carbonyl is maintained, depending on the relative rates of its formation and its reaction with the Grignard reagent. At any time that the main process is stopped by hydrolysis of the Grignard reagent, only this equilibrium quantity of nickel carbonyl is obtainable from the mixture.

With respect to nickel carbonyl, this method of formation is of theoretical interest only. However, with chromium, molybdenum, and tungsten carbonyls it is the only practicable method of preparation; in fact, with chromium carbonyl it is the only method of formation that has been discovered.

Behavior of nickel carbonyl

Nickel carbonyl is soluble in, in fact, completely miscible with, organic solvents in general. It is not markedly soluble in water. It is without action with aqueous acids and alkalies.

When nickel carbonyl is formed from nickel and carbon monoxide, the latter substances suffer a most complete change of their physical properties, but only a very slight change of chemical properties. In fact, some of the chemical properties which they exhibit in the free state seem to be enhanced by their combination in the nickel carbonyl.

Nickel carbonyl reacts vigorously and quantitatively with bromine

$$Ni(CO)_4 + Br_2 \rightarrow NiBr_2 + 4CO$$

the reaction being applicable to gas analytical procedure.

It reacts with the other halogens, with oxygen, and with sulfur in similar fashion, the nickel giving halide, oxide (hydroxide), and sulfide, respectively, and the carbon monoxide remaining free. Nickel carbonyl reacts slowly with oxygen, either dry or in the presence of water. Various observers have reported products which appear as crusts or deposits of the most varied appearance and composition. Berthelot (3) gives a composition $C_2O_3Ni_3 \cdot 10H_2O$; Lenher and Loos (56), $Ni(CO)_4 \cdot Ni(OH)_2 \cdot 4H_2O$; Thorne (90), a basic carbonate of nickel. These variable results apparently arise from the fact that nickel carbonyl is so volatile that during the long period of the reaction most of it escapes, even through water seals. Carbon dioxide of the air enters during the period to form carbonate. Blanchard and Gilliland (4) found that the oxidation product contained about 4 equivalents of formate per 100 equivalents of nickel. When the oxidation took place in a sealed vessel containing nickel carbonyl, water, and oxygen, after several weeks the residual gases consisted of carbon monoxide and unused oxygen and nickel carbonyl vapor, with no trace of carbon dioxide. The light green residue dissolved completely in dilute acid without trace of effervescence. It thus consisted solely of nickelous hydroxide and a little nickel formate but no nickel carbonate. The presence of formate is accounted for by the slow hydration of carbon monoxide to formic acid under the catalytic effect of the nickel carbonyl.

In contrast to the halogens, etc., which react only with the nickel, Grignard reagents act solely upon the carbon monoxide of the nickel carbonyl, and leave the nickel uncombined as a jet-black residue. Grignard reagents are as a rule without action on carbon monoxide alone, but react vigorously with the carbon monoxide of nickel carbonyl. This reaction has proved of great value in the study of Grignard syntheses from carbon monoxide; in fact, it has been found that a very small amount of nickel carbonyl is sufficient to effect such syntheses, the nickel acting as a carrier for the carbon monoxide (19).

The nickelous ion forms complexes with many amines, for example, $[Ni(NH_3)_4]^{++}$. Nickel carbonyl is the corresponding complex of zero valent nickel. No unmixed amine complexes of zero valent nickel are known, but several mixed amine carbonyl complexes are on record. When nickel carbonyl is treated with pyridine a slow effervescence is noted; removal of the carbon monoxide by pumping allows the reaction to proceed more fully, and finally it is possible to obtain crystallized products. Hieber, Mühlbauer, and Ehman (35) have identified three such products of the compositions $Ni_2(CO)_4py$, $Ni(CO)_2py$, and $Ni_2(CO)_3py_2$; with *o*-phenanthroline these authors have obtained the much more stable compound $Ni(CO)_2(o\text{-phthr})$, in the form of ruby-red needles as much as 1 cm. long.

The behavior of these mixed carbonyl amine complexes with acids is of interest, and particularly so when comparison is made with the behavior of similar cobalt and iron complexes. If we allow Am to stand for the amine part of the complex, the reactions shown in equations 1 and 2 take place

$$Ni(CO)_2Am + 3H^+ \rightarrow Ni^{++} + 2CO + H_2 + AmH^+ \qquad (1)$$

$$2Ni(CO)_2Am + 2H^+ \rightarrow Ni(CO)_4 + Ni^{++} + H_2 + 2AmH^+ \qquad (2)$$

with equation 1 predominating. In the unsubstituted nickel carbonyl complex the nickel does not enter into reaction with hydrogen ions.

Nickel carbonyl and oxides of nitrogen

The behavior of nickel carbonyl with oxides of nitrogen has recently (1936) been studied by Frazer and Trout (14). They find that nitrogen dioxide, NO_2, reacts exothermically even at a temperature as low as --78°C.; as much as 98 per cent of the carbon monoxide of the carbonyl and a small amount of carbon dioxide are found in the gaseous products. The solid product contains all of the nickel and appears to be a mixture of nitrate and nitrite in about the ratio of 3:1.

Nitrogen trioxide, N_2O_3, reacts similarly to the dioxide.

Nitric oxide, NO, reacts with liquid nickel carbonyl from $-11°$ to 0°C. to form a blue gelatinous solid product, which becomes almost white when excess of nickel carbonyl is removed. At room temperature bronze to olive-green deposits are obtained. These solid products are insoluble in water, but soluble in dilute sulfuric acid with evolution of red fumes. The analyses of the solid product are very variable, but practically all of the original carbon monoxide and a small amount of carbon dioxide are found in the gaseous products.

Nitrous oxide, N_2O, does not undergo any slow reaction with nickel carbonyl. The gas mixture explodes when ignited with a gas flame.

A green solid is obtained when a solution of nickel carbonyl in not anhydrous methyl alcohol is treated with nitric oxide. This substance is stable in air. Reihlen (83, 84) gives its composition as $NO \cdot NiOH \cdot OCH_3 + CH_3OH$. On the other hand, Anderson (2) gives its composition as $N_2O_2 \cdot Ni(OH)_2 + 4CH_3OH$.

There still appears to be much uncertainty as to the nature of the nitrosyl compounds of nickel, but it is at least significant that no volatile nitrosyl or nitrosyl carbonyl has been discovered.

COBALT CARBONYLS

Preparation of cobalt carbonyls

Direct synthesis. Finely divided cobalt (pumice soaked with cobalt salt solution and reduced in hydrogen at a low temperature) reacts a little with carbon monoxide, a trace of vapor being entrained which gives a faint cobalt mirror in a heated tube. When this cobalt is treated with a mixture of carbon monoxide and nitric oxide, the volatile cobalt nitrosyl carbonyl, $Co(CO)_3NO$, is produced rather freely (5).

Cyanide method. An alkaline suspension of cobalt cyanide absorbs a considerable amount of carbon monoxide, but no identifiable carbonyl can be isolated, either as a vapor or by extraction with solvents. However, the moment nitric oxide is introduced the apparatus becomes filled with the deep yellow-brown vapor of cobalt nitrosyl carbonyl. This is a very serviceable method of preparation of the cobalt nitrosyl carbonyl (5).

