CHEMISTRY OF THE METAL CARBONYLS

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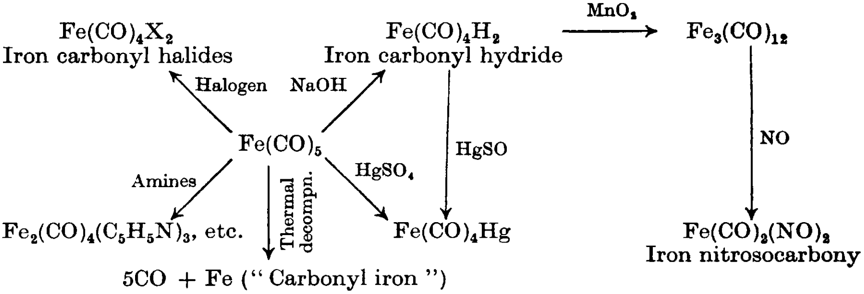
I. *General.*—The special interest attaching to the chemistry of the metal carbonyls arises from several causes. Whilst quite distinct from the organometallic compounds, they differ in physical properties (*e.g.*, their volatility) from all other compounds of the transition metals. Chemically, they constitute a group of compounds in which the formal valency of the metal atoms is zero, and in this respect (apart, perhaps, from the ammoniates of the alkali metals) they are comparable only with the recently discovered compounds $K_4[Ni(CN)_4]$ [1] and $K_4[Pd(CN)_4]$.[2] Their constitution, and that of their derivatives, accordingly raises a number of problems for interpretation by valence theory.

As a class, the carbonyls are reactive compounds, and a number of new types of inorganic compound has been discovered, largely through the work of W. Hieber and his school. The various classes of derivative obtainable from iron pentacarbonyl—which, with cobalt and nickel carbonyls, has hitherto been most closely studied—are indicated in Table I.

Table I



Since the discovery of nickel carbonyl by Mond and Langer [3] in 1888, the carbonyls of the iron group and of tungsten and molybdenum have found important technical applications—*e.g.*, in the Mond nickel process, and for the preparation of the metals in a state of subdivision and of purity suitable for powder metallurgy, for catalysts, etc. The reaction mechanism of the processes developed for producing the carbonyls technically has only recently received its interpretation.

Within the space of a review it is necessary to limit discussion to a few topics. Particular stress has accordingly been laid upon (*a*) the chemical

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[1] J. W. Eastes and W. M. Burgess, *J. Amer. Chem. Soc.*, 1942, **64**, 1187.

[2] J. T. Burbage and W. C. Fernelius, *ibid.*, 1943, **65**, 1484.

[3] *J.*, 1890, **57**, 749.

mechanism of the reactions undergone by the carbonyls, and especially of synthetic reactions; (*b*) the newly discovered carbonyls of the platinum metals; and (*c*) the present status of the structural problem.

The known carbonyls are listed in Table II.

II. *The Formation and Properties of the Metal Carbonyls.*—(1) *Direct synthesis of carbonyls.* The original discovery of the carbonyls, as also the large-scale preparation of the compounds, hinges on the direct reaction between carbon monoxide and the free, reactive metals. Two adsorption processes are thereby involved: activated adsorption of carbon monoxide, promoted by preparing the metal in a highly active state by reduction at low temperatures; [4, 5] and adsorption of the carbonyl, which blocks access of carbon monoxide to the metal surface. One effect of operating at high temperatures and high pressures is doubtless to change the relative importance of these adsorption equilibria, as well as to shift the chemical equilibrium between metal, carbon monoxide, and metal carbonyl. Only nickel carbonyl can be readily obtained at atmospheric pressure (cf. the original preparation of iron pentacarbonyl [6]), and in the I.-G. high-pressure process (200°, 50—200 atm. CO) the gas is continuously circulated to keep the iron carbonyl concentration below 2%, so avoiding excessive adsorption.

Although the direct synthesis reaction is inhibited by oxygen, yet it is promoted, even at ordinary pressures, by traces of sulphur. At high pressures, material consisting largely of iron or nickel sulphides may be converted directly and nearly quantitatively into the volatile carbonyls.[7] In the presence of sulphides, and of iron or copper to act as ultimate acceptor of the sulphur, molybdenum or tungsten can be converted directly into the hexacarbonyls on the technical scale.[8] In contrast with this, iridium, osmium, and rhenium metals do not react with carbon monoxide under any conditions of temperature or pressure, though their carbonyls have been prepared by the action of carbon monoxide on their compounds (II, 4).

(2) *Preparation of carbonyls by the Grignard reaction.* A. Job and his co-workers [9] observed that the slow reaction between carbon monoxide and the Grignard reagent was accelerated by salts of the transition metals, and particularly by anhydrous chromic chloride. The organic products of this reaction are complex, but an ether-soluble compound of chromium could be isolated in small yield; this proved to be chromium hexacarbonyl, $Cr(CO)_6$. A. Job and J. Rouvillois [9a] subsequently prepared tungsten hexacarbonyl, $W(CO)_6$, in the same way from tungsten hexachloride.

The mechanism of this process has not yet been worked out. W. Hieber and E. Romberg [10] showed that no chromium carbonyl is formed before

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[4] Cf. F. W. Laird, *Rec. Trav. chim.*, 1927, **46**, 177; C. F. van Duin, *ibid.*, p. 381.

[5] A. Mittasch, *Z. angew. Chem.*, 1928, **41**, 827; *Z. physikal. Chem.*, 1902, **40**, 1.

[6] M. Berthelot, *Compt. rend.*, 1891, **112**, 1343; L. Mond and F. Quincke, *J.*, 1891, **59**, 604.

[7] I. G. Patents: D.R.-P. 535,437 (*Chem. Zentr.*, 1930, II, 601); 618,108 (*ibid.*, 1933, II, 3606); E.PP. 394,906, 438,893 (*ibid.*, 1936, I, 2168).

[8] E.P. 367,481; F.PP. 708,260, 708,379 (*ibid.*, 1931, II, 2041).

[9] *Compt. rend.*, 1926, **183**, 392; *Bull. Soc. chim.*, 1927, **41**, 1041.

[9a] *Compt. rend.*, 1928, **187**, 564.

[10] *Z. anorg. Chem.*, 1935, **221**, 321.

TABLE II

Carbonyls and Carbonyl Hydrides

Cr (24).	Mn (25).	Fe (26).	Co (27).	Ni (28).
$Cr(CO)_6$, sublimes, rhombic, colourless	—	$Fe(CO)_5$, m.p. − 20°, b.p. + 103°, yellow; $Fe_2(CO)_9$, decomp. 100°, yellow, triclinic; $Fe_3(CO)_{12}$, decomp. 140°, green, monoclinic	$Co_2(CO)_8$, m.p. 51°, orange-red; $Co_4(CO)_{12}$, decomp. 60°, black, crystalline	$Ni(CO)_4$ m.p. − 25°, b.p. + 43°, colourless
		$Fe(CO)_4H_2$, m.p. − 70°, colourless	$Co(CO)_4H$, m.p. − 26°, yellow	
Mo (42).	**— (43).**	**Ru (44).**	**Rh (45).**	**Pd (46).**
$Mo(CO)_6$, sublimes, rhombic, colourless	—	$Ru(CO)_5$, m.p. − 22°, colourless; $Ru_2(CO)_9$, orange, monoclinic; $Ru_3(CO)_{12}$, green needles	$Rh_2(CO)_8$, orange, cryst., m.p. 76° (decomp.); $[Rh(CO)_3]_n$, red, cryst.; $[Rh_4(CO)_{11}]_m$, black	—
			$Rh(CO)_4H$, m.p. −10°, pale yellow	
W (74).	**Re (75).**	**Os (76).**	**Ir (77).**	**Pt (78).**
$W(CO)_6$, sublimes, rhombic, colourless	$Re_2(CO)_{10}$, colourless, m.p. 177°, sublimes, monoclinic	$Os(CO)_5$, colourless, m.p. − 15°; $Os_2(CO)_9$, bright yellow, sublimes, m.p. 224°	$Ir_2(CO)_8$, yellow-green, crystalline, sublimes; $[Ir(CO)_3]_x$, canary-yellow, decomp. 210°, rhombohedral	
	$Re(CO)_5H$ (?)	$Os(CO)_4H_2$	$Ir(CO)_4H$	

the stage of hydrolysis of the Grignard reagent, so the first product must be some organo-chromium carbonyl, which is decomposed by acid forming Cr^{3+} ion and $Cr(CO)_6$ amongst other products—*e.g.*,

$$(2, 1)\quad 3Cr(CO)_2R_4 + 6H^+ \longrightarrow Cr(CO)_6 + 2Cr^{3+} + 12R + 6H \longrightarrow \text{organic products} + H_2$$

This type of dismutation is commonly observed in the acid decomposition of substituted carbonyls. F. Hein's work [11] has shown that in such circumstances organo-chromium compounds are indeed formed, and do undergo the required type of valency disproportionation. Only the non-polar halides ($CrCl_3$, $MoCl_5$, WCl_6) enter into the Grignard reaction; stable complex salts do not react, even though non-electrolytes, the metal atom being presumably blocked from some initial step of co-ordinative union with carbon monoxide.

(3) *Indirect formation of carbonyls by reactions in solution.* The valency disproportionation involved in the Grignard synthesis is analogous to a number of reactions in aqueous solutions whereby metal carbonyls are formed. For instance, the complex cyanide of univalent nickel, $K_2[Ni(CN)_3]$,[12] absorbs carbon monoxide, presumably forming $K_2[Ni(CN)_3(CO)]$.[13] When this is acidified, or when NiCN itself is treated with carbon monoxide, nickel carbonyl is formed. Nickel(II) cyanide, $Ni(CN)_2$, suspended in sodium hydroxide solution, also absorbs carbon monoxide,[14] as also do nickel sulphide and the mercaptide.[15] Manchot and Gall [13] suggested that the reaction proceeded in two steps: formation of a carbonyl complex of univalent nickel (2, 2), followed by disproportionation (2, 3):

$$(2, 2)\quad 2NiX_2 + 2nCO \longrightarrow 2Ni(CO)_nX + X_2 \qquad (X_2 \text{ absorbed by alkali; } X = -OH, -SH, -SR)$$

$$(2, 3)\quad 2Ni(I) \longrightarrow Ni(II) + Ni(0)$$
$$2Ni(CO)_nX + (4 - 2n)CO \longrightarrow Ni(CO)_4 + NiX_2$$

Later work by W. Hieber, A. Schlecht, and H. Behrens [16] has shown the peculiar aptitude of organic and inorganic thio-salts for this reaction, *e.g.*, nickel thiosalicylate, xanthate, etc., or hexamminonickel thio-salts such as $[Ni(NH_3)_6]MoS_4$. Whereas, however, the maximum absorption amounts to 4 molecules of CO per atom of Ni, they found only *half* the nickel appearing as nickel carbonyl. The reaction thus presents some features still needing explanation.

