The Chemistry of Transition-metal Carbonyls: Synthesis and Reactivity

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1 Introduction

Earlier[1] we surveyed the stereochemistry and bonding in the metal carbonyls and their derivatives. Herein we shall review their chemistry from the standpoint of synthesis and reactivity. In the last five years several aspects of metal carbonyl chemistry have been reviewed in depth, and Table 1 lists several important surveys for those who wish to study this subject in more detail than can be given here.

We have previously tabulated the formulae of the known metal carbonyls and the reader is referred to Tables 2, 4, and 5 of the previous article[1] in *Quarterly Reviews* as an aid to understanding this article. The common abbreviations we have used are given in Table 2.

2 Preparation of the Metal Carbonyls

Few metal carbonyls can be prepared as simply as was tetracarbonylnickel by Mond, Langer, and Quincke in 1891.[1] The only metals which react readily with carbon monoxide are nickel and iron. Indeed, carbon monoxide stored in iron cylinders can contain appreciable amounts of $Fe(CO)_5$.

Since the oxidation state of a metal atom in a metal carbonyl is lower than in the complex from which it is derived, all carbonylations of metal compounds are reductions. Most syntheses, therefore, depend upon reducing a transition-metal compound in the presence of carbon monoxide under pressure (Table 3). Common reducing agents are sodium, aluminium alkyls, or carbon monoxide itself, the latter sometimes mixed with hydrogen. The term 'reductive carbonylation' has been coined for reactions of this kind.[2] Mechanistic studies on such syntheses are lacking, but it is reasonable to assume that successive reduction steps are accompanied by simultaneous co-ordination of carbon monoxide groups. This is supported by the reactions which occur between ruthenium or rhodium trihalides and carbon monoxide. Carbonylation of ruthenium trichloride in methanol affords the dinuclear ruthenium(II) complex $[Ru(CO)_3Cl_2]_2$, but the same reaction carried out in the presence of zinc as a halide acceptor, or under higher carbon monoxide pressures, affords the carbonyl $Ru_3(CO)_{12}$.[3] Passage of

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[1] E. W. Abel and F. G. A. Stone, *Quart. Rev.*, 1969, **23**, 325.
[2] H. E. Podall, *J. Chem. Educ.*, 1961, **38**, 187.
[3] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1967, 1238.

carbon monoxide at atmospheric pressure over rhodium(III) chloride trihydrate at 100 °C represents a good route to the binuclear rhodium(I) carbonyl halide $[Rh(CO)_2Cl]_2$,[4] whereas if the reaction is carried out in methanol at 60 °C using CO at 40 atm. the hexanuclear carbonyl $Rh_6(CO)_{16}$ is formed.[5] Moreover, in a series of elegant experiments, Chini and Martinengo[6] have shown that $[Rh(CO)_2Cl]_2$ can be reduced to $Rh_4(CO)_{12}$ by carbon monoxide and water at room temperature and atmospheric pressure, and that in the presence of alkali and alkali metals further reduction occurs:

$$[Rh(CO)_2Cl[_2 \xrightarrow[H_2O]{CO} Rh_4(CO)_{12} \xrightarrow[OH^-]{CO} [Rh_{12}(CO)_{30}]^{2-} \xrightarrow[OH^-]{CO} [Rh_7(CO)_{16}]^{3-}$$

$$\xrightarrow[OH^-]{CO} [Rh_6(CO)_{14}]^{4-} \xrightarrow[Na\text{-}THF]{CO} [Rh(CO)_4]^-$$

In some syntheses, particularly when electropositive metals (Na, Mg) are used as reducing agents, the products of reductive carbonylation are not the neutral carbonyls but anionic species. Hence the final reaction step involves oxidation, *e.g.*

$$\begin{tikzcd} VCl_3 + 4Na + 6CO\ (200)^{*} \arrow[r, "\text{diglyme}", "160\ ^{\circ}C"'] & {[Na(\text{diglyme})_2][V(CO)_6] + 3NaCl} \arrow[d, "HCl\text{-}Et_2O"] \\ & V(CO)_6 \end{tikzcd}$$

(refs. 7, 8)

$$\begin{tikzcd} CrCl_3 + 5Na + 5CO\ (150) \arrow[r, "\text{diglyme}", "0\text{–}25\ ^{\circ}C"'] & {[(\text{diglyme})_2Na]_2[Cr(CO)_5] + 3NaCl} \arrow[d, "0\ ^{\circ}C"', "{CO\ (50),\ H_2SO_4}"] \\ & Cr(CO)_6 \end{tikzcd}$$

(ref. 9)

With diglyme as solvent, electron transfer from sodium to the transition metal is probably facilitated by the solubility of the alkali metal in the polyether which is accompanied by some charge transfer. Hence the first act of the reduction is an attack by the solvent on the transition-metal halide. Support for this idea comes from the existence of well developed syntheses involving radical carbanions. Thus in one preparation of decacarbonyldimanganese, manganese(II) chloride is treated with sodium benzophenone ketyl and carbon monoxide.[8,10]

$$2MnCl_2 + 4Ph_2CONa + 10CO\ (200) \xrightarrow[200\ ^{\circ}C]{THF} Mn_2(CO)_{10} + 4NaCl + 4Ph_2CO$$

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[*] Figures in parentheses in this and subsequent equations refer to CO pressure in atmospheres.

[4] J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

[5] S. H. H. Chaston and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 500.

[6] P. Chini and S. Martinengo, *Chem. Comm.*, 1969, 1092; *Inorg. Chim. Acta*, 1969, **3**, 21, 299 and 315.

[7] F. Calderazzo and R. Ercoli, *Chim. Ind.* (*Milan*), 1962, **44**, 990.

[8] R. B. King, 'Organometallic Syntheses' Volume I, Transition Metal Compounds, Academic Press, 1965.

[9] H. E. Podall, H. B. Prestridge, and H. Shapiro, *J. Amer. Chem. Soc.*, 1961, **83**, 2057.

[10] R. D. Closson, L. R. Buzbee, and G. C. Eçke, *J. Amer. Chem. Soc.*, 1960, **82**, 1325.

Table 1 *Reviews of chemistry of the metal carbonyls and their derivatives**

Topic	*Authors*	*Reference*
Preparation, Structure and Properties	F. Calderazzo, R. Ercoli, and G. Natta	Chapter 1, 'Organic Syntheses via Metal Carbonyls', ed. I. Wender and P. Pino, Interscience, 1968.
Synthesis and Identification†	J. C. Hileman	*Prep. Inorg. React.*, 1964, **1**, 77
Structural Chemistry	(*a*) E. W. Abel and F. G. A. Stone	*Quart. Rev.*, 1969, **23**, 325
	(*b*) M. R. Churchill and R. Mason	*Adv. Organometallic Chem.*, 1967, **5**, 93
Metal Carbonyl Clusters	P. Chini	*Inorg. Chim. Acta Rev.*, 1968, **2**, 31
Kinetics and Mechanisms of Substitution Reactions of Metal Carbonyl Complexes	R. J. Angelici	*Organometallic Chem. Rev.*, 1968, **3**, 173
Metal Carbonyl Cations	E. W. Abel and S. Tyfield	*Adv. Organometallic Chem.*, 1970, **8**, 117
Alkali Metal Derivatives of Metal Carbonyls	R. B. King	*Adv. Organometallic Chem.*, 1964, **2**, 157
Lewis Base-Metal Carbonyl Complexes	T. A. Manuel	*Adv. Organometallic Chem.*, 1965, **3**, 181
Substitution Complexes of Cr, Mo and W Carbonyls	G. R. Dobson, I. W. Stolz and R. K. Sheline	*Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 1
Sulphur and Phosphorus Bridged Metal Carbonyl Complexes	R. G. Hayter	*Prep. Inorg. React.*, 1965, **2**, 211
Sulphur-containing Metal Carbonyls	E. W. Abel and B. C. Crosse	*Organometallic Chem. Revs.*, 1967, **2**, 443
Metal Carbonyl Hydrides	(*a*) M. L. H. Green and D. J. Jones	*Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 115
	(*b*) M. L. H. Green	*Angew Chem.*, 1960, **72**, 719
	(*c*) A. Ginsberg	*Progr. Trans. Metal. Chem.*, 1965, **1**, 111
Halogeno Metal Carbonyls	F. Calderazzo	'Halogen Chemistry,' Vol. 3, ed. V. Gutmann, Academic Press, 1967
Halogenocarbonyls of Cr, Mo and W	M. W. Anker, R. Colton, and I. B. Tomkins	*Rev. Pure Appl. Chem.*, 1968, **18**, 23

Carbonyl Complexes of Transition Metals in Positive Oxidation States	M. H. B. Stiddard	*Rev. Chim. minérale*, 1966, 801
Fluorocarbon-metal Carbonyl Complexes	M. I. Bruce and F. G. A. Stone	*Prep. Inorg. React.*, 1968, **4**, 177
Cyclopentadienyl and Arene Metal Carbonyls	R. L. Pruett	*Prep. Inorg. React.*, 1965, **2**, 187
Carbonyl Complexes with Hydrocarbon Ligands	E. O. Fischer and H. Werner	'Metal π-Complexes', Elsevier, 1966
Metal Carbonyls and Acetylenic Compounds	(*a*) W. Hubel	Chapter 2, 'Organic Syntheses via Metal Carbonyls', ed. I. Wender and P. Pino, Interscience, 1968
	(*b*) F. L. Bowden and A. P. Lever	*Organometallic Chem. Rev.*, 1968, **3**, 227
Catalysis by Cobalt Carbonyls	A. J. Chalk and J. F. Harrod	*Adv. Organometallic Chem.*, 1968, **6**, 119
Alkyl- and Acyl-cobalt Carbonyls	R. F. Heck	*Adv. Organometallic Chem.*, 1966, **4**, 243
Diene-Iron Carbonyl Complexes	R. Pettit and G. F. Emerson	*Adv. Organometallic Chem.*, 1964, **1**, 1
Metal Carbonyl Complexes with Si, Ge, Sn or Pb Atoms as Ligands	(*a*) J. F. Young	*Adv. Inorg. Chem. Radiochem.*, 1968, **11**, 92
	(*b*) F. G. A. Stone	'New Pathways in Inorganic Chemistry', eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968, p. 283
Ruthenium Carbonyl	M. I. Bruce and F. G. A. Stone	*Angew. Chem. Internat. Edn.*, 1968, **7**, 427
Infrared Spectra of Metal Carbonyl Complexes	L. M. Haines and M. H. B. Stiddard	*Adv. Inorg. Chem. Radiochem.*, 1970, **12**, 53

[*] Annual Reports of the Chemical Society 1965–69 contain excellent review sections on recent progress.

[†] Various syntheses of metal carbonyls and their derivatives are described in detail in 'Organometallic Syntheses', by R. B. King (Academic Press, 1965), in the various volumes of 'Inorganic Syntheses' (McGraw-Hill), and in 'Handbook of Preparative Inorganic Chemistry' (Ed. G. Brauer) Volumes 1 and 2, Academic Press.

Table 2 *Abbreviations*

acac	acetylacetonate
π-C_3H_5	π-allyl
Bu	n-butyl
π-C_5H_5	π-cyclopentadienyl
π-C_7H_7	π-cycloheptatrienyl
den	diethylenetriamine
diars	*o*-phenylenebis(dimethylarsine)
diglyme	2,2′-dimethoxydiethyl ether
diphos	1,2-bis(diphenylphosphino)ethane
dipy	2,2′-dipyridyl
DMF	dimethylformamide
en	ethylenediamine
Et	ethyl
ffars	1,2-dimethylarsinoperfluorocyclobutene
ffos	1,2-diphenylphosphinoperfluorocyclobutene
HMPT	hexamethylphosphoramide
Me	methyl
Ph	phenyl
phen	phenanthroline
py	pyridine
THF	tetrahydrofuran
o-triars	bis(*o*-dimethylarsinophenyl)methylarsine

Table 3 *Synthesis of metal carbonyls**

Compound	*Reactants*	*Yield(%)*	*Reference*
$V(CO)_6$	VCl_3, Na, CO, diglyme	55†	*a*
$Cr(CO)_6$	$CrCl_3$, Al, $AlCl_3$, CO, C_6H_6	80	*a, b*
	$Cr(acac)_3$, Mg, CO, THF, I_2, py	80	*a, c*
	$CrCl_3$, Na, CO, diglyme or naphthalene	80	*d*
	$CrCl_3$, Et_3Al, CO	40	*e*
$Mo(CO)_6$	$MoCl_5$, Et_3Al, CO	75	*e*
	$MoCl_5$, Na, CO, diglyme	65	*d*
$W(CO)_6$	WCl_6, Et_3Al, CO	90	*e*
	WCl_6, $Fe(CO)_5$, H_2, Et_2O	85	*f*
$Mn_2(CO)_{10}$	$MnCl_2$, Ph_2CO, Na, CO, THF	35	*a, g*
	$MeC_5H_4Mn(CO)_3$, Na, CO, diglyme	20	*h*
	$Mn(OAc)_2$, Et_3Al, CO, $Pr^i{}_2O$	60	*e*
$Tc_2(CO)_{10}$	Tc_2O_7, CO	50	*i*
$Re_2(CO)_{10}$	Re_2O_7, CO	60	*a, j, k*
$Fe(CO)_5$	Fe, S(catalyst), CO	90	*l*
$Fe_2(CO)_9$	u.v. irradiation of $Fe(CO)_5$ in glacial acetic acid	70	*a, m*
$Fe_3(CO)_{12}$	$HFe(CO)_4^-$, NH_4Cl, MnO_2	70	*a, n*
	$Fe(CO)_5$, Et_3N–H_2O, MeOH, HCl	70	*o*

$Ru(CO)_5$	$Ru(acac)_3$, CO, H_2, heptane	50	*p*
$Ru_3(CO)_{12}$	$Ru(acac)_3$, CO, H_2, MeOH	70	*q*
	$RuCl_3{\cdot}3H_2O$, CO, MeOH	~70	*t*
$Os(CO)_5$	OsO_4, CO, heptane	~30	*p*
$Os_3(CO)_{12}$	OsO_4, CO, xylene	70	*s*
	OsO_4, CO, methanol	80	*t*
$Co_2(CO)_8$	$Co(OAc)_2$, $(AcO)_2O$, CO, H_2	60	*a*
	$CoCO_3$, CO, H_2, petroleum ether	80	*u*
	$CoCl_2$, CO, KOH, H_2O, KCN	30	*v*
$Co_4(CO)_{12}$	$Co_2(CO)_8$, $Co(C_7H_{15}CO_2)_2$, H_2, heptane	95	*a, w*
$Rh_4(CO)_{12}$	$[Rh(CO)_2Cl]_2$, CO, H_2O, $NaHCO_3$ n-hexane	80	*x*
$Rh_6(CO)_{16}$	$RhCl_3{:}3H_2O$, CO, MeOH	90	*y*
	$[Rh(CO)_2Cl]_2$, LiOAc, CO, MeOH	80	*x*
$Ir_4(CO)_{12}$	$IrCl_3,3H_2O$, CO, MeOH	60	*y*
$Ni(CO)_4$	Ni, CO		*z*

• For a more detailed listing, see the articles by Hileman, and by Calderazzo, Ercoli, and Natta given in Table 1. The compounds $Fe(CO)_5$, $Ni(CO)_4$, $Mo(CO)_6$, and $W(CO)_6$ are readily available commercially, hence the methods of preparation of these four carbonyls are included only for the sake of completeness.

† Yield of the salt $[Na(diglyme)_2][V(CO)_6]$, see text. Vanadium hexacarbonyl is formed by adding 4N-hydrochloric acid in diethyl ether. The carbonyl is air sensitive and thermally unstable, the latter factor contributing to a lower yield from the salt.

[a] R. B. King, 'Organometallic Syntheses', Vol 1, Academic Press, 1965. [b] E. O. Fischer, W. Hafner, and K. Öfele, *Chem. Ber.*, 1959, **92**, 3050. [c] R. Ercoli, F. Calderazzo, and G. Bernardi, *Gazzetta*, 1959, **89**, 809. [d] H. E. Podall, H. B. Prestridge, and H. Shapiro, *J. Amer. Chem. Soc.*, 1961, **83**, 2057. H. Shapiro and H. E. Podall, *J. Inorg. Nuclear Chem.*, 1963, **24**, 925. [e] H. E. Podall, J. H. Dunn, and H. Shapiro, *J. Amer. Chem. Soc.*, 1960, **82**, 1325. [f] A. N. Nesmeyanov, K. N. Anisimov, E. P. Mikheev, V. L. Volkov, and Z. P. Valueva, *Zhur. Neorg. Khim.*, 1959, **4**, 249. [g] R. D. Closson, L. R. Buzbee, and G. C. Ecke, *J. Amer. Chem. Soc.*, 1958, **80**, 6167. [h] R. B. King, J. C. Stokes, and T. F. Korenowski, *J. Organometallic Chem.*, 1968, **11**, 641. [i] J. C. Hileman, *Preparative Inorg. React.*, 1964, **1**, 102. [j] W. Hieber and H. Fuchs, *Z. anorg. Chem.*, 1941, **248**, 256. [k] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1962, **1**, 933. [l] W. Hieber and O. Geisenberger, *Z. anorg. Chem.*, 1950, **262**, 15. [m] E. H. Braye and W. Hübel, *Inorg. Synth.*, 1966, **8**, 178. [n] R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 193. [o] W. McFarlane and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 181. [p] F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, 1967, **6**, 1220. [q] G. Braca, G. Sbrana, and P. Pino, *Chim. Ind. Italy*, 1964, **46**, 206; 'Progress in Co-ordination Chemistry', Ed. M. Cais, Elsevier, 1968, pA19. [r] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. (A)*, 1967, 1238. [s] C. W. Bradford and R. S. Nyholm, *Chem. Comm.*, 1967, 384. [t] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc. (A)*, 1968, 2859. [u] W. L. Jolly, 'Synthetic Inorganic Chemistry', Prentice Hall, Englewood Cliffs, New Jersey, 1960, p. 168; I. Wender, H. W. Sternberg, S. Metlin, and M. Orchin, *Inorg. Synth.*, 1957, **5**, 190. [v] R. J. Clark, S. E. Whiddon, and R. E. Serfass, *J. Organometallic Chem.*, 1968, **11**, 640. [w] R. Ercoli, P. Chini, and M. Massi-Mauri, *Chim. Ind. Italy*, 1959, **41**, 132. [x] P. Chini and S. Martinengo, *Inorg. Chim. Acta*, 1969, **3**, 315. [y] S. H. H. Chaston and F. G. A. Stone, *J. Chem. Soc. (A)*, 1969, 500. [z] A. E. Rea, 'Nickel Carbonyl', The International Nickel Co., New York, 1955; 55 Patents on the production of the carbonyl listed.

Interestingly, some additional manganese carbonyl is often obtained by acidification of the product mixture, suggesting that sufficient electron transfer from the radical anion occurs to form some $NaMn(CO)_5$.

If the above description in terms of an electron transfer process is correct, electrochemical synthesis of metal carbonyls suggests itself. Indeed, preliminary results show that the 'electrocarbonylation' of metal acetylacetonates dissolved in anhydrous pyridine under CO pressures of from 50—200 atm., in the presence of an auxiliary electrolyte (Bu_4NBr), affords a variety of metal carbonyls or carbonylmetallates.[11]

In some chemical reduction processes involving metal oxides, carbon monoxide is sufficiently reducing in character that addition of a further reducing agent is unnecessary. The oxides Re_2O_7, Tc_2O_7, and OsO_4 can be converted to their respective carbonyls in this manner, *e.g.*,[12]

$$Re_2O_7 + 17CO\,(180) \xrightarrow{250\ ^\circ C} Re_2(CO)_{10} + 7CO_2$$

A mixture of carbon monoxide and hydrogen can be a useful source of both the reducing agent and the ligand. Thus octacarbonyldicobalt can be made conveniently from cobalt(II) acetate, carbon monoxide, and hydrogen, in acetic anhydride solution.[8,13]

$$2[Co(H_2O)_4][OAc]_2 + 8(Ac)_2O + 8CO\,(160) + 2H_2\,(40) \xrightarrow{170\ ^\circ C} Co_2(CO)_8 + 20\,HOAc$$

For metals which form stable hydrides, addition of hydrogen as a reactant can lead to formation of carbonyl hydrides rather than the carbonyls. By heating OsO_4 with CO the carbonyls $Os_3(CO)_{12}$[14–16] or $Os(CO)_5$[14,17] can be obtained, depending on the reaction conditions. However, with CO and H_2, osmium tetroxide affords $H_2Os(CO)_4$,[18] as well as small amounts of novel polynuclear hydrides, $H_2Os_2(CO)_8$ and $H_2Os_3(CO)_{12}$.[19]

Pentacarbonyliron has been used both as a reducing agent and a carbonylating agent in the preparation of molybdenum and tungsten carbonyls from the halides $MoCl_5$ and WCl_6 respectively.[20] A similar method was used to obtain $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ from $[Ru(CO)_3Cl_2]_2$,[21] $Co_2(CO)_8$ from $CoCl_2$, and $Rh_6(CO)_{16}$ from $RhCl_3$ or $[Rh(CO)_2Cl]_2$.[22]

Most preparative methods for the metal carbonyls require high-pressure

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[11] R. Ercoli, M. Guainazzi, and G. Silvestri, *Chem. Comm.*, 1967, 927.

[12] W. Hieber and H. Fuchs, *Z. anorg. Chem.*, 1941, **248**, 256; see also reference 8.

[13] P. Szabó, L. Markó, and G. Bor, *Chem. Tech.* (*Berlin*), 1961, **13**, 549.

[14] W. Hieber and H. Stallman, *Z. Elektrochem.*, 1943, **49**, 288.

[15] C. W. Bradford and R. S. Nyholm, *Chem. Comm.*, 1967, 384.

[16] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc.* (*A*), 1968, 2859.

[17] F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, 1967, **6**, 1220.

[18] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 1967, **6**, 2092.

[19] J. R. Moss and W. A. G. Graham, *Chem. Comm.*, 1969, 800; *J. Organometallic Chem.*, 1970, **23**, C 47.

[20] A. N. Nesmeyanov, E. P. Mikheev, K. N. Anisimov, V. L. Volkov, and Z. P. Valueva, *Zhur. Neorg. Khim.*, 1959, **4**, 249, 503; *Russ. J. Inorg. Chem.*, 1959, **4**, 107, 228.

[21] D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 502.

[22] B. L. Booth, M. J. Else, R. Fields, H. Goldwhite, and R. N. Haszeldine, *J. Organometallic Chem.*, 1968, **14**, 417.

equipment. Clearly the development of alternative syntheses which operate at atmospheric pressure is desirable. In one such method, decacarbonyldimanganese is obtained by the reaction of π-$MeC_5H_4Mn(CO)_3$ with CO in refluxing diglyme containing dispersed sodium.[23] Although the yields are only in the 16—20% range, the availability of commercial supplies of $MeC_5H_4Mn(CO)_3$* makes the synthesis an attractive one. Octacarbonyldicobalt can also be prepared in 10—100 g. batches from carbon monoxide at atmospheric pressure. The method depends on a sequence of reactions which afford thermally unstable $HCo(CO)_4$.[24,25]

$$CoCl_2 + 6KCN \rightarrow K_4Co(CN)_6 + 2KCl$$

$$2K_4Co(CN)_6 + 12KOH + 11CO \rightarrow 2KCo(CO)_4 + 3K_2CO_3 + 12KCN + 6H_2O$$

$$KCo(CO)_4 + HCl \rightarrow HCo(CO)_4 + KCl$$

$$2HCo(CO)_4 \rightarrow Co_2(CO)_8 + H_2$$

Methods for preparing polynuclear carbonyls depend mainly on starting from the simpler carbonyls where these exist.