Cysteine method: preparation of cobalt tetracarbonyl hydride. Schubert (86), in making a study of the absorption of carbon monoxide by the cysteine complexes of cobalt and iron, found that with iron the potassium and sodium salts of the carbonyl complex could be isolated,

$$Fe(SCH_2CHNH_2COOK)_2 \cdot 2CO \cdot 2H_2O$$

and also the free acid,

$$Fe(SCH_2CHNH_2COOH)_2 \cdot 2CO \cdot H_2O$$

With cobalt, although similar complexes may represent intermediate stages, they could not be isolated; a disproportionation of the cobalt took place with formation of a cysteine complex of trivalent cobalt and a carbonyl complex containing no cysteine. Acidification of the latter complex caused separation of cobalt tetracarbonyl. Schubert worked out the following reactions (in the equations R stands for the part of the formula of cysteine, $HS[-CH_2CHNH_2COO-]H$, enclosed in brackets):

$$CoCl_2 + 2HSRH \cdot HCl + 6KOH \rightarrow K_2Co(SR)_2 + 4KCl + 6H_2O \quad (1)$$

Equation 1 shows the formation of the cobaltous cysteinate complex.

$$9K_2Co(SR)_2 + 8CO + 2H_2O \rightarrow 6K_3Co(SR)_3 + 2HCo(CO)_4 + Co(OH)_2 \quad (2)$$

Reaction 2 takes place in moderately concentrated alkali and shows the disproportionation of the cobalt into a cobaltic cysteine complex and the carbonyl complex $HCo(CO)_4$, which contains no cysteine.

$$K_3Co(SR)_3 + 6CO + 7KOH \rightarrow 3K_2RS + HCo(CO)_4 + 2K_2CO_3 + 3H_2O \quad (3)$$

Reaction 3 takes place in concentrated alkali solution and shows the oxidation of carbon monoxide to a carbonate and the reduction of the trivalent cobalt to the same carbonyl cobalt complex. The validity of these reactions was tested by very careful analysis. In particular, existence of the hydride $HCo(CO)_4$ was confirmed by the precipitation and analysis of both the mercuric and silver salts, $Hg[Co(CO)_4]_2$ and $AgCo(CO)_4$.

Coleman and Blanchard (10), in seeking improved methods of preparing cobalt nitrosyl carbonyl, tried the use of cysteine. They first noted that consolidation of the three equations given by Schubert gave

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

according to which all of the cysteine is regenerated and a part of the carbon monoxide acts as the reducing agent.

Actually they found that no absorption of carbon monoxide at all takes place in the absence of cysteine; nevertheless a small amount of cysteine brings about the absorption of a much larger proportion of carbon monoxide than shown in equations 2 and 3. In fact, they found rather more carbon monoxide absorbed than demanded by equation 4 on the basis of the cobaltous salt taken.

They found that in contrast to the alkaline cobaltous cyanide solution saturated with carbon monoxide, this alkaline cysteine solution did not yield any cobalt nitrosyl carbonyl upon treatment with nitric oxide. After acidifying, however, the case was quite different (see later). The immediate effect of acidification (without nitric oxide) was to liberate the hydride $HCo(CO)_4$.

Preparation of cobalt carbonyl hydride. Coleman and Blanchard found that acidification of the solution described above (containing the salt $KCo(CO)_4$) produced effervescence (carbon dioxide). In agreement with Schubert they observed that the escaping gases had an almost intolerably vile odor. They swept the acidified solution with carbon monoxide and passed the entrained gases through phosphorus pentoxide and then through a trap immersed in solid carbon dioxide and alcohol, and obtained a light yellow crystalline solid. This substance had a perfectly sharp melting point at about $-33°C$. It gave a clear, straw-yellow liquid. After being several times resolidified and remelted the substance began to acquire a reddish-brown color, and when it approached room temperature it effervesced strongly and changed to a dark colored solid. This residue was shown to be cobalt tetracarbonyl, $[Co(CO)_4]_2$, and the gas which escaped was found to be hydrogen. The vapor which condensed to the light yellow solid was the hydride, $HCo(CO)_4$. In the best run an amount of hydride was obtained which corresponded to 26 per cent of the cobalt taken.

Preparation of cobalt nitrosyl carbonyl. If, after acidification of the alkaline solution in the cysteine method, the sweeping with carbon monoxide is withheld for sometime, a black scum of cobalt tetracarbonyl rises to the surface. Then on introducing nitric oxide the shaking vessel becomes filled with reddish-brown vapors. These were swept with nitric oxide through phosphorus pentoxide into a trap in solid carbon dioxide and alcohol. Light yellow crystalline cobalt nitrosyl carbonyl was obtained. After several days with occasional sweeping the total yield of cobalt nitrosyl carbonyl, based on the cobalt salt taken, was 54 per cent.

Cobalt nitrosyl carbonyl has been found to react quantitatively with bromine.

$$Co(CO)_3NO + Br_2 \rightarrow CoBr_2 + 3CO + NO$$

The escape of free nitric oxide as well as carbon monoxide tends to support the postulate that the nitrosyl and carbonyl groups function similarly in the complex (10, 25).

Other assistants in the preparation of cobalt carbonyls. Coleman and Blanchard found many other substances besides sulfide, cyanide, and cysteine which would promote the absorption of carbon monoxide by alkaline cobalt salt solution. The most effective of these proved to be tartaric acid and, although this did not cause as rapid an absorption as did cysteine, it was employed in the preparation of batches of both the carbonyl hydride and the nitrosyl carbonyl.

Properties of cobalt tetracarbonyl

Cobalt tetracarbonyl usually is obtained as a dark colored solid, but when it is entirely pure it exists as yellow crystals. Its molecular weight, as determined by the freezing-point method in benzene and also in iron pentacarbonyl, gives it the dimeric formula $[Co(CO)_4]_2$ (35).

It melts at 51°C.; slightly above this temperature it begins to decompose, giving off carbon monoxide and leaving a residue of cobalt tricarbonyl. The latter is sparingly soluble in benzene and pentane, and can be purified by recrystallization from these solvents. It consists of pitch-black glistening crystals. By the freezing-point method in iron pentacarbonyl it is shown to have the tetrameric formula $[Co(CO)_3]_4$.

Behavior with alkalies. According to Hieber and Schulten (40, 41) cobalt tetracarbonyl reacts with strong bases as follows:

$$3Co(CO)_4 + 2OH^- \rightarrow 2HCo(CO)_4 + Co(CO)_3 \text{ (polymer)} + CO_3^{--}$$

with weak bases, e.g., ammonia, as follows:

$$3Co(CO)_4 + 2H_2O \rightarrow 2HCo(CO)_4 + Co(OH)_2 + 4CO$$

The presence of the hydride was confirmed by the addition of ammoniacal silver nitrate and the precipitation of the silver salt, to which they give the formula $AgCo(CO)_4 \cdot 1/2CO \cdot 1/2H_2O$. Further confirmation of the presence of the $[Co(CO)_4]^-$ ion they find in the formation of crystalline salts upon the addition of complex cobaltous, nickel, and silver ions, e.g.,

$$[Co(o\text{-phthr})_3]Cl_2 + 2KCo(CO)_4 \rightarrow [Co(o\text{-phthr})_3][Co(CO)_4]_2 + 2KCl$$

Behavior with amines. Hieber and his coworkers have extensively investigated the behavior of the carbonyls with the complex-forming amines. They find in general that, as with nickel carbonyl, the amines displace a part but never all of the carbonyl group of the cobalt carbonyls with the formation of mixed complexes. These new complexes can be isolated as crystalline substances of definite composition, but there is no indication that any of them are volatile. Furthermore, the multiplicity of such complexes is increased through the ability of the cobalt to disproportionate.

For example, either cobalt tetracarbonyl or cobalt tricarbonyl placed in pyridine causes effervescence (escaping carbon monoxide), and crystalline $Co_2(CO)_5py_4$ finally crystallizes out. In similar fashion such complexes as $Co(CO)_3(o\text{-phthr})_2$, $Co_2(CO)_5 \cdot CH_3OH$, and $Co_2(CO)_5 \cdot 1.5C_2H_5OH$ have been isolated. When such complexes are treated with acid there is obtained a small amount of a cobalt compound with a very bad odor. This was the first observation of the cobalt carbonyl hydride (35).