No analogous reactions are available for the formation of iron pentacarbonyl, but cobalt compounds react similarly, forming, not the carbonyl, but cobalt carbonyl hydride, $Co(CO)_4H$ (cf. III, 4).

In the reactions undergone by substituted carbonyls and polynuclear carbonyls, a second type of disproportionation is typical—redistribution of CO groups to give a free carbonyl [*e.g.*, $Fe(CO)_5$] and products poorer in CO (*e.g.*, Fe^{2+}). Thus, decomposition of the substituted iron carbonyls

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[11] *J. pr. Chem.*, 1931, **132**, 59.

[12] J. Belucci, *Z. anorg. Chem.*, 1914, **86**, 88.

[13] W. Manchot and H. Gall, *Ber.*, 1926, **59**, 1060.

[14] A. A. Blanchard, J. R. Rafter, and W. B. Adams, *J. Amer. Chem. Soc.*, 1934, **56**, 16.

[15] W. Manchot and H. Gall, *Ber.*, 1929, **62**, 678.

[16] Not yet published; cf. W. Hieber, *Die Chemie*, 1942, **55**, 7.

$Fe(CO)_3,A$ (A = MeOH, etc.) furnishes $Fe(CO)_5$ and Fe^{2+} as if the reaction were that of a $Fe(CO)_3$ radical :[17]

(2, 4) $$3Fe(CO)_3 \longrightarrow Fe(CO)_5 + 2Fe(CO)_2$$

(2, 5) $$Fe(CO)_2 + 2H^+ \rightarrow Fe^{2+} + H_2 + 2CO$$

The hexacarbonyls of Cr and Mo are formed similarly in the decomposition of their derivatives $M(CO)_3py_3$ (py = pyridine),[18] and $Ni(CO)_4$ from $Ni(CO)_2$phenan (phenan = *o*-phenanthroline).[19] Similarly, a considerable part of the carbon monoxide displaced from iron tetracarbonyl by reaction with pyridine, methyl alcohol, nitric oxide, etc., appears as iron pentacarbonyl :

(2, 6) $$2[Fe(CO)_4]_3 + 3py \rightarrow 3Fe(CO)_3,py + 3Fe(CO)_5$$

Reactions of this kind originate in the ready reversibility of the *metal carbonyl + substituted carbonyl +* CO system. With some carbonyls [*e.g.*, $Ni(CO)_4$, $Fe(NO)_2(CO)_2$], substitution of CO by pyridine can be effected only if the carbon monoxide is removed continuously ; [19] at high temperatures and CO pressures, $Cr(CO)_6$ forms $Cr(CO)_4,py_2$, but if the back reaction of (2, 7) is obviated, $Cr(CO)_3,py_3$ is formed :

(2, 7) $$Cr(CO)_4,py_2 + py \rightleftharpoons Cr(CO)_3,py_3 + CO$$

(4) *New carbonyls of the platinum metals : the high-pressure synthesis.* Ruthenium carbonyl. That compounds of the metals could be converted directly into carbonyls, by carbon monoxide at high pressures, was shown by W. Manchot and W. J. Manchot [20] in their preparation of ruthenium pentacarbonyl, $Ru(CO)_5$. Ruthenium iodide, RuI_3, reacts with carbon monoxide even at the ordinary pressure, the carbonyl iodide, $Ru(CO)_2I_2$, being formed by partial displacement of iodine. If mixed with an acceptor for iodine, such as finely divided copper or silver, the carbonyl iodide undergoes further ready reaction with carbon monoxide—especially at high pressures—forming $Ru(CO)_5$.

Although metallic ruthenium does react with carbon monoxide,[21] it is unlikely that RuI_3 or $Ru(CO)_2I_2$ is reduced to free metal as the initial step, for carbonyls of iridium and osmium—metals which are quite inert towards carbon monoxide—have been prepared similarly. The reaction is better regarded as involving a series of displacement equilibria, whereby the formal valency of the metal is lowered at each step :

(2, 8) $$2RuI_3 + 4CO \rightleftharpoons 2Ru(CO)_2I_2 + I_2$$

(2, 9) $$RuI_3 \rightleftharpoons Ru(CO)_2I_2 \rightleftharpoons Ru(CO)_nI \rightleftharpoons Ru(CO)_5$$

A carbonyl bromide, Ru(CO)Br, containing formally univalent ruthenium was described earlier by W. Manchot and E. Enk.[22]

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[17] W. Hieber and E. Becker, *Ber.*, 1930, **63,** 1405.

[18] W. Hieber and F. Mühlbauer, *Z. anorg. Chem.*, 1935, **221,** 337.

[19] W. Hieber, F. Mühlbauer, and E. A. Ehmann, *Ber.*, 1932, **65,** 1090.

[20] *Z. anorg. Chem.*, 1936, **226,** 385.

[21] Contrast R. L. Mond and A. E. Wallis, *J.*, 1922, **121,** 29.

[22] *Ber.*, 1930, **63,** 1635.

Iridium carbonyls, $Ir_2(CO)_8$, $[Ir(CO)_3]_x$. W. Hieber and H. Lagally [23] and W. Hieber, H. Lagally, and A. Mayr [24] confirm the mechanism of equation (2, 9) by their work on iridium carbonyls. The iridium halides react with carbon monoxide (110°, ordinary pressure), the first stage being described by (2, 10) or (2, 11):

(2, 10) $2IrX_3 + 5CO \rightarrow 2Ir(CO)_2X_2 + COX_2$ (X = Cl or Br)
(2, 11) $2IrI_3 + 4CO \rightarrow 2Ir(CO)_2I_2 + I_2$

This reaction was observed previously by W. Manchot and H. Gall [25]; it may be followed successively by reactions (2, 12) and (2, 13):

(2, 12) $2Ir(CO)_2X_2 + 3CO \rightarrow 2Ir(CO)_3X + COX_2$
(2, 13) $2Ir(CO)_3X + CO \rightarrow [Ir(CO)_3]_x + COX_2$

In these changes, the exothermic formation of carbonyl chloride or bromide at each stage plays an essential part in determining the course of reaction under ordinary pressure of carbon monoxide. As COI_2 is non-existent, the reaction with IrI_3 stops at (2, 11); only with $IrCl_3$ does the third stage (2, 13) occur, though the main product is $Ir(CO)_3Cl$. In the presence of silver or copper to combine with halogen, and at high pressures of carbon monoxide, ultimate formation of carbonyl is favoured, and it may logically be inferred that the tricarbonyl, formed in reaction (2, 13), is the precursor of $[Ir(CO)_4]_2$, the final product. Under these conditions the over-all process is as equation (2, 14), and the ease with which halogen is split out of the

(2, 14) $IrX_3 + 3Cu + 3CO \rightarrow 3CuX + [Ir(CO)_3]_x \xrightarrow{+\,CO} [Ir(CO)_4]_2$

iridium halides is more important than the heat of formation of COX_2; conversion into carbonyl then proceeds with increasing ease in the sequence chloride → bromide → iodide. Little or no formation of carbonyl takes place if reduction to metal occurs—as in *mixtures* of iridium halides with copper or silver powder.

Osmium carbonyls, $Os(CO)_5$, $Os_2(CO)_9$. These have been prepared, like the carbonyls of iridium, by high-pressure synthesis from the osmium halides,[26] by reactions hinging on the intermediate formation of the carbonyl halides $Os(CO)_4X_2$. These CO-richest compounds (see Table IV) are formed from the halides ($OsCl_3$, Os_2Br_9, osmium " oxyiodide ") in carbon monoxide (120°, 200 atm. pressure).[27] In the presence of silver or copper—from the lining of the autoclave—partial conversion into the pure carbonyl occurs, increasing in extent in the order $Os(CO)_4Cl_2 < Os(CO)_4Br_2 < Os(CO)_4I_2$. Osmium carbonyl is most readily obtained, however, by an exceptional reaction, *viz.*, the direct action of carbon monoxide on the covalent highest oxide:

(2, 15) $OsO_4 + 9CO \rightarrow Os(CO)_5 + 4CO_2$

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[23] *Z. anorg. Chem.*, 1940, **245**, 321.

[24] *Ibid.*, 1941, **246**, 138.

[25] *Ber.*, 1925, **58**, 232.

[26] W. Hieber and H. Stallmann, *Z. Elektrochem.*, 1943, **49**, 288.

[27] *Idem, Ber.*, 1942, **75**, 1472; cf. W. Manchot and J. König, *ibid.*, 1925, **58**, 229.

This reaction occurs fairly readily (100°, 50 atm.), presumably by way of an intermediate oxy-carbonyl, since metallic osmium formed by reduction in a side reaction is without action upon carbon monoxide.

Rhodium carbonyls, $[Rh(CO)_4]_2$, $[Rh(CO)_3]_x$, $[Rh_4(CO)_{11}]_y$. The existence of rhodium carbonyls is to be expected, since cobalt and iridium form compounds of similar nature. W. Hieber and H. Lagally [28] have shown that rhodium does, indeed, stand between cobalt and iridium in its reaction with carbon monoxide. As with cobalt, $[Rh(CO)_4]_2$ is most readily formed by direct union of carbon monoxide with metallic rhodium at high pressures. The halides RhX_3 react with carbon monoxide, like those of iridium, forming the rhodium carbonyl halides $Rh(CO)_2X$ and the carbonyls $[Rh(CO)_3]_x$, $Rh_2(CO)_8$. The pure carbonyls, especially the very stable lower carbonyl $[Rh(CO)_3]_x$, are formed even at low temperatures in the presence of a halogen-acceptor (Ag or Cu) ; the use of zinc or cadmium as halogen-acceptors does not, however, lead to the formation of mixed carbonyls, as it does with cobalt carbonyl (see III, 6). The superior stability of the tricarbonyl is striking, and at higher temperatures ($>$ 100°) a yet more highly condensed carbonyl is formed in the high-pressure synthesis, *viz.*, $Rh_4(CO)_{11}$ or a polymer thereof.

