The Chemistry of Transition-metal Carbonyls: Structural Considerations

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1 Introduction

One of the most active areas for research at the present time is the study of transition-metal complexes wherein carbon monoxide groups are ligands. This is likely to remain so for many years to come. Indeed, during the last two decades preparative and structural work involving metal carbonyl compounds has provided as great a stimulus for the development of inorganic chemistry as have the great advances in boron hydride chemistry, fluorine chemistry, or the chemistry of the so-called π-complexes. In the case of the latter, progress has been intimately connected with the work on the carbonyl complexes. Schutzenberger[1] first recognised carbon monoxide as a ligand in his preparation and characterisation of $Pt(CO)_2Cl_2$, but the first binary metal carbonyl, tetracarbonylnickel, was discovered[2] in 1890. It is one of the interesting coincidences of chemistry that on June 15th, 1891, Mond[3] in London and Berthelot[4] in Paris were describing their independent discoveries of pentacarbonyliron to the Chemical Society and the French Academy of Sciences, respectively. In the ensuing fifty years, as in many areas of inorganic chemistry, progress was slow. Some of the metal carbonyls discovered in this period were $Co_2(CO)_8$ (1910), $Mo(CO)_6$ (1910), $Cr(CO)_6$ (1926), $Ru(CO)_5$ (1936), $Ir_4(CO)_{12}$ (1940), and $Re_2(CO)_{10}$ (1941). Paralleling these early syntheses, and the discovery of some carbonyl derivatives, was the realisation that the new substances had novel properties, notably high volatility for compounds containing such heavy metal atoms. Moreover, they posed a problem from the standpoint of the then current theories of valency. Some early studies, such as that which established the tetrahedral configuration of $Ni(CO)_4$,[5] as well as Sidgwick's and Bailey's[6] concept relating the formulae of the then known metal carbonyls to an 'effective atomic number' rule (see later), were of fundamental importance. It was during this period that W. Hieber[7] and his students made the first of their many significant experimental contributions, including the synthesis of several metal carbonyls, and the discovery of the first carbonyl anions and hydrides. However,

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[1] P. Schutzenberger, *Compt., Rend.* 1870, **70**, 1134; *J. Chem. Soc.*, 1871, 1008.
[2] L. Mond, C. Langer, and F. Quincke, *J. Chem. Soc.*, 1890, 749.
[3] (*a*) L. Mond and F. Quincke, *Chem. News.*, 1891, **63**, 301; (*b*) L. Mond and C. Langer, *J. Chem. Soc.*, 1891, 1090.
[4] M. Berthelot, *Compt. Rend.*, 1891, **112**, 1343.
[5] L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, 1935, **3**, 828.
[6] N. V. Sidgwick and R. W. Bailey, *Proc. Roy. Soc.*, 1934, **144**, 521.
[7] W. Hieber, *Adv. Organometallic Chem.*, 1970, **8**, 1.

it was not until after the discovery of ferrocene in 1951[8] and 1952,[9] and dibenzenechromium in 1955,[10] that the field of metal carbonyl chemistry began to grow with very great rapidity. Some measure of this growth can be gained by scanning Annual Reports of the Chemical Society. In the 1952 Volume, in the section concerned with inorganic chemistry, there were some six references to carbonyl compounds. However, by 1966 there were *ca.* 300 references to this topic. This research activity has stemmed mainly from the realisation that the metal carbonyls form numerous derivatives, and in part from the amenability of many of the compounds to study by physical methods. The scope of the field can be illustrated by reference to Table 1 which shows several different types of carbonyl complex derived from one metal. Moreover, carbonyl complexes of the transition metals wherein more than one type of ligand is present are legion. Thus from decacarbonyldimanganese it is possible to obtain such complexes as $HMn(CO)_4PPh_3$, $MeMn(CO)_4PPh_3$, p-$NC_5F_4Mn(CO)_4PPh_3$, $Ph_3SnMn(CO)_4$-PPh_3, $Ph_3PAuMn(CO)_4PPh_3$, π-$C_5H_5Mn(CO)_2PPh_3$, and $BrMn(CO)_3(PPh_3)_2$.

In the neutral complexes in which CO groups are the only ligands, the metals have a formal oxidation state of zero, and for many years these compounds were the only well-authenticated examples of the zerovalent state. It is now known that many other ligands can stabilise this valence state, and CO groups have lost their uniqueness in this respect. For example, nickel is formally zerovalent in all of its compounds $K_4Ni(CN)_4$, $Ni(PF_3)_4$, $(C_6H_5NC)_4Ni$, and $(C_8H_{12})_2Ni$ (C_8H_{12} = cyclo-octa-1,5-diene), as it is in $Ni(CO)_4$. This group of complexes also serves to illustrate the convergence of co-ordination chemistry and organometallic chemistry. Since an organometallic compound is one containing a carbon atom or atoms directly bonded to a metal atom, a carbonyl derivative is both an organometallic and a co-ordination compound, and any distinction between these two fields is lost as far as the transition metals are concerned.

In this Review we shall be concerned with a necessarily non-comprehensive survey of the bonding and stereochemistry of carbonyl complexes. In a subsequent article we shall summarise methods of synthesis, the more important of the numerous chemical reactions, and certain physical properties.

2 The Metal–Carbon Bond in Metal Carbonyl Complexes[11,12]

The ability of the CO group to stabilise metal atoms in low-positive, zero, or low-negative oxidation states is believed to be due to a so-called 'synergic' bonding effect.[13] A metal–carbon σ-bond is formed by overlap of a filled *sp*-hybrid orbital of carbon and a vacant hybrid orbital of the metal, for example, sp^3 of Ni in $Ni(CO)_4$, dsp^3 of Fe in $Fe(CO)_5$, and d^2sp^3 of Cr in $Cr(CO)_6$. In addition, π-bonds are formed by overlap of filled *d* orbitals of the metal with

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[8] T. J. Kealy and P. L. Pauson, *Nature*, 1951, **168**, 1039.

[9] S. A. Miller, J. A. Tebboth, and J. F. Tremaine, *J. Chem. Soc.*, 1952, 632.

[10] E. O. Fischer and W. Hafner, *Z. Naturforsch.*, 1955, **10b**, 665.

[11] E. W. Abel, *Quart. Res.*, 1963, **17**, 133.

[12] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, New York, 2nd Ed., p. 719.

[13] L. E. Orgel, 'An Introduction to Transition Metal Chemistry,' Methuen, London, 2nd Edn. 1966.

Table 1 *Some carbonyl complexes of manganese*

Complex	*Example*	*Complex*	
The carbonyl	$Mn_2(CO)_{10}$	Carbonyl nitrosyls	$Mn(CO)_4NO$
Mixed metal carbonyls	$MnRe(CO)_{10}$		$Mn(CO)(NO)_3$
	$MnFe(CO)_7(\pi\text{-}C_5H_5)$	Organometal carbonyls	
	$MnReFe(CO)_{14}$	(a) Sigma complexes	$MeMn(CO)_5$
Anionic	$[Mn(CO)_5]^-$		$HCF_2CF_2Mn(CO)_5$
	$[MnFe_2(CO)_{12}]^-$		$C_6F_5Mn(CO)_5$
	$[MnCr(CO)_{10}]^-$	(b) Pi complexes	$\pi\text{-}C_3H_5Mn(CO)_4$
Cationic	$[Mn(CO)_6]^+$		$\pi\text{-}C_5H_5Mn(CO)_3$
			$[\pi\text{-}B_9C_2H_{11}Mn(CO)_3]^-$
Phosphine and other Lewis base complexes	$[Ph_3PMn(CO)_4]_2$	With post-transition metals as ligands	
	$[Me_2AsMn(CO)_4]_2$		
	$[MeSMn(CO)_4]_2$	(a) Ib and IIb metals	$Ph_3PAuMn(CO)_5$
	$Mn_2(CO)_9PF_3$		$Hg[Mn(CO)_5]_2$
Carbonyl halides	$Mn(CO)_5Cl$	(b) IVb metals	$Cl_3SiMn(CO)_5$
	$[Mn(CO)_4Br]_2$		$H_2Ge[(Mn(CO)_5]_2$
Carbonyl hydrides	$HMn(CO)_5$		$Ph_3SnMn(CO)_5$
	$[HMn(CO)_4]_3$		$MeSn[Mn(CO)_5]_3$

empty antibonding orbitals of the CO groups. Consequently, charge transfer in the σ-bond is in the opposite direction to that in the π-bond, and the latter is considered to be crucial in serving to remove negative charge on the metal atom.

The two-way electron-transfer process between a CO group and a metal atom can be considered in an alternative way. The CO group transfers an electron to the metal while the latter similarly transfers an electron to a π^* orbital of the CO group. The net effect is to raise the CO molecule to an excited state for which the energy required is *ca.* 6 ev. Interestingly, the same process for 'end-on' bonding of molecular N_2, isoelectronic with CO, requires *ca.* 7·3 ev. Molecular nitrogen complexes are now known but are less stable than carbonyl compounds.

A major consequence of the presence of electrons in the π-antibonding orbital of carbon monoxide is the reduction of CO bond order. Hence in the i.r. spectrum of free carbon monoxide ν_{CO} occurs at 2155 cm.$^{-1}$, whereas the corresponding frequencies for carbonyl groups MCO (M = a metal) occur at lower frequency (*ca.* 2000 cm.$^{-1}$). Considerable support for resonance in metal carbonyls involving the two canonical forms (*a*) and (*b*) comes from comparing carbonyl stretching frequencies in the i.r.

$$\underset{(a)}{M \leftarrow C \equiv O} \qquad \underset{(b)}{M \underset{\rightarrow}{=} C = O}$$

Thus the synergic effect would lead to the prediction that as negative charge is added to the metal ν_{CO}(max) would decrease, as it does in the two isoelectronic series:

$Mn(CO)_6^+$	$Cr(CO)_6$	$V(CO)_6^-$
2096	2000	1859 cm.$^{-1}$
$Ni(CO)_4$	$Co(CO)_4^-$	$Fe(CO)_4^{2-}$
2046	1883	1788 cm.$^{-1}$

Moreover, the i.r. metal–carbon vibrational stretching frequency would be expected to increase regularly with decreasing metal oxidation state, *viz.* $Mn(CO)_6^+$ (416 cm.$^{-1}$), $Cr(CO)_6$ (441) and $V(CO)_6^-$ (460). The foregoing argument concerning the effect of formal positive charge on the metal customarily assumes no alteration in the σ-bond strengths between carbon and oxygen, and carbon and the metal, while electron populations in π-orbitals of these two bonds change. Semi-empirical molecular orbital calculations, it has been suggested,[14] support this premise. However, if only changes in the degree of π-bonding occur, the rhenium–carbon bond in $Re(CO)_6^+$ (ν_{CO} 2085 cm.$^{-1}$) should be weaker than the tungsten–carbon bond in isoelectronic $W(CO)_6$ (ν_{CO} 1978 cm.$^{-1}$), yet the approximate M—C force constants are 2·76 and 2·73 mdynes/Å, respectively.[15] It would appear, therefore, that for these hexacarbonyl complexes any loss in π-bonding is compensated by improved σ-donation.

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[14] K. G. Caulton and R. F. Fenske, *J. Amer. Chem. Soc.*, 1968, **7**, 1273.

[15] E. W. Abel, R. A. N. McLean, M. G. Norton, and S. P. Tyfield, *Chem. Comm.*, 1968, 900.

As CO groups in a carbonyl complex are replaced by other ligands which are stronger σ donors but weaker π acceptors, ν_{CO} (max) will also decrease, *e.g.*, $Ni(CO)_4$ [2128 (Raman), 2046 cm.$^{-1}$], $Me_3PNi(CO)_3$ (2063, 1943 cm.$^{-1}$), and $(Me_3P)_2Ni(CO)_2$ (1994, 1934 cm.$^{-1}$). Conversely, ligands which tend to inhibit transfer of electron density from the metal to the π^* CO orbital by placing a positive charge on the metal cause ν_{CO} (max) to rise, *e.g.* $ClMn(CO)_5$ (2138, 2054, 1999 cm.$^{-1}$), $BrMn(CO)_5$ (2133, 2050, 2001 cm.$^{-1}$) and $IMn(CO)_5$ (2125, 2044; 2003 cm.$^{-1}$). Subtle changes in CO stretching frequencies are also observed as groups bonded to ligand atoms are changed. Thus, for example, in complexes of the type *cis*-$(R_3P)_3Mo(CO)_3$, ν_{CO} (max) decreases with decreasing electronegativity of the groups R, *viz.* $(F_3P)_3Mo(CO)_3$ (2074, 2026 cm.$^{-1}$), $(Cl_3P)_3Mo(CO)_3$ (2041, 1989 cm.$^{-1}$), $(C_6H_5PCl_2)_3Mo(CO)_3$ (2016, 1943 cm.$^{-1}$), $[(C_6H_5)_2PCl]_3Mo(CO)_3$ (1977, 1885 cm.$^{-1}$), and $[(C_6H_5)_3P]_3Mo(CO)_3$ (1949, 1835 cm.$^{-1}$). It is commonly assumed that phosphines are similar to carbonyl groups in being able to both donate and accept electrons in a metal complex. In the phosphines the 3*d* orbitals of the phosphorus atoms are vacant, but the degree with which they can effectively overlap with a filled metal *d* orbital depends on the nature of the groups attached to the ligand atoms. Electronegative substituents such as fluorine effectively contract the phosphorus 3*d* orbitals, making π-bonding between phosphorus and the metal possible. Chlorine and phenyl groups are less effective in this respect and, moreover, tend to reduce the σ-donor power of phosphorus less than do fluorine atoms. Consequently, there is an increased flow of charge to the metal atom in the σ-bond, and the increase in electron density at the metal has then to be compensated by additional charge transfer from the metal to the CO π^* orbitals, leading to a decrease in ν_{CO} (max), as is observed.

As the extent of back donation to the CO group increases for structurally related compounds, the metal–carbon bond might be expected to become shorter and the carbon–oxygen bond longer. With regard to the latter, a change in bond order from three to two produces little change in bond length. Thus considering the two complexes $Mo(CO)_6$ and dien $Mo(CO)_3$ (dien = diethylenetriamine) a purported change in Mo—C bond order from 1·5 to 2·0 in going from the former complex to the latter would only cause the CO bond lengths to change by *ca.* 0·025 Å.[16] The relationship between metal–carbon bond distances and bond orders is complex since it is difficult to assess the expected bond distance for a single bond. However, recently it has been possible to obtain evidence for metal–carbon bond shortening in a number of metal carbonyl compounds. From *X*-ray studies on *cis*-dien $Mo(CO)_3$[16] and on π-$C_5H_5Mo(CO)_3(\sigma$-$C_2H_5)$[17] accurate bond lengths are available. It is reasonable to assume that in *cis*-dien $Mo(CO)_3$ the Mo—N distance corresponds to a single σ-bond, and that this is also the case for the Mo—C (ethyl) distance in π-$C_5H_5Mo(CO)_3(\sigma$-$C_2H_5)$. In order to estimate the hypothetical Mo—C(O) single σ-bond distance it is necessary to correct the observed (2·38 Å) Mo—C (ethyl) distance by subtracting 0·07 Å

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[16] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

[17] R. Mason and M. J. Bennett, *Proc. Chem. Soc.*, 1963, 273.

for the radius change on going from sp^3 to sp hybridised carbon. Similarly, for the tetrahedrally hybridised nitrogen atoms in *cis*-dien $Mo(CO)_3$, the correction for the change from sp^3 nitrogen to sp^3 carbon is +0·07 Å, followed by a hybridisation change for carbon. This leads to the conclusion that the observed Mo—N (sp^3) distance (2·32 Å) can be regarded as the expected Mo—C (sp) single bond distance. The observed Mo—C(O) distance in the diethylenetriamine complex is, however, 1·94 Å; while for π-$C_5H_5Mo(CO)_3C_2H_5$ it is 1·97 Å as against a predicted distance of 2·31 Å for a single σ-bond. These bond shortenings are consistent and support the concept of metal–carbonyl π bonding in these molecules.[16] Several years ago Pauling[18] explained the stability of tetracarbonylnickel and the apparently short nickel–carbon bond distances in this molecule as being due to resonance between tetrahedral structures with single and double bonds between carbon and nickel. The subsequent discovery of nickel (0) compounds with ligands such as PCl_3,[19] PF_3,[20,21] and PR_3,[22] led to a logical extension of the above bonding hypothesis, with the criterion that the donor groups have low σ-donor capacity coupled with vacant low-energy orbitals of proper symmetry for overlapping with the filled non-bonding *d* orbitals of the metal in order to form a π-bond. A still further extension of the concept was made to account for the bonding of olefins[23,24] to metals, and subsequently for hydrocarbon π-complexes such as ferrocene.[25] With the unsaturated hydrocarbon ligands π-electrons are donated to the metal atom in the σ-bond, and back donation occurs by overlap of filled metal *d* orbitals with the π^* antibonding orbitals of the hydrocarbon moieties.[13] With the possible exception of PF_3,[26] it seems that none of these ligands is as effective a π-acceptor as CO, but all are stronger σ-donors. Nevertheless, this is only a matter of degree, and the legion of known hydrocarbon(carbonyl)metal complexes becomes readily understandable in terms of a delicate balance between donor and acceptor bonding.