Although $Co_4(CO)_{12}$ does form by thermal decomposition of $Co_2(CO)_8$, it is better obtained by the reaction of cobalt(II) 2-ethylhexanoate, octacarbonyldicobalt, and hydrogen.[8,26]

$$3Co_2(CO)_8 + 2Co(C_7H_{15}CO_2)_2 + 2H_2\ (60) \rightarrow 2Co_4(CO)_{12} + 4C_7H_{15}CO_2H$$

Treatment of $Co_4(CO)_{12}$ with alkali metals in tetrahydrofuran at room temperature affords solutions containing the $[Co_6(CO)_{15}]^{2-}$ and $[Co_6(CO)_{14}]^{4-}$ anions. Mild oxidising agents such as $FeCl_3$ react with these anions to give $Co_6(CO)_{16}$.[27]

$$[Co_6(CO)_{15}]^{2-} + CO + 2FeCl_3 \xrightarrow{\text{water}} Co_6(CO)_{16} + 2FeCl_2 + 2Cl^-$$

Polynuclear $Ir_6(CO)_{16}$ has similarly been obtained[27a] from $Ir_4(CO)_{12}$ *via* $[Ir_6(CO)_{15}]^{2-}$.

Dodecacarbonyltri-iron can also be obtained by oxidation of a solution of an anion.[8]

$$Fe(CO)_5 + 2OH^- \rightarrow HFe(CO)_4^- + HCO_3^-$$

$$3HFe(CO)_4^- + 3MnO_2 \rightarrow Fe_3(CO)_{12} + 3OH^- + 3MnO$$

The role of the manganese(IV) oxide is obscure, but it probably increases the rate of formation of the polynuclear anion $HFe_3(CO)_{11}^-$. The last step of the synthesis involves treatment of the mixture with concentrated sulphuric acid. Dodeca-

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* This compound is a combustion improver for fuel oils.

[23] R. B. King, J. C. Stokes, and T. F. Korenowski, *J. Organometallic Chem.*, 1968, **11**, 641.
[24] R. J. Clark, S. E. Whiddon, and R. E. Serfass, *J. Organometallic Chem.*, 1968, **11**, 637.
[25] P. Gilmont and A. A. Blanchard, *Inorg. Synth.*, 1946, **2**, 238.
[26] R. Ercoli, P. Chini, and M. Massi-Mauri, *Chim. Ind.* (*Milan*), 1959, **41**, 132.
[27] P. Chini, *Chem. Comm.*, 1967, **29**, 440.
[27a] L. Malatesta, G. Caglio, and M. Angoletta, *Chem. Comm.*, 1970, 532.

carbonyltri-iron is also readily prepared by reacting pentacarbonyliron with triethylamine followed by acidification.[28,29]

$$3Fe(CO)_5 + Et_3N + 2H_2O \rightarrow [Et_3NH][HFe_3(CO)_{11}] + 2CO_2 + 2CO + H_2$$

$$12[Et_3NH][HFe_3(CO)_{11}] + 18HCl \rightarrow 11Fe_3(CO)_{12} + 15H_2 + 3FeCl_2 + 12Et_3NHCl.$$

Enneacarbonyldi-iron is prepared by irradiating pentacarbonyliron.[8,30]

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

Recently[30a] $Os_2(CO)_9$ has been similarly prepared from $Os(CO)_5$ at −40 °C.

Numerous bi-, tri- and poly-nuclear carbonyls are known which contain more than one transition element (see ref. 1, Table 5). The majority of these complexes are obtained by one or other of the following methods.

(*a*) *Metathetical reactions involving carbonyl anions and carbonyl halides.* As described later, some carbonyl anions are nucleophilic in character, permitting reactions of the following kind.

$$NaMn(CO)_5 + Re(CO)_5Cl \rightarrow (OC)_5MnRe(CO)_5 + NaCl \qquad \text{(refs. 31, 32)}$$

$$NaCo(CO)_4 + Mn(CO)_5Br \rightarrow (OC)_5MnCo(CO)_4 + NaBr \qquad \text{(ref. 33)}$$

$$Zn[Co(CO)_4]_2 + [Rh(CO)_2Cl]_2 \rightarrow Co_2Rh_2(CO)_{12} + ZnCl_2 \qquad \text{(ref. 34)}$$

(*b*) *Intramolecular redox processses in a carbonylmetallate containing a transition metal cation.*

$$[Re(CO)_6][Co(CO)_4] \xrightarrow{60\ °C} (OC)_5ReCo(CO)_4 + CO \qquad \text{(ref. 35)}$$

Similar decompositions of salt-like carbonyls probably occur in the formation of certain polynuclear carbonyl hydrides such as $HMCo_3(CO)_{12}$[M=Fe,[36] Ru,[5,37] or Os[37]] and $H_2FeRu_3(CO)_{13}$[21,38] (see later).

(*c*) *Condensation of co-ordinatively unsaturated species.* Under the influence of heat or u.v. irradiation, it is a general characteristic of carbonyl complexes to dissociate, either by loss of CO groups or by rupture of metal–metal bonds. The fragments so produced are co-ordinatively unsaturated and can recombine to

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[28] N. von Kutepow and H. Kindler, *Angew. Chem.*, 1960, **72**, 802.
[29] W. McFarlane and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 181.
[30] E. H. Braye and W. Hübel, *Inorg. Synth.*, 1966, **8**, 178.
[30a] J. R. Moss and W. A. G. Graham, *Chem. Comm.*, 1970, 835.
[31] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and I. S. Kolomnikov, *Izvest. Akad. Nauk, S.S.S.R., Otdel. khim. Nauk.*, 1963, 194.
[32] N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1964, **3**, 1123.
[33] K. K. Joshi and P. L. Pauson, *Z. Naturforsch.*, 1962, **17b**, 565.
[34] P. Chini, S. Martinengo, and V. Albano, Proceedings of a Symposium on Metal Carbonyls, Venice, 1968.
[35] T. Kruck and M. Hofler, *Angew Chem. Internat. Edn.*, 1964, **3**, 701.
[36] P. Chini, L. Colli, and M. Peraldo, *Gazetta*, 1960, **90**, 1005.
[37] M. J. Mays and R. N. F. Simpson, *J. Chem. Soc.* (*A*), 1968, 1444.
[38] J. Knight and M. J. Mays, *Chem. Ind.*, 1968, 1159.

form new compounds. In this manner, several 'mixed' metal carbonyls have been obtained.

$$Mn_2(CO)_{10} + Re_2(CO)_{10} \xrightarrow[\text{hexane}]{h\nu} ReMn(CO)_{10} \xrightarrow[\text{Fe(CO)}_5\text{, hexane}]{h\nu} (OC)_4Fe[Mn(CO)_5][Re(CO)_5] + CO \qquad \text{(ref. 39)}$$

$$3Fe(CO)_5 + Ru_3(CO)_{12} \xrightarrow[\text{sealed tube}]{110\ ^\circ C} FeRu_2(CO)_{12} + FeRu(CO)_{12} + 3CO \qquad \text{(ref. 21)}$$

In the latter reaction the 'mixed' hydride $H_2FeRu_3(CO)_{13}$ also forms, probably arising from traces of water in commercial pentacarbonyliron. Similarly, treatment of $Fe_2(CO)_9$ with $H_2Os(CO)_4$ affords $Fe_2Os(CO)_{12}$ (70%) and $H_2FeOs_3(CO)_{13}$ (6%), while $Co_2(CO)_8$ and $H_2Os(CO)_4$ yield $Co_2Os(CO)_{11}$.[39a]

In our previous article[1] mention was made of many polynuclear metal carbonyl complexes wherein non-metal atoms such as hydrogen form an intrinsic part of the structure. Special mention may be made of the 'carbide' complexes. The first of these to be characterised was $CFe_5(CO)_{15}$,[40] obtained in trace amounts from reactions between $Fe_3(CO)_{12}$ and n-PrC≡CH or MeC≡CPh. The compound $CRu_6(CO)_{17}$ has been obtained by heating $Ru_3(CO)_{12}$ in n-octane or n-nonane. It is also produced together with complexes $CRu_6(CO)_{14}$ (arene) [arene = $Me_3C_6H_3$, *m*-$Me_2C_6H_4$, or MeC_6H_5], by reacting $Ru_3(CO)_{12}$ with the appropriate arene.[41] In these reactions the carbon atoms probably arise by reduction of a CO group.

Octacarbonyldicobalt reacts with carbon tetrachloride in ethanol to afford a complex $ClCCo_3(CO)_9$[42] in which an aliphatic carbon atom is bonded to three cobalt atoms which are bonded to each other forming a CCo_3 core.[43] If $ClCCo_3(CO)_9$ is heated in mesitylene a series of novel cobalt carbonyl carbide complexes of formula $HC_3Co_5(CO)_{15}$, $C_4Co_6(CO)_{18}$, and $C_6Co_8(CO)_{24}$ are produced.[44]* The source of the C_2 and C_4 fragments in these molecules may be the carbon atoms of mesitylene, in which case the compounds would be formed by a process which is essentially the reverse of the commonly observed trimerisation of acetylenes by metal carbonyls.

* The structures of these complexes have recently been elucidated by *X*-ray crystallographic studies. In $C_4Co_6(CO)_{18}$ two $CCo_3(CO)_9$ clusters are linked by a C_2 group. In $HC_3Co_5(CO)_{15}$ a $CCo_3(CO)_9$ cluster is attached to a $Co_2(CO)_6$ group by a C_2H bridge; while the structure of $C_6Co_8(CO)_{24}$ is derived from that of $HC_3Co_5(CO)_{15}$ by replacement of the H atom by a $C_2CCo_3(CO)_9$ group.[45]

[39] G. O. Evans and R. K. Sheline, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2862.

[39a] J. R. Moss and W. A. G. Graham, *J. Organometallic Chem.*, 1970, **23**, C 23.

[40] E. H. Braye, W. Hübel, L. F. Dahl, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1962, **84**, 4633.

[41] B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc.* (*A*), 1968, 2865.

[42] W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc.*, 1961, 169.

[43] P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 261.

[44] B. H. Robinson, J. Spencer, and R. Hodges, *Chem. Comm.*, 1968, 1480.

[45] B. R. Penfold, private communication.

The synthesis of several compounds wherein metals of the Main Groups of the Periodic Table are incorporated into a polynuclear carbonyl structure is described in a later Section of this article.

3 Anionic and Cationic Carbonyl Complexes[46,47]

Among the earliest reactions of pentacarbonyliron to be discovered were those with nitrogen bases, forming mono- or poly-nuclear carbonylferrates.[48] The anion produced depends on the nature of the base and on the reaction conditions.[49]

$$5Fe(CO)_5 + 6py \rightarrow [py_6Fe][Fe_4(CO)_{13}] + 12CO$$

$$2Fe(CO)_5 + 6NH_3 + H_2O \rightarrow [(NH_3)_6Fe][HFe(CO)_4]_2 + CO + CO_2$$

More anionic carbonyls are known than are neutral carbonyls. Thus $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ have been isolated[50] whereas the neutral carbonyls have not. Moreover, nickel forms the carbonylnickelate anions $[Ni_2(CO)_6]^{2-}$, $[Ni_3(CO)_8]^{2-}$, $[Ni_4(CO)_9]^{2-}$, and $[Ni_5(CO)_9]^{2-}$, yet only a tetracarbonyl is known for this metal.

'Mixed-metal' carbonyl anions have been characterised which are isoelectronic with neutral di-, tri-, and tetra-nuclear carbonyls. For example, the anions $[CrMn(CO)_{10}]^-$,[51,52] $[FeCo(CO)_8]^-$,[51] $[Fe_2Mn(CO)_{12}]^-$,[53] and $[FeCo_3(CO)_{12}]^-$ [36] are isoelectronic with $Mn_2(CO)_{10}$, $Co_2(CO)_8$, $Fe_3(CO)_{12}$, and $Co_4(CO)_{12}$, respectively.

Countless anionic complexes are known wherein other ligands besides CO are present. Among the more important classes are the hydrido- and cyclopentadienyl-carbonyl anions, and phosphine derivatives, *e.g.*

$[HCr_2(CO)_{10}]^-$ $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ $[Ph_3PMn(CO)_4]^-$

$[H_2Re_3(CO)_{12}]^-$ $[(\pi\text{-}C_5H_5)W(CO)_3]^-$ $[Ph_3PCo(CO)_3]^-$

There can be an electronic relationship between the neutral carbonyl, the carbonyl anion, the hydrido-carbonyl, and the hydrido-carbonyl anion. This arises because a CO group can formally be replaced by (i) two electrons, (ii) a hydrogen atom and an electron, or (iii) two hydrogen atoms. This is well illustrated by four parallel series of iron carbonyl complexes.[54]

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[46] R. B. King, *Adv. Organometallic Chem.*, 1964, **2**, 157.
[47] E. W. Abel and S. Tyfield, *Adv. Organometallic Chem.*, 1969, **8**, 117.
[48] W. Hieber, *Adv. Organometallic Chem.*, 1970, **8**, 1.
[49] W. Hieber, W. Beck, and G. Brown, *Angew. Chem.*, 1960, **72**, 795.
[50] R. P. M. Werner and H. E. Podall, *Chem. and Ind.*, 1961, 144.
[51] J. K. Ruff, *Inorg. Chem.*, 1968, **7**, 1818.
[52] U. Anders and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1967, **89**, 539.
[53] U. Anders and W. A. G. Graham, *Chem. Comm.*, 1966, 291.
[54] K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1969, 2339

$Fe(CO)_5$	$Fe_2(CO)_9$	$Fe_3(CO)_{12}$	—*
$[Fe(CO)_4]^{2-}$	$[Fe_2(CO)_8]^{2-}$	$[Fe_3(CO)_{11}]^{2-}$	$[Fe_4(CO)_{13}]^{2-}$
$[Fe(CO)_4H]^-$	$[Fe_2(CO)_8H]^-$	$[Fe_3(CO)_{11}H]^-$	$[Fe_4(CO)_{13}H]^-$
$Fe(CO)_4H_2$	$Fe_2(CO)_8H_2$	$Fe_3(CO)_{11}H_2$	$Fe_4(CO)_{13}H_2$

* The neutral carbonyl $Fe_4(CO)_{14}$ is not known (see ref. 55).

Moreover, the recent discovery of the series $Co_6(CO)_{16}$, $Co_6(CO)_{15}{}^{2-}$ and $Co_6(CO)_{14}{}^{4-}$ shows that in certain circumstances more than one molecule of CO can be replaced by pairs of electrons.[27]

The existence of cationic metal carbonyl species was postulated some years before such complexes were isolated. Compounds in which the only ligands in the cation are CO groups, are known in much fewer numbers than are the corresponding anions. This is generally understandable since removal of negative charge from a metal atom, or group of metal atoms, in a carbonyl complex leads to less π-bonding with the CO groups and hence to destabilisation.[1] Not surprisingly, it has been possible to prepare numerous cationic complexes in which ligands are present which are less demanding as π acceptors than CO, *e.g.* phosphine groups, or unsaturated hydrocarbons.

$$Co_2(CO)_8 + 2R_3P \rightarrow [Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^- + CO \qquad \text{(refs. 56, 57)}$$

$$2V(CO)_6 + \text{arene} \rightarrow [V(CO)_4\text{arene}]^+[V(CO)_6]^- + 2CO \qquad \text{(refs. 58, 59)}$$

The existence of the cobalt(I) cations $[(R_3P)_2Co(CO)_3]^+$ is interesting in view of the suggestion that the unstable product obtained from $Co_2(CO)_8$ and CO at high pressures may be formulated as $[Co(CO)_5][Co(CO)_4]$.[60] The characterisation of complexes such as $[Mn(CO)_6]^+[V(CO)_6]^-$ or $[Re(CO)_6]^+[Co(CO)_4]^-$ leaves no doubt, however, that 'salt-like' carbonyls can exist.[61] Numerous isoelectronic series, *e.g.* $Ta(CO)_6{}^-$, $W(CO)_6$ and $Re(CO)_6{}^+$, demonstrate the relationship between anionic and cationic species, and the observance of the effective atomic number formalism.[1]

Mention was made above of polynuclear hydridocarbonyl anions. Some corresponding protonic species are known, *viz.* $[HM_3(CO)_{12}]^+$ ($M = Ru$, or Os)[62]

A. Synthesis.—(i) *Anions.* There is no specific reagent which will convert all metal carbonyls into anionic species. Depending on the metal, several different reactions are used to obtain the carbonyl anion.[46]

(*a*) *Reaction between a metal carbonyl and a 'hard' base such as hydroxide ion, aqueous ammonia, amines, or pyridine.* For several metals (*e.g.* Fe, Ni, Rh, Ru)

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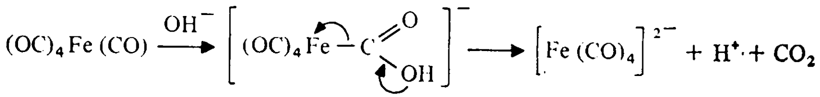
[55] R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 4847.
[56] A. Sacco and M. Freni, *Ann. Chim.* (*Italy*), 1958, **48**, 218.
[57] W. Hieber and W. Freyer, *Chem. Ber.*, 1958, **91**, 1230.
[58] F. Calderazzo, *Inorg. Chem.*, 1964, **3**, 1207; 1965, **4**, 223.
[59] F. Calderazzo and R. Cini, *J. Chem. Soc.*, 1965, 818.
[60] S. Metlin, I. Wender, and H. W. Sternberg, *Nature*, 1969, **183**, 457.
[61] T. Kruck and M. Hofler, *Chem. Ber.*, 1964, **97**, 2289.
[62] J. Knight and M. J. Mays, *J. Chem. Soc.* (*A*), 1970, 711.

these reactions are complicated, the nature of the product depending markedly on the pH and temperatures of the solutions. The mechanism of the reaction with hydroxide ion solutions is not well understood, but a plausible one, in view of the mode of formation of carbene-metal complexes (see later), would involve attack by the hydroxyl anion on the carbon atom of a carbonyl group. Electron transfer to the metal would then follow with release of CO_2 (*i.e.* formation of CO_3^{2-} in the presence of base).[63]



With nitrogen bases, or with alcohols, disproportionation reactions can take place, as exemplified by the reaction of octacarbonyldicobalt with ethanol to give a solution containing the anion $[Co(CO)_4]^-$.[64] In those reactions of $Co_2(CO)_8$ with Lewis bases which afford $[Co(CO)_4]^-$, the first step is probably formation of Co^I and Co^{-I} *viz.*

$$Co_2(CO)_8 + L \rightarrow [Co(CO)_4L][Co(CO)_4]$$

With additional ligand molecules further electron transfer, coupled with loss of CO, can then occur so as to yield a final product containing cobalt(II) and cobalt(−I); the former stabilized by co-ordination to the nitrogen base, for example, as $[en_3Co]^{2+}$, $[py_6Co]^{2+}$, or $[(PhCN)_6Co]^{2+}$. The postulated formation of intermediate Co^I complexes is supported by detection of the cationic species $[Co(CO)_4ROH]^+$ during the reaction of $Co_2(CO)_8$ with alcohols.[65]

The various carbonylferrates are satisfactorily obtained by the reactions shown in the accompanying scheme. The dodecacarbonyls of ruthenium and osmium react with aqueous potassium hydroxide in methanol to afford polynuclear anions of these metals, the formulations of which are not known. Acidification affords a series of polynuclear hydrides (see later).[16,73]

(*b*) *Reduction of metal carbonyls with alkali metals, alkali metal amalgams, or borohydrides.* A number of dinuclear metal carbonyls react with sodium amalgam in tetrahydrofuran to afford solutions of the appropriate anion. In this manner

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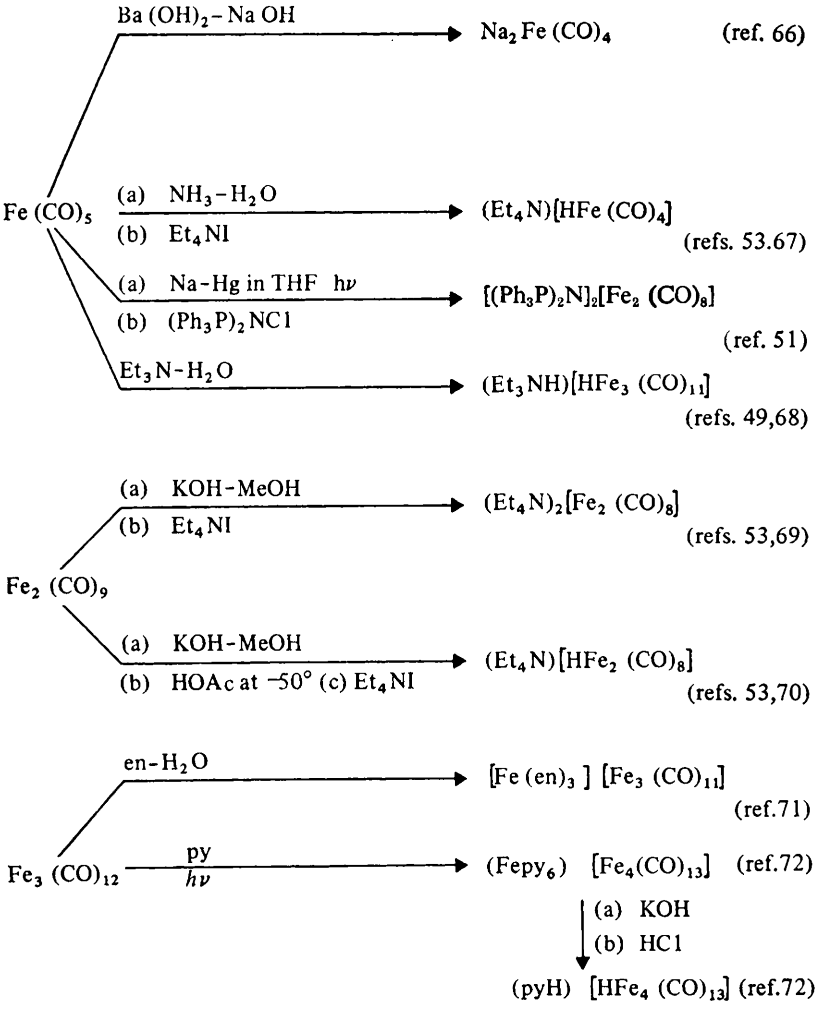
[63] T. Kruck, M. Hofler, and M. Noack, *Chem. Ber.*, 1966, **99**, 1153.
[64] I. Wender, H. W. Sternberg, and M. Orchin, *J. Amer. Chem. Soc.*, 1952, **74**, 1216.
[65] E. R. Tucci and B. H. Gwynn, *J. Amer. Chem. Soc.*, 1964, **86**, 4838.
[66] H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras, and S. Bril. *J. Chem. Phys.*, 1960, **32**, 1482.
[67] W. Hieber and E. Fach, *Z. anorg. Chem.*, 1938, **236**, 83.
[68] J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 1960, 4632.
[69] W. Hieber and N. Kahlen, *Chem. Ber.*, 1958, **91**, 2234.
[70] W. Hieber and G. Brendal, *Z. anorg. Chem.*, 1957, **289**, 324.
[71] W. Hieber, J. Sedlmeier, and R. Werner, *Chem. Ber.*, 1957, **90**, 278.
[72] W. Hieber and R. Werner, *Chem Ber.*, 1957, **90**, 286.
[73] B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2856.



