Structural Chemistry of Binuclear Metal Centres. Crystal and Molecular Structures of the μ-Vinyl and μ-Methylcarbene Complexes $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2][BF_4]$ and $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ *

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Protonation of $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2H_2\}(\eta\text{-}C_5H_5)_2]$ with $HBF_4\cdot OEt_2$ affords the μ-vinyl cation of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2][BF_4]$ (1). Reaction of (1) with $NaBH_4$ yields the μ-carbene complex $[Fe(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ (2). Both (1) and (2) have been studied using *X*-ray diffraction methods. Complex (1) crystallizes in the orthorhombic space group *Pnma* (no. 62) with unit-cell dimensions $a = 12.149(4)$, $b = 10.745(3)$, $c = 12.470(3)$ Å, and $Z = 4$. The structure has been refined to *R* 0.083 for 1 281 intensity data, and consists of isolated $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\mu\text{-}C_5H_5)]^+$ cations and $[BF_4]^-$ anions, each lying on sites of crystallographic mirror symmetry. The cations show orientational disorder, with the methylene function of the μ-vinyl group occupying two sites of occupancy 0.5 related by the mirror plane. The iron atoms are singly bonded to one another and are separated by 2.595(2) Å, being bridged both by vinyl and carbonyl ligands. In addition each iron atom carries one terminal carbonyl ligand and an η^5-cyclopentadienyl moiety. The molecular cation adopts a conformation which places the cyclopentadienyl ligands mutually *cis* with the vinylic methylene *anti* to these groups. Complex (2) crystallizes in the orthorhombic space group *Pnma* (no. 62) with unit-cell dimensions $a = 15.096(9)$, $b = 14.414(8)$, $c = 6.336(4)$ Å, and $Z = 4$. The structure has been refined to *R* 0.046 for 1 631 intensity data, and consists of isolated molecules of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)(\eta\text{-}C_5H_5)_2]$ each lying on sites of crystallographic mirror symmetry. The Fe–Fe distance is 2.520(2) Å and is indicative of a bond order of unity, the bond being bridged both by methylcarbene and carbonyl ligands. In addition each iron atom carries one terminal carbonyl ligand and an η^5-bound cyclopentadienyl moiety. The conformation of the molecule of (2) is similar to that of (1) having mutually *cis* cyclopentadienyl groups and the methyl group oriented *anti* to these.

The previous paper [1] describes the synthesis and spectroscopic properties of binuclear complexes of iron and ruthenium in which the metal–metal bond is bridged by a variety of vinyl and carbene ligands. In particular protonation of the alkyne derived metallacycle $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2H_2\}(\eta\text{-}C_5H_5)_2]$ with $HBF_4\cdot OEt_2$ in dichloromethane gives the μ-vinyl cation of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2][BF_4]$ (1) a structural study of which is reported in this paper. Treatment of (1) with $NaBH_4$ in acetone yields the μ-carbene complex $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ (2), whose crystal and molecular structure is likewise reported herein. Complexes (1) and (2) are representatives of large classes of complexes which are accessible *via* the synthetic routes discussed in the preceding paper and for this reason were chosen for structural characterisation. The μ-vinyl cation of complex (1) and related species show interesting dynamic processes in solution, as studied by n.m.r. spectroscopy, the solid-state structure is hence shown to be consistent with a ground state for these processes where the cyclopentadienyl and terminal CO ligands are in a *cis* conformation and the vinylic methylene group is *anti* with respect to the C_5H_5 rings. Similarly (2) has the *cis* conformation in the solid state and the methyl substituent on the bridging carbene carbon oriented *anti* to the cyclopentadienyl groups. In (1) and (2) the iron atoms are separated by typical Fe–Fe single bond lengths, this bond being bridged by a CO ligand in both, and the μ-vinyl and μ-carbene moieties respectively. The *X*-ray studies allow examination of the relationship between the vinyl and carbene ligands and comparison of their structural characteristics. A preliminary account of the structure of (2) has appeared previously,[2] and other workers have also reported an *X*-ray study of (2).[3] The synthetic and structural chemistry of μ-carbene complexes and their relationship to industrially important catalytic processes have been extensively reviewed.[4]