It may be mentioned in passing that terminal M—C—O bonds are often bent. Molecular-orbital arguments have shown that the π^*-orbitals of tricarbonyl groups can be divided into two symmetry sets which are orthogonal. This leads to a difference in the degree of occupation of the orbitals and hence to bending of the M—C—O bonds.[27]

In addition to the M—CO bond so far discussed, many metal carbonyl compounds contain carbon monoxide groups bonded simultaneously to two or three metal atoms. Until recently it was thought that 'bridging' carbonyls

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[18] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1939.

[19] J. W. Irvine and G. Wilkinson, *Science*, 1951, **113**, 742.

[20] G. Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 5501; *Nature*, 1951, **168**, 514.

[21] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 1951, 3061.

[22] W. Reppe and W. J. Schweckendiek, *Annalen*, 1948, **560**, 104.

[23] M. J. S. Dewar, *Bull. Soc. chim. France*, 1951, **18**, C79.

[24] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.

[25] G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, 1959, **1**, 3, and references cited therein.

[26] Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.

[27] S. F. A. Kettle, *Inorg. Chem.*, 1965, **4**, 1661.

were confined to metals of the first transition series. This is no longer true, and as described below there are structures now known in which CO groups bridge two or three atoms of the second or the third transition-metal series. However, no carbonyl complexes are known wherein carbonyl groups function as bridging ligands between metal atoms of the first transition series on the one hand and the second or third on the other.

In structures in which a CO group bridges two metal atoms, it is customarily assumed that the CO group contributes one electron to each of the metal atoms to form localised σ-bonds by pairing with metal electrons. For CO groups which bridge three metal atoms simultaneously no such simple picture is possible, and multicentre bonding must be invoked with bonding electrons assigned to molecular orbitals. The question of π-bonding with bridging carbonyl groups is more complicated than with terminal CO ligands but undoubtedly occurs, and may also be multicentre in character. In the i.r., a bridging carbonyl group shows a stretching frequency around 1850 cm.$^{-1}$ but this is very variable, the lowest reported so far being 1616 cm.$^{-1}$ in $[\pi\text{-}C_5H_5RuCO]_4$.[28] The observation of a carbonyl stretching frequency in the region of 1850 cm.$^{-1}$ does not necessarily imply the presence of a bridging carbonyl group unless only CO ligands are present in a neutral species. If strong σ-donor ligands with no π-acceptor capacity are bonded to the metal atoms, transfer of electron density from the metal to the antibonding orbitals of the CO group will be relatively extensive with a commensurate reduction in C—O bond order. Thus the i.r. spectrum of the complex dien $Mo(CO)_3$ shows ν_{CO} (max) at 1883 and 1723 cm.$^{-1}$.[29]

3 Molecular Structures of the Metal Carbonyls and their Derivatives

I.r. and Raman measurements, dipole moment studies, n.m.r. and Mössbauer spectroscopy, magnetic susceptibility measurements, electron diffraction, and mass spectroscopy have all given useful information about the structures of metal carbonyls and their derivatives. However, *X*-ray diffraction studies have undoubtedly been the most important in elucidating structures, with the important caveat that the molecular structure in the crystal may not be preserved in solution. It has recently been recognised that intramolecular rearrangement of CO groups in metal carbonyl structures is extensive.

A. The Metal Carbonyls.—(i) *Homonuclear complexes.* Table 2 lists for each transition element the carbonyl of simplest molecular formula. Except for paramagnetic vanadium hexacarbonyl, all these carbonyls are diamagnetic and obey the Sidgwick–Bailey[6] effective atomic number (EAN) rule. A carbon monoxide group is regarded as a source of two valence electrons, so that in the simple 'binary' carbonyls $M(CO)_y$ with one metallic atom in the molecule the EAN of the metal (atomic number $+ 2y$) is always the atomic number of the next noble gas, *e.g.*, 36 in $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$, and 86 in $W(CO)_6$, $Os(CO)_5$, and $Pt(CO)_4$. For metals of odd atomic number the rule implied that

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[28] T. Blackmore, J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2931.
[29] E. W. Abel, M. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 2323.

Table 2 *Mononuclear and binuclear metal carbonyls*[a]

$V(CO)_6$ Black green dec. *ca.* 70°	$Cr(CO)_6$ White dec. 130°	$Mn_2(CO)_{10}$ Golden yellow 154—155°	$Fe(CO)_5$[b] Yellow −20°[c]	$Co_2(CO)_8$ Orange red dec. 51°	$Ni(CO)_4$ Colourless −19·3°[e]
	$Mo(CO)_6$ White	$Tc_2(CO)_{10}$ White 160°	$Ru(CO)_5$ Colourless −22°	$Rh_2(CO)_8$[d] Orange dec. 76°	
	$W(CO)_6$ White	$Re_2(CO)_{10}$ White 177°	$Os(CO)_5$ Colourless *ca.* −15°	$Ir_2(CO)_8$[d] Yellow green	$Pt(CO)_4$[f]

[a] Binuclear species in this Table are limited to homonuclear complexes. See Table 5 for heteronuclear compounds. Temperatures given are those at which the carbonyl melts or decomposes. [b] Iron also forms a binuclear carbonyl $Fe_2(CO)_9$ (see cursive text). [c] B.p. 103–104°. [d] No other reports known, apart from that of the discoverers. [e] B.p. 42°. [f] See text.

there would be no stable simple mononuclear carbonyls, but it was extended to include binuclear and certain polynuclear carbonyls. Although there are several metal-carbonyl complexes which do not obey the EAN rule, and, moreover, the rule is formalistic in character, it has been very useful in preparative work in both accounting for and even predicting the stoicheiometries of complexes. With the advent of ligand-field theory, the diamagnetism of the majority of carbonyl complexes is understandable in terms of the relatively high ligand-field strength of CO which will operate to force a metal atom in a complex into a low-spin state, if necessary by forming metal–metal bonds (see later). The formula of vanadium carbonyl might have been expected to be $V_2(CO)_{12}$ (diamagnetic) rather than $V(CO)_6$ (paramagnetic). Vanadium's preference for the mononuclear formula is not well understood, although it is possible that steric factors inhibit formation of a vanadium–vanadium bond.

The structures of the mononuclear carbonyls $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have been firmly established (Table 3). The three

Table 3 *Structures of mononuclear metal carbonyls*

Compound	*Metal σ bonds*	*Structure*	*Physical technique*	*Reference*
$Ni(CO)_4$	sp^3	Tetrahedral	Electron diffraction	*a*
		T_d	*X*-ray diffraction	*b*
			Infrared spectra	*c*
$Fe(CO)_5$	dsp^3	Trigonal bipyramid	Electron diffraction	*d—f*
		D_{3h}	*X*-Ray diffraction	*g*, *h*
			Mössbauer	*i*
			Infrared	*j—l*
$Cr(CO)_6$	d^2sp^3	Octahedral	*X*-Ray	*m*
		O_h	Electron diffraction	*n*
			Infrared	*o*
$V(CO)_6$	d^2sp^3	Octahedral	*X*-ray	*p*
		O_h	Infrared	*q*
			Magnetic susceptibility	*p*, *r*

[a] L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, 1935, **3**, 828. [b] J. Ladell, B. Post, and I. Fankuchen, *Acta. Cryst.*, 1952, **5**, 795. [c] L. H. Jones, *Spectrochim. Acta*, 1963, **19**, 1899; *J. Chem. Phys.*, 1958, **28**, 1215. [d] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, 1939, **35**, 681. [e] M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, 1965, **69**, 3405. [f] G. M. Sheldrick, personal communication. [g] A. W. Hanson, *Acta Cryst.*, 1962, **15**, 930; but see reference *h*. [h] J. Donohue and A. Caron, *Acta Cryst.*, 1964, **17**, 663. [i] R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, 1963, **2**, 153. [j] W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, 1963, **19**, 863. [k] A. Reckziegel and M. Bigorgne, *J. Organometallic Chem.*, 1965, **3**, 341. [l] L. H. Jones and R. S. McDowell, *Spectrochim. Acta.*, 1964, **20**, 248. [m] W. Rudorff and U. Hofmann, *Z. phys. Chem.* (*B*), 1935, **28**, 351. [n] L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, 1938, **34**, 1350. [o] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432. [p] G. Natta, R. Ercoli, F. Calderazzo, A. Alberola, P. Corradini, and G. Allegra, *Atti. Accad. Naz. Lincei, Rend. Classe Sci. fis. mat. nat.* (8), 1959, **27**, 107. [q] W. Beck and R. E. Nitzchmann, *Z. Naturforsch.*, 1962, **17b**, 577. [r] F. Calderazzo, R. Cini and R. Ercoli, *Chem. and Ind.*, 1960, 934.

structural types (tetrahedral, trigonal bipyramidal, and octahedral) are encountered repeatedly among derivatives of these carbonyls, and also with isoelectronic species, *e.g.*, $Mn(NO)_3CO$, $[Ni(CO)_4]$; $Mn(CO)_4NO$, $[Fe(CO)_5]$; $Mn(CO)_6^+$, $[Cr(CO)_6]$.

There has been considerable discussion as to whether or not there are two kinds of Fe—C bond distance in $Fe(CO)_5$.[30,31] The most recent electron diffraction study (Table 3, ref. *f*) confirms that in the gas phase, although there is no distortion from D_{3h} symmetry, Fe—C (equatorial) [1·8331 ± 0·0024 Å] is somewhat longer than Fe—C (axial) [1·8062 ± 0·0031 Å]. It should be mentioned in passing that the *X*-ray crystallographic study of $Fe(CO)_5$ (Table 3, ref. *h*) establishes that the bonding is Fe—C—O rather than Fe—O—C. The question of whether in metal carbonyls the structures involve $M—(OC)_n$ linkages rather than $M—(CO)_n$ is one sometimes raised.

The pentacarbonyls of ruthenium and osmium[32] very probably have trigonal bipyramidal structures like $Fe(CO)_5$. Tetracarbonylplatinum, which has but a fleeting existence,[26] probably has a molecular structure similar to that of nickel carbonyl.

The molecular structures of $Mn_2(CO)_{10}$ (I),[33] $Co_2(CO)_8$ (II),[34] and $Fe_2(CO)_9$(III)[35] have all been established by *X*-ray studies. As expected $Tc_2(CO)_{10}$[36] and $Re_2(CO)_{10}$[37] are isomorphous with $Mn_2(CO)_{10}$. Other related carbonyl structures in which two halves of a molecule are held together by a covalent metal–metal bond, unsupported by bridging ligands, are $[Et_3PMn(CO)_4]_2$ (from *X*-ray studies[38]), and $[IFe(CO)_4]_2$,[39] $[IM(CO)_4]_2^{2-}$ (M = Mn, Re),[40] $[Cr(CO)_5]_2^{2-}$,[41] and $[R_3SiRu(CO)_4]_2$[42] (from i.r. studies).

In structures (I)—(III) the metal atoms obey the noble gas formalism. Manganese(0) in $Mn(CO)_5$ can be regarded as receiving 10 electrons from the CO ligands, and since the 'magic number'* for Mn(0) is eleven, two $Mn(CO)_5$

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* In this field, so-called 'magic numbers' can often be used to predict the formula of carbonyl compounds for a given set of ligands. The magic number is the number of additional valence electrons needed by a metal atom in a complex in order to equal the number of electrons in the succeeding noble-gas atom. For the transition elements which form carbonyl complexes these numbers are:

	Sub-group						
Oxidation State	Ti	V	Cr	Mn	Fe	Co	Ni
I	15	14	13	12	11	10	9
O	14	13	12	11	10	9	8
—I	13	12	11	10	9	8	7

[30] M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, 1967, **71**, 775.

[31] J. Donohue and A. Caron, *J. Phys. Chem.*, 1966, **70**, 603; 1967, **71**, 777.

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

[33] L. F. Dahl and R. E. Rundle, *Acta. Cryst.*, 1963, **16**, 419.

[34] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta. Cryst.*, 1964, **17**, 732.

[35] (*a*) R. Brill, *Z. Krist.*, 1927, **65**, 85; (*b*) H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 1939, 286.

[36] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1140.

[37] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.

[38] M. J. Bennett and R. Mason, *J. Chem. Soc.* (*A*), 1968, 75.

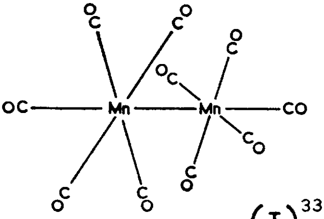
[39] F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, 1967, **6**, 2113.

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

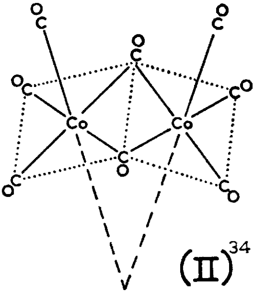
[41] W. Hieber, W. Beck, and R. Braun, *Angew Chem.*, 1960, **72**, 795.

[42] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, in the press.

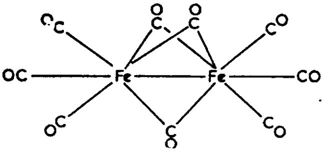
groups dimerise to form $Mn_2(CO)_{10}$. The structure can be regarded as involving two octahedra sharing a common apex with the fourfold axes of the two octahedra coincident but rotated 45° with respect to each other. The molecule retains a D_{4d} configuration, but in each half of the molecule the four equatorial Mn—CO bonds are bent inward toward the other half of the molecule so that the manganese atom is 0·12 Å out of the plane of the carbon atoms. In octacarbonyldicobalt each cobalt atom acquires nine electrons, six from terminal CO groups, two from bridging carbonyl groups, and one by formation of a cobalt–cobalt bond. As with $Mn_2(CO)_{10}$, the environment of the metal atoms is octahedral if one assumes a bent metal–metal bond (cobalt hybridised d^2sp^3), so that two octahedra share a common face.



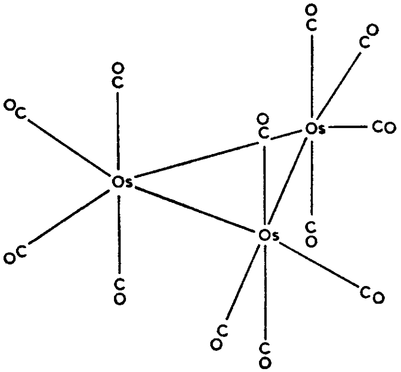
(I)[33]



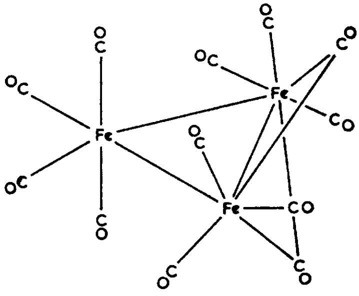
(II)[34]



(III)[35]



(IV)[54]



(V)[52]

There is no good reason yet known as to why octacarbonyldicobalt has structure (II) in the crystal, rather than one with a cobalt–cobalt bond without bridging CO ligands, since the EAN formalism would equally apply. Indeed i.r. spectral studies have established that there are two tautomeric forms of $Co_2(CO)_8$ in solution, one structure corresponding to (II) [bridging ν_{CO} (max) 1866 and 1857 cm.$^{-1}$], the other having no bridging CO groups, *viz.* $(OC)_4CoCo(CO)_4$.[43,44] The two forms are related by a temperature-dependent equilibrium. At room temperature a pentane solution of the carbonyl contains *ca.* 45% of the CO-bridged isomer (II) and *ca.* 55% of the non-bridged form.

If $Co_2(CO)_8$ is sublimed on to a probe at $-196°$ paramagnetic $Co(CO)_4$ is formed.[45]

Interestingly, the i.r. spectrum of the dimeric complex $[Co(CO)_3PPh_3]_2$ does not show any stretching mode attributable to bridging carbon monoxide ligands.[46] Moreover, an *X*-ray crystallographic study of $[Co(CO)_3PBu_3{}^n]_2$ reveals a linear PCoCoP unit with an unbridged Co—Co bond.[47] The molecular symmetry is D_{3d} (carbonyl groups staggered).