Formation of carbonylferrates

$[Mn(CO)_5]^-$,[8,74] $[Mn(CO)_4PPh_3]^-$,[75] $[Re(CO)_5]^-$,[76] $[Co(CO)_4]^-$,[8] $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$,[8] and $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$,[77] *etc.*, can be conveniently obtained. These and other mononuclear metal carbonyl anions can be

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[74] R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 198.
[75] P. Jolly, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5830.
[76] W. Beck, W. Hieber, and G. Braun, *Z. anorg. Chem.*, 1961, **308**, 23.
[77] R. G. Hayter, *Inorg. Chem.*, 1963, **2**, 1031.

stored as salts of the bis(triphenylphosphine)iminium cation.[51,78] The cation $[(Ph_3P)_2N]^+$ imparts stability to the anions which are normally air sensitive.

The hexacarbonyls of the Group VI elements react with sodium in liquid ammonia to give carbonylmetallates.[79-81] First prepared by this route, and also by using sodium borohydride in liquid ammonia, were the species $[M(CO)_5]^{2-}$, $[M_2(CO)_{10}]^{2-}$ and $[M_2(CO)_9]^{4-}$. More recently, studies using tetrahydrofuran, or even hexamethylphosphoramide, as solvent, and alkali metals or amalgams as reducing agents, have given a clearer picture as to the nature of the anions involved and their inter-relationships.[82-84] The anions are precipitated as their Et_4N^+, $[(Ph_3P)_2N]^+$, or even Cs^+ salts.

$$2M(CO)_6 \xrightarrow[h\nu]{\text{Na-Hg THF}} [M_2(CO)_{10}]^{2-} + 2CO \qquad \text{(ref. 83)}$$

$$2M(CO)_6 \xrightarrow[\text{THF}]{\text{Na, dipy}} [M_2(CO)_{10}]^{2-} + 2CO \qquad \text{(ref. 84)}$$

Treatment of $(Et_4N)_2[Cr_2(CO)_{10}]$ with sodium in HMPT affords the anion $[HMPTCr(CO)_5]^{2-}$.

The first stage in the reduction of $M(CO)_6$ is probably the formation of an intermediate $[(OC)_5MCO]^-$, much like an organic ketyl $[R_2CO]^-$, which releases CO to give a solvent stabilised monoanion $[SM(CO)_5]^-$ (S = THF or HMPT). The latter may then dimerise to give $[M_2(CO)_{10}]^{2-}$,* or add an electron to form $[SM(CO)_5]^{2-}$.[82] Oxidation of the latter species, or protonation of $[M_2(CO)_{10}]^{2-}$, gives the hydridocarbonyl anions $[HM_2(CO)_{10}]^-$. These hydrido ions are, however, conveniently prepared directly by reducing the hexacarbonyls with sodium borohydride in tetrahydrofuran (see later).[83,85]

Decacarbonyldirhenium reacts[86] with sodium borohydride in tetrahydrofuran to afford among other species the tetranuclear anions $[Re_4(CO)_{16}]^{2-}$ and $[H_6Re_4(CO)_{12}]^{2-}$.

(*c*) *Displacement of CO from a metal carbonyl with an anion.* It has been known for some time that the carbonyls of the chromium and manganese sub-groups react at elevated temperatures with various nucleophilic anions in tetrahydro-

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* The observation of i.r. bands due to CO below 1800 cm^{-1} in the spectra of these anions is not due to bridging CO groups, but to the negative charge and ion pair effects (see refs. 82, 84, and 1). The anions are isostructural with the neutral carbonyls $M_2(CO)_{10}$ [M = Mn, Tc, or Re]. Interestingly, the anion $[Cr_2(CO)_9]^{4-}$ is isoelectronic with $Fe_2(CO)_9$.

[78] J. K. Ruff and W. J. Schlientz, *Inorg. Synth.*, 1970, **14**, in press.

[79] H. Behrens and R. Weber, *Z. anorg. Chem.*, 1957, **291**, 123.

[80] H. Behrens and J. Vogl, *Chem. Ber.*, 1963, **96**, 2220.

[81] H. Behrens and W. Haag, *Chem. Ber.*, 1961, **94**, 312, 320.

[82] W. C. Kaska, *J. Amer. Chem. Soc.*, 1968, **90**, 6340.

[83] R. G. Hayter, *J. Amer. Chem. Soc.*, 1966, **88**, 4376.

[84] E. Lindner, H. Behrens, and S. Birkle, *J. Organometallic Chem.*, 1968, **15**, 165.

[85] W. A. G. Graham and U. Anders, *Chem. Comm.*, 1965, 499.

[86] (*a*) R. Bau, B. Fontal, H. D. Kaesz, and M. R. Churchill, *J. Amer. Chem. Soc.*, 1967, **89**, 6374; (*b*) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *ibid*, 1969, **91**, 1021.

furan, diglyme, or DMF with release of CO. This type of reaction was first used to prepare cyclopentadienylcarbonyl anions,[87,88] *e.g.*

$$Mo(CO)_6 + K(Na)C_5H_5 \rightarrow [K(Na)][Mo(CO)_3(\pi\text{-}C_5H_5)] + 3CO \quad \text{(refs. 89, 90)}$$

Subsequently it was shown that iodide ion was a sufficiently strong Lewis base to displace CO groups from the hexacarbonyls;[91,92] indeed the complete series of $[MX(CO)_5]^-$ anions (M=Cr, Mo, or W; X = Cl, Br, or I) has been prepared.[93]

$$R_4NX + M(CO)_6 \rightarrow R_4N[MX(CO)_5] + CO$$

Decacarbonyldimanganese will react in the same manner[94]

$$2R_4NX + Mn_2(CO)_{10} \rightarrow (R_4N)_2[Mn_2X_2(CO)_8] + 2CO$$

Similarly, by photolytically activating the hexacarbonyls of the chromium group, difluorodithiophosphate and difluorothiophosphate anions will replace carbonyl groups.[95] Interestingly, the $[PF_2S_2]^-$ anion acts as a bidentate ligand.

$$M(CO)_6 + [PF_2S_2]^- \rightarrow [M(CO)_4PF_2S_2]^- + 2CO$$

$$M(CO)_6 + [PF_2OS]^- \rightarrow [M(CO)_5PF_2OS]^- + CO$$

There appears to be no limit to the number of novel anions which will undergo this type of reaction. For instance anionic complexes $[M(CO)_4B_3H_8]^-$ are formed from the hexacarbonyls and $[B_3H_8]^-$.[96]

Even more novel is the reaction between $[B_{10}H_{13}]^-$ and $M(CO)_6$ which forms anions $[(B_{10}H_{10}COH)M(CO)_4]^-$. With sodium hydride the latter yield anions $[B_{10}H_{10}\overline{COM}CO(CO)_3]^-$ containing an ether linkage between a carbonyl ligand and an icosahedral framework.[96a]

Recently it has been recognised that certain mononuclear carbonyl anions can function as nucleophiles towards neutral carbonyls. The formation of $[MnFe_2(CO)_{12}]^-$ from $[Mn(CO)_5]^-$ and $Fe(CO)_5$ was mentioned earlier.[52] The trinuclear species $[MnFe_2(CO)_{12}]^-$ is probably formed *via* an unstable mixed-metal dinuclear anion $[FeMn(CO)_9]^-$. Indeed, by using u.v. irradiation as a means of activating pentacarbonyliron both this binuclear anion and $[FeCo(CO)_8]^-$ have been prepared.[51]

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[87] T. S. Piper and G. Wilkinson, *Naturwiss.*, 1955, **42**, 625; *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[88] E. O. Fischer, W. Hafner and H. O. Stahl, *Z. anorg. Chem.*, 1955, **282**, 47.

[89] W. L. Jolly, *Inorg. Synth.*, 1968, **11**, 116.

[90] R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 99.

[91] E. O. Fischer and K. Öfele, *Chem. Ber.*, 1960, **93**, 1156.

[92] E. W. Abel, M. A. Bennett, and G. Wilkinson, *Chem. Ind.*, 1960, 442.

[93] E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 1963, 2068.

[94] E. W. Abel and I. S. Butler, *J. Chem. Soc.*, 1964, 434.

[95] J. K. Ruff and M. Lustig, *Inorg. Chem.*, 1968, **7**, 2171.

[96] F. Klanberg and L. J. Guggenberger, *Chem. Comm.*, 1967, 1293.

[96a] P. A. Wegner, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 3473.

$$Fe(CO)_5 + [Mn(CO)_5]^- \xrightarrow{h\nu} [FeMn(CO)_9]^- + CO$$

$$Fe(CO)_5 + [Co(CO)_4]^- \xrightarrow{h\nu} [FeCo(CO)_8]^- + CO$$

In a related reaction, both $[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$ react with the hexacarbonyls $M(CO)_6$ [M = Cr, Mo, or W] in diglyme at 160 °C to give the six possible anions $[(OC)_5M'M(CO)_5]^-$ (M′ = Mn or Re), precipitated as their tetraethylammonium salts.[52] The manganese anions have also been prepared under milder conditions by the reaction.[51]

$$[(Ph_3P)_2N]_2[M_2(CO)_{10}] + Mn_2(CO)_{10} \xrightarrow[50^\circ]{THF} 2[(Ph_3P)_2N][MMn(CO)_{10}]$$

(ii) *Cations.* Cationic metal carbonyl complexes are usually obtained by one of the following types of reaction, of which methods (*a*) and (*b*) have been used most widely.

(*a*) *Removal of halide ion from a carbonylmetal halide with a Lewis acid in the presence of a suitable neutral ligand.* The preparation of the cations $[M(CO)_6]^+$ (M = Mn, Tc, or Re) typifies this route.[97–100]

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

The existence of many substituted cationic species was mentioned earlier, and many such complexes, often precipitated as their PF_6^- salts, have been similarly obtained.

$$BrMn(CO)_5 + \text{arene} + AlCl_3 \xrightarrow{-CO} [(\text{arene})Mn(CO)_3][AlCl_3Br] \quad \text{(refs. 101,102)}$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2Br + CO + AlBr_3 \rightarrow [(\pi\text{-}C_5H_5)Fe(CO)_3][AlBr_4] \quad \text{(ref. 103)}$$

Halides rather than carbonylhalides, have been used in these syntheses provided CO is added as a ligand.

$$(Ph_3P)_2PtCl_2 + CO + 2BF_3 \rightarrow [(Ph_3P)_2Pt(CO)Cl][BF_4] + (BF_2Cl) \quad \text{(ref. 104)}$$

Removal of halide without addition of CO is also possible, as in the synthesis of (π-allyl)(tricarbonyl)iron cation.

$$(\pi\text{-}C_3H_5)Fe(CO)_3Cl + AgBF_4 \rightarrow [(\pi\text{-}C_3H_5)Fe(CO)_3][BF_4] + AgCl$$

The resultant cation is particularly interesting since it is two electrons short of the number required for iron to attain its effective atomic number.[105]

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[97] E. O. Fischer and K. Öfele, *Angew. Chem.*, 1961, **73**, 581; 1962, **74**, 76.
[98] E. O. Fischer, K. Fichtel, and K. Öfele, *Chem. Ber.*, 1962, **95**, 249.
[99] W. Hieber and T. Kruck, *Angew. Chem.*, 1961, **73**, 580; *Z. Naturforsch.*, 1961, **16b**, 709.
[100] W. Hieber, F. Lux, and C. Herget, *Z. Naturforsch.*, 1965, **20b**, 1159.
[101] T. H. Coffield, V. Sandel, and R. D. Closson, *J. Amer. Chem. Soc.*, 1957, **79**, 5826.
[102] G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 3807; G. Winkhaus, *Z. anorg. Chem.*, 1963, **319**, 404.
[103] E. O. Fischer and K. Fichtel, *Chem. Ber.*, 1961, **94**, 1200.
[104] H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, 1969, **90**, 2259.

Chlorocomplexes of the platinum metals are sufficiently labile to react directly with CO in the presence of perchlorate anion.[106]

$$(Ph_3P)_2Ir(CO)Cl + 2CO + ClO_4^- \rightarrow [(Ph_3P)_2Ir(CO)_3][ClO_4] + Cl^-$$

$$(Et_3P)_2PtCl_2 + CO + ClO_4^- \rightarrow [(Et_3P)_2Pt(CO)Cl][ClO_4] + Cl^-$$

(*b*) *Protonation of metal carbonyl complexes.*[106a] Several metal carbonyl derivatives dissolve in strong acids, and n.m.r. studies have shown that metal–hydrogen bonds form.[107] Cationic species have been isolated in only a few cases, *viz.* $[\pi\text{-}C_5H_5FeMn(CO)_7H]^+$,[107] $[HFe(CO)_5]^+$,[108] and $[HM_3(CO)_{12}]^+$ (M = Ru or Os).[62] In contrast, with HBF_4, HPF_6, or even HCl, many crystalline complexes have been isolated by protonation of the organocarbonyls obtained from unsaturated hydrocarbons and metal carbonyls. Some representative examples of this behaviour are shown in Table 4.

(*c*) *Removal of hydride ion from organometal carbonyls.* This method involves use of the reagent trityl borofluoride, and is limited to those complexes containing hydrocarbon groups. It was first applied in the synthesis of the (π-cycloheptatrienyl)(tricarbonyl)molybdenum cation.[109]

$$(\pi\text{-}C_7H_8)Mo(CO)_3 + Ph_3C^+BF_4^- \rightarrow [(\pi\text{-}C_7H_7)Mo(CO)_3]^+[BF_4]^- + Ph_3CH$$
$(C_7H_8$ = cycloheptatriene)

The method has been applied most widely to the hydrocarbon(carbonyl) complexes of iron, a few examples being given in Table 5.

(*d*) *Disproportionation of metal carbonyls in reactions with electron donors.* The disproportionation reactions which afford the cations $[(R_3P)_2Co(CO)_3]^+$ and $[(arene)V(CO)_4]^+$ were mentioned earlier. This type of reaction is of very limited applicability in the synthesis of cations. The mechanism of formation of the cations probably involves initial formation of uncharged substitution products which are then oxidised by a second molecule of the carbonyl. The stability of the anions $[V(CO)_6]^-$ and $[Co(CO)_4]^-$ is undoubtedly an important factor in determining the course of the reactions.

B. Anionic and Cationic Carbonyl Complexes in Synthesis.—Cationic and anionic carbonyls, particularly mononuclear anions, are important intermediates in further syntheses.

Several mononuclear carbonyl anions are very reactive, and many examples of their use in preparative chemistry will be given in later Sections. Here may be mentioned:

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[105] G. F. Emerson, K. Ehrlich, W. J. Jacobs, and R. Pettit, *Chem. and Ind.*, 1964, 836.
[106] M. J. Church and M. J. Mays, *Chem. Comm.*, 1968, 435.
[106a] D. F. Shriver, *Accounts Chem. Res.*, 1970, **3**, 231.
[107] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3653.
[108] Z. Iqbal and T. C. Waddington, *J. Chem. Soc. (A)*, 1968, 2958.
[109] H. J. Dauben and L. R. Honnen, *J. Amer. Chem. Soc.*, 1958 **80**, 5570.

Table 4 *Formation of cationic carbonyl iron complexes by protonation*

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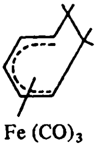
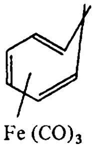
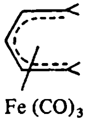
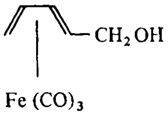
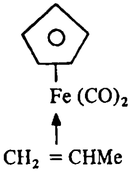
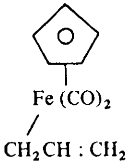
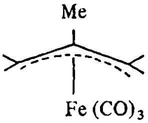
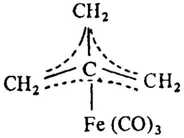
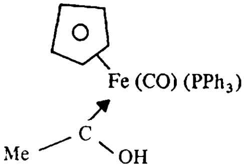
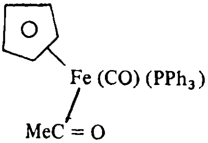
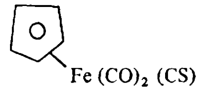
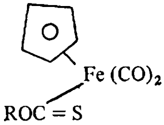
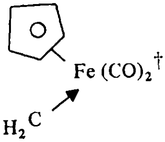
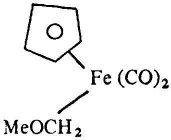
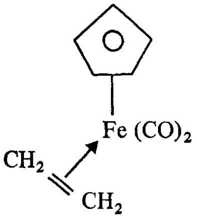
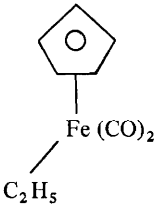
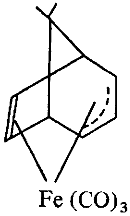
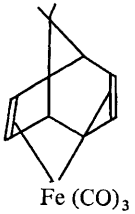
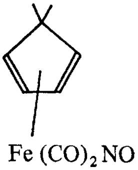
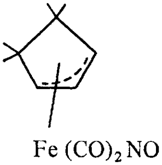
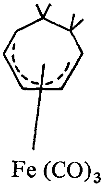
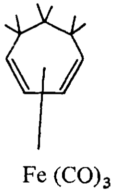
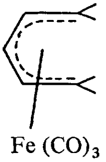
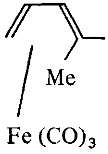
		*a*
		*b*
		*c*
		*d*
		*e*
		*f*
		*g*

* All species in this column carry a uni-positive charge, probably delocalised between the hydrocarbon moiety and the metal atom.

† Carbene complex cation not isolated, but its intermediacy can be argued from its chemistry (ref. g).

[a] H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 497. [b] J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3955. [c] M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 1962, 189. [d] G. F. Emerson, K. Erhlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1966, **88**, 3172. [e] M. L. H. Green and C. R. Hurley, *J. Organometallic Chem.*, 1967, **10**, 188. [f] L. Busetto and R. J. Angelici, *J. Amer. Chem. Soc.*, 1968, **90**, 3283; L. Busetto, U. Belluco, and R. J. Angelici, *J. Organometallic Chem.*, 1969, **18**, 213. [g] P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 5044.

Table 5 *Formation of cationic iron carbonyl complexes by removal of hydride ion from organometallic carbonyls with Ph_3CBF_4*

*Cation**	*Neutral compound*	*Reference*
		*a*
		*b*
		*c*
		*d*
		*e*

* All species in this column carry a uni-positive charge, probably delocalised between the hydrocarbon moiety and the iron atom.

[a] M. L. H. Green and P. L. I. Nagy, *J. Amer. Chem. Soc.*, 1962, **84**, 1310; *J. Organometallic Chem.*, 1963, **1**, 58. [b] T. N. Margulis, L. Schiff, and M. Rosenblum, *J. Amer. Chem. Soc.*, 1965, **87**, 3269. [c] F. M. Chaudhari and P. L. Pauson. See P. L. Pauson, *Pure and Appl. Chem.*, 1968, **17**, 235. [d] H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 497. [e] J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3955.

(*a*) *Synthesis of organometal carbonyls*

$[Mn(CO)_5]^- + CH_2{:}CHCH_2Cl \rightarrow \sigma\text{-}CH_2{:}CHCH_2Mn(CO)_5 + Cl^-$ (refs. 110, 111)

$[Mn(CO)_5]^- + C_5F_5N \rightarrow \sigma\text{-}NC_5F_4Mn(CO)_5 + F^-$ (ref. 112)

(*b*) *Preparation of complexes with covalent metal–metal bonds*

$[Mn(CO)_5]^- + (\pi\text{-}C_5H_5)Fe(CO)_2I \rightarrow (\pi\text{-}C_5H_5)FeMn(CO)_7 + I^-$ (ref. 113)

$[Mn(CO)_5]^- + Ph_3PAuCl \rightarrow Ph_3PAuMn(CO)_5 + Cl^-$ (ref. 114)

$[Mn(CO)_5]^- + Ph_3SnCl \rightarrow Ph_3SnMn(CO)_5 + Cl^-$ (ref. 115)

$[Mn(CO)_5]^- + 2\text{-}ClB_5H_8 \rightarrow 2\text{-}[Mn(CO)_5]B_5H_8 + Cl^-$ (ref. 116)

(*c*) *Synthesis of carbonyl hydrides*

$[Mn(CO)_5]^- + H_3PO_4 \rightarrow HMn(CO)_5 + [H_2PO_4]^-$ (ref. 117)

Reactions (*a*)—(*c*) depend on the nucleophilicity of the mononuclear anions which is approximately in the order $[Re(CO)_5]^- \approx [(\pi\text{-}C_5H_5)Fe(CO)_2] > [(\pi\text{-}C_5H_5)Ru(CO)_2]^- \approx [Mn(CO)_4PPh_3]^- > [Mn(CO)_5]^- > [(\pi\text{-}C_5H_5)Mo(CO)_3]^- > [Co(CO)_4]^-$.[118] Pentacarbonylrhenate(−I) generally reacts to give products in good yield uncontaminated by side reactions (see the accompanying chart). The anion $[Re(CO)_5]^-$ is sufficiently nucleophilic to react with diborane to give $[H_3BRe(CO)_5]^-$, precipitated as its tetra-alkylammonium salt.[119] Related to the formation of $[H_3BRe(CO)_5]^-$, are reactions[120] between the Lewis acids $GaBr_3$ or $InBr_3$ and the anions $[Fe(CO)_4]^{2-}$ or $[Co(CO)_4]^-$.

$$[(Ph_3P)_2N][Co(CO)_4] + GaBr_3 \xrightarrow{CH_2Cl_2} [(Ph_3P)_2N][Br_3GaCo(CO)_4]$$

$$Na_2[Fe(CO)_4] + InBr_3 + 2(Ph_3P)_2NBr \xrightarrow{THF} [(Ph_3P)_2N]_2[Br_3InFe(CO)_4] + 2NaBr$$

Polynuclear carbonyl anions have little tendency to act as nucleophiles, presumably because the negative charge is delocalized over two or more metal atoms. Nevertheless, protonation often provides a useful route to polynuclear carbonyl hydrides (see later).

The chemistry of cationic carbonyl complexes has been less studied, but some

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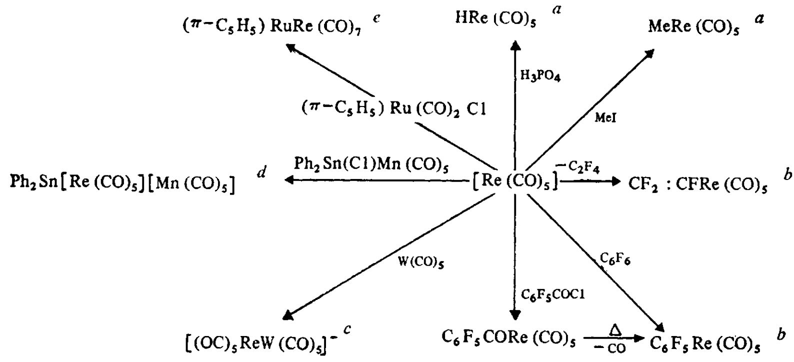
[110] H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, 1960, **15b**, 682.
[111] W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601.
[112] J. Cooke, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 173.
[113] R. B. King, P. M. Treichel, and F. G. A. Stone, *Chem. and Ind.*, 1961, 747.
[114] C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1964, 1741.
[115] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.
[116] D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, 1968, **7**, 1041.
[117] W. Hieber and G. Wagner, *Z. Naturforsch.*, 1957, **12b**, 478; 1958, **13b**, 339.
[118] M. I. Bruce, D. N. Sharrocks, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 680.
[119] G. W. Parshall, *J. Amer. Chem. Soc.*, 1964, **86**, 361.
[120] J. K. Ruff, *Inorg. Chem.*, 1968, **7**, 1499.