Results

Crystal Structure of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2][BF_4]$ (1).—An illustration of the molecular cation of (1), with the labelling scheme adopted, is given in Figure 1. Bond lengths and inter-bond angles are given in Tables 1 and 2. Both the cation and anion lie at sites of crystallographic mirror symmetry. This imposes orientational disorder on the $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]^+$ cation, affecting in particular the bridging vinyl moiety. This disorder forces the observed C(1) position to bridge the Fe–Fe′ vector symmetrically and C(2) to lie in sites of occupancy 0.5 either side of the mirror plane bonded to Fe and Fe′ respectively. In addition the thermal parameters reflect the superposition of two orientations of the molecular cation rather than simply the vibrational motion of atoms (see Figure 1). The cation adopts a solid-state conformation that has the cyclopentadienyl groups *cis* with respect to one another, and the vinyl oriented *anti* to these groups. This conformation is consistent with the spectroscopic (n.m.r. and i.r.) properties of the major isomer present in solution at ambient temperature.[1] This conformation directs the bulkier substituent (*i.e.*, CH_2) at the bridging carbon C(1) away from the cyclopentadienyl groups and is therefore favoured on steric grounds. Each iron atom carries a terminal carbonyl group and an η^5-bound cyclo-

* μ-Carbonyl-[μ-vinyl-C^1(Fe):C^1—C^2(Fe′)]-bis[carbonyl(η^5-cyclopentadienyl)iron](*Fe*—*Fe*)tetrafluoroborate and μ-carbonyl-μ-ethylidene-bis[carbonyl(η^5-cyclopentadienyl)iron](*Fe*—*Fe*) respectively.

Supplementary data available (No. SUP 23590, 34 pp.): structure factors, H-atom co-ordinates, thermal parameters, full bond distances and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

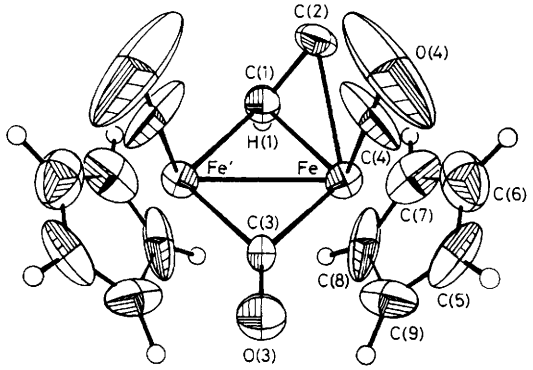


Figure 1. Molecular geometry of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]^+$ with ellipsoids drawn to enclose 50% probability density. Only one of the equally occupied sites for C(2) is shown. Hydrogen atoms are drawn as spheres of arbitrary radius

Table 1. Bond lengths (Å) * for (1)

Fe–Fe′	2.595(2)	Fe–C(2)	2.21(2)
Fe–C(1)	1.980(8)	Fe–C(4)	1.731(10)
Fe–C(3)	1.963(8)	Fe–C(6)	2.075(13)
Fe–C(5)	2.072(13)	Fe–C(8)	2.084(13)
Fe–C(7)	2.117(11)	B–F(2)	1.34(2)
Fe–C(9)	2.075(11)	C(2)–C(1)	1.40(2)
B–F(1)	1.37(2)	C(3)–O(3)	1.167(13)
B–F(3)	1.333(14)	C(4)–O(4)	1.155(15)
C(5)–C(6)	1.32(2)	C(5)–C(9)	1.37(2)
C(6)–C(7)	1.30(2)	C(7)–C(8)	1.40(2)
C(8)–C(9)	1.45(2)	C(1)–H(1)	1.10(10)

* Estimated standard deviations in parentheses, here and throughout this paper.

pentadienyl ligand. The remaining carbonyl ligand bridges the Fe–Fe′ vector symmetrically.

Crystal Structure of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ (2).—The molecular structure of (2) is illustrated in Figure 2, which gives the labelling scheme used. Bond lengths and inter-bond angles are listed in Tables 3 and 4. The molecule of (2) lies at a site of crystallographic mirror symmetry. The solid-state geometry is therefore in accord with molecular C_s symmetry as indicated by the spectroscopic properties of (2).[1] The Fe–Fe′ vector is symmetrically bridged by the μ-methylcarbene moiety and one carbonyl ligand. In addition each iron atom carries one terminal carbonyl ligand and an η^5-bound cyclopentadienyl group. The solid-state conformation of (2) is therefore similar to (1) in having the $\eta\text{-}C_5H_5$ rings mutually *cis* and the bulkier substituent (here CH_3) on the bridging carbon, C(1), oriented away from these groups. This structure is therefore consistent with the spectroscopic properties of the major isomer of (2) present in solution.[1] The results of this analysis agree very well with those of Meyer *et al.*[3] whose excellent discussion of the structure of (2) will not be repeated here.