The structure of enneacarbonyldi-iron (III) can be described in terms of two octahedra sharing a common face formed by the carbon atoms of the bridging carbonyl groups. The insolubility of this compound is something of an enigma, and prevents a study of the i.r. spectrum in solution. It is also surprising that the carbonyl sublimes so much less readily than does octacarbonyldicobalt.[48] Nevertheless, the molecular structure (III) in the crystal has been firmly established.[35] It is customarily assumed that each terminal CO group contributes two electrons to the iron atom to which it is attached, and that each bridging molecule contributes one electron to each of the metal atoms. Hence each iron atom shares nine ligand electrons which together with its own eight electrons gives seventeen in all. Since the molecule is diamagnetic it is assumed that the odd electrons become paired in a metal–metal bond. This is consistent with the observed iron–iron distance (2·46 Å) which is at the lower range of metal–metal distances found in other iron complexes in which such bonding has been invoked.* The electronic structure of $Fe_2(CO)_9$ can be described as follows.[13] Since the environment of each iron atom is approximately octahedral it is reasonable to regard the metal atoms as using e_g *d*-orbitals, as well as 4*s* and 4*p* orbitals, in forming six σ-bonds to the carbonyl ligands. The CO groups will

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* *E.g.* $[EtSFe(CO)_3]_2$ (2.54Å),[49] $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (2.49 Å),[50] $Fe_5(CO)_{15}C$ (2.64 Å),[51] $Fe_3(CO)_{12}$ (2.56 and 2.67 Å),[52] $Sn[Fe(CO)_4]_4$ (2.78 Å).[53] In iron metal the interatomic distance is 2.48 Å.

[43] K. Noack, *Spectrochim. Acta.*, 1963, **19**, 1925; *Helv. Chim. Acta.*, 1964, **47**, 1555.

[44] G. Bor, *Spectrochim. Acta.*, 1963, **19**, 2065.

[45] H. J. Keller, and H. Wawersik, *Z. Naturforsch.*, 1965, **20b**, 938.

[46] O. Vohler, *Chem. Ber.*, 1958, **91**, 1235.

[47] J. A. Ibers, *J. Organometallic Chem.*, 1968, **14**, 423.

[48] M. H. Chisholm, A. G. Massey, and N. R. Thompson, *Nature*, 1966, **211**, 67.

[49] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 1963, **2**, 328.

[50] O. S. Mills, *Acta. Cryst.*, 1958, **11**, 620.

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

[52] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 1821; 1969, **91**, 1351.

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

supply nine electrons per iron atom and each of the latter will contribute a further three electrons for σ-bonding. The remaining five electrons on each iron atom are then assigned to the remaining three t_{2g} d-orbitals. Of these orbitals, one, a d_{z^2} type orbital arising from a linear combination of the t_{2g} set, can overlap strongly with the corresponding orbital of the other iron atom, while the other two orbitals overlap much less with orbitals of similar symmetry. The bonding combination of d_{z^2} type orbitals can then be assumed to contain an electron pair and the anti-bonding combination is empty, thus accounting for the diamagnetism. Alternatively since diamagnetism requires only a weak coupling of unpaired spins this could arise through multicentre iron–carbon–iron bonding involving the bridging carbonyl groups.

It is interesting to consider the increasing degree of polymerisation in the sequence $W(CO)_6$, $[Re(CO)_5]_2$, $[Os(CO)_4]_3$, and $[Ir(CO)_3]_4$ reflecting an increasing tendency to form metal–metal bonds. The molecular structures of $Os_3(CO)_{12}$ (IV)[54] and $Ru_3(CO)_{12}$[55] are similar (D_{3h}). The molecular structure of $Fe_3(CO)_{12}$ (V)[52] is, however, different in that one of the iron–iron bonds is supported by bridging carbonyl groups, so that the three metal atoms are at the corners of an isosceles triangle rather than the equilateral triangle of (IV). The structure (V) may be regarded as being derived from that of $Fe_2(CO)_9$ by replacing one of the bridging CO groups by an $Fe(CO)_4$ group. The latter is bonded by two iron–iron bonds, 2·67 Å in length. The other metal–metal bond is 2·56 Å long, and the two bridging carbonyl groups are somewhat unsymmetrically located. The twelve carbonyl groups are approximately disposed at the vertices of an icosahedron.

The i.r. spectrum of $Fe_3(CO)_{12}$ has been a matter of interest because although bands attributable to bridging carbonyl groups are observed, their intensity is much lower than expected on the basis of structure (V). Moreover, the two observed terminal carbonyl bands are far fewer than the nine expected. It would appear that in solution dodecacarbonyl-tri-iron rearranges to some extent to another structure. On cooling solutions of $Fe_3(CO)_{12}$ in dichloromethane to −78° the intensity of the peaks due to the bridging carbonyl groups increases relative to those due to the terminal carbonyl bands.[56] This suggests that there is an equilibrium in solution perhaps between structure (IV) and one consisting of three identical $Fe(CO)_3$ groups positioned at the vertices of an equilateral triangle and linked in pairs to one another by a bridging carbonyl group and an iron–iron bond.[52]

In the cobalt sub-group a structural change also occurs between polynuclear carbonyls of similar formulae, $M_4(CO)_{12}$. However, for this group the change operates between the second and third elements rather than between the first and the second. Both $Co_4(CO)_{12}$[52,57] and $Rh_4(CO)_{12}$[58] (VI) have tetrahedrally arranged metal atoms. Apical $M(CO)_3$ groups are symmetrically bonded by

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[54] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, **1**, 521.

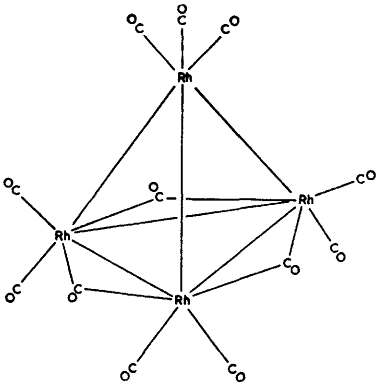
[55] R. Mason and A. I. M. Rae, *J. Chem. Soc.* (*A*), 1968, 778.

[56] J. Dalton and F. G. A. Stone, unpublished observations.

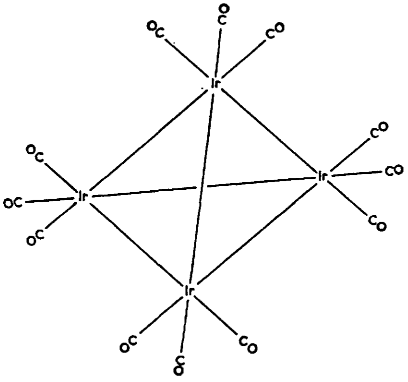
[57] P. Corradini and A. Sirigu, *Ricerca sci.*, 1966, **36**, 188.

[58] C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 4792.

only metal–metal bonds to basal $M_3(CO)_9$ fragments containing three identical $M(CO)_2$ groups located at the vertices of an equilateral triangle and linked in pairs to one another by both a bridging carbonyl group and a metal–metal bond. As with (V), the twelve CO groups in (VI) are disposed at the corners of an icosahedron which encompasses the tetrahedron of metal atoms. In $[Ir(CO)_3]_4$ (VII), however, the tetrahedron of metal atoms is stabilised without bridging carbonyl groups. The molecule has T_d symmetry, and the twelve carbonyl ligands are disposed in a cubo-octahedral arrangement around the iridium atom cluster. The i.r. spectrum of $Co_4(CO)_{12}$ in pentane solution contains only four bands in the terminal carbonyl stretching region and one in the bridging region, whereas the structure (C_{3v}) determined for the crystal should give rise to six and two bands in these regions respectively. It was, therefore, suggested[59] that a structure (D_{2d}) with a Co_4 tetrahedron with four bridging carbonyl groups and two terminal groups on each cobalt atom would account for the spectrum, thus raising the possibility of a change in structure on dissolving the crystals.[60] However, measurements of the ^{59}Co n.m.r. spectrum of $Co_4(CO)_{12}$ in hydrocarbon solvents[61,62] reveal two resonances with integrated intensities of 3 : 1 in accord with Corradini's structure (C_{3v}).[52,57,63] Since intramolecular transformations between different structures in solution appear to be ruled out, it must be assumed that the character of the i.r. spectrum arises through accidental degeneracy of bands or the extreme weakness of certain bands.



(VI)[58]



(VII)[58]

No homopentanuclear metal carbonyls have yet been described, but hexanuclear species $M_6(CO)_{16}$ (M = Co, Rh, or Ir) are known. The structure of $Rh_6(CO)_{16}$ (VIII),[64] provides an interesting example of a case where

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[59] D. L. Smith, *J. Chem. Phys.*, 1965, **42**, 1460.

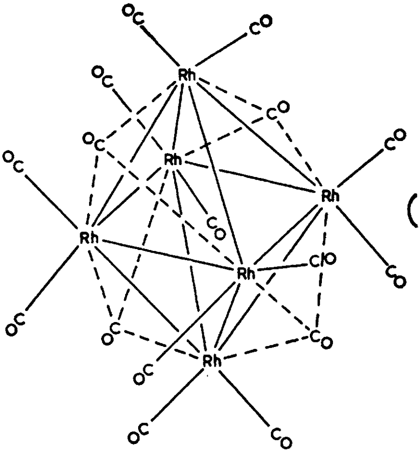
[60] F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1083.

[61] H. Haas and R. K. Sheline, *J. Inorg. Nuclear Chem.*, 1967, **29**, 693.

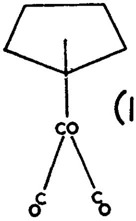
[62] E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc.* (*A*), 1967, 148.

[63] P. Corradini, *J. Chem. Phys.*, 1959, **31**, 1676.

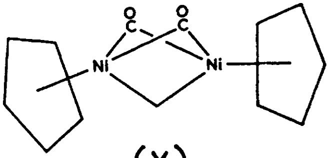
[64] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.



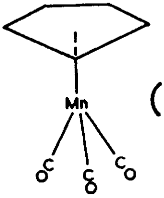
(VIII)[64]



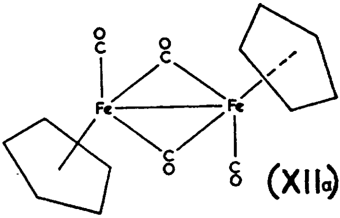
(IX)



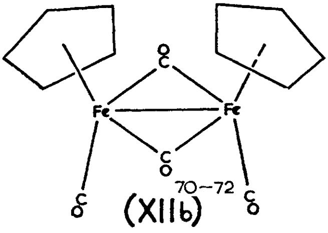
(X)



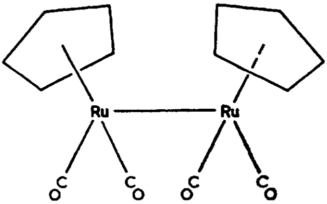
(XI)



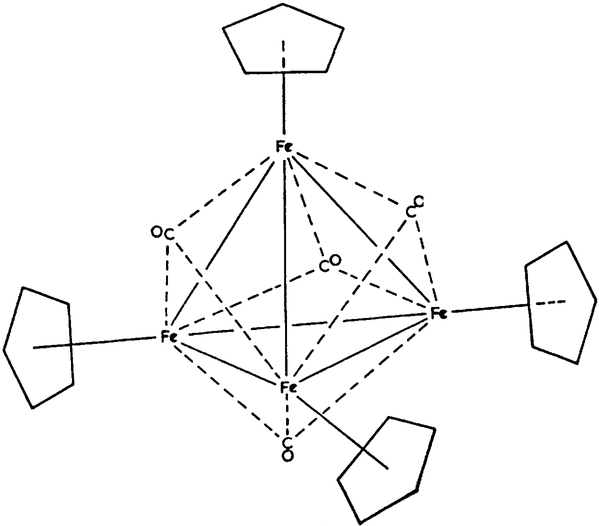
(XIIa)[69]



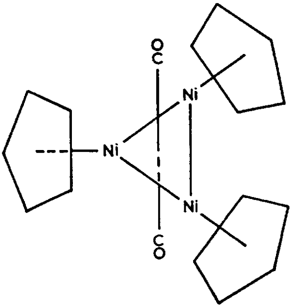
(XIIb)[70–72]



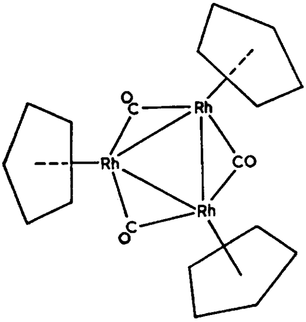
(XIII)[70–72]



(XIV)[75]



(XV)[76]



(XVI)[77]

a crystal-structure determination led to a revision of a molecular formula; on the basis of analysis $Rh_4(CO)_{11}$ had been previously assigned. Structure (VIII) was one of the first to establish that carbonyl groups could bridge three metal atoms. The four such ligands in (VIII) are bonded to alternate faces of the octahedron of rhodium atoms, and give rise to ν_{CO} (max) at 1800 cm.$^{-1}$.[65] Although $Rh_6(CO)_{16}$ does not obey the EAN formalism the compound is essentially diamagnetic. The spin pairing of all the electrons can be rationalised from MO symmetry arguments.[64] Recently discovered $Co_6(CO)_{16}$[66] has a very similar i.r. spectrum to that of (VIII) and presumably the two carbonyls have

---

[65] W. Beck and K. Lottes, *Chem. Ber.*, 1961, **94**, 2578.

[66] P. Chini, *Chem. Comm.*, 1967, 440; *Inorg Chem.*, 1969, **8**, 1206.

similar structures. The hexanuclear carbonyl purported[67a] to be $Ru_6(CO)_{18}$ has recently been characterised as a 'carbide' complex $CRu_6(CO)_{17}$;[67b] its structure is described later.

The convergence of metal carbonyl chemistry with that of the π-complexes was mentioned in the Introduction. In this respect the π-cyclopentadienylmetal carbonyls are important.[68] The π-C_5H_5 group can formally be regarded as a five-electron donor, and with the EAN concept in mind, the formulae of the mononuclear and binuclear complexes listed in Table 4 are understandable, as is the relationship between these diamagnetic compounds and those of Table 2. With the cyclopentadienylmetal carbonyls, mononuclear species occur with metals of odd atomic number and binuclear species with metals of even atomic number.

The cyclopentadienyl group can formally, but qualitatively, be regarded as a terdentate ligand, so that there are some structural analogies between metal carbonyls and cyclopentadienylmetal carbonyls, *e.g.* $Fe(CO)_5$ and π-$C_5H_5Co(CO)_2$ (IX); $Co_2(CO)_8$ (II) and $[\pi$-$C_5H_5NiCO]_2$ (X); and $Cr(CO)_6$ and π-$C_5H_5Mn(CO)_3$ (XI). Interestingly, the molecular structure of $[\pi$-$C_5H_5Fe(CO)_2]_2$ in the crystal (XIIa)[69] is not analogous to that of $Mn_2(CO)_{10}$ (I). The cyclopentadienylmetal carbonyls $[\pi$-$C_5H_5M(CO)_2]_2$ (M = Fe, Ru, or Os) provide another interesting example of tautomerism in which a structure containing a metal–metal bond with bridging carbonyl groups can be interconverted with a structure having the metal-metal bond but without bridging ligands. On the basis of infrared studies[70–72] it was concluded that the principal form of $[\pi$-$C_5H_5Fe(CO)_2]_2$ in solution was (XIIb),[70,71] while under the same conditions the ruthenium analogue exists as a mixture of two isomers, one with *cis*-cyclopentadienyl groups and bridging carbonyl groups analogous to (XIIb), and the other with structure (XIII). A study of the spectra of the iron compound in several solvents, however, has led to the conclusion that *cis*-, *trans*-, and non-bridged structures are all present, and this is likely to be so for the ruthenium compound also.[72] The osmium compound $[\pi$-$C_5H_5Os(CO)_2]_2$ very probably has a structure without carbonyl bridges both in solution and in the solid state.[70]

The binuclear rhodium complex $[\pi$-$C_5H_5RhCO]_2$-μ-CO has an unusual structure since two $(\pi$-$C_5H_5)(OC)Rh$ groups are held together by a single bridging CO group and a rhodium–rhodium bond.[73] From i.r. studies it appears that a singly bridging CO group also supports a metal–metal bond in $[\pi$-$C_5H_5(OC)_2V]_2$-μ-CO.[74] A number of polynuclear cyclopentadienylmetal carbonyls are known, for example, $[\pi$-$C_5H_5FeCO]_4$[75] (XIV), paramagnetic

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[67] (*a*) F. Piacenti, M. Bianchi, and E. Benedetti, *Chem. Comm.*, 1967, 775; (*b*) A. Sirigu, M. Bianchi, and E. Benedetti, *Chem Comm.*, 1969, 596.

[68] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' vol. 2, Methuen, London, 1968.

[69] O. S. Mills, *Acta. Cryst.*, 1958, **11**, 620.

[70] R. D. Fischer, A. Vogler, and K. Noack, *J. Organometallic Chem.*, 1967, **7**, 135.

[71] F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, 1967, **6**, 15.

[72] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1319.

[73] J. P. Nice, and O. S. Mills, *J. Organometallic Chem.*, 1967, **10**, 337.

[74] E. O. Fischer and R. J. J. Schneider, *Angew. Chem. Internationat. Edn.*, 1967, **6**, 569.

[75] R. B. King, *Inorg. Chem.*, 1966, **5**, 2227.

