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# $\mu_2$ BRIDGING CARBONYL SYSTEMS IN TRANSITION METAL COMPLEXES

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## CONTENTS

## ABBREVIATIONS

| | |
|---|---|
| acac | acetyl acetonyl |
| Et | ethyl |
| Bu | butyl |
| dam | bis(diphenylarsino)methane |
| dpm | bis(diphenylphosphino)methane |
| dipy | 2,2′ dipyridyl |
| ffars | 1,2 bis(dimethylarsino)tetrafluorocyclobutene |
| Me | methyl |
| Ph | phenyl |

## A. INTRODUCTION

The main aims of this review are to survey the known crystal structures involving $\mu_2$-carbonyl bridges between two transition metal atoms and to emphasise the wide variety of structural features involved. It is now well known that in solution there is usually facile exchange between $\mu_2$ bridging and terminal carbonyl groups in transition metal complexes, which must involve intermediate unsymmetrical bridging structures. The activation energies of these exchange processes in solution are very low and show that intermediate situations between symmetrical bridging and terminal carbonyls are all very similar in energy. Lattice packing forces are at least comparable with, and probably greater than, the exchange activation energies and thus it will emerge that these recently discovered exchange processes have a considerable bearing on the interpretation of many structures in the solid state.

The carbonyl group, CO, is a most versatile ligand. X-ray crystallography has so far shown that it can coordinate to transition metals in the ways shown in Fig. 1 and described below:

(i) Terminal (linear) in which the carbonyl group is associated with only one metal atom. The group is usually linear, but in some cases significant distortion does occur due to steric interactions.

(ii) Symmetrical $\mu_2$ bridging in which the two metal—carbon lengths are not significantly different. The C—O vector is approximately at right angles to the M—M vector, although the M—C—M angle is usually rather small, typically in the range 77—90°. This small angle at carbon has been used as an argument against the so-called 'ketonic' mode of carbonyl bonding [125] and this point will be discussed later.

(iii) Asymmetric $\mu_2$ bridging in which the two metal carbon bond lengths are significantly different, although the C—O vector is still approximately normal to the M—M axis. It has been suggested by Cotton and Troup [40] that asymmetric bridges, which often occur in compensating pairs, represent intermediate stages in the entire range from symmetrically bridged to non-bridged

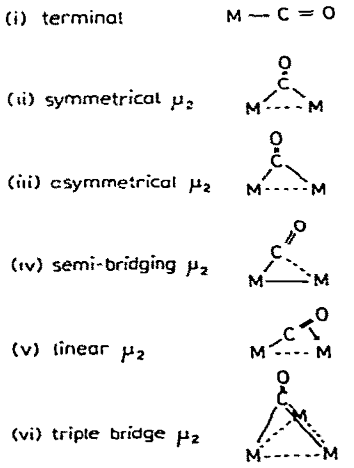


Fig. 1. Modes of coordination of the carbonyl group.

extremes, and that in a particular compound the asymmetry represents a 'stopped action' view of the intermediate stages of concerted opening and closing of pairs of carbonyl bridges. We certainly agree with this general view, but in addition to the cases presented by Cotton to support the above arguments there are many examples of single carbonyl bridges which are asymmetric and also pairs which are not asymmetric to the same extent. We believe all these variations can be rationalised in terms of intra- and inter-molecular packing forces (steric forces) and we shall pursue this line of argument in more detail after the crystal structures themselves have been described.

(iv) Semi-bridging ($\mu_2$) in which the two metal—carbon bonds are now markedly different and the two M—C—O angles are also different such that the C—O vector is no longer at right angles to the metal—metal direction. Cotton and Troup [38] have suggested that one reason for the occurrence of semi-bridging groups is to neutralise unequal charge distribution within unsymmetrical molecules. However, there are a number of examples which have semi-bridging groups between electronically equivalent metal atoms. We will discuss later the concept that this type of bridging group is also caused by steric pressures.

(v) Linear $\mu_2$ bridging in which the bridging group is now linear. In this situation the carbonyl is regarded as a four electron donor via a $\sigma$-bond to one metal and a $\mu$-bond (cf. olefins and acetylenes) to the other.

(vi) Triple bridging in which the carbonyl is associated with three metal atoms. This type of bridging will not be considered in detail in this article.

A word on the criteria used for classification of types (ii)—(iv) is in order. These types are not distinct but they merge into one another. An extreme case of semi-bridging is easy to recognize, but there are compounds in which the carbonyl group could be classed as asymmetric or semi-bridging. Similarly, criteria of significant difference in bond lengths are necessary to distinguish between symmetric and asymmetric bridging. We have adopted the commonly used crystallographic criteria of significance, namely, a bridge is deemed to be symmetrical if

$3\sigma >$ the difference in the metal—carbon bond lengths

where $\sigma = \sqrt{(a)^2 + (b)^2}$, $a$ and $b$ being the e.s.d.'s of the bond lengths [126]. Our arbitrary distinction between asymmetric and semi-bridging is that provided the difference in the M—C bond lengths is less than 0.3 Å and the difference in the M—C—O angles is less than 20° we refer to the bridging carbonyl group as asymmetric. Larger bond differences and larger angular differences at the bridging carbon classify the carbonyl group as semi-bridging. Some authors have used different criteria of significance, so that occasionally our description of a bridging group is different to theirs; this in no way implies any criticism of their description.

In addition to the basic types of carbonyl linkages described above, there are examples known in which the oxygen atom of the carbonyl group is coordinated to another (usually non-transition) metal as well as the normal car-

TABLE 1

Distribution of complexes containing $\mu_2$ carbonyl groups

| | | | | | | |
|---|---|---|---|---|---|---|
| Homonuclear $M_2$ | V<br>1 | Cr<br>— | Mn<br>5 | Fe<br>44 | Co<br>23 | Ni<br>5 |
| | | Mo<br>3 | Tc<br>— | Ru<br>7 | Rh<br>19 | Pd<br>2 |
| | | | Re<br>1 | Os<br>1 | Ir<br>2 | Pt<br>1 |
| Heteronuclear M—M′ | Fe—Co<br>6 | Fe—Rh<br>3 | Fe—Ru<br>1 | Co—Ni<br>3 | Co—Pt<br>1 | Ru—Pt<br>1 |

bon coordination to the transition metal. This can occur for both terminal and bridging carbonyl groups.

Approximately 120 crystal structures which contain one or more $\mu_2$ carbonyl groups are included in this survey. A number of additional structures have been reported, usually as preliminary communications, but insufficient data were presented to allow us to make detailed comments on the role of the $\mu_2$ carbonyl groups. It is instructive to show the distribution of these carbonyl bridges throughout the Periodic Table and this is done in Table 1. Ninety three structures with $\mu_2$ carbonyls bridging homonuclear pairs of metal atoms occur for the four elements Fe, Co, Ru and Rh. In addition, at least one of these elements is involved in all 15 structures reported in which a $\mu_2$ carbonyl spans a heteronuclear pair of metal atoms. There are only 21 structures included in our survey which do not contain one of these four elements. Clearly these elements, and in particular iron, dominate the chemistry of $\mu_2$ carbonyl derivatives, and for this reason complexes of these elements will be discussed first in the section on X-ray structures which follows. In this section each complex will be given a number, which also corresponds with the reference number, so that in the later discussion sections individual compounds can easily be referred to without laborious repetition of names.

## B. X-RAY STRUCTURES

### *(i) Homonuclear structures — iron*

### *1. Symmetrically bridged complexes*

Structural details for the carbonyl bridge region of each molecule in this section are given in Table 2. Brief descriptions are given where appropriate.

$Fe_2(\mu\text{-}CO)_3(CO)_6$ (compound 1) was the first carbonyl bridged complex whose structure was determined by X-ray crystallography [1a]. The data tabulated are from a recent accurate re-determination of the structure [1b].

The three bridging groups are equivalent and highly symmetrical. The hydride [Fe$_2$($\mu$-CO)$_2$($\mu$-H)(CO)$_6$]$^-$ has a similar structure [2] with the hydride replacing one bridging carbonyl. The length of the Fe—Fe bond is not affected, but the Fe—C bond lengths of the remaining bridging carbonyls are shortened.

Fe$_2$($\mu$-CO)($\mu$-GePh$_2$)$_2$(CO)$_6$ [3] is included at this point, even though the carbonyl bridge is asymmetric, because the complex is so closely related to Fe$_2$(CO)$_9$. The effects of replacing two of the carbonyl bridges by $\mu$-GePh$_2$ groups are to substantially increase the Fe—Fe distance and to introduce asymmetry into the remaining carbonyl bridge. Still further increase in the Fe—Fe distance to 2.75 Å is reported in the case where all the bridging positions are occupied by GeMe$_2$ groups [127].

Although few details are available for compound 4, Fe$_2$($\mu$-CO)$_3$[C$_4$Ph$_2$Bu$_2$]$_2$, it is included because of its highly unusual character. The structure is essentially the Fe$_2$(CO)$_3$ core of Fe$_2$(CO)$_9$ with the three terminal carbonyls on each metal atom replaced by 1,2-diphenyl-3,4-di-*t*-butylcyclobutadiene groups. The Fe—Fe distance is dramatically reduced to 2.177 Å and is thought to be the result of an iron—iron triple bond. As a result the angle at the bridging carbon atoms is reduced to 66.9°(av.), the lowest value recorded.

*Cis*-Fe$_2$($\mu$-CO)$_2$(CO)$_2$(C$_5$H$_5$)$_2$ [5] is a key compound in this review, firstly because it can be regarded as the parent compound of a large number of derivatives whose structures have been determined, and secondly because it was the first complex in which the facile exchange between bridging and terminal carbonyl groups was unambiguously demonstrated. This latter aspect will be discussed later. The structure of Fe$_2$($\mu$-CO)$_2$(CO)$_2$(C$_5$H$_5$)$_2$ is shown in Fig. 2; the bridges are symmetrical. The Fe$_2$($\mu$-CO)$_2$ system is non-planar and the dihedral angle between the two Fe$_2$CO planes is 164°.

The crystal structures of a number of compounds closely related to compound 5 have been reported in which every group in the parent complex is varied. For example, the terminal groups may be substituted, the cyclopentadienyl groups may be replaced by other groups are alternatively linked by organic groups. The bridging carbonyl groups may be substituted and even further coordinated to AlEt$_3$ moieties.

No significant effects on the Fe—Fe distance and the geometry of the Fe$_2$($\mu$-CO)$_2$ system are usually produced by substitution of one of the terminal carbonyl groups (compounds 6—8). Although one of the carbonyl bridges in compound 8 is slightly asymmetric, this is not thought to be significant for reasons which will be discussed later. Similarly, linking the cyclopentadienyl groups via organic or silicon side chains (compounds 9—11) produces minimal effects.

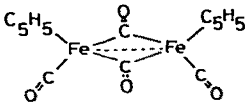


Fig. 2. Molecular structure of Fe$_2$($\mu$-CO)$_2$(CO)$_2$(C$_5$H$_5$)$_2$ (compound 5).

TABLE 2

Structural data for symmetrically bridged iron complexes

| Cpd. No. | Formula | Fe—Fe (Å) | Fe—C (Å) | | Fe—C—Fe (°) | Ref. |
|---|---|---|---|---|---|---|
| 1 | $Fe_2(\mu\text{-}CO)_3(CO)_6$ | 2.523(1) | 3x[2.016(3) | 2.016(3) | 77.6(1)] | 1 |
| 2 | $[Fe_2(\mu\text{-}CO)_2(\mu\text{-}H)(CO)_6]^-$ | 2.521(1) | 1.966(12)<br>1.961(10) | 1.981(11)<br>1.971(12) | 79.4(5)<br>79.7(4) | 2 |
| 3 | $Fe_2(\mu\text{-}CO)[\mu\text{-}GePh_2]_2(CO)_6$ | 2.666(3) | 1.98(1) | 2.08(1) | 82.1(5) | 3 |
| 4 | $Fe_2(\mu\text{-}CO)_3[C_4Ph_2Bu_2]_2$ | 2.177(3) | | 1.974(av) | 66.9(av) | 4 |
| 5 | *cis* $Fe_2(\mu\text{-}CO)_2(CO)_2(C_5H_5)_2$ | 2.531(2) | 1.908(7)<br>1.917(7) | 1.918(7)<br>1.925(7) | 82.8(3)<br>82.4(3) | 5 |
| 6 | *cis* $Fe_2(\mu\text{-}CO)_2CO[P(OPh)_3](C_5H_5)_2$ | 2.543(3) | 1.90(2) | 1.92(2) | 83.4(6) | 6 |
| | (there are two independent molecules in the unit cell, but their dimensions are very similar) | | | | | |
| 7 | *cis* $Fe_2(\mu\text{-}CO)_2CO(i\text{-}butNC)(C_5H_5)_2$ | 2.524(3) | 1.899(15)<br>1.901(17) | 1.915(13)<br>1.924(14) | 82.9(5)<br>82.6(6) | 7 |
| 8 | *cis* $Fe_2(\mu\text{-}CO)_2CO(t\text{-}butNC)(C_5H_5)_2$ | 2.523(2) | 1.86(1)<br>1.88(1) | 1.94(1)<br>1.92(1) | 83.0(4)<br>83.2(4) | 8 |
| 9 | *cis* $Fe_2(\mu\text{-}CO)_2L$<br>($L = C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4$) | 2.510(1) | 1.926(8)<br>1.916 | 1.932(8)<br>1.928(8) | 81.2(3)<br>81.5(3) | 9 |
| 10 | *cis* $Fe_2(\mu\text{-}CO)_2(CO)_2[C_6H_4CMe_2CMe_2C_6H_4]$ | 2.500(2) | 1.908(7) (av) | | 81.7(3) | 10 |
| 11 | *cis* $Fe_2(\mu\text{-}CO)_2(CO)_2[C_5H_4SiMe_2C_5H_4]$ | 2.512(3) | 1.87(1)<br>1.88(1) | 1.92(1)<br>1.89(1) | 83.0(5)<br>83.7(5) | 11a |
| | | 2.520(1) | 1.920(av) | | 82.0 | 11b |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 12 | *cis* $Fe_2(\mu\text{-}CO)_2(CO)_2[C_{10}H_8Fe(CO)_3]_2$ | 2.508(3) | 2x[1.923(6) | 1.938(6) | 81.0(3)] | 12 |
| 13 | *cis* $Fe_2(\mu\text{-}CO)_2(CO)_2(C_5H_5B)_2$ | 2.574(2) | 1.926(6) (av) |  | 83.9 | 13 |
| 14 | *cis* $Fe_2(\mu\text{-}CO)_2(CO)_2[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2$ | 2.591(5) | 1.900(14)<br>1.895(13) | 1.987(13)<br>1.981(12) | 83.6(5)<br>83.9(5) | 14 |
| 15 | *cis* $Fe_2(\mu\text{-}CO)[\mu\text{-}CC(CN)_2](CO)_2(C_5H_5)_2$ | 2.509(4) | 1.91(3) | 1.97(3) | 80(1) | 15 |
|  | (there are two independent molecules in the unit cell but their dimensions are very similar) |  |  |  |  |  |
| 16 | *cis*$[Fe_2(\mu\text{-}CO)(\mu\text{-}CSEt)(CO)_2(C_5H_5)_2]^+$ | 2.510(2) | 1.923(10) | 1.949(11) | 80.8(4) | 16 |
| 17 | *cis* $Fe_2(\mu\text{-}CO)(\mu\text{-}PhNC)(CO)_2(C_5H_5)_2$ | 2.532 | 1.920(av) |  | 83.1 | 17 |
| 18 | *cis* $Fe_2(\mu\text{-}CO)(\mu\text{-}GeMe_2)(CO)_2(C_5H_5)_2$ | 2.628(1) | 1.902(6) | 1.923(6) | 86.8(2) | 18 |
| 19 | *cis* $Fe_2(\mu\text{-}CO)(\mu\text{-}SO_2)(CO)_2(C_5H_5)_2$ | 2.584(1)<br>2.597(1) | 1.920(4)<br>1.925(4) | 1.951(4)<br>1.939(4) | 83.74(16)<br>84.45(15) | 19 |
| 20 | *cis* $Fe_2(\mu\text{-}CO)(\mu\text{-}PMe_2)(CO)_4(C_5H_5)$ | 2.615(2)<br>2.638(2) | 1.92(1)<br>1.90(1) | 1.95(1)<br>1.96(1) | 84.9(4)<br>86.2(4) | 20 |
| 21 | *cis* $Fe_2[\mu\text{-}COAl(C_2H_5)_3]_2(CO)_2(C_5H_5)_2$ | 2.491 | 1.88(av) |  | 83.0 | 21 |
| 22 | *trans* $Fe_2(\mu\text{-}CO)_2(CO)_2(C_5H_5)_2$ | 2.534(2) | 2x[1.910(5) | 1.918(5) | 82.9(2)] | 22 |
| 23 | *trans* $Fe_2(\mu\text{-}CO)_2(CO)_2(C_{10}H_{13})_2$ | 2.553(2) | 2x[1.892(9) | 1.925(9) | 83.9(4)] | 23 |
| 24 | $Fe_3(\mu\text{-}CO)_2(CO)_7(PMe_2Ph)_3$ | 2.540(7) | 1.97(2)<br>2.02(3) | 1.97(3)<br>2.04(3) | 80.3<br>77.5 | 24 |
| 25 | $Fe_2(\mu\text{-}CO)(CO)_4(C_8H_8)$ | 2.742(3) | 2x1.986(17) |  | 87.3 | 25 |
| 26 | $Fe_2(\mu\text{-}CO)(CO)_4[C_8H_4(CH_3)_4]$ | 2.724(4) | 1.91(2) | 1.97(2) | 89(1) | 26 |
| 27 | $Fe_2(\mu\text{-}CO)(\mu\text{-}dpm)(CO)_6$ | 2.709(2) | 1.98(1) | 2.01(1) | 85.6(5) | 27 |

Replacing the cyclopentadienyl groups by other $\pi$-bonding ligands does have some effect in some cases. In compound 12 the $C_5H_5^-$ groups of 5 are replaced by azulene ligands which are also coordinated to other $Fe(CO)_3$ moieties. In this case the only noticeable difference in this complex is that the iron-bridging carbonyl bond is slightly longer than usual. However, in compound 13, in which 'borabenzene' replaces $C_5H_5^-$, there is a significant increase in both the Fe—Fe distance and in the bridge—Fe distances, although the bridges remain symmetrical. In compound 14 a different carborane containing more carbon causes the Fe—Fe distance to increase still further and a slight asymmetry in the carbonyl bridges now becomes apparent.