Discussion

Both the cation of (1) and molecule (2) show Fe–Fe′ distances consistent with an iron–iron bond order of unity, as would be predicted by the effective atomic number rule [Fe–Fe′ 2.595(2) and 2.520(2) Å in (1) and (2) respectively]. Similar Fe–Fe bond lengths have been observed for a variety of

Table 2. Inter-bond angles (°) for (1)

C(2)–Fe–C(1)	38.4(5)	C(2)–Fe–C(3)	117.3(5)
C(1)–Fe–C(3)	97.4(3)	C(2)–Fe–C(4)	69.8(6)
C(1)–Fe–C(4)	100.0(5)	C(3)–Fe–C(4)	86.1(5)
C(2)–Fe–C(5)	134.1(6)	C(1)–Fe–C(5)	154.8(4)
C(3)–Fe–C(5)	103.8(4)	C(4)–Fe–C(5)	94.9(5)
C(2)–Fe–C(6)	99.0(6)	C(1)–Fe–C(6)	120.9(5)
C(3)–Fe–C(6)	140.9(5)	C(4)–Fe–C(6)	94.1(5)
C(5)–Fe–C(6)	37.2(5)	C(2)–Fe–C(7)	89.2(5)
C(1)–Fe–C(7)	92.1(4)	C(3)–Fe–C(7)	147.1(4)
C(4)–Fe–C(7)	123.2(5)	C(5)–Fe–C(7)	62.7(5)
C(6)–Fe–C(7)	36.2(5)	C(2)–Fe–C(8)	115.1(6)
C(1)–Fe–C(8)	95.1(5)	C(3)–Fe–C(8)	108.6(5)
C(4)–Fe–C(8)	157.4(4)	C(5)–Fe–C(8)	65.5(5)
C(6)–Fe–C(8)	63.7(5)	C(7)–Fe–C(8)	39.0(5)
C(2)–Fe–C(9)	153.9(6)	C(1)–Fe–C(9)	132.2(5)
C(3)–Fe–C(9)	85.5(4)	C(4)–Fe–C(9)	127.8(5)
C(5)–Fe–C(9)	38.7(5)	C(6)–Fe–C(9)	63.8(5)
C(7)–Fe–C(9)	65.3(5)	C(8)–Fe–C(9)	40.7(5)
C(2)–Fe–Fe′	78.4(4)	C(1)–Fe–Fe′	49.1(2)
C(3)–Fe–Fe′	48.6(2)	C(4)–Fe–Fe′	99.1(3)
C(5)–Fe–Fe′	147.5(4)	C(6)–Fe–Fe′	164.7(4)
C(7)–Fe–Fe′	128.5(3)	C(8)–Fe–Fe′	103.5(3)
C(9)–Fe–Fe′	112.7(3)	F(1)–B–F(2)	108.6(12)
F(1)–B–F(3)	109.5(8)	F(2)–B–F(3)	107.5(9)
F(3)–B–F(3′)	113.9(14)	Fe–C(2)–C(1)	61.9(7)
Fe–C(1)–C(2)	79.6(7)	Fe–C(1)–Fe′	81.8(4)
F(2)–C(1)–Fe′	128.4(10)	Fe–C(3)–O(3)	138.6(2)
Fe–C(3)–Fe′	82.7(4)	Fe–C(5)–C(6)	71.6(8)
Fe–C(4)–O(4)	175.9(11)	C(6)–C(5)–C(9)	108.9(12)
Fe–C(5)–C(9)	70.8(7)	Fe–C(6)–C(7)	73.6(8)
Fe–C(6)–C(5)	71.3(8)	Fe–C(7)–C(6)	70.2(7)
C(5)–C(6)–C(7)	112.3(12)	C(6)–C(7)–C(8)	108.3(11)
Fe–C(7)–C(8)	69.2(7)	Fe–C(8)–C(9)	69.3(7)
Fe–C(8)–C(7)	71.8(7)	Fe–C(9)–C(5)	70.5(7)
C(7)–C(8)–C(9)	105.0(10)	C(5)–C(9)–C(8)	105.6(10)
Fe–C(9)–C(8)	70.0(7)	Fe–C(1)–H(1)	109(4)
C(2)–C(1)–H(1)	122(4)		