Table 4 *Mononuclear and binuclear π-cyclopentadienylmetal carbonyls**

π $C_5H_5V(CO)_4$ orange decomp. 138°	$[\pi\text{-}C_5H_5Cr(CO)_3]_2$ deep green decomp. 163°	$\pi\text{-}C_5H_5Mn(CO)_3$ yellow 77°	$[\pi\text{-}C_5H_5Fe(CO)_2]_2$† red-purple 194°	$\pi\text{-}C_5H_5Co(CO)_2$ red −22°	$[\pi\text{-}C_5H_5NiCO]_2$ red 146°
π $C_5H_5Nb(CO)_4$ orange 144°	$[\pi\text{-}C_5H_5Mo(CO)_3]_2$ red-violet 215°	$\pi\text{-}C_5H_5Tc(CO)_3$ white	$[\pi\text{-}C_5H_5Ru(CO)_2]_2$ orange red 185° decomp.	$\pi\text{-}C_5H_5Rh(CO)_2$ orange −11°	
$\pi\text{-}C_5H_5Ta(CO)_4$ orange 171°	$[\pi\text{-}C_5H_5W(CO)_3]_2$ red-purple	$\pi\text{-}C_5H_5Re(CO)_3$ white 111°	$[\pi\text{-}C_5H_5Os(CO)_2]_2$ yellow 198°	$\pi\text{-}C_5H_5Ir(CO)_2$ yellow-liquid	$[\pi\text{-}C_5H_5PtCO]_2$ red 103°

* Mononuclear $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ is also known, as are the binuclear compounds $[\pi\text{-}C_5H_5V(CO)_2]\text{-}\mu\text{-}CO$ and $[\pi\text{-}C_5H_5RhCO]_2\text{-}\mu\text{-}CO$, and the polynuclear complexes $[\pi\text{-}C_5H_5RhCO]_3$, $\pi\text{-}C_5H_5(OC)Rh[Rh(CO)\pi\text{-}C_5H_5]_2$, $[\pi\text{-}C_5H_5CoCO]_3$, $[\pi\text{-}C_5H_5Ni]_3(CO)_2$, and $[\pi\text{-}C_5H_5MCO]_4$ (M = Fe, Ru). Temperatures given are melting or decomposition points.

† A mononuclear complex $\pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}C_5H_5)$ is also known.

Table 5 *Some heteronuclear metal carbonyls*

$(OC)_5MnCo(CO)_4$[a]
$(OC)_5MnRe(CO)_4$[b]
$[(OC)_5Mn]_2Fe(CO)_4$[c]
$[(OC)_5Mn]\,[(OC)_5Re]Fe(CO)_4$[d]
$(Phen)(OC)_3MnCo(CO)_4$[a]
$(OC)_5ReCo(CO)_4$[e]
$(Phen)(OC)_3ReCo(CO)_4$[e]
$[(OC)_5Re]_2Fe(CO)_4$[f]
$Fe_2Ru(CO)_{12}$[g]

$FeRu_2(CO)_{12}$
$Ru_2Os(CO)_{12}$[h]
$RuOs_2(CO)_{12}$[h]
$Co_2Rh_2(CO)_{12}$[i]
$Co_2Rh_4(CO)_{16}$[j]
$(\pi\text{-}C_5H_5)(OC)_2FeMn(CO)_5$[k]
$(\pi\text{-}C_5H_5)(OC)_2FeRe(CO)_5$[l]
$(\pi\text{-}C_5H_5)(OC)\overline{Fe(CO)_2Co}(CO)_3$[a]
$(\pi\text{-}C_5H_5)(OC)\overline{Fe(CO)_2Ni}(\pi\text{-}C_5H_5)$[m]

$(\pi\text{-}C_5H_5)(OC)_2FeMo(CO)_3(\pi\text{-}C_5H_5)$[k]
$(\pi\text{-}C_5H_5)(OC)_2RuRe(CO)_5$[n]
$(\pi\text{-}C_5H_5)(OC)_2RuCo(CO)_4$[n]
$(\pi\text{-}C_5H_5)(OC)_3MoMn(CO)_5$[o]
$(\pi\text{-}C_5H_5)(OC)_3MoRe(CO)_5$[o]
$(\pi\text{-}C_7H_7)(OC)_2MoMn(CO)_5$[p]
$(\pi\text{-}C_5H_5)(OC)_3MoW(CO)_3(\pi\text{-}C_5H_5)$[q]
$(\pi\text{-}C_5H_5)(OC)_3WMn(CO)_5$[o]
$(\pi\text{-}C_5H_5)(OC)_3WRe(CO)_5$[o]

[a] K. K. Joshi and P. L. Pauson, *Z. Naturforsch.*, 1962, **17b**, 565; T. Krück and M. Höfler, *Chem. Ber.*, 1964, **97**, 2289. [b] 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; N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1964, **3**, 1123. [c] E. H. Schubert and R. K. Sheline, *Z. Naturforsch.*, 1965, **20b**, 1306; P. A. Agron, R. D. Ellison, and H. A. Levy, *Acta Cryst.*, 1967, **23**, 1079. [d] G. O. Evans and R. K. Sheline, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2862. [e] T. Krück and M. Höfler, *Angew. Chem.*, 1964, **76**, 786. [f] G. O. Evans, J. P. Hargaden, and R. K. Sheline, *Chem. Comm.*, 1967, 186. [g] D. B. W. Yawney and F. G. A. Stone, *Chem. Comm.*, 1968, 619; *J. Chem. Soc.* (*A*), 1969, 502; J. Knight and M. J. Mays, *Chem. and Ind.*, 1968, 1159. [h] B. F. G. Johnson, R. D. Johnston, J. Lewis, I. G. Williams, and P. A. Kilty, *Chem. Comm.*, 1968, 861. [i] P. Chini, S. Martinengo, and V. Albano, *Inorg. Chim. Acta*, First Internat. Sympos. on Metal Carbonyls. P. A3. [j] S. H. H. Chaston and F. G. A. Stone, unpublished observations. [k] R. B. King, P. M. Treichel, and F. G. A. Stone, *Chem. and Ind.*, 1961, 747; P. J. Hansen and R. J. Jacobson, *J. Organometallic Chem.*, 1966, **6**, 389. [l] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Doklady Akad. Nauk S.S.S.R.*, 1964, **156**, 383. [m] J. F. Tilney-Bassett, *J. Chem. Soc.*, 1963, 4784. [n] T. Blackmore, J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2931. [o] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. S. Beschastnov, *Doklady Akad. Nauk S.S.S.R.*, 1964, **159**, 377; B. P. Bir'yukov, Yu T. Struchkov, K. N. Anisimov, N. E. Kolobova, and A. S. Beschastnov, *Chem. Comm.*, 1968, 667. [p] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 785. [q] E. W. Abel, A. Singh, and G. Wilkinson, *J. Chem. Soc.*, 1960, 1321.

$[\pi\text{-}C_5H_5Ni]_3(CO)_2$[76] (XV), and $[\pi\text{-}C_5H_5RhCO]_3$[77] (XVI). An isomer of the latter $\pi\text{-}C_5H_5(OC)Rh[\pi\text{-}C_5H_5Rh(CO)]_2$ is also known.[78]

(ii) *Heteronuclear Complexes.* Many mixed metal carbonyls are known (Table 5). These polynuclear compounds have either a sequence or a cluster of metal atoms. Thus examination of $Mn_2Fe(CO)_{14}$ (XVII) by *X*-ray[79] reveals a linear Mn·Fe·Mn sequence, while the i.r. spectra of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ suggest[80] molecular structures for these compounds based on triangular clusters similar to structures (V) and (IV), respectively. Several of the binuclear compounds have molecular structures closely related to those of the homonuclear species from which they are derived, for example $MnRe(CO)_{10}$ and (I), and $(\pi\text{-}C_5H_5)_2MoW(CO)_6$ and (XVIII), and $(\pi\text{-}C_5H_5)(OC)\overline{Fe(CO)_2Co}(CO)_3$ and (II) or (XIIa).

Many polynuclear metal carbonyl complexes have been characterised wherein non-metal atoms form an intrinsic part of the structure, for example, $C[Fe(CO)_3]_5$[51] (XIX), $S[Co(CO)_3]_3$[81] (XX), and $HRe_2Mn(CO)_{14}$[82] (XXI), the structures being established by *X*-ray methods.

Several 'carbide' cluster compounds have been recently discovered, but for only two of these complexes are the structures as yet known with certainty. The compound $CRu_6(CO)_{14}(C_6H_3Me_3)$ (XXII), isoelectronic with (VIII), has a carbide atom located close to the centre of a slightly distorted octahedron of ruthenium atoms.[83] The compound $CRu_6(CO)_{17}$[84] has a structure[67b] very similar to (XXII) with the mesitylene ring replaced by three CO groups terminally bound to the ruthenium atom. Cobalt carbonyl carbide complexes $C_3HCo_5(CO)_{15}$, $C_5Co_6(CO)_{17}$, $C_4Co_6(CO)_{18}$ have been described.[85] It is possible that their structures are based on that of the dimer $[CCo_3(CO)_9]_2$, mentioned below.

The sulphur atom in paramagnetic $SCo_3(CO)_9$ (XX) bridges three metal atoms.[81] The analogue $SFeCo_2(CO)_9$ is diamagnetic and isomorphous. The average metal–metal bond length is 0·08 Å shorter than the average Co—Co bond length in (XX). These results suggest that a formal removal of the unpaired electron by substitution of iron for cobalt strengthens the metal–metal bonds thereby indicating that the unpaired electron in (XX) must be accommodated in an antibonding or non-bonding orbital.

A structure related to (XX) is one in which the S atom is replaced by the MeC group.[86] The bromo-analogue $BrCCo_3(CO)_9$ in boiling toluene dimerises

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[76] A. A. Hock and O. S. Mills, 'Advances in the Chemistry of Co-ordination Compounds,' ed. S. Kirschner, Macmillan, New York, 1961, p. 640.

[77] O. S. Mills and E. F. Paulus, *Chem. Comm.*, 1966, 815.

[78] E. F. Paulus, E. O. Fischer, H. P. Fritz, and H. S. Woldan, *J. Organometallic Chem.*, 1967, **10**, P3.

[79] P. A. Agron, R. D. Ellison, and H. A. Levy, *Acta. Cryst.*, 1967, **23**, 1079.

[80] D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 502; *Chem. Comm.*, 1968, 619.

[81] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1229.

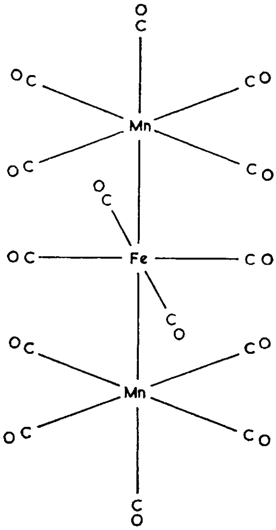
[82] M. R. Churchill and R. Bau, *Inorg. Chem.*, 1967, **6**, 2086.

[83] R. Mason and W. R. Robinson, *Chem. Comm.*, 1968, 468.

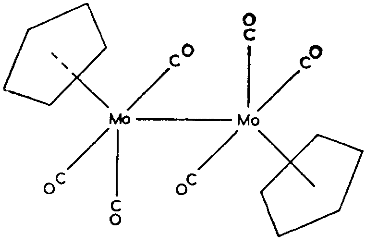
[84] B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc.* (*A*), 1968, 2865.

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

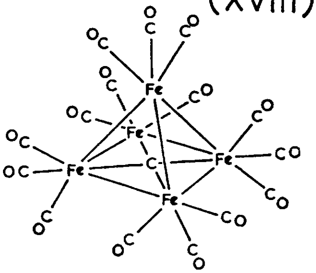
[86] P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 261.



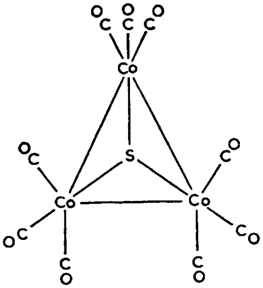
(XVII)[79]



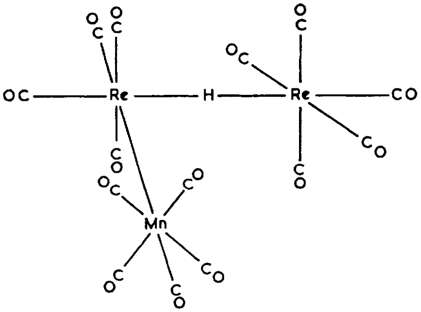
(XVIII)



(XIX)[51]



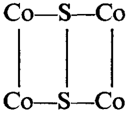
(XX)[81]



(XXI)[82]

to yield $[CCo_3(CO)_9]_2$ as well as an insertion product $[Co_3(CO)_9C]_2CO$.[87] These compounds have Co_3C tetrahedra as the basic structural feature, with the tetrahedra joined by a C—C bond in the former case, and a ketonic carbonyl group in the latter. Another structure known to contain the $CCo_3(CO)_9$ core is $Co_3(CO)_{10}BH_2NEt_3$ (XXIII).[88] Although the structure contains an apical triply-bridging CO group, in a formal sense it is best regarded as a $Co_3(CO)_9C$-substituted derivative of a hydroxyborane.

Complex (XX) can be regarded as the parent substance of a variety of other cobalt carbonyl sulphur compounds, the majority of which have been discovered by Marko and Bor and co-workers.[89] In $[SCo_3(CO)_7]_2S_2$ two *cis*-equatorial carbonyl groups of two $SCo_3(CO)_9$ units (XX) are replaced by an S_2 group which acts as a bridge,[90] *viz.*



$$\begin{array}{ccccc} Co & — & S & — & Co \\ | & & | & & | \\ Co & — & S & — & Co \end{array}$$

Wei and Dahl[91] have characterised by *X*-ray diffraction the mercaptocobalt cluster complexes $Co_3[(SC_2H_5)_5CO](CO)_3$, $Co_5(CO)_{10}(SC_2H_5)_5$, and $SCo_6(CO)_{11}(SC_2H_5)_4$. In the trinuclear compound, the three cobalt atoms form a ring with three coplanar terminal carbonyl groups each attached to a cobalt atom. The remaining carbonyl group and the five EtS ligands are located in pairs above and below the tricobalt plane to give doubly bridging groups. In $Co_5(CO)_{10}(SC_2H_5)_5$ there is a $Co_3[(SC_2H_5)_4(CO)_2](CO)_3$ residue bonded by bridging mercapto-groups to a $Co_2(CO)_5(SC_2H_5)$ fragment. The sulphur(carbonyl group) polyhedron of the trimeric residue closely resembles that of the molecular complex $Co_3[(SC_2H_5)_5CO](CO)_3$. The structure of the hexameric cobalt complex $SCo_6(CO)_{11}(SC_2H_5)_4$ is as shown (XXIV).

Other metal carbonyls also react with sulphur or sulphur compounds to yield polynuclear species wherein sulphur atoms are an intricate part of the structure, for example (XXV) and (XXVI).[92,93] Trinuclear iron carbonyls $Fe_3(CO)_9X_2$ (X = S, Se) (XXVII) are also known.[94,95]

In $HRe_2Mn(CO)_{14}$ (XXI)[82] the rhenium–manganese distance is as expected on the basis of the metal–metal bond lengths in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ but the rhenium–rhenium distance is 0·37 Å longer than anticipated for a simple σ bond. Hence it is reasonable to assume that the hydrogen atom is located between the two rhenium atoms. Assuming a linear symmetric Re—H—Re

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[87] G. Allegra, R. Ercoli, and E. M. Peronaci, *Chem. Comm.*, 1966, 549.

[88] F. Klanberg, W. B. Askew, and L. J. Guggenberger, *Inorg. Chem.*, 1968, **7**, 2265.

[89] E. Klump, L. Markó, and G. Bor, *Chem. Ber.*, 1964, **97**, 926; 1967, **100**, 1451; and references cited therein.

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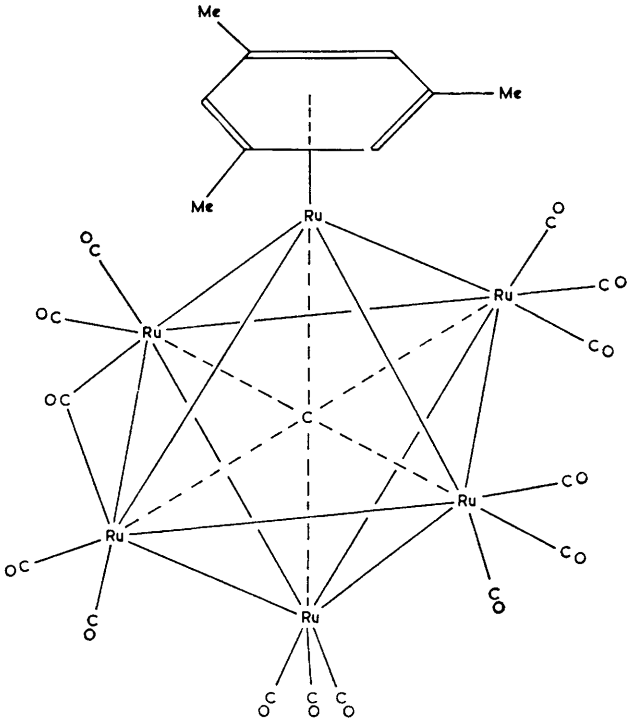
[91] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1968, **90**, 3960, 3969, 3977.