Substitution of the carbonyl bridges has perhaps the most significant effect on both the Fe—Fe distance and on the remaining carbonyl bridge. In compounds 15—18 the carbonyl bridge remains symmetrical, although in the latter two complexes there are very significant increases in the Fe—Fe distance. In compound 19 there are two independent molecules in the unit cell, both have long metal—metal distances and there is now some asymmetry in the carbonyl bridge.

$Fe_2(\mu\text{-}CO)(\mu\text{-}PMe_2)(CO)_4(C_5H_5)$ [20] is particularly interesting as the distribution of ligands within the molecule is quite different to that of the preceding examples and yet the same basic structure is retained as shown in Fig. 3. The ligand and electronic environment of the two metal atoms are nonequivalent. One iron has no $C_5H_5^-$ group attached and its only coordination to a negative group is to the bridging $PMe_2^-$ group. There are again two independent molecules in the unit cell, both have very long Fe—Fe distances and slight asymmetry in the carbonyl bridge.

Compound 21 (Fig. 4) is an interesting variation on *cis*-$Fe_2(\mu\text{-}CO)_2(CO)_2(C_5H_5)_2$ in which the bridging carbonyls are bonded to $AlEt_3$ moieties via the carbonyl oxygen atoms. There are no major differences in the geometry of the $Fe_2(\mu\text{-}CO)_2$ system compared with compound 5, but both the Fe—Fe and Fe—bridge distances are reduced.

Reaction of *cis*-$Fe_2(\mu\text{-}CO)_2(CO)_2(C_5H_5)_2$ with $CH_3N(PF_2)_2$ gives a two step reaction, first replacing the terminal carbonyl groups to give a complex in which the iron atoms are bridged by two carbonyls and the ligand coordinated via its phosphorus atoms. Further reaction replaces the bridging carbonyls

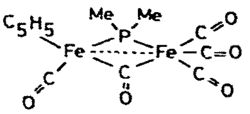


Fig. 3. Molecular structure of $Fe_2(\mu\text{-}CO)(\mu PMe_2)(CO)_4(C_5H_5)_2$ (compound 20).

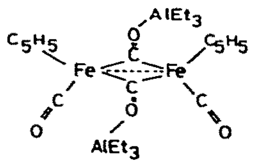


Fig. 4. Molecular structure of $Fe_2(\mu\text{-}COAlEt_3)_2(CO)_4(C_5H_5)_2$ (compound 21).

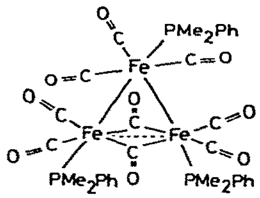


Fig. 5. Molecular structure of $Fe_3(\mu\text{-}CO)_2(CO)_7(PPhMe_2)_3$ (compound 24).

but not in a simple manner; the second molecule of ligand is cleaved to generate a $PF_2^-$ group and a $CH_3NPF_2^-$ ligand which bridges via N and P. Both these new ligands act as 3 electron donors so the iron atoms now attain the 18 electron configuration independently with the result that the Fe—Fe distance increases to 3.646 Å. Presumably steric interactions between the cyclopentadienyl groups and the fluorine atoms of the ligand prevent a second $CH_3N(PF_2)_2$ coordinating via phosphorus and this remarkable re-arrangement occurs instead [128].

*Trans*-$Fe_2(\mu\text{-}CO)_2(CO)_2(C_5H_5)_2$ [22] has molecular dimensions virtually identical to that of the *cis* isomer. In this case the $Fe_2(\mu\text{-}CO)_2$ is planar by a crystallographic requirement. A very similar structure occurs for compound 23, $Fe_2(\mu\text{-}CO)_2(CO)_2L$ where L = 2, 3, 4, 5, 6-pentahaptotricyclo[6.2.0.0.$^{2,6}$]-deca-2, 4-dien-6-yl which is a substituted cyclopentadienyl group.

The compound $Fe_3(\mu\text{-}CO)_2(CO)_7(PPhMe_2)_3$ [24] is derived from $Fe_3(CO)_{12}$ by substitution of a terminal group on each iron atom, (Fig. 5). The doubly bridged $Fe_2$ system is retained, but in contrast to the parent carbonyl (see below), the carbonyl bridges are both symmetrical.

Finally in this section, the structures of a few dinuclear complexes of iron with only a single bridge have been reported [25—27]. In each case the bridge is symmetrical.

### 2. *Asymmetrically bridged complexes*

In this section a brief description of each structure containing an asymmetric carbonyl bridge between two iron atoms will be given, although the emphasis at this stage will be on the carbonyl bridge portion of the molecule. Table 3 lists the structural features of interest.

Triirondodecacarbonyl, $Fe_3(\mu\text{-}CO)_2(CO)_{10}$ [28] has been the subject of a number of crystallographic studies because the structure was difficult to solve due to severe disorder problems within the crystal. The latest and most accurate study is that of Cotton and Troup [28] in which the disorder problem was overcome. A triangle of iron atoms is bridged along only one edge by a

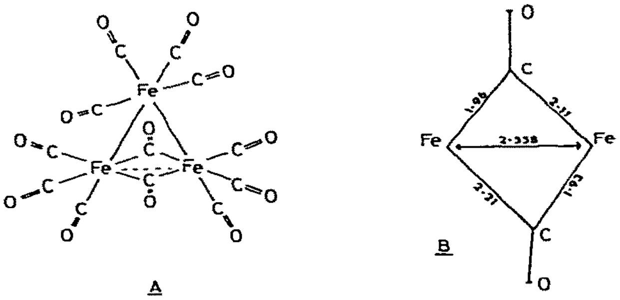
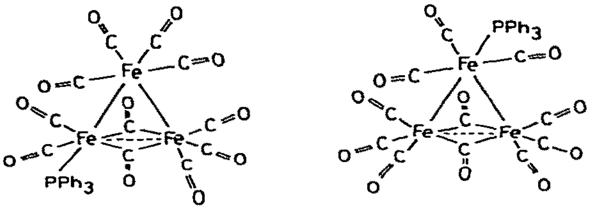


Fig. 6. A, Molecular structure of $Fe_3(\mu\text{-}CO)_2(CO)_{10}$ (compound 28). B, Details of the carbonyl bridge system (planar projection, drawn to scale).

TABLE 3

Structural data for asymmetrically bridged iron complexes

| Cpd. No. | Formula | Fe—Fe (Å) | Fe—C (Å) |  | Fe—C—Fe (°) | Fe—C—O (°) |  | Ref. |
|---|---|---|---|---|---|---|---|---|
| 28 | $Fe_3(\mu\text{-}CO)_2(CO)_{10}$ | 2.558(1) | 1.93(2) | 2.21(3) | 76 | 132(2) | 152(3) | 28 |
|  |  |  | 1.96(4) | 2.11(4) | 77 | 140(3) | 143(3) |  |
| 29 | $Fe_3(\mu\text{-}CO)_2(CO)_9(PPh_3)$ Isomer A | 2.568(8) | 1.86(4) | 2.04(4) | 82(2) | 132(3) | 144(4) | 29 |
|  |  |  | 1.90(4) | 1.99(4) | 83(2) | 139(3) | 139(3) |  |
|  | Isomer B | 2.558(9) | 1.85(5) | 2.04(5) | 82(2) | 136(4) | 142(4) |  |
|  |  |  | 1.86(4) | 2.07(4) | 81(2) | 135(3) | 144(3) |  |
| 30 | $Fe_3(\mu\text{-}CO)_2(CO)_6(PhC_2Ph)_2$ | 2.428(3) | 1.842(19) | 1.991(19) | 78.5(7) | 137.7(1.5) | 143.8(1.5) | 30 |
|  |  | 2.435(3) | 1.771(21) | 1.988(21) | 80.5(8) | 131.2(1.6) | 148.2(1.7) |  |
| 31 | $Fe_3(\mu\text{-}CO)_2(CO)_6L$ | 2.515(3) | 1.884(5) | 2.004(4) | 80.5(2) | 138.3(3) | 141.2(3) | 31 |
|  | ($L = \eta$-1,3-dimethyl-2-vinylcyclopentadiene) | 2.525(3) | 1.875(4) | 2.031(4) | 80.5(2) | 136.0(3) | 143.5(3) |  |
| 32 | $Fe_3(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_6L$<br>($L = Ph_2PC(CO_2Me)C(CF_3)C_2CF_3$) | 2.543(2) | 1.874(9) | 2.166(10) | 77.6(6) | 132.5 | 150 | 32 |



Isomer A Isomer B

Fig. 7. Molecular structures of the isomers of $Fe_3(\mu\text{-}CO)_2(CO)_9(PPh_3)$ (compound 29).

pair of carbonyl groups as shown in Fig. 6. The disorder in the crystal leads to rather large e.s.d.'s but nevertheless it was shown quite clearly that one of the bridges is asymmetric and the other is on the borderline between asymmetric and symmetric. This difference between the bridges is also seen in the angular differences at the bridging carbons (Table 3). The dihedral angle between the $Fe_2CO$ planes is 139.6°.

$Fe_3(\mu\text{-}CO)_2(CO)_9(PPh_3)$ [29] is obtained by the interaction of $Fe_3(CO)_{12}$ and $PPh_3$ and it retains many of the features of the parent carbonyl. Remarkably, the crystal structure contains equal numbers of two distinct clusters, isomer A in which a terminal carbonyl on one of the carbonyl bridged iron atoms is substituted, and isomer B in which a carbonyl on the apical iron is substituted (Fig. 7). Within our criteria of $3\sigma$ difference between Fe—C bonds, three of the four carbonyl bridges in the two isomers are very slightly asymmetric, while the fourth (isomer A) is not significantly different from symmetrical.

There are two isomers of $Fe_3(CO)_8(PhC_2Ph)_2$ [30]. The violet isomer contains two separate diphenylacetylene groups and only terminal carbonyl groups. However, on heating in benzene it forms the black isomer $Fe_3(\mu\text{-}CO)_2$-

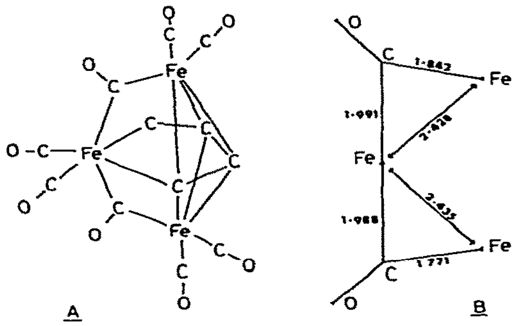


Fig. 8. A, Skeleton in the molecular structure of $Fe_3(\mu\text{-}CO)_2(CO)_6(PhC_2Ph)_2$ (compound 30). B, Details of the carbonyl bridge system (drawn to scale).

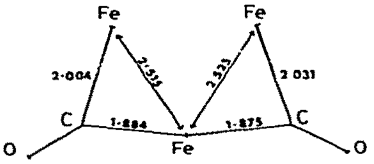


Fig. 9. Details of the carbonyl bridge system in $Fe_3(\mu\text{-}CO)_2(CO)_6(CEt)[C_5H_2Me_2(C_2H_3)]$ (compound 31). (Drawn to scale.)

$(CO)_6(PhC_2Ph)_2$ which contains two fused acetylene groups forming a ferrocyclopentadiene ring with one iron atom. This unique metal atom has a single asymmetric carbonyl bridge to each of the other two iron atoms as shown in Fig. 8. In this case the bridges are definitely asymmetrical although the angular differences at carbon are not large.

$Fe_3(\mu\text{-}CO)_2(CO)_6(CEt)[C_5H_2Me_2(C_2H_3)]$ [31] is formed by the interaction of $Fe_3(CO)_{12}$ and methylacetylene. It contains an $Fe_3C$ cluster unit with a complex organic group attached to one iron atom. Two edges of the iron triangle are each bridged by an asymmetric carbonyl group as shown in Fig. 9.

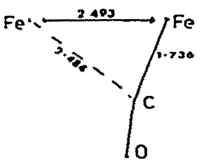
Compound 32 contains a triangle of iron atoms, one edge bridged by an asymmetric carbonyl group and another by a $PPh_2^-$ group.

### 3. *Semi-bridged complexes*

The semi-bridging carbonyl group is characterised by markedly different metal—carbon lengths and also markedly different M—C—O angles. Usually, one of the M—C—O angles is within 25° of 180° so the M—C—O group is tending to be linear. Table 4 contains structural details of semi-bridged iron complexes.

$Fe_2(\mu\text{-}CO)(CO)_5[CH_3C_2(COH)]_2$ [33] was the first complex in which a semi-bridging carbonyl was recognised. This complex (Fig. 10) and compounds 34 and 35 (Fig. 11) are closely related. They all contain a ferrocarbon ring with a second iron $\pi$-bonded to the ring. In each case a carbonyl on the second iron is semi-bridged to the ferrocarbon iron atom. In these three complexes the difference in the Fe—C bond lengths is about 0.7 Å and the angular differences at the bridging carbons range from 37° to 46°. In the similar compound 36 the differences are even greater and this bridge could be regarded as very borderline. $Fe_2(\mu\text{-}CO)(CO)_3(PhC_2C_6H_4C_2Ph)$ [37] is basically similar to the previous examples as far as the semi-bridging carbonyl is concerned. The major difference in the structure is that two terminal groups on the non-ferrocarbon iron atom have been replaced by a substituted cyclobutadiene group.

The interesting complex $Fe_2(\mu\text{-}CO)_2(CO)_5dipy$ [38] is an example of a dinuclear iron complex containing two carbonyl bridging groups, one semi-bridging and the other asymmetric.



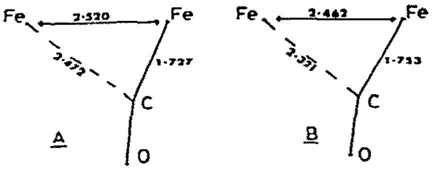


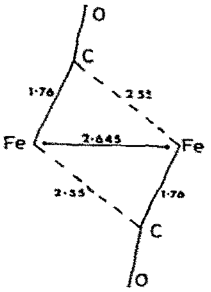
Fig. 10. Details of the carbonyl bridge system in $Fe_2(\mu\text{-}CO)(CO)_5[MeC_2(COH)]_2$ (compound 33). (Drawn to scale.)

Fig. 11. Details of the carbonyl bridge systems in A, $Fe_2(\mu\text{-}CO)(CO)_5[PhC_2Ph]$ (compound 34); and B, $Fe_2(\mu\text{-}CO)(CO)_5(C_{12}H_{16})$ (compound 35). (Drawn to scale.)