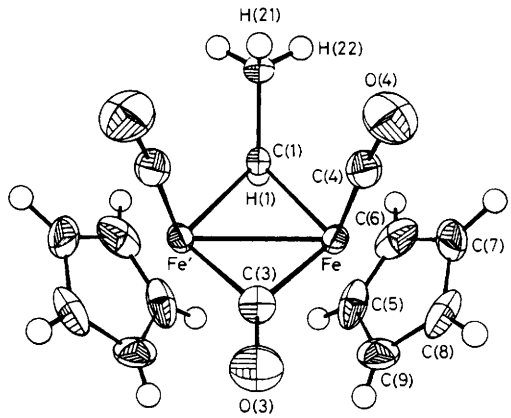


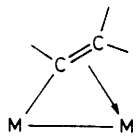
Figure 2. Molecular geometry of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ (2) with ellipsoids drawn to enclose 50% probability density. Hydrogen atoms are drawn as spheres of arbitrary radius

carbonyl- and carbene-bridged iron dimers {*e.g.* $[Fe_2(CO)_9]$[5] 2.523, $[Fe_2(CO)_8(CH_2)]$[3] 2.504, and *cis*-$[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$[6] 2.531 Å}.

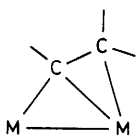
The bonding of vinyl fragments bridging across metal–metal bonds has usually been described as involving σ + π donation [7,8] [as in (I)]. The n.m.r. spectroscopic properties[1] of the bridging carbon in (1) (^{13}C δ 185.8 p.p.m.) and its attached hydrogen (^1H δ 12.57 p.p.m.) [*cf.* 172.9 and 11.60 p.p.m for (2)] prompt the use of description (II) which

Table 3. Bond lengths (Å) for (2)

Fe–Fe′	2.520(2)	Fe–C(3)	1.903(3)
Fe–C(1)	1.986(3)	Fe–C(5)	2.130(4)
Fe–C(4)	1.748(3)	Fe–C(7)	2.091(3)
Fe–C(6)	2.120(4)	Fe–C(9)	2.122(3)
Fe–C(8)	2.096(4)	C(1)–C(2)	1.514(5)
C(3)–O(3)	1.183(5)	C(4)–O(4)	1.149(4)
C(5)–C(6)	1.395(6)	C(5)–C(9)	1.402(6)
C(6)–C(7)	1.377(6)	C(7)–C(8)	1.392(6)
C(8)–C(9)	1.385(5)		



(I)



(II)

emphasises the μ-carbenoid nature of this carbon [C(1) here]. Indeed in terms of bond lengths such bridging carbons in μ-vinyl groups show carbon–metal distances which are sometimes near symmetrical {*e.g.* $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-CH-CH}_2)]$ [7] Os–C 2.107(3), 2.273(3) Å; $[Os_4(CO)_{11}(\mu\text{-H})_3(\mu\text{-CHCHPh})]$ [8] 2.154(10), 2.151(13) Å; and $[Rh_2(\eta\text{-}C_9H_7)_2(CO)_2\{\mu\text{-C(Me)CH}_2\}]^+$ [9] 2.046(4), 2.099(4) Å (the first number in each case refers to the C–M 'σ' interaction)}. The non-bridging carbon–metal distance in these complexes is uniformly longer [2.362(3), 2.299(13), and 2.223(5) Å respectively for the three examples above]. The μ-vinyl C–Fe distances in the cation of (1) follow these trends with C(1)–Fe 1.980(8) and C(2)–Fe 2.21(2) Å [where C(1)–Fe is equivalent to C(1)–Fe′]. This bridging C(1)–Fe distance is the same, within experimental uncertainty, as that for the μ-carbene carbon in (2) [1.986(3) Å] providing some support for description (II) above. The C(1)–C(2) distance in the vinyl ligand is typical of μ-vinyl complexes [1.40(2) Å; *cf.* 1.396(4), 1.36(2), and 1.402(8) Å respectively for the three complexes above]. This C(1)–C(2) distance is compatible with a C–C bond order between one and two as would be expected for some population of the π* orbital of the vinyl fragment on co-ordination as in (I). The C(1)–C(2) bond length in (2) [1.514(5) Å] shows the expected increase relative to that in (1) on reduction of the C–C bond order to unity.