[92] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1.

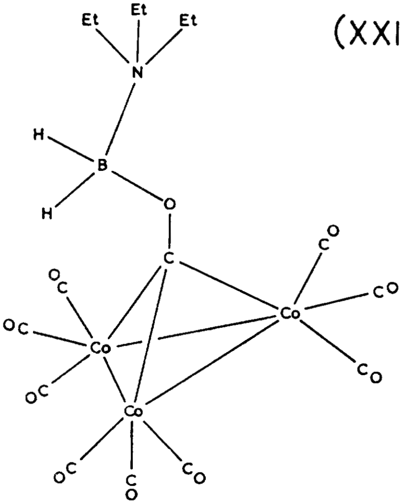
[93] J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1236.

[94] L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, 1963, **2**, 1067.

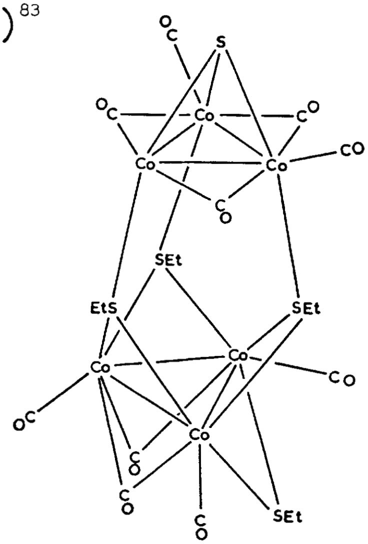
[95] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 493.



(XXII)[83]



(XXIII)[88]

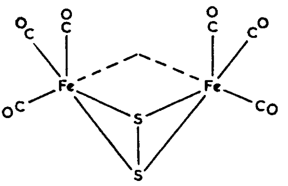


(XXIV)[91]

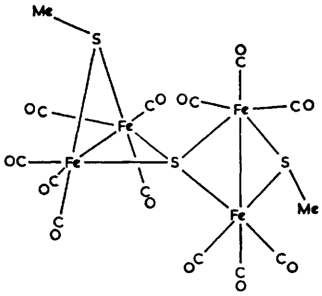
bond, the Re—H distance (1·696 Å) is very close to that found (1·68 Å) in K_2ReH_9 by neutron diffraction.[96] Interestingly, the $(OC)_4Re(H)Re(CO)_5$ portion of the molecule has an eclipsed configuration of carbonyl groups, as in the anion $[HCr_2(CO)_{10}]^-$ (see below), whereas in the $(OC)_4Re—Mn(CO)_5$ portion of the molecule the carbonyl groups are staggered as in (I).

B. Derivatives of the Metal Carbonyls.—The more important derivatives of the metal carbonyls are the carbonyl hydrides, the anionic and cationic species, carbonyl halides, complexes in which CO groups have been replaced by electron-pair donors, organometal carbonyls and complexes in which Si, Ge, Sn, or Pb atoms, or post-transition metal atoms such as Hg, are ligands. The molecular structures of many derivatives have been established by one or other of the physical techniques mentioned earlier. The results quoted in this section are necessarily illustrative rather than comprehensive.

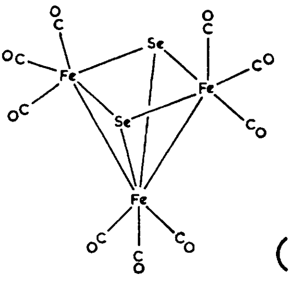
(i) *Metal Carbonyl Hydrides.* Historically these compounds are of particular significance because $HCo(CO)_4$ and $H_2Fe(CO)_4$ were the first compounds in which direct hydrogen-to-transitional-metal covalent bonds were proposed (1931).[7] Of the *ca.* 250 transition-metal hydride complexes presently known, *ca.* 100 are metal carbonyl hydrides. Single-crystal *X*-ray diffraction studies have revealed that the hydrogen atoms in the carbonyl hydrides occupy definite co-ordination positions. Consequently, the structures can be compared with those



(XXV)[92]



(XXVI)[93]



(XXVII)[95]

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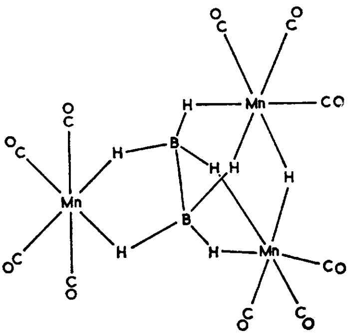
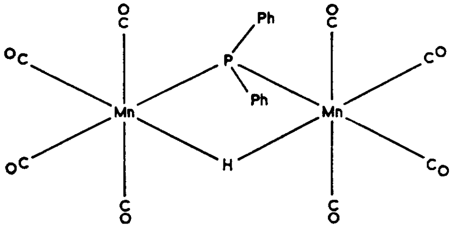
[96] S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 1964, 3, 558.



(XXVIII)[105]



(XXIX)[111]

in which other ligands, notably halogen atoms or alkyl groups, are bonded to the metals.

Usually the co-ordinates of the hydrogen atom have to be inferred from the positions of the other ligands, since the heavy atoms present mask hydrogen in the diffraction pattern. Fortunately, two physical properties of transition-metal hydrides lead to their ready identification. In the i.r., terminal metal-hydrogen stretching vibrations occur in the range 2200–1700 cm.$^{-1}$. Although this is also the region of most carbonyl stretching vibrations, a distinction between the two types of absorption is possible *via* synthesis of the corresponding deuteride. In this way the M—D frequency falls by a factor of *ca.* 1·4 compared with the corresponding M—H absorption, to appear in the range 1600—1200 cm.$^{-1}$. Transition-metal hydrides also have characteristic high-field ^{1}H n.m.r. signals (τ 12—45). It is therefore relatively easy to establish qualitatively the presence of the metal–hydrogen group, provided the complex is soluble enough. In order to establish the molecular symmetry, resort must be made to analysis of the vibrational spectrum, or better to *X*-ray or neutron or electron diffraction techniques. Often a combination of the various methods settles the structure beyond doubt.

A single-crystal *X*-ray diffraction study[97] of $HMn(CO)_5$ failed to locate the hydrogen atom, but showed that the five carbonyl groups occupy five of the six corners of a nearly regular octahedron. Interestingly, as with $Mn_2(CO)_{10}$ (I), the manganese atom lies slightly above the based plane along the fourfold axis toward the apical carbonyl group. The i.r. spectrum of the hydride is also in accord with C_{4v} symmetry.[98] The high resolution n.m.r. spectrum of $HMn(CO)_5$ shows a sharp line at τ 17·5. Broad-line n.m.r. studies[99] of the compound in the solid state led to an erroneous conclusion for the Mn—H bond length, but

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[97] S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, 1964, **3**, 1491.

[98] W. F. Edgell, J. W. Fischer, G. Asato, and W. M. Risen, *Inorg. Chem.*, 1969, **8**, 1103.

[99] T. C. Farrar, S. W. Ryan, A. Davison, and J. W. Faller, *J. Amer. Chem. Soc.*, 1966, **88**, 184; T. C. Farrar, F. E. Brinckman, T. D. Coyle, A. Davison, and J. W. Faller, *Inorg. Chem.*, 1967, **6**, 161.

reinterpretation[100] of the data afforded a bond length of 1·44 ± 0·03 Å. A recent electron-diffraction study[101] has given an Mn—H distance of 1·425 ± 0·046 Å, assuming the molecular point group C_{4v}, in excellent agreement with the revised estimate from the observed second moment of the solid-state n.m.r. spectrum. Moreover, the bond distance is as expected for a covalent bond, so that previous ideas concerning very short metal–hydrogen bond distances are no longer tenable.

In an *X*-ray diffraction study[102] of $(Ph_3P)_3Rh(CO)(H)$ the peak from the hydrogen atom was actually discernible. The conformation of the ligands around the rhodium atom is that of a trigonal bipyramid with the three phosphorus atoms in the basal plane and a Rh—H distance of 1·60 ± 0·12 Å.

Reference was made earlier to the bridging hydrogen atom in $HRe_2Mn(CO)_{14}$ (XXI). Many examples of metal–hydrogen–metal linkages are now known and three types may be distinguished. Those in which the hydrogen atom is the only bridging group, as in (XXI) and in the anion $[HCr_2(CO)_{10}]^-$; those in which the hydrogen atom is part of a double bridge, as in $(OC)_4Mn(H)(PPh_2)Mn(CO)_4$; and those in which the hydrogen atom is part of a multiple bridge, as in the anion $[HFe_3(CO)_{11}]^-$.

A linear symmetric Cr(H)Cr bond is consistent with spectroscopic and diffraction data for the anion $[HCr_2(CO)_{10}]^-$.[103,104] The *X*-ray study failed to locate the hydrogen atom in the anion but showed that two $Cr(CO)_5$ groups are held together through a Cr—Cr distance of 3·41 Å. The two halves of the anion are related to each other by a centre of symmetry so that the carbonyl groups perpendicular to the fourfold axis in the two halves of the molecule are eclipsed (D_{4h} symmetry). The metal–hydrogen–metal bonding may be described in terms of a delocalised three-centre two-electron bond. Assuming that each chromium atom is d^2sp^3 hydridised, a combination of two such hybrids, one from each chromium atom, and a hydrogen *s* atomic orbital affords three molecular orbitals which are bonding, non-bonding, and anti-bonding. The bonding orbital then contains two electrons derived from the hydrogen atom and the anionic charge. In this manner both chromium atoms have a closed-shell electronic configuration, and the bonding is reminiscent of that in the B(H)B bridge bonds of the boron hydrides.

The close relationship between the bridge bonding in the transition metals and in the boron hydrides is well illustrated by the characterisation of several mixed hydrides such as $HMn_3(CO)_{10}(BH_3)_2$ (XXVIII)[105] and $[Cr(CO)_4B_3H_8]^-$. In the anion, chromium is in an essentially octahedral environment bonded to a B_3H_8 moiety *via* two *cis* Cr(H)B linkages.[106]

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[100] G. M. Sheldrick, *Chem. Comm.*, 1967, 751.

[101] A. G. Robiette, G. M. Sheldrick, and R. N. F. Simpson, *Chem. Comm.*, 1968, 506.

[102] S. J. PaPlaca and J. A. Ibers, *Acta. Cryst.*, 1965, **18**, 511.

[103] L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Amer. Chem. Soc.*, 1966, **88**, 366.

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

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

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

The compounds $(OC)_4Mn(H)(PPh_2)Mn(CO)_4$[107,108] and $(\pi\text{-}C_5H_5)(OC)_2Mo(H)(PMe_2)Mo(CO)_2(\pi\text{-}C_5H_5)$[109] are examples of carbonyl hydrides in which the hydrogen ligand is part of a double bridge system, and the two structures are closely related.[110,111] In the molybdenum complex[110] the hydrogen atom was not located by *X*-ray diffraction, but because of the similar co-ordination around each of the molybdenum atoms there is strong support for the equivalence of the hydrogen interaction with both metal atoms. In the manganese complex (XXIX) the bridging hydrogen atom was located.[111] The structure[112] of the anion $[HFe_3(CO)_{11}]^-$ is related to that of $Fe_3(CO)_{12}$ (V), and can be regarded as one in which a bridging carbonyl group of $Fe_3(CO)_{12}$ is replaced by H^-, although the charge would not be localised on hydrogen in the anion. Hydrogen is also part of a multiple bridge system in the anion $[HFe_2(CO)_8]^-$, the structure of which, elucidated by i.r. and Mössbauer spectroscopy,[113] is similar to that of $Fe_2(CO)_9$ with a bridging CO group replaced by hydride.

Many polynuclear hydrido-carbonyls of the iron and cobalt subgroups have been characterised, but as yet their structures are not known with any degree of certainty, *e.g.* $HFeCo_3(CO)_{12}$,[114,115] $HRuCo_3(CO)_{12}$,[115,116] $H_2Ru_4(CO)_{13}$,[117] $H_2FeRu_3(CO)_{13}$,[80,118] $\alpha\text{-}H_4Ru_4(CO)_{12}$, $\beta\text{-}H_4Ru_4(CO)_{12}$,[117] $H_4Os_4(CO)_{12}$,[119] $H_2Os_4(CO)_{13}$,[119] $H_2Os_3(CO)_{10}$,[119] $HOs_3(CO)_{10}(OMe)$,[119] $HM_3(CO)_{10}(SR)$ (M = Ru, Os).[120,121] The iron compounds $H_2Fe_3(CO)_{11}$[122,123] and $H_2Fe_4(CO)_{13}$[124] were discovered earlier.

On the basis of i.r. and mass spectroscopy it has been suggested[115] that the hydrides $HMCo_3(CO)_{12}$ (M = Fe or Ru) have structures similar to that of $M_4(CO)_{12}$ [M = Co or Rh, (VI)] with the hydrogen atom located inside the metal atom cluster.

Since the hydrides $H_2Ru_4(CO)_{13}$, $\alpha\text{-}H_4Ru_4(CO)_{12}$, and $\beta\text{-}H_4Ru_4(CO)_{12}$ are isoelectronic with $Rh_4(CO)_{12}$, and the hydride $H_2Fe_4(CO)_{13}$ is isoelectronic with $Co_4(CO)_{12}$, it is reasonable to assume that the metal atoms in these hydrides have a tetrahedral arrangement. On the basis of i.r. and n.m.r. data, the structure

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

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

[109] R. G. Hayter, *Inorg. Chem.*, 1963, **2**, 1031.

[110] R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2576.

[111] R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1967, **89**, 4323.

[112] L. F. Dahl and J. F. Blount, *Inorg. Chem.*, 1965, **4**, 1373.

[113] F. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *Chem. Comm.*, 1968, 593.

[114] P. Chini, L. Colli, and M. Peraldo, *Gazzetta*, 1960, **90**, 1005.

[115] M. J. Mays and R. N. F. Simpson, *J. Chem. Soc.* (*A*), 1968, 1444.

[116] M. J. Mays and R. N. F. Simpson, *Chem. Comm.*, 1967, 1024.

[117] B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2856.

[118] J. Knight and M. J. Mays, *Chem. and Ind.*, 1968, 1159.

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

[120] B. F. G. Johnson, R. D. Johnston, J. Lewis, I. G. Williams, and P. A. Kilty, *Chem. Comm.*, 1968, 861.

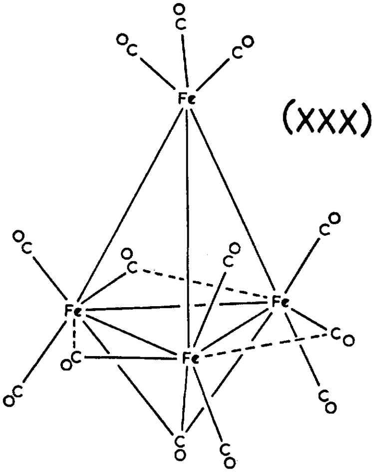
[121] G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1969, 797.

[122] W. Hieber and G. Brendel, *Z. anorg. Chem.*, 1957, **289**, 324.

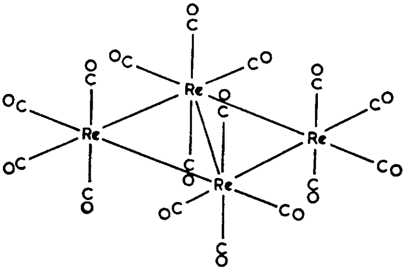
[123] W. Hieber and H. Beutner, *Z. Naturforsch.*, 1962, **176**, 211.

[124] W. Hieber and R. Werner, *Chem. Ber.*, 1957, **90**, 286.

of $H_2Ru_4(CO)_{13}$ may be similar to that of the anion $[Fe_4(CO)_{13}]^{2-}$ (XXX) (see later) but with two Ru(H)Ru bridges.[117] Similar bridge bonding probably occurs in the α- and β- forms of $H_4Ru_4(CO)_{12}$. Mass spectral, i.r., and n.m.r. studies[119,121] suggest that the hydrides $Os_3(CO)_{10}(H)(X)$ (X = H, OH, or OMe) and $HRu_3(CO)_{10}(SR)$ are structurally similar to $Fe_3(CO)_{12}$ (V) with H and X, and H and SR groups, respectively, replacing the two bridging carbonyl groups. Such a structure has recently been confirmed for $Os_3(CO)_{10}(OMe)_2$ and $H_2Os_3(CO)_{10}$.[125]



(XXX)[132]



(XXXI)[133]

(ii) *Anionic and Cationic Metal Carbonyls.* It is generally assumed that the structures of the mononuclear carbonyl anions and cations are the same as those of isoelectronic neutral carbonyls, and i.r. and Raman studies support this view. Thus $Fe(CO)_4{}^{2-}$, $Co(CO)_4{}^{-}$, and $Ni(CO)_4$ all possess a single i.r.-active carbonyl stretching band consistent with a tetrahedral structure.[126,127] Moreover,

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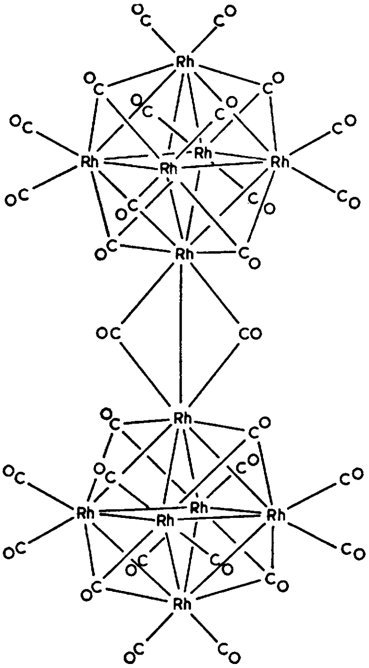
[125] R. Mason and V. Duckworth, to be published.