Rhenium carbonyl, $[Re(CO)_5]_2$. The carbonyl derivatives of rhenium are of special systematic importance, as bridging the gap between the complete series of hexacarbonyls $M(CO)_6$ of Group VI (M = Cr, Mo, W) and the complete series of pentacarbonyls $M'(CO)_5$ and carbonyl halides $M'(CO)_4X_2$ of the iron group (M′ = Fe, Ru, Os). The compounds are of the types expected : [29] carbonyl halides, $Re(CO)_5X$, and dimeric carbonyl, $[Re(CO)_5]_2$. Rhenium carbonyl halides are so stable, and so readily formed, that they are the sole and invariable products of high-pressure syntheses from the halides or complex halides of rhenium. Thus, from $ReCl_5$, K_2ReCl_6 or K_2ReBr_6 in the presence of copper, $Re(CO)_5Cl$ and $Re(CO)_5Br$ respectively are formed (230°, 50 atm. of CO) ; carbon monoxide forms $Re(CO)_5I$ from K_2ReI_6 even at the ordinary pressure. This great tendency to form the carbonyl halides is demonstrated by their formation from metallic rhenium or its oxygen compounds in the presence of the reducible halides of transition metals ; *e.g.* :

$$Re + CuX_2 + 6CO \longrightarrow Re(CO)_5X + Cu(CO)X \tag{2, 16}$$
$$2Re + NiX_2 + 14CO \longrightarrow 2Re(CO)_5X + Ni(CO)_4 \tag{2, 17}$$

or by chlorination with, *e.g.*, carbon tetrachloride :

$$KReO_4 + CCl_4 + 8CO \longrightarrow KCl + Re(CO)_5Cl + COCl_2 + 3CO_2 \tag{2, 18}$$

Their stability is such that the conversion of these carbonyl halides into rhenium carbonyl has not been observed under any conditions investigated. $[Re(CO)_5]_2$ is formed, however, directly from the sulphide Re_2S_7 and the oxygen compounds, Re_2O_7, $KReO_4$ (250°, 200 atm. of CO).

The dimeric carbonyl,  $(CO)_4Re\overset{CO}{\underset{CO}{}}Re(CO)_4$, resembles the co-ordina-

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[28] *Z. anorg. Chem.*, 1943, **251**, 96.

[29] W. Hieber and H. Schulten, *ibid.*, 1939, **243**, 164 ; W. Hieber, R. Schuh, and H. Fuchs, *ibid.*, 1941, **248**, 243 ; W. Hieber and H. Fuchs, *ibid.*, p. 256.

tively saturated hexacarbonyls [$Cr(CO)_6$, etc.] in its stability and chemical inertness. It is not decomposed by alkalis or concentrated mineral acids, and although, as a polynuclear compound, it is not very volatile, it can be sublimed in carbon monoxide at 200°. It reacts with gaseous halogens, forming the stable carbonyl halides.

(5) *High-pressure synthesis of the iron-group carbonyls.* Numerous patent specifications [30] record the conditions found empirically to promote the formation of metal carbonyls under technical conditions. These can now be correlated with systematic studies by Hieber and his co-workers on the mechanism of the high-pressure synthesis. Carbonyls can be formed from the compounds of iron, cobalt, and nickel with highly polarisable non-metals ; *i.e.*, from solids in which the lattice forces are not of purely ionic type. Thus, cobalt sulphide (NiAs structure) is quantitatively converted into $Co_2(CO)_8$ (200°, 200 atm.), but cobalt oxide does not react : [31]

(2, 19) $2CoS + 8CO + 4Cu$ (autoclave lining) $\longrightarrow Co_2(CO)_8 + 2Cu_2S$

Of the halides, CoF_2 (rutile structure, purely ionic) is without reaction, whereas the other halides (layer lattice structures) increase in reactivity in the order $CoCl_2 < CoBr_2 < CoI_2$. Thus, in carbon monoxide at 250°, 200 atm., and without direct contact with a free metal (so that halogen must be bound by reaction of some volatile compound with the silver or copper autoclave lining) relative conversion of halides into carbonyl according to (2, 20) is :

X =	Cl.	Br.	I.
% $Co_2(CO)_8$ formed =	3·5	9	100

(2, 20) $2CoX_2 + 4Cu + 8CO \longrightarrow Co_2(CO)_8 + 4CuX$

The volatile compounds involved might be (*a*) $COCl_2$, $COBr_2$, or (from CoI_2) free I_2 ; or (*b*) a volatile cobalt carbonyl halide. No formation of $COCl_2$ or $COBr_2$ has been detected, and where the reaction mechanism definitely involves these compounds, the sequence of reactivity appears to be iodide < bromide < chloride (cf. iridium carbonyl). H. Schulten [32] has, however, found that at the ordinary temperature, under 100 atm. of carbon monoxide, cobalt iodide reacts to form a cobalt carbonyl iodide, $Co(CO)I_2$, a dark brown crystalline solid with a high dissociation pressure of carbon monoxide, which is perceptibly volatile even at room temperature. The relative efficiency of the cobalt halides as reactants in the carbonyl synthesis would be consistent with an increase in stability of cobalt carbonyl halides in the sequence chloride < bromide < iodide which holds for the iron carbonyl halides.

A second factor involved in the reaction is the rôle of the metal added as halogen acceptor. In intimate mixtures of cobalt bromide with finely divided metals, the efficiency of various metals (Au, Ag, Cu, etc.) in removing halogen and forming cobalt carbonyl increases in the order of the heat of

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[30] Cf. refs. (5) and (7), and the compilation of patent refs. by R. L. Mond (*J. Soc. Chem. Ind.*, 1930, **49**, 288T).

[31] W. Hieber, H. Schulten, and R. Marin, *Z. anorg. Chem.*, 1939, **240**, 261.

[32] *Ibid.*, 1939, **243**, 145.

formation of their bromides. The displacement reaction (2, 21) would, for

$$\text{(2, 21)} \qquad CoBr_2 + 2M \longrightarrow 2MBr + Co + Q \text{ cal.}$$

the metals cited, be endothermic. Endothermic processes involving only solid reactants and resultants can take place only if the formation of solid solutions provides an increase in entropy. There is, in fact, limited miscibility between AgBr or CuBr and $CoBr_2$, so that in mixtures of $CoBr_2$ + Ag (or Cu), heated in argon under conditions comparable with those of the carbonyl synthesis, some metallic cobalt is set free. However, as is shown by the data of Table III, the yield of reaction (2, 21) in argon, compared with that of the (over-all exothermic) reaction (2, 22) in carbon monoxide, suggests that something more than the reaction of carbon monoxide with freshly liberated metallic cobalt is involved in carbonyl formation.

$$\text{(2, 22)} \quad CoBr_2 + 4Ag + 8CO \longrightarrow Co_2(CO)_8 + 4AgBr + (Q_f - 15{\cdot}2) \text{ kg.-cal.}$$
$$[Q_f = \text{unknown heat of formation of } Co_2(CO)_8 \text{, in kg.-cal.}]$$

TABLE III

M.	Ratio $CoBr_2$: M.	Temp.	% Reaction at 200 atm.	
			In argon.	In CO.
Ag	1 : 3	250°	6·2	29
Cu	1 : 4	250	12·5	76
Cd	1 : 1·5	180	20	100
Zn	1 : 2	180	23	100

This conclusion is borne out by experiments with zinc and cadmium as halogen acceptors. With these, reaction (2, 21) is incomplete under the experimental conditions, although exothermic. In carbon monoxide, however, dehalogenation is quantitative, and cobalt is converted completely, not into $[Co(CO)_4]_2$, but into the mixed carbonyl compounds $[Co(CO)_4]_2Zn$, $[Co(CO)_4]_2Cd$.

Similar results were found by W. Hieber, H. Behrens, and U. Teller[33] in comparable experiments with iron and nickel halides. The chlorides and bromides FeX_2, NiX_2 undergo but little reaction when heated in carbon monoxide without direct contact with a halogen acceptor. Quantitative conversion of NiI_2 into $Ni(CO)_4$, and 50—75% conversion of FeI_2 into $Fe(CO)_5$ occurred ; in the latter case the iron is largely left as $Fe(CO)_4I_2$ which, because of its stability, slows down the last stage of carbonyl formation. Although no nickel carbonyl iodide was isolated, the results suggest the formation of such a compound, stable only under high pressures of carbon monoxide.

The catalytic rôle of iodine in carbonyl formation is now apparent, since it can enter into a cyclic set of reactions whereby the metallic iodide is formed, and converted at each stage into the carbonyl iodide, and thence

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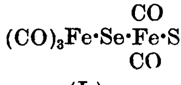
[33] *Ibid.*, 1942, **251**, 26.

into carbonyl and metallic iodide. The function of sulphur in the technical carbonyl processes must be analogous. No metal carbonyl sulphides are known, but they presumably exist as intermediates, and the isolation of an iron carbonyl selenide $Fe_3Se_2(CO)_8$,[34] formulated by Hieber as (I), may be taken as evidence that such is the case.



$$(CO)_3Fe\cdot Se\cdot \overset{CO}{\underset{CO}{Fe}}\cdot Se\cdot Fe(CO)_3$$

(I.)

III. *Metal Carbonyl Hydrides and their Derivatives.*—(1) *The hydrolysis of iron pentacarbonyl.* It was early observed [35] that iron pentacarbonyl was soluble in alcoholic potassium hydroxide, giving a solution which turned red in air. Such solutions have powerful reducing properties,[36] and absorb oxygen from the air. W. Hieber and F. Leutert [37] found that, in complete absence of oxygen, a volatile, very unstable iron carbonyl hydride, $Fe(CO)_4H_2$, is liberated when the solutions are acidified. This is formed by the hydrolysis reaction : [38]

$$Fe(CO)_5 + 2OH^- \longrightarrow Fe(CO)_4H_2 + CO_3^{2-} \tag{3, 1}$$

With caustic alkalis, formation of carbonate approaches one molecule per molecule of iron pentacarbonyl when a suitable excess of base is used ; with ammonia, ethylenediamine, etc., carbamic acids $NHR\cdot CO_2H$ are formed as primary products. The carbonyl hydride formed in the process can be oxidised and titrated with methylene-blue. Mild oxidising agents (*e.g.*, manganese dioxide) oxidise iron carbonyl hydride in concentrated solutions to iron tetracarbonyl, in almost quantitative yield : [39]

$$3Fe(CO)_4H_2 + 3MnO_2 + 3H_2SO_4 \longrightarrow 3MnSO_4 + 3H_2O + [Fe(CO)_4]_3 \tag{3, 2}$$

Drastic oxidants (*e.g.*, hydrogen peroxide) bring about complete oxidation to ferric hydroxide, carbon monoxide, and carbon dioxide.

Iron carbonyl hydride is a pale yellow liquid, m.p. − 70°, with a nauseating smell. Above − 10° it decomposes rapidly, giving free hydrogen and, by disproportionation of the resulting $Fe(CO)_4$ radical, iron pentacarbonyl and ill-defined products with a lower CO : Fe ratio :

$$Fe(CO)_4H_2 \longrightarrow H_2 + Fe(CO)_4 \tag{3, 3}$$

$$2Fe(CO)_4 \longrightarrow Fe(CO)_5 + Fe(CO)_3, \text{ etc.} \tag{3, 4}$$

followed by reactions (2, 4), (2, 5).