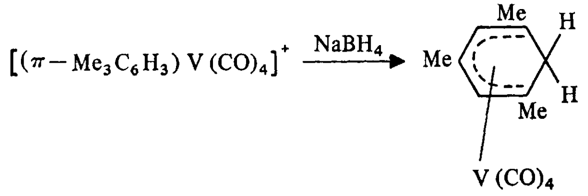


Some representative reactions of pentacarbonylrhenate(−I)

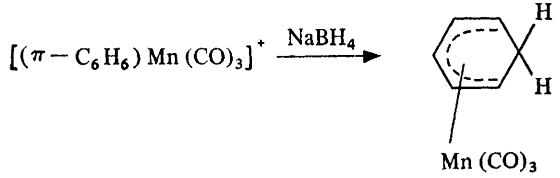
[a]W. Hieber and G. Braun, *Z. Naturforsch.*, 1959, **14b**, 132; W. Beck, W. Hieber, and G. Braun, *Z. Anorg. Chem.*, 1961, **308**, 23. [b]P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5830. [c]U. Anders and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1967, **89**, 539. [d]A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and M. Ya. Zakharova, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1965, 1122. [e]T. Blackmore, J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 2931.

important reactions have been observed. Many cationic complexes containing hydrocarbon ligands are susceptible to attack by nucleophiles (H^-, R^-, or OR^-, *etc.*) sometimes giving novel neutral carbonyl compounds.

$[(\pi\text{-}C_7H_7)Mo(CO)_3]^+ + R^- \rightarrow \pi\text{-}RC_7H_7Mo(CO)_3$ (ref. 121)
($R^- = CN^-$, OMe^- or Ph^-) (RC_7H_7 = substituted cycloheptatriene)



(ref. 122)



(ref. 102)

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[121] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3475, 3479, 3484.
[122] F. Calderazzo, *Inorg. Chem.*, 1966, **5**, 429.

Alkoxide ion attacks CO groups in cationic carbonyls of iridium,[123] manganese,[124] rhodium,[125] and platinum.[126] *e.g.*

$$[(Ph_3P)_2Ir(CO)_3][ClO_4] + NaOMe \rightarrow (Ph_3P)_2Ir(CO_2Me)(CO)_2 + NaClO_4$$

$$[(Ph_3P)_2Pt(CO)Cl][BF_4] + MeOH \rightarrow (Ph_3P)_2Pt(CO_2Me)Cl + HBF_4$$

In water most cationic carbonyls decompose, thus $[Mn(CO)_6]^+$ affords $HMn(CO)_5$,[99] and $[(Et_3P)_2Pt(CO)Cl]^+$ yields $(Et_3P)_2Pt(H)Cl$.[126]

4 Metal Carbonyl Derivatives

In the following Sections the chemistry of the metal carbonyls is reviewed according to the kinds of derivative involved. Although this subdivision is convenient, since each class of carbonyl complex has its own special properties often giving rise to an extensive chemistry, allocation of a complex to a particular class is often arbitrary. This is a consequence of it being possible for several different kinds of ligand to be present in the co-ordination sphere of a metal in a low oxidation state. Thus, for example, using the classification selected below, the compound $(\pi\text{-}C_5H_5)Mo(CO)_2[P(OPh)_3](H)$ could equally well be treated as an organometal carbonyl, a Lewis base complex of a carbonyl, or a hydrido metal carbonyl, and will display properties accordingly. Moreover, cationic and anionic species are found with all types of carbonyl complex.

A. 'Lewis Base' Complexes of the Metal Carbonyls.—Numerous complexes are known wherein other donor groups are associated with CO in low valency transition-metal compounds. The commonest ligands are those involving atoms of the Group V elements, especially phosphorus. Such donor groups may be classified according to whether they are, for example, two, three, four, or six electron donors:

Two-electron donors:	R_3P, $(RO)_3P$, R_3As, PF_3, py, RCN, PH_3 and less commonly R_2S and NH_3.
Three-electron donors:	NO; and R_2P, R_2As, RS and RSe when these ligands occur as bridging groups; and occasionally acac.
Four-electron donors:	diphos, dipy, phen, diars, en.
Six-electron donors:	diglyme, den, triars.

Among methods of preparation, the direct reaction between a metal carbonyl and the ligand has been by far the most common. The effects on reaction of such variables as solvent, temperature, or u.v. irradiation are profound. Indirect methods of synthesis involving displacement of one ligand by another have been extensively used, particularly in the preparation of complexes of a required stoicheiometry or stereochemistry.

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[123] L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 1965, 6974.
[124] T. Kruck and M. Noack, *Chem. Ber.*, 1964, **97**, 1693.
[125] W. Hieber and V. Frey, *Chem. Ber.*, 1966, **99**, 2614.
[126] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, 1969, **91**, 1346.

In most instances the ligands have π-acceptor properties, but with the possible exceptions of PF_3 and NO they are invariably less effective π-acceptors than CO*. This is argued from relative changes in the observed CO frequencies. Indeed, this is the most thoroughly studied physical property, providing information about bonding and stereochemistry.[1]

As CO groups are replaced by other ligands further substitution usually becomes increasingly difficult because the strength of the remaining carbon–metal bonds normally increases. This is due to enhanced metal–carbon π bonding resulting from addition to the co-ordination sphere of the metal atom of ligands which are better σ donors but are poorer π acceptors than CO. Illustrating this behaviour the complexes $LFe(CO)_4$ and $L_2Fe(CO)_3$ [$L = Ph_3E$; E = P, As, or Sb] are readily prepared by heating pentacarbonyliron with the triphenyl derivatives of the Group V elements in an appropriate solvent.[128] Substitution of more than two CO groups of $Fe(CO)_5$ by these ligands does not occur. Similarly, the strong chelating ligand diars either on heating to 140 °C,[129] or on u.v. irradiation,[130] affords (diars)$Fe(CO)_3$. However, the latter will react further with diars on strong heating to yield the monocarbonyl complex $(diars)_2Fe(CO)$.[129]

The effect of temperature on the nature of the products is shown in the reactions of phosphines with octacarbonyldicobalt. Mention was made previously of the ionic complexes $[(R_3P)_2Co(CO)_3][Co(CO)_4]$.[56,57] These compounds form rapidly at 0 °C in solvents such as methylene chloride, and reactions have been observed even at − 70 °C.[131] However, if the compounds are heated in solution binuclear disubstitution products are formed.[132,133]

$$[(R_3P)_2Co(CO)_3][Co(CO)_4] \xrightarrow{> 40\ ^\circ C} [R_3PCo(CO)_3]_2 + CO$$

Mono-phosphine-substituted binuclear cobalt complexes can be obtained by the reaction:[133]

$$[R_3PCo(CO)_3]_2 + Co_2(CO)_8 \xrightarrow{CO} 2Co_2(CO)_7(PR_3)$$

Like the species $[R_3PCo(CO)_3]_2$, the compounds $Co_2(CO)_7(PR_3)$ have a molecular structure with a Co—Co bond without bridging CO groups. Interestingly, tertiary phosphites and octacarbonyldicobalt afford covalent complexes $[(RO)_3P]_2Co_2(CO)_6$ and $[(RO)_3P]Co_2(CO)_7$, and only trace amounts of the ionic

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* The sequence of relative π-bonding ability is approximately: NO ≈ CO ≈ $PF_3 > PCl_3 > P(OR)_3 > PPh_3 > SR_2 > PR_3 >$ py $> R_3N$.[127] However, there can be no consistent order of overall π-bonding, for this will depend on the competition from other ligands. Moreover, acceptor and donor action by the same ligand are mutually supportive, thereby affecting bond strengths and changing orders of displacement of one ligand by another.

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[128] A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, 1963, **2**, 151; *Inorg. Synth.*, 1966, **8**, 185.

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compounds can be obtained. This is undoubtedly related to the relatively greater π acceptor and weaker σ donor properties of phosphites compared with tertiary phosphines, so that the latter can stabilise the Co^I cation (see earlier).

The displacement of one ligand by another has been extensively used for the synthesis of compounds of the type described in this section. Thus acetonitrile groups in $(MeCN)_3M(CO)_3$ (M = Cr, Mo or W)[134] are readily replaced by other groups, and recent examples of this approach include the synthesis of compounds containing the tris(dimethylamino)borane[135] and hexamethylborazole[136] ligands.

$$(Me_2N)_3B + (MeCN)_3W(CO)_3 \rightarrow (Me_2N)_3BW(CO)_3 + 3MeCN$$

$$Me_6B_3N_3 + (MeCN)_3Cr(CO)_3 \rightarrow (Me_6B_3N_3)Cr(CO)_3 + 3MeCN$$

This technique was used some years ago to obtain the complexes $L_3M(CO)_3$ [L = Ph_3P, $(PhO)_3P$, Ph_3As, *etc.*] as their *fac* isomers, by reactions of the donor molecules L with either cycloheptatriene- or arene-tricarbonylmetal complexes of Cr, Mo, or W.[137,138] More recently the trisubstituted complexes $L_3M(CO)_3$ [L = aniline or cyclohexylamine; M = Cr, Mo or W] have been obtained from reaction of aniline or cyclohexylamine with (norbornadiene)$M(CO)_4$.[139] The ligand displacement technique has also been used as one method of obtaining a carbonyl complex with acetylacetone as a ligand.[140]

$$(Me_2CHNH_2)Ir(CO)_2Cl + C_5H_8O_2 \rightarrow (OC)_2Ir(acac) + (C_3H_7NH_3)Cl$$

Among the unidentate ligands, NO, PF_3, and PH_3 are of special interest. Nitrosyl metal carbonyls have been known for over fifty years; PF_3 complexes have a very extensive though relatively recently developed chemistry; and PH_3 complexes of the carbonyls have only recently been discovered. Moreover, the NO, PF_3, and PH_3 carbonyl derivatives are especially suitable for spectroscopic studies. All three ligands give rise to characteristic bands in the i.r. region, while the two phosphorus ligands can be further characterised by their n.m.r. spectra (^{31}P, ^{1}H, or ^{19}F).

The two isosteric series: $Ni(CO)_4$, $Co(NO)(CO)_3$, $Fe(NO)_2(CO)_2$, and $Mn(NO)_3CO$; and $Fe(CO)_5$, $Mn(NO)(CO)_4$ were discussed in our previous article.[1] The cobalt compound is probably still best prepared by the reaction which led to its discovery:[141]

$$Co_2(CO)_8 + 2NO \xrightarrow{40\ ^\circ C} 2Co(NO)(CO)_3 + 2CO$$

Interestingly, $Co(NO)(CO)_3$ reacts further with NO to give $Co(NO)_3$.[141a]

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[134] D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.
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[137] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 2323.
[138] C. N. Matthews, T. A. Magee, and J. H. Wotiz, *J. Amer. Chem. Soc.*, 1961, **83**, 3200.
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[141a] I. H. Sabherwal and A. B. Burg, *Chem. Comm.*, 1970, 1001.

Of the several methods for preparing the iron nitrosyl, that involving treatment of an alkaline solution of Na[$HFe(CO)_4$] with sodium nitrite and acetic acid is probably the most satisfactory.[8,142] The compound $Mn(NO)_3CO$[143] was prepared by the action of NO on $Mn(CO)_5I$ at *ca.* 100 °C, while $Mn(NO)(CO)_4$ was first obtained by treating $HMn(CO)_5$ with *N*-nitroso-*N*-methyl-*p*-toly-sulphonamide.[8,144] Tetracarbonyl(nitrosyl)manganese can also be prepared by the reaction of $(Ph_3P)_2Mn_2(CO)_8$ with nitric oxide at 90 °C in tetralin. The complex $Mn(CO)_4NO$ is also a convenient source of $Mn(NO)_3CO$ which forms on treatment of the mononitrosyl with nitric oxide.[145]

No unsubstituted carbonylnitrosyls of the Group VI metals have been obtained as yet, although complexes such as $Cr(CO)_3(NO)_2$, isoelectronic with $Fe(CO)_5$, might reasonably be expected to exist. Vanadium hexacarbonyl reacts with nitric oxide to form a very unstable nitrosyl $V(CO)_5NO$.[146] There seems no reason why polynuclear carbonylnitrosyls should not exist, and in this respect the recent synthesis of $Ru_3(CO)_{10}(NO)_2$ from $Ru_3(CO)_{12}$ and nitric oxide (containing no NO_2 or H_2O) is of considerable interest.[147]

Although unsubstituted carbonylnitrosyls are relatively few in number, it should be noted that a great many carbonylnitrosyls with other ligands present in the molecule are known, *e.g.* $(\pi\text{-}C_5H_5)V(NO_2)(CO)$,[148] $(\pi\text{-}C_5H_5)Mo(NO)(CO)_2$,[149] or $(Ph_3P)_2Ru(NO)(CO)(Cl)$.[150] Anionic and cationic complexes are also found, *e.g.* $Hg[Fe(CO)_3NO]_2$[151] or $[(Ph_3P)_2Ir(NO)(CO)I][BF_4]$, C_6H_6.[152] In the former complex[153] the nitrosyl group functions as a σ donor (Lewis base), in which the Fe—N—O linkage is very probably linear, as established in many related uncharged nitrosyls. Back bonding from the metal to the NO group will occur.[1] However, in the cationic complex the NO ligand acts as a σ-acceptor (Lewis acid). Consequently, the Ir—N—O linkage is bent to 125°, the nitrogen atom being sp^2 hybridised, with iridium(I) acting as a weak Lewis base.[152]

Phosphorus trifluoride is capable of substituting more or less randomly to almost any extent into metal carbonyls. This was first observed[154] with $Ni(CO)_4$, and subsequently complexes $Ni(CO)_{4-x}(PF_3)_x$ ($x = 1$—4) were isolated by chromatography.[155] Similar studies have been carried out with other metal

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carbonyls, for example those of iron,[156,157] molybdenum[158] or manganese[159]; as well as with derivatives of carbonyls, such as $HMn(CO)_5$,[160] $Co(CO)_3NO$,[161] $CF_3Co(CO)_4$,[162] and (butadiene)$Fe(CO)_3$.[163] Preparation of the compounds involves treating the carbonyl complex with PF_3 under pressure, and either heating the mixture, or exposing it to u.v. irradiation. The various products, for example all possible compositions of the type $Fe(CO)_x(PF_3)_{5-x}$ or $CF_3Co(PF_3)_x(CO)_{4-x}$ have been isolated, are separated by gas-liquid partition chromatography. With these systems a great variety of stereochemical situations is possible. Thus with $Mn_2(CO)_{10}$, assuming free rotation about the metal–metal bond, substitution by PF_3 could produce 2, 6, 9, 17, 14, 17, 9, 6, 2, and 1 isomers for mono, di, tri, *etc.* substitution, for a total of 84 species. These correspond to eleven compositions including as yet unreported $Mn_2(PF_3)_{10}$. If free rotation about the Mn—Mn bond is restricted, the possibilities are even greater.[159] In practice four PF_3 complexes have been clearly identified, and good evidence for four others obtained. The pentacarbonyliron system is much more labile, and the compositions $Fe(CO)_x(PF_3)_{5-x}$ consist of a random mixture of isomers. These isomers are stereochemically non-rigid and exist in a ready equilibrium.[157,164] It has been estimated, for example, that the composition $Fe(CO)_4PF_3$ consists of 33% axial substitution by PF_3 and 67% equatorial.[165]

Although fully substituted PF_3 complexes can be obtained by many of the exchange reactions cited above, they can be prepared more directly by 'reductive fluorophosphination' of metal salts:[166]

$$MX_x \xrightarrow[\text{Heat Cu or Zn}]{PF_3 \text{ under pressure}} M(PF_3)_n + CuX \text{ or } ZnX_2$$

Compounds $XM(PF_3)_n$ are sometimes formed, while addition of hydrogen as a reactant can yield hydrido-complexes $H_yM(PF_3)_x$. These syntheses clearly parallel those described earlier for metal carbonyls. The close similarity of PF_3 and CO as ligands is further demonstrated by the existence of numerous compounds of similar formula, *e.g.*

$Co(NO)(PF_3)_3$	$Co(NO)(CO)_3$	$Fe(PF_3)_4I_2$	$Fe(CO)_4I_2$
$Fe(PPh_3)_2(PF_3)_3$	$Fe(PPh_3)_2(CO)_3$	$(\pi\text{-}C_5H_5)Co(PF_3)_2$	$(\pi\text{-}C_5H_5)Co(CO)_2$
$HMn(PF_3)_5$	$HMn(CO)_5$	$(\pi\text{-}Me_3C_6H_3)Mo(PF_3)_3$	$(\pi\text{-}Me_3C_6H_3)Mo(CO)_3$

The phosphorus trifluoride complexes which do not contain CO groups seem to

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have a less extensive derivative chemistry than the carbonyls. This may be due to PF_3 being too effective as a ligand in removing charge from a transition metal atom, so that those many reactions of carbonyl complexes which depend on their nucleophilicity are not observed, or occur only to a minor degree. Thus although the trifluorophosphinemetallates (*e.g.* $[Re(PF_3)_5]^-$) can be protonated, they are only weak reducing agents. The salt $[Mn(CO)_6][Co(PF_3)_4]$ is, for example, thermally stable; whereas as mentioned in a previous Section $[Mn(CO)_6][Co(CO)_4]$ readily affords $(OC)_5MnCo(CO)_4$ with release of CO.

A new development in the chemistry of 'Lewis base' complexes of the carbonyls has been the discovery of phosphine derivatives*, obtained by methods involving displacement of carbonyl, organophosphine, borane, carbene, or hexamethylborazole ligands, *e.g.*

$$(\pi\text{-}C_5H_5)V(CO)_4 + PH_3 \xrightarrow{h\nu} (\pi\text{-}C_5H_5)V(CO)_3(PH_3) + CO \qquad \text{(ref. 169)}$$

$$(Ph_3P)_2Ir(CO)Cl + PH_3 \xrightarrow{\Delta} (Ph_3P)(PH_3)Ir(CO)Cl + Ph_3P \qquad \text{(ref. 170)}$$

$$[(OC)_4WB_3H_8]^- + 2PH_3 \xrightarrow{\Delta} (PH_3)_2W(CO)_4 + [B_3H_8]^- \qquad \text{(ref. 170)}$$

$$(OC)_5CrC(OMe)Me + 2PH_3 \xrightarrow{h\nu} (PH_3)_2Cr(CO)_4 + CH_2{:}CHOMe + CO \qquad \text{(ref. 171}a\dagger)$$

$$(Me_6B_3N_3)Cr(CO)_3 + 3PH_3 \xrightarrow{\Delta} (PH_3)_3Cr(CO)_3 + Me_6B_3N_3 \qquad \text{(ref. 171}c)$$

A phosphine(carbonyl)nitrosyl has also been prepared.[172]

$$Co(CO)_3NO + PH_3 \rightarrow Co(CO)_2(NO)(PH_3) + CO$$

Phosphine will even displace PF_3 from a complex, as in the formation of $HCo(PF_3)_3(PH_3)$ from $HCo(PF_3)_4$.[173] An interesting phenomenon in phosphine-(carbonyl) chemistry is the synthesis of the metal cluster compounds $Ru_3(CO)_8(PH_3)_4$ and $Rh_6(CO)_8(PH_3)_8$ from relatively simple carbonyl halides.[170]

Complexes wherein CO groups of polynuclear metal carbonyls have been replaced by electron pair donors are as yet comparatively few in number, but

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* It should be noted that NH_3 complexes also exist. Treatment of $M(CO)_6$ [M = Cr, Mo, W] with ammonia at elevated temperatures affords $(H_3N)_3M(CO)_3$. At lower temperatures $H_3NCr(CO)_5$ has been prepared.[167] Cationic complexes, *e.g.* $[(\pi\text{-}C_5H_5)Mo(CO)_3NH_3]^+$ are also known.[168] Many other ammonia(carbonyl)–metal complexes are probably capable of synthesis.

† A complex, $Cr(PH_3)_4(CO)_2$, in which four CO groups in $Cr(CO)_6$ have been replaced by PH_3 has also been isolated.[171b]

[167] H. Behrens and N. Harder, *Chem. Ber.*, 1964, **97**, 433; and references cited therein.

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[171] (*a*) E. O. Fischer, E. Louis, and W. Bathelt, *J. Organometallic Chem.*, 1969, **20**, 147. (*b*) E. O. Fischer and E. Louis, *ibid*, 1969, **18**, P26, (*c*) E. O. Fischer and C. G. Kreiter, *Angew. Chem. Internat. Edn.*, 1969, **8**, 377.

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include for example, the compounds $Fe_3(CO)_{11}L$ [L = Ph_3P,[174] $(MeO)_3P$[175]], $Fe_3(CO)_{10}[P(OMe)_3]_2$,[175] $Fe_3(CO)_9L_3$ [L = $PhPMe_2$,[176] $(MeO)_3P$[175]], $Co_3(CO)_6L_3$ [L = Bu_3P, Ph_2PBu],[177] $Co_4(CO)_{11}L$ [L = Ph_3P, Ph_3As, Ph_3Sb],[178] $Ir_4(CO)_9(PPh_3)_3$,[179] $M_3(CO)_9L_3$ [M = Ru or Os, L = PPh_3],[180] $Ru_3(CO)_{10}(AsPh_3)_2$,[181] $YCCo_3(CO)_8L$ and $YCCo_3(CO)_7L_2$ [Y = Cl, Br etc.; L = R_3P and R_3As].[182] No doubt as the chemistry of polynuclear carbonyls continues to expand many similar derivatives will be described.

Countless carbonyl complexes are known containing chelating ligands. Mention was made earlier of diars derivatives of pentacarbonyliron. Of similar vintage are several 1,2-bis(diphenylphosphino)ethane complexes such as (diphos)-$Ni(CO)_2$[183] or (diphos)$Cr(CO)_4$.[184] Recent trends have been towards preparing complexes containing more exotic bidentates. Space does not permit more than a cursory summary, but among the derivatives which may be mentioned are those involving dithioketones [*e.g.* $(Me_2C_2S_2)_2W(CO)_2$],[185] 1,4-diazabutadienes {*e.g.* $[Me_2C_2N_2(OMe)_2]Mo(CO)_4$},[186] organometallic bases {*e.g.* $[Me_2Si(AsMe_2)_2]$-$Ni(CO)_2$},[187] and 1,2-arsino- or -phosphino-perfluorocyclobutenes [*e.g.* (ffars)$Mo(CO)_4$, (ffos)$Ni(CO)_2$,[188] (ffars)$Fe_2(CO)_6$[189]]. Similar compounds have been prepared from 1,2-diphenylphosphinoperfluorocyclopentene,[189] *e.g.* ($f_6$fos)$Fe(CO)_3$. In (ffars)$Fe_2(CO)_6$ the arsenic atoms chelate to one iron atom while the double bond of the cyclobutene group co-ordinates to the second iron atom. There is also an Fe—Fe donor–acceptor bond.*

Chelate complexes have also been prepared in which pairs of nitrogen and phosphorus atoms, or phosphorus and sulphur atoms are co-ordinated to metal carbonyl groups, *e.g.* $[Ph_2PC_2H_4NEt_2]Cr(CO)_4$[190] and $[Ph_2PCH_2CH_2SMe]$-$W(CO)_4$.[191] In yet another type of bidentate ligand, electron pairs are contributed by a phosphorus atom and by a carbon–carbon double bond *e.g.* [*o*-$Ph_2PC_6H_4$-CH:CHMe]$Mo(CO)_4$.[192] Interestingly in these complexes containing the 2-*cis*-propenylphenyl-diphenylphosphine ligand the reactant was the allyl com-

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*For other examples of this type of metal–metal interaction see reference 1.