[126] W. F. Edgell, J. Huff, J. Thomas, H. Lehmann, G. Angell, and G. Astata, *J. Amer. Chem. Soc.*, 1960, **82**, 1254.

[127] W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Amer. Chem. Soc.*, 1965, **87**, 3080.



(XXXII)[135]

the spectra of the species $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ are all similar suggesting the same octahedral symmetry.[128]

Trinuclear anions $[MFe_2(CO)_{12}]^-$ (M = Mn, Tc, or Re) have recently been discovered.[129–131] Their structures are of particular interest. On the basis of i.r. studies, it appears likely that they are closely related to that of $Fe_3(CO)_{12}$ (V) with Mn, Tc, or Re atoms replacing the iron atom of the apical $Fe(CO)_4$ group. As with $Fe_3(CO)_{12}$ (see earlier), the carbonyl bands of the anions in the bridging region are of relatively weak intensity.

X-Ray work on carbonyl anions and cations has been rather limited as yet; however very important stereochemical information has been obtained by a three-dimensional single-crystal *X*-ray examination of the salt $[py_6Fe]$ $[Fe_4(CO_{13}]$.[132] In the anion (XXX) a carbonyl group triply bridges the three basal iron atoms. Perhaps the most interesting feature of the structure is the

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[128] E. W. Abel, R.A.N. McLean, S. P. Tyfield, P. S. Braterman, A. P. Walker, and P. J. Hendra, *J. Mol. Spectroscopy*, 1969, **30**, 29.

[129] U. Anders and W. A. G. Graham, *Chem. Comm.*, 1966, 291.

[130] G. O. Evans, J. P. Hargaden, and R. K. Sheline, *Chem. Comm.*, 1967, 186.

[131] M. W. Lindauer, G. O. Evans, and R. K. Sheline, *Inorg. Chem.*, 1968, **7**, 1249.

[132] R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 4847.

weak interaction between the three 'terminal' carbonyl groups which are in the Fe_3 basal plane and the adjacent iron atoms so that these carbonyl groups are slightly deformed towards a doubly bridging configuration. The deviation from linearity leads to three Fe—C—O bond angles (*ca.* 155°) which are significantly smaller than the other nine terminal Fe—C—O angles of which the smallest is 167°. Moreover, the average distance from each of the three basal carbonyl carbon atoms to the second basal iron atom is only 2·28 Å, which is to be contrasted with the other closest intramolecular non-bonding Fe—CO distances of, on average, 2·74 Å. Similar deformations of terminal carbonyl groups towards doubly bridging situations have been observed in other structures. These results confirm that carbonyl groups in metal carbonyl complexes may take on a number of configurations which are intermediate between terminal and symmetrically doubly bridging cases. In (XXX) the basal iron atoms are either seven- or eight- co-ordinated depending on whether the weak iron–carbon interaction is considered in determining the co-ordination number.

Other novel anions, the structures of which have been elucidated by *X*-ray crystallographic studies, are $[Re_4(CO)_{16}]^{2-}$ (XXXI)[133] and $[H_2Re_3(CO)_{12}]^-$.[134] The rhenium atom skeleton in (XXXI) consists of two fused coplanar approximately equilateral triangles. Each of the observed rhenium–rhenium bond lengths (2·956—3·024 Å) is close to the value (3·02 Å) found for the Re—Re distance in $Re_2(CO)_{10}$.[37] Each rhenium atom is bonded to four terminal carbonyl groups, two of which are approximately axial and two approximately equatorial. It should be noted that the two doubly-bridging rhenium atoms are octahedrally co-ordinated, whereas the two triply-bridging rhenium atoms are associated with a distorted pentagonal–bipyramidal stereochemistry. It is not uncommon in the polynuclear metal carbonyl structures to have metal atoms with different co-ordination numbers [see (VI) or (XIX)], and sometimes even the assignment of co-ordination numbers to particular atoms is difficult [*e.g.* (XXX)]. The structure of $[H_2Re_3(CO)_{12}]^-$ is based on three rhenium atoms defining an isosceles triangle. Four terminal CO groups are bonded to each rhenium atom; two occupy axial sites and two occupy equatorial sites. Although hydrogen atoms were not detected by the *X*-ray study, there is evidence that they form two ReHRe bridges in the Re_3 plane. The ^1H n.m.r. spectrum shows a signal at τ 27·2.[134]

It is likely that the chemistry of polynuclear carbonyl anions will be considerably extended in the next few years by the elucidation of the structures of more complex species by *X*-ray methods, and this field may well develop in the manner of the polyhedral borane anions. Thus an anion $[Rh_{12}(CO)_{30}]^{2-}$ has recently been prepared and the structure (XXXII) established by *X*-ray analysis.[135] The structure is related to that of $Rh_6(CO)_{16}$ (VIII) by substitution of two

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[133] M. R. Churchill, and R. Bau, *Inorg. Chem.*, 1968, **7**, 2606.

[134] M. R. Churchill, P. M. Bird, H. D. Kaesz, R. Bau, and B. Fontal. *J. Amer. Chem. Soc.*, 1968, **90**, 7135.

[135] P. Chini, V. Albano, and S. Martinengo, 'Progress in Co-ordination Chemistry,' ed. M. Cais, Elsevier, Amsterdam, 1968, p. 211.

terminal carbon monoxide groups on each octahedral cluster with two bridging carbon monoxide groups. Deviation from the EAN rule is maintained but the bonding can be satisfactorily accounted for in molecular orbital terms.

The probable structures of two cationic carbonyl complexes are worthy of note. Cobalt forms a cluster cation $\{[C_6H_6Co]_3(CO)_2\}^+$ the structure of which is almost certainly similar to (XV).[136,137] It will be evident to the reader that structures in which carbonyl groups bridge three metal atoms are now fairly common. A remarkable di-iron carbonyl azide cation $[Fe_2(CO)_4(N_3)_2]^{2+}$ has been reported.[138] A planar (D_{2h}) structure has been proposed, the azido-groups being bridging and the carbonyl groups terminal. The cation has the highest recorded paramagnetism (5·29 B.M.) for a metal carbonyl derivative.

(iii) *Metal Carbonyl Halides.* The halogeno-metal carbonyls for which complete structures are known from *X*-ray work are $[Rh(CO)_2Cl]_2$ (XXXIII),[139] $[Mn(CO)_4Br]_2$ (XXXIV),[140] $[Ru(CO)_3Br_2]_2$ (XXXV),[141] and $Ru(CO)_4I_2$.[142] The latter compound has an octahedral arrangement of ligands with the iodine atoms *cis* to one another. Structures (XXXIII)—(XXXV) all involve halogen bridges. The EAN formalism is obeyed, assuming the bridging halogen atoms act as three electron donors. Structure (XXXIII) contains an intramolecular metal–metal bond [compare (II)]. but the rhodium atoms are in actuality in an essentially octahedral environment since in the crystal the dimeric $[Rh(CO)_2Cl]_2$ units are joined by intermolecular rhodium–rhodium bonds (3·31 Å).

I.r. spectroscopy has played an important part in determining the molecular symmetry of a number of metal carbonyl halides. This is also true of the structures of many organometal carbonyls and Lewis base complexes of the carbonyls discussed later. The number of i.r.-active CO stretching bands is governed by the overall molecular symmetry of a carbonyl complex and hence a study of the region around 2000 cm.$^{-1}$ can often provide information about the relative positions of the ligands in the co-ordination sphere of the metal. It has to be emphasised, however, that one sometimes observes coincidences of bands which should be separated, and that certain solvents tend to lead to broadening of bands so that other bands that should be seen are masked. Moreover, in arriving at the number of i.r.-active carbonyl stretching bands expected for a particular symmetry it is assumed that the ligands are spherically symmetric. This is generally not the case and sometimes the asymmetry of the ligand is sufficient to reduce the overall molecular symmetry so that additional bands appear. Bearing these pitfalls in mind, much structural information can be obtained about the species present in solution. Thus a monosubstituted pentacarbonyl octahedral complex such as $ClMn(CO)_5$ has C_{4v} symmetry. Group

[136] P. Chini and R. Ercoli, *Gazzetta*, 1958, **88**, 1170.

[137] E. O. Fischer and O. Beckert, *Angew. Chem.*, 1958, **70**, 744.

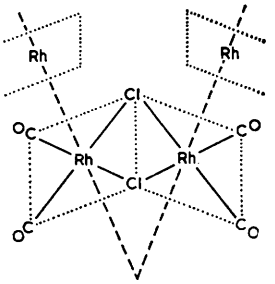
[138] G. Lange and K. Dehnicke, *Z. anorg. Chem.*, 1966, **344**, 167.

[139] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1761.

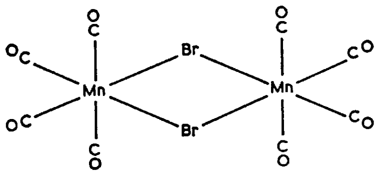
[140] L. F. Dahl and C. H. Wei, *Acta. Cryst.*, 1963, **16**, 611.

[141] S. Merlino and G. Montagnoli, *Acta. Cryst.*, 1968, **324**, 424.

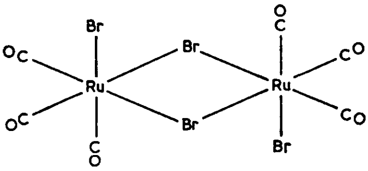
[142] L. F. Dahl and D. L. Wampler, *Acta. Cryst.*, 1962, **15**, 946.



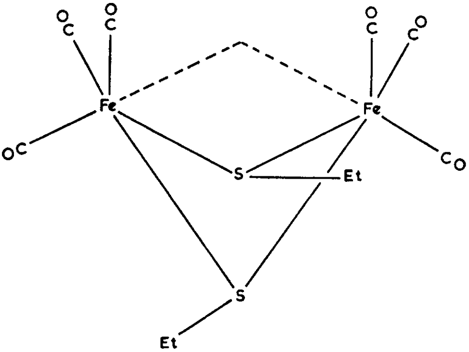
(XXXIII)[139]



(XXXIV)[40]



(XXXV)[141]



(XXXVI)[49]

theory shows that the carbonyl vibrations are of type E, $2A_1$, and B_1, and that the latter is not i.r.-active.[143,144] In accord with this prediction the spectrum of $ClMn(CO)_5$ shows bands at 2139, 2055, and 1999 cm.$^{-1}$, assigned

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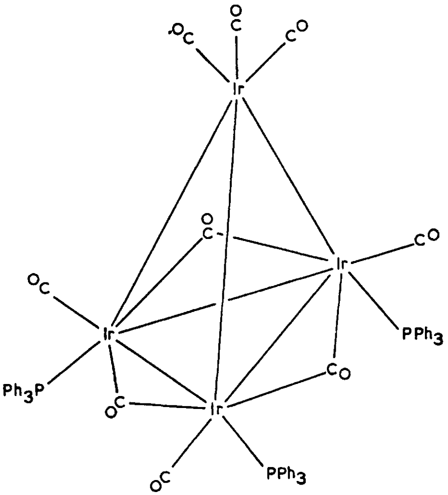
[143] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.
[144] M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectroscopy*, 1962, **9**, 310.



(XXXVII)[162]

to $A_1^{(1)}$, E, and $A_1^{(2)}$ vibration modes respectively.[145] However, there are many subtleties in the spectra of even such relatively simple molecules as the pentacarbonyl halides.[146] For example, in the spectrum of $ClRe(CO)_5$ the high energy A_1 mode is barely detectable.[144] Tetracarbonyl halide dimers of Mn, Tc, and Re, such as (XXIV), show three strong absorptions and a relatively weak high-energy band in the carbonyl stretching region.[147] This is in accord with a D_{2h} halogen bridging structure (XXXIII). As mentioned above, in the crystal, $I_2Ru(CO)_4$ has a *cis*-I_2Ru arrangement. Such a structure (C_{2v}) should give rise to four i.r.-active carbonyl stretching bands. In fact five bands are observed, albeit one is very weak.[148] The band pattern may be due to the presence of both the *cis*- and the *trans*-isomers in solution. Interestingly, the spectrum of $Br_2Ru(CO)_4$ shows four bands only, in agreement with C_{2v} symmetry. The halogeno-derivatives $X_2Fe(CO)_4$ show four stretching vibrations between 2100 and 2045 cm.$^{-1}$.[149] Noack,[150] however, showed that the spectrum of $I_2Fe(CO)_4$ changed with time under irradiation of light from the spectrometer and a new band appeared suggesting isomerisation. Irradiation of *cis*-$I_2Fe(CO)_4$ was subsequently shown to produce the *trans*-isomer.[151]

Examination[152] of the vibrational spectra of the polynuclear halides

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[145] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc.*, 1967, **89**, 2844.
[146] P. S. Braterman, R. Bau, and H. D. Kaesz, *Inorg. Chem.*, 1967, **6**, 2097.
[147] M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, 1963, **2**, 158.
[148] E. R. Corey, M. V. Evans, and L. F. Dahl, *J. Inorg. Nuclear Chem.*, 1962, **24**, 926.
[149] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1961, 2582.
[150] K. Noack, *Helv. Chim. Acta.*, 1962, **45**, 1847.
[151] M. Pankowski and M. Bigorgne, *Compt. rend.*, 1966, **263**, 239.
[152] D. Hartley, P. A. Kilty, and M. J. Ware, *Chem. Comm.*, 1968, 493.

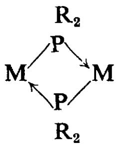
$Os_3(CO)_{12}X_2$ (X = Cl, Br, or I) has provided strong evidence for a linear XOs_3X skeleton.

(iv) *'Lewis Base' Complexes of the Metal Carbonyls.* Countless derivatives of the metal carbonyls are known wherein carbon monoxide groups are associated with other electron-pair donating ligands. Most of these complexes involve co-ordinate bonds from atoms of the fifth or sixth main groups of the Periodic Table, such as for example, tertiary phosphines or dialkyl sulphides.

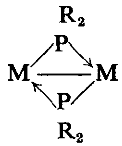
The metal carbonyl nitrosyls can be regarded as a special class of Lewis base complex, the nitrosyl group being a three-electron donor. Alternatively, one can visualise the bonding as involving transfer of an electron from nitric oxide to the metal atom, with a consequential decrease of one unit in oxidation state, followed by donation of an electron pair from the nitrosyl cation NO^+ (isoelectronic with CO) to the metal through the nitrogen atom. Thus one has a related series of isoelectronic carbonyl-nitrosyls $Ni(CO)_4$, $Co(NO)(CO)_3$, $Fe(NO)_2(CO)_2$, and $Mn(NO)_3CO$. As with terminal metal carbonyl groups, back donation to the ligand is possible through resonance: $M^{-}\leftarrow N\equiv O^{+} \longleftrightarrow M{=}N{=}O$, with a corresponding effect on nitrosyl stretching frequencies in the i.r.

No *X*-ray studies have been reported for the *pseudo*-nickel carbonyl nitrosyls, but an early electron diffraction study indicated a tetrahedral arrangement of CO and NO groups around the metal atoms in $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$.[153] A manganese nitrosyl $Mn(NO)(CO)_4$, isoelectronic with pentacarbonyliron, is now known and its i.r. spectrum[154] is consistent with a trigonal bipyramidal structure having the NO group at an apex. An *X*-ray study[155] of a triphenylphosphine derivative $(Ph_3P)_2Mn(NO)(CO)_2$ reveals a trigonal bipyramidal structure with co-planar nitrosyl and carbonyl groups and the two triphenylphosphine groups at the apices of the trigonal bipyramid.

The groups R_2P, R_2As, RS, and RSe function as three-electron donors when they are bridging ligands, as in $[EtSFe(CO)_3]_2$ (XXXVI).[49] The two iron atoms and two sulphur atoms adopt a butterfly-like arrangement, and the structure is very like that of (XXV). The iron atoms are in essentially an octahedral environment if the metal–metal bond is regarded as being bent by being formed by overlap of a d^2sp^3 hybrid from each iron. Isomers of (XXXVI) are possible according to whether the alkyl groups are *syn* or *anti* to one another. Two stereoisomers of $[MeSFe(CO)_3]_2$ have been characterised.[156] Many carbonyl complexes are known in which two halves of a molecule are held together with two R_2P or R_2As bridges: *e.g.*



or



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[153] L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.*, 1937, **33**, 1233.