Cobalt carbonyl hydride

This very volatile substance was first observed by Hieber, Mühlbauer, and Ehman (35); its salts, or the corresponding salts of iron carbonyl hydride, were recognized by Hock and Stuhlman (47), Feigl and Krumholz (12, 13), and Schubert (86), but the cobalt carbonyl hydride was definitely isolated and identified first by Hieber (24). Hieber and Schulten (41) treated cobalt tetracarbonyl with barium hydroxide solution, by means of which the disproportionation outlined in the previous paragraph was effected. Thereafter, treatment with phosphoric acid and vacuum distillation into a trap cooled with liquid air gave the cobalt carbonyl hydride. Hieber and Schulten give its melting point as $-26.2°C$. The light yellow liquid soon turns dark, and at $-18°C$. it effervesces with escape of hydrogen.

Originally Hieber maintained that both the hydride and the metal derivatives of the hydride were non-ionic in nature. In 1937 he admits that the metal derivatives are ionic and that the ion $Co(CO)_4^-$ possesses a symmetrical electron shell, but he still contends that the hydride is non-ionic, in fact, he postulates a composite pseudo nickel atom (24),—a coalition of the cobalt and hydrogen atoms, with atomic number 28,—as the center of the complex.

In spite of the instability of cobalt carbonyl hydride in the pure state, it can be carried from one vessel to another as a vapor highly diluted with carbon monoxide at room temperature with practically no decomposition. It dissolves out of such a stream of carbon monoxide in water at 0°C., and although the solution decomposes in a few minutes, it, nevertheless, persists long enough for a rough estimate of its acid strength to be made. Coleman (9) passed carbon monoxide carrying the hydride vapors through a rotary absorption tower containing 200 cc. of distilled water and some methyl orange. The indicator quickly turned red, although somewhat short of the clear red produced by strong acids. Addition of 0.1 *N* potassium hydroxide changed the color to yellow. In all, 3 cc. of 0.1 *N* potassium hydroxide was added, and even in the presence of the salt, $KCo(CO)_4$, absorption of additional hydride caused the methyl orange to turn red. After about ten minutes the red color faded and a little flocculent deposit was noted due to the decomposition of the hydride. Postulating the acid nature,

$$HCo(CO)_4 \rightleftharpoons H^+ + Co(CO)_4^-$$

and making rough estimates of the amount of acid and its neutral salt indicate an ionization constant between that of acetic acid, 1.8×10^{-5}, and that of formic acid, 2×10^{-4}.

It is hard to understand Hieber's point of view, but certainly, according to all ordinary standards, the acid-to-salt relation holds between the cobalt carbonyl hydride and its sodium, potassium, and barium salts. The latter are soluble; although they have not been isolated in the dry condition they must exist in water solution in the ionized condition. It is true, of course, that the mercuric and silver derivatives are insoluble in water and soluble in organic solvents,—benzene, acetone, chloroform, ether,—and, perhaps, complete salt-like nature should not be attributed to them.

IRON CARBONYLS

There are three different well-defined iron carbonyls,—the pentacarbonyl, $Fe(CO)_5$, the tetracarbonyl, $[Fe(CO)_4]_3$, and the enneacarbonyl, $Fe_2(CO)_9$. Of these, the pentacarbonyl is the only one which is distinctly volatile, and it is the only one which can be prepared directly from the metal and carbon monoxide.

Preparation of iron pentacarbonyl

Iron pentacarbonyl is prepared on a large scale by industrial processes (75). It is in general prepared by the action of carbon monoxide upon finely divided iron reduced from the oxide or some other iron compound. High pressure and somewhat elevated temperature (up to 200°C.) work advantageously. Oxygen and carbon disulfide vapor decrease the activity of the iron. Hydrogen sulfide is reported to be without effect.

In addition to its poisonous effects, iron pentacarbonyl is dangerous on account of the liability of spontaneous combustion. This danger is lessened by the common practice of mixing it with kerosene or other organic solvents.

Properties of iron pentacarbonyl

In contact with air iron pentacarbonyl is oxidized, ferric oxide (Fe_2O_3) is deposited, and usually carbon monoxide is set free, although under some conditions carbon dioxide is formed. Spontaneous ignition frequently occurs, and the products of burning are ferric oxide and carbon dioxide. When it is shaken with a large amount of distilled water and hydrogen peroxide a deep red transparent ferric oxide sol can be prepared that will remain clear for from two to three months (18, 16).

Halogens do not react as rapidly or as definitely as with nickel carbonyl. The tendency is to form ferrous or ferric halide with liberation of carbon monoxide, but intermediate stages can be identified. At low temperature the addition compounds $Fe(CO)_5X_2$ (X = halogen) can be isolated. At room temperature these lose carbon monoxide to leave $Fe(CO)_4X_2$. With water complete change to the salt-like form of FeX_2 occurs and all of the carbon monoxide escapes (26, 27).

Dilute acids are without effect. Solutions of hydrogen chloride and hydrogen bromide in chloroform and anhydrous gaseous hydrogen iodide give ferrous halide, carbon monoxide, and free hydrogen (55).

Preparation of iron enneacarbonyl

Subjected to the action of sunlight iron pentacarbonyl, either pure or in solvents or in the vapor form, decomposes (89).

$$2Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO$$

The yellow to orange crystals may be washed free of surplus pentacarbonyl with ether. The above reaction is subject to a slow reversal in the dark.

The enneacarbonyl is insoluble in ether, petroleum ether, and benzene, somewhat soluble in alcohol, and more so in pyridine.

Its decomposition begins at about 80°C. and proceeds according to the following reactions, depending on pressure, solvents, etc.,

$$2Fe_2(CO)_9 \rightarrow 2Fe(CO)_5 + 2Fe(CO)_4$$

$$2Fe(CO)_4 \rightarrow Fe(CO)_5 + Fe + 3CO$$

The dry crystals of iron enneacarbonyl are very stable in dry air. Moistened with iron pentacarbonyl they quickly lose their luster and frequently ignite spontaneously.

The halogens decompose the enneacarbonyl; for example, bromine water dissolves the crystals and carbon monoxide is liberated. The reactions of the halogens are not as complete as with nickel carbonyl and an intermediate compound, $Fe_2(CO)_7Br_4$, has been identified (21).

Dilute hydrochloric and sulfuric acids have no action on the enneacarbonyl.

Potassium hydroxide dissolves the enneacarbonyl.

Preparation of iron tetracarbonyl

In general, iron tetracarbonyl is a product of the regulated thermal decomposition of iron enneacarbonyl (15, 17, 11). Specifically, if 1 part of the enneacarbonyl and 20 parts of toluene are heated in a sealed, air-free tube to 95°C. with shaking until the crystals have disappeared, and then the tube is allowed to cool slowly, green crystals of the tetracarbonyl separate out. These crystals may be washed with toluene.

Iron tetracarbonyl is soluble in benzene, petroleum ether, ether, acetone, nickel carbonyl, and iron pentacarbonyl. The solutions are dark green.

A very effective method of preparing iron tetracarbonyl direct from the pentacarbonyl has been devised by Hieber and Leutert (32). The pentacarbonyl is shaken with alkali, barium hydroxide or sodium methoxide, and a suspension of manganese dioxide is added. The pentacarbonyl disproportionates with the formation of the hydride.

$$Fe(CO)_5 + Ba(OH)_2 \rightarrow Fe(CO)_4H_2 + BaCO_3$$

$$Fe(CO)_5 + CH_3ONa + H_2O \rightarrow Fe(CO)_4H_2 + CH_3O \cdot CO \cdot ONa$$

The hydride is oxidized:

$$Fe(CO)_4H_2 + MnO_2 \rightarrow 1/3[Fe(CO)_4]_3 + H_2O + MnO$$

The excess of manganese dioxide is dissolved with ferrous sulfate and sulfuric acid and the iron tetracarbonyl is collected on a filter.