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[175] P. J. Pollick and A. Wojcicki, *J. Organometallic Chem.*, 1968, **14**, 469.

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[189] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, 1969, **8**, 95, 1464.

[190] G. R. Dobson and R. C. Taylor, *Inorg. Chem.*, 1967, **6**, 1929.

[191] E. P. Ross and G. R. Dobson, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2363.

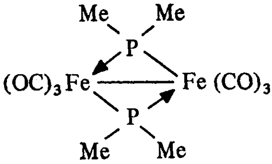
[192] L. V. Interrante, M. A. Bennett, and R. S. Nyholm, *Inorg. Chem.*, 1966, **5**, 2212.

pound *o*-CH_2:$CHCH_2C_6H_4PPh_2$ which isomerised during reaction. As mentioned later, metal carbonyls readily isomerise double bonds.

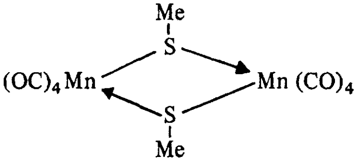
Several metal carbonyl complexes have been prepared containing phosphorus ligands which are bi- or even poly-functional but which are non-chelating. For example, with tetracarbonylnickel the oxide P_4O_6 forms the novel tetranuclear nickel complex $P_4O_6[Ni(CO)_3]_4$,[193] and the ligands $(CF_3)_2POP(CF_3)_2$ and $(CF_3)_2PN(Me)P(CF_3)_2$ afford compounds $[(CF_3)_2POP(CF_3)_2]_2Ni_2(CO)_4$, and $[(CF_3)_2PN(Me)P(CF_3)_2]_2Ni_2(CO)_3$, respectively.[194] The compound from $(CF_3)_2POP(CF_3)_2$ probably has a structure based on an eight-membered ring containing two $Ni(CO)_2$ groups and two molecules of the ligand. A related eight-membered ring structure occurs in the complexes $[(CF_3)_2PCNM(CO)_4]_2$ formed by reacting the cyanophosphine ligand $(CF_3)_2PCN$ with the bicycloheptadiene complexes $C_7H_8M(CO)_4$ [M = Cr or Mo].[195]

With the non-chelating bifunctional phosphorus ligands both mono- and bi-nuclear metal carbonyl complexes are possible. Thus $P(OCH_2)_3P$ reacts with the hexacarbonyls of the chromium group to give two series of compounds $(OC)_5MP(OCH_2)_3P$ and $(OC)_5MP(OCH_2)_3PM(CO)_5$ [M = Cr, Mo, or W]; and with $Fe(CO)_5$ the three complexes $(OC)_4FeP(OCH_2)_3P$, $(OC)_4FeP(CH_2O)_3P$, and $(OC)_4FeP(OCH_2)_3PFe(CO)_4$ have been prepared.[196]

Diphosphines and disulphides, R_2PPR_2 and RSSR, and related compounds involving As, Se or Te, react with metal carbonyls either on heating or under u.v.



(1)



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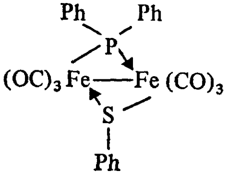

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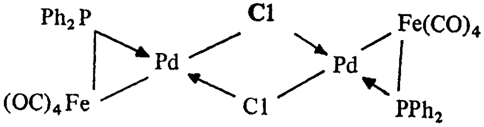

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[194] R. A. Sinclair and A. B. Burg, *J. Amer. Chem. Soc.*, 1966, **88**, 5354; *Inorg. Chem.*, 1968, **7**, 2160.

[195] J. F. Nixon and J. R. Swain, *J. Organometallic Chem.*, 1970, **27**, P13.

[196] R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 71.

irradiation to give bridge complexes such as (1)[197] or (2)[198] which may or may not contain metal–metal bonds.[1] Innumerable compounds similar to (1) and (2) have been prepared.[*] Diphosphines also give rise to compounds of the type $(OC)_4FePR_2{\cdot}R_2PFe(CO)_4$,[197,199] which are precursors to complexes like (1). Not surprisingly it has been possible to prepare from Ph_2PSPh the compound (3),[200] which combines the features of (1) and (2). Several complexes are known in which a single R_2P group bridges two metal carbonyl groups either by itself or in parallel with hydrido or halogenbridges, *e.g.* $(OC)_5Mn(Me_2P)Mn(CO)_4(PMe_2)$,[201] $(OC)_4Mn(PPh_2)(H)Mn\ (CO_4)$,[201,202] and $(OC)_4Mn[P(CF_3)_2](I)Mn(CO)_4$.[203] Some novel related bridge compounds, *e.g.* (4), $(OC)_4\overline{Fe(PPh_2)Co}(CO)_3$, and $(OC)_4\overline{Fe(PPh_2)Mn}(CO)_4$,containing metal–metal bonds between dissimilar metal atoms have been prepared by reactions between $Ph_2(H)PFe(CO)_4$ and allyl complexes.[204]

$$2Ph_2(H)PFe(CO)_4 + [(\pi\text{-}C_3H_5)PdCl]_2 \rightarrow (4) + C_3H_6$$

As indicated at several points in this and the preceding Section, many reactions of carbonyl complexes with electron donors occur upon u.v. light irradiation of the reactants. These photochemically induced reactions[205] probably proceed *via* co-ordinatively unsaturated species such as $W(CO)_5$ or $Fe(CO)_4$, for which there is spectroscopic evidence.[206] It is most interesting that in reactions of this kind another transition-metal atom can act as a Lewis Base. The photochemical formation of anions containing dissimilar metal atoms, *e.g.* $[(OC)_4FeMn(CO)_5]^-$ was mentioned earlier; another example is the formation of complexes such as $(\pi\text{-}C_5H_5)_2(H)_2WW(CO)_5$[207] where bis(cyclopentadienyl)-molybdenum or -tungsten dihydrides function as Lewis Bases.

Most of the reactions described in this Section have involved displacement of CO groups especially by phosphines. It is worth reminding the reader that the reverse process can occur with the platinum metals. Treatment of $(Ph_3P)_nPt$ ($n = 3$ or 4) with CO affords several triphenylphosphine platinum carbonyl compounds.[208,209]

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[*] See the article by R. G. Hayter listed in Table 1.

[197] J. Chatt and D. A. Thornton, *J. Chem. Soc.*, 1964, 1005.

[198] P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 1963, 720.

[199] K. Issleib and M. Keil, *Z. anorg. Chem.*, 1964, **333**, 10.

[200] B. E. Job, R. A. N. McLean, and D. T. Thompson, *Chem. Comm.*, 1966, 895.

[201] R. G. Hayter, *J. Amer. Chem. Soc.*, 1964, **86**, 823.

[202] M. L. H. Green and J. T. Moelwyn-Hughes, *Z. Naturforsch.*, 1962, **17b**, 783.

[203] J. Grobe, *Z. anorg. Chem.*, 1964, **331**, 63.

[204] B. C. Benson, R Jackson, K. K. Joshi, and D. T. Thompson, *Chem. Comm.*, 1968, 1507.

[205] W. Strohmeier, *Angew. Chem. Internat. Edn.*, 1964, **3**, 730.

[206] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, 1963, **85**, 1013.

[207] B. Deubzer and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1968, **90**, 3276.

[208] V. G. Albano, G. M. B. Ricci, and B. L. Bellon, *Inorg. Chem.*, 1969, **8**, 2109; and references cited therein.

[209] R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Amer. Chem. Soc.*, 1969, **91**, 1574; P. Chini and G. Longini, *J. Chem. Soc.* (*A*), 1970 1542; and references cited therein.

B. Metal Carbonyl Hydrides.—The metal carbonyl hydrides are of particular significance historically in that $HCo(CO)_4$ and $H_2Fe(CO)_4$ were the first compounds to be obtained having direct hydrogen to transition metal bonds.[48] In addition to mononuclear compounds, polynuclear species *e.g.* $H_3Re_3(CO)_{12}$ and $HRe_3(CO)_{14}$ abound. Moreover, as indicated in a previous Section, anionic hydridocarbonyls, *e.g.* $[H_6Re_4(CO)_{12}]^{2-}$, $[H_2Re_3(CO)_{12}]^-$, and $[H_3Re_2(CO)_6]^-$, are well known; cationic species less so.

The thermal stabilities of the simple unsubstituted carbonyl hydrides vary considerably. For example, only above *ca.* 80 °C does $HMn(CO)_5$ rapidly afford hydrogen and manganese carbonyl, whereas $H_2Fe(CO)_4$ and $HCo(CO)_4$ decompose rapidly into the carbonyls and hydrogen even below room temperature. For the cobalt compound this is known to be a reversible process, and to involve $HCo(CO)_3$,[210] with important implications for the hydroformylation reaction mentioned in a later Section. The hydride $HV(CO)_6$ has not been isolated, but the oxonium salt $[Et_2OH][V(CO)_6]$ is known.[7] Although $H_2Ru(CO)_4$[211] is similar to $H_2Fe(CO)_4$ in decomposing even below 0 °C, $H_2Os(CO)_4$[18] is stable at 100 °C.

Substituted carbonyl hydrides and polynuclear species generally have enhanced stability. For example, $HCo(CO)_3PPh_3$ decomposes at 70 °C,[212] π-$C_5H_5Fe(CO)_2H$ slowly at room temperature,[213] and $HV(CO)_5PPh_3$ has been prepared and can be studied in aqueous solution in which it is a weak acid ($k = 1{\cdot}5 \times 10^{-7}$).[214] Mononuclear carbonyl hydrides have varying degrees of acidity. Aqueous solutions of $H_2Fe(CO)_4$ are slightly more acidic than acetic acid ($k_1 = 3{\cdot}6 \times 10^{-5}$ and $k_2 = 1{\cdot}1 \times 10^{-14}$), and although $HCo(CO)_4$ is only slightly soluble in water, measurements in methanol show that it is as strong an acid as nitric acid. Manganese pentacarbonyl hydride is a weak acid ($k = 0{\cdot}8 \times 10^{-7}$).[117] Unsubstituted mononuclear carbonyl hydrides are very air sensitive, but the substituted or polynuclear hydrides are much less susceptible to oxidation.

Several methods have been used to make carbonylmetal hydrides. The most commonly used route, briefly mentioned earlier, involves protonation of carbonyl anions. A few illustrative examples are given on page 530.

As mentioned previously, treatment of iron carbonyls with aqueous solutions of ammonia or amines affords hydrido(carbonyl)ferrates.

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[210] F. Ungváry and L. Marko, *J. Organometallic Chem.*, 1969, **20**, 205.

[211] J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2162.

[212] W. Hieber and E. Linder, *Z. Naturforsch.*, 1961, **16b**, 137.

[213] M. L. H. Green and P. L. I. Nagy, *J. Organometallic Chem.*, 1963, **1**, 58.

[214] W. Hieber, E. Winter, and E. Schubert, *Chem. Ber.*, 1962, **95**, 3070.

[215] H. W. Sternberg, I. Wender, and M. Orchin, *Inorg. Synth.*, 1957, **5**, 192.

[216] (*a*) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1964, **86**, 4841. (*b*) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau and B. Fontal, *J. Amer. Chem. Soc.*, 1968, **90**, 7135.

[217] H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2753.

[218] B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *J. Organometallic Chem.*, 1967, **10**, 105.

[219] W. Fellmann and H. D. Kaesz, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 63.

[220] E. O. Fischer, *Inorg. Synth.*, 1963, **7**, 136.

$$Co_2(CO)_8 \xrightarrow{py} [py_6Co][Co(CO)_4]_2 \xrightarrow{H_2SO_4} HCo(CO)_4 \qquad \text{(ref. 215)}$$

$$\begin{tikzcd}
 & {[Re(CO)_5]^-} \arrow[r, "H_3PO_4"] & HRe(CO)_5 & & & \text{(ref. 76)} \\
e_2\ CO)_{10} \arrow[ur, "Na\text{-}Hg"] \arrow[dr, "a"'] & & & & & \\
 & \text{Mixture of anions*} \arrow[r, "H_3PO_4"] \arrow[dr, "(a)\ {[Re(CO)_5]^-}", "(b)\ H_3PO_4"'] & {[HRe(CO)_4]_3}\ \text{(ref. 216}a\dagger\text{)} \arrow[r, "OH^-\ EtOH"] & {[H_2Re_3(CO)_{12}]^-} & & \text{(ref. 216}b\text{)} \\
 & & {[HRe_3(CO)_{14}]} & & & \text{(ref. 219)}
\end{tikzcd}$$

$$Mo(CO)_6 \xrightarrow[THF]{C_5H_5Na} [(\pi\text{-}C_5H_5)Mo(CO)_3]^- \xrightarrow{HOAc} HMo(CO)_3(\pi\text{-}C_5H_5) \qquad \text{(refs. 8, 87, 220)}$$

$$Os_3(CO)_{12} \xrightarrow[\text{or } NaBH_4 \text{ in THF}]{KOH\text{-}MeOH} \text{(uncharacterised anions)} \xrightarrow{H_3PO_4} \begin{matrix} H_2Os_3(CO)_{10} \\ HOs_3(CO)_{10}OH \\ H_2Os_4(CO)_{13} \\ H_4Os_4(CO)_{12} \end{matrix} \qquad \text{(ref. 16)}$$

$$Ru_3(CO)_{12} \xrightarrow[{[Mn(CO)_5]^-}]{\text{reduction with}} \text{uncharacterised anion} \xrightarrow{H_3PO_4} H_2Ru_6(CO)_{18} \qquad \text{(ref. 220}a\text{)}$$

$$Co_2(CO)_8 + Ru_3(CO)_{12} \xrightarrow{\text{acetone}} [RuCo_3(CO)_{12}]^- \xrightarrow{HCl} HRuCo_3(CO)_{12} \qquad \text{(ref. 37)}$$

$$Cr(CO)_6 \xrightarrow[Et_4NBr]{NaBH_4\text{-}THF} [Et_4N][(OC)_5Cr(H)Cr(CO)_5] \qquad \text{(refs. 83, 85)}$$

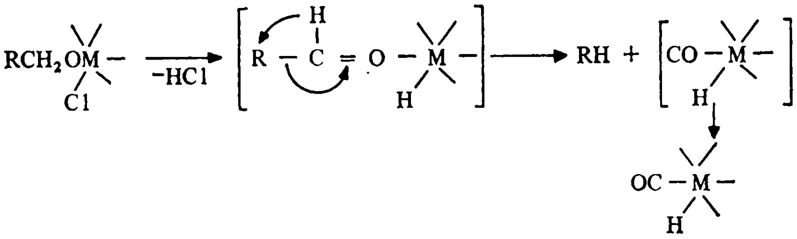
For hydridocarbonyl complexes of the platinum metals the common method of syntheses involves reduction of halide complexes.

$$(Ph_3P)_2Rh(CO)Cl \xrightarrow[Ph_3P/ROH]{N_2H_4} HRh(CO)(PPh_3)_3 \qquad \text{(ref. 221)}$$

$$(NH_4)_2OsBr_6 \xrightarrow[\text{2-methoxyethanol}]{Ph_3P} HOs(CO)(PPh_3)_3Br \qquad \text{(ref. 222)}$$

$$[Ru_2Cl_3(PEt_2Ph)_6]Cl \xrightarrow{KOH\text{-}EtOH} HRu(CO)(PEt_2Ph)_3Cl \qquad \text{(ref. 223)}$$

Tracer studies with D- and ^{14}C-labelled alcohols have shown that the alcohols are the source of the H and CO ligands in reactions such as the last two above.[223,224]



A number of carbonyl complexes in which the metal has a d^8 configuration react directly with molecular hydrogen, affording carbonyl hydrides of these elements, *e.g.*,

$$Os(CO)_5 + 2Ph_3P \xrightarrow{130\ ^\circ C} (Ph_3P)_2Os(CO)_3 \xrightarrow[120\ \text{atm.}\ -130\ ^\circ C]{H_2\text{-THF}} H_2Os(CO)_2(PPh_3)_2 \qquad \text{(ref. 225)}$$

$$IrCl_3 + Ph_3P \xrightarrow[\text{boil}]{DMF} (Ph_3P)_2Ir(CO)Cl \qquad \text{(ref. 226)}$$

[220a] M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Comm.*, 1970, 458.
[221] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.
[222] L. Vaska, *J. Amer. Chem. Soc.*, 1964, **86**, 1943.
[223] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466.
[224] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 4989.
[225] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 1968, **7**, 1290.
[226] J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Synth.*, 1968, **11**, 101.

Footnotes to Scheme on facing page

* Reduction of $Re_2(CO)_{10}$ affords several polynuclear carbonylrhenium anions,[220b] including $[Re_4(CO)_{16}]^{2-}$ and $[H_6Re_4(CO)_{12}]^{2-}$.

† In the corresponding synthesis of $[HMn(CO)_4]_3$ the novel complex $HMn_3(CO)_{10}(BH_3)_2$ is a by-product (see refs. 1 and 217). Formation of the borane species can be avoided by treating $Mn_2(CO)_{10}$ with 15M aqueous KOH, followed by H_3PO_4, giving trinuclear $[HMn(CO)_4]_3$ in 80% yield.[218]

Then $(Ph_3P)_2Ir(CO)Cl \xrightarrow[1\ atm.]{H_2} H_2Ir(CO)(PPh_3)_2Cl$ (refs. 227, 228)

The tendency for transition-metal complexes in low oxidation states to form stable covalent bonds with hydrogen is so great that in several reactions hydrido-complexes have been formed unexpectedly, hydrogen having been abstracted from the solvent, or a ligand. Two examples from metal carbonyl chemistry are:

$$Mn_2(CO)_{10} \xrightarrow[\text{reflux in xylene}]{L\,=\,Ph_3P\text{ or }(PhO)_3P} HMn(CO)_3L_2 \qquad \text{(ref. 229)}$$

$$[(\pi\text{-}C_5H_5)Mo(CO)_3]^- \xrightarrow[THF]{Me_2PCl} (\pi\text{-}C_5H_5)(OC)_2Mo\cdot\mu(H)(PMe_2)\cdot Mo(CO)_2(\pi\text{-}C_5H_5)$$

(refs. 77, 230)

As mentioned previously, some substituted metal carbonyl complexes can be readily protonated, and the protonated species occasionally isolated as salts, *e.g.* $[(\pi\text{-}C_5H_5)(OC)_2Fe(H)Mn(CO)_5]^+$.[107] It seems likely that in the binuclear cations the proton is part of a symmetrically bridged system, in view of the more recent discovery and establishment of the structure of the anionic and the neutral polynuclear bridged species such as $[(OC)_5Cr(H)Cr(CO)_5]^-$ or $(OC)_5Mn(OC)_4Re(H)Re(CO)_5$, referred to earlier.[1] In the novel anion $[H_3Re_2(CO)_6]^-$, prepared by treating ReH_9^{2-} with CO in 2-propanol, two $Re(CO)_3$ groups are probably linked through three bridging hydrogen atoms.[230a]

Several chemical reactions of $HMn(CO)_5$ are summarised in the accompanying chart. Many of these reactions have their counterparts in the chemistry of other mononuclear carbonyl hydrides less well investigated. Thus halogenation, insertion, and substitution reactions have been observed with many different hydrides, *e.g.*,

$$(\pi\text{-}C_5H_5)Mo(CO)_3H + CHCl_3 \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_3Cl + CH_2Cl_2 \qquad \text{(ref. 87)}$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2H + CH_2{:}CHCN \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2CH(CN)Me \qquad \text{(ref. 231)}$$

$$H_2Ru(CO)_4 + 2Ph_3P \rightarrow H_2Ru(CO)_2(PPh_3)_2 + 2CO \qquad \text{(ref. 211)}$$

A number of carbonyl complexes isomerise olefins and catalyse the conversion of non-conjugated into conjugated dienes. Intramolecular transfer of hydrogen between metal and hydrogen undoubtedly occurs in these reactions, and the following mechanism has been proposed for the conjugation of dienes.[232]

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[227] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.

[228] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 53; and references cited therein.

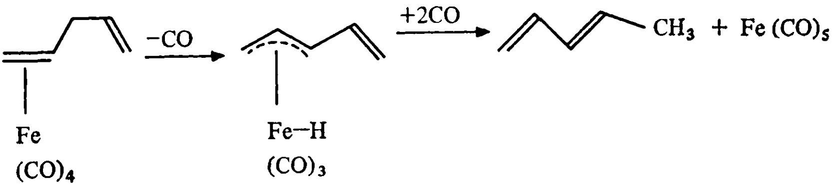
[229] R. Ugo and F. Bonati, *J. Organometallic Chem.*, 1967, **8**, 189.

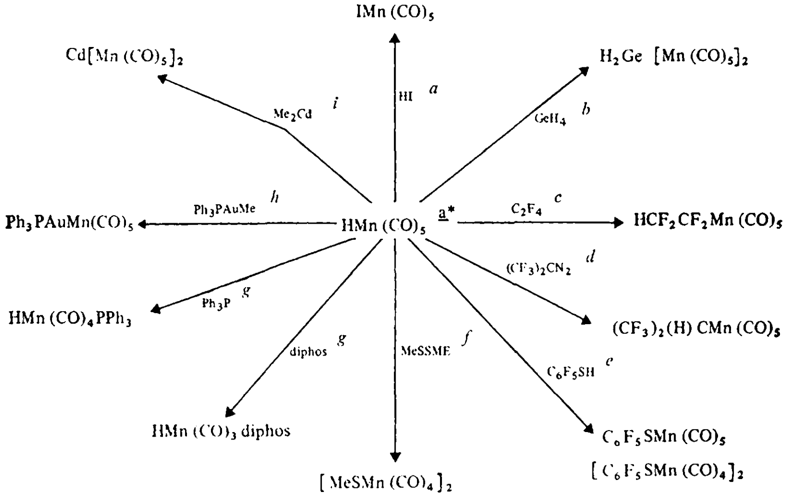
[230] R. G. Hayter, *J. Amer. Chem. Soc.*, 1963, **85**, 3120.

[230a] A. P. Ginsberg and M. J. Hawkes, *J. Amer. Chem. Soc.*, 1968, **90**, 5930.

[231] J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 1963, 2976.

[232] R. Pettit and G. F. Emerson, *Adv. Organometallic Chem.*, 1964, **1**, 1.





Some reactions of manganese pentacarbonyl hydride (m.p. − 24·6: b.p. 111 °C)

* For the most recent information on the i.r. spectrum, see W. F. Edgell, J. W. Fischer, G. Asato, and W. Risen, *Inorg. Chem.*, 1969, **8**, 1103.