The most important reactions of iron carbonyl hydride are those giving rise to metal derivatives. These, together with derivatives of cobalt carbonyl hydride, are considered in III, 3.

(2) *Hydrolysis of cobalt carbonyl.* The reaction of cobalt tetracarbonyl with bases, although formally more complex than that of iron pentacarbonyl,

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[34] W. Hieber and O. Geisenheimer, unpubl. ; cf. ref. (16).

[35] J. Dewar and H. O. Jones, *Proc. Roy. Soc.*, 1905, *A*, **76**, 558 ; 1906, *A*, **79**, 66.

[36] H. Freundlich and W. Malchow, *Ber.*, 1923, **56**, 2264 ; *Z. anorg. Chem.*, 1924, **141**, 317.

[37] *Naturwiss.*, 1931, **19**, 360.

[38] W. Hieber and F. Leutert, *Z. anorg. Chem.*, 1932, **204**, 145.

[39] W. Hieber, *ibid.*, p. 165.

conforms to the same pattern.[40] With strong bases [$Ba(OH)_2$, KOH] the reaction is

(3, 5) $$3[Co(CO)_4]_2 + 4OH^- \rightarrow 4Co(CO)_4H + 2CO_3^{2-} + 2[Co(CO)_3] \text{ polymer}$$

At lower hydroxyl-ion concentrations (ammonia), an alternative hydrolysis reaction is favoured :

(3, 6) $$3[Co(CO)_4]_2 + 4H_2O \rightarrow 4Co(CO)_4H + 2Co(OH)_2 + 8CO$$

The dilute solutions obtained by hydrolysis have properties similar to those of iron carbonyl hydride : they reduce methylene-blue, and are very easily oxidised by air or mild oxidants, forming cobalt tetracarbonyl. From such a solution (baryta hydrolysis), W. Hieber and H. Schulten [41] isolated the free hydride, by the action of phosphoric acid. $Co(CO)_4H$ is extremely unstable, and decomposes into cobalt tetracarbonyl and hydrogen at temperatures above its melting point (— 26·2°).

(3) *Derivatives of metal carbonyl hydrides.* The carbonyl hydrides behave as very weak monobasic acids, forming true salts only with the alkali metals and with bulky ammine cations ; compounds formed with the heavier metals do not have the properties of typical salts. F. Feigl and P. Krumholz [42] isolated a salt $Fe(CO)_4HNa,MeOH$ as the immediate product of hydrolysing iron pentacarbonyl with sodium methoxide ; calcium or magnesium hydroxides similarly form $[Fe(CO)_4H]_2Ca$ and $[Fe(CO)_4H]_2Mg$.[43] Amines, *e.g.*, pyridine and *o*-phenanthroline, also react with iron carbonyl hydride solutions, giving stable addition compounds which can be formulated as salts,[44] *e.g.*, $[Fe(CO)_4H_2],2C_5H_5N$ or $[Fe(CO)_4][C_5H_5NH]_2$, $[Fe(CO)_4]$[phenan,H_2]. The electrically conducting solution formed by iron carbonyl hydride in pyridine accords with this view. This behaviour is in contrast to the action of pyridine on the pure carbonyls and all other classes of derivative ; in general, reaction leads to displacement of carbon monoxide and substitution of pyridine.

From solutions of iron carbonyl hydride, sparingly soluble derivatives may be precipitated by reaction with solutions of the ammines and salts of the heavy metals.[45, 46] With solutions containing the hexammine cations $[M(NH_3)_6]^{2+}$ ($M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}$), the crystalline compounds $[Fe(CO)_4H]_2[M(NH_3)_6]$ are obtained ; no analogous salt is formed by the hexamminocobaltic ion, $[Co(NH_3)_6]^{3+}$, as this acts as an oxidant, forming $[Fe(CO)_4]_3$. In the hydrolysis of iron pentacarbonyl with ammonia, a little of the salt $[Fe(CO)_4H]_2[Fe(NH_3)_6]$ is invariably formed, through reactions analogous to (3, 3), (3, 4), (2, 5), followed by

(3, 7) $$Fe^{2+} + 6NH_3 \rightarrow [Fe(NH_3)_6]^{2+}$$

Very sparingly soluble salts, $[Fe(CO)_4H]_2[M\ phenan_3]$ ($M = Fe^{II}, Co^{II}$,

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[40] *Idem*, *Z. Elektrochem.*, 1934, **40**, 158.

[41] *Z. anorg. Chem.*, 1937, **232**, 29.

[42] *Monatsh.*, 1932, **59**, 314.

[43] F. Hein and H. Pobloth, *Z. anorg. Chem.*, 1941, **248**, 84.

[44] W. Hieber and H. Vetter, *ibid.*, 1933, **212**, 145.

[45] F. Feigl and P. Krumholz, *ibid.*, 1933, **215**, 242.

[46] W. Hieber and E. Fack, *ibid.*, 1938, **236**, 83.

Ni^{II}) are also formed by the trisphenanthroline cations, $[M\,phenan_3]^{2+}$; these are precipitated almost quantitatively.

Solutions of these carbonyl hydride salts of complex cations in acetone or methyl alcohol have conductivities typical of solutions of strong electrolytes,[46] and it may be inferred that the compounds are true salts.

The reactions of cobalt carbonyl hydride solutions are analogous;[47] with ammoniacal nickel or cobalt solutions, the salts $[Co(CO)_4]_2[Ni(NH_3)_6]$, $[Co(CO)_4]_2[Co(NH_3)_6]$ are obtained, the latter being formed (by reaction 3, 6) in small amounts in the hydrolysis of cobalt carbonyl with ammonia. Gaseous ammonia also reacts directly with cobalt carbonyl:

$$3[Co(CO)_4]_2 + 12NH_3 \rightarrow 2[Co(CO)_4]_2[Co(NH_3)_6] + 8CO \tag{3, 8}$$

Derivatives of markedly different properties are formed by the metals of the zinc and copper groups. Although formally related to the carbonyl hydrides, their properties are not those of typical salts, and they can be regarded rather as polynuclear complex compounds.

That iron pentacarbonyl reacts with mercuric salts was observed[48] before iron carbonyl hydride was discovered:

$$Fe(CO)_5 + HgSO_4 + H_2O \rightarrow H_2SO_4 + CO_2 + Fe(CO)_4Hg \tag{3, 9}$$

With a further molecular proportion of mercuric salt, compounds of the type $Fe(CO)_4Hg_2X_2$ are obtained. $Fe(CO)_4Hg$ is a very stable yellow substance, insoluble in all solvents. It is quite unchanged in air, and does not react with boiling pyridine, but reacts with iodine, forming iron carbonyl iodide:

$$Fe(CO)_4Hg + 2I_2 \rightarrow HgI_2 + Fe(CO)_4I_2 \tag{3, 10}$$

It is decomposed at 150° into mercury, iron, and carbon monoxide. Its formal relation to $Fe(CO)_4H_2$ is shown by its precipitation from iron carbonyl hydride solutions:

$$Fe(CO)_4H_2 + HgCl_2 \rightarrow 2HCl + Fe(CO)_4Hg \tag{3, 11}$$

Similar reactions with ammoniacal zinc or cadmium solutions form the insoluble compounds $[Fe(CO)_4][Zn(NH_3)_3]$, $[Fe(CO)_4][Cd(NH_3)_2]$, $[Fe(CO)_4][Cd\,py_2]$. In these derivatives of the Group IIB metals there is a clear gradation of properties

$$\begin{array}{lll}
Fe(CO)_4Zn(NH_3)_3 & \xrightarrow{\qquad\quad HOAc \quad\qquad} & Fe(CO)_4H_2 \\
Fe(CO)_4Cd(NH_3)_2 & \xrightarrow{HOAc} Fe(CO)_4Cd \xrightarrow{HCl} & Fe(CO)_4H_2 \\
 & Fe(CO)_4Hg \ldots \text{unaffected by acids} &
\end{array}$$

Similar in type are the copper and silver compounds $Fe(CO)_4Cu_2(NH_3)_2$, $Fe(CO)_4Ag_2phenan$.

These compounds are not derived from stable ammine cations, and in

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[47] W. Hieber and H. Schulten, *Z. anorg. Chem.*, 1937, **232**, 17.

[48] H. Hock and H. Stuhlmann, *Ber.*, 1928, **61**, 2097; 1929, **62**, 2690.

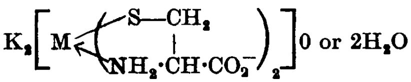
them—in contrast to its behaviour in truly ionic compounds—$Fe(CO)_4H_2$ functions as formally dibasic.

Some rather unstable organometallic derivatives have been described by F. Hein and E. Heuser.[49] Methylmercuric hydroxide, $CH_3 \cdot HgOH$, reacts with iron carbonyl hydride, forming $Fe(CO)_4(Hg \cdot CH_3)_2$. This substance is soluble in organic solvents [contrast $Fe(CO)_4Hg$], and presumably has a normal molecular weight. It slowly disproportionates into $Fe(CO)_4Hg$ and $Hg(CH_3)_2$; the corresponding ethylmercury and phenylmercury compounds are too unstable to be isolated, and decompose immediately in a similar manner. A diethyl-lead derivative, $Fe(CO)_4Pb(C_2H_5)_2$, has also been described;[43] it is formed by the action of $(C_2H_5)_3PbOH$ on iron carbonyl hydride, and is soluble in organic solvents.

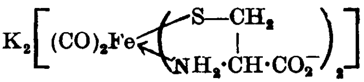
Cobalt carbonyl hydride solutions yield heavy-metal compounds of similar character, *e.g.*, $[Co(CO)_4]_2Cd$, $[Co(CO)_4]_2Hg$. These (compare the iron compounds) are monomeric, and soluble in organic solvents, but insoluble in water.

(4) *Formation of carbonyl hydrides by reactions in solution.* The tendency to form cobalt carbonyl hydride is so great that it may be formed from carbon monoxide and cobalt(II) compounds, by reactions parallel to those described in II, 3 for the preparation of nickel carbonyl.

Cysteine, $SH \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$ (= H_2SR, below) forms, with bivalent iron and cobalt, complex salts of the type (I). Alkaline solutions



(I.)



(II.)

of these inner complex salts are sensitive to oxygen, and also absorb carbon monoxide.[50] From the ferrous dicysteine complex, a dicarbonyl derivative (II) is formed. The cobalt(II)–cysteine complex absorbs one molecule of CO per atom of cobalt, but no addition compound can be isolated; the complex undergoes disproportionation, the cysteine being recovered in the form of a cobalt(III) complex, $K_3[Co(SR)_3],3H_2O$, and the complementary product of reaction being cobalt carbonyl hydride:

$$(3, 12) \quad 9[Co(SR)_2]^{2-} + 8CO + 2H_2O \longrightarrow 6[Co(SR)_3]^{3-} + Co(OH)_2 + 2Co(CO)_4H$$

Prolonged action of carbon monoxide forms the carbonyl hydride in increased amount, by reaction with the cobaltitriscysteinate formed in reaction (3, 12):

$$(3, 13) \quad [Co(SR)_3]^{3-} + 6CO + 7OH^- \longrightarrow 2CO_3^{2-} + 3SR^{2-} + 3H_2O + Co(CO)_4H$$

The net effect of (3, 12) and (3, 13) is to regenerate the cysteine, so that, as was found by G. W. Coleman and A. A. Blanchard,[51] a small amount of cysteine suffices to bring about absorption of carbon monoxide corresponding to nearly complete conversion of the cobalt salt.