Iron carbonyl hydride, $Fe(CO)_4H_2$

As outlined in the preceding paragraph, treatment of iron pentacarbonyl with alkalies yields iron tetracarbonyl hydride, or its salt. In alkaline solution the hydride is comparatively stable except from attack by oxidizing agents; it is particularly susceptible to air and it can be prepared only in oxygen-free atmospheres. The stability of the hydride in alkalies is quite obviously a consequence of salt formation, although Hieber at first strongly contested this view. However, when the solution is acidified the free acid is formed. This is extremely unstable and breaks down in a variety of ways, liberating hydrogen and other products. By immediate vacuum distillation of the acidified solution or by sweeping with carbon monoxide the volatile hydride can be transferred to a trap cooled with liquid air and obtained in a pure condition.

The iron tetracarbonyl hydride was first isolated and identified by Hieber and Leutert (30). Previous to that its existence had been surmised. Hock and Stuhlman (47) treated iron pentacarbonyl with mercuric salts,

$$Fe(CO)_5 + HgSO_4 + H_2O \rightarrow Fe(CO)_4Hg + H_2SO_4 + CO_2$$

obtaining the mercury compound as a dark yellow precipitate insoluble in water, acids, acetone, ether, and pyridine. This compound decomposes at 150°C. into carbon monoxide, mercury, and iron. With excess mercuric sulfate the salt $Fe(CO)_4Hg \cdot HgSO_4$ is obtained; it is somewhat soluble. With mercuric chloride the salt $Fe(CO)_4Hg_2Cl_2$ is obtained.

Feigl and Krumholz (12) acidified the salts of $H_2Fe(CO)_4$ and, by sweeping with carbon monoxide into a solution of mercuric salt, succeeded in carrying over a volatile compound which again precipitated the same mercury compound. Feigl and Krumholz (13) also prepared $[Fe(CO)_4]NaH \cdot CH_3OH$ and the corresponding ethyl alcoholate by treating iron pentacarbonyl with sodium methylate and sodium ethylate in alcohol solution. They believed that the salt-like nature of these compounds, that is, the ionic character of $Fe(CO)_4^{--}$, was demonstrated by the precipitation with metal ammine solutions of such complexes as $[Fe(CO)_4]$-$[Cd(NH_3)_6]$ and $[Fe(CO)_4H]_2[Fe(o\text{-phthr})_3]$.

Coleman (9) found the acid strength of the iron carbonyl hydride much less than that of the cobalt carbonyl hydride. He condensed the vapors in a trap cooled with solid carbon dioxide; after sweeping out all carbon dioxide from the trap he allowed the trap to warm up slowly and then swept the carbonyl hydride vapors into a rotary absorption tower containing indicators. Methyl orange and methyl red were not affected, but phenolphthalein, reddened with a drop of 0.1 *N* potassium hydroxide, was quickly decolorized. In fact, the absorption of the carbonyl hydride could be sharply followed by titration with the 0.1 *N* potassium hydroxide, several cubic centimeters of which were used. The acid strength of iron carbonyl hydride is thus of about the same order of magnitude as that of carbonic acid.

Iron nitrosyl carbonyl

Mond and Wallis (80) in 1922 showed that a volatile nitrosyl carbonyl was formed by the action of nitric oxide on iron enneacarbonyl, but they were unable to separate it from the pentacarbonyl formed at the same time and they did not derive its correct formula. Nitric oxide does not react with iron pentacarbonyl alone, and it does not react completely with the enneacarbonyl nor with the tetracarbonyl alone. But Anderson (1) in 1932 used a solution of iron tetracarbonyl in iron pentacarbonyl, allowing nitric oxide to act at 95°C. with a return condenser. The mixture of pentacarbonyl and nitrosyl carbonyl was separated by fractionation at -15°C. At 0°C. the vapor pressures are as follows: $Fe(CO)_5$, 6 mm.; $Fe(CO)_2(NO)_2$, 4.5 mm. At -15°C. the difference is greater. The fractionation was continued until the melting point indicated the purity of the nitrosyl carbonyl.

The iron nitrosyl carbonyl has the formula $Fe(CO)_2(NO)_2$. It consists of dark red crystals melting at 18.5°C. The red liquid easily supercools. It is generally soluble in organic solvents but not in water. Its vapor decomposes considerably at 70°C. and a little even at -15°C. It is quickly oxidized by air and the halogens. Bromine liberates nitric oxide and carbon monoxide completely, but the latter is partly converted to bromphosgene. Iodine in benzene solution liberates carbon monoxide, a small part of which is oxidized to carbon dioxide, and the compound $Fe(NO)_2I_2$ can be isolated. The latter reacts with silver giving silver iodide, and no gas escapes. This may indicate that a polymer $[Fe(NO)_2]_n$ is formed. Aqueous hydrogen peroxide and sodium hydroxide liberate carbon monoxide with a considerable amount of carbon dioxide and the nitric oxide is converted to a mixture of sodium nitrite and nitrate.

Non-volatile iron nitrosyls

Two non-volatile iron nitrosyls which contain no carbonyl groups have been reported. Manchot and Gall (68) shook 10 cc. of iron pentacarbonyl and 50 cc. of anhydrous methyl alcohol at room temperature for twenty-four hours with nitric oxide and obtained a completely black precipitate which seemed to have the formula $FeNO \cdot 2CH_3OH$. Manchot and Enk (61) placed about 1 cc. of iron pentacarbonyl in a glass tube and condensed solid nitric oxide by immersing the tube in liquid air. The open tube was placed in a brass autoclave filled with nitric oxide, and the autoclave was slowly warmed to 44–45°C. and kept at that temperature. More rapid heating to higher temperature caused explosive reactions. After some time the autoclave was cooled with carbon dioxide and acetone, and opened; the glass tube was found filled with matted, thread-like, black crystals. These would smoke in the air as they warmed up and nitric oxide would escape, but the crystals themselves appeared to be not volatile. Analysis showed the formula $Fe(NO)_4$ and complete absence of carbon monoxide. These crystals reacted strongly with ammonia, pyridine, and hydrazine, but the products were not identified.

$Fe(NO)_2I_2$ has been mentioned above.

$Fe_2(NO)_4I_3$ has been prepared by Hieber and Bader (27). Nitric oxide does not react with $Fe(CO)_4I_2$ below its decomposition temperature of 75°C., but when the latter is held in a current of nitric oxide at 75–80°C. it melts and all of the carbon monoxide is expelled quickly together with some iodine; there is left after cooling a black solid of the composition $Fe_2(NO)_4I_3$. This is barely sublimable in a current of nitrogen. It is unstable in air. With pyridine and dilute acids nitric oxide is rapidly evolved and a ferrous salt is left. Dry heating drives off nitric oxide.

Mixed ammine complexes of the iron carbonyls

The number of complex substances derived from iron carbonyls which have been identified is very large. This may be attributed to two reasons: first, the practical one that the reactions of iron carbonyl have been most extensively studied; and second, the theoretical reason that since the electron requirements of the iron atom can not be satisfied in so simple a manner as that of nickel in nickel carbonyl, the number of ways in which this may be accomplished is multiplied.

The following tabulation of mixed carbonyl ammine complexes compiled by Hieber and Becker in 1930 (28) shows the range of 5, 3, 2.5, and 2 moles of carbon monoxide per atom of iron.

$Fe(CO)_5NH_3$ $Fe(CO)_5en$*	$Fe(CO)_3(NH_3)_2$ $Fe(CO)_3py$ $Fe(CO)_3en$ $Fe_4(CO)_{12}en_3$ $Fe(CO)_3\cdot CH_3OH$	$Fe_2(CO)_5en_2$	$Fe_2(CO)_4py_3$ $Fe_2(CO)_4en_3$

* py = pyridine; en = ethylenediamine.

It has already been noted that in the formation of mixed ammine and alcohol neutral complexes of cobalt and nickel, the carbonyl groups are never wholly replaced by the other groups. The same statement holds for iron carbonyls. The only compounds of iron in which the carbonyl groups are entirely replaced by zero valent groups are the nitrosyls $FeNO\cdot CH_3OH$ and $Fe(NO)_4$, mentioned in the preceding section. It is to be noted that these compounds are not volatile and that their chemical nature is as yet very obscure.