TABLE 4

Structural data for semi-bridged iron complexes

| Cpd. No. | Formula | Fe—Fe (Å) | Fe—C (Å) | | Fe—C—Fe (°) | | Fe—C—O (°) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 33 | $Fe_2(\mu\text{-}CO)(CO)_5[C(OH)CMe]_2$ | 2.4930(18) | 1.736(8) | 2.484(8) | 69.9 | 122.1 | 168.0(7) | 33 |
| 34 | $Fe_2(\mu\text{-}CO)(CO)_5[PhC_2Ph]$ | 2.520(3) | 1.727(13) | 2.472(13) | 71.3(4) | 123.9(9) | 164.8(1.1) | 34 |
| 35 | $Fe_2(\mu\text{-}CO)(CO)_5(C_{12}H_{16})$ | 2.462(3) | 1.753(21) | 2.321(19) | 72.8(7) | 125.1(2.6) | 161.9(2.8) | 35 |
| 36 | $Fe_2(\mu\text{-}CO)(CO)_5L$ ($L = N(SO_2 \cdot C_6H_4 \cdot CH_3)C\cdot(OCH_3)(CH)_2C(OCH_3)$) | 2.6362(2) | 1.732(12) | 2.804(11) | 66.2 | 121.7 | 172.1(1) | 36 |
| 37 | $Fe_2(\mu\text{-}CO)(CO)_3[PhC_2C_6H_4C_2Ph]$ | 2.494(5) | 1.741(20) | 2.388(20) | 72.4 | 120.3(1.5) | 166.4(1.7) | 37 |
| 38 | $Fe_2(\mu\text{-}CO)_2(CO)_5dipy$ | 2.611 | 1.80 | 2.37 | 76.2 | 123.3 | 160.5 | 38 |
| | (asym) | | 1.89 | 2.08 | 82.1 | | | |
| 39 | $Fe_2(\mu\text{-}CO)(\mu\text{-}C_2Ph)(CO)_6(C_5H_5)$ | 2.524(1) | 1.788(5) | 2.273(6) | 75.82(22) | 126.35(46) | 157.63(56) | 39 |
| 40 | $Fe_3(\mu\text{-}CO)_2(\mu\text{-}C_4H_8S)_2(CO)_6$ | 2.645(2) | 2 x [1.76(1) | 2.55(1) | 73.1 | 119.4(6) | 167.4(7)] | 40 |
| 41 | $Fe_3Rh(\mu\text{-}CO)_4(CO)_7(C_5H_5)$ | 2.553(3) | 1.871(20) | 2.356(20) | 73.3 | 129.4 | 157.3(1.8) | 41 |
| | | 2.586(3) | 1.820(21) | 2.478(21) | 72.1 | 124.1 | 163.8(1.9) | |
| 42 | $[Fe_2(\mu\text{-}CO)_4(CO)_9]^{2-}$ | 2.500(6) | 1.80(4) | 2.24 | 75.6 | 133.4 | 151 | 42 |
| | | 2.500(6) | 1.81(4) | 2.28 | 74.4 | 130.6 | 155 | |
| | | 2.500(6) | 1.85(3) | 2.33 | 72.4 | 129.6 | 158 | |
| 43 | $Fe_4(\mu\text{-}CO)_3(CO)_8(NEt)(ONEt)$ | 2.484(4) | 1.83(1) | 2.47(1) | 68.7 | 128.51 | 162.56 | 43 |
| | | 2.487(4) | 1.78(1) | 2.45(1) | 70.0 | 125.25 | 164.66 | |
| | (symm) | 2.552(4) | 1.91(1) | 1.95(1) | 82.8 | | | |
| 44 | $[Fe_6(\mu\text{-}CO)_3(CO)_{13}C]^{2-}$ | | | | | | | |
| | molecule 1 | 2x[2.632(10) | 1.780(43) | 2.163(43) | 83.2(2.1) | 125.8(4.9) | 151.0(3.7)] | 44 |
| | | 2.609(10) | 1.969(60) | 2.326(61) | 74.3(4.1) | 121.5(5.0) | 164.2(5.7) | |
| | molecule 2 | 2x[2.621(9) | 1.791(60) | 2.213(60) | 81.0(2.3) | 126.2(4.2) | 152.6(4.9)] | |
| | | 2.553(10) | 1.905(63) | 2.005(63) | 81.5(4.3) | 133.2(5.1) | 145.3(5.3) | |



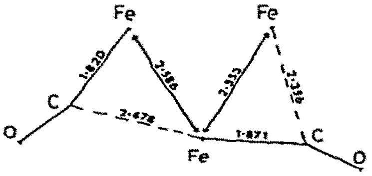


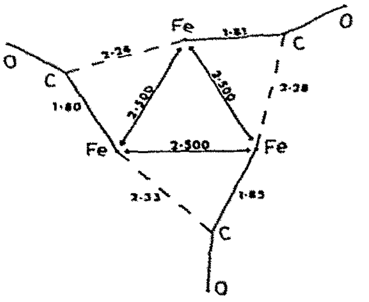
Fig. 12. Details of the carbonyl bridge system in $Fe_3(\mu\text{-}CO)_2(\mu\text{-}C_4H_8S)_2(CO)_6$ (compound 40). (Drawn to scale.)

Fig. 13. Details of the carbonyl bridge system between iron atoms in $Fe_3Rh(\mu\text{-}CO)_4(CO)_7(C_5H_5)$ (compound 41). (Drawn to scale.)

$Fe_3(\mu\text{-}CO)(\mu\text{-}C_2C_6H_5)(CO)_6(C_5H_5)$ [39] contains a phenylethynyl group σ-bonded to one iron atom and symmetrically π-bonded to the other two. This latter pair of iron atoms is bridged by a semi-bridging carbonyl group. $Fe_3(\mu\text{-}CO)_2(\mu\text{-}C_4H_8S)_2(CO)_6$ [40] contains a mirror plane with two semi-bridging carbonyl groups spanning one pair of iron atoms (Fig. 12). The other edges of the iron triangle are bridged by $SC_4H_8$ groups in which the sulphur atoms are considered to be four electron donors.

$Fe_3Rh(\mu\text{-}CO)_4(CO)_7(C_5H_5)$ [41] contains a tetrahedron of metal atoms with the $C_5H_5^-$ group coordinated to rhodium. There are two carbonyl bridges between iron and rhodium, but these will be discussed in the section on heteronuclear bridges. In addition, there are two semi-bridging carbonyl groups spanning two pairs of iron atoms as shown in Fig. 13.

The $[Fe_4(\mu\text{-}CO)_4(CO)_9]^{2-}$ anion [42] has a tetrahedron of metal atoms and



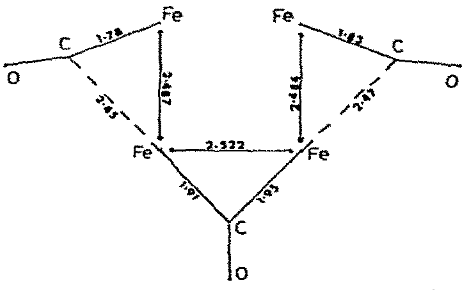


Fig. 14. Details of the $\mu_2$ carbonyl bridge system in the $[Fe_4(\mu\text{-}CO)_4(CO)_9]^{2-}$ anion (compound 42). (Drawn to scale.)

Fig. 15. Details of the carbonyl bridge system in $Fe_4(\mu\text{-}CO)_3(CO)_8(NEt)(ONEt)$ (compound 43). (Drawn to scale.)

the basal $Fe_3$ unit is spanned by a triply bridging carbonyl group. The apical iron atom has three terminal carbonyls and each iron in the basal plane is also associated with another three carbonyl groups although in this case one is semi-bridging to its neighbour in the basal plane in the cyclic manner shown in Fig. 14.

The extraordinary complex $Fe_4(\mu\text{-}CO)_3(CO)_8(NEt)(ONEt)$ [43] consists of a square of iron atoms bridged along one edge by a symmetrical carbonyl group and along the two adjacent edges by semi-bridging ones (Fig. 15). The NEt and ONEt groups are above and below the plane of the iron atoms and are each connected to all four metal atoms.

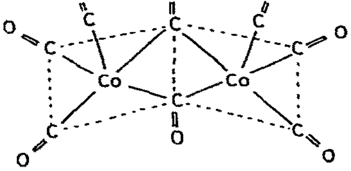
Finally in this section, the $[Fe_6(\mu\text{-}CO)_3(CO)_{13}C]^{2-}$ anion [44] has an octahedron of metal atoms enclosing the carbon atom. The metal atoms are not all equivalent and three edges of the metal octahedron are spanned by carbonyl groups, two of which are crystallographically equivalent. The unit cell of the crystal contains two independent clusters which differ significantly in their dimensions although their basic structures are the same. For example, the unique carbonyl bridge in molecule 2 is actually symmetric within the experimental error whilst the corresponding bridge in molecule 1 is semi-bridging. The pair of equivalent bridges in each molecule are both semi-bridging.

### *(ii) Homonuclear structures — cobalt*

#### *1. Symmetrically bridged complexes*

Dicobalt octacarbonyl $Co_2(\mu\text{-}CO)_2(CO)_6$ [45] has two symmetrical carbonyl bridges spanning a Co—Co distance of 2.52 Å. The asymmetric unit contains two molecules which have similar dimensions and the two carbonyl bridges within each molecule are crystallographically equivalent. The structure may be regarded as composed of two square pyramids sharing an edge (Fig. 16). Structural details for this compound and other symmetrically bridged cobalt complexes are given in Table 5.

Compound 46 maintains the essential geometry of $Co_2(CO)_8$, but a terminal carbonyl on each cobalt is substituted by the bridging diarsine ligand. The geometry of *cis*-$Co_2(\mu\text{-}CO)_2(CO)_2(C_6H_8)_2$ [47] is analogous to that of the iso-



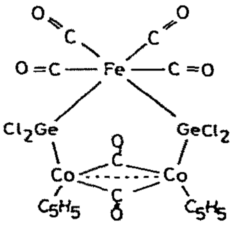


Fig. 16. Molecular structure of $Co_2(\mu\text{-}CO)_2(CO)_6$ (compound 45).

Fig. 17. Molecular structure of $Co_2(\mu\text{-}CO)_2[\mu\text{-}(GeCl_2)_2Fe(CO)_4](C_5H_5)_2$ (compound 50).

TABLE 5

Structural data for symmetrically bridged cobalt complexes

| Cpd. No. | Formula | Co–Co (Å) | Co–C (Å) | | Co–C–Co (°) | Ref. |
|---|---|---|---|---|---|---|
| 45 | $Co_2(\mu\text{-}CO)_2(CO)_6$ | 2.522(2) | 2x[1.883(12) | 1.925(12) | 82.9] | 45 |
| 46 | $Co_2(\mu\text{-}CO)_2(CO)_4(ffars)$ | 2.843(4) | 1.91(2) | 1.94(3) | 80.4(9) | 46 |
| 47 | *cis* $Co_2(\mu\text{-}CO)_2(CO)_2(C_6H_8)_2$ | 2.559(3) | 1.911(10)(av) | | 80.6 | 47 |
| 48 | *trans* $Co_2(\mu\text{-}CO)_2(C_6H_{10})_2$ | 2.549(1) | 2x[1.922(4) | 1.931(4) | 82.9(2)] | 48 |
| 49 | $[Co_2(\mu\text{-}CO)_2(C_5H_5)_2]^-$ | 2.36 | 1.82 | 1.83 | 80.6 | 49 |
| 50 | $Co_2(\mu\text{-}CO)_2[(\mu\text{-}GeCl_2)_2Fe(CO)_4](C_5H_5)_2$ | 2.434(5) | 1.85(3)<br>1.87(3) | 1.86(3)<br>1.91(3) | 82.0(1)<br>80.0(1) | 50 |
| 51 | $Co_2(\mu\text{-}CO)(\mu\text{-}C_4H_2O_2)(CO)_6$ | 2.45(1) | 1.90(8) | 1.96(8) | 79 | 51 |
| 52 | $Co_2(\mu\text{-}CO)[\mu\text{-}Sn(acac)_2](CO)_6$ | 2.626(4) | 1.85(2) | 1.89(2) | 89.2(9) | 52 |
| 53 | $Co_2Pt_2(\mu\text{-}CO)_3(CO)_5(PPh_3)$ | 2.498(3) | 1.929(19) | 1.998(17) | 78.95(49) | 53 |
| 54 | $Co_3(\mu\text{-}CO)(\mu\text{-}SC_2H_5)_5(CO)_3$ | 2.485(7) | 1.94(3) | 1.96(3) | 79.1 | 54 |
| 55 | $Co_4(\mu\text{-}CO)_3(CO)_9$ | 2.457(3)<br>2.479(3)<br>2.512(2) | 2.118(22)<br>1.958(9)<br>1.958(9) | 2.191(17)<br>2.010(9)<br>2.024(9) | 69.5(7)<br>77.3(3)<br>78.2(4) | 55 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 56a | $Co_4(\mu\text{-}CO)_3(CO)_6(C_6H_6)$ | 3×[2.457(2) | 1.939(9) | 1.956(9) | 78.2(3)] | 56 |
| 56b | $Co_4(\mu\text{-}CO)_3(CO)_6[C_6H_4(CH_3)_2]$ | 2.451(2) | 1.911(10) | 1.949(11) | 78.8(4) | 56 |
| | | 2.456(2) | 1.926(12) | 1.938(12) | 78.9(5) | |
| | (asymm) | 2.456(2) | 1.865(12) | 1.946(12) | 80.2(4) | |
| 57 | $FeCo_3(\mu\text{-}CO)_3(\mu_3\text{-}H)(CO)_6[P(OMe)_3]_3$ | 2.499(1) | 1.950(6) | 1.964(6) | 79.4(2) | 57a |
| | | 2.476(1) | 1.929(6) | 1.961(6) | 79.1(2) | |
| | | 2.488(1) | 1.958(6) | 1.959(6) | 78.9(2) | |
| 58 | $Co_2Ir_2(\mu\text{-}CO)_3(CO)_9$ | 2.594(6) | 1.91(6) | 2.21(6) | 78(2) | 58 |
| | | 2.615(6) | 1.91(6) | 2.06(6) | 82(2) | |
| | | 2.644(9) | 1.88(6) | 2.03(6) | 85(2) | |
| 59 | $CO_4(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2(CO)_8$ | 2.519(2) | | | | 59 |
| 60 | $Co_5(\mu\text{-}CO)_3[\mu\text{-}SC_2H_5]_5(CO)_7$ | 2.430(6) | 1.82(3) | 1.85(3) | 83.0(1.4) | 60 |
| | | 2.487(7) | 1.84(3) | 1.96(4) | 81.2(1.5) | |
| | | 2.491(6) | 1.82(5) | 1.82(5) | 86.2(2.2) | |
| 61 | $[Co_6(\mu\text{-}CO)_3(CO)_{12}]^{2-}$ | 2.454(4) | 1.90(2) | 1.95(2) | 79.2 | 61 |
| | | 2.475(4) | 1.86(3) | 1.88(2) | 82.9 | |
| | | 2.475(5) | 1.91(3) | 1.93(2) | 80.3 | |
| 62 | $Co_6(\mu\text{-}CO)_5(\mu\text{-}SC_2H_5)_4(CO)_6S$ | 2.450(7) | 1.91(4) | 1.95(3) | 78.8(1.3) | 62 |
| | | 2.459(7) | 1.89(4) | 2.01(4) | 78.1(1.4) | |
| | | 2.471(8) | 1.82(3) | 1.89(3) | 83.6(1.4) | |
| | (asymm) | 2.481(7) | 1.78(3) | 1.97(3) | 82.5(1.2) | |
| | | 2.488(7) | 1.82(4) | 1.84(4) | 85.5(1.8) | |

electronic $Fe_2(\mu\text{-}CO)_2(CO)_2(C_5H_5)_2$ series. A *trans* complex, $Co_2(\mu\text{-}CO)_2(CO)_2(C_6H_{10})_2$ [48] has very similar interatomic distances.

The simple molecular structure of $Co_2(\mu\text{-}CO)_2(C_5H_5)_2$ [49] consists of two cobalt atoms bridged by two equivalent carbonyl groups with the $C_5H_5^-$ groups attached to each cobalt at right angles to the Co—Co direction. The very short metal—metal distance is notable. An interesting comparison is provided between compounds 49 and 50, $Co_2(\mu\text{-}CO)_2[\mu\text{-}(GeCl_2)_2Fe(CO)_4](C_5H_5)_2$; in which the cobalt atoms are bridged by the complex germanium ligand as well as the two carbonyl groups as shown in Fig. 17. The Co—Co distance is now significantly longer than in compound 49, although it is still a little shorter than most Co—Co distances (Table 5). The major stereochemical effect of the additional bridging ligand is that the $C_5H_5^-$ groups are no longer normal to the Co—Co vector.

Compound 51 is a simple derivative of $Co_2(CO)_8$ containing a single carbonyl bridge and a lactone bridge between the metal atoms. The basic structure of two square pyramids sharing an edge is retained. It is also retained in compound 52, $Co_2(\mu\text{-}CO)_2[\mu\text{-}Sn(acac)_2](CO)_6$, but this time the Co—Co distance is very long at 2.626 Å. Since the cobalt—carbon distances are normal, the angle at the bridging carbons is large at 89.2°.

The heteronuclear cluster compound $Co_2Pt_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2$ [53] contains a butterfly arrangement of the four metal atoms and a single carbonyl group bridges the two cobalt atoms symmetrically.

A number of polynuclear complexes derived from cobalt carbonyl and the $(SC_2H_5)^-$ ligand have been characterised by structural studies. In $Co_3(\mu\text{-}CO)(\mu\text{-}SC_2H_5)_5(CO)_3$ [54] the single carbonyl group is symmetrical.

The determination of the structure of $Co_4(\mu\text{-}CO)_3(CO)_9$ [55] has, like that of $Fe_3(CO)_{12}$, proved to be a difficult problem due to disorder in the structure. The structure suggested by Wei [82] has been refined by Cotton and co-workers [55] and it consists of a tetrahedral array of cobalt atoms in which the apical cobalt carries three terminal carbonyls and is directly bonded to the other three cobalt atoms. Each of these carries two terminal carbonyls and each edge of the basal triangle is bridged by a symmetrical carbonyl as shown in Fig. 18.

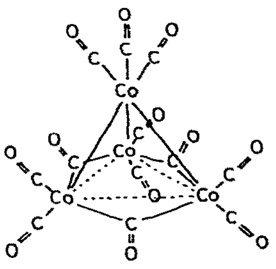


Fig. 18. Molecular structure of $Co_4(\mu\text{-}CO)_3(CO)_9$ (compound 55).

In compounds 56a and 56b the structures are derived from $Co_4(CO)_{12}$ by replacing the three terminal carbonyls on the apical cobalt by an arene group, benzene or xylene respectively. In 56b there is a disordered mixture of *o* and *m* xylene and one of the carbonyl bridges is asymmetric.

$HFeCo_3(CO)_{12}$ is thought to have a structure similar to that of $Co_4(CO)_{12}$ and very recently the structure of a derivative, $HFeCO_3(\mu\text{-}CO)_3(CO)_6\text{-}[P(OMe)_3]_3$ [57a], has been determined at —139°C. The structure is based on $Co_4(CO)_{12}$ with the iron atom in the apical position. An axial terminal carbonyl on each cobalt is substituted by the phosphite. A neutron diffraction study [57b] has revealed that the hydride is outside the cluster, triply bridging the $Co_3$ face.

In $Co_2Ir_2(\mu\text{-}CO)_3(CO)_9$ [58] the mixed metal cluster has the same stereochemistry as $Co_4(CO)_{12}$. There is disorder in the metal distribution but iridium shows a marked tendency to occupy the apical (non-bridged) position in keeping with the general trends in group chemistry. One of the bridges is slightly asymmetric, but this is probably not significant in view of the disordered nature of the structure.

$Co_4(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2(CO)_8$ [59] displays an unusual square arrangement of cobalt atoms, two opposite edges of which are each bridged symmetrically by a carbonyl group.