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[49] *Z. anorg. Chem.*, 1942, **249**, 293.

[50] M. P. Schubert, *J. Amer. Chem. Soc.*, 1933, **55**, 4563.

[51] *Ibid.*, 1936, **58**, 2160.

The cobalt carbonyl hydride formed in these processes was characterised by precipitating the silver and mercury derivatives. Formation of cobalt carbonyl, by decomposition, when the solution is acidified, provides a convenient means of preparing that substance. In alkaline solutions, cobalt carbonyl itself reacts with free cysteine, forming the carbonyl hydride :

$$(3, 14)\quad 2[Co(CO)_4]_2 + 3H_2SR + 3OH^- \longrightarrow 3Co(CO)_4H + [Co(SR)_3]^{3-} + 4CO + 3H_2O$$

Analogous reactions take place with cobalt(II) salts and other thio-compounds that form inner complex salts.[52] Absorption of carbon monoxide first forms a substituted cobalt carbonyl derivative [53] (3, 15), which furnishes cobalt carbonyl hydride when decomposed with acid (3, 16). Thus, with potassium xanthate, KXa ($Xa = C_2H_5{\cdot}O{\cdot}CS{\cdot}S{-}$) :

$$(3, 15)\quad 6CoCl_2 + 12KXa + 5CO + EtOH \longrightarrow 12KCl + 4CoXa_3 + Co_2(CO)_5,EtOH$$

$$(3, 16)\quad Co_2(CO)_5,EtOH + 2H^+ \longrightarrow EtOH + Co^{2+} + Co(CO)_4H + CO + \tfrac{1}{2}H_2$$

The foregoing reactions are applicable only to the preparation of cobalt carbonyl hydride, but if the sequence of properties in the pairs Ru–Rh, Os–Ir recapitulates that of the pair Fe–Co, similar methods may be available for the preparation of $Rh(CO)_4H$ and $Ir(CO)_4H$. Reaction (3, 16), however, is typical of the acid decomposition of substituted carbonyls, involving a disproportionation of valencies and redistribution of carbonyl groups. Formation of ferrous ion and iron carbonyl hydride occurs to some extent in the acid decomposition of amine- or alcohol-substituted iron carbonyls, especially those with the ratio CO : Fe = 3 : 1 or 2 : 1. Thus, the ethylenediamine compound $Fe_2(CO)_4en_3$ reacts quantitatively according to (3, 17) : [54]

$$(3, 17)\quad Fe_2(CO)_4en_3 + 2H^+ \longrightarrow Fe^{2+} + Fe(CO)_4H_2 + 3\,en$$

With tricarbonyl derivatives, the corresponding reaction occurs to a smaller extent, possible products [55, 56] being :

$$(3, 18)\quad 3Fe(CO)_3,X + 2H^+ \longrightarrow Fe^{2+} + Fe(CO)_4H_2 + Fe(CO)_5 + 3X$$

$$(3, 19)\quad 2Fe(CO)_3,X + 2H^+ \longrightarrow Fe^{2+} + Fe(CO)_4H_2 + 2CO + 2X$$

It may be noted that, although the quantitative formation of iron carbonyl hydride in reaction (3, 17) has led to the suggestion [45] that the amine compounds could be formulated as carbonyl hydride salts, yet no salts with similar complex cations, $[M\,en_3]^{2+}$, could be prepared synthetically.[46]

The nickel and cobalt hexammine salts of iron carbonyl hydride react with carbon monoxide,[52] the final products being iron carbonyl hydride

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[52] W. Hieber, *Z. Elektrochem.*, 1937, **43**, 290 ; *Angew. Chem.*, 1936, **49**, 463 ; *Die Chemie*, 1942, **55**, 7.

[53] Cf. ref. (19).

[54] W. Hieber and F. Leutert, *Ber.*, 1931, **64**, 2832.

[55] Cf. ref. (17).

[56] W. Hieber and H. Vetter, *Ber.*, 1931, **64**, 2340.

and either nickel carbonyl or cobalt carbonyl hydride. Hieber considers that mixed carbonyls, not yet isolated, are formed as intermediates :

$$[Fe(CO)_4H]_2[Ni(NH_3)_6] \rightarrow [Fe(CO)_4H]_2[Ni(CO)_n] \rightarrow Fe(CO)_4H_2 + [Fe(CO)_4]_3 + Ni(CO)_4$$

$$[Fe(CO)_4H]_2[Co(NH_3)_6] \rightarrow [Fe(CO)_4H]_2[Co(CO)_4] \rightarrow Fe(CO)_4H_2 + [Fe(CO)_4]_3 + Co(CO)_4H \rightarrow [Co(CO)_4]_2 + H_2$$

(5) *Formation of metal carbonyl hydrides in the high-pressure synthesis.* Hieber's recent work on the high-pressure synthesis has disclosed a number of new reactions by which the carbonyl hydrides may be formed. These are of interest, not only in themselves, but also in that they emphasise the peculiar ease of formation of cobalt carbonyl hydride, and suggest similar properties for the compounds of the related elements, rhodium and iridium.

In their study of the synthesis of cobalt carbonyl, W. Hieber, H. Schulten, and R. Marin [31] found that the gases blown off from the autoclave frequently contained a volatile carbonyl compound, although reagents that could lead to contamination with nickel carbonyl or iron pentacarbonyl were carefully avoided. By precipitation of $Co(CO)_4HgCl,\frac{1}{2}H_2O$ from mercuric chloride solution, the volatile compound was shown to be $Co(CO)_4H$, which formed when the reactants contained traces of moisture. When cobalt sulphide or iodide was deliberately moistened, formation of the carbonyl hydride took place very readily, by some process such as :

$$(3, 20) \qquad 2CoS + H_2O + 9CO + 4Cu \rightarrow 2Co(CO)_4H + CO_2 + 2Cu_2S$$

The formation of $Rh(CO)_4H$, $Ir(CO)_4H$ and probably $Os(CO)_4H_2$ and $Re(CO)_5H$ occurs under similar conditions.

Total synthesis of cobalt carbonyl hydride. Hieber, Schulten, and Marin found, further, that cobalt carbonyl hydride is formed in circumstances which amount to a total synthesis from its constituents. Thus, cobalt carbonyl is partly converted into the carbonyl hydride when it is heated in hydrogen (120 atm.) and carbon monoxide (150 atm., to prevent decomposition) at 165° :

$$(3, 21) \qquad [Co(CO)_4]_2 + H_2 \rightarrow 2Co(CO)_4H$$

Reaction (3, 21) is thus reversible, the synthesis being the converse of the spontaneous decomposition of the hydride at ordinary pressures. Partial conversion into hydride also occurs when metallic cobalt or cobalt sulphide is heated in hydrogen (50 atm.) and carbon monoxide :

$$(3, 22) \qquad 2Co + 8CO + H_2 \rightarrow 2Co(CO)_4H$$

$$(3, 23) \qquad 2CoS + 8CO + H_2 + 4Cu \rightarrow 2Co(CO)_4H + 2Cu_2S$$

Rather better conversion into the hydride was found in the action of carbon monoxide on T. Weichselfelder's cobalt hydride, CoH_2.[57] Hieber attributes the ready formation of cobalt carbonyl hydride in this case to the preexistence of the Co–H bond, but this view is not compatible with current models for the constitution of the carbonyl hydrides.

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[57] *Annalen*, 1926, **447**, 64.

Rhodium carbonyl hydride has also been obtained by reaction (3, 22). By contrast, iron carbonyl hydride is formed only in solution, by the reactions cited in III (1) and III (4). Careful investigation [58] has shown that none of the methods cited in this section yields any iron carbonyl hydride, neither is any formed when iron tetracarbonyl or iron carbonyl iodide is heated in hydrogen and carbon monoxide. In every case the product of reaction is iron pentacarbonyl.

(6) *High-pressure synthesis of mixed carbonyls.* The ease of formation of cobalt carbonyl hydride is reflected by the direct formation of its heavy-metal derivatives at high pressures. As was discussed in II (5), the rôle of silver or copper in the synthesis turns upon the coupling of the exothermic formation of carbonyl with the endothermic reduction of cobalt sulphide or halide. Using metals baser than copper, so that the reduction also is exothermic, reaction with carbon monoxide becomes quantitative; the product is not $[Co(CO)_4]_2$, however, but the corresponding heavy-metal derivative, *e.g.*, $[Co(CO)_4]_2Zn$. The compounds

$Co(CO)_4Tl$ (yellow)
$[Co(CO)_4]_2M^{II}$ $[M^{II}$ = Zn, Cd, Hg, Sn, Pb (?)] yellow or orange
$[Co(CO)_4]_3M^{III}$ $[M^{III}$ = Ga (?), In (red), Tl (violet)]

have been obtained by three types of reaction : [59]

(*a*) The reaction just discussed, typified by

(3, 24) $$2CoBr_2 + 3Zn + 8CO \longrightarrow 2ZnBr_2 + [Co(CO)_4]_2Zn$$

The thermochemistry of the process makes it possible to form the mercury compound by a reversal of the rôles of halogen acceptor and free metal:

(3, 25) $$HgX_2 + 3Co + 8CO \longrightarrow CoX_2 + [Co(CO)_4]_2Hg \quad (X = Cl, Br, I)$$

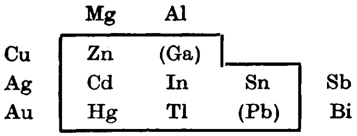
(*b*) Total synthesis :

(3, 26) $$2Co + Zn + 8CO \longrightarrow [Co(CO)_4]Zn$$

(*c*) From pre-formed cobalt carbonyl and zinc, cadmium, or mercury in carbon monoxide at high pressures :

(3, 27) $$[Co(CO)_4]_2 + Cd \longrightarrow [Co(CO)_4]_2Cd$$

The ability to form heavy-metal derivatives in this way is restricted to the metals in the portion of the Periodic Table shown inset, the tendency to do so being greatest for mercury.