Iron pentacarbonyl does not react directly with anhydrous ammonia, or even with liquid ammonia, and the same is true of the ennea- and tetracarbonyls. In the presence of pyridine, however, the ammonia compound, $Fe(CO)_3(NH_3)_2$, has been prepared (44).

With pyridine alone, iron pentacarbonyl reacts vigorously, carbon monoxide escaping; at first no definite compounds could be isolated (42), but later, when 5 moles of pyridine were used to 1 mole of iron pentacarbonyl, red crystals of $Fe(CO)_5py$ were isolated (43). After a few days a more abundant crop of crystals of $Fe(CO)_4py$ was obtained, and after ten to fourteen days, crystals of $Fe(CO)_4py_2$. Removal of the carbon monoxide was necessary to obtain the last-named product; in other words the replacement of carbon monoxide by pyridine is a reversible reaction. These mixed complexes are formed as crystalline compounds only under very special conditions,—often very low temperature, and always absence of air and moisture. When isolated, such complexes show no sign of being volatile without decomposition, but they are always of little stability. The pyridine complexes just mentioned are pyrophoric. A further pyridine complex of the formula $Fe_2(CO)_4py_3$ was isolated (44) and when iodine also was present a substance of the formula $Fe(CO)_3py_2I_2$ could be separated; the latter on standing in pyridine finally gave $FeI_2 \cdot 6C_5H_5N$. The last is either a completely polar compound or it needs only an ionizing solvent to make it so.

The straight carbonyls are without action with dilute non-oxidizing acids. The substituted carbonyls, particularly where the substituents are basic amines, react readily with acids. In such cases the amines are removed as the hydrochlorides, the CO groups are reapportioned, and ferrous ions are produced at the expense of hydrogen liberated. A few examples of such behavior are shown by the following equations:

$$Fe(CO)_3py_2 + 4HX \rightarrow FeX_2 + 2C_5H_5N \cdot HX + 3CO + H_2$$

$$2Fe(CO)_3py_2 + 6HX \rightarrow FeX_2 + Fe(CO)_4 + 4C_5H_5N \cdot HX + 2CO + H_2 \quad (43)$$

$$2Fe_2(CO)_4py_3 + 12H^+ \rightarrow 3Fe^{++} + Fe(CO)_4 + 6C_5H_5N \cdot H^+ + 3H_2 + 4CO \quad (44)$$

$$Fe_2(CO)_5en_2 + 6HX \rightarrow FeX_2 + Fe(CO)_5 + 2C_2H_4(NH_2)_2 \cdot HX + H_2$$

$$Fe_2(CO)_4en_2 + 6HX \rightarrow FeX_2 + Fe(CO)_4 + 2C_2H_4(NH_2)_2 \cdot HX + CO + H_2 \quad (42)$$

Mixed halogen carbonyl complexes

In the absence of water and of solvents which may form solvates, the halogens seem to be able to play somewhat the same rôle in complex building as do the carbonyl, nitrosyl, and amine groups. For example, dry halogen and dry iron pentacarbonyl yield $Fe(CO)_4X_2$ with liberation of one CO (26). Excess of halogen fails to displace more than one CO. These complexes are shown to be monomolecular by the freezing-point method in indifferent solvents (27, 36). $Fe(CO)_4Cl_2$ is pure yellow. It decomposes at 10°C. into $FeCl_2$ and 4CO. The corresponding bromide,

$Fe(CO)_4Br_2$, is darker colored and decomposes at 55°C. $Fe(CO)_4I_2$ is deep brown and decomposes at 75°C. These halogen complexes cannot be prepared from the simple iron halides and carbon monoxide. The complexes decompose with water,

$$Fe(CO)_4X_2 + aq \rightarrow FeX_2 \cdot aq + 4CO$$

instantly in the case of the chloride, slowly in the case of the iodide. Similar decompositions take place with ammonia, amines, alcohols, esters, ketones, and aldehydes. On the other hand, all three of these carbonyl halides are stable in glacial acetic acid.

Just as addition products of iron pentacarbonyl with amines, e.g., $Fe(CO)_5en$ (43) can be isolated, prior to the escape of carbon monoxide, so in similar manner addition products with the halogens have been isolated without escape of carbon monoxide. Equimolal amounts of $Fe(CO)_5$ and of halogen in ether or petroleum ether at −80°C. give a precipitate of $Fe(CO)_5X_2$. The chloride is yellow, the bromide is a darker yellow, and the iodide is a deep brown-red solution. The chloride decomposes at −35°C. into $Fe(CO)_4Cl_2$ and carbon monoxide; the bromide decomposes at −10°C., and the iodide only at 0°C.

TABLE 7

Mixed carbonyl halides

$Fe(CO)_5X_2$*	$Fe(CO)_4X_2$	$Fe(CO)_3Hg_2I_2$	$Fe(CO)_2py_2I_2$	$Fe(CO)py_2I_2$
	$Fe(CO)_4en_2I_2$		$Fe(CO)_2(o\text{-phen})_2I_2$	
			$Fe(CO)_2(o\text{-phthr})_2I_2$	$[Fe(CN)_2(CO)]K_3$
			$Fe(CO)_2(CN)_2py$	

* X = Cl, Br, or I; *o*-phen = *o*-phenylenediamine; *o*-phthr = *o*-phenanthroline.

A particularly stable substnace is obtained (27) by treating diiron tetracarbonyl tripyridine with cyanogen

$$Fe_2(CO)_4py_3 + 2(CN)_2 \rightarrow 2Fe(CO)_2(CN)_2py + C_5H_5N$$

The substance is stable up to 100°C. and is not decomposed by potassium cyanide, acids, or pyridine.

Hieber and Bader give an interesting table (table 7) of the mixed carbonyl halides, showing a complete range from one to five carbonyl groups for each iron atom.

REACTIONS OF NITROSYL CARBONYLS WITH AMINES

The nitrosyl carbonyls show much the same kind of behavior with amines as do the straight carbonyls, but it is noteworthy that in such reaction only the carbonyl group is displaced. For example, Hieber (25) reports the formation of the following complexes: $Fe_2(NO)_4py_3$; $Fe(NO)_2$(*o*-phthr); $Co_2(NO)_2COpy_2$; $CoNO(CO)_2$(*o*-phthr); CoNOCO(*o*-phthr). The halogens on the other hand, as already mentioned, displace both carbon monoxide and nitric oxide with the formation of cobaltous and ferrous halides. Chlorine and bromine do so without the formation of intermediate products, while iodine in benzene solution displaces the carbon monoxide and the intermediate product $Fe(NO)_2I_2$ can be separated.

Anderson and Hieber find in the easier displacement of carbon monoxide evidence for a different electronic binding of carbon monoxide and nitric oxide to the central atom. For carbon monoxide they find the bonding to be of the "coördinative covalence" type (i.e., M:C:::O:, as designated earlier in this paper under formula I, p. 9), whereas for nitric oxide they hold that the bonding is a composite of the coördinative covalence and pure covalence types (M::N::O::, as shown in formula II).

Although it is recognized that either type I or type II is a possible method of bonding for either carbon monoxide or nitric oxide, it hardly seems probable that replacement of CO by NO in a series of complexes of such very similar properties as $Ni(CO)_4$, $Co(NO)(CO)_3$, and $Fe(NO)_2(CO)_2$ should be accompanied by a change of the electron symmetry of the central atom. It is far simpler to attribute the greater tenacity of the nitric oxide bonding to the different distribution of the positive kernel charges.

RUTHENIUM CARBONYLS

It had been known for some time that metals of the platinum family as well as copper, silver, gold, and mercury could form mixed carbonyl compounds, many of them capable of being sublimed. In fact, Mond had prepared a straight carbonyl of ruthenium (76, 80) by heating ruthenium sponge in carbon monoxide under a pressure of 400 atmospheres at 300°C. He obtained a yellow-orange precipitate and a metal mirror in the tube. The yellow compound was insoluble in hydrochloric acid but dissolved in nitric acid and bromine water with evolution of carbon monoxide. Its composition approximated the formula $Ru(CO)_2$.