The orientation of the bridging methylcarbene moiety in (2) is exactly perpendicular to the metal–metal vector. This orientation is favoured on electronic grounds.[10] Both theoretical [10] and experimental [11] studies have shown that small deviations (<6°) from strict perpendicularity of the M–M vector and the CR′R plane are possible for complexes containing the metallacyclopropane unit M_2CRR'. In contrast, in (1) the plane through C(1), C(2), and H(1) makes an angle of 57° with the Fe–Fe′ vector. This aspect of the vinyl ligand geometry emphasises the differing nature of the acceptor function on the $CHCH_2$ moiety as compared with the $CHCH_3$ ligand in (2), therefore favouring description (I) above. It is noticeable that the transition state in the solution state dynamic process observed by variable-temperature n.m.r.,[1] in which C(2) exchanges between sites on either metal atom, would presumably have the C(1)H(1)C(2) plane perpendicular to Fe–Fe′. The disorder affecting the cation of (1) precludes any detailed analysis of the orientation of the hydrogen atoms on the vinyl ligand. Previous workers [9] have noted deviations from planarity in μ-vinyl ligands explicable in terms of twisting about the C–C bond; a distortion consonant with description (II). The increased Fe–Fe′ bond length in (1) as compared with (2) [2.595(2) *vs.* 2.520(2) Å] seems likely to be a consequence of the larger bite of the vinyl as compared with the methylcarbene ligand. Similar variation in metal–metal bond length has been observed in osmium complexes {in $[Os_4(CO)_{11}(\mu\text{-H})_3(\mu\text{-CHCHPh})]$ [8] and $[Os_4(CO)_{11}H_2(\mu\text{-CHCH}_2\text{-Ph})]$ [12] bridged Os–Os are 2.830(3) and 2.755(2) Å; in $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-CHCH}_2)]$ [7] and $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-CHCH}_2\text{-PMe}_2\text{Ph})]$ [13] bridged Os–Os are 2.845(1) and 2.800(2) Å respectively}.

Table 4. Inter-bond angles (°) for (2)

C(1)–Fe–C(3)	93.1(1)	C(1)–Fe–C(4)	98.1(1)
C(3)–Fe–C(4)	89.8(2)	C(1)–Fe–C(5)	98.8(1)
C(3)–Fe–C(5)	156.8(1)	C(4)–Fe–C(5)	108.0(2)
C(1)–Fe–C(6)	91.8(1)	C(3)–Fe–C(6)	122.0(2)
C(4)–Fe–C(6)	146.2(2)	C(5)–Fe–C(6)	38.3(2)
C(1)–Fe–C(7)	119.7(1)	C(3)–Fe–C(7)	92.6(1)
C(4)–Fe–C(7)	141.9(2)	C(5)–Fe–C(7)	64.2(1)
C(6)–Fe–C(7)	38.1(2)	C(1)–Fe–C(8)	156.2(1)
C(3)–Fe–C(8)	97.5(1)	C(4)–Fe–C(8)	103.2(1)
C(5)–Fe–C(8)	64.5(1)	C(6)–Fe–C(8)	64.5(2)
C(7)–Fe–C(8)	38.8(2)	C(1)–Fe–C(9)	134.5(2)
C(3)–Fe–C(9)	132.3(1)	C(4)–Fe–C(9)	86.5(2)
C(5)–Fe–C(9)	38.5(2)	C(6)–Fe–C(9)	64.1(2)
C(7)–Fe–C(9)	64.3(1)	C(8)–Fe–C(9)	38.3(1)
C(1)–Fe–Fe′	50.6(1)	C(3)–Fe–Fe′	100.4(1)
C(4)–Fe–Fe′	48.5(1)	C(5)–Fe–Fe′	102.6(1)
C(6)–Fe–Fe′	125.8(1)	C(7)–Fe–Fe′	163.9(1)
C(8)–Fe–Fe′	145.9(1)	C(9)–Fe–Fe′	111.8(1)
Fe–C(1)–C(2)	123.7(2)	Fe–C(1)–Fe′	78.8(1)
Fe–C(3)–O(3)	138.5(1)	Fe–C(4)–O(4)	176.3(3)
Fe–C(5)–C(9)	70.5(2)	Fe–C(4)–Fe′	82.9(2)
Fe–C(6)–C(5)	71.2(2)	Fe–C(5)–C(6)	70.5(2)
C(5)–C(6)–C(7)	108.2(4)	C(6)–C(5)–C(9)	107.3(3)
Fe–C(7)–C(8)	70.8(2)	Fe–C(6)–C(7)	69.8(2)
Fe–C(8)–C(7)	70.4(2)	Fe–C(7)–C(6)	72.1(2)
C(7)–C(8)–C(9)	107.7(4)	C(6)–C(7)–C(8)	108.6(3)
Fe–C(9)–C(8)	69.8(2)	Fe–C(8)–C(9)	71.9(2)
		Fe–C(9)–C(5)	71.0(2)
		C(5)–C(9)–C(8)	108.1(3)