Compound 60 consists essentially of a $Co_3(\mu\text{-}CO)_2(\mu\text{-}SC_2H_5)_4(CO)_3$ residue bonding via its bridging thioalkyl groups to a $Co_2(\mu\text{-}CO)(\mu\text{-}SC_2H_5)(CO)_4$ moiety. All the carbonyl bridges are symmetrical.

The $[Co_6(\mu\text{-}CO)_3(CO)_{12}]^{3-}$ anion [61] contains an octahedral array of cobalt atoms and three of its edges are bridged by symmetrical carbonyl groups.

The complex $Co_6(\mu\text{-}CO)_5(\mu\text{-}SC_2H_5)_4(CO)_6S$ [62] contains a $Co_3(\mu\text{-}CO)_2(\mu\text{-}SC_2H_5)_4(CO)_3$ unit linked via sulphur atoms to a $SCo_3(\mu\text{-}CO)_3(CO)_3$ fragment. Of the five carbonyl bridges, four are symmetric and one, in the $Co_3(\mu\text{-}CO)_2\text{-}(\mu\text{-}SC_2H_5)_4(CO)_3$ unit, is asymmetric.

### 2. *Asymmetrically bridged complexes*

The unsymmetrical molecule $Co_2(\mu\text{-}CO)_2(CO)_4(C_7H_8)$ [63] can be regarded as a substitution product of $Co_2(CO)_8$ with two terminal carbonyls on one cobalt replaced by norbornadiene. The carbonyl bridges become asymmetric. Details of this and other complexes with asymmetric bridges between two cobalt atoms are given in Table 6.

Compound 64 contains a trinuclear cluster of cobalt atoms each pair of which is bridged by a carbonyl group. Within the criteria used in this review one of the bridges is symmetrical but the other two are asymmetric.

Compound 65, $Co_4(\mu\text{-}CO)_2(CO)_8(EtC_2Et)$, contains a butterfly arrangement of four cobalt atoms. Two sets of non-equivalent cobalt atoms (one in the fold, one in the wing of the butterfly) are each bridged by a single asymmetric carbonyl group.

### 3. *Semi-bridged complexes*

Three compounds only have been reported to contain semi-bridging car-

TABLE 6

Structural data for asymmetrically bridged cobalt complexes

| Cpd. no. | Formula | Co—Co (Å) | Co—C (Å) | | Co—C—Co (°) | Co—C—O (°) | | Ref. |
|---|---|---|---|---|---|---|---|---|
| 63 | $Co_2(\mu\text{-}CO)_2(CO)_4(C_7H_8)$ | 2.531(1) | 1.867(4) | 1.993(5) | 81.9(2) | 136.1(4) | 142.0(4) | 63 |
| 64 | $Co_3(\mu\text{-}CO)_3(CO)_4(ffars)$ (symm) | 2.440(1) | 1.915(7) | 1.937(7) | 78.6(3) | 140.6(6) | 140.7(6) | 64 |
| | | 2.470(2) | 1.940(9) | 1.986(8) | 78.0(3) | 138.3(7) | 143.7(7) | |
| | | 2.479(2) | 1.892(7) | 1.983(7) | 79.5(3) | 135.4(6) | 145.0(6) | |
| 65 | $Co_4(\mu\text{-}CO)_2(CO)_8(EtC_2Et)$ | 2.433(5) | | | | | | 65 |
| | | 2.438(5) | | | | | | |

TABLE 7

Structural data for semi-bridged complexes of cobalt

| Cpd. no. | Formula | Co—Co (Å) | Co—C (Å) | | Co—C—Co (°) | Co—C—O (°) | | Ref. |
|---|---|---|---|---|---|---|---|---|
| 66 | $Co_4(\mu\text{-}CO)_3(CO)_5(ffars)_2$ | 2.343 | 1.69 | 2.58 | 62.5 | 138.5 | 159 | 66 |
| | | 2.412 | 1.77 | 2.54 | 65.2 | 133.8 | 161 | |
| | | 2.446 | 1.84(2) | 2.61 | 64.0 | 137 | 159(1) | |
| 67 | $Co_3(\mu\text{-}CO)_3(C_5H_5)_3$ (asymm) | 2.440(4) | 1.78(3) | 1.99(3) | 80.5 | 130.9 | 148.6(7) | 67 |
| | | 2.458(4) | 1.75(4) | 2.11(4) | 78.5 | 128.3 | 153.2(7) | |
| 68 | $[Co_8(\mu\text{-}CO)_{10}(CO)_8C]^{2-}$ | 2.515(4) | 1.79(2) | 2.26(2) | 75.8 | 131(1) | 153(1) | 68 |
| | | 2.517(4) | 1.74(2) | 2.35(2) | 74.3 | 125(1) | 161(1) | |
| | | 2.522(4) | 1.80(2) | 2.27(2) | 75.6 | 130(2) | 165(2) | |
| | | 2.553(4) | 1.79(2) | 2.63(2) | 67.5 | 126(2) | 165(2) | |
| | (asymm) | 2.482(4) | 1.82(2) | 2.12(2) | 77.7 | 135(1) | 147(1) | |
| | (asymm) | 2.501(4) | 1.82(2) | 2.12(2) | 78.4 | 132(1) | 149(1) | |
| | (There are also 4 symmetrical $\mu_2$ carbonyls in this molecule) | | | | | | | |

bonyl groups between two cobalt atoms. In compound 66 there are three very weakly semi-bridging groups (Table 7). $Co_3(\mu\text{-}CO)_3(C_5H_5)_3$ [67] is based on an isosceles triangle of cobalt atoms. Each metal is associated with a $C_5H_5^-$ group and one carbonyl is triple bridging to all three cobalt atoms. The other two carbonyls span two edges of the metal triangle, one is asymmetric and the other semi-bridging as shown in Fig. 19.

The $[Co_8(\mu\text{-}CO)_{10}(CO)_8C]^{2-}$ ion [68] consists of a carbide surrounded by a distorted tetragonal prism of cobalt atoms, each of which carries a terminal carbonyl. The edge bridging carbonyls range from symmetric to grossly semi-bridging.

### *(iii) Homonuclear structures — ruthenium*

Table 8 gives structural details for all compounds containing a $\mu_2$ carbonyl group bridging two ruthenium atoms.

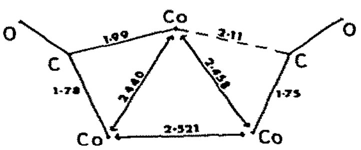
*Cis*-$Ru_2(\mu\text{-}CO)_2(CO)_2(C_5H_5)_2$ [69] is similar in every respect to its iron analogue, compound 5.

In $Ru_3(\mu\text{-}CO)(CO)_6(C_{10}H_8)$ [70] there are two independent molecules in the asymmetric unit, but they have similar stereochemistry and similar dimensions. An isosceles triangle of ruthenium atoms is bound to the azulene group and a single carbonyl symmetrically bridges the two equivalent metal atoms.

Compound 71, $Ru_6(\mu\text{-}CO)(CO)_{13}(C_6H_3Me_3)C$, consists of an octahedron of ruthenium atoms surrounding a central carbon atom. One ruthenium is bonded to the mesitylene group and a single pair of metal atoms is bridged by a symmetrical carbonyl group.

The compound $Ru_3(\mu\text{-}CO)_3(CO)_7(C_4H_4N_2)$ [72] contains a triangle of ruthenium atoms each pair of which is bridged by an asymmetric carbonyl group, but not in a cyclic manner.

$Ru_3(\mu\text{-}CO)_2(CO)_4(C_7H_7)(C_7H_9)$ [73] provides an interesting example of a triangle of ruthenium atoms in which one edge is non-bridged, the second is asymmetrically bridged and the third is semi-bridged (Fig. 20). The same ruthenium atom is associated with the short Ru—C distance for both bridges



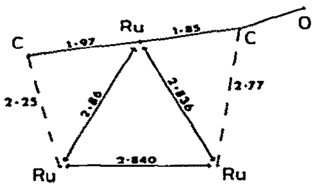


Fig. 19. Details of the $\mu_2$ carbonyl system in $Co_3(\mu\text{-}CO)_3(C_5H_5)_3$ (compound 67). (Drawn to scale.)

Fig. 20. Details of the carbonyl bridge system in $Ru_3(\mu\text{-}CO)_2(CO)_4(C_7H_7)(C_7H_9)$ (compound 73). (Drawn to scale.)

TABLE 8

Structural data for $\mu_2$ carbonyl bridged complexes of ruthenium

| Cpd. no. | Formula | Ru—Ru (Å) | Ru—C (Å) | | Ru—C—Ru (°) | Ru—C—O (°) | | Ref. |
|---|---|---|---|---|---|---|---|---|
| Symmetrical bridges | | | | | | | | |
| 69 | *cis* $Ru_2(\mu\text{-}CO)_2(CO)_2(C_5H_5)_2$ | 2.735(2) | 2x[1.975(13) | 1.998(13) | 87.0(5)] | | | 69 |
| 70 | $Ru_3(\mu\text{-}CO)(CO)_6(C_{10}H_8)$ | 2.740(4) | 2.037(37) | 2.051(37) | 84.1(1.3) | | | 70 |
| | (There are two independent molecules in the unit cell with very similar dimensions) | | | | | | | |
| 71 | $Ru_6(\mu\text{-}CO)(CO)_{13}C(C_6H_3Me_3)$ | 2.853(7) | 2.06(av) | | 87.7 | | | 71 |
| Asymmetrical bridges | | | | | | | | |
| 72 | $Ru_3(\mu\text{-}CO)_3(CO)_7(C_4H_4N_2)$ | 2.744(1) | 2.101(8) | 2.175(5) | 79.8(2) | 136.2(4) | 142.8(4) | 72 |
| | | 2.859(1) | 2.073(5) | 2.219(6) | 83.5(2) | 132.5(5) | 144.0(5) | |
| | | 2.861(1) | 2.108(6) | 2.189(6) | 83.5(2) | 134.9(4) | 141.6(4) | |
| 73 | $Ru_3(\mu\text{-}CO)_2(CO)_4(C_7H_7)$-$(C_7H_9)$ | 2.86 | 1.97 | 2.25 | 85.1 | | | 73 |
| | (semi) | 2.836 | 1.85 | 2.77 | 72.6 | 118.4 | 169 | |
| 74 | $Ru_3(\mu\text{-}CO)_2(CO)_4(C_8H_9)_2$ | 2x[2.835 | 1.86 | 2.54 | 78.6 | 111.5 | 160.9] | 74 |
| 75 | $Ru_4(\mu\text{-}CO)_2(CO)_{11}H_2$ | | | | | | | |
| | Molecule A | 2.762(7) | 1.89(5) | 2.31(5) | 82(2) | 130(4) | 149(4) | 75 |
| | | 2.764(7) | 1.90(5) | 2.47(5) | 77(2) | 129(4) | 154(5) | |
| | Molecule B | 2.778(7) | 1.94(5) | 2.40(4) | 79(2) | 129(4) | 152(4) | |
| | | 2.786(7) | 2.01(7) | 2.42(5) | 77(2) | 133(5) | 144(5) | |

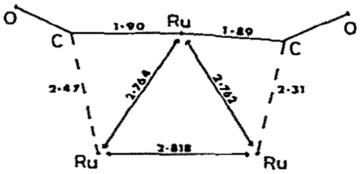


Fig. 21. Details of the carbonyl bridge system in $Ru_4(\mu\text{-}CO)_2(CO)_{11}H_2$ (compound 75). (Drawn to scale.)

and has no other carbonyl groups. Compound 74 is somewhat similar in its $Ru_3(\mu\text{-}CO)_2(CO)_4$ core, the only difference being that both bridges are now semi-bridging.

The carbonyl hydride $Ru_4(\mu\text{-}CO)_2(CO)_{11}H_2$ [75] has two independent molecules in the unit cell, although they have the same general stereochemistry. The ruthenium atoms are arranged in a tetrahedron and the apical metal is not bridged to the basal $Ru_3$ plane. Within this plane, one ruthenium is associated with a semi-bridging carbonyl to each of the other two metals as shown in Fig. 21.

### *(iv) Homonuclear structures — rhodium*

Structural details for all the compounds containing carbonyl bridges between two rhodium atoms are given in Table 9.

The $\mu_2$ carbonyl portion of $[Rh_{12}(\mu\text{-}CO)_2(CO)_{28}]^{2-}$ [76] is comparatively simple despite the complexity of the whole anion. Essentially the anion consists of two fragments, each closely resembling $Rh_6(CO)_{16}$, joined by a double carbonyl bridge system between a single rhodium atom in each cluster.

Compounds 77 and 78 are interesting isomers of $Rh_3(CO)_3(C_5H_5)_3$. Each contain a triangle of rhodium atoms with a $C_5H_5^-$ group bonded to each metal; the differences lie in the carbonyl and $C_5H_5^-$ arrangements. Compound 77 has a double carbonyl bridge between a pair of rhodium atoms, one bridge symmetrical and the other asymmetrical, with the third rhodium retaining a terminal carbonyl. Compound 78 has a single symmetric carbonyl bridge on each edge of the metal triangle. There appears to be little significant difference between the complexes in any of the molecular dimensions. In contrast however, the closely related complex $Rh_2(\mu\text{-}CO)(CO)_2(C_5H_5)_2$ [79] which has a terminal group on each rhodium has a significantly longer Rh—Rh distance.

$Rh_3(\mu\text{-}CO)(C_6F_5C_2C_6F_5)(C_5H_5)_3$ [80] also contains a triangle of rhodium atoms each bonded to a $C_5H_5^-$ group. The fluoroacetylene is considered to be $\sigma$-bonded to two rhodium atoms and $\pi$ -bonded to the third. The carbonyl bridges the two equivalent metal atoms. A point of interest is that in the analogous complex with the non-fluorinated acetylene, i.e. with diphenylacetylene, a similar structure is adopted except that the carbonyl now triply bridges to all three metal atoms [80].

The unusual complex $Rh_2(\mu\text{-}CO)(\mu\text{-}CPh_2)_2Cl_2(C_5H_5N)_2$ [81] is included even

TABLE 9

Structural data for $\mu_2$ carbonyl bridged complexes of rhodium

| Cpd. no. | Formula | Rh—Rh (Å) | Rh—C (Å) | | Rh—C—Rh (°) | Rh—C—O (°) | Ref. |
|---|---|---|---|---|---|---|---|
| 76 | $[Rh_{12}(\mu\text{-}CO)_2(CO)_{28}]^{2-}$ | 2.819 | 2×[1.99(2) | 2.01(2) | 90(1)] | | 76 |
| 77 | $Rh_3(\mu\text{-}CO)_2(CO)(C_5H_5)_3$ (asymm) | 2.620(2) | 1.947(14)<br>1.890(14) | 1.972(14)<br>2.003(14) | 83.9(5)<br>84.5(5) | | 77 |
| 78 | $Rh_3(\mu\text{-}CO)_3(C_5H_5)_3$ | 2×[2.617(3)<br>2.622(3) | 2.00(2)<br>1.99(2) | 2.01(2)<br>1.99(2) | 81.4(9)]<br>82.4(9) | | 78 |
| 79 | $Rh_2(\mu\text{-}CO)(CO)_2(C_5H_5)_2$ | 2.681(2) | 1.990(7) | 2.017(17) | 84.0(6) | | 79 |
| 80 | $Rh_3(\mu\text{-}CO)(C_6F_5C_2C_6F_5)\text{-}(C_5H_5)_3$ | 2.672(1) | 1.96(1) | 1.96(1) | 86.0(6) | | 80 |
| 81 | $Rh_2(\mu\text{-}CO)(\mu\text{-}CPh_2)_2Cl_2\text{-}(C_5H_5N)_2$ | 2.51 | | | | | 81 |
| 82 | $Rh_4(\mu\text{-}CO)_3(CO)_9$ | 2.716(6)<br>2.734(7)<br>2.796(8) | 2.01(6)<br>1.93(11)<br>1.92(5) | 2.18(6)<br>1.98(11)<br>1.94(5) | 80.6(2.1)<br>88.8(4.8)<br>92.9(2.1) | | 82 |
| 83 | $Rh_4(\mu\text{-}CO)_3(CO)_5[P(OPh)_3]_4$ | 2.72(av) | 2.00(av) | | | | 83 |
| 84 | $Rh_4(\mu\text{-}CO)_3(CO)_5(dpm)_2$ | 2.671(1)<br>2.740(1)<br>2.735(1) | 2.079(16)<br>2.107(16)<br>2.027(13) | 2.086(14)<br>2.116(15)<br>2.101(15) | 79.8(6)<br>80.9(6) | | 84 |
| 85 | $Rh_2Fe_2(\mu\text{-}CO)_3(CO)_5(C_5H_5)_2$ | 2.648(3) | 1.97(4) | 1.97(4) | 85(2) | | 85 |
| 86 | $[Rh_6(\mu\text{-}CO)_9(CO)_6C]^{2-}$ | 2×[2.772(2) | 2.10(1) | 2.11(1) | 82.4(5)] | | 86 |