	Mg	Al		
Cu	Zn	(Ga)		
Ag	Cd	In	Sn	Sb
Au	Hg	Tl	(Pb)	Bi

The heavy-metal compounds obtained in this way are identical with some prepared from solutions of cobalt carbonyl hydride (cf. III, 3). All are soluble in organic solvents, with normal molecular weights. They are distinctly more stable than cobalt carbonyl itself, may be sublimed, and melt with some decomposition above 70°. They are decomposed by an excess of halogen, but with one molecular proportion, cobalt carbonyl and

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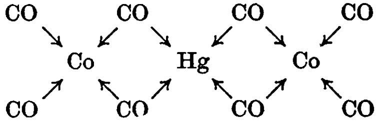
[58] W. Hieber and U. Teller, *Z. anorg. Chem.*, 1942, **249**, 58.

[59] *Idem, ibid.*, p. 43.

the halide of the metal are formed. Nitric oxide reacts to form cobalt nitrosocarbonyl; with $[Co(CO)_4]_2Cd$, just half the cobalt is converted into $Co(CO)_3NO$. Pyridine does not displace carbon monoxide, but forms addition compounds in which it is presumably linked to the second metal.

In view of their properties, these compounds are formulated by Hieber and Teller as polynuclear complexes, *e.g.*, (I). Similar constitutions can be assigned to the amminated derivatives of iron and cobalt carbonyl hydrides, obtained from solution. Mercury iron tetracarbonyl, $Fe(CO)_4Hg$, could obviously acquire a structure essentially similar to (I) by a process of infinite polymerisation, and it is significant that it is, in fact, an insoluble, completely non-volatile compound, in contrast to $[Co(CO)_4]_2Hg$.



(I.)

IV. *Metal Carbonyl Halides.*—(1) The halogen compounds of the metals, with co-ordinated carbon monoxide, are of interest in that they link the chemistry of the carbonyls with the more familiar chemistry of co-ordination compounds, especially of the platinum metals. The ability to form such compounds does not coincide exactly with the formation of pure carbonyls, as is indicated by the inset. An extension of the range of conditions experimentally accessible would doubtless increase the number of known compounds, as the recent isolation of $Co(CO)I_2$ shows. The experimental evidence points to the existence of an analogous nickel carbonyl iodide at high pressures; at the ordinary pressure the existence of $K_2[Ni(CN)_3(CO)]$ has been established.[13] The sulphate Ag_2SO_4,CO is the only known carbonyl derivative of silver.[60]

V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Nb	Mo		Ru	Rh	Pd	Ag	Cd
Ta	W	Re	Os	Ir	Pt	Au	Hg

Metals enclosed ——— form carbonyls.
Metals enclosed – – – – form carbonyl halides.

For the metals Pd, Pt, Cu, Au, which form no pure carbonyls, the sequence of stability of the carbonyl halides appears to be iodide $<$ bromide $<$ chloride.[61] The stability, ease of formation, and volatility of the compounds of the carbonyl-forming metals, however, all trend in the opposite sequence, running parallel with the polarisability of the halogen and the increasingly covalent character of the M–X valency forces.

The formation of the platinum-metal carbonyl halides, by direct combination of carbon monoxide with the metallic halides, was observed before systematic investigation coupled their reactions with those of the carbonyls proper (*e.g.*, the platinum carbonyl halides,[62] ruthenium carbonyl

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[60] W. Manchot and J. König, *Ber.*, 1927, **60**, 2183.

[61] Cf. O. H. Wagner, *Z. anorg. Chem.*, 1931, **196**, 364.

[62] P. Schützenberger, *Ann. Chim.*, 1868, **15**, 100; 1870, **21**, 350; F. Mylius and F. Foerster, *Ber.*, 1891, **24**, 2424, 3751.

bromide[63] and the carbonyl chlorides of palladium,[64] gold,[65] iridium,[66] and osmium[67]). The general chemistry of compounds of this type has been summarised elsewhere,[68] and those aspects which are relevant to the chemistry of the carbonyls have received notice in discussing the synthesis of the platinum-metal carbonyls (II, 4).

Table IV collects together the known types of carbonyl halides, and makes apparent the tendency to form compounds in which the stable co-ordination numbers 6 or 4 (probably square planar configuration) are attained either in monomeric compounds—*e.g.*, $Re(CO)_5X$, $Os(CO)_4X_2$, $Ir(CO)_3X$, $Pt(CO)_2X_2$—or by formation of a binuclear complex, as in $[Os(CO)_4X]_2$, $[Rh(CO)_2X]_2$.

TABLE IV

Metallic Carbonyl Halides and Related Compounds

Mn —	$Fe(CO)_5X_2$ $Fe(CO)_4X_2$ $[Fe(CO)_3Br_2]_3$ $Fe(CO)_2X_2$ $Fe(CO)_2I$ $K_3[Fe(CN)_5CO]$	$Co(CO)I_2$ $K_3[Co(CN)_5CO]$	Ni — $K_2[Ni(CN)_3CO]$	$Cu(CO)X$
	$Ru(CO)_2X_2$ $Ru(CO)Br$	$[Rh(CO)_2X]_2$	$[Pd(CO)Cl_2]_n$ $H[Pd(CO)Cl_3]$	Ag_2SO_4,CO
$Re(CO)_5X$	$Os(CO)_4X_2$ $Os(CO)_3X_2$ $Os(CO)_2X_2$ $[Os(CO)_4X]_2$	$Ir(CO)_3X$ $Ir(CO)_2X_2$	$Pt(CO)_2Cl_2$ $[Pt(CO)X_2]_2$ $H[Pt(CO)X_3]$	$Au(CO)Cl$

(2) *Iron carbonyl halides.* An adequate discussion of the chemistry of the carbonyl halides is possible only for the iron compounds. The range of known compounds, including the substituted carbonyl halides, is summarised in Table V ; the ratio CO : Fe varies in these from 5 : 1 to 1 : 1, the

TABLE V

$Fe(CO)_5X_2$	$Fe(CO)_4X_2$ $Fe(CO)_4XY$ $Fe(CO)_4en_2I_2$	$[Fe(CO)_3Br_2]_3$ $Fe(CO)_3Hg_2I_2$	$Fe(CO)_2I_2$ $Fe(CO)_2I$ $Fe(CO)_2py_2X_2$ $Fe(CO)_2phenanX_2$	$Fe(CO)py_2I_2$

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[63] W. Manchot and E. Enk, *ibid.*, 1930, **63**, 1635.

[64] W. Manchot and J. König, *ibid.*, 1926, **59**, 883.

[65] W. Manchot and H. Gall, *ibid.*, 1925, **58**, 2175 ; M. S. Kharasch and H. S. Isbell, *J. Amer. Chem. Soc.*, 1930, **52**, 2918.

[66] W. Manchot and H. Gall, *Ber.*, 1925, **58**, 232.

[67] W. Manchot and J. König, *ibid.*, p. 229.

[68] H. J. Emeléus and J. S. Anderson, " Modern Aspects of Inorganic Chemistry ", Routledge, London, 1938, Chap. 12.

substances poorer in carbon monoxide being formed directly under more drastic conditions, or formed and stabilised through the replacement of CO groups by amine molecules.

Whereas nickel and cobalt carbonyls are completely decomposed by free halogens, iron pentacarbonyl forms, first, the addition compounds $Fe(CO)_5X_2$, isolable only at low temperatures, and then, by spontaneous loss of carbon monoxide, the relatively stable tetracarbonyl halides.[69] The reaction of iron tetracarbonyl with bromine is more complex,[70] and it has been inferred that a mixture of $Fe(CO)_4Br_2$ with $[Fe(CO)_3Br_2]_3$ is formed, although the second compound was not isolated.

The iron carbonyl halides are non-electrolytes, soluble in inert organic solvents. Their stability rises progressively in the order chloride < bromide < iodide, as is evident from the comparison of decomposition temperatures, photochemical sensitivity, and thermochemical data [71] shown in Table VI, where Q and Q' are given in kg.-cal.

TABLE VI

X =	Cl.	Br.	I.
Decomposition temp. of $Fe(CO)_5X_2$	− 35°	− 10°	0°
Decomposition temp. of $Fe(CO)_4X_2$	+ 10°	+ 55°	+ 75°
$FeX_2 + 4CO \longrightarrow Fe(CO)_4X_2 + Q$	$Q = 17{\cdot}9$	28·3	38·9
$Fe(CO)_5 + X_2(g) \longrightarrow Fe(CO)_4X_2 + CO + Q'$	$Q' = 45{\cdot}8$	43·4	23·1
Stability of $Fe(CO)_2py_2X_2$ . .	Non-existent	Decomp. 0°	Stable, photosensitive
Stability of $Fe(CO)_2phenanX_2$	Decomp. − 10°	Stable, photosensitive	Stable, not photosensitive

Iron tetracarbonyl iodide is stable enough to sublime unchanged in a vacuum. If it is heated in hydrogen, the lower carbonyl iodide $Fe(CO)_2I_2$ is obtained as a bright red sublimate, although complete decomposition (to Fe + 4CO) occurs extensively also.[72] The same lower iodide is formed directly, by the action of iron pentacarbonyl on iodine dissolved in boiling benzene. Another mode of partial decomposition has been observed, on heating $Fe(CO)_4I_2$ in carbon dioxide. In addition to iron and carbon monoxide, FeI_3 and the unstable $Fe(CO)_2I$ [compare $Fe(NO)_2I$ [73]] are formed in small amount. Decomposition of the latter compound furnishes the hitherto unknown, bright red, unstable FeI.

The decomposition reaction (4, 1) proceeds to completion at room temperature, and is brought about by water, or by pyridine in excess ; it

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[69] W. Hieber and G. Bader, *Ber.*, 1928, **61,** 1717.

[70] *Idem, Z. anorg. Chem.*, 1931, **201,** 329.

[71] W. Hieber and A. Woerner, *Z. Elektrochem.*, 1934, **40,** 287.

[72] W. Hieber and H. Lagally, *Z. anorg. Chem.*, 1940, **245,** 295.