It remained, however, for Manchot and Manchot (73) in 1936 to show that ruthenium can form a very volatile carbonyl,—in fact, a series of carbonyls closely resembling iron pentacarbonyl, iron enneacarbonyl, and and iron tetracarbonyl, the pentacarbonyl being the volatile member of the series with ruthenium as well as with iron. The volatile ruthenium carbonyl stands in the same relation to the inert gas xenon that iron pentacarbonyl does to krypton.

The pentacarbonyl was first prepared by these men from ruthenium sponge and carbon monoxide at 700 atmospheres and 400°C. The high pressure was produced by condensing the carbon monoxide with liquid nitrogen in a brass vessel connected with the autoclave containing the ruthenium sponge. Accumulation of the pentacarbonyl in the ruthenium sponge soon inhibited the reaction, but occasional opening of the exit valve allowed this to be swept out and its formation in the autoclave to proceed. The vapors of the ruthenium pentacarbonyl were condensed at low temperature from the carbon monoxide stream. A more effective method of preparing the pentacarbonyl was soon devised: A mixture of 1 g. of ruthenium triiodide and 5 g. of finely divided silver subjected in an autoclave to carbon monoxide under 455 atmospheres at 170°C. gave in twenty-four hours a large yield of the pentacarbonyl.

Ruthenium pentacarbonyl condenses to colorless crystals which melt at -22°C. to a colorless liquid of high vapor pressure. The liquid decomposes slowly above its melting point into the enneacarbonyl, $Ru_2(CO)_9$. However, by working rapidly in a vacuum the liquid may be completely vaporized to a colorless gas, which can again be condensed at -23°C. to colorless crystals or supercooled liquid.

Ruthenium pentacarbonyl is soluble in benzene, alcohol, etc., but it is unstable in these solvents. Like iron pentacarbonyl it decomposes in the light. Ruthenium pentacarbonyl vapors passed into a concentrated (1:1) potassium hydroxide solution give a brown-red solution of strong reducing properties.

From the breakdown of the pentacarbonyl the enneacarbonyl is obtained. This is an orange colored substance. It is quite stable against air and light, and it can be sublimed. Its decomposition yields a green substance which is probably the polymer of the tetracarbonyl, although a reliable analysis has not been achieved.

From the enneacarbonyl and iodine the mixed carbonyl halide, $Ru(CO)_2I_2$, is obtained. The latter, warmed with silver in a current of carbon monoxide, gives the pentacarbonyl.

This carbonyl halide had been prepared in 1924 by Manchot and König (69) by heating ruthenium triiodide in a current of carbon monoxide at atmospheric pressure at 250°C. The residue, $Ru(CO)_2I_2$, is an ochre-colored powder, very unreactive toward hydrochloric and concentrated sulfuric acids and insoluble in organic solvents. Similar compounds, $Ru(CO)_2Br_2$ and $Ru(CO)_2Cl_2$, were prepared. These can be sublimed. The enneacarbonyl, heated to 190°C. under high pressure in nitric oxide, yields a red nitrosyl, free from carbon monoxide; the uncertain analysis indicates its formula as $Ru(NO)_4$ or $Ru(NO)_5$, and it would seem to correspond to the non-volatile iron nitrosyl $Fe(NO)_4$.

CARBONYLS OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

A volatile carbonyl of molybdenum was prepared as early as 1910 by Mond (76) by direct synthesis at high pressure and temperature. The amount obtained was small and the analysis, giving the formula $Mo_5(CO)_{26}$, was uncertain. The pressure method for obtaining molybdenum and tungsten carbonyls, $Mo(CO)_6$ and $W(CO)_6$, in larger amounts was improved and patents were taken out by the I. G. Farbenindustrie A.-G. (49) in 1931. Chromium, however, utterly fails to yield the carbonyl in this manner.

Meanwhile, Job and Cassal (51) had applied to the problem the discoveries of Job and Reich regarding the behavior of carbon monoxide and the Grignard reagent in the presence of metal salts. Carbon monoxide is absorbed with reasonable rapidity about in proportion to the Grignard reagent used when a little chromic chloride is present. Upon hydrolysis of the Grignard mixture an amount of chromium hexacarbonyl small in proportion to the carbon monoxide used is recovered. Small as the yield is, the substance is obtained in great purity and in amount sufficient for its identification and a study of its properties. Later the same method was employed with molybdenum pentachloride and tungsten hexachloride for the preparation of the hexacarbonyls of molybdenum and tungsten, respectively.

Chromium hexacarbonyl was prepared in 1934 by this method by Windsor and Blanchard (92), who confirmed the formula $Cr(CO)_6$ by analysis and vapor density measurements. The vapor pressure ranges from 0.04 mm. at 0°C. to 66.5 mm. at 100°C. At 100°C. slow decomposition takes place and interferes with the vapor pressure determination.

Hieber and Romberg (37) in 1935 prepared the hexacarbonyls of chromium, molybdenum, and tungsten by the Grignard method. All three form beautiful, colorless, strongly refracting crystals. The hexacarbonyls are remarkably stable in comparison with the other carbonyls, the vapors decomposing noticeably only at about 120°C. and thereby depositing a very pure metallic mirror. At ordinary temperature concentrated hydrochloric and sulfuric acids are without effect; chromium carbonyl is in fact stable toward bromine and iodine. Concentrated nitric acid oxidizes the hexacarbonyl rapidly. With alkalies there is no formation of carbonate or of carbonyl hydride; in this respect the behavior is the same as that of nickel carbonyl. The reaction with halogens does not give carbonyl halides, but the displacement of carbon monoxide is quantitative.

$$2Cr(CO)_6 + 3Cl_2 \rightarrow 2CrCl_3 + 12CO \text{ (with some phosgene)}$$

$$Mo(CO)_6 + 2Br_2 \rightarrow MoBr_4 + 6CO$$

$$W(CO)_6 + 3Br_2 \rightarrow WBr_6 + 6CO$$

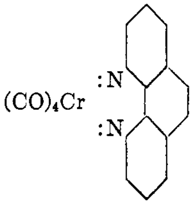
The volatility of the hexacarbonyls decreases slightly in the order chromium, molybdenum, tungsten. Extrapolating from the vapor pressure curves Hieber and Romberg (38) obtained the following boiling points: $Cr(CO)_6$, 420.5°A.; $Mo(CO)_6$, 429.4°A.; $W(CO)_6$, 448.0°A.

Amine-substituted carbonyls

The greater stability of these hexacarbonyls as compared with the carbonyls of nickel, cobalt, and iron is also reflected in the greater difficulty with which amine substitutions are effected (34, 39). Hieber and Mühlbauer and Hieber and Romberg have succeeded in isolating the following compounds:

$Cr(CO)_4py_2$	$Mo(CO)_3py_3$	$W(CO)_3py_3$
$Cr_2(CO)_7py_5$	$Mo(CO)_3py_2$	$W(CO)_4py_2$
$Cr(CO)_3py_3$	$Mo(CO)_4$(*o*-phthr)	$W(CO)_4$(*o*-phthr)
$Cr(CO)_4$(*o*-phthr)*	$Mo(CO)_3py$(*o*-phthr)	$W(CO)_3py$(*o*-phthr)
$Cr_2(CO)_6py_3$	$Mo_2(CO)_6en_3$	

*



The behavior of these amine-substituted carbonyls with acids is very similar to that of the corresponding compounds of nickel, cobalt, and iron; the carbonyl groups are reapportioned with the formation of hexacarbonyl and escape of carbon monoxide, and metal ions and a corresponding amount of free hydrogen are formed.