[a] W. Hieber and G. Wagner, *Z. Naturforsch.*, 1958, **13b**, 339; for laboratory syntheses see R. B. King 'Organometallic Syntheses,' vol. 1. p. 158, Academic Press, 1965, or R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963. **7**, 198. [b] A. G. Massey, A. J. Park, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1963, **85**, 2021. [c] P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, 1962, **1**, 511. [d] Joan Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 1872. [e] A. G. Osborne and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1143. [f] P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 1963, 720. [g] B. L. Booth and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1966, 157. [h] C. M. Mitchell and F. G. A. Stone, unpublished observations. [i] N. A. D Carey and J. G. Noltes, *Chem. Comm.*, 1968, 1471.

C. Metal Carbonyl Halides.—As with the other classes of carbonyl derivative, it is possible for metal carbonyl halides to exist as neutral molecules [*e.g.* $Mo(CO)_4Cl_2$], as anions (*e.g.* $[Mo(CO)_5I]^-$), or as cations (*e.g.* $[Mo(CO)_2(diars)_2Br]^+$). The latter species serves to illustrate the frequently found combination in a complex of carbonyl, halogen, and electron pair donating ligand; in this case a chelating diarsine group.

The halogens of many metal carbonyl halides are present as bridges between two metal atoms,* *e.g.* $[IMn(CO)_4]_2$ or $[Ru(CO)_3Br_2]_2$. Although the majority

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* The compound $Mo(CO)_4Cl_2$ is probably dimeric with halogen bridges and seven-coordinate molybdenum, the metal atoms thus conforming with the effective atomic number rule.[222]

of the complexes are diamagnetic, a number of paramagnetic species are known, for example, $Cr(CO)_5I$ and $py_2Mo(CO)_2Cl_2$. For simple halogeno-metal carbonyls, *e.g.*, $Fe(CO)_4X_2$ (X = Cl, Br, or I) the thermal stabilities generally increase in the order of Cl < Br < I. No metal carbonyl fluorides have as yet been characterised unambiguously although there is some evidence for a cationic species $[Ru(CO)_2F]^+$. A compound thought to have been $Pt(CO)_2F_8$ probably did not contain fluorine.[234] It is not surprising that simple carbonyl fluorides would have low stability. Both COF_2 and metal fluorides are thermodynamically very stable species, and these compounds are likely to form readily by conventional methods which might be used in attempting to prepare such species as $Fe(CO)_4F_2$. In other words, mononuclear metal carbonyl fluorides have not been authenticated so far, simply because something else is even more stable. A similar argument may be used to account for the relative stabilities of the iron carbonyl halides mentioned above. Under certain conditions, however, probably with fluoride as a bridging ligand in a polymeric complex, it may be possible to obtain a metal carbonyl fluoride.

Metal carbonyl halides are customarily prepared in one of two ways:

(i) *Carbonylation of a metal halide.* This is the customary route to carbonyl halides of the platinum group metals. The syntheses of $[Ru(CO)_3Cl_2]_2$[3] and of $[Rh(CO)_2Cl]_2$[4] were described earlier. The compound $(Ph_3P)_2Rh(CO)Cl$ is conveniently prepared by adding $RhCl_3,3H_2O$ to boiling ethanol containing triphenylphosphine, and treating the solution with aqueous formaldehyde.[235] The latter reagent is the source of the CO group, and the reaction should be compared with the previously indicated syntheses of $(Ph_3P)_2Ir(CO)Cl$ and $HOs(CO)(PPh_3)_3Br$.

Treatment of platinum chloride of empirical composition $PtCl_3$ with CO (40—120 atm.) at 110 °C affords $Pt(CO)_2Cl_2$ and phosgene. The dicarbonyl-platinum complex on heating loses CO and forms $[Pt(CO)Cl_2]_2$.[236] Of more interest are complexes of the type *cis*-$R_3PPt(CO)X_2$ readily obtained by cleavage of the metal halogen bridges in $[R_3PPtX_2]_2$ with CO.[237,238] A bridge splitting reaction also occurs in the synthesis of $[(Et_3P)_2Pd(CO)Cl][BF_4]$ by treating $[(Et_3P)_4Pd_2Cl_2][BF_4]_2$ with CO.[239]

(ii) *Reactions between metal carbonyls and halogens.* Carbonylmetal halides of many types have been prepared by this method, *e.g.*,

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[233] M. W. Anker, R. Colton, and I. B. Tomkins, *Rev. Pure and Appl. Chem.*, 1968, **18**, 23.

[234] R. D. W. Kemmitt, R. D. Peacock, and I. L. Wilson, *Chem. Comm.*, 1968, 772.

[235] D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Synth.*, 1968, **11**, 99.

[236] (*a*) J. M. Lutton and R. W. Parry, *J. Amer. Chem. Soc.*, 1954, **76**, 4271; (*b*) P. Schutzenberger, *Compt. rend.*, 1870, **70**, 1134; *J. Chem. Soc.*, 1871, 1008.

[237] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1662.

[238] A. C. Smithies, M. Rycheck, and M. Orchin, *J. Organometallic Chem.*, 1968, **12**, 199.

[239] H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, 1969, **91**, 596.

$$\mathrm{Re_2(CO)_{10}} \xrightarrow{\mathrm{Br_2}} \mathrm{Re(CO)_5Br}\ \text{(ref. 240)} \xrightarrow[-\mathrm{CO}]{\Delta} \mathrm{[Re(CO)_4Br]_2} \qquad \text{(ref. 241)}$$

$$\mathrm{Mo(CO)_6} \xrightarrow{\mathrm{Cl_2}} \mathrm{[Mo(CO)_4Cl_2]_2} \qquad \text{(ref. 242)}$$

$$\mathrm{Os_3(CO)_{12}} \xrightarrow{\mathrm{Cl_2}} \mathrm{ClOs(CO)_4{\cdot}Os(CO)_4{\cdot}Os(CO)_4Cl} \qquad \text{(ref. 16*)}$$

$$\mathrm{Cr(diars)_2(CO)_2} \xrightarrow{\mathrm{I_2}} \mathrm{[Cr(diars)_2(CO)_2I]I} \qquad \text{(ref. 244)}$$

The seven-co-ordinate chromium(II) complex formed in the latter reaction is an example of a large number of similar seven-co-ordinate carbonyl halides of $\mathrm{Cr^{II}}$, $\mathrm{Mo^{II}}$ and $\mathrm{W^{II}}$ that have been isolated and characterised.[233] Oxidation of the compound (diars)$\mathrm{Fe(CO)_3}$ with one equivalent of iodine yields the paramagnetic five-co-ordinate product (diars)$\mathrm{Fe(CO)_2I}$.[129]

Interestingly, halogen-containing organic compounds often oxidise metal carbonyl complexes, and this kind of reaction has found frequent use in synthesis.

$$\mathrm{(MeCN)_3Mo(CO)_3} \xrightarrow{\mathrm{CH_2{:}CHCH_2Cl}} \mathrm{(MeCN)_2Mo(CO)_2(\pi\text{-}C_3H_5)(Cl)} \qquad \text{(ref. 245)}$$

$$\mathrm{H_2Os(CO)_4} \xrightarrow{\mathrm{CCl_4}} \mathrm{Cl_2Os(CO)_4} \qquad \text{(ref. 18)}$$

$$\mathrm{[Ph_3PCo(CO)_3]^-} \xrightarrow{\mathrm{CF_3I}} \mathrm{ICo(CO)_3PPh_3} \qquad \text{(ref. 246)}$$

The product of the last reaction is of interest in that $\mathrm{ICo(CO)_4}$, analogous to $\mathrm{I_2Fe(CO)_4}$, has only a fleeting existence, being obtained by iodine cleavage of the cobalt–metal bonds in complexes such as $\mathrm{Et_3PbCo(CO)_4}$.[247] The carbonyls of nickel, cobalt, and vanadium react rapidly with halogens giving the corresponding metal halides.

It has been known for many years that pentacarbonyliron and iodine react to give $\mathrm{I_2Fe(CO)_4}$.[248] Treatment of dodecacarbonyltri-iron with iodine in tetrahydrofuran affords $\mathrm{Fe_2(CO)_8I_2}$ for which a D_{4d} structure has been proposed.[249] The reaction $\mathrm{Fe(CO)_5 + I_2 \rightarrow I_2Fe(CO)_4 + CO}$ is an example of an oxidative-elimination process.[228] Iron(0)(d^8) is oxidised to iron(II)(d^6) with an increase in

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* This reaction contrasts with that between $\mathrm{Ru_3(CO)_{12}}$ and halogens which initially affords $\mathrm{[Ru(CO)_3X_2]_2}$ or *cis*-$\mathrm{X_2Ru(CO)_4}$ depending on the conditions. The difference in behaviour between osmium ana ruthenium carbonyl is probably due to an enhanced metal–metal bond strength in the former case.[243]

[240] W. Hieber, R. Schuh, and H. Fuchs, *Z. anorg. Chem.*, 1941, **248**, 243.

[241] E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 1958, 3149.

[242] R. Colton and I. B. Tomkins, *Austral. J. Chem.*, 1966, **19**, 1143; see also ref. 233.

[243] B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc.* (*A*), 1969, 792.

[244] J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 3009.

[245] R. G. Hayter, *J. Organometallic Chem.*, 1968, **13**, P1.

[246] W. Hieber and H. Duchatsch, *Chem. Ber.*, 1965, **98**, 2530.

[247] M. Pankowski and M. Bigorgne, *Compt. rend.*, 1967, **264**, *C*, 1382.

[248] W. Hieber and G. Bader, *Z. anorg. Chem.*, 1930, **190**, 193, 215.

[249] F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, 1967, **6**, 2113.

co-ordination number of the metal from five to six. Metal carbonyl complexes in which the metal atom has a d^8 configuration have a marked propensity to become oxidised to the d^6 state by reaction with halogen-containing compounds. The products so obtained can be regarded as falling within the definition of being carbonyl halides:

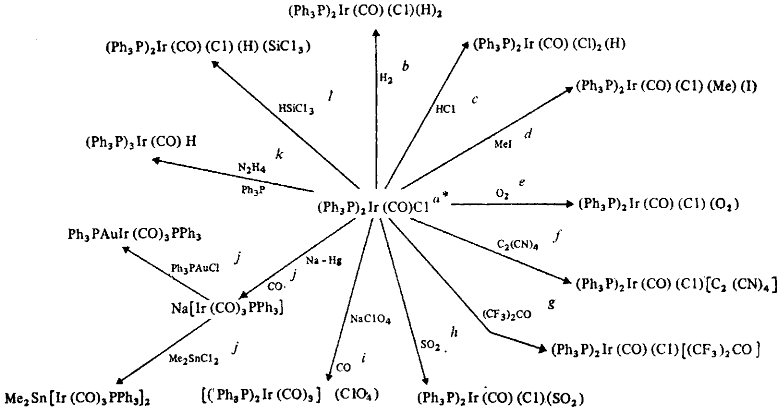
$$\mathrm{MeI} + \mathrm{(Ph_3P)_2Ru(CO)_3} \xrightarrow{-\mathrm{CO}} \mathrm{(Ph_3P)_2Ru(CO)_2(Me)(I)} \qquad \text{(ref. 228)}$$

$$\mathrm{Ph_3PAuCl} + \mathrm{Os_3(CO)_{12}} \longrightarrow \mathrm{ClOs(CO)_4{\cdot}Os(CO)_4{\cdot}Os(CO)_4AuPPh_3} \qquad \text{(ref. 250)}$$

$$\mathrm{GeI_4} + (\pi\text{-}\mathrm{C_5H_5})\mathrm{Co(CO)_2} \xrightarrow{-\mathrm{CO}} (\pi\text{-}\mathrm{C_5H_5})\mathrm{Co(GeI_3)(I)(CO)} \qquad \text{(ref. 251)}$$

$$\mathrm{HgCl_2} + \mathrm{(Ph_3P)_2Ir(CO)Cl} \longrightarrow \mathrm{(Ph_3P)_2Ir(CO)(Cl)_2(HgCl)} \qquad \text{(ref. 252)}$$

The last reaction exemplifies the marked reactivity of the iridium(I) carbonyl



Some reactions of chlorocarbonylbis(triphenylphosphine)iridium(I)

* For laboratory syntheses see *Inorg. Synth.*, 1968, **11**, 101.
[a]L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1961, **83**, 2784; J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, 1967, **89**, 844; J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *ibid.*, 1968, **90**, 5430; J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 604. [b]L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679. [c]L. Vaska, *J. Amer. Chem. Soc.*, 1966, **88**, 5325; L. Vaska, *Accounts Chem. Res.*, 1968, **1**, 335. [d]R. F. Heck, *J. Org. Chem.*, 1963, **28**, 604. [e]L. Vaska, *Science*, 1963, **140**, 809; S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 2581. [f]W. H. Baddley, *J. Amer. Chem. Soc.*, 1968, **90**, 3705. [g]Beverley Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 167. L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, 1966, **88**, 1333; S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1966, **5**, 405. [i]M. J. Church and M. J. Mays, *Chem. Comm.*, 1968, 435. [j]J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, 1968, **90**, 2282. [k]L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, 1963, **85**, 3500. [l]A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1965, **87**, 16.

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[250] C. W. Bradford and R. S. Nyholm, *Chem. Comm.*, 1968, 867.
[251] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 523.
[252] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5337.

halide complex $(Ph_3P)_2Ir(CO)Cl$, some of the chemistry of which is shown in the accompanying chart. Most of these reactions involve the formal oxidation of iridium(I) to iridium(III), so that a sixteen-electron carbonyl complex becomes one in which eighteen electrons are in the valence shell of the metal.

Reactions of the metal carbonyl halides have been widely studied, those involving nucleophilic attack by neutral ligands able to replace carbon monoxide being particularly common, *e.g.*,

$$I_2Fe(CO)_4 + 2Ph_3P \xrightarrow{-2CO} I_2Fe(CO)_2(PPh_3)_2 \qquad \text{(ref. 253)}$$

$$ClRe(CO)_5 + \text{diars} \xrightarrow{-2CO} ClRe(CO)_3(\text{diars}) \qquad \text{(ref. 254)}$$

$$IMo(CO)_3(\pi\text{-}C_5H_5) + (Me_2N)_3P \xrightarrow{-CO} IMo(CO)_2(\pi\text{-}C_5H_5)[P(NMe_2)_3] \qquad \text{(ref. 255)}$$

With binuclear carbonyl halides, bridge splitting reactions occur:

$$[Cl_2W(CO)_4]_2 + 2Ph_3P \xrightarrow{-2CO} 2Cl_2W(CO)_3(PPh_3)_2{}^* \qquad \text{(ref. 233)}$$

$$[IRe(CO)_4]_2 + 4py \xrightarrow{-2CO} 2IRe(CO)_3py_2 \qquad \text{(ref. 241)}$$

Bridge cleavage reactions are also observed without release of CO:

$$[Br_2Ru(CO)_2PPh_3]_2 \xrightarrow{2PPh_3} 2(Ph_3P)_2Ru(CO)_2Br_2 \qquad \text{(ref. 180)}$$

$$[Cl_2Pt(CO)]_2 \xrightarrow{2NH_3} 2(H_3N)Pt(CO)Cl_2 \qquad \text{(ref. 256)}$$

In an earlier Section of this review reference was made to the synthesis of the nine anions $[M(CO)_5X]^-$ (M = Cr, Mo, or W; X = Cl, Br, or I) by nucleophilic displacement of CO from $M(CO)_6$ by X^-. The isoelectronic halogenocarbonyls $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) also react with tetra-alkylammonium halides to give both single and mixed-halogen anions.[94,257,258]

$$M(CO)_5X + Y^- \rightarrow [M(CO)_4XY]^- + CO.$$
$$(M = \text{Mn or Re; X and Y = Cl, Br, or I})$$

Several syntheses have been carried out with the anions $[M(CO)_5X]^-$. When

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* Interestingly, seven-co-ordinate complexes of this type decompose in refluxing dichloromethane to give deep blue compounds of formula $L_2M(CO)_2X_2$. The latter absorb CO quantitatively reverting to $L_2M(CO)_3X_2$.[233] *X*-Ray analysis has shown that $(Ph_3P)_2M(CO)_2Br_2$ has essentially a seven-co-ordinate structure but with only six ligands. The structure is a capped octahedron with one octahedral site vacant.

[253] W. Hieber and A. Thalhofer, *Angew. Chem.*, 1956, **68**, 679.

[254] W. J. Kirkham, A. G. Osborne, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 550.

[255] R. B. King, *Inorg. Chem.*, 1963, **2**, 936.

[256] R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 1957, 2018.

[257] R. J. Angelici, *Inorg. Chem.*, 1964, **3**, 1099.

[258] E. W. Abel, I. S. Butler, M. C. Ganorkar, C. R. Jenkins, and M. H. B. Stiddard, *Inorg. Chem.*, 1966, **5**, 25.

M = Mo or W, and X = Br or I, treatment[259,260] with halogens gives the seven-co-ordinate anionic metal species $[M(CO)_4X_3]^-$. The latter with triphenylphosphine gives $[M(CO)_3(PPh_3)X_3]^-$. However, with bidentate ligands (diphos, diars, *etc.*) neutral complexes $M(CO)_3(LL)X_2$ are formed, while certain terdentate ligands afford $M(CO)_2(LLL)X_2$.[261]

Mild oxidation of $[Cr(CO)_5I]^-$ with I_2, Fe^{3+}, or H_2O_2 is stated[262] to afford blue paramagnetic $Cr(CO)_5I$, also prepared by the action of iodine upon the ion $[Cr_2(CO)_{10}]^{2-}$. However, under somewhat different conditions $[Cr(CO)_5I]^-$ was found to be the product of the latter reaction.[263]

Anions of the type $[M(CO)_5I]^-$ react with an excess of $M(CO)_6$ under photolytic conditions to form binuclear species $[M_2(CO)_{10}I]^-$. Even 'mixed' species have been obtained by this technique:[263]

$$[Cr(CO)_5I]^- + W(CO)_6 \xrightarrow[THF]{h\nu} [CrW(CO)_{10}I]^- + CO$$

Apparently iodide in $[M(CO)_5I]^-$ is sufficiently basic to complex with '$M(CO)_5$' generated by photolysis. The binuclear anions have bridged structures $[(OC)_5M(I)M(CO)_5]^-$. However, unlike in electron deficient $[(OC)_5M(H)M(CO)_5]^-$ the M(X)M bridge in the halides is bent. Related species $[(OC)_5M(X)M(CO)_5]^-$ (X = SCN, CN, or SR) are also known.[264]

As mentioned in an earlier Section, carbonylmetal halides are important intermediates in the synthesis of cationic carbonyl complexes. Moreover, several examples have been given earlier of syntheses involving treatment with alkali metal derivatives of carbonyl anions. Of great importance also are the many known reactions with metallo-organics, *e.g.*,

$$(\pi\text{-}C_5H_5)Fe(CO)_2Cl + CH_2{:}CHLi \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2(CH{:}CH_2) + LiCl \quad \text{(ref. 265)}$$

$$[Ru(CO)_3Cl_2]_2 + 2C_5H_5Tl \rightarrow 2(\pi\text{-}C_5H_5)Ru(CO)_2Cl + 2TlCl + 2CO \quad \text{(ref. 266)}$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2I + AgC(CN)_3 \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2C(CN)_3 + AgI \quad \text{(ref. 267)}$$

Mention was made earlier of the incompatibility of F and CO as ligands; this is due in part to the oxidising properties of the reagents available for the synthesis of carbonyl fluorides so that metal fluorides readily form. The nitrate group is also a good oxidising agent and therefore NO_3 and CO are also likely to be

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[259] R. B. King, *Inorg. Chem.*, 1964, **3**, 1039.
[260] M. C. Ganorkar and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 3494.
[261] W. S. Tsang, D. W. Meek, and A. Wojcicki, *Inorg. Chem.*, 1968, **7**, 1263.
[262] H. Behrens and H. Zizlsperger, *Z. Naturforsch.*, 1961, **16b**, 349.
[263] J. K. Ruff, *Inorg. Chem.*, 1968, **7**, 1821.
[264] J. K. Ruff and R. B. King, *Inorg. Chem.*, 1969, **8**, 180.
[265] M. L. H. Green, M. Ishaq and T. Mole, *Z. Naturforsch.*, 1965, **20b**, 598.
[266] T. Blackmore, J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2931.
[267] W. Beck, R. E. Nitzschmann, and G. Neumair, *Angew. Chem.*, 1964, **76**, 346.

incompatible. However, the compounds $M(CO)_5(NO_3)$ ($M = Mn$[268] or Re[269]) have been made:

$$Re_2(CO_{10}) + 2N_2O_4 \xrightarrow{0\,°C} 2Re(CO)_5(NO_3) + 2NO$$

The nitratopentacarbonyls are less stable than the corresponding carbonyl halides, and treatment of other metal carbonyls with dinitrogen tetroxide results in complete cleavage of CO groups.

The acetylacetone ligand is also oxidising, and treatment of several metal carbonyls with 2,4-pentanedione yields only acetylacetonate complexes.[270] However, the synthesis of $(OC)_2Ir(acac)$ was mentioned in an earlier Section, and several β-diketone carbonyl complexes of Ir and Rh are known.[140] Moreover, thallium hexafluoroacetylacetonate reacts with $BrMn(CO)_5$ to give the stable complex $(hfac)Mn(CO)_4$.[271] The latter reacts with several unidentate phosphine ligands to give compounds $(hfac)Mn(CO)_2L_2$ [$L = Ph_3P$, $(MeO)_3P$, Ph_2PMe, *etc.*].

D. Organo(carbonyl)metal Complexes.—Numerous compounds of this type exist. Indeed, following the discovery of the cyclopentadienylmetal carbonyls, the arene metal carbonyls, and simple alkyl metal carbonyls [*e.g.* $MeMn(CO)_5$] it became apparent that all manner of organic groups could act as ligands in association with CO. Moreover, many of these hydrocarbon derivatives were obtained very simply by reacting together a metal carbonyl and an organic compound. Hence, for example, the reaction between tungsten hexacarbonyl and cyclo-octa-1,5-diene which gives $(\pi\text{-}C_8H_{12})W(CO)_4$ is similar in character to the corresponding reaction with triphenylphosphine which gives $(Ph_3P)_2W(CO)_4$.

In this article only a very cursory treatment of the organometal carbonyls is possible. Several of the reviews listed in Table 1 deal with the topic in depth. Previously (ref. 1, p. 362) we have drawn attention to a convenient classification[272] of organometal carbonyls according to the number of electrons which are formally considered to be donated to the metal by the organic ligand. This classification is useful in understanding the formula of the compounds considered in this Section. Most organometal carbonyls have been prepared by one of the following three methods, of which the first and second are by far the most common.

(i) *Direct reaction between an organic compound and a metal carbonyl or metal carbonyl derivative leading to displacement of CO or other ligands.* It is generally necessary to heat the reactants, or to initiate reaction photochemically.

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[268] C. C. Addison, M. Kilner, and A. Wojcicki, *J. Chem. Soc.*, 1961, 4839; C. C. Addison and M. Kilner, *ibid.*, 1968, 1539.

[269] C. C. Addison, R. Davis, and N. Logan, *Inorg. Chem.*, 1967, **6**, 1926.

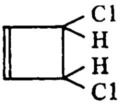
[270] M. Kilner and A. Wojcicki, *Inorg. Chem.*, 1965, **4**, 591; and references cited therein.