|  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  | 2x[2.773(2) | 2.12(1) | 2.13(1) | 81.6(4)] |  |  |  |
|  |  |  | 2x[2.783(2) | 2.12(1) | 2.13(1) | 81.9(4)] |  |  |  |
|  |  |  | 2x[2.817(2) | 2.04(1) | 2.06(1) | 86.9(5)] |  |  |  |
|  |  |  | 2.817(2) | 2.03(1) | 2.03(1) | 87.8(7) |  |  |  |
| 87 | $[Rh_7(\mu\text{-}CO)_2(\mu\text{-}I)(CO)_{14}]^{2-}$ |  | 2.886(5) | 1.96(2) | 2.04(3) | 92.3 |  |  | 87 |
| 88 | $[Rh_{13}(\mu\text{-}CO)_{12}(CO)_{12}H_2]^{3-}$ |  | 2.777(3) | 1.99(2) | 1.99(2) | 88(2) |  |  | 88 |
|  | (There are 11 other $\mu_2$ carbonyl bridges in this complex, all of similar dimensions) |  |  |  |  |  |  |  |  |
| 89 | $[Rh_{15}(\mu\text{-}CO)_{14}(CO)_{14}C_2]^-$ |  |  |  |  |  |  |  |  |
|  |  | (asymm) | 2x[2.734(3) | 1.98(1) | 2.11(1) | 83.8] |  |  | 89 |
|  |  | (asymm) | 2x[2.738(3) | 1.97(1) | 2.11(1) | 84.2] |  |  |  |
|  |  |  | 2x[2.800(3) | 2.02(1) | 2.04(1) | 87.2] |  |  |  |
|  |  | (asymm) | 2x[2.809(3) | 1.98(1) | 2.03(1) | 88.9] |  |  |  |
|  |  |  | 2x[2.826(3) | 2.02(1) | 2.05(1) | 87.9] |  |  |  |
|  |  | (asymm) | 2x[2.829(3) | 1.97(1) | 2.05(1) | 89.4] |  |  |  |
|  |  |  | 2x[2.833(3) | 2.00(2) | 2.02(2) | 89.6] |  |  |  |
| 90 | $Rh_{12}(\mu\text{-}CO)_{11}(CO)_{14}C_2$ |  |  |  |  |  |  |  |  |
|  |  | (asymm) | 2.784(2) | 1.96(2) | 2.14(2) | 85.4 | 133 | 142 | 90 |
|  |  | (asymm) | 2.575(2) | 1.98(2) | 2.14(2) | 83.9 | 129 | 147 |  |
|  | (There are also 8 symmetrical $\mu_2$ carbonyls in this complex) |  |  |  |  |  |  |  |  |
| 91 | $Rh_2(\mu\text{-}CO)_2(CO)_2(PPh_3)_4$ |  |  |  |  |  |  |  |  |
|  |  | (asymm) | 2x[2.630(1) | 1.956(7) | 2.051(6) | 82.0(3)] |  |  | 91 |
| 92 | $Rh_2(\mu\text{-}CO)(C_7H_8)_2(C_8H_8O)$ |  |  |  |  |  |  |  |  |
|  |  | (asymm) |  | 1.99 | 2.15 | 84.3 | 136.8 | 138.6 | 92 |
| 93 | $[Rh_2(\mu\text{-}CO)(\mu\text{-}Cl)(\mu\text{-}dpm)_2\text{-}(CO)]^+$ |  | 2.841(1) | 2.01 | 2.09(1) | 87.7(4) |  |  | 93 |
| 94 | $Rh_8(\mu\text{-}CO)_8(CO)_{11}C$ |  |  |  |  |  |  |  |  |
|  |  | (asymm) | 2.699(3) | 2.033(6) | 2.124(9) | 80.9 |  |  | 94 |
|  |  | (asymm) | 2.741(3) | 2.007(7) | 2.144(7) | 82.6 |  |  |  |
|  |  |  | 2.752(3) | 2.058(6) | 2.059(6) | 83.9 |  |  |  |
|  |  |  | 2.784(3) | 1.976 | 2.195 | 83.6 |  |  |  |
|  |  | (asymm) | 2.795(3) | 1.997(6) | 2.050(7) | 87.4 |  |  |  |
|  |  |  | 2.841(3) | 2.025(6) | 2.040(7) | 88.7 |  |  |  |
|  |  | (semi) | 2.755(3) | 1.99(9) | 2.796(8) | 67.9 | 121.1 | 171.0 |  |
|  |  | (semi) | 2.899(3) | 1.91(7) | 2.831(9) | 72.4 | 116.5 | 171.9 |  |

though few details of its structure are available. The stereochemistry about the rhodium atoms is approximately square pyramidal which share an edge (the $\mu$-$CPh_2$ groups) and have a common apex at the carbonyl. The Rh—Rh distance is short.

Compound 82, $Rh_4(\mu\text{-}CO)_3(CO)_9$, has a structure similar to that of its cobalt analogue. Although it was suggested that one of the carbonyl bridges may be asymmetric, they are in fact all symmetric within the criteria used in this survey. $Rh_4(\mu\text{-}CO)_3(CO)_5[P(OPh)_3]_4$ [83] is a simple derivative of $Rh_4(CO)_{12}$ in which a terminal carbonyl on each rhodium is substituted by the phosphite. The overall stereochemical features of the parent are retained. In compound 84, $Rh_4(\mu\text{-}CO)_3(CO)_5(dpm)_2$, the basal carbonyl bridges of $Rh_4(CO)_{12}$ are retained but one terminal carbonyl on each metal is substituted by phosphorus. This means that one edge of the metal tetrahedron is bridged by both carbonyl and dpm, but it appears to make little difference to the carbonyl bridges.

$Rh_2Fe_2(\mu\text{-}CO)_3(CO)_5(C_5H_5)_2$ [85] contains an irregular tetrahedron of metal atoms. There is a symmetrical carbonyl bridge between the two rhodium atoms and also two asymmetrical bridges between rhodium and iron which will be discussed later.

The ion $[Rh_6(\mu\text{-}CO)_9(CO)_6C]^{2-}$ [86] contains the first reported trigonal prismatic array of metal atoms and the carbon atom occupies the centre of the prism. Each rhodium has a terminal carbonyl and each edge of the prism (9 in all) is bridged by a carbonyl, although there are only five crystallographically independent bridging groups. All are symmetrical with normal Rh—Rh and Rh—C separations.

The anion $[Rh_7(\mu\text{-}CO)_2(CO)_{14}I]^{2-}$ [87], contains two bridging carbonyl groups and a bridging iodine atom. However, there is considerable disorder between the iodo group and one bridging carbonyl with the result that only the other bridge is well defined. The distance spanned by this group is the largest in Table 9 and the bridge is just symmetrical within the limits of the e.s.d.'s.

The geometry of $[Rh_{13}(\mu\text{-}CO)_{12}(CO)_{12}H_3]^{2-}$ [88] consists of three nearly parallel layers of rhodium atoms representing a fragment from a hexagonal close packed array and the central metal atom is 12-coordinated to the other metals. Each outer metal atom has a terminal carbonyl and the other 12 carbonyls bridge half the edges of the metal polyhedron.

The equally impressive cluster $[Rh_{15}(\mu\text{-}CO)_{14}(CO)_{14}C_2]^-$ [89] contains an array of rhodium atoms described as a centred and tetracapped pentagonal prism. Each of the 14 peripheral rhodiums has a terminal carbonyl and the remaining carbonyls bridge edges of the metal polyhedron in such a way that each metal is associated with three carbonyl groups. Since the molecule has $C_2$ symmetry there are only seven crystallographically independent carbonyl bridges. Asymmetric carbonyl groups are rare for rhodium, but this compound shows a mixture of symmetric and asymmetric bridges.

$Rh_{12}(\mu\text{-}CO)_{11}(CO)_{14}C_2$ [90] is the most unsymmetrical metal cluster known.

A $C_2$ unit lies within the metal polygon and there are ten $\mu_2$ carbonyls and one $\mu_3$ carbonyl. Two of the edge bridges are asymmetric.

Only three examples have been reported which contain asymmetric bridges between rhodium atoms without there also being symmetric bridges in the molecule. $Rh_2(\mu\text{-}CO)_2(CO)_2(PPh_3)_4$ [91] contains two crystallographically identical asymmetric bridges. The coordination about each rhodium is completed by a terminal carbonyl and two $PPh_3$ groups. Compound 92, $Rh_2(\mu\text{-}CO)(C_7H_8)_2(C_8H_8O)$, contains the novel ligand $C_8H_8O$ which σ and π-bonds to both rhodium atoms and an asymmetrical carbonyl group also spans the metals.

The cation $[Rh_2(\mu\text{-}CO)(\mu\text{-}Cl)(CO)_2(dpm)_2]^+$ [93] contains two bridging dpm ligands and the bridging carbonyl and chlorine in a plane at right angles to the $Rh_2P_4$ plane. The carbonyl may be reversibly removed.

Finally, in this section another polymeric cluster, $Rh_8(\mu\text{-}CO)_8(CO)_{11}C$ [94] provides the only examples of semi-bridging carbonyl groups between two rhodium atoms. The cluster also contains symmetric and asymmetric bridges.

### *(v) Homonuclear structures — other elements*

There are some 21 structures which contain $\mu_2$ carbonyl bridges between homonuclear pairs of metal atoms other than iron, cobalt, ruthenium and rhodium. These elements appear reluctant to form carbonyl bridges, but when they are persuaded to do so the resulting structures are often unusual and several of them will feature prominantly in the later discussion sections. Structural details for these complexes are given in Table 10.

$V_2(\mu\text{-}CO)_2(CO)_3(C_5H_5)_2$ [95] contains two non-equivalent vanadium atoms. Each has a $C_5H_5^-$ group but one has a single terminal carbonyl group while the other has two. Two semi-bridging carbonyls span the metals as shown in Fig. 22.

$Mo_2(\mu\text{-}CO)_4(C_5H_5)_2$ [96] has a short metal—metal distance and there are four semi-bridging carbonyl groups, two in each direction. Compounds 97 and 98 are very similar and have the formulae $Mo_2(\mu\text{-}CO)(\mu\text{-}RC_2R)(CO)_3(C_5H_5)_2$ (R = Et [97] and R = H [98]). In each case the carbonyl is semi-bridging and it is specifically suggested that intramolecular forces cause the carbonyl to be semi-bridging.

In $Mn_2(\mu\text{-}CO)(\mu\text{-}NO)(CO)(NO)(C_5H_5)_2$ [99] there is a crystallographically imposed centre of symmetry which makes both terminal and bridging carbonyl and nitrosyl groups disordered. Thus the values given in Table 10 are averaged for the two ligands. $Mn_2(\mu\text{-}CO)(\mu\text{-}GeMe_2)(CO)_8$ [100] contains an asymmetric carbonyl bridge and a symmetric $GeMe_2$ one.

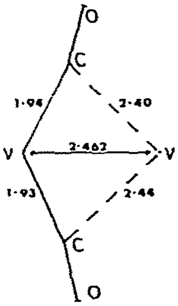
Compound 101, $Mn_2(\mu\text{-}CO)[\mu\text{-}(CF_3)_2CN]_2(CO)_6$, has a structure basically similar to $Fe_2(CO)_9$ but the carbonyl bridge is not symmetric. It is actually on the arbitrary borderline between asymmetric and semi-bridging, but within our criteria it is classed as asymmetric. Compound 102, $Mn_2(\mu\text{-}CO)(\mu\text{-}AsMe_2)(CO)_5(C_5H_5)_2$ contains a semi-bridging carbonyl group, and although

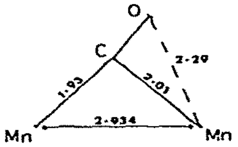
TABLE 10

*Structural data for $\mu_2$ carbonyl bridged complexes for homonuclear pairs*

| Cpd. no. | Formula | | M–M (Å) | M–C (Å) | | M–C–M (°) | M–C–O (°) | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 95 | $V_2(\mu\text{-}CO)_2(CO)_3(C_5H_5)_2$ | (semi) | 2.462(2) | 1.94(1) | 2.40(1) | 68.2 | 1.228 | 169.0 | 95 |
| 96 | $Mo_2(\mu\text{-}CO)_4(C_5H_5)_2$ | (semi) | 2.448(1) | 2×[2.14(2) | 2.51(2) | 62.9 | 120.8 | 176.3(16)] | 96 |
| | | (semi) | | 2×[2.06(2) | 2.52(2) | 63.7 | 121.0 | 175.3(16)] | |
| 97 | $Mo_2(\mu\text{-}CO)(\mu\text{-}EtC_2Et)(CO)_3\cdot(C_5H_5)_2$ | (semi) | 2.977(1) | 1.936(6) | 2.826(6) | 73.8 | 116.8(4) | 168.1(5) | 97 |
| 98 | $Mo_2(\mu\text{-}CO)(\mu\text{-}HC_2H)(CO)_3\cdot(C_5H_5)_2$ | (semi) | 2.980(1) | 1.951(4) | 2.902(4) | 72.8 | 118.4(3) | 168.5(4) | 98 |
| 99 | $Mn_2(\mu\text{-}CO)(\mu\text{-}NO)(CO)(NO)\cdot(C_5H_5)_2$ | | 2.571(1) | 2×[1.901(3) | 1.911(4) | 84.8] | | | 99 |
| 100 | $Mn_2(\mu\text{-}CO)(\mu\text{-}GeMe_2)(CO)_8$ | (asymm) | 2.854(2) | 2.037(8) | 2.154(7) | 85.8(3) | 134.1 | 140.0 | 100 |
| 101 | $Mn_2(\mu\text{-}CO)[\mu\text{-}(CF_3)_2CN]_2(CO)_6$ | (asymm) | 2.5183(24) | 1.994(9) | 2.173(9) | 75.19(34) | 133.83(77) | 150.96(77) | 101 |
| 102 | $Mn_2(\mu\text{-}CO)(\mu\text{-}AsMe_2)(CO)_5\cdot(C_5H_5)$ | (semi) | 2.912(4) | 1.83(2) | 2.57 | | | 160.0(2) | 102 |
| 103 | $Mn_2(\mu\text{-}CO)(\mu\text{-}dpm)_2(CO)_4$ | (linear) | 2.934(6) | 1.93(3) | 2.01(3) | 96(1) | 90.2 | 173(3) | 103 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 104 | $Re_2(\mu\text{-}CO)(CO)_4(C_5H_5)_2$ | | 2.957(1) | 2.06(2) | 2.06(2) | 91.7 | | | 104 |
| 105 | $Os_3(\mu\text{-}CO)_2(CO)_8(PhC_2Ph)$ | (semi) | 2.844(1) | 1.961(9) | 2.745(8) | 72.2 | 121.1(7) | 166.6(8) | 105 |
| | | (semi) | 2.883(1) | 1.944(12) | 2.765(10) | 73.2 | 120.0(8) | 166.6(9) | |
| 106a | $Ir_4(\mu\text{-}CO)_3(CO)_6(PPh_3)_3$ | | 2.73(av) | 2.1(av) | | | | | 106 |
| 106b | $Ir_4(\mu\text{-}CO)_3(CO)_7(PPh_3)_2$ | | 2.73(av) | 2.1(av) | | | | | 106 |
| 107 | $Ni_2(\mu\text{-}CO)(L{-}L)_2(CO)_2$<br>$(L{-}L = (CF_3)_2PSP(CF_3)_2)$ | | 2.577(5) | 1.983(20) | 1.983(20) | 81.0(1.0) | | | 107 |
| 108a | $[Ni_3Mo_2(\mu\text{-}CO)_3(CO)_{13}]^{2-}$ | | 2.327(10)<br>2.347(11)<br>2.350(8) | 1.94(5)<br>1.88(5)<br>1.86(4) | 1.97(5)<br>1.91(5)<br>1.87(4) | 73(2)<br>76(3)<br>78(2) | | | 108 |
| 108b | $[Ni_3W_2(\mu\text{-}CO)_3(CO)_{13}]^{2-}$ | | 2.324(12)<br>2.334(9)<br>2.360(12) | 1.81(6)<br>1.79(5)<br>1.76(5) | 1.90(6)<br>1.84(5)<br>1.79(5) | 78(3)<br>80(2)<br>83(3) | | | 108 |
| 109 | $Ni_4(\mu\text{-}CO)_6[P(C_2H_4CN)_3]_4$ | | 3×[2.506(5)<br>3×[2.512(6) | 1.889(19)<br>1.852(22) | 1.922(18)<br>1.881(22) | 82.2(7)]<br>84.6(9)] | | | 109 |
| 110 | $[Ni_6(\mu\text{-}CO)_6(CO)_6]^{2-}$ | | 2.38(av) | 1.90(av) | | 77.6(av) | | | 110 |
| 111 | $Pd_2(\mu\text{-}CO)(\mu\text{-}dam)_2Cl_2$ | | 3.274(8) | 1.84(5) | 1.95(6) | 119(3) | | | 111 |
| 112 | $Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4$<br>$\cdot (AcOH)_2$ | | 2×[2.663(1) | 2×[1.97 | 2.01 | 84.2]] | | | 112 |
| 113 | $Pt_2Ru(\mu\text{-}CO)_3(CO)_2\text{-}$<br>$[PMePh_2]_3$ | | 2.647(2) | 2.07(3) | 2.09(3) | 79.0(1.1) | | | 113 |





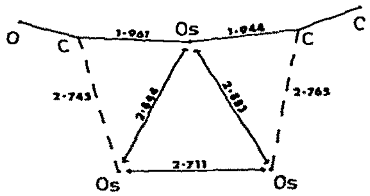


Fig. 22. Details of the carbonyl bridge system in $V_2(\mu\text{-}CO)_2(CO)_3(C_5H_5)_2$ (compound 95). (Planar projection, drawn to scale.)

Fig. 23. Details of the carbonyl bridge system in $Mn_2(\mu\text{-}CO)(\mu\text{-}dpm)_2(CO)_4$ (compound 103). (Drawn to scale.)

Fig. 24. Details of the carbonyl bridge system in $Os_3(\mu\text{-}CO)_2(CO)_8(PhC_2Ph)$ (compound 105). (Drawn to scale.)

the metal atoms are non-equivalent electronically it was suggested that steric forces are responsible for this configuration.

$Mn_2(\mu\text{-}CO)(\mu\text{-}dpm)_2(CO)_4$ [103] contains a radically different type of carbonyl bridge as shown in Figure 23. The bridging carbonyl is essentially linear and is thought to act as a four electron donor by σ-bond formation to one metal and by μ-donation to the other.