[73] J. S. Anderson and W. Hieber, *ibid.*, 1933, **211,** 132.

may be compared with (4, 2), which is typical of the aqueous decomposition

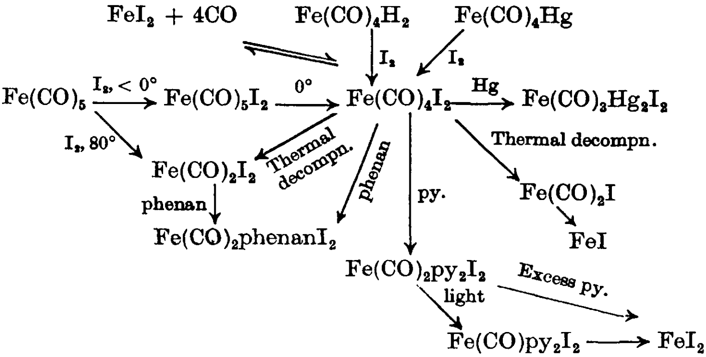
$$(4, 1) \qquad Fe(CO)_4I_2 \longrightarrow FeI_2 + 4CO$$

$$(4, 2) \qquad Pt(CO)Cl_2 + H_2O \longrightarrow 2HCl + CO_2 + Pt$$

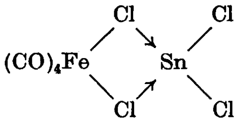
of the platinum-metal carbonyl halides. At high pressures, (4, 1) is reversible; at room temperature the equilibrium pressure is probably about 6 atm., and ethereal solutions of ferrous iodide are slowly and completely converted into $Fe(CO)_4I_2$ by carbon monoxide at high pressures.[74] Copper and other metals react with iron carbonyl iodide, forming cuprous iodide and the products of disproportionation of the $Fe(CO)_4$ radical.[75] Every step involved in the mechanism of the high-pressure synthesis (II, 4 ; II, 5) can thus be realised for the iron compounds.

Pyridine and other amines can effect partial replacement of carbon monoxide, the substituted compounds [75] being relatively stable (Table VI). These reactions, with others mentioned previously [76], are summarised in Table VII.

TABLE VII



Mixed carbonyl halides, $Fe(CO)_4XY$ ($X = I$, $Y = Cl$ or Br) have been obtained by W. Hieber and A. Wirsching [77] by the action of ICl or IBr on iron pentacarbonyl. These are intermediate in stability and properties between the corresponding simple carbonyl halides ; their chemical individuality is, perhaps, not certain. Compounds such as $SbCl_5$ or $SnCl_4$, which can act as halogenating agents, react with iron pentacarbonyl, forming $Fe(CO)_4SbCl_5$ and $Fe(CO)_4SnCl_4$ respectively. The latter, with a normal molecular weight in benzene, may be represented as (I). The former has, in benzene, only half the expected molecular weight, and as the electrical conductivity of its nitrobenzene solutions is negligibly small, it probably dissociates into $Fe(CO)_4Cl_2 + SbCl_3$.



(I.)

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[74] W. Hieber and H. Lagally, *Z. anorg. Chem.*, 1940, **245**, 305.

[75] W. Hieber, *Z. Elektrochem.*, 1937, **43**, 390.

[76] W. Hieber and G. Bader, *Z. anorg. Chem.*, 1930, **190**, 193.

[77] *Ibid.*, 1940, **245**, 38.

Sulphuryl chloride reacts additively with iron pentacarbonyl at low temperatures, but effects complete decomposition at 0°. It also reacts with $Fe(CO)_4I_2$, displacing both iodine and carbon monoxide. and forming the previously unknown compound $Fe(CO)_2Cl_2$.

V. *The Constitution of the Metal Carbonyls.*—(1) The constitution of the metal carbonyls has, since the discovery of nickel carbonyl, presented a problem in every formulation of a theory of valency. Their non-polar molecular constitution (which renders them volatile) and the diamagnetism of the simple carbonyls and all their substitution products stand in contrast with the properties of other classes of compound formed by the transition elements. Although the formal valency of the metals is not immediately apparent, some simple systematic relation clearly exists between the atomic numbers of the metals and the composition of their simplest carbonyls.

It is, in the first place, clear that the CO groups exist as such within the molecules, and that these groups retain, on the whole, the bond character of the free carbon monoxide molecule. The former point is assured by the ease with which carbon monoxide is liberated as such, and by the partial replacement of CO by neutral molecules—every stage of progressive replacement being capable of realisation with certain classes of compounds (cf. Table V). The second contention is supported by several lines of evidence. Nickel carbonyl has a zero dipole moment,[78] which implies collinearity of the Ni–C–O bonds. Unless the Ni–C and C–O linkages are both double bonds (Ni=C=O), which would involve very high covalencies in $Fe(CO)_5$ or $Cr(CO)_6$, the carbon and oxygen must be effectively triply linked (Ni—C≡O), as in carbon monoxide itself. That this is so is confirmed, not only by the bond length, but also by the strongest Raman frequency of nickel carbonyl [79, 80] (2039 cm.$^{-1}$; cf. 2155 cm.$^{-1}$ in the Raman spectrum of carbon monoxide, and the usual magnitude of double- and triple-bond frequencies).

The CO group in the carbonyls can accordingly be regarded as a little-modified carbon monoxide molecule, co-ordinated to a central metal *atom*, as other neutral molecules or ions are linked, in most types of co-ordination compound, to central *cations*. The essential equivalence of CO and of ammino-groups is demonstrated in the chemistry of the carbonyls, and also by the simplest carbonyl compound, borine carbonyl BH_3,CO, which is precisely analogous to BH_3,NMe_3 or to BF_3,NH_3. On this hypothesis, the composition of the monometallic carbonyls is determined by the requirement that the effective atomic number (E.A.N.) of the central atom shall be made up to that of the next inert gas :

$Fe(CO)_5$	Fe = 26	E.A.N. =	26 + 5 × 2 = 36
$Ni(CO)_4$	Ni = 28		28 + 4 × 2 = 36
$Mo(CO)_6$	Mo = 42		42 + 6 × 2 = 54
$Ru(CO)_5$	Ru = 44		44 + 5 × 2 = 54
$Os(CO)_5$	Os = 76		76 + 5 × 2 = 86

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[78] L. E. Sutton and J. B. Bentley, *J.*, 1933, 652.

[79] J. S. Anderson, *Nature*, 1932, **130**, 1002.

[80] *J. Chem. Physics*, 1934, **2**, 636.

It is significant that the elements of odd atomic number—Co, Rh, Re, Ir—form no monometallic carbonyls. The requisite condition of molecular stability is reached by some further formation of co-ordinate links within bi-nuclear molecules.

(2) *Stereochemistry and bond character in the carbonyls.* Pauling's hypothesis that 4 or 6 equivalent σ-type bonds are formed in co-ordination compounds by suitable hybridisation of *d*-, *s*-, and *p*-type orbitals, makes the spatial arrangement of co-ordinated groups an index of the bond type. Particular interest therefore attaches to the detailed interpretation of the structure of the carbonyls.

Crystal-structure studies [81] of the solid hexacarbonyls of chromium, molybdenum, and tungsten, and electron-diffraction investigations of their vapours [82] have established the octahedral configuration of CO groups around the central atom. Few complexes of co-ordination number 5 are known, and the configuration of iron pentacarbonyl was for some time in doubt. A trigonal bipyramidal structure should have zero dipole moment, whereas that of iron pentacarbonyl is finite, though small,[83] suggesting either a tetragonal pyramidal molecule, or non-equivalence of the Fe–CO bonds. The regular trigonal bipyramid, as in PF_5, appears to be the only structure in accord with the electron-diffraction data.[84] For 4-co-ordinate compounds based on the Ni^{2+} ion, a square planar configuration has been rigorously established. A. B. F. Duncan and J. W. Murray [80] wrongly inferred from the Raman spectrum that the same steric arrangement obtained in nickel carbonyl, but electron-diffraction measurements [85] clearly indicate that the molecule is tetrahedral, as also are the nitrosocarbonyls and carbonyl hydrides isoelectronic with it (see below).

Bond lengths deduced from the electron-diffraction data are summarised in Table VIII. The C–O distances are those expected for :C:::O: (cf. 1·13 A. in carbon monoxide itself). The M–C distances are, however, shorter in every case than the sum of the covalent radii of carbon and the central atom. Even if the covalent radius of triply-bonded carbon is uncertain by as much as 0·08 A. (cf. ref. 82), the residual discrepancies are significant. Brockway and his co-workers have accordingly regarded this as indicative of a real bond shortening due to resonance between the bond arrangements (I) and (II). Structure (II) has the merit of avoiding an accumulated negative charge on the metal atoms, which have low electronegativities. Only in nickel carbonyl could all the CO groups be so linked to the metal; the

$$\underset{\text{(I.)}}{M \leftarrow C{\equiv}O} \qquad\qquad \underset{\text{(II.)}}{M{=}C{=}O}$$

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[81] W. Rüdorff and U. Hofmann, *Z. physikal. Chem.*, 1935, *B*, **28,** 351.

[82] L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, 1938, **34,** 1350.

[83] W. Graffunder and E. Heymann, *Z. physikal. Chem.*, 1932, *B*, **15,** 377; E. Bergmann and L. Engel, *ibid.*, 1931, *B*, **13,** 236.

[84] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, 1939, **35,** 681.

[85] L. O. Brockway and P. C. Cross, *J. Chem. Physics*, 1935, **3,** 828.

TABLE VIII

Inter-atomic Distances in Metal Carbonyls from Electron-diffraction Data (in A. *units)*

	C–O.	M–C.	N–O.	M–N.	M–C, calc.	Bond shortening.
$Ni(CO)_4$	1·15	1·82			1·98	– 0·16
$Fe(CO)_5$	1·15	1·84			2·00	– 0·16
$Cr(CO)_6$	1·15	1·92			2·02	– 0·10
$Mo(CO)_6$	1·15	2·08			?	?
$W(CO)_6$	1·13	2·06			?	?
$Co(CO)_3NO$ . . .	1·14	1·83	1·10	1·76	1·99	– 0·16
$Fe(CO)_2(NO)_2$ . .	1·15	1·84	1·12	1·77	2·00	– 0·16
$Co(CO)_4H$	1·16	1·83*			1·99	– 0·16
$Fe(CO)_4H_2$ . . .	1·15	1·82*			2·00	– 0·18

* Average bond lengths, taken to be weighted means of M–C–O and M–C–OH groupings.

type (I) bonding—which determines the stereochemical properties in any case—must be increasingly important in $Fe(CO)_5$ and the hexacarbonyls, as the last column of Table VIII shows. Hieber [86] has suggested that the evidence for effective octavalency of nickel is not cogent, and that the bond shortening might arise from a secondary interaction between the π-electrons of the C≡O bond and the 3*d* electrons of the nickel atom. The accurate structure determination of $[Fe(C{\equiv}N{-}CH_3)_6]Cl_2,3H_2O$,[87] in which (see below) the $C{\equiv}N{-}CH_3$ group plays a similar rôle to that of C≡O in the carbonyls, does, however, substantiate the idea of resonance between (I) and (II).

In deducing the bond type in the carbonyls and their derivatives, isosteric relations with other classes of co-ordination compound may be noted. The :C:::O: group, the CN^- ion :C:::N:, and the NO^+ group :N:::O: are isosteric and isoelectronic. The Cr atom is (by the displacement rule) similarly isoelectronic with the Fe^{2+} and Co^{3+} ions. Hence the electrostatically neutral $Cr(CO)_6$ has the same electronic configuration and steric arrangement as a number of diamagnetic complex cyano-anions (Table IX), all based on the formation of σ-type (d^2sp^3) covalencies about a ^1S core.