[271] F. A. Hartman, M. Kilner, and A. Wojcicki, *Inorg. Chem.*, 1967, **6**, 34.

[272] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds' Vol. 2 (by M. L. H. Green), Methuen, London, 1968.

$$Co_2(CO)_8 + C_5H_6 \xrightarrow[-[H]]{-CO} (\pi-C_5H_5)Co(CO)_2$$ (refs. 8,273)

$$Fe(CO)_5 + CH_2:CHCH:CH_2 \xrightarrow{-CO} (\pi-C_4H_6)Fe(CO)_3$$ (refs. 274,275)

$Fe_2(CO)_9 +$  $\xrightarrow[-[Cl^-]]{-CO} (\pi-C_4H_4)Fe(CO)_3$ (refs. 276)

cis

$$Mn_2(CO)_{10} + C_4H_5N \xrightarrow[-[H]]{-CO} (\pi\text{-}C_4H_4N)Mn(CO)_3$$ (ref.277)

$$Cr(CO)_6 + C_4H_4S \xrightarrow{-CO} (\pi\text{-}C_4H_4S)Cr(CO)_3$$ (ref. 278)

$$(MeCN)_3W(CO)_3 + Et_2C_2 \xrightarrow[-MeCN]{-CO} (\pi\text{-}Et_2C_2)_3W(CO)$$ (ref. 279)

$$Mn_2(CO)_{10} + MeC_3B_3H_6^* \xrightarrow[-[H]]{-CO} (\pi\text{-}MeC_3B_3H_5)Mn(CO)_3$$ (ref. 280)

$$Mo(CO)_6 + [MeC{\equiv}C]^- \xrightarrow{-CO} [MeC{\equiv}CMo(CO)_5]^-$$ (ref. 281)

$$Re(CO)_5Cl + C_2H_4 \xrightarrow[AlCl_3]{-CO/-Cl^-} [(C_2H_4)_2Re(CO)_4]^+$$ (ref. 97)

Although monoacetylene(carbonyl)metal complexes are known, it is a general characteristic of reactions between acetylenes and metal carbonyls to give products in which acetylene groups have dimerized or trimerized.[1,272]†

(ii) *Metathetical Reactions.*

$$CH_2:CHCH_2Cl + [Co(CO)_4]^- \xrightarrow[-Cl^-]{-CO} (\pi\text{-}C_3H_5)Co(CO)_3$$ (ref. 282)

$$[Rh(CO)_2Cl]_2 + C_5H_5^- \xrightarrow[-Cl^-]{} (\pi\text{-}C_5H_5)Rh(CO)_2$$ (ref. 283)

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[*] 2-Methyltricarbahexaborane(7).

[†] See especially the article by Hübel (Table 1).

[273] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.

[274] H. Reihlen, A. Gruhl, G. von Hessling, and O. Pfrengle, *Annalen*, 1930, **482**, 161.

[275] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 1958, 642.

[276] G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 132.

[277] R. B. King and A. Efraty, *J. Organometallic Chem.*, 1969, **20**, 264.

[278] E. O. Fischer and K. Öfele, *Chem. Ber.*, 1958, **91**, 2395.

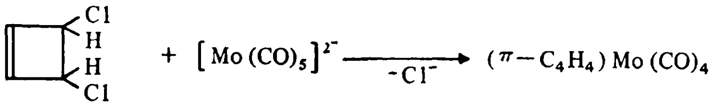
[279] D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasselle, *J. Amer. Chem. Soc.*, 1964, **86**, 3261.

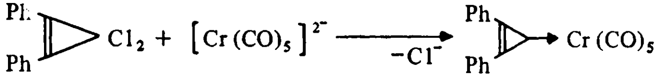
[280] J. W. Howard and R. N. Grimes, *J. Amer. Chem. Soc.*, 1969, **91**, 6499.

[281] W. J. Schlientz and J. K. Ruff, *Chem. Comm.*, 1969, 1363.

[282] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1960, **82**, 4438; 1961, **83**, 1097.

[283] E. O. Fischer and K. Bittler, *Z. Naturforsch.*, 1961, **16b**, 225, 835.

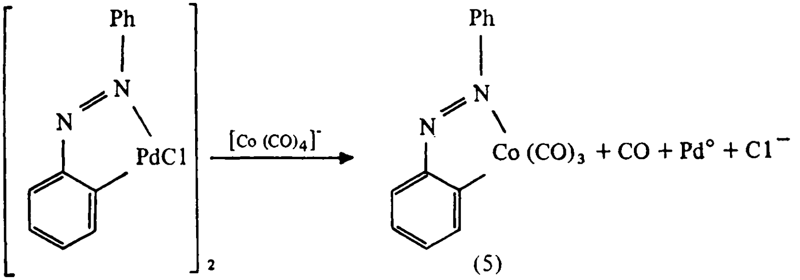

(ref. 284)


(ref. 285)

$$(\pi\text{-}C_7H_7)Mo(CO)_2I + B(pz)_4^- \xrightarrow[-I^-]{} (\pi\text{-}C_7H_7)Mo[B(pz)_4](CO)_2$$ (ref. 286*)

$$Mn(CO)_5Br + [C_2B_9H_{11}]^{2-} \xrightarrow[-Br^-]{-2CO} [(\pi\text{-}C_2B_9H_{11})Mn(CO)_3]^-$$ (ref. 288†)

(iii) *Ligand exchange reactions.* So far this method of synthesis has been used relatively little; examples include the transfer of tetraphenylcyclobutadiene,[290] allylic,[291] and 2-(phenylazo)phenyl[291] ligands from palladium to cobalt carbonyl groups *e.g*:



(5)

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* Several organometal carbonyls containing poly(1-pyrazolyl)borate anions have been prepared.[286] The ligands $HB(pz)_3^-$ and $B(pz)_4^-$ act as terdentate groups, and form sandwich compounds analogous to those formed by the cyclopentadienyl ligand, *e.g.* compare $[HB(pz)_3]Mn(CO)_3$ and $(\pi\text{-}C_5H_5)Mn(CO)_3$. The complex $(\pi\text{-}C_7H_7)Mo[B(pz)_4](CO)_2$ presents an interesting structural problem, namely, utilisation of all ligand electrons would lead to eight-co-ordinate Mo with 20 electrons. Assuming a formal seven-co-ordination and a xenon configuration for molybdenum, one possibility would involve a normal terdentate $B(pz)_4$ group and an allylic $\pi\text{-}C_7H_7$ ligand, as in the fluxional molecule $(\pi\text{-}C_7H_7)Mo(\pi\text{-}C_5H_5)(CO)_2$.[287] However, an alternative formulation in which the $B(pz)_4$ group has become bidentate and the $\pi\text{-}C_7H_7$ group has an uncomplexed double bond is preferred.[286]

† Several metal carbonyl complexes are known in which carborane groups are ligands. These include compounds derived from the anions $[C_2B_9H_{11}]^{2-}$, $[CB_{10}H_{11}]^{3-}$, $[C_2B_7H_9]^{2-}$ and $[C_2B_6H_8]^{2-}$. All have sandwich-like structures,[289] and the series is likely to be extended. Indeed, the complex $(\pi\text{-}MeC_3B_3H_5)Mn(CO)_3$,[180] isoelectronic with $(\pi\text{-}C_5H_5)Mn(CO)_3$, was mentioned above. Moreover, just as 'mixed metal' cyclopentadienyl carbonyls, e.g. $(\pi\text{-}C_5H_5)(OC)_3MoMn(CO)_5$,[1] are known so are related complexes with the $[C_2B_9H_{11}]^{2-}$ ligand, *viz.*[289]

$$[(\pi\text{-}C_2B_9H_{11})Mo(CO)_3]^{2-} + W(CO)_6 \xrightarrow{h\nu} [(\pi\text{-}C_2B_9H_{11})(OC)_3MoW(CO)_5]^{2-} + CO$$

This reaction is reminiscent of those described earlier which gave anions such as $[FeMn(CO)_9]^-$ and $[(OC)_5MnW(CO)_5]^-$.

[284] R. G. Amiet, P. C. Reeves, and R. Pettit, *Chem. Comm.*, 1967, 1208.

[285] K. Öfele, *Angew. Chem. Internat. Edn.*, 1968, **7**, 950.

[286] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 588, 3183.

[287] M. A. Bennett, R. Bramley, and R. Watt, *J. Amer. Chem. Soc.*, 1969, **91**, 3089.

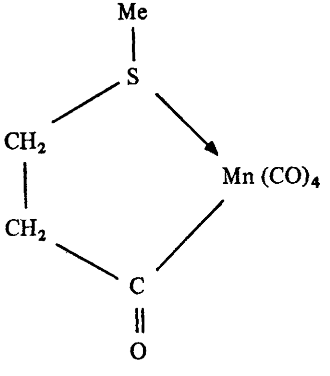
[288] M. F. Hawthorne and T. D. Andrews, *J. Amer. Chem. Soc.*, 1965, **87**, 2496.

[289] M. F. Hawthorne, *Accounts Chem. Res.*, 1967, **1**, 281; and references cited therein.

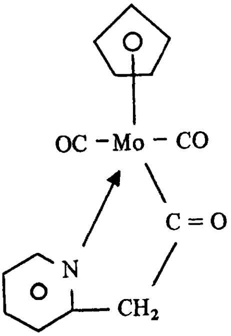
[290] P. M. Maitlis and A. Efraty, *J. Organometallic Chem.*, 1965, **4**, 175.

[291] R. F. Heck, *J. Amer. Chem. Soc.*, 1968, **90**, 313, 317.

Complex (5) is similar to many others in having a metal-carbonyl group bound to a ligand both by a carbon-metal σ bond and a donor–acceptor bond. For example, treatment of $MeRe(CO)_5$ with azobenzene affords tetracarbonyl-2-(phenylazo) phenylrhenium,[292] and 2-chloroethylmethylsulphide and 2-chloromethylpyridine react with the anions $[Mn(CO)_5]^-$ and $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$ to give complexes (6) and (7), respectively.[293]



(6)



(7)

Simple alkyl- or aryl-metal carbonyls are relatively few in number, being confined to compounds of type $RCo(CO)_4$ and $RM(CO)_5$ (M = Mn or Re). Tetracarbonyl(alkyl)cobalt complexes are very unstable, under normal conditions decomposing below 0 °C. As with the carbonylmetal hydrides, replacement of CO by other groups, notably R_3P or $\pi\text{-}C_5H_5$, enhances the stability so that a wide variety of substituted derivatives are known, *e.g.* $(\pi\text{-}C_5H_5)Fe(CO)_2Me$, $(\pi\text{-}C_5H_5)Mo(CO)_3{}^iPr$, and $C_6H_5CH_2Co(CO)_3(PPh_3)$.

The reactivity of alkylcobalt tetracarbonyls is crucial to the success of the hydroformylation reaction whereby octacarbonyldicobalt or its phosphine derivatives catalyse the formation of aldehydes as the principal products from olefins, carbon monoxide, and hydrogen at elevated temperatures and pressures.[294] There is strong evidence for the participation in the reaction of co-ordinatively

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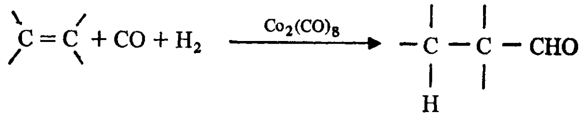
[292] M. Z. Iqbal, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, in the press.

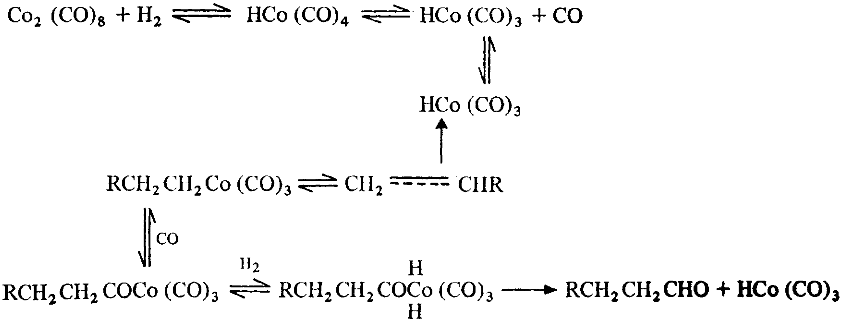
[293] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1965, **4**, 486; *ibid*, 1966, **5**, 293.

[294] A. J. Chalk and J. F. Harrod, *Adv. Organometallic Chem.*, 1968, **6**, 119; and references cited therein.



$$\rangle C{=}C\langle + CO + H_2 \xrightarrow{Co_2(CO)_8} -\underset{H}{C}-C-CHO$$

unsaturated carbonyl complexes, and it is generally accepted that cobalt hydrocarbonyls are key intermediates. Although several steps in the reaction are susceptible to an S_N1 or an S_N2 interpretation, the following sequence, or slight variations of it, seems to accord with the experimental observations.[228,294] The insertion of CO into the cobalt–carbon bond in alkylcobalt carbonyls is well established,[272] and cobalt carbonyl complexes were possibly the earliest known compounds believed capable of activating molecular hydrogen under homogeneous conditions.[294]



Many of the reactions postulated to occur with alkylcobalt tetracarbonyls are well documented for the more stable organomanganese carbonyls. Methylmanganese pentacarbonyl undergoes numerous insertion reactions (see Chart), several of which are similar in nature to those proposed for hydroformylation. Moreover, the acyl derivative $EtCOMn(CO)_5$ is one of the decomposition products of the very unstable $EtMn(CO)_5$, and treatment of the latter with Ph_3CBF_4 affords $[C_2H_4Mn(CO)_5][BF_4]$,[213] *i.e.* a σ complex is converted into a π complex, the reverse of one of the proposed steps in hydroformylation. Examples of the conversion of π into σ complexes may be found elsewhere.[272]

In the last decade it has become well recognised that the reactivity of unsaturated hydrocarbons is altered on co-ordination to metal carbonyl groups, thereby permitting reactions which do not occur with the free hydrocarbon ligand. Indeed, the latter may not even exist in the free state but its chemistry may be examined by co-ordination to a metal. Notable among such systems is the extensive chemistry associated with the cyclobutadiene group in $(\pi\text{-}C_4H_4)Fe(CO)_3$.[295] In this review of metal carbonyl chemistry, space does not

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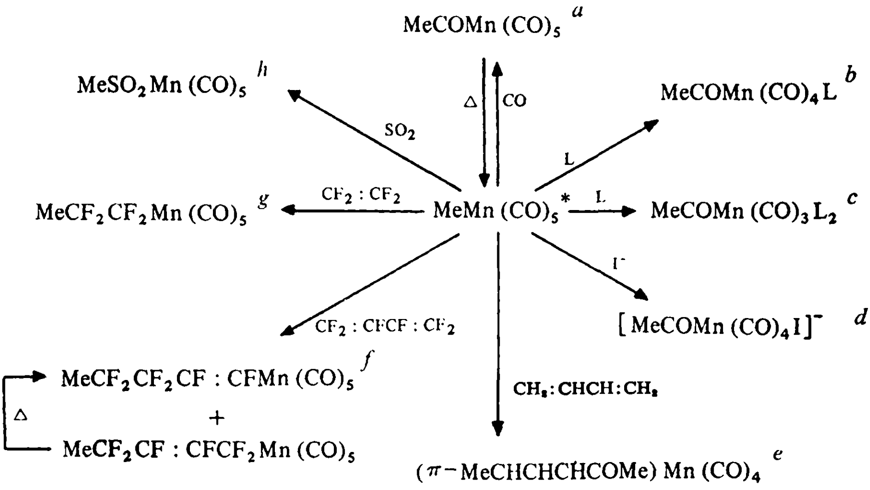
[295] R. Pettit, *Pure Appl. Chem.*, 1968, **17**, 253; see also L. Watts and R. Pettit, 'Advances in Chemistry Series No. 62, Werner Centennial' 1966 p. 549, and R. G. Amiet, K. Nicholas, and R. Pettit, *Chem. Comm.*, 1970, 161.

permit discussion of the reactions of the co-ordinated hydrocarbon ligands, but passing mention may be made of certain ring expansion reactions,[121,296] of electrophilic substitution reactions of cyclo-octatetraene- and cycloheptatriene-(tricarbonyl)iron,[297] and of Friedel–Crafts intermediates in acylation[298] and sulphination[299] of butadiene-(tricarbonyl)iron.

Two classes of organometal carbonyl call for special comment, those containing carbene or fluorocarbon groups.



Some reactions of methylmanganese pentacarbonyl (m.p. 94 °C)

* For the synthesis of this compound see ref. 8. For its i.r. spectrum see J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 389.

[a]T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, 1957, **22**, 598. For ^{13}CO studies see K. Noack and F. Calderazzo, *J. Organometallic Chem.*, 1967, **10**, 101. [b]For L = *cyclo*-$C_6H_{11}NH_2$, $C_6H_5NH_2$, NH_3 *etc.*, see K. A. Keblys and A. H. Filbey, *J. Amer. Chem. Soc.*, 1960, **82**, 4204. For L = cyclohexylamine see also R. J. Mawby, F. Basolo, and R. G. Pearson, *ibid.*, 1964, **86**, 3994. For L = PPh_3, $AsPh_3$, and $SbPh_3$ see W. D. Bannister B. L. Booth, M. Green, and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1969, 698. For L = PPh_3 see also Mawby *et al.*, *ibid.*, and P. K. Maples and C. A. Kraihanzel, *J. Amer. Chem. Soc.*, 1965, **87**, 5267. For L = $P(OCH_2)_3CMe$ see M. Green and D. C. Wood, *ibid.*, 1966, **88**, 4106 and P. K. Maples and C. S. Kraihanzel, *Chem. Comm.*, 1968, 922. [c]For L_2 = diphos, $2P(OPh)_3$, or $2P(Me)(OPh)_2$ see Bannister *et al.*, *loc. cit.* [d]F. Calderazzo and K. Noack, *J. Organometallic Chem.*, 1965, **4**, 250. [e](3-Acetyl-1-methyl-π-allyl)(tetracarbonyl)manganese. See W. D. Bannister, M. Green, and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1966, 194. [f]P. Craig, M. Green, A. J. Rest, and F. G. A. Stone, *J. Organometallic Chem.*, 1968, **12**, 548. [g]J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometallic Chem.*, 1964, **2**, 119. [h]F. A. Hartman and A. Wojcicki, *J. Amer. Chem. Soc.*, 1968, **7**, 1504. See also *Inorg. Chim. Acta*, 1968, **2**, 351 for reactions of this complex with bipy, py, I^-, PPh_3 etc.

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[296] J. Lewis and A. W. Parkins, *Chem. Comm.*, 1968, 1194.

[297] B. F. G. Johnson, J. Lewis, A. W. Parkins, and G. L. P. Randall, *Chem. Comm.*, 1969, 595; B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *ibid*, p. 1274.

[298] E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Comm.*, 1969, 1124.

[299] M. R. Churchill, J. Wormald, D. A. T. Young, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 7201.

Several reactions were mentioned previously wherein nucleophiles attack the metal atoms in the hexacarbonyls $M(CO)_6$ to give anionic complexes, *e.g.* $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$, $[(OC)_5ReCr(CO)_5]^-$, or $[W(CO)_5I]^-$. In contrast, methyl- or phenyl-lithium attack CO groups affording ions $[M(CO)_5COR]^-$. The latter on treatment with aqueous acid and diazomethane yield carbene complexes, *e.g.*[300]

$$Mo(CO)_6 + MeLi \xrightarrow[Me_4NBr\text{-}H_2O]{ether} (Me_4N)[Mo(CO)_5COMe]$$

$$\xrightarrow[CH_2N_2]{H^+} (OC)_5MoC(OMe)Me$$

Cyclopentadienyl(tricarbonyl)manganese, which is very similar in chemical behaviour to $Cr(CO)_6$, behaves in the same way yielding the carbene complex $(\pi\text{-}C_5H_5)Mn(CO)_2[C(OMe)Ph]$. In like manner $Mn_2(CO)_{10}$ affords $Mn_2(CO)_9$-$[C(OMe)Me]$.[301] A considerable chemistry of these complexes is developing, for example,

$$(OC)_5Cr[C(OMe)Me] \xrightarrow{R_3P} (OC)_4(R_3P)Cr[C(OMe)Me]^* \qquad \text{(ref. 302)}$$

$$\xrightarrow{BuNH_2} (OC)_5Cr[C(NHBu)Me] \qquad \text{(ref. 303)}$$

$$\xrightarrow{py} pyCr(CO)_5 + MeOCH{:}CH_2 \qquad \text{(ref. 304)}$$

$$\xrightarrow{PhSeH} (OC)_5CrSe(C_6H_5)CH(OMe)Me \qquad \text{(ref. 305)}$$

$$\xrightarrow{PhSH} (OC)_5Cr[C(SPh)Me] \qquad \text{(ref. 306)}$$

Due to restricted rotation about the carbon–oxygen bond in the carbene complexes discrete *cis*- and *trans*-isomers (8a and b) exist, both in the solid and in solution.[307]

Fluorocarbon groups form stable bonds with transition metal ions, and as a consequence several hundred complexes with this type of ligand are known, and many of these contain carbonyl groups.[308,309] There are three chief methods of synthesis, and the first two of these depend on the nucleophilicity of carbonyls or

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[*] See ref. 1, structure XLII; in the formula given in this reference Ph_3P should appear, rather than Ph_3CP.

[300] E. O. Fischer and A. Maasböl, *Chem. Ber.*, 1967, **100**, 2445.

[301] E. O. Fischer and E. Offhaus, *Chem. Ber.*, 1969, **102**, 2449.

[302] H. Werner and H. Rascher, *Inorg. Chim. Acta*, 1968, **2**, 181.

[303] J. A. Connor and E. O. Fischer, *J. Chem. Soc.* (*A*), 1969, 578.

[304] E. O. Fischer and A. Maasböl, *J. Organometallic Chem.*, 1968, **12**, P15.

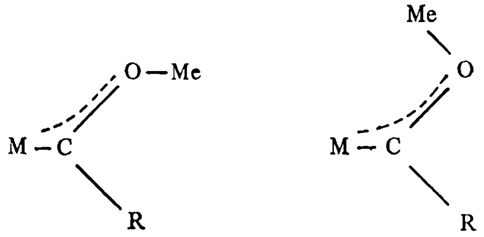
[305] E. O. Fischer and V. Kiener, *Angew. Chem. Internat. Edn.*, 1967, **6**, 961.

[306] U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, 1967, **89**, 7141.

[307] C. G. Kreiter and E. O. Fischer, *Angew. Chem. Internat. Edn.*, 1969, **8**, 761; and references cited therein.

[308] M. I. Bruce and F. G. A. Stone, *Prep. Inorg. Reactions*, 1968, **4**, 177; and references cited therein.

[309] M. I. Bruce and F. G. A. Stone, *Angew. Chem. Internat. Edn.*, 1968, **7**, 747.



(a) *cis* (8) (b) *trans*

their derivatives and the corresponding electrophilic character of unsaturated fluorocarbons.