$Re_2(\mu\text{-}CO)(CO)_4(C_5H_5)_2$ [104] contains a single symmetrical carbonyl bridge.

Compound 105, $Os_3(\mu\text{-}CO)_2(CO)_8(PhC_2Ph)$, contains a triangle of osmium atoms and the acetylene is bound to all the metals. Two osmiums have three terminal carbonyl groups and the other has four, two of which are semi-bridging to the other two metal atoms as shown in Fig. 24.

Few structural details are available for compounds 106a and 106b, but they are included because of the contrast between their structures and that of the parent carbonyl $Ir_4(CO)_{12}$. $Ir_4(\mu\text{-}CO)_3(CO)_6(PPh_3)_3$ (Compound 106a) has a structure based on a form of $Ir_4(CO)_{12}$ with the configuration of $Co_4(CO)_{12}$ even though the iridium carbonyl itself has the non-bridged tetrahedral structure [129]. The apical iridium has three terminal carbonyls and is directly bonded to the three iridiums of the basal plane. Each of these has a $PPh_3$ group and the basal triangle is edge bridged by three symmetrical carbonyls. Compound 106b is similar, the only difference being that one basal iridium has an extra terminal carbonyl instead of $PPh_3$.

Compound 107, $Ni_2(\mu\text{-}CO)[\mu\text{-}(CF_3)_2PSP(CF_3)_2]_2(CO)_2$, contains a single symmetrical carbonyl bridge and the two bridging diphosphine ligands are distorted to accommodate the short Ni—Ni separation. Compounds 108a and 108b, $[Ni_3M_2(\mu\text{-}CO)_3(CO)_{13}]^{2-}$ (M = Mo, W respectively) contain a trigonal bipyramidal arrangement of metal atoms with $Ni_3$ in the equatorial plane. Each edge of the nickel triangle is bridged by a symmetrical carbonyl. $Ni_4(\mu\text{-}CO)_6[P(C_2H_4CN)_3]_4$ [109] is a highly symmetrical structure containing a tetrahedron of metal atoms, each edge of which is bridged by a symmetrical carbonyl group. Compound 110, $[Ni_6(\mu\text{-}CO)_6(CO)_6]^{2-}$, contains a trigonal antiprismatic (elongated octahedron) arrangement of nickel atoms and may be envisaged as being formed from the dimerization of two planar $Ni_3(\mu\text{-}CO)_3(CO)_3$ units.

Compound 111, $Pd_2(\mu\text{-}CO)(\mu\text{-}dam)_2Cl_2$, is unique in that it is the only carbonyl bridged complex which definitely does not also contain a metal—metal bond. The symmetrical bridge spans a Pd—Pd distance of 3.274 Å and the angle at the bridging carbon is 120°.

$Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4 \cdot (CH_3COOH)_2$ [112] contains a parallelogram of palladium atoms. Two opposite edges are each spanned by two symmetrical carbonyl groups and the other two edges each by two acetate groups. The acetic acid occurs as separate dimer units in the crystal lattice.

Compound 113, $Pt_2Ru(\mu\text{-}CO)_3(CO)_2[PMePh_2]_3$, contains a triangle of metal atoms each edge of which is bridged by a symmetrical carbonyl. Each metal is coordinated to a phosphine ligand and in addition the ruthenium carries two terminal carbonyl groups.

### *(vi) Heteronuclear structures*

#### *1. Complexes containing iron*

In compounds 114—118, which all contain iron and cobalt and are all very similar, the $C_5H_5^-$ group is attached to iron. $FeCo(\mu\text{-}CO)_2(CO)_2(C_7H_8)(C_5H_5)$ [114] has rather symmetrical bridges despite the different identity of the metals. Table 11 lists the structural details for this and the other heteronuclear complexes containing iron. Compound 115 shows distortion of one carbonyl group even though both bridges are in equivalent environments. This distortion involves a lengthening of the Co—C bond and a corresponding decrease in the Fe—C bond compared with compound 114 and the bridge may be described as slightly asymmetric. Similar slight distortions are apparent in compounds 116 and 117. In compound 118, $FeCo(\mu\text{-}CO)_2(CO)_2(PMePh_2)(C_5H_5)$, this non-equivalence in the bridges is still more obvious, but in this case the environments of the bridges are not the same. One bridge is symmetrical, but the other is grossly asymmetric, bordering on semi-bridging.

In the simple anion $[FeCo(\mu\text{-}CO)(CO)_7]^-$ [119] the single bridge is now truly semi-bridging, but this time from cobalt to iron as shown in Fig. 25.

Compound 120, $[Fe_2Rh(\mu\text{-}CO)_2(\mu\text{-}PPh_2)_2(CO)_2(C_5H_4Me)_2]^+$, contains a non-closed triangular arrangement of metal atoms, each Fe—Rh linkage being spanned by both a bridging carbonyl and $PPh_2^-$ group.

In compound 41, $Fe_3Rh(\mu\text{-}CO)_4(CO)_7(C_5H_5)$, there is a tetrahedron of metal atoms and two of the Fe—Rh edges are bridged by carbonyls. Although there are some slight angular distortions at the bridging carbon, the metal—

TABLE 11

Structural data for carbonyl bridged heteronuclear pairs containing iron

| Cpd. no. | Formula | Fe—M (Å) | Fe—C (Å) | M—C (Å) | Fe—C—M (°) | Fe(M)—C—O (°) | | Ref. |
|---|---|---|---|---|---|---|---|---|
| 114 | $FeCo(\mu\text{-}CO)_2(CO)_2(C_7H_8)\cdot(C_5H_5)$ | 2.503(1) | 1.903(4)<br>1.911(5) | 1.905(4)<br>1.918(4) | 83.2<br>82.7(2) | | | 114 |
| 115 | $FeCo(\mu\text{-}CO)_2(CO)_2(C_6H_{10})\cdot(C_5H_4Me)$ | 2.5460(10) | 1.897(6)<br>1.916(6) | 1.966(7)<br>1.933(6) | 82.5(3)<br>82.8(3) | 136.5(6) | 141.1(6) | 115 |
| 116 | $FeCo(\mu\text{-}CO)_2(CO)_4(C_5H_5)$ | 2.545(1) | 2×[1.882(7) | 2.036(7) | 80.9(3) | 134.6(6) | 144.5(6)] | 116 |
| 117 | $FeCo(\mu\text{-}CO)_2(CO)_4C_9H_7$ | 2.552(2) | 1.838(12)<br>1.916(13) | 2.054(12)<br>1.960(13) | 81.8(4)<br>82.4(5) | 129.9(1.0)<br>138.8(1.1) | 143.8(1.1)<br>138.8(1.1) | 117 |
| 118 | $FeCo(\mu\text{-}CO)_2(CO)_3(PMePh_2)C_5H_5$ | 2.540(4) | 1.797(16)<br>1.967(19) | 2.027(20)<br>1.907(17) | 83.0(7)<br>81.9(6) | 129.6(1.5)<br>134.0(1.6) | 147.1(1.7)<br>144.1(1.7) | 118 |
| 119 | $[FeCo(\mu\text{-}CO)(CO)_7]^-$ | 2.585(3) | 2.210(19) | 1.774(20) | 80.1 | 128.7(1.4) | 151.2(1.6) | 119 |
| 120 | $[Fe_2Rh(\mu\text{-}CO)_2(\mu\text{-}PPh_2)_2\cdot(CO)_2(C_5H_4Me)_2]^+$ | 2.659(2)<br>2.674(1) | 1.88(1)<br>1.89(9) | 2.025(10)<br>2.023(9) | 85.4(4)<br>86.1(6) | 130.5(7)<br>129.7(6) | 143.0(8)<br>143.5(7) | 120 |
| 41 | $Fe_3Rh(\mu\text{-}CO)_4(CO)_7(C_5H_5)$ | 2.568(3)<br>2.615(3) | 1.934(23)<br>1.861(23) | 2.086(23)<br>2.096(23) | 79.3(9)<br>82.5(9) | 134.9(1.9)<br>130.5(1.8) | 144.1(1.9)<br>146.9(2.0) | 41 |
| 85 | $Fe_2Rh_2(\mu\text{-}CO)_3(CO)_5(C_5H_5)$ | 2×[2.598(5) | 1.79(4) | 2.18(3) | 81(1) | 125(3) | 152(3)] | 85 |
| 121 | $FeRu_3(\mu\text{-}CO)_2(CO)_{11}H_2$ | | | | | | | |
| | Molecule A | 2.624(9)<br>2.661(12) | 1.78(6)<br>1.84(5) | 2.32(6)<br>2.25(5) | 78(2)<br>81(2) | 131(6)<br>134(4) | 150(7)<br>145(4) | 121 |
| | Molecule B | 2.619(9)<br>2.654(9) | 1.68(5)<br>1.86(4) | 2.23(5)<br>2.32(4) | 84(2)<br>78(2) | 120(4)<br>123(4) | 156(4)<br>153(4) | |

TABLE 12

Structural data for carbonyl bridged complexes containing other heteronuclear pairs

| Cpd. no. | Formula | M–M′ (Å) | Co–C (Å) | Ni–C (Å) | M–C–M′ (°) | M(M′)–C–O (°) | | Ref. |
|---|---|---|---|---|---|---|---|---|
| 122 | $CoNi(\mu\text{-}CO)_2(CO)_2[PPh_2(C_6H_{11}]\text{-}(C_5H_4Me)$ | 2.418(2) | 1.928(10)<br>1.929(10) | 1.863(9)<br>1.842(11) | 79.3(4)<br>79.7(4) | 137.2(8)<br>139.3(9) | 143.5(8)<br>140.5(8) | 122 |
| 123 | $CoNi(\mu\text{-}CO)_2(CO)_2PEt_3(C_5H_5)$ | 2.4097(8) | 1.890(5)<br>1.956(6) | 1.900(6)<br>1.825(6) | 79.0(2)<br>79.1(2) | 134.3(5)<br>139.8(5) | 146.7(5)<br>141.0(5) | 123 |
| 124 | $CoNi(\mu\text{-}CO)_2(CO)_2[P(p\text{-}C_6H_4F)_3]\text{-}(C_5H_5)$ | 2.425(2) | 1.904(11)<br>2.026(12) | 1.894(11)<br>1.823(14) | 79.4(4)<br>77.9(5) | 134.5(9)<br>138.0(11) | 145.4(10)<br>143.8(11) | 124 |
| | | | Co–C (Å) | Pt–C (Å) | | | | |
| 53 | $Co_2Pt_2(\mu\text{-}CO)_3(CO)_5PPh_3$ | 2.540(2)<br>2.579(2) | 1.961(17)<br>2.188(19) | 2.053(21)<br>1.988(20) | 78.47(44)<br>76.11(42) | 140.53(1.18)<br>132.23(1.23) | 140.66(1.28)<br>151.29(1.22) | 53 |
| | | | Ru–C (Å) | Pt–C (Å) | | | | |
| 113 | $RuPt_2(\mu\text{-}CO)_3(CO)_2[PMePh_2]_3$ | 2.707(2)<br>2.729(2) | 2.07(2)<br>2.19(2) | 2.08(2)<br>2.09(2) | 81.4(9)<br>79.1(8) | 137.7(19)<br>137.6(20) | 140.7(19)<br>143.1(20) | 113 |

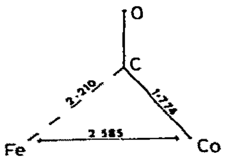


Fig. 25. Details of the carbonyl bridge system in the $[FeCo(\mu\text{-}CO)(CO)_7]^-$ anion (compound 119). (Drawn to scale.)

carbon bond lengths are normal. However, compound 85, $Fe_2Rh_2(\mu\text{-}CO)_3(CO)_5(C_5H_5)_2$, which also contains a metal tetrahedron, has two semi-bridging carbonyls from both rhodium atoms to one iron.

$FeRu_3(\mu\text{-}CO)_2(CO)_{11}H_2$ [121] has two independent molecules in the unit cell which differ significantly in their dimensions. Each cluster contains a metal tetrahedron with two Fe—Ru edges bridged by asymmetric carbonyl groups in molecule A and by semi-bridging groups in molecule B.

### 2. *Complexes not containing iron*

Compounds 122—124 are all very similar; they all contain a cobalt—nickel pair bridged by two carbonyls and the nickel coordination is completed by a cyclopentadienyl group. The cobalt atom has two terminal carbonyls and a phosphine ligand whose identity varies between the complexes. As shown in Table 12 in compound 122 the bridges are equivalent in the sense that both Co—C bond lengths are almost equal as are both Ni—C bonds. In compound 123, however, this is not true; one bridge is very similar to the previous case, but for the other the Co—C distance is decreased significantly with a corresponding lengthening of the Ni—C bond. The overall effect is that in one bridge the Co—C bond is longer than Ni—C, and in the other bridge the reverse is true. In compound 124 neither the Co—C nor the Ni—C pairs of bonds are similar in length, but in this case the Co—C bond length is the greater in both bridges.

Compound 53, $Co_2Pt_2(\mu\text{-}CO)_3(CO)_5(PPh_3)$, contains two carbonyl bridges between each of the cobalt atoms and one platinum. One is symmetrical with the Co—C shorter than Pt—C as expected, but the second bridge is very asymmetric with a long Co—C bond. This asymmetry is, according to the authors, due to steric crowding about the carbonyl group.

$RuPt_2(\mu\text{-}CO)_3(CO)_2(PMePh_2)_3$ [113] has both ruthenium—platinum edges of the metal triangle bridged by symmetrical carbonyl groups.

## C. DISCUSSION

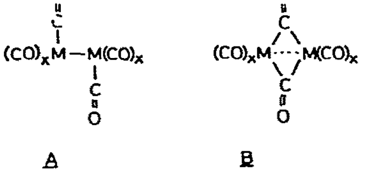
Although this discussion section is notionally divided into three parts, the component sections of structural considerations, electronic considerations and fluxional behaviour of carbonyls in solution are intimately interwoven. We have chosen to consider the solid phase structures as the first discussion topic, but it is necessary, we believe, to take into account the results of studies on solutions of the carbonyl complexes to fully appreciate the significance of features in the solid state. In particular, the very low activation energies of exchange between terminal and bridging carbonyl groups and the concept of intermediate stages in this exchange involving non-symmetric bridging carbonyls are important.

### *(i) Structural considerations*

When two or more metal atoms come together to form a polynuclear metal complex the metal atoms can be linked in two extreme ways as shown in Fig. 26 which are equivalent in terms of electronic book-keeping. In A each carbonyl formally donates two electrons to one metal only and an unsupported metal—metal bond pairs the odd electron on each metal to form the only linkage between them. In B each bridging carbonyl donates a single electron to each metal. The spin pairing in the invariably diamagnetic complex is usually assumed to occur via a metal—metal bond, although an alternative mechanism exists via the bridging carbonyl group.

It is also well known that there is a distinct tendency for the larger metals of the second and third transition series to favour the unbridged structure whilst their first row analogues prefer the bridged structure. For example, $Fe_3(CO)_{12}$ has bridging carbonyls along one edge of the metal triangle, but $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ do not.

Prior to the NMR work described later, there had been indications that these two extreme types of structure were almost equi-energetic, at least in some cases such as $Co_2(CO)_8$. This molecule has a double carbonyl bridged structure in the solid state [45], but in solution IR spectroscopic studies inferred the existence of substantial quantities of the non-bridged form [130,131] and indeed the crystal structures of some simple derivatives of $Co_2(CO)_8$ had been



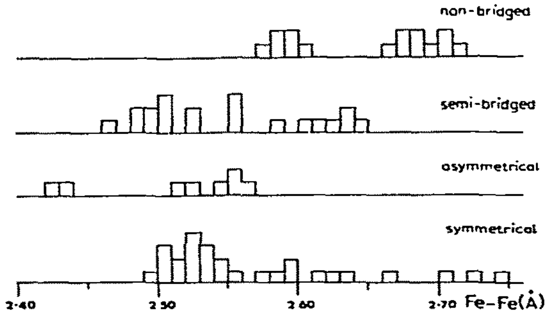


Fig. 26. Equivalent ways of linking two metal atoms: A, terminal carbonyl groups and a metal—metal σ bond; B, two bridging carbonyl groups.

Fig. 27. Distribution of Fe—Fe distances for compounds in Tables 1—3 according to the carbonyl bridge type.

shown to contain non-bridged cobalt atoms [132].

There appears to be no correlation between metal—metal separation and the type of carbonyl bridge spanning the metals. Fig. 27 shows a histogram of iron—iron separations against the type of carbonyl bridge for all the complexes in Tables 1—3. The three symmetrical bridges with long bond lengths are compounds 25—27 which have only single carbonyl bridges and a diene or dpm as the other bridge. It is likely that this second bridge largely determines the metal—metal distance (see later). Apart from these compounds, there is little difference between the distribution of metal separations with bridge type. It might be noted that Cotton and co-workers [133] have made the point that the length of metal—metal bonds, especially those of lower order, depend strongly upon the number, size, arrangement and character of the bridging groups.

Also included in Fig. 27 are the iron—iron distances for non-bridged metal contacts for iron complexes in Tables 1—3. These are derived from trinuclear and higher clusters in which not all the edges are carbonyl bridged. As will be seen from the figure, the unbridged Fe—Fe distances are also not significantly longer than the bridged contacts. However, this is a very restricted sample of non-bridged Fe—Fe contacts and much larger iron—iron separations are found in other compounds not within the scope of this review [23] and in addition in a particular compound carbonyl bridged metal contacts are always shorter than unbridged ones.

The conformation of molecules in a solid state lattice is subject not only to the electronic effects within the molecule itself, but also to both intra- and intermolecular packing forces. We believe that the occurrence of a particular type of bridge, including semi-bridging, or indeed the absence of carbonyl bridges in some cases, is largely determined by packing forces within the crystal.