Both the cation of (1) and molecule (2) are in the *cis* conformation where the C(O)–Fe–Fe–C(O) torsion angle is 0° [here this angle is constrained by symmetry to this value, although in (1) this is an artefact of the disorder]. Similar geometries are adopted by a number of closely related μ-carbene species of the type $[Fe_2(CO)_2(\mu\text{-CO})(\eta\text{-}C_5H_5)_2(\mu\text{-L})]$ where L = $CHCO_2Bu^t$,[14a] CH_2,[14b] and CC(Ph)CH_2Ph.[14c] As in the parent *cis*-$[Fe_2(CO)_2(\mu\text{-CO})_2(\eta\text{-}C_5H_5)_2]$ [5] these complexes all have a non-planar $Fe_2(\mu\text{-C})_2$ central core, a feature which has been analysed by molecular-orbital techniques.[15] The degree of non-planarity of the $Fe_2(\mu\text{-C})_2$ units in (1) and (2), as measured by the dihedral angle between the FeFe′C(1) and FeFe′C(3) planes, is typical of this class of compound {8.1 and 14.2° for (1) and (2) respectively, *cf.* 16° for *cis*-$[Fe_2(CO)_2(\mu\text{-CO})_2(\eta\text{-}C_5H_5)_2]$}.

The *anti* conformation of the bridging C_2 ligand displayed here in (1) and (2) is clearly sterically preferable in that it prevents short contacts between C(2) and the cyclopentadienyl group atoms. The shortest such contacts are C(2) · · · C(7) 3.04 and C(2) · · · C(6) 3.24 Å in (1) and C(2) · · · C(6) 3.9 Å in (2). The H(1) · · · other atom intramolecular contacts in both (1) and (2) are not remarkably short [no H(1) · · · C shorter than 2.72 Å in either] indicating that this conformation is indeed sterically 'comfortable'. Likewise no very short intermolecular contacts are present in (1) or (2).

The major difference in bond lengths between (1) and (2), as regards the $Fe_2(CO)_2(\mu\text{-CO})(\eta\text{-}C_5H_5)$ fragment concerns the

Table 5. Atomic positional (fractional co-ordinates) parameters for (1)

Atom	*x*	*y*	*z*
Fe	0.220 47(8)	0.129 27(10)	0.115 39(8)
B	0.002 3(14)	0.75	0.264 3(12)
F(1)	−0.015 9(7)	0.75	0.373 1(6)
F(2)	0.111 5(8)	0.75	0.246 8(8)
F(3)	−0.038 4(10)	0.854 0(12)	0.221 6(7)
C(1)	0.330 1(9)	0.25	0.170 2(10)
C(2)	0.321 3(14)	0.171(2)	0.258 3(13)
C(3)	0.105 9(9)	0.25	0.076 7(8)
O(3)	0.014 7(7)	0.25	0.047 3(7)
C(4)	0.144 7(9)	0.103 8(10)	0.230 9(8)
O(4)	0.089 0(11)	0.090 3(11)	0.305 1(9)
C(5)	0.170 4(11)	−0.033 4(13)	0.040 6(11)
C(6)	0.260 9(13)	−0.057 0(12)	0.095 8(10)
C(7)	0.345 0(9)	0.006 7(12)	0.061 2(10)
C(8)	0.309 2(13)	0.084 1(10)	−0.022 3(10)
C(9)	0.193 7(11)	0.054 7(12)	−0.035 9(9)

bridging carbonyl ligand [Fe–C(3) 1.963(8) and 1.903(3) Å in (1) and (2) respectively]. This change is compatible with the charge on the cation of (1) reducing the π-back donation to this carbonyl and hence the Fe–C(3) bond order. Remaining differences in this part of the molecules are insignificant and are hidden by the effects of the disorder in (1). The averaged molecular parameters for (1) [and (2) in parentheses] are Fe–C(O) terminal 1.731(10) [1.748(3)], Fe–C(of C_5H_5) 2.085(8) [2.112(8)], C(3)–O(3) (bridging CO) 1.167(13) [1.183(5)], C(4)–O(4) (terminal CO) 1.155(15) [1.149(4)], C–C(of C_5H_5) 1.37(3) [1.390(4) Å].