(*a*) *Oxidative-addition or oxidative-elimination reactions.* Carbonyl compounds in which the metal has a d^8 or d^{10} configuration readily undergo this kind of reaction, first observed[310] with pentacarbonyliron. With the d^{10} systems studied to date all CO groups are eliminated and the resulting complex is not an organometal carbonyl. However, with the d^8 compounds CO groups are retained, for example,

$$Fe(CO)_5 + C_3F_7I \rightarrow C_3F_7Fe(CO)_4I + CO$$

$$Fe_2(CO)_9 + \text{DHFB}^{*} \rightarrow (\text{DHFB})Fe(CO)_4 + (OC)_4Fe(\text{DHFB})Fe(CO)_4$$

$$(\pi\text{-}C_5H_5)Co(CO)_2 + 2C_2F_4 \rightarrow \overline{CF_2\,(CF_2)_2CF_2Co}(\pi\text{-}C_5H_5)(CO) + CO$$

$$(Ph_3P)_2Ir(CO)Cl + (CF_3)_2CO \rightarrow (Ph_3P)_2Ir(CO)[(CF_3)_2CO]Cl$$

(*b*) *Reactions of carbonylmetal anions with fluorocarbons*[309]

$$C_6F_6 + [Re(CO)_5]^- \rightarrow C_6F_5Re(CO)_5 + F^-$$

$$C_4F_6 + [(\pi\text{-}C_5H_5)Fe(CO)_2]^- \rightarrow CF_2{:}CFCF{:}CFFe(CO)_2(\pi\text{-}C_5H_5) + F^-$$

$$CF_3C_2CF_3 + [Re(CO)_5]^- \rightarrow CF_2{:}C{:}C(CF_3)Re(CO)_5 + F^-$$

$$C_4F_4N_2 + [(\pi\text{-}C_5H_5)Mo(CO)_3]^- \rightarrow N_2C_4F_3Mo(CO)_3(\pi\text{-}C_5H_5) + F^-$$

$$CF_3CF{:}CF_2 + [(\pi\text{-}C_5H_5)W(CO)_3]^- \rightarrow CF_3CF{:}CFW(CO)_3(\pi\text{-}C_5H_5) + F^-$$

$$\text{cyclo-}C_6F_{10} + [(\pi\text{-}C_5H_5)Ru(CO)_2]^- \rightarrow \text{cyclo-}C_6F_9Ru(CO)_2(\pi\text{-}C_5H_5) + F^-$$

In the above reactions the carbonyl anions vary in their nucleophilic power in the sequence mentioned in an earlier Section. Thus, for example $[Mn(CO)_5]^-$ will not react with hexafluorobenzene, and $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ is more reactive than $[(\pi\text{-}C_5H_5)Ru(CO)_2]^-$.

[*] DHFB is hexafluorobicyclo[2,2,0]hexa-2,5-diene or 'Dewar hexafluorobenzene' with two CF:CF groups available for bonding.

[310] T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 249.

(*c*) *Insertion reactions into metal–hydrogen or metal–carbon bonds*

$HMn(CO)_5 + CF_2{:}CF_2 \rightarrow HCF_2CF_2Mn(CO)_5$

$HCo(CO)_4 + CF_2{:}CF_2 \rightarrow HCF_2CF_2Co(CO)_4$

$HW(CO)_3(\pi\text{-}C_5H_5) + CF_2{:}CF_2 \rightarrow HCF_2CF_2W(CO)_3(\pi\text{-}C_5H_5)$

$HRe(CO)_5 + C_4F_6 \rightarrow HCF_2CF_2CF{:}CFRe(CO)_5$

$PhMn(CO)_5 + CF_2{:}CF_2 \rightarrow PhCF_2CF_2Mn(CO)_5$

$MeMn(CO)_5 + CF_2{:}CFCl \rightarrow MeCF_2CFClMn(CO)_5$

$HMn(CO)_5 + (CF_3)_2CN_2 \rightarrow (CF_3)_2CHMn(CO)_5 + N_2$

The chemistry of the fluorocarbon(carbonyl)metal compounds is reviewed elsewhere.[308,309,311]

E. Complexes with Main-group Metals or Metalloids, or Post-transition Metals as Ligands.—An extensive chemistry is associated with carbonyl complexes in which elements such as boron, silicon, tin, mercury, zinc, *etc.*, are also ligands. Mercury derivatives such as $[HgFe(CO)_4]_n$ have been known for as long as carbonyls have been studied,[48] and the first complexes in which Group IVb elements were ligands were described over twenty-five years ago.[312,313] The field of the Group IVb element–(carbonyl)metal complexes has become very wide in scope, and is certain to expand much more. Apparently the valence orbitals of Si, Ge, or Sn atoms are such that they are energetically particularly compatible with the d^2sp^3, dsp^3, or dsp^2 orbitals of transition metals so that stable σ bonds readily form. Indeed, there is some evidence that in certain of the compounds the covalent metal–metal bonds thus produced have π as well as σ components. In any event it has become clear that this area of endeavour presents more possibilities than when hydrocarbon groups are bonded to metal carbonyl moieties solely by two-centre two-electron σ bonds.

The majority of complexes in which silicon or its congeners are linked to carbonymetal groups are prepared by one of four methods. Only a few examples of each type can be given.

(*a*) *Metathetical reactions involving carbonylmetal anions.*

$SiH_3I + [Co(CO)_4]^- \rightarrow H_3SiCo(CO)_4 + I^-$ (ref. 314)

$Me_2SnCl_2 + 2[Re(CO)_5]^- \rightarrow Me_2Sn[Re(CO)_5]_2 + 2Cl^-$ (ref. 315)

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[311] P. M. Treichel and F. G. A. Stone, *Adv. Organometallic Chem.*, 1964, **1**, 143.
[312] F. Hein and H. Pobloth, *Z. anorg. Chem.*, 1941, **248**, 84.
[313] W. Hieber and U. Teller, *Z. anorg. Chem.*, 1942, **249**, 43.
[314] B. J. Aylett and J. M. Campbell, *J. Chem. Soc.* (*A*), 1969, 1910, 1916, 1920.
[315] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2217.

$2Et_3PbCl + [Fe(CO)_4]^{2-} \rightarrow (Et_3Pb)_2Fe(CO)_4 + 2Cl^-$ (refs. 316, 317)

(*b*) *Reactions involving elimination of a neutral molecule.*

$GeH_4 + 2HMn(CO)_5 \rightarrow H_2Ge[Mn(CO)_5]_2 + 2H_2$ (ref. 318)

$2Me_3SiH + Co_2(CO)_8 \rightarrow 2Me_3SiCo(CO)_4 + H_2$ (ref. 319)

$Ph_4AsGeCl_3 + Cr(CO)_6 \rightarrow [Ph_4As][Cl_3GeCr(CO)_5] + CO$ (ref. 320)

$SnCl_2 + (\pi\text{-}C_5H_5)Fe(CO)_2HgCl \rightarrow Cl_3SnFe(CO)_2(\pi\text{-}C_5H_5) + Hg$ (ref. 321)

$Me_3SnNMe_2 + (\pi\text{-}C_5H_5)W(CO)_3H \rightarrow Me_3SnW(CO)_3(\pi\text{-}C_5H_5) + Me_2NH$ (ref. 322)

$SnCl_4 + H_2Os(CO)_4 \rightarrow Cl_3SnOs(CO)_4H + HCl$ (ref. 323)

(*c*) *Oxidative-addition and oxidative-elimination reactions.*

$(EtO)_3SiH + (Ph_3P)_2Ir(CO)Cl \rightarrow (EtO)_3SiIr(H)(Cl)(CO)(PPh_3)_2$ (ref. 324)

$SnCl_4 + Fe(CO)_5 \rightarrow (OC)_4Fe(SnCl_3)Cl + CO$ (ref. 325)

$6Me_3SiH + 2Ru_3(CO)_{12} \rightarrow 3[Me_3SiRu(CO)_4]_2 + 3H_2{}^*$ (ref. 326)

$3Me_3SnH + Os_3(CO)_{12} \rightarrow 3Me_3SnOs(CO)_4H$ (ref. 326)

$\sigma\text{-}C_5H_5GeMe_3 + (MeCN)_3Cr(CO)_3 \rightarrow (\pi\text{-}C_5H_5)Cr(GeMe_3)(CO)_3 + 3MeCN$ (ref. 327)

$MeSnCl_3 + bipyMo(CO)_4 \rightarrow MeCl_2SnMo(CO)_3(bipy)Cl + CO$ (ref. 310)

(*d*) *Insertion reactions into metal–metal bonds by germanium*(II)- *or tin*(II)-*halides.*

$SnCl_2 + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \rightarrow Cl_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ (ref. 328)

$GeI_2 + Co_2(CO)_8 \rightarrow I_2Ge[Co(CO)_4]_2$ (ref. 329)

$GeI_2 + [W_2(CO)_{10}]^{2-} \rightarrow [(OC)_5WGeI_2W(CO)_5]^{2-}$ (ref. 320)

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* The initial reaction between Me_3SiH and '$Ru(CO)_4$' is undoubtedly an oxidative–addition process to give very unstable $Me_3SiRu(CO)_4H$. The latter then decomposes to give mainly $[Me_3SiRu(CO)_4]_2$ with some $(Me_3Si)_2Ru(CO)_4$.[326]

[316] F. Hein and W. Jehn, *Annalen*, 1965, **684**, 4.

[317] O. Kahn and M. Bigorgne, *Compt. rend.*, 1965, **261**, 2483.

[318] A. G. Massey, A. J. Park, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1963, **85**, 2021.

[319] Y. L. Baay and A. G. MacDiarmid, *Inorg. Chem.*, 1969, **8**, 986.

[320] J. K. Ruff, *Inorg. Chem.*, 1967, **6**, 1502, 2080.

[321] F. Bonati, S. Cenini, D. Morelli, and R. Ugo, *J. Chem. Soc.* (*A*), 1966, 1052.

[322] D. J. Cardin and M. F. Lappert, *Chem. Comm.*, 1966, 506.

[323] J. R. Moss and W. A. G. Graham, *J. Organometallic Chem.*, 1969, **18**, 24.

[324] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1965, **87**, 16, 1133.

[325] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 310, 1208.

[326] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2559; 1970, 3147.

[327] S. A. Keppie and M. F. Lappert, *J. Organometallic Chem.*, 1969, **19**, P5.

[328] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179.

[329] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1405.

Some brief comments on the various syntheses are pertinent. The metal carbonyl anion reaction has been used to attach as many as four transition metal carbonyl groups to a Group IV element.[330]

$$SnCl_4 + 4[(\pi\text{-}C_5H_5)Fe(CO)_2]^- \rightarrow Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_4 + 4Cl^-$$

A combination of the metal carbonyl anion and insertion reaction methods has also been used to obtain heteronuclear complexes containing as many as five metal atoms.[331]

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \xrightarrow{SnCl_4} Cl_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2 \xrightarrow{[(\pi\text{-}C_5H_5)Mo(CO)_3]^-} [(\pi\text{-}C_5H_5)Fe(CO)_2]_2Sn[Mo(CO)_3(\pi\text{-}C_5H_5)]_2$$

Syntheses involving carbonylmetal anions sometimes afford unexpected products, for example, a ditin compound $[(OC)_5Re]_3SnSn[Re(CO)_5]_3$ is obtained from $[Re(CO)_5]^-$ and $Br_3SnRe(CO)_5$,[332] treatment of $MeSnCl_3$ with $[Fe(CO)_4]^{2-}$ yields $Me_4Sn_3Fe_4(CO)_{16}$,[333]* and $(acac)_2SnCl_2$ reacts with $[Co(CO)_4]^-$ to give $(acac)_2SnCo_2(CO)_7$.[334]

Of major importance in this field is the discovery of rapidly increasing numbers of polynuclear complexes. These form *via* compounds with one or two metal–metal bonds which then subsequently afford polynuclear species either by thermal decomposition, or by further reaction with one or other of the reactants. This is clearly shown by the reactions of germanium tetrahalides with pentacarbonyliron.[325] The initial oxidative-addition product $(OC)_4Fe(GeX_3)X$ yields $(OC)_4Fe(GeX_3)_2$, which reacts with more $Fe(CO)_5$ in a ring closure reaction to give complexes $[X_2GeFe(CO)_4]_2$. Earlier it had been observed that Me_2SnH_2 and $Fe(CO)_5$ afford $[Me_2SnFe(CO)_4]_2$;[335] in this reaction the initial products are not isolated owing to the instability of iron–hydrogen bonds. The compounds $[R_2MFe(CO)_4]_2$ are examples of metal–metal heterocycles with four membered rings. With diphenylgermane, $Fe_3(CO)_{12}$ and $Co_2(CO)_8$ afford the complexes $Ph_2Ge[Fe(CO)_4]_2$[336] and $Ph_2GeCo_2(CO)_7$,[337] respectively, which contain three-membered rings. Interestingly, in the spiro-compound $Sn[Fe(CO)_4]_4$ two $SnFe_2$ rings are found.[338] The first example of a five-metal atom ring has recently been established for $(OC)_4Fe[GeCl_2Co(CO)(\pi\text{-}C_5H_5)]_2$, a product of the ring closure reaction between $(\pi\text{-}C_5H_5)(OC)Co(GeCl_3)_2$ and $Fe(CO)_5$.[339] Reactions between

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* See ref. 1 for the structure of this and several related complexes mentioned in this Section.

[330] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1966, 1292.

[331] S. V. Dighe and M. Orchin, *J. Amer. Chem. Soc.*, 1965, **87**, 1146.

[332] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Doklady Akad. Nauk. S.S.S.R.*, 1964, **156**, 383.

[333] C. J. Fritchie, R. M. Sweet, and R. Schunn, *Inorg. Chem.*, 1967, **6**, 749.

[334] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1967, **6**, 1879.

[335] J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1967, 264.

[336] E. H. Brooks, M. Elder, W. A. G. Graham, and D. Hall, *J. Amer. Chem. Soc.*, 1968, **90**, 3587.

[337] S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *Chem. Comm.*, 1969, 1297.

[338] P. F. Lindley and P. Woodward, *J. Chem. Soc.* (*A*), 1967, 382.

[339] M. J. Bennett, W. Brooks, M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *J. Amer. Chem. Soc.* 1970, **92**, 208.

$Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ and organohydrides of silicon, germanium or tin give rise to numerous polynuclear species.[326,340] Initially formed complexes $Me_3M^{IV}M(CO)_4H$ and $(Me_3M^{IV})_2M(CO)_4$, depending on M and M^{IV}, decompose according to reactions such as the following:

$$2Me_3SiOs(CO)_4H \rightarrow [Me_3SiOs(CO)_4]_2 + H_2$$

$$(Me_3Si)_2Ru(CO)_4 \rightarrow [Me_3SiRu(CO)_4]_2 + (Me_3Si)_2O^*$$

$$(Me_3Sn)_2Ru(CO)_4 \rightarrow [Me_3SnRu(CO)_3\text{-}\mu\text{-}SnMe_2]_2 + Me_4Sn$$

$$(Me_3Ge)_2Ru(CO)_4 \rightarrow [Me_2GeRu(CO)_3]_3 + (Me_2Ge)_3Ru_2(CO)_6$$

The complex $[Me_2GeRu(CO)_3]_3$ probably contains an Ru_3 moiety supported by bridging Me_2Ge groups so that effectively there is a ring of six metal atoms. Not all the polynuclear compounds, however, have metal–metal heterocyclic structures. Complexes $[Me_3SiM(CO)_4]_2$ have M—M bonds, and accordingly react with sodium amalgam to give anions $[Me_3SiM(CO)_4]^-$. The latter have an extensive chemistry reacting with halides to give such complexes as $(Me_3Si)(Ph_3PAu)Ru(CO)_4$, $(Me_3Si)[(OC)_5Mn]Ru(CO)_4$, $(Me_3Si)(Me_3Sn)Os(CO)_4$, and $(Me_3Si)(Me)Os(CO)_4$.[326]

The thermal stability of the transition-metal carbonyl derivatives of the Group IVb elements is greater than that of the simple alkyl metal carbonyls. Thus $H_3SiCo(CO)_4$ is thermally stable up to 85 °C[314] whereas, as mentioned previously, $MeCo(CO)_4$ decomposes below room temperature. Moreover, attachment of electronegative groups to the Group IV element enhances the stability of the metal–metal bonds. Thus $F_3SiCo(CO)_4$[341] is thermally more stable than $H_3SiCo(CO)_4$, just as $F_3CCo(CO)_4$ is more stable than $MeCo(CO)_4$.

The reactivity of the various complexes naturally depends on the particular metals involved, the nature of the attached ligands, and on the reactants. It might be thought that the metal–metal bonds would always be the most reactive centres in these compounds but this is not always so, for example:

$$Ph_2Sn[Mn(CO)_5]_2 + 2HCl \rightarrow Cl_2Sn[Mn(CO)_5]_2 + 2C_6H_6 \qquad \text{(ref. 115)}$$

$$Cl_2Ge[Fe(CO)_2(\pi\text{-}C_5H_5)]_2 \xrightarrow{NaBH_4} H_2Ge[Fe(CO)_2(\pi\text{-}C_5H_5)]_2 + H_2 \qquad \text{(ref. 342)}$$

$$H_3SiMn(CO)_5 + 2HCl \xrightarrow{\Delta} SiHCl_2Mn(CO)_5 + 2H_2 \qquad \text{(ref. 314)}$$

However, in many reactions cleavage of the bonds between the Group IV element and the transition metal, or between the transition metal atoms, occurs, *e.g.*

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* Several of the alkylsilicon transition metal carbonyl complexes decompose with release of disiloxanes, *e.g.* $Me_3SiCo(CO)_4$.[319] It appears that the silicon atoms abstract oxygen from CO groups.

[340] J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2758.

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$SiH_3Mn(CO)_5 + bipy \rightarrow [bipySiH_3][Mn(CO)_5]$ (ref. 314)

$Me_3SnMn(CO)_5 + CF_2{:}CFH \rightarrow CFH{:}CFMn(CO)_5 + Me_3SnF$ (ref. 343)

$[Me_3SiRu(CO)_4]_2 \xrightarrow{I_2} Me_3SiRu(CO)_4I \xrightarrow{\Delta} [Me_3SiRu(CO)_3I]_2$ (ref. 344)

In addition to the carborane complexes mentioned previously, with their electronically delocalised array of boron and carbon atoms, several carbonyl derivatives are known in which boron atoms are directly bonded to metal carbonyl groups. The compounds $(Et_4N)[H_3BRe(CO)_5]$[119] and $H_8B_5Mn(CO)_5$[116] were briefly noted. Reactions between boron halides and carbonylmetal anions have afforded several boron bonded species, for example,[345,346]

$$(Me_2N)_2BCl + [Mn(CO)_5]^- \rightarrow (Me_2N)_2BMn(CO)_5 + Cl^-$$

$$Ph_2BCl + [W(CO)_3(\pi\text{-}C_5H_5)]^- \rightarrow Ph_2BW(CO)_3(\pi\text{-}C_5H_5) + Cl^-$$

There are several known carbonyl complexes with other Group III elements as ligands, obtained from reactions between halides and metal carbonyls or carbonyl anions. Indium(I) bromide and octacarbonyldicobalt afford either $[(OC)_4Co]_2InBr(THF)$ or $In_3Br_3Co_4(CO)_{15}$ depending on the solvent used in the reaction.[347] The anions $[Fe(CO)_4]^{2-}$ and $[Co(CO)_4]^-$ form adducts[120] with $InBr_3$ and $GaBr_3$, as mentioned earlier when the nucleophilic character of carbonyl anions was discussed. A novel example of a Lewis acid–Lewis base interaction is demonstrated in the compound $[(\pi\text{-}C_5H_5)Fe(CO)]_2(COAlEt_3)_2$ in which Et_3Al groups co-ordinate with the two bridging carbonyl groups in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$.[348] A terminal CO group is a site for Lewis basicity in the adduct formed between Me_3Al and (triphenylphosphoniumcyclopentadienylide)-(tricarbonyl)molybdenum.[349]

So many mercury derivatives of the metal carbonyls are known that it would appear that all metals which form binary carbonyls can form these compounds, as well as some which do not [*e.g.* $MeHgTa(CO)_6$[350]]. The mercury derivatives can be prepared by oxidative–elimination reactions, *via* carbonyl metal anion reactions, by insertion reactions, or by exchange reactions, as the following examples indicate.

$(bipy)W(CO)_4 + 2HgCl_2 \rightarrow (bipy)W(CO)_3(HgCl)_2 + COCl_2(?)$ (ref. 351)

$Fe(CO)_5 + 2HgCl_2 \rightarrow (ClHg)_2Fe(CO)_4 + COCl_2$ (refs. 352, 353)

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$Os_3(CO)_{12} + HgCl_2 \rightarrow ClHgOs(CO)_4Cl + (ClHg)_2Os(CO)_4$ (ref. 354)

$2[Mn(CO)_5]^- + Hg(CN)_2 \rightarrow Hg[Mn(CO)_5]_2 + 2CN^-$ (ref. 355)

$Co_2(CO)_8 + Hg \rightarrow Hg[Co(CO)_4]_2$ (ref. 356*)

$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg + HgI_2 \rightarrow 2(\pi\text{-}C_5H_5)Mo(CO)_3HgI$ (ref. 357)

$[(\pi\text{-}C_5H_5)W(CO)_3]_2Hg + Hg[Co(CO)_4]_2 \rightarrow 2(\pi\text{-}C_5H_5)(OC)_3WHgCo(CO)_4$ (ref. 357)

Similar syntheses have been used to obtain compounds containing copper, zinc, silver, cadmium, and gold, *e.g.*

$(o\text{-triars})CuBr + [Fe(CO)_4]^{2-} \rightarrow [(o\text{-triars})Cu]_2Fe(CO)_4 + Br^-$ (ref. 358)

$(o\text{-triars})AgBr + [Co(CO)_4]^- \rightarrow (o\text{-triars})AgCo(CO)_4 + Br^-$ (ref. 358)

$Ph_3PAuCl + [(\pi\text{-}C_5H_5)W(CO)_3]^- \rightarrow Ph_3PAuW(CO)_3(\pi\text{-}C_5H_5) + Cl^-$ (ref. 114)

$Zn + Mn_2(CO)_{10} \xrightarrow[\text{diglyme}]{120^\circ\text{ C}} Zn[Mn(CO)_5]_2$ (ref. 359)

$Cd + Hg[Co(CO)_4]_2 \rightarrow Cd[Co(CO)_4]_2 + Hg$ (ref. 359)

The tendency of the metals of Groups Ib and IIb to readily form bonds with metal carbonyl groups can be attributed to their relatively high electronegativities. Not surprisingly the metal–metal bonds so formed are cleaved homolytically by reagents such as halogens or hydrogen halides.[114] Of considerable interest is the observation that some of these covalent bonds undergo heterolytic cleavage in polar solvents. The zinc compounds dissociate essentially completely, *e.g.* into Zn^{2+} and $[Co(CO)_4]^-$, the cadmium compounds only partially, and the mercury derivations not at all. With trimetallic $(\pi\text{-}C_5H_5)(OC)_2FeZnCo(CO)_4$ only the $Co(CO)_4$ group ionizes.[360] Moreover, whereas $Ph_3SnCo(CO)_4$ is not appreciably dissociated in acetonitrile, upon addition of tetraethylammonium bromide complete conversion to $[Co(CO)_4]^-$ and Ph_3SnBr occurs. These and related observations[360] may be interpreted in terms of nucleophilic displacement of a carbonyl anion from the main group metal by halide ion.

5 Conclusion

With a current rate of approximately 1500 publications per annum concerned with metal carbonyl complexes, this review and our previous article can only hope to give an abbreviated summary of developments in this field. Many branches of metal carbonyl chemistry have now deservedly been the subject of individual reviews (Table 1).

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[*] There are several alternative methods for preparing this compound. See ref. 8.

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