TABLE IX

Complexes MX_6—$M(KL3s^23p^63d^6)\ \sigma\text{-}[(3d^24s4p^3)]^{12}(A{\equiv}B)_6$

M-CN⁻.	M-CO.	M-NO⁺.
$[Mn^I(CN)_6]^{5-}$ $[Fe^{II}(CN)_6]^{4-}$ $[Co^{III}(CN)_6]^{3-}$	$Cr^0(CO)_6$ $[Fe^{II}(CN)_5(CO)]^{3-}$	$[Mn^I(CN)_5(NO)]^{3-}$ $[Fe^{II}(CN)_5(NO)]^{2-}$

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[86] W. Hieber, *Die Chemie*, 1942, **55**, 25.

[87] H. M. Powell and G. W. R. Bartindale, *J.*, 1945, 799.

In the case of $Ni(CO)_4$, the central atom is Ni^0, $^1S(KL3s^23p^63d^{10})$, isoelectronic with Cu^+ and Zn^{++}. No $3d$ orbits are available for hybridisation [to give four co-planar dsp^2 bonds], so that in $Ni(CO)_4$, as in the complex ions $[Cu^I(CN)_4]^{3-}$ and $[Zn^{II}(CN)_4]^{2-}$, a tetrahedral configuration is imposed by the formation of four $(4s4p^3)$ bonds.

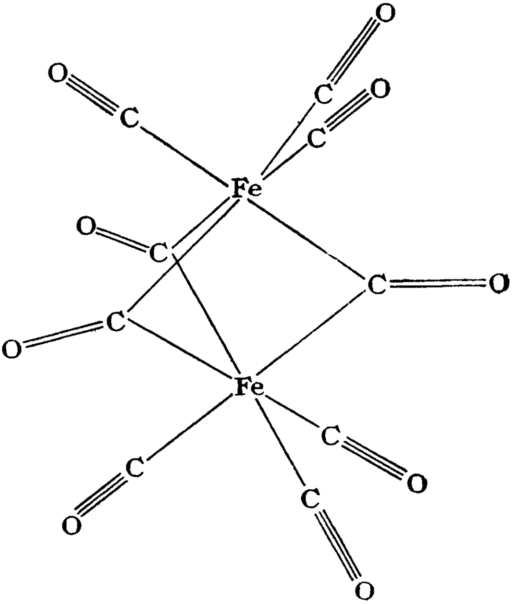
(3) *Polynuclear carbonyls.* If the central metal atom cannot otherwise attain a closed electronic configuration (*e.g.*, with metals of odd atomic number, or with lower CO : metal ratios than the maximum), polynuclear carbonyls are formed. The constitution of these has probably not yet been finally settled.

N. V. Sidgwick and R. W. Bailey [88] suggested a general principle for formulating polynuclear carbonyls and nitrosyls, based on the hypotheses (*a*) that all the metal atoms should acquire the effective atomic number of an inert gas, and (*b*) that the CO group can form two collinear co-ordinate links. $Fe_2(CO)_9$ then receives the constitution (I). The isoelectronic CN^- group can undoubtedly form two such collinear links—*e.g.*, in crystalline AgCN,[89] and in $[(C_3H_7)_2AuCN]_4$ [90]—but participation of CO in similar structures would involve residual positive charges on the adjacent carbon and oxygen atoms, and so is less likely.

Brill's inference [91] that the molecule of $Fe_2(CO)_9$ has trigonal symmetry

$(CO)_4Fe \leftarrow C{\equiv}O \rightarrow Fe(CO)_4$

(I.)



(II.)

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[88] *Proc. Roy. Soc.*, 1934, *A*, **144**, 521.

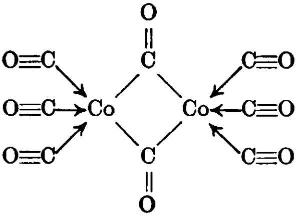
[89] R. D. West, *Z. Krist.*, 1934, **88**, 173 ; 1935, **90**, 555.

[90] R. F. Phillips and H. M. Powell, *Proc. Roy. Soc.*, 1939, *A*, **173**, 147.

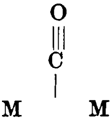
[91] R. Brill, *Z. Krist.*, 1927, **65**, 85.

has been confirmed by a detailed *X*-ray crystallographic study,[92] which has shown conclusively that the structure is that shown in (II); the Sidgwick–Bailey rules are not apparently valid.

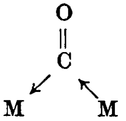
The terminal CO groups are collinear with the co-ordinate links, but the bridge CO groups are linked by the *carbon* atom to both iron atoms. Their C–O distance (1·3 A.), is longer than that in the terminal CO groups, and approximates to that of the C=O group. Whilst the geometry of the molecule is thereby established, inferences as to the bond character must be critically examined for their wider implications. The obvious conclusion, that each iron atom forms three ordinary covalencies [in place of the effective zero-valency of iron in $Fe(CO)_5$], gives to it the effective atomic number 35, and leaves it with one unpaired electronic spin. The diamagnetism of $Fe_2(CO)_9$[93] can then be explained only by the supplementary hypothesis of spin coupling between the unpaired electrons of the two relatively closely spaced iron atoms. An analogous formulation of $Co_2(CO)_8$ as (III) would present the same difficulty.



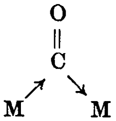
(III.)



(IV.)

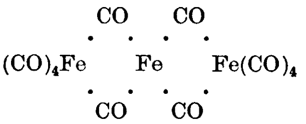


(V.)



(VI.)

If, however, the bond pattern advanced for $Fe_2(CO)_9$ is extended to $Fe_3(CO)_{12}$, $Co_4(CO)_{12}$, etc., the problem is more acute, and supplementary hypotheses are less plausible. Detailed structure analyses for these compounds are lacking, but R. Brill[94] considers that the space-group data for $Fe_3(CO)_{12}$ indicate the two-fold symmetry of structure (VII). This structure, on the Powell and Ewens model, would confer a ^1S configuration on the outer iron atoms, but the central iron atom would be quadrivalent, with E.A.N. = 30; the molecule would certainly be paramagnetic. Similar difficulties arise for the "mixed carbonyl" derivatives of iron and cobalt carbonyl hydrides (cf. III, 6).



(VII.)

Any distinction between two substantially different kinds of metal–CO binding within the polynuclear carbonyls seems out of harmony with the general chemistry of these compounds, as compared with the simple carbonyls. In this connection the considerations of K. A. Jensen[95] on the constitution of polynuclear complexes are of interest. He suggests for the linking of the

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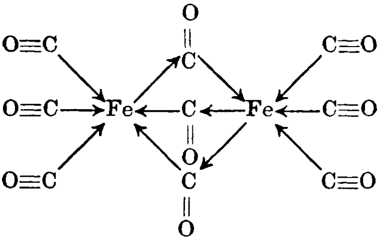
[92] H. M. Powell and R. V. G. Ewens, *J.*, 1939, 286.

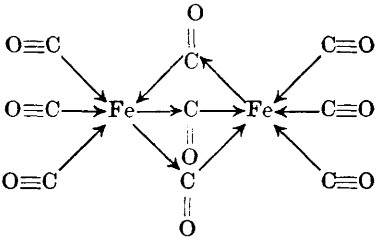
[93] W. Klemm, H. Jacobi, and J. Tilk, *Z. anorg. Chem.*, 1931, **201**, 1.

[94] *Z. Krist.*, 1931, **77**, 36.

[95] *Z. anorg. Chem.*, 1944, **252**, 234.

bridge groups a resonance between the forms (IV), (V), and (VI) ; $Fe_2(CO)_9$ would then be regarded as a resonance hybrid of (VIII) and (IX), which would fit the observed bond lengths, and would be compatible, without supplementary hypotheses, with the observed diamagnetism.


(VIII.)


(IX.)

(4) *Nitrosocarbonyls and carbonyl hydrides.* The structural principle underlying the existence and composition of the two series

$Fe(CO)_2(NO)_2$	$Co(CO)_3NO$	$Ni(CO)_4$
$Fe(CO)_4H_2$	$Co(CO)_4H$	$Ni(CO)_4$

is clearly the attainment of the same closed electronic configuration throughout—that of the nickel carbonyl molecule.

In the nitrosocarbonyls, $(:N:::O:)^+$ groups replace $(:C:::O:)$ groups progressively, as the diamagnetic susceptibilities show. The NO^+ groups arise from the transfer of the odd electron of the nitric oxide molecule to the iron or cobalt atoms, which thereby become " pseudo-nickel " atoms :

$(O{\equiv}C)_4{-}Ni$	$(O{\equiv}C)_3{-}Co{-}N{\equiv}O$	$(O{\equiv}C)_2{-}Fe{-}(N{\equiv}O)_2$
$8 + 28 = 36$	$6 + 27 + 1 + 2 = 36$	$4 + 26 + 2 + 4 = 36$

Electron-diffraction data [96] (Table VIII) show that the nitrosocarbonyls are closely isosteric with nickel carbonyl. The somewhat enhanced polarity of the nitrosocarbonyl structure is reflected in their lower volatility [97] and other physical properties.

The carbonyl hydrides have also been proved to have the tetrahedral $Ni(CO)_4$ structure, but the mode of linkage of the hydrogen [84] is, perhaps, not certainly established by the electron-diffraction data. Hieber's view [38, 86] that the hydrogen atoms are incorporated in some way as protons within the core of the cobalt and iron atoms (which become " pseudo-nickel " atoms) is difficult to accept as a physical model, though it is not very different in principle from K. S. Pitzer's recently advocated borane structure.[98] Ewens and Lister [84] suggested that an electron is transferred to the metal atom, and that a proton is linked to the lone pair of electrons of the CO oxygen atom. The resulting group $(:C:::O:H)^+$ would be isoelectronic with, and not too different sterically from, the

[96] L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.*, 1937, **33,** 1233.
[97] W. Hieber and J. S. Anderson, *Z. anorg. Chem.*, 1932, **208,** 232.
[98] *J. Amer. Chem. Soc.*, 1945, **67,** 1126.

(:N:::O:)$^+$ group, so that the carbonyl hydrides are the analogues of the nitrosocarbonyls. However, Hieber [86] has pointed out that the formulation involves, in effect, a quaternary oxonium group which would be unique ; this should be stabilised by alkylation, whereas the carbonyl hydrides form no alkyl derivatives under any conditions yet found. Moreover, no cogent evidence has been advanced that there are two types of M–C and C–O bond dimension within the molecules. This question should therefore be regarded as open. Critical consideration of the structural problems, presented by this whole group of compounds, serves to lay salutary emphasis on the caution that is needed in drawing conclusions from purely metrical data as to the intimate constitution of molecules of unusual type.