Experimental

Structure Determination of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2][BF_4]$ (1).—Dark purple (1) crystallises from dichloromethane as plates elongated along *a*; a single crystal of approximate dimensions 0.04 × 0.14 × 0.31 mm was mounted in a thin-walled glass capillary under N_2 for *X*-ray structure analysis. Preliminary oscillation and Weissenberg photography established approximate cell dimensions and indicated the space group to be either *Pna*2_1 (no. 33) or *Pnma* (no. 62). A full octant of intensity data in the range $3 < 2\theta < 60°$ was collected at 240 K on a Nicolet P3m diffractometer. Integrated intensities were measured by the θ—2θ scan technique with scan widths $2.0° + \Delta_{\alpha_1\alpha_2}$ (difference in 2θ of Mo-$K_{\alpha 1}$ and Mo-$K_{\alpha 2}$ wavelengths) and scan speeds varying between 1.0 and 29.3° min^{-1} based on a 2-s prescan of the reflection. Two check reflections remeasured after every 40 data were constant within ±3% throughout the course of data collection. A numerical absorption correction, based on the indexed crystal faces (0 1 1), (0 $\bar{1}$ $\bar{1}$), (0 1 $\bar{1}$), (0 $\bar{1}$ 1), (2 1 1), ($\bar{1}$ 1 1), and ($\bar{1}$ $\bar{1}$ 1) was applied to the 2 898 data collected. Averaging of duplicate measurements and symmetry related reflections and deletion of systematic absences yielded 2 334 unique data; after application of Lorentz and polarisation corrections the 1 281 data with $F^2 > 2\sigma(F^2)$ were used in structure solution and refinement.

Crystal data for (1). $C_{15}H_{13}BF_4FeO_3$, $M = 439.5$, Orthorhombic, $a = 12.149(4)$, $b = 10.745(3)$, $c = 12.470(3)$ Å, $U = 1\,628(1)$ Å^3, $Z = 4$, $D_c = 1.79$ g cm^{-3}, $F(000) = 880$, space group *Pnma* (no. 62) (by refinement), Mo-K_α *X*-radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 18.3 cm^{-1}, $T = 240$ K.

Structure solution and refinement for (1). The structure was solved by heavy-atom methods, the unique iron atom was located by inspection of the Patterson function and the remaining non-hydrogen atoms located in subsequent difference Fourier maps. Refinement proved more satisfactory in the centric space group *Pnma* requiring disorder of the vinyl group across the crystallographic mirror plane which bisects both cation and anion. Refinement of a model in *Pna*2_1 did not lead to significantly reduced indices of fit and proved unstable, leading to unreasonable molecular geometry still showing two orientations for the vinyl group. The final refined model allowed anisotropic thermal parameters for all non-hydrogen atoms, with atoms C(1), C(3), O(3), H(2), B, F(1), and F(2) constrained to lie on the crystallographic mirror plane. The hydrogen atom H(1) (attached to the bridging carbon of the vinyl group) was located in a difference electron-density map and refined with an isotropic thermal parameter without positional constraints. A common isotropic thermal parameter for the cyclopentadienyl hydrogen atoms was refined, these atoms were constrained to idealised geometries with C–H bond distances fixed at 0.96 Å. The hydrogen atoms attached to C(2), the disordered (50% occupancy of each site) carbon atom of the vinyl group, were not included in the refined structure. Refinement was by blocked-cascade, full-matrix least squares, with data assigned weight $w = [\{\sigma^2(F_o^2)/4F_o^2\} + gF_o^2]^{-1}$ where $\sigma^2(F_o^2)$ is the variance in F_o^2 estimated from counting statistics and *g* was given the value 0.0003. Final indices of fit were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.083$ and $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_c| = 0.072$; inspection of the variance function $w(|F_o| - |F_c|)^2$ showed no significant dependence on $|F_o|$, sin θ, or indices. A final electron-density synthesis showed no peaks >1.1 or < −1.1 e Å^{-3}, the largest features being close to the $[BF_4]^-$ anion. Complex neutral-atom scattering factors were taken from ref. 16. All computations were carried out with programs of the SHELXTL software package on a Nicolet R3m structure determination system. Non-hydrogen atomic positional parameters are given in Table 5.

Table 6. Atomic positional (fractional co-ordinates) parameters for (2)

Atom	*x*	*y*	*z*
Fe	0.601 94(2)	0.337 43(2)	0.316 08(6)
C(1)	0.534 0(3)	0.25	0.496 2(6)
C(2)	0.434 0(3)	0.25	0.512 6(8)
C(3)	0.645 9(3)	0.25	0.116 9(7)
O(3)	0.684 7(3)	0.25	−0.045 5(5)
C(4)	0.511 4(2)	0.359 3(2)	0.151 3(5)
O(4)	0.454 2(2)	0.377 9(2)	0.039 3(5)
C(5)	0.706 2(3)	0.369 6(3)	0.530 5(7)
C(6)	0.632 1(3)	0.423 4(3)	0.577 9(7)
C(7)	0.612 4(3)	0.476 8(3)	0.404 0(8)
C(8)	0.674 0(3)	0.457 9(3)	0.246 6(7)
C(9)	0.732 4(2)	0.392 2(3)	0.324 5(7)