[154] P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 2593.

[155] J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 1575.

[156] R. B. King, *J. Amer. Chem. Soc.*, 1962, **84**, 2460.

The intermetallic distances depend on whether or not a metal–metal bond is present. Conformational differences can arise according to whether or not the two halves of the molecule are folded along the P . . . . P line. The molecular structure of $Et_3P(OC)_3\overline{Mo(PMe_2)_2Mo}(CO)_3PEt_3$ has been determined by *X*-ray methods.[157] The two metal atoms are linked by a planar di-μ-phosphido-bridge, and there is a metal–metal bond 3·09 Å long. This may be compared with a Mo—Mo distance of 3·22 Å in (XVIII). It is a general feature of this field that metal–metal bonds unsupported by bridging ligands are longer than those where such ligands are present. Moreover, in the di-μ-phosphido-molybdenum complex the $Mo\widehat{P}Mo$ angles are reduced to 78° and the $P\widehat{Mo}P$ angles are increased to 102° to accommodate the Mo—Mo distance. Although a single-crystal *X*-ray study has not been carried out on $[Me_2PFe(CO)_3]_2$ it is very probable that the $(PFe)_2$ bridging system has the 'butterfly' configuration of (XXXVI), to accommodate the iron–iron bond. Treatment of $[Me_2PFe(CO)_3]_2$ with one mole of iodine cleaves the metal–metal bond and affords $(OC)_3(I)Fe(PMe_2)_2Fe(I)(CO)_3$. An *X*-ray study[158] reveals a centrosymmetrical dioctahedral structure with the iodine atoms *trans* to one another and lying above and below a planar di-μ-phosphido-bridge. The iron–iron distance (3·59 Å) is outside the range of possible metal–metal interactions.

The structures of the complexes $(OC)_3NiPPh_2{\cdot}PPh_2Ni(CO)_3$[159] and $(OC)_4FePMe_2{\cdot}PMe_2Fe(CO)_4$[160] have also been determined by *X*-ray diffraction. The molecules are centrosymmetric and have a staggered conformation of substituents about the metal–phosphorus and phosphorus–phosphorus bonds, thereby producing a condition of minimum steric interaction. A further binuclear-metal phosphine complex with a structure firmly established by *X*-ray is $[Et_3PMn(CO)_4]_2$. As mentioned on page 334, the molecular configuration strongly resembles that of $Mn_2(CO)_{10}$, with the carbonyl groups *trans* to the metal–metal bond replaced by two triethylphosphine ligands.[38]

The molecular structures of some polynuclear metal-atom carbonyltriphenylphosphine complexes are worthy of note. Two structural isomers of $Ph_3PFe_3(CO)_{11}$ have been identified by *X*-ray crystallographic work.[161] Both isomers occur in the unit cell and have structures similar to that of $Fe_3(CO)_{12}$ (V); in one isomer one terminal carbonyl group of the bridging $Fe(CO)_4$ unit is replaced by the phosphine, and in the other isomer a terminal carbonyl group of the $Fe_2(CO)_8$ fragment is substituted by the phosphine. Of particular interest is the asymmetry of the bridging carbonyl groups of both isomers with the

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[157] R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 1735.

[158] G. R. Davies, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 1251.

[159] R. H. B. Mais, P. G. Owston, D. T. Thompson, and A. M. Wood, *J. Chem. Soc.* (*A*), 1967, 144.

[160] J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 622.

[161] D. J. Dahm and R. A. Jacobson, *J. Amer. Chem. Soc.*, 1968, **90**, 5106.

longer Fe—C distances averaging 1·98 Å and the shorter 1·81 Å. There is evidence for a similar asymmetry in structure (V).

The structures of the polynuclear iridium compounds $(Ph_3P)_2Ir_4(CO)_{10}$ and $(Ph_3P)_3Ir_4(CO)_9$ have also been determined.[162] Both structures are based on a tetrahedron of iridium atoms with edges 2·73 Å in length. Three carbonyl groups are bridged to basal iridium atoms which also carry the triphenylphosphine substituents (XXXVII). The presence of the bridging carbonyl groups between a third-row transition element is unusual, but is evidently a real possibility when the metal–metal distances are below *ca.* 2·8 Å.

The i.r. spectrum is doubtless the most widely reported property of the Lewis base carbonyl complexes. As mentioned previously, the number of i.r.-active CO stretching bands observed in the spectrum of a complex is related to its molecular symmetry. Structural information about binuclear or even polynuclear complexes can often be obtained by assuming that coupling between parts of such molecules can be neglected, so that selection rules based upon local symmetry may be applied. In order to obtain CO stretching force constants, correct band assignments must be made. This has been done by considering relative band positions and intensities, by taking Raman spectra, and by using 'non-rigorous' energy factored secular equations to obtain consistent sets of force constants. The reader is referred to two papers by Orgel[143] and Bigorgne,[163] and to several papers by Bigorgne[164] and by Cotton[165] and their respective co-workers for analysis of the spectra of numerous phosphine and other Lewis-base substituted carbonyl compounds. The subject has recently been thoroughly reviewed.[166] The information in Table 6 indicates how band patterns may be used to deduce molecular symmetry.

In a series of papers[167] the spectra of molecules belonging to the point groups C_{4v} [*e.g.*, $Me_3PMo(CO)_5$], C_{3v} [*e.g.*, $Et_3PFe(CO)_4$], C_{2v} (*e.g.* $[C_6F_5SMn(CO)_4]_2$), and C_s *e.g.*, $[(MeO)_3P(dipy)Mo(CO)_3]$ have been analysed. Molecules $LM(CO)_5$ [M = Cr, Mo, or W with L = R_3E (E = P, As, Sb, or Bi; R = Ph, Me, MeO, Cl, or F)] belonging to the point group C_{4v} exhibit three i.r. active bands ($A_1^{(1)}$, $A_1^{(2)}$, and E modes). Often, however a weak fourth band (B_1) is observed in the spectra of such complexes. This is because $LM(CO)_5$ complexes arise from

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[162] V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Comm.*, 1967, 730.

[163] M. Bigorgne, *Bull. Soc. chim. France*, 1960, 1986.

[164] (*a*) R. Poilblanc and M. Bigorgne, *Bull. Soc. chim. France*, 1962, 1301; (*b*) R. Poilblanc and M. Bigorgne, *J. Organometallic Chem.*, 1966 **5**, 93; (*c*) D. Benlian and M. Bigorgne, *Bull. Soc. chim. France*, 1963, 1583; (*d*) M. Bigorgne, *J. Organometallic Chem.*, 1963, **1**, 101; (*e*) A. Reckziegel and M. Bigorgne, *J. Organometallic Chem.*, 1965, **3**, 341; (*f*) A. Reckziegel and M. Bigorgne, *Compt. rend.*, 1964, **258**, 4065; (*g*) M. Bigorgne and J. Bénard, *Rev. Chim, minérale*, 1966, **3**, 831; (*h*) J. B. P. Tripathi and M. Bigorgne, *J. Organometallic Chem.*, 1967, **9**, 307.

[165] (*a*) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432; (*b*) F. A. Cotton and C. S. Kraihanzel, *Inorg. Chem.*, 1963, **2**, 533; (*c*) F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

[166] L. M. Bower and M. H. B. Stiddard, *Inorg. Chim. Acta.*, 1967, **1**, 231.

[167] (*a*) J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1195; (*b*) J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *ibid.*, p. 1199; (*c*) E. W. Abel, J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *ibid.*, p. 1203; (*d*) J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *ibid.*, p. 1208.

Table 6 *Infrared active carbonyl vibrations in octahedral and in trigonal bipyramidal complexes*[a]

	Octahedral[b]				*Trigonal bipyramidal*[c]		
Structure	Symmetry	Modes	Number	Structure	Symmetry	Modes	Number
$[M(CO)_5L]$	C_{4v}	$2A_1 + E$	3	$[M(CO)_4L]$			
cis-$[M(CO)_4L_2]$	C_{2v}	$2A_1 + B_1 + B_2$	4	Axial trigonal			
				bipyramid	C_{3v}	$2A_1 + E$	3
trans-$[M(CO)_4L_2]$	D_{4h}	E_u	1	Equatorial trigonal			
				bipyramid	C_{2v}	$2A_1 + B_1 + B_2$	4
cis-$[M(CO)_3L_3]$	C_{3v}	$A_1 + E$	2	$[M(CO)_3L_2]$			
trans-$[M(CO)_3L_3]$	C_{2v}	$2A_1 + B_1$	3	*trans*-trigonal			
				bipyramid	D_{3h}	E'	1
cis-$[M(CO)_2L_4]$	C_{2v}	$A_1 + B_1$	2	*cis*-trigonal	$\left\{ C_{2v} \right.$	$2A_1 + B_1$	3
trans-$[M(CO)_2L_4]$	D_{4h}	A_{2u}	1	bipyramid	$\left. C_s \right.$	$2A' + A''$	3
$[M(CO)L_5]$	C_{4v}	A_1	1	$[M(CO)_2L_3]$			
				trans-trigonal			
				bipyramid	D_3	A_2''	1
				cis-trigonal	$\left\{ C_{2v} \right.$	$A_1 + B_1$	2
				bipyramid	C_s	$A' + A''$	2
				$[M(CO)L_4]$	$\left\{ C_{2v} \right.$	A_1	1
					C_{3v}	A_1	1

[a] For a more complete summary see T. A. Manuel, *Adv. Organometallic Chem.*, 1965, **3**, 181. [b] For a thorough review see G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 1. Secular equations are given by F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432. [c] For a complete treatment see J. B. P. Tripathi and M. Bigorgne, *J. Organometallic Chem.*, 1967, **9**, 307; and references cited therein; see also J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1199.

fusion of a C_{3v} unit (R_3E) with a C_{4v} unit [$M(CO)_5$] so that the overall molecular symmetry is reduced to C_s, and a 'pseudo-B_1' mode which is not i.r.-active for vigorous C_{4v} symmetry gains some intensity.[165a,167a] Similarly, the presence of different R groups in $R_3EM(CO)_4$ can lower the symmetry from C_{3v} to C_s and a fourth i.r.-active band can appear.[167b] Although binuclear complexes [$LM(CO)_4$]$_2$ have a D_{2h} molecular configuration, they may also be treated according to the local symmetry (C_{2v}) of the metal atoms M. Hence there are four i.r.-active modes B_1, B_2, $A_1^{(1)}$, and $A_1^{(2)}$,[167c] for example 1995, 2045, 2100, and 2020 cm.$^{-1}$ for the μ-SC_6F_5 bridged complex [$C_6F_5SMn(CO)_4$]$_2$. Sometimes, however, the spectra of [$LM(CO)_4$]$_2$ complexes show more than four bands, in which case weak bands, as with other complexes of different symmetry, may be due to ^{13}CO stretching modes. The bridged species [$Me_2PMn(CO)_4$]$_2$, on the other hand, shows only three bands in 1,2-dichloroethane.[168] However, this solvent is known to affect band resolution, and in cyclohexane the spectrum of [$Ph_2PMn(CO)_4$]$_2$ shows the expected four bands.[169] From the foregoing it is evident that assignments of molecular symmetry on the basis of the number of observed carbonyl stretching modes in the i.r. is not always clear cut.

(v) *Organometal Carbonyls.* We have referred previously to the cyclopentadienyl-metal carbonyls which are representatives of this class of complex. Countless organometal carbonyls have been discovered in the last decade. One useful way of classifying these complexes is according to the number of electrons which are formally considered as being donated to the metal by the ligand,[68] *viz.*:

Number of electrons	*Class*	*Example*
1	alkyl	$MeMn(CO)_5$
2	alkene	$[C_2H_4Mn(CO)_5]^+$
3	allyl	π-$C_3H_5Mn(CO)_4$
4	diene	π-$C_6H_8Mn(CO)_3H$
5	cyclopentadienyl	π-$C_5H_5Mn(CO)_3$
6	arene	$[\pi$-$C_6H_6Mn(CO)_3]^+$

Since this review is concerned with the chemistry of the metal carbonyls rather than with organo-derivatives of the transition metals and, moreover, since the main interest in the structures of the organometal carbonyls is in the stereochemistry of the organic moieties, the reader is referred elsewhere for a survey of this topic.[68,170] Nevertheless, several structures are important in the present context, both in demonstrating relationships with parent metal carbonyls and also in illustrating the ability of metal carbonyl groups in stabilising unusual organic ligands.

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[168] R. G. Hayter, *J. Amer. Chem. Soc.*, 1964, **86**, 823.
[169] E. W. Abel and I. H. Sabherwal, *J. Organometallic Chem.*, 1967, **10**, 491.
[170] M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, 1967, **5**, 93.

Structures (XXXVIII)—(XLII),[171–175] established by *X*-ray diffraction methods, involve the attachment of a novel ligand to a metal carbonyl group. There is currently considerable interest in the structures of carbonyl–carbene–metal complexes.[176–179] The structure of (XLIII) has been determined by electron diffraction,[180] and that of the phenyl derivative $[\pi\text{-}(CH_2)_2C(CHPh)]Fe(CO)_3$ by *X*-ray diffraction.[181] Many other examples could be quoted of highly reactive or often even intrinsically unstable organic species having been stabilised by co-ordination to a metal carbonyl group.

Structures (XLIV)—(XLIX)[182–187] are illustrative of binuclear complexes wherein an organic group bridges two metal atoms. The relationship between structures (XLIV)—(XLVI) and that of $Co_2(CO)_8$ (II) will be obvious. One can regard the bridging ligand in (XLVII) as either a substituted ethylene or perhaps better as a carbene.[185] Complex (XLVIII)[186] is of interest on account of the bridging isocyanide ligand. Compound (XLIX)[187] is one of many known ferracyclopentadiene complexes. The iron–iron distance (2·49 Å) is similar to that found in $Fe_2(CO)_9$ (III), and in order for the EAN formalism to be obeyed it is necessary to regard the π-diene-bonded iron atom as donating an electron-pair to the iron atom of the heterocyclic ring. A further novelty of the structure arises in the apparent interaction between the ring iron atom and the carbonyl group in closest proximity bonded to the other iron atom. This is exemplified by an Fe—C distance of 2·48 Å. Moreover, this carbonyl group is terminally bonded to its iron atom in such a way as to give an $\mathrm{Fe\hat{C}O}$ angle of 168° [see (XXX)]. A number of other organoiron carbonyl complexes are formed from reactions between acetylenes and iron carbonyls. Several of these compounds are binuclear or trinuclear. Examples of the latter situation are structures (L)—(LII), all three confirmed by *X*-ray diffraction studies.[188,189] Complexes (LI) and (LII) are isomeric and the former is converted into the latter when boiled in benzene. Moreover (LI) is formed from (L) by addition of diphenyl-

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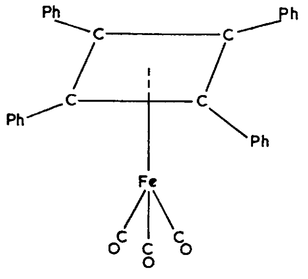
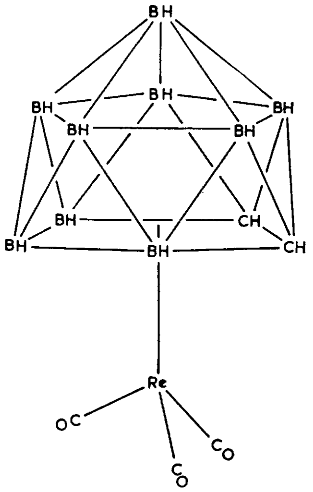
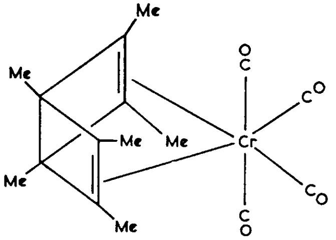
[171] R. P. Dodge and V. Schomaker, *Acta Cryst.*, 1965. **18**, 614.
[172] A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, 1966, **5**, 1189.
[173] G. Huttner and O. S. Mills, *Chem. Comm.*, 1968, 344.
[174] R. J. Doedens, *Chem. Comm.*, 1968, 1271.
[175] O. S. Mills and A. D. Redhouse, *Chem. Comm.*, 1966, 814.
[176] O. S. Mills and A. D. Redhouse, *Angew. Chem. Internat. Edn.*, 1965, **4**, 1082.
[177] P. E. Baikie, E. O. Fischer, and O. S. Mills, *Chem. Comm.*, 1967, 1199.
[178] E. O. Fischer, V. Kiener, D. St. P. Bunbury, E. Frank, P. F. Lindley, and O. S. Mills, *Chem. Comm.*, 1968, 1378.
[179] J. A. Connor and O. S. Mills, *J. Chem. Soc.* (*A*), 1969, 334.
[180] A. Almenningen, A. Haaland, and K. Wahl, *Chem. Comm.*, 1968, 1027.
[181] M. R. Churchill and K. Gold, *Chem. Comm.*, 1968, 693.
[182] W. G. Sly, *J. Amer. Chem. Soc.*, 1959, **81**, 18.
[183] O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 1959, 156; *Inorg. Chim. Acta.*, 1967, **1**, 61.
[184] N. A. Bailey and R. Mason, *J. Chem. Soc.* (*A*), 1968, 1293.
[185] O. S. Mills and A. D. Redhouse, *J. Chem. Soc.* (*A*), 1968, 1282.
[186] K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Comm.*, 1965, 181.
[187] A. A. Hock and O. S. Mills, *Acta. Cryst.*, 1961, **14**, 139.
[188] J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Amer. Chem. Soc.*, 1966, **88**, 292.
[189] R. P. Dodge and V. Schomaker, *J. Organometallic Chem.*, 1965, **3**, 274.