Authors of some individual papers have already attributed the occurrence of asymmetric and semi-bridging carbonyl bridges to steric forces, but the only general discussions of these types of bridges have been by Cotton and his co-workers and they have discussed them in terms of electronic considerations, as outlined very briefly in the Introduction to this review. The reasons put forward by Cotton for the occurrence of asymmetric and semi-bridging carbonyls are different for the two types, thus implying a fundamental difference between them. We believe, however, that they merge into each other and that they differ only in degree rather than in kind. For this reason we include semi-bridging groups in the discussion of bridge—terminal exchange (see later) and treat them together in the discussion of structural effects.

In order to make a case that these non-symmetric carbonyl bridges are the result of steric forces and not electronic, it is necessary to describe a fairly large number of molecular structures in these terms and we ask that it be kept in mind that, as far as the energetics of the bridging system are concerned, there is little preference for any particular configuration in solution (in the absence of lattice effects) as shown by the $^{13}C$ NMR experiments.

In $Fe_3(CO)_{12}$ [28] the two bridges are both asymmetric, but to markedly different degrees. There is no apparent electronic reason within the molecule to cause either the asymmetry or the difference between the bridges, but it can be readily ascribed to crowding of the carbonyl groups about the metal triangle. Two substitution products of $Fe_3(CO)_{12}$ are of interest in this context. $Fe_3(\mu\text{-}CO)_2(CO)_7(PPhMe_2)_3$ [24] has a terminal carbonyl on each iron atom substituted by the phosphine. The presence of the phosphines would decrease the crowding by 'opening out' the ligand polyhedron and the two carbonyl bridges which were asymmetric in the parent are now symmetrical. On the other hand, $Fe_3(\mu\text{-}CO)_2(CO)_9(PPh_3)$ [29] crystallises with equal numbers of two isomers as described earlier. The authors comment that the reason there are two isomers is that the packing is more favourable for two isomers together than for either one separately (and we would add that the fluxional behaviour in solution during the crystallisation process provides a ready source of either isomer). The authors also suggest that perhaps the asymmetrical bridges are an artifact of the forces which produce the octahedral arrangement about each iron atom.

In $[Fe_4(\mu\text{-}CO)_4(CO)_9]^-$ [42] the three iron atoms in the basal plane are equivalent and yet the carbonyl bridges along the edges are not symmetrical, as might be expected on electronic grounds, but semi-bridging. A more significant example is provided by the $[Fe_6(\mu\text{-}CO)_3(CO)_{13}C]^{2-}$ ion [44]. The unit cell of this crystal contains two crystallographically independent clusters which are oriented differently in the lattice. The Fe—Fe distances in the two clusters are closely similar but, as noted earlier, there are very marked differences in the bridging groups in the two clusters, one particular bridge is symmetrical in one and semi-bridging in the other. There are, of course, no electronic reasons for these differences and the complex provides a particularly nice example for discussing packing factors and their effects on carbonyl configuration. A rather similar situation occurs with compound 118 which also has two crystallographically independent clusters with different orientations in the unit cell. In one molecule the bridges are asymmetric and in the other semi-bridging.

In $Ru_3(\mu\text{-}CO)_2(CO)_4(C_7H_7)(C_7H_9)$ [73] (Fig. 20) each ruthenium has two carbonyl groups, but those on one metal are $\mu_2$ bridging (one asymmetric and one semi-bridging) to the other two metal atoms. This ruthenium is bound to the $C_7H_9$ group which coordinates as a diolefin and this is probably responsible for the configuration of the bridges through intramolecular steric effects. In any event, the other two ruthenium atoms are equivalent and on electronic grounds the bridging carbonyls should be equivalent also.

In the description of the crystal structure of compound 99 the authors state that the asymmetric carbonyl linkage between the two equivalent metal atoms is due to intra- and intermolecular forces. Similar comments were made concerning the semi-bridging carbonyl groups in compound 41 and Doedens and Dahl [42] go so far as to suggest in their paper on the already crowded $[Fe_4(CO)_{13}]^-$ (see above) that the neutral complex $Fe_4(CO)_{14}$ could not exist because of the steric pressures among the carbonyl groups.

Compounds 56b, 66, 72, 73, 96 and 100 provide further examples of asymmetric and semi-bridging groups between equivalent metal atoms.

The paper describing the structure of $Fe_2(\mu\text{-}CO)(CO)_5[MeC_2COH]_2$ [33] is a remarkable one. It includes the first direct evidence of the shortening of M—C bonds in terminal carbonyl groups by comparison with a $\sigma$ M—C bond, and also the first example of a semi-bridging carbonyl group. Although the bridge spans two quite inequivalent metal atoms, so that electronic effects cannot be ruled out, the point is made by the authors that there is a close intermolecular contact between a ring substituted oxygen of one molecule and the bridging carbonyl oxygen of the neighbouring molecule.

Among the complexes in this review there are many examples of asymmetric and semi-bridging carbonyl groups between non-equivalent metal atoms. Discussions based on individual compounds have tended to emphasise electronic considerations and while such arguments cannot be refuted, it seems to us that the more general concept of lattice effects is useful. For example, it is difficult to explain on electronic grounds why one bridge in $Fe_2(\mu\text{-}CO)_2\text{-}(CO)_5$dipy [38] is asymmetric and the other semi-bridging. Even in heteronuclear complexes there are sometimes indications of steric forces causing non-symmetrical bridges as in compound 53.

There are also some examples of symmetrical bridges spanning metal atoms which are in very different electronic environments. Such seemingly "normal" bridges attract little attention in crystallographic discussions, but they provide a challenge to any argument in which asymmetry is based solely on electronic considerations. Such examples are provided by compounds 6, 20 and 115.

Johnson [134] has proposed a rationalisation of the structures of polynuclear binary carbonyls in the solid phase which not only emphasises the importance of intramolecular lattice effects, but also provides a satisfying explanation of the long established differences between the structures of the first row transition metal carbonyls and those of their second and third row homologues. Thus while $Fe_3(CO)_{12}$ has the edge bridged structure, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ adopt the non-bridged configuration [135,136]. Similarly, $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ have an edge bridged structure, $Ir_4(CO)_{12}$ has the non-bridged structure [129].

Johnson's arguments are similar in some respects to radius ratio concepts in ionic solids, and although they embody all the usual assumptions and limitations of a hard sphere approach, it does appear that useful correlations can be made. There are two polyhedra with 12 vertices, the icosahedron and the cubooctahedron * [137]. It is important to note that all the vertices are equivalent in both polyhedra but only the icosahedron has equivalent faces. While the icosahedron is the more symmetrical polyhedron from the point of view

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* The cubooctahedron is derived from cubic close packing of spheres, the closely related (and equally space filling) "twinned" cubooctahedron is derived from hexagonal close packing. The non-bridged dodecacarbonyls actually adopt this latter structure.

of an enclosed metal core, the cubooctahedron is the more efficient in space filling in the crystal lattice, so there will always be some interplay between intra- and intermolecular forces in the selection of the carbonyl polyhedron.

The interstitial hole in the icosahedron is smaller than that provided by the cubooctahedron. Thus, while the metal cores $Fe_3$, $Co_4$ and $Rh_4$ can fit into the interstitial hole of the icosahedron, this building block is used. However, when the metal core is too large, such as $Ru_3$, $Os_3$, and $Ir_4$ the less favoured cubooctahedron is utilised. Inspection of the polyhedra will show that inserting a triangle or tetrahedron of metal atoms into the icosahedron provides carbonyl groups which are naturally equidistant from two metal atoms (i.e. bridging). The cubooctahedron, on the other hand, has a disposition of carbonyl groups favouring terminal coordination thus providing a structural explanation of the group trends which have usually been discussed, rather unsuccessfully, in electronic terms.

Johnson [134] also put forward similar arguments to account for the structures of $Fe_2(CO)_9$ (compound 1) and $Os_2(CO)_9$ which is believed to have only a single carbonyl bridge [138]. Each may be expected to be based on a tricapped trigonal prismatic arrangement of carbonyl groups and indeed $Fe_2(CO)_9$ can be regarded as having this structure. However, the larger $Os_2$ unit cannot be accommodated in the holes of a trigonal prism and it is proposed that rotation about one of the $C_2$ axes produces the geometry expected for $Os_2(CO)_9$. Johnson's ideas, especially for the $(CO)_{12}$ structures emphasise the significance of intramolecular packing forces. In addition, he has also used them to provide a possible mechanism for the fluxional behaviour of $Fe_3(CO)_{12}$ which involves rotation of the metal triangle within the icosahedron [139]. It is a fact that many polynuclear binary carbonyls show disorder in their crystal structures and it may be that this disorder arises from different orientations of the metal core within the carbonyl polyhedron. Examples of disorder are provided by $Fe_3(CO)_{12}$ [28], $Co_4(CO)_{12}$ [55] and $Ni_3M_2(CO)_{16}$ [108].

It would be pointless to try to apply these ideas to grossly unsymmetrical molecules with a variety of ligands in the same molecule. However, there may be some value in cases where comparatively little substitution of the parent carbonyl has occurred and yet a structural change has resulted.

Perhaps the best example is provided by compounds 106a and 106b, $Ir_4(\mu\text{-}CO)_3(CO)_6(PPh_3)_3$ and $Ir_4(\mu\text{-}CO)_3(CO)_7(PPh_3)_2$ respectively which have stereochemistries based on the $Co_4(CO)_{12}$ structure rather than the unbridged $Ir_4(CO)_{12}$. The introduction of phosphorus into the ligand coordination sphere would no doubt cause an increase in the size of the interstitial hole by "opening out" the carbonyls, thus enabling the $Ir_4$ core to be accommodated in a polyhedron close to an icosahedron which could readily be attained by only minor shifts of the ligands [137]. Even if the polyhedron remained cubooctahedral the effect of the phenyl rings on the phosphine would be to drastically reduce the space filling properties of this polyhedron and this effect may well contribute to the change of polyhedron. This change in stereochemistry on substituting $Ir_4(CO)_{12}$ may be a fairly general phenomenon as other cases of the formation of carbonyl bridged derivatives have been detected by spectroscopic methods [140].

The isoelectronic series $Co_2(\mu\text{-}CO)_2(CO)_6$ [45], $[FeCo(\mu\text{-}CO)(CO)_7]^-$ and the non-bridged $[Fe_2(CO)_8]^{2-}$ provide an interesting example of changing stereochemistry with change of metal rather than change of ligand. Johnson [134] has related these three structures by rotation of the $M_2$ group within the carbonyl polyhedron, assumed to be a bicapped trigonal prism. However, there is a difficulty in applying Johnson's scheme as there is a change in the carbonyl polyhedron from bicapped trigonal prism in $Co_2(CO)_8$ to end capped anti-prismatic in $[Fe_2(CO)_8]^{2-}$ [119], but it is interesting that this same geometry is adopted by $Co_2(CO)_6(PBu_3)_2$ [132], which is made simply by substituting $Co_2(CO)_8$. An added difficulty with the mixed metal ion is that the crystal structure shows the metals to be quite inequivalent since the iron atom is five coordinate and the cobalt atom only four coordinate. It is in this sort of situation that simple "hard sphere" models break down. We would prefer to suggest that lattice effects, involving the cations in all probability, are responsible for the different configurations. Similar effects on changing the counter ion have been observed in cobalt dioxygen complexes [141,142] and in the fluoroanions of zirconium [143].

There are several other examples of changes in stereochemistry on substitution of a parent carbonyl, but in these cases the ligands are such that considerable changes must occur in the ligand polyhedron and there may also be considerable changes in the electronic structure of the molecule. For these reasons we shall not attempt to rationalise the changes which occur, but merely give a few examples to illustrate the effects which can occur. Cotton and co-workers have prepared two derivatives of $Fe_2(CO)_9$ which both differ in their stereochemistry from the parent. $Fe_2(CO)_7$dipy has one asymmetric and one semi-bridging carbonyl spanning two non-equivalent metal atoms and $Fe_2(CO)_7$dpm has a single symmetrical carbonyl between the two metal atoms.

Compound 64 is basically a derivative of the $Co_3(CO)_9CR$ series which contain only terminal groups, in which a carbonyl on each of two cobalts is substituted by the ditertiary arsine ffars. However, the remaining carbonyls rearrange to give a bridging group along each edge of the metal triangle.

Two derivatives of the unbridged $Ru_3(CO)_{12}$ have been isolated which retain the metal triangle, but edges are now bridged. In compound 70, $Ru_3(\mu\text{-}CO)(CO)_9(C_{10}H_8)$, there is one symmetrical carbonyl bridge and in $Ru_3(\mu\text{-}CO)_3(CO)_7(C_4H_4N_2)$ [72] all three edges of the metal triangle are bridged by asymmetric carbonyl groups.

Deprotonation of $H_4Ru_4(CO)_{12}$, which contains only terminal carbonyl groups gives first $[H_3Ru_4(CO)_{12}]^-$ which also has only terminal carbonyls and then $[H_2Ru_4(CO)_{12}]^{2-}$ which has three $\mu_2$ carbonyl groups in a structure thought to be similar to $Co_4(CO)_{12}$ on the basis of IR and $^{13}C$ NMR spectroscopy [144].

In the solid state compound 67, $Co_3(\mu\text{-}CO)_3(C_5H_5)_3$, contains one triple

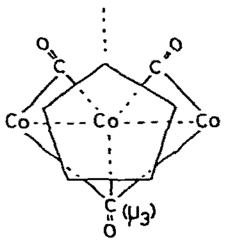


Fig. 28. Molecular structure of $Co_3(\mu\text{-}CO)_3(C_5H_5)_3$ (compound 67) viewed down the unique $Co—C_5H_5$ axis.

carbonyl bridge and two $\mu_2$ bridges (one asymmetric and one semi-bridging) along two edges of the metal triangle bent away from the triple bridge. There is a plane of symmetry in the molecule through the doubly bridged cobalt atom and the triple bridging carbonyl as shown in Fig. 28 and together with the diagram in the original publication [67] it can be seen that the three carbonyls are almost stereochemically equivalent about a "three fold axis" and occupying the volume between the cyclopentadiene rings. This automatically makes two of the carbonyls edge bridging and one triple bridging. In solution the IR spectrum varies markedly with solvent, but is always quite different to the solid state spectrum, thus demonstrating that the structure adopted in the solid state is the result of lattice effects.

Our general conclusion is that the type of carbonyl bridge observed in the solid state is largely a result of intermolecular and intramolecular forces. We acknowledge that it is impossible to distinguish between electronic and steric effects in unsymmetrical molecules, and that electronic factors may have some importance in these situations, but there are so many examples of non-symmetrical bridges which can clearly be ascribed to steric forces that we believe a case for the generality of their causal effect can be substantiated.

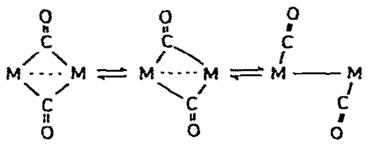
### *(ii) Fluxional behaviour in carbonyls*

One of the most interesting discoveries in the last decade or so is that many molecules undergo rapid intramolecular rearrangements in solution. A rather spectacular version of this general phenomenon is the interchange between bridging and terminal carbonyl groups in polynuclear metal derivatives. The process was first suggested by Cotton and co-workers [145] on the basis of the temperature variation of the $^1H$ NMR spectrum of $Fe_2(\mu\text{-}CO)_2(CO)_2(C_5H_5)_2$ (compound 5) and the subsequent observation of the $^{13}C$ NMR spectrum [146] confirmed the process. In the last few years there has been intense activity in this field and the interchange between terminal and bridging carbonyl groups has become a very common observation.

Fortunately, in many cases, the rate of exchange is amenable to study by NMR techniques and the observation of the spectra as a function of temperature in suitable cases leads to a limiting spectrum at low temperature and the full exchange situation at high temperature. From these studies the activation energy of the process can be determined and fine detail of the exchange process explored. In other cases, such as Fe$_3$(CO)$_{12}$, the exchange is so facile that even at the lowest temperatures obtainable there is still only a single carbonyl resonance in the NMR spectrum, implying that the activation energy for the process is very low indeed.

Cotton [147] has suggested that unsymmetrical bridging groups fall into two main types, namely compensated sets of two asymmetric bridges as in Fe$_3$(CO)$_{12}$, and semi-bridging carbonyls which he has suggested serve the function of equalising charge distribution within the molecule. Cotton then invokes the compensating sets in the exchange between terminal and bridging carbonyls as shown in Fig. 29. The unsymmetrical bridges merely represent intermediate stages in the entire range between nonbridged and symmetrical bridged extremes, under conditions where the total energy of the system varies little from one limiting structure to the other. It should be noted at this point that Cotton and his co-workers have amply demonstrated that at least in compound 5 and many closely related complexes [148], the nonbridged form is indeed an intermediate in the exchange process.

We would agree with all that Cotton has suggested about the exchange process, but we would widen the concept somewhat. For reasons given earlier, we regard asymmetric and semi-bridging groups as basically similar and we would therefore include semi-bridging carbonyls in the exchange process. We would also remove any arbitrary distinction between symmetrical bridges with angles in the common range of 77—90° and those with angles close to 120°. At present, the only published example of this latter type is Pd$_2$($\mu$-CO)($\mu$-dam)$_2$Cl$_2$ [111], which has no terminal carbonyls to exchange, but when further examples containing this type of bridge are found, we would expect the usual exchange to occur. In other words, we regard the carbonyl bridge in compound 111 to be merely one extreme in the wide spectrum of carbonyl bridging envisaged by Cotton and not a radically different ligand as suggested by Robinson [149]. These views are confirmed by the very recent observation [150] that Pt$_2$($\mu$-CO)($\mu$-dpm)$_2$Cl$_2$ has a structure very similar to compound 111 and that in solution it partially isomerises to a terminal carbonyl deriva-



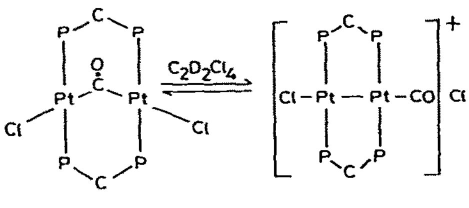


Fig. 29. Bridge—terminal exchange scheme invoking asymmetrically bridged intermediates.