The following equations are given as typical (34):

$$3Mo(CO)_3py_3 + 15HCl \rightarrow Mo(CO)_6 + 2[MoCl_6](py\cdot H)_3 + 3C_5H_5N\cdot HCl + 3CO + 3H_2$$

$$4Mo(CO)_4py_3 + 21HCl \rightarrow Mo(CO)_6 + 3[MoCl_6](py\cdot H)_3 + 3C_5H_5N\cdot HCl + 6CO + 4.5H_2$$

$$3Cr(CO)_3py_3 + 15HCl + 2H_2O \rightarrow Cr(CO)_6 + 2[CrCl_5(OH_2)](py\cdot H)_2 + 5C_5H_5N\cdot HCl + 3CO + 3H_2$$

BORINE CARBONYL

Burg and Schlesinger (8) have very recently shown the existence of a compound of the formula BH_3CO. This substance can exist in gaseous mixture in equilibrium with diborane and carbon monoxide,

$$2BH_3CO \rightleftharpoons B_2H_6 + 2CO$$

an idea of its stability being given by the statement that a sample of pure BH_3CO at an initial pressure of 200 mm at 100°C. would be 95 per cent decomposed when equilibrium was reached (neglecting minor side reactions in which a little hydrogen and some less volatile products are produced). It is best prepared by heating a mixture of carbon monoxide and diborane at 90°C. for 15 min.; under these conditions the gaseous equilibrium mentioned above is practically attained. The borine carbonyl may be isolated by condensation at low temperatures. At -111.8°C. its vapor pressure is 25.4 mm. Its melting point is estimated at -137°C., and its boiling point at -64°C. It hydrolyzes according to the equation

$$BH_3CO + 3H_2O \rightarrow B(OH)_3 + 3H_2 + CO$$

the reaction being quantitative after three hours at 100°C. From the volume changes during formation and decomposition this substance is shown to be monomolecular according to the formula BH_3CO.

The above authors were interested in the study of this compound as a means of indicating the transitory existence of monomolecular borine, BH_3. The electron arrangement of the ordinary diborane, B_2H_6, is still a puzzle. For the borine carbonyl they favor the structure in which "borine and carbon monoxide are joined by a coördinate link consisting of electrons furnished by the carbon monoxide". This would correspond to the carbonyl linkage I (see p. 9) as follows: $H_3B{:}C{:}{:}{:}O{:}$ and boron would have the effective atomic number of 10. Carbonyl linkage II would not fit this compound.

It is very evident that borine carbonyl has the distinguishing characteristics of the volatile metal carbonyls and should be included in that classification.

CARBONYL HALIDES OF THE NOBLE METALS

Platinum compounds with carbon monoxide were first prepared in 1868 by Schützenberger (87), who passed chlorine and carbon monoxide over platinum sponge at 250°C. and obtained a yellow sublimate (or liquid which crystallized on cooling). This sublimate dissolved in carbon tetrachloride and three distinct compounds were isolated: $PtCl_2 \cdot CO$, $PtCl_2 \cdot 2CO$, and $2PtCl_2 \cdot 3CO$. These compounds are convertible into one another under the right conditions. They dissolve unchanged in carbon tetrachloride but are decomposed with water:

$$PtCl_2 \cdot CO + H_2O \rightarrow Pt + 2HCl + CO_2$$

The other two carbonyl halides give the same products and the surplus carbon monoxide escapes. Schützenberger's experiments were confirmed much later by others, especially Mylius and Foerster (81) and Manchot (59). By treating a carbon tetrachloride solution of the platinum compounds with ammonia the compounds $PtCl_2 \cdot CO \cdot 2NH_3$ and $PtCl_2 \cdot 2CO \cdot 2NH_3$ were isolated; with ethylene the compound $PtCl \cdot CO \cdot C_2H_3$ was isolated. Manchot made use of the volatility of the platinum chloride carbonyls as a practical method of separating platinum from palladium.

Iridium. Manchot and Gall prepared a similar sublimable carbonyl chloride of iridium (64). Dry iridium trichloride in a current of completely dry carbon monoxide at 150°C. yields a white, sublimable, crystalline substance of the composition $Ir(CO)_2Cl_2$. This decomposes in water with the evolution of carbon monoxide.

Osmium. Manchot and König (70) heated osmium trichloride in a stream of carbon monoxide at 1 atmosphere at 270°C. and obtained a white sublimate whose composition approximated the formula $OsCl_2 \cdot 3CO$. This compound is indifferent to water and acids. It dissolves in sodium hydroxide solution; after neutralization with nitric acid all of the chlorine is precipitated by silver nitrate, leaving the osmium and carbon monoxide in solution as an apparently stable complex.

Palladium forms the least stable halogen carbonyl complex of all of the platinum metals. Complexes of the others can be sublimed away leaving only the palladium untouched. At low temperature, however, Manchot and König (72) succeeded in isolating a compound of the composition $PdCl_2 \cdot CO$. Strangely enough, the presence of alcohol favored the formation of this compound. Dry carbon monoxide saturated with the vapor of methyl alcohol was passed over dry $PdCl_2$ at 0°C. and the latter was converted to the light yellow-brown complex. The latter is decomposed by water.

$$PdCl_2 \cdot CO + H_2O \rightarrow Pd + CO_2 + 2HCl$$

Rhodium differs from the other platinum metals in that no simple carbonyl halide has been discovered, but the compound $RhCl_2 \cdot RhO \cdot 3CO$, prepared by Manchot and König (71), excells all of the carbonyl halides of this series in volatility. No results were obtained by heating anhydrous rhodium trichloride in carbon monoxide even to high temperatures, but when carbon monoxide was passed over moist rhodium trichloride a change began at 50°C. At 140°C. beautiful, ruby-red, needle-like crystals sublimed, sometimes 3 cm. in length. At 300°C. decomposition of the substance takes place with the deposit of a metallic mirror. Analysis gives the formula as shown above, and the molecular weight by the freezing-point method in benzene corresponds closely to that formula. The substance dissolves with difficulty in cold water, but more rapidly in warm water with an orange-red color. On further warming or after a long time in the cold the solution grows cloudy and metallic rhodium deposits. At 125.5°C. the substance melts to a brown liquid; meanwhile a part vaporizes with a strong blue fluorescence. It is somewhat volatile at ordinary temperature, because on standing the walls of the vessel become dark. It is soluble in carbon tetrachloride, benzene, and glacial acetic acid.

Ruthenium trihalides react with carbon monoxide according to the equation

$$RuX_3 + 2CO \rightarrow Ru(CO)_2X_2 + 1/2\, X_2$$

At 250°C. and 1 atmosphere the black triiodide reacts completely in 30 min., an ochre-colored residue remaining and iodine vapors escaping. This residue of $Ru(CO)_2I_2$ is insoluble in water and in organic solvents. It is very resistant to concentrated hydrochloric acid and concentrated sulfuric acid (69).

The similar reaction with ruthenium tribromide is very much slower, but, unlike the carbonyl iodide, the product, $Ru(CO)_2Br_2$, sublimes and is obtained distinct from the unaffected residue. At very high carbon monoxide pressure at 185–188°C. there is a further reduction of the bromide to RuCOBr (62). This new carbonyl bromide is a colorless crystalline substance. Heated to 200°C. in an indifferent gas it disproportionates into $Ru(CO)_2Br_2$, which sublimes, and ruthenium.

The ruthenium trichloride reacts with carbon monoxide much more slowly than the iodide or the bromide. The product is the same, $Ru(CO)_2Cl_2$, and it sublimes away from the unaffected residue even more easily than the carbonyl bromide. High pressure of carbon monoxide fails to produce a compound similar to RuCOBr, but it does give a very small quantity of a halogen-free product which appears to be identical with the non-volatile carbonyl of Mond. This halogen-free carbonyl is also produced in small amounts from the iodide.