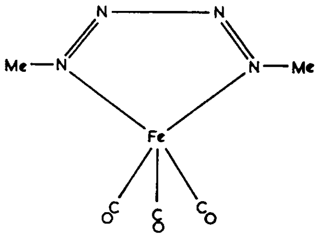
(XXXVIII)[171]



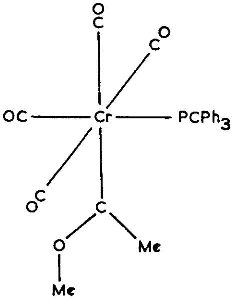
(XXXIX)[172]



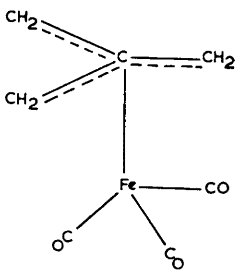
(XL)[173]



(XLI)[174]



(XLII)[175]



(XLIII)[180]

acetylene and loss of CO. The reader is referred to Hübel's review[190] for a survey of many other organometal complexes derived from acetylenes.

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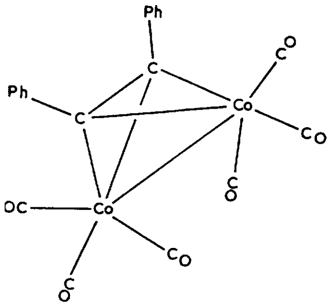
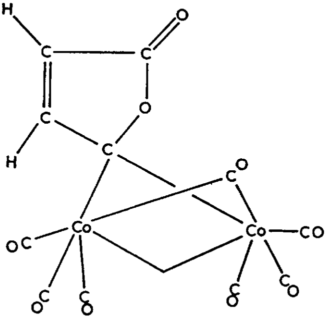
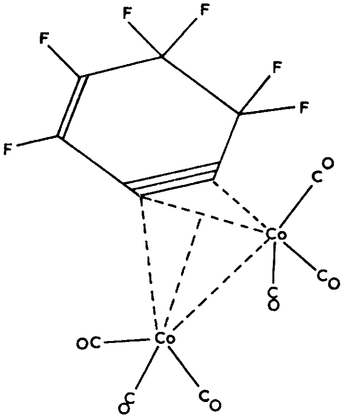
[190] W. Hübel, 'Organic Syntheses *via* Metal Carbonyls,' eds., I. Wender and P. Pino, Interscience, New York, Vol. 1, 1968, p. 273.



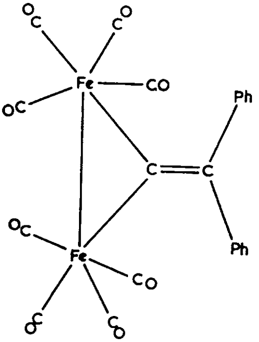
(XLIV)[182]



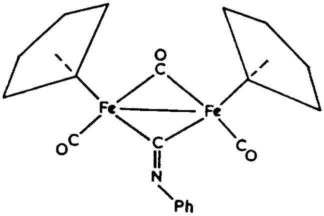
(XLV)[183]



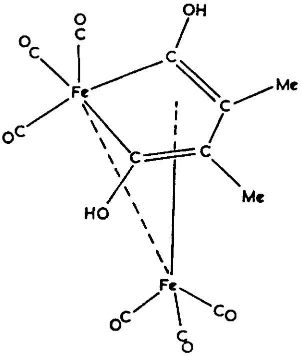
(XLVI)[184]



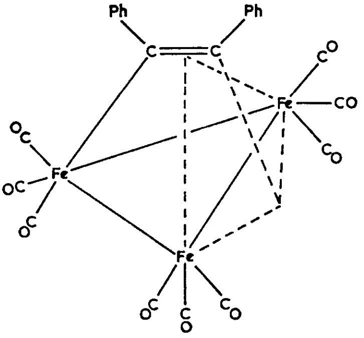
(XLVII)[185]



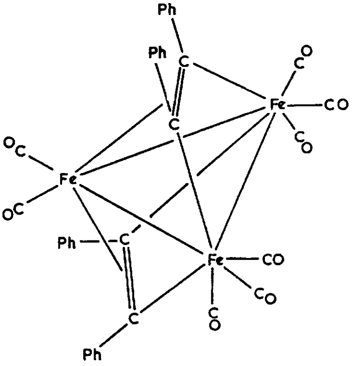
(XLVIII)[185]



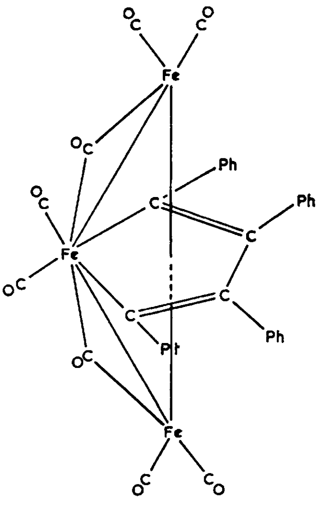
(XLIX)[187]



(L)[188]



(LI)[189]



(LII)[189]

Azulene and its derivatives react with metal carbonyls to form binuclear metal complexes of various kinds.[191] In $C_{10}H_8Fe_2(CO)_5$ the iron atoms of an $Fe(CO)_3$ and an $Fe(CO)_2$ group are bonded to the same side of the hydrocarbon. The carbon atoms from the five-membered ring of azulene form a π-cyclopentadienyl system which is bonded to the $Fe(CO)_2$ group, while three atoms of the seven-membered ring form a π-allyl linkage to the $Fe(CO)_3$ group. There is an iron–iron

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[191] P. H. Bird and M. R. Churchill, *Inorg. Chem.*, 1968, **7**, 349.

bond (2·782 Å).[192] The molecular structure of $C_{10}H_8Mo_2(CO)_6$ is similar in that the hydrocarbon bridges two $Mo(CO)_3$ groups and there is a molybdenum–molybdenum bond.[193,194] However, the $Mo(CO)_3$ group attached to the seven-membered ring is bonded *via* a π-pentadienyl–metal bond.[193] Acenaphthylene(pentacarbonyl)di-iron has a structure like the azulene complex $C_{10}H_8Fe_2(CO)_5$ in that the carbon atoms from the five-membered ring form a π-cyclopentadienyl system to an $Fe(CO)_2$ group, while the second iron atom is associated with three carbonyl groups and bonds to three atoms of the acenaphthylene system *via* a π-allyl linkage. The iron–iron distance of 2·768 Å is indicative of a metal–metal bond in keeping with the observed diamagnetism.[195] There are a number of other examples known of carbonyl derivatives in which a large hydrocarbon ligand bridges and supports a metal–metal bond. Notable among these are cyclo-octatetraene complexes of iron and ruthenium carbonyls, *e.g.*, $C_8H_8Ru_2(CO)_6$, $C_8H_8Fe_2(CO)_5$, and $(C_8H_8)_2Ru_3(CO)_4$.[196]

(vi) *Carbonyl Complexes in which Silicon, Germanium, and Tin, or Post-transition Metals are Ligands.* Compounds in which silicon or a Group IVb metal are bonded to a transition metal are being described in ever-increasing numbers. The first direct physical proof of bonding between metal atoms of different elements in these complexes came from an *X*-ray crystallographic study of $Ph_3SnMn(CO)_4PPh_3$.[197] *X*-ray diffraction studies (Table 7) have revealed several novel molecular structures, for example (LIII)—(LVI).

In $Sn[Fe(CO)_4]_4$ (LIII) there are two iron–iron distances (4·65 and 2·87 Å).[53] The complex is diamagnetic, and, therefore, spin-pairing of electrons on adjacent iron atoms must occur. Whilst it is possible to envisage direct interaction between the pairs of iron atoms 2·87 Å apart, this distance is longer than that found in the majority of complexes that have been examined and in which normal covalent iron–iron bonding occurs, *viz*, 2·46 Å in (III), 2·67 Å for the two equal sides of the isosceles triangle in (V), 2·635 Å in (L), and 2·78 Å in $C_{10}H_8Fe_2(CO)_5$, mentioned in the previous section. In (LIII), however, interaction between the pairs of iron atoms separated by 2·87 Å is possible through two equivalent three-centre bonds involving a vacant *d* orbital on the tin atom. Interestingly, establishment of the iron–iron distance of 2·87 Å leads to a very considerable distortion of the regular tetrahedral valencies of tin. In (LIII) one pair of angles has closed to 69° and the other pair has opened out to 133°. The complex $Me_4Sn_3[Fe(CO)_4]_4$ has a structure[198] related to (LIII) with two Me_2Sn groups formally inserted into the iron–iron bonds.

Structure (LIV) is novel in that it contains an intramolecular Sn—Cl—Mo bridge bond making the co-ordination of molybdenum a capped octahedron

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[192] M. R. Churchill, *Inorg. Chem.*, 1967, **6**, 190.
[193] M. R. Churchill and P. H. Bird, *Chem. Comm.*, 1967, 746.
[194] J. S. McKechnie and I. C. Paul, *Chem. Comm.*, 1967, 747.
[195] M. R. Churchill and J. Wormald, *Chem. Comm.*, 1968, 1597.
[196] F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257.
[197] R. F. Bryan, *Proc. Chem. Soc.*, 1964, 232, *J. Chem. Soc.* (*A*), 1967, 172.
[198] C. J. Fritchie, R. M. Sweet, and R. Schunn, *Inorg. Chem.*, 1967, **6**, 749.

Table 7 *X-ray crystallographic studies of metal carbonyl derivatives of the Group* IVB *elements**

Compound	*Metal–metal distance* (Å)	*Reference*
$Ph_3SnMn(CO)_5$	2·675 ± 0·004	*a*
$Me_3SnMn(CO)_5$	2·674 ± 0·003	*b*
$Ph_3SnMn(CO)_4PPh_3$	2·627 ± 0·01	*c*
$Ph_2Sn[Mn(CO)_5]_2$	2·70 ± 0·01	*d*
$ClSn[Mn(CO)_5]_3$	2·737 ± 0·006	*e*
$Ph_3GeMn(CO)_5$	2·535 ± 0·02	*f*
$Cl_3SiCo(CO)_4$	2·254 ± 0·003	*g*
$Ph_2Sn[Mn(CO)_5][Co(CO)_4]$	Sn—Co 2·66 ± 0·01 Sn—Mn 2·73 ± 0·01	*h*
$MeCl_2SnMo(Cl)(CO)_3bipy$	2·75 ± 0·01	*i*
$Ph_3SnFe(CO)_2(\pi\text{-}C_5H_5)$	2·536 ± 0·003	*j*
$Ph_3PbMo(CO)_3(\pi\text{-}C_5H_5)$	2·90	*k*
$Cl_2Ge[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2·36 ± 0·01	*l*
$Cl_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2·492 ± 0·008	*m*
$Me_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2·603 ± 0·005	*n*
$[\sigma\text{-}C_5H_5]_2Sn\text{-}[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2·56 ± 0·004	*o*
$(ONO)_2Sn\text{-}[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2·56	*p*
$(PhOSO)_2Sn\text{-}[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2·50 ± 0·01	*q*
$Sn[Fe(CO)_4]_4$	Sn—Fe 2·54 ± 0·01 Fe—Fe 2·87 ± 0·01	*r*
$Me_4Sn_3[Fe(CO)_4]_4$	Sn—Fe (interior) 2·747 ± 0·008 Sn—Fe (terminal) 2·625 ± 0·008	*s*
$ClSn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2[Mo(CO)_3(\pi\text{-}C_5H_5)]$	Sn—Fe 2·590 ± 0·007 Sn—Mo 2·891 ± 0·005	*t*
$Me_6Ge_3Fe_2(CO)_6$	Fe—Fe 2·74 ± 0·1 Fe—Ge 2·398 ± 0·005	*u*
$[Me_3SnRu(CO)_3\text{-}\mu\text{-}SnMe_2]_2$	Me_3Sn—Ru 2·686 Me_2Sn—Ru 2·638 & 2·694 Ru—Ru 3·12	*v*
$In_3Br_3Co_4(CO)_5$	In—Co 2·57—2·63 and 2·53—2·58	*w*

Table 7 *Continued*

* An electron diffraction study has been made on the compound $H_3SiCo(CO)_4$ (A. C. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J. Aylett, and J. A. Campbell, *J. Organometallic Chem.*, 1968, **14**, 279). The Co—Si distance is 2·381 ± 0·007 Å.
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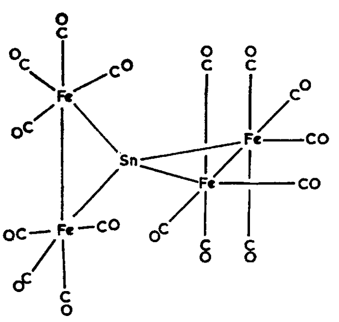
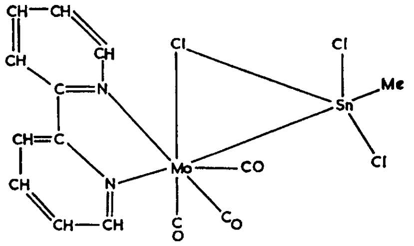
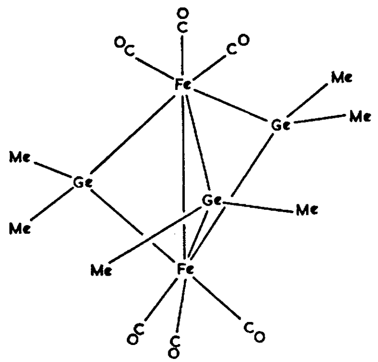


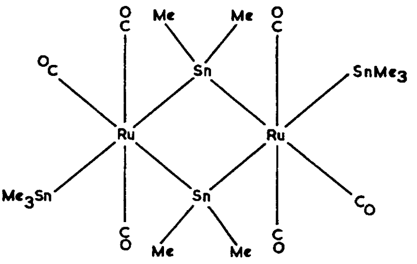
(LIII)[53]



(LIV)[199]



(LV)[200]



(LVI)[201]

comprising an octahedral bipy(OC)$_3$ClMo grouping with the tin atom located over the octahedral face defined by the chlorine atom and two of the carbonyl ligands.[199] Structure (LV)[200] is closely related to that of Fe$_2$(CO)$_9$ (III). The iron–iron bond is 2·74 Å in length, substantially longer than that in (III); but to establish an Fe—Fe distance of 2·74 Å the $\mathrm{Fe\widehat{Ge}Fe}$ angles have had to close to 70°. The complex (LVI)[201] is diamagnetic and spin-pairing of electrons between the ruthenium atoms is required. This could occur *via* the bridging Me$_2$Sn groups or possibly *via* a direct ruthenium–ruthenium bond. The Ru—Ru distance is 3·12 Å compared with 2·85 Å in [Ru(CO)$_4$]$_3$. However, in [Ru(CO)$_3$Br$_2$]$_2$, where no Ru—Ru bond is required for the effective atomic number formalism to be obeyed, the Ru—Ru distance is 3·75 Å.

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Metals of the copper and zinc sub-groups also form bonds to metal carbonyl groups. In $Hg[Co(CO)_4]_2$[202] and $Hg[Co(CO)_3PEt_3]_2$[203] the Co—Hg—Co units are linear, the carbonyl groups perpendicular to the CoHgCo axis being staggered with respect to one another. The equatorial carbonyls are bent by *ca.* 7° towards the mercury atom, as they are towards the gold atom in $Ph_3PAuCo(CO)_4$.[204] Crystal structures of $Zn[Co(CO)_4]_2$,[205] $(BrHg)_2Fe(CO)_4$,[206] $TTAsCuMn(CO)_5$,*[204] $Ph_3PAuW(CO)_3(\pi\text{-}C_5H_5)$,[207] and $(\pi\text{-}C_5H_5)(OC)_2\text{-}CoHgCl_2$[208] have also been determined. In the latter complex, mercury is three-co-ordinate and apparently accepts an electron pair from the cobalt atom of $\pi\text{-}C_5H_5Co(CO)_2$ which acts as a Lewis base. In a subsequent article we shall refer to the metal–metal donor–acceptor interaction in $(\pi\text{-}C_5H_5)_2(H)_2MoMo(CO)_5$.[208]

* TTAs = bis(o-dimethylarsinophenyl)methylarsine.

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