Fig. 30. Bridge—terminal carbonyl equilibrium in Pt$_2$($\mu$-CO)($\mu$-dpm)$_2$Cl$_2$. (Phenyl groups omitted for clarity.)

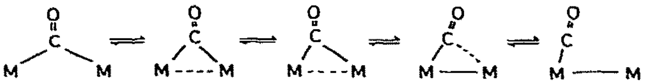


Fig. 31. Extended bridge—terminal carbonyl exchange scheme invoking semi-bridged species as intermediates.

tive which has a direct metal—metal bond as shown in Fig. 30.

Our complete exchange scheme, which is merely an extension of Cotton's is shown in Fig. 31. The majority of complexes will not reach the extreme left hand side of the exchange scheme, because of intramolecular factors which are discussed below, but this does not affect the ability to exchange terminal and bridging carbonyl groups.

In this sequence several clearly defined steps can be envisaged:

(i) Gradual opening of the M—C—O angle from 120° to 180° at the two extremes which is equivalent, in the extremes, to a change in hybridisation at carbon from $sp^2$ to $sp$.

(ii) Gradual weakening of one metal—carbon bond and strengthening of the other, which occurs simultaneously, although not necessarily at the same rate, in both the $\sigma$ and $\pi$ frameworks.

(iii) Gradual increase in the strength of the M—M bond from zero at the left hand side to a complete bond at the right hand side. At first this bond is likely to be a $\pi$ interaction and only as the carbonyl bridge becomes asymmetric and the coordination sphere about each metal rotates slightly [28,139] will it become a $\sigma$ interaction.

The energetics of the exchange process have not been examined in detail. Several independent lines of evidence suggest that the metal to bridging carbonyl bond is strong. X-ray crystallography gives a comparison of Fe—C $\sigma$ bonds in compounds 30 and 33—35 (which range from 1.94—2.06 Å) with Fe—symmetrical bridge distances which are all less than 2.0 Å (except for one bridge in compound 24) and most are less than 1.94 Å. Less direct indications of the strength of M—bridge bonds are provided by IR spectroscopy and $^{13}C$ NMR. On the conventional view of bonding of carbonyl groups to transition metals, the decrease in the carbonyl stretching frequency compared with free carbon monoxide to lower values for terminal carbonyls is attributed to back donation to the empty $\pi^*$ orbital of the ligand, thus giving multiple character to the M—C bond, which also has crystallographic confirmation [33,151]. Bridging carbonyls have even lower stretching frequencies and, although two M—C bonds are now involved, there must still be significant $\pi$ bonding involved. Carbon NMR shifts have been correlated [152] with electron density at carbon. Terminal carbonyls give signals which occur at extremely low field indicating considerable electron density at the carbon, but bridging carbonyls are invariably at still lower field.

There is therefore an abundance of evidence that the metal—bridge carbonyl bond is strong, and yet the activation energies for exchange in very many complexes are of the order of 15 kcal or less, for a process which has been shown unequivocally to involve breaking of a metal—bridge bond. Clearly, the observed activation energy must merely be the difference between the energy required to break the bridge bond and some compensating process or processes which release a very similar amount of energy. One obvious possibility is an increase in the strength of one metal—carbon bond as the carbonyl group changes from bridging to terminal. A second process is the gradual increase in the strength of the metal—metal bond.

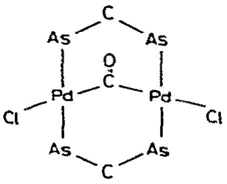
As noted above, towards the left of the exchange scheme the spin-pairing of the metal electrons will be via a $\pi$-interaction which may be either direct metal—metal interaction or via the bridging carbonyls [153]. If this is accepted considerable simplification in stereochemistry of metals in polynuclear complexes can be achieved because it is no longer necessary to postulate a direct $\sigma$-bond between the metals. For example, we would regard the iron atoms in $Fe_2(CO)_9$ as almost octahedral with the spin-pairing occurring through a weak $\pi$-interaction between the metals which is not stereochemically significant. If a direct $\sigma$-bond is postulated a seven coordinate stereochemistry is required which is sterically unlikely (see below). Similarly, if a direct Fe—Fe $\sigma$-bond is not demanded for the carbonyl bridged edge in $Fe_3(CO)_{12}$, the stereochemistry of each metal atom is close to octahedral.

### *(iii) Electronic and further structural considerations*

The conventional view of the bond of terminal carbonyl groups to transition metals is too well-known to need repeating here. In contrast, there are few descriptions of the bonding situation in bridged carbonyls although Braterman [125] has argued against the idea of "ketonic" carbonyl groups in favour of a delocalised molecular orbital description.

In every case known to the authors in which bridging carbonyls occur, the pair of metal atoms involved are short of the number of electrons required to obey the 18 electron rule, usually by one. However, since the complexes are invariably diamagnetic spin-pairing must occur. Although it has long been recognised that this may occur via the bridging carbonyl [153], the discovery of the first unsupported metal—metal bonds and their rapid proliferation in the last twenty years has led to a situation where it becomes almost automatic to assume a metal—metal bond is always responsible for the spin-pairing. Indeed, it has been explicitly proposed that, "bridging carbonyl groups never occur unless the bridged metal atoms are formally bound to each other" [154].

Compound 111, $Pd_2(\mu\text{-}CO)(\mu\text{-}dam)_2Cl_2$, provides the first proven exception to this proposed rule. The molecular structure is shown in Fig. 32. The palladium atoms are 3.274 Å apart and are square planar coordinated, sharing the carbonyl group. In all other palladium(I) dimers the Pd—Pd distance is less than 2.7 Å [111] and since the diameter of non-bonded palladium is about 2.75 Å it is clear that direct metal—metal interaction cannot occur.



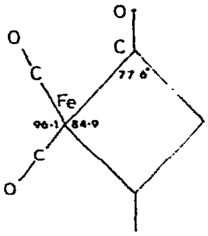


Fig. 32. Molecular structure of $Pd_2(\mu\text{-}CO)(\mu\text{-}dam)_2Cl_2$ (compound 111). (Phenyl groups omitted for clarity.)

Fig. 33. Angles in $Fe_2(\mu\text{-}CO)_3(CO)_6$. (Only two bridging and two terminal carbonyl groups shown for clarity.)

The metal—carbon bond lengths are normal, so that considerable opening out of the Pd—C—Pd angle occurs; in fact the angle is approximately 120° and the bridging carbonyl closely resembles an organic ketone group. This analogy is supported further by the carbonyl stretching frequency which is 1720 $cm^{-1}$. Compound 111 is diamagnetic, and as there is no mechanism for spin-pairing via the saturated diarsine ligands, it must occur via the carbonyl bridge. We envisage that the carbon at the bridge is $sp^2$ hybridised with a single electron in each of the two lobes directed towards the metal atoms. If we assume $dsp^2$ hybridisation for palladium, there will be one electron in one of the $\sigma$ hybrid orbitals of each metal with the other four unhybridised $d$ orbitals full. We regard every ligand except the carbonyl to be a two electron donor and spin-pairing to occur to give a covalent bond between each Pd and carbonyl. In this way the metal electrons are paired, but not with each other.

Apart from any electronic consideration, the existence of this structure effectively demolishes all arguments concerned with the lack of carbonyl bridges between metals about 3.0 Å apart (e.g. $Mn_2(CO)_{10}$) when these arguments are based simply on the presumption that the carbonyl ligand cannot span such a large metal separation.

In the preceding section we suggested that spin-pairing of the metal electrons may be via a $\pi$-system and thus be stereochemically not significant; we shall now consider some consequences of this assumption.

Consider the case of $Fe_2(CO)_9$; in their paper on its structure Powell and Ewens [1a] called the carbonyl groups ketonic and assumed them to be two electron donors to both metal atoms, thus making the ligands $CO^{2-}$ and the metals formally Fe(III). This is clearly an unreasonable approach, but it is an unnecessary one, since the bonding can be considered covalent as in the previous case of compound 111. The iron atom can then be regarded as Fe(O) with octahedral coordination, but three of the metal hybrid orbitals would each contain one electron to pair up with the three carbonyl electrons. The remaining unpaired electron on the metal is in an orbital of $\pi$ symmetry which may pair up either directly or via the carbonyls in a two electron three centre MO system. If it is accepted that this is a reasonable description of the

$\sigma$ framework, it is reasonable to ask why the angle at carbon is only 77.6° instead of 120°. We believe the answer to this question lies in intermolecular forces as suggested by Powell and Ewens. The detailed geometry of the bridge system is shown in Fig. 33 in which the angles are those reported in the re-determination of the structure by Cotton and Troup [1b]. Any increase in the angle at carbon would lead to a decrease in the angle at iron. This in turn would lead to gross interaction between the three bridging carbonyl groups and also a further decrease in overlap between the metal hybrid orbitals and those of the carbonyl. Conversely, any increase in the angle at iron would further decrease the angle at carbon. Thus the steric arrangement can be considered to be a compromise between the conflicting stereochemical requirements of the metal and the carbonyls. As Cotton and Troup [1b] have pointed out, the angle at carbon in the compound is low (see Tables), and we believe this is due simply to the fact that there are three bridging carbonyl groups, and any distortion of the angles at the metal quickly causes intramolecular repulsions.

Incidentally, if a direct $\sigma$-bond is postulated between the metal atoms it would pass through the compressed faces of the metal coordination spheres, thus adding to an already crowded situation.

It is worth noting at this point that the generally small angle at bridging carbonyls, which has attracted considerable attention [125], is nothing unusual or unique to carbonyls, but is in fact a universal phenomenon at all bridging groups in similar environments. Thus, in compounds 3 and 18 the angles at the bridging germanium are 66.8° and 68.15° respectively. The angle at sulphur in compound 19 is 72.9° and in the range 67—70° in compound 54. In the complex $[Co(\mu\text{-}PPh_2)(C_5H_5)]_2$ [155] the angle at phosphorus is 72° and in $[Mn(\mu\text{-}SiPh_2)(CO)_4]_2$ [156] it is 73.4° at silicon. Many other examples could be cited to show that this is a general effect and not restricted to carbonyl groups. This in turn suggests a general cause for the effect, which we believe to be steric, as outlined above.

Compound 27, $Fe_2(\mu\text{-}CO)(CO)_6$dpm, provides a particularly nice example in which to examine intramolecular bonding effects. Each iron atom is essentially trigonal bipyramidal (omitting an Fe—Fe $\sigma$-bond), the diphosphine occupying axial positions on each metal. A carbonyl in the trigonal plane is symmetrically shared between the metals as shown in Fig. 34 which also shows the details of the carbonyl bridge. In this case the opening out of the angle at carbon to 120° would have no effect on the stereochemistry about the iron atoms, but the diphosphine is a constraint on the carbon angle. We have shown that in the bridging mode of coordination dpm and dam are rather rigid ligands in the sense that they resist opening and closing of the angle at the methylene carbon. In situations in which the natural separation of the ligand donor atoms (P—P 3.0 Å, As—As 3.3 Å) matches the metal—metal separation (e.g. compound 103) no distortion of the ligand or the metal coordination sphere occurs. In cases where the metal—metal separation is greater than the bite of the ligand, there is distortion of the coordination

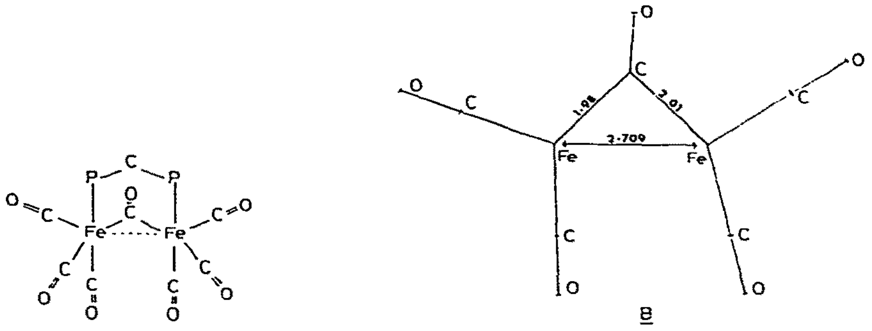


Fig. 34. A, Molecular structure of $Fe_2(\mu\text{-}CO)(\mu\text{-}dpm)(CO)_6$ (compound 27). (Phenyl groups omitted for clarity.) B, Details of the planar $Fe_2(\mu\text{-}CO)(CO)_4$ system.

sphere of the metal rather than of the ligand. An example is $Re_2(\mu\text{-}Cl)_2(\mu\text{-}dam)(CO)_6$ [157] which has a metal separation of 3.8062 Å. On the other hand, for metal separations shorter than the ligand bite there is either a twist of the dimeric molecule to effectively reduce the bite of the molecule as in $[PdBr(\mu\text{-}dpm)]_2$ [158] or, as in the case of compound 27, a slight twist about the metal—metal axis combined with a slight distortion of the metal coordination sphere. Thus we see this long Fe—Fe separation of 2.709 Å as resulting mainly from a compromise between the requirements of the bridging carbonyl and the diphosphine ligand. It would be an interesting test of these ideas to prepare a corresponding derivative with dam to see if the Fe—Fe distance did increase and the carbonyl angle open out as a result of the larger ligand bite.

If we now return briefly to $Pd_2(\mu\text{-}CO)(\mu\text{-}dam)_2Cl_2$ it can be seen from the structure that there is no restraint on the angle at the carbonyl bridge opening out to the optimum value of 120° since this produces a metal—metal separation ideal for dam to bridge.

It should be emphasised again that in these examples it makes no difference whether spin-pairing occurs via the carbonyl groups or via a $\pi$ interaction between the metals. All that is important is that there should be no strong $\sigma$ interaction between the metals.

### *(iv) Linear $\mu_2$ bridging and semi-bridging carbonyls*

In compound 103, $Mn_2(\mu\text{-}CO)(\mu\text{-}dpm)_2(CO)_4$, it is suggested that there is a radically different type of carbonyl bridge as shown in Fig. 23. The evidence that this is not just an extreme case of semi-bridging is, (i) the metal—carbon bonds are closely similar and (ii) the stretching frequency of the bridging carbonyl which occurs at 1645 cm$^{-1}$. This very low value is consistent with a group which is not only bonded in a normal terminal fashion to one metal, but also donates from its filled $\pi$ orbitals to the second metal. Ordinary semi-bridging groups have stretching frequencies close to those shown by terminal carbonyls in keeping with the idea that they have predominantly terminal character.

In our original papers on this compound [103,159] we suggested the presence of a Mn—Mn bond to account for the diamagnetism of the complex in accord with the metal—metal separation which is similar to that found in $Mn_2(CO)_{10}$ [160]. We now favour a bonding scheme involving spin-pairing via the carbonyl bridge and we have some evidence which may support this view [161]. We have found that $Mn_2(\mu\text{-dpm})(CO)_8$ and $Mn_2(\mu\text{-dpm})_2(CO)_6$, which are intermediates in the preparation of compound 100, have stretching modes in their Raman spectra close to that observed for $Mn_2(CO)_{10}$ at about 170 $cm^{-1}$ which is assigned to the metal—metal stretch [162]. There is no way other than by a metal—metal bond that spin-pairing can occur, so by analogy we assign the bands in these complexes to the stretch of the metal—metal bond. However, in compound 103 there is no such stretching mode; the spectrum is clear in this region and as the mode is very strong in the other complexes we feel there is no chance the vibration has been missed. Since the intermediates show that the presence of the bridging dpm ligands does not alter the position of the band, clearly something dramatic happens when the bridging carbonyl is introduced. We suggest it is loss of the metal—metal $\sigma$-bond.

Very recently Klinger et al. [96a] have claimed that compound 96, $Mo_2(\mu\text{-CO})_4(C_5H_5)_2$, contains four carbonyl groups which are linear $\mu_2$ bridges, two in each direction. We reject this suggestion on the grounds that, (i) the metal carbon bonds at the bridges differ by about 0.5 Å in each case and (ii) the carbonyl stretching frequencies of 1900 and 1850 $cm^{-1}$ are close to normal terminal values. We prefer to classify these bridges as borderline semibridging, which was the opinion of the authors themselves in their preliminary communication [96b].

### *(v) $\mu_3$ carbonyl groups*

A number of structures are known in which a carbonyl group bridges three metal atoms, either symmetrically or asymmetrically. It is also known that the triply bridged carbonyl can undergo facile exchange with $\mu_2$ carbonyl groups or terminal carbonyls, for example compound 67. Although we have not made a study of $\mu_3$ carbonyls we feel it is likely that steric forces are also responsible for their appearance in the solid state. For example, compound 80, $Rh_3(\mu\text{-CO})(C_6F_5C_2C_6F_5)(C_5H_5)_3$, contains a single $\mu_2$ carbonyl, but if diphenylacetylene is used instead of its perfluoro analogue the carbonyl becomes $\mu_3$, with other features of the structure remaining essentially unchanged.

## D. CONCLUSIONS

It seems to us that a good case can be put forward to account for the detailed conformation of carbonyl bridged systems in the solid state in terms of intra- and intermolecular forces. Over the years since their discovery, carbonyl compounds have presented an impressive number of challenges to bonding theories. If our proposals are correct, then they add another. There is little point in trying to rationalise the detailed stereochemistry of a molecule in the solid state if the predominant force causing that stereochemistry is ignored by the theory. In solution, yet another problem arises in bonding theory due to the dynamic character of the molecules.

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