Structure Determination of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ (2).—Complex (2) was obtained as red-black prisms elongated along *c*, from dichloromethane solution. A crystal of approximate dimensions 0.07 × 0.15 × 0.33 mm was mounted in a thin-walled glass capillary under N_2 for *X*-ray structure analysis. Following a preliminary photographic study as for (1), the crystal was cooled to 220 K on a Nicolet P3m diffractometer for data collection. A full octant of intensity data in the range $3 < 2\theta < 65°$ was collected following the same procedure as for (1) above. The intensities of two check reflections remeasured after every 30 data were constant within ±2% over the period of data collection. A numerical absorption correction [crystal faces (2 1 0), ($\bar{2}$ $\bar{1}$ 0), (0 0 1), (1 $\bar{2}$ 0), ($\bar{1}$ $\bar{2}$ 0), (0 1 1), (0 −1 1)] was applied to all 2 762 data,

further data reduction as for (1) gave 2 309 unique data of which 1 631 with $F^2 > 1.5\ \sigma(F^2)$ were used in structure solution and refinement.

Crystal data for (2). $C_{15}H_{14}Fe_2O_3$, $M = 353.7$, Orthorhombic, $a = 15.096(9)$, $b = 14.414(8)$, $c = 6.336(4)$ Å, $U = 1\ 379(2)$ Å^3, $Z = 4$, $D_c = 1.70$ g cm^{-3}, $F(000) = 720$, space group *Pnma* (no. 62) (by refinement), Mo-K_α *X*-radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 21.06 cm^{-1}, $T = 220$ K.

Structure solution and refinement for (2). This proceeded as for (1) with the exceptions that no disorder was observed, all hydrogen atoms were located on difference electron-density maps and refined without positional constraints; a common isotropic thermal parameter was refined for the methyl hydrogens and for the cyclopentadienyl hydrogens. Atoms C(1), C(2), H(21), H(1), C(4), and O(4) were constrained to lie on the crystallographic mirror plane which bisects the molecule. Satisfactory behaviour of the variance function was obtained with the weighting scheme as for (1) ($g = 0.0003$); final indices of fit were $R = 0.046$ and $R' = 0.038$. A final difference Fourier synthesis showed no peaks >0.6 or <0.7 e Å^{-3}, all features being in regions of no chemical significance. Computational details of refinement, scattering factors, and programs were as for (1).

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References

1 A. F. Dyke, S. A. R. Knox, M. J. Morris, and P. J. Naish, preceding paper.
2 A. F. Dyke, S. A. R. Knox, P. J. Naish, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1980, 441.
3 B. B. Meyer, P. E. Riley, and R. E. Davis, *Inorg. Chem.*, 1981, **20**, 3024.
4 W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117; *Pure Appl. Chem.*, 1982, **54**, 65.
5 F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.*, 1974, 800.
6 R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, 1970, 3068.
7 A. G. Orpen, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *Acta Crystallogr., Sect. B*, 1978, **34**, 2466.
8 B. F. G. Johnson, J. Lewis, A. G. Orpen, P. R. Raithby, and K. D. Rouse, *J. Chem. Soc., Dalton Trans.*, 1981, 788.
9 Y. N. Al-Obaidi, P. K. Baker, M. Green, N. D. White, and G. E. Taylor, *J. Chem. Soc., Dalton Trans.*, 1981, 2321.
10 P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 554.
11 F. Takusagawa, A. Fumagalli, T. F. Koetzle, and W. A. Herrmann, *Inorg. Chem.*, 1981, **20**, 3060; D. A. Clemente, B. Rees, G. Bandoli, M. C. Biagini, B. Reiter, and W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 887; A. J. Schultz, J. M. Williams, R. B. Calvert, J. R. Shapley, and G. D. Stucky, *Inorg. Chem.*, 1979, **18**, 319.
12 B. F. G. Johnson, J. W. Kelland, J. Lewis, A. L. Mann, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 547.
13 M. R. Churchill, B. G. DeBoer, J. R. Shapley, and J. B. Keister, *J. Am. Chem. Soc.*, 1976, **98**, 2357.
14 (*a*) W. A. Herrmann, J. Plank, I. Bernal, and M. Creswick, *Z. Naturforsch., Teil B*, 1980, **35**, 680; (*b*) R. Korswagen, R. Alt, D. Speth, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1049; (*c*) M. B. Hossain, D. J. Hanlon, D. F. Marten, D. Van der Helm, and E. V. Dehmlow, *Acta Crystallogr., Sect. B*, 1982, **38**, 1457.
15 E. D. Jemmis, A. R. Pinhas, and R. J. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 2576.
16 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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