Copper. The familiar use of either acidic or ammoniacal solutions of cuprous chloride as an absorbent for carbon monoxide in gas analysis rests on the formation of a copper carbonyl halide. Manchot and Friend (63) found the upper limit of the absorption ratio CO:CuCl to be 1:1. At 0°C. they succeeded in obtaining colorless crystals of the composition $CuCl \cdot CO \cdot 2H_2O$ independent of whether the solution were acid, neutral, or weakly ammoniacal. These crystals immediately began to give off carbon monoxide when taken out of the atmosphere of that gas.

Silver. The absorption of carbon monoxide by silver salt under very unusual conditions has been observed by Manchot (60). Aqueous silver salt solutions have no action with carbon monoxide, but sulfuric acid solutions do absorb the gas, in fact, the more concentrated the solution, even up to fuming acid of 50 per cent SO_3 content, the greater the absorption. It is evident that the effect of the sulfuric acid is due to its dehydrating action, because similar effects are obtained by adding phosphoric anhydride to the dilute solutions. The maximum absorption ratio is 1CO to $1Ag_2SO_4$, and the formula of the complex is deduced as $Ag_2SO_4 \cdot CO$.

Gold. Anhydrous gold trichloride, subjected to the action of dry carbon monoxide, begins to show a sublimate at 55°C. At higher temperatures the reaction is more rapid, but reduction to metallic gold complicates the process. The best procedure (65) proved to be to pass dry carbon monoxide mixed with 10 per cent of dry chlorine over dry gold trichloride at 115–120°C.

A similar sublimate was obtained with AuCl and carbon monoxide (without the chlorine). The sublimate consisted of beautiful, lustrous, colorless, very transparent crystals several millimeters in length. The substance is extraordinarily sensitive to water, even to the moisture of the air. The ratio Au:Cl:CO in the substance was shown to be 1:1:1, which indicates the composition $AuCl \cdot CO$.

Mercury. Alcoholic mercuric acetate absorbs carbon monoxide freely, but there is controversy over the nature of the product. Schoeller, Schrauth, and Essers (85) regard it as a mercury-substituted ester of formic acid, $CH_3COOHg \cdot CO \cdot OR$; Manchot (58) regards it as a carbonyl with the characteristic metal-carbonyl bond, $CO \cdot Hg(OC_2H_5)(COOCH_3)$.

DISCUSSION

It is very difficult to appraise the significance of the volatility of the carbonyl halides of the platinum metals. It is quite clear that the volatility is of a lower order of magnitude than that of the carbonyls that have been listed as volatile. Even chromium carbonyl (vapor pressure 0.26 mm. at 20°C.) has probably a much higher vapor pressure than the most volatile of the carbonyl halides, $RuCl_2 \cdot RhO \cdot 3CO$, which is the only one to show evidence of vaporization at room temperature. No vapor density determinations of the carbonyl halides have been made, and there is no certainty that dissociation does not take place during the process of sublimation (as with ammonium chloride). It would seem nearly certain that the carbonyl linkage to the metal atom is the same as in the volatile carbonyls, because even although the breakup of the complex often gives carbon dioxide, owing to the oxidation of the carbonyl group, there is clear evidence of the dissociability of the carbonyl linkage in this series of compounds.

The great range of the stability of the carbonyls is remarkable,—from those which can exist only at temperatures well below 0°C. to those, like $Ru(CO)_2I_2$, which withstand fairly high temperatures and strong chemicals. There is apparently little relationship between the structural forms which produce volatility and those which produce stability of the carbonyl linkage. There is no apparent relationship among the carbonyl halides between the progressive atomic numbers of the central atoms and the number of carbonyl groups, or the substitution of nitrosyl for carbonyl groups as in the series $\mathrm{Ni(CO)_4}$, $\mathrm{Co(CO)_2NO}$, and $\mathrm{Fe(CO)_2(NO)_2}$. There is, in fact, no evidence of a tendency among the carbonyl halides for the central atom to acquire the effective atomic number of an inert gas.

The study of the carbonyls seems to establish the principle that the effective atomic number of the central atom of a complex has an important influence on the field of the complex. This field will be self-contained and the complex be volatile only when the effective atomic number is equal to that of an inert gas. Obviously the effective atomic number of the central atom is not of itself enough to establish a self-contained field over the whole complex. The symmetry of the structure and the charges of the surrounding groups must coördinate with that of the central atom.

TABLE 8

Volatile carbonyls already known (in Roman type) or to be sought (in italics)

$\mathrm{Ni(CO)_4}$	$\mathit{Pd(CO)_4}$	$\mathit{Pt(CO)_4}$
$\mathrm{Fe(CO)_5}$	$\mathrm{Ru(CO)_5}$	$\mathit{Os(CO)_5}$
$\mathrm{Cr(CO)_6}$	$\mathrm{Mo(CO)_6}$	$\mathrm{W(CO)_6}$
$\mathrm{CoNO(CO)_3}$	$\mathit{RhNO(CO)_3}$	$\mathit{IrNO(CO)_3}$
$\mathrm{Co(CO)_4H}$	$\mathit{Rh(CO)_4H}$	$\mathit{Ir(CO)_4H}$
$\mathrm{Fe(NO)_2(CO)_2}$	$\mathit{Ru(NO)_2(CO)_2}$	$\mathit{Os(NO)_2(CO)_2}$
$\mathrm{Fe(CO)_4H_2}$	$\mathit{Ru(CO)_4H_2}$	$\mathit{Os(CO)_4H_2}$

$\mathrm{Ni(CO)_4}$	$\mathrm{CoNO(CO)_3}$	$\mathrm{Fe(NO)_2(CO)_2}$	$\mathit{Mn(NO)_3CO}$	$\mathit{Cr(NO)_4}$
$\mathrm{Ni(CO)_4}$	$\mathrm{Co(CO)_4H}$	$\mathrm{Fe(CO)_4H_2}$	$\mathit{Mn(CO)_4H_3}$	$\mathit{Cr(CO)_4H_4}$

The influence of the effective atomic number of the central atom in complex ions can be compared with its influence in the electrically neutral carbonyl complexes. When the complex is charged it cannot escape from the electrostatic influence of the oppositely charged ions and volatility is not to be expected. On the other hand, the ionic condition itself is dependent on the uniformity of the electrostatic field of the whole ion. The net charge not being segregated in any one spot in the ion lessens its chance of degenerating into a non-polar chemical bond. It is naturally far more difficult to trace the connection between effective atomic numbers and the formation of complex ions, because of the greater uncertainties of the latter problem. For example, the degree of solvation of the ion is difficult to estimate, but it does affect the effective atomic number of the central atom.

The effective atomic number concept serves so well in systematizing the very volatile carbonyls that are already known, that we may well conclude this review by making a list of the additional volatile compounds which the concept would lead us to expect. The stability of such substances may be very low, but, according to the concept, if the molecule would hold together at all it would have little external field and the substance would be volatile. The recent success of Manchot in preparing the very volatile ruthenium pentacarbonyl gives some ground for hoping that some other members of the series may be experimentally verified. In table 8 the as yet undiscovered members of the several series (horizontal lines) are printed in italics.

In addition to the compounds listed in table 8, there might be added, with a question mark, $Ni(NO)_2CO$ and $Co(NO)_3$. The effective atomic number concept would allow of such compounds if the arrangement of three groups around the central atom could allow a self-contained field. It is recalled that no such compound of nickel has been discovered, although many experiments, particularly those of Frazer and Trout (14), have been made in which the formation of such a compound might have been noted. A cobalt nitrosyl, $Co(NO)_3$, is mentioned by Hieber (24) with the implication that it is also a volatile compound, but no authoritative description of its formation or of its properties has as yet appeared.

It is noteworthy that no carbonyl compound whatever of manganese has been prepared.

Omitting manganese, mazurium, and rhenium, the metals with which the peculiar dissociable carbonyl linkage occurs occupy a solid block of the periodic arrangement:

Cr — Fe Co Ni Cu
Mo — Ru Rh Pd Ag
W — Os Ir Pt Au Hg

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