Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 15.[1] Reactions of the Complex $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) with Iron Carbonyls; Crystal Structures of $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ and $[FeW_2(\mu_3\text{-}RC_2R)(CO)_5L(\eta\text{-}C_5H_5)_2]$ (L = CO or O) *

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The compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) in diethyl ether at room temperature reacts with $[Fe_2(CO)_9]$ to give the dimetal complex $[FeW(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ (1), and the two trimetal species $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (2) and $[FeW_2(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$ (3). Compound (2) with PMe_2Ph or $Ph_2PCH_2PPh_2$ (dppm) affords $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_6L_2(\eta\text{-}C_5H_5)]$ [$L = PMe_2Ph$ (4), L_2 = dppm (5)], complexes in which the phosphine ligands are bonded to the two iron atoms. From the reaction between the complexes $[Fe_3(CO)_{12}]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$, the trimetal compounds (2), (3), and $[FeW_2(O)(\mu_3\text{-}RC_2R)(CO)_5(\eta\text{-}C_5H_5)_2]$ (6) were isolated. Spectroscopic data (infrared and n.m.r.) for the new compounds are reported, and discussed in relation to their structures, which were firmly established for (2), (3), and (6) by single-crystal *X*-ray diffraction studies. Crystals of (2) are orthorhombic, space group $P2_12_12_1$, $Z = 4$, in a unit cell with lattice parameters $a = 10.078(8)$, $b = 13.115(8)$, and $c = 16.785(8)$ Å. The structure was refined to *R* 0.030 (*R*′ 0.031) for 5 837 reflections having $2\theta \leqslant 60°$ (Mo-K_α *X*-radiation) collected at 200 K. The molecule consists of a Fe_2W triangle [Fe–W 2.805(2) and 2.756(2), Fe–Fe 2.538(2)Å] capped by a triply bridging tolylidyne ligand [μ_3-C–W 2.093(5), μ_3-C–Fe 1.969(5) and 2.036(5) Å]. The Fe–Fe bond is bridged by a CO group, the remaining carbonyl ligands being terminally bonded, two to the tungsten and three to each iron. Crystals of (3) are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with $a = 8.622(2)$, $b = 12.799(4)$, $c = 13.443(8)$ Å, $\alpha = 90.72(4)$, $\beta = 108.45(4)$, and $\gamma = 93.34(2)°$. The structure has been refined to *R* 0.037 (*R*′ 0.039) for 4 337 reflections having $2\theta \leqslant 50°$ collected at room temperature. The molecule consists of a FeW_2 triangle, the W–W distance [2.747(1) Å] suggesting double bonding. The Fe–W separations [2.731(1) and 2.745(1)] are perceptibly different, and the shorter is transversely bridged by a RC_2R alkyne group; one of the carbon atoms of the alkyne triply bridges the metal triangle [μ_3-C–W 2.289(5) and 2.264(7), μ_3-C–Fe 2.011(5) Å]. There are five terminally bound CO ligands, three attached to the iron atom and one to each tungsten. In addition, the tungsten atom σ-bonded to the alkyne carries a CO group which semi-bridges the W–W edge [W–C–O 164.9(7)°]. Crystals of (6) are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with $a = 8.694(2)$, $b = 12.540(4)$, $c = 13.365(7)$ Å, $\alpha = 88.03(4)$, $\beta = 108.44(3)$, and $\gamma = 97.54(2)°$. The structure has been refined to to *R* 0.049 (*R*′ 0.050) for 3 916 reflections having $2\theta \leqslant 50°$ collected at room temperature. The molecule has a structure very similar to that of (3) except that an oxygen atom has replaced the terminal CO ligand bonded to the tungsten atom μ-η^2 co-ordinated to the alkyne.

We have previously shown[2] that the compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) reacts with $[Co_2(CO)_8]$ to give the trimetal species $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$, in a reaction which parallels those which readily occur between octacarbonyldicobalt and alkynes, affording the bridged complexes $[Co_2(\mu\text{-}RC_2R)(CO)_6]$. Similarly, $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ yield the compound $[Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3]$.[1] These, and other, reactions[3] demonstrate similar reactivity patterns for $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and for alkynes which follow from the isolobal relationship between CR and $W(CO)_2(\eta\text{-}C_5H_5)$ groups.[4] Hence many complexes containing tungsten bonded to other transition elements should be accessible by treating $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with low-valent metal species. In this context we have investigated reactions between the mononuclear alkylidyne tungsten compound[5] and the iron carbonyls $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$. A preliminary account of some of the work has been given.[6]

Results and Discussion

Reactions between the compounds $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, or $[Fe_3(CO)_{12}]$ and alkynes are known to afford many types of organoiron complex,[7–9] and it was therefore expected that a mixture of products would be obtained by treating $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with iron carbonyls. In an attempt to simplify the system, the reaction between the alkylidynetungsten compound and $[Fe_2(CO)_9]$ in tetrahydrofuran (thf) was first studied, because it is known that in this solvent enneacarbonyldi-iron affords $[Fe(CO)_4(thf)]$ and $[Fe(CO)_5]$.[10] However, it was subsequently found that use of diethyl ether as the reaction medium allowed the nature of the products to be controlled more satisfactorily.

The initial product obtained by mixing $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with $[Fe_2(CO)_9]$ in diethyl ether at 25 °C is compound

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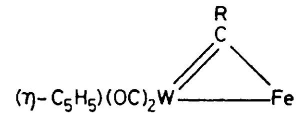
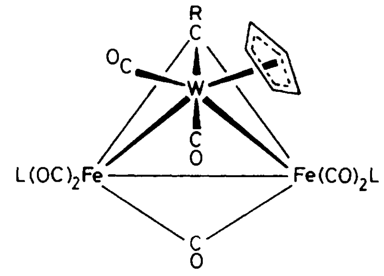
* 1,2-μ-Carbonyl-1,1,1,2,2,2,3,3-octacarbonyl-3-(η-cyclopentadienyl)-μ_3-*p*-tolylmethylidyne-*triangulo*-di-irontungsten; μ_3-[bis(*p*-tolyl)acetylene-$C^{1-2}(Fe^1 : W^3)C^2(W^2)$]-1,1,1,2,2,3-hexacarbonyl-2,3-bis(η-cyclopentadienyl)-*triangulo*-ironditungsten; and μ_3-[bis(*p*-tolyl)acetylene-$C^{1-2}(Fe^1 : W^3)C^2(W^2)$]-1,1,1,2,2-pentacarbonyl-2,3-bis(η-cyclopentadienyl)-3-oxo-*triangulo*-ironditungsten.

Supplementary data available (No. SUP 23425, 114 pp.): H-atom co-ordinates, thermal parameters, structure factors, complete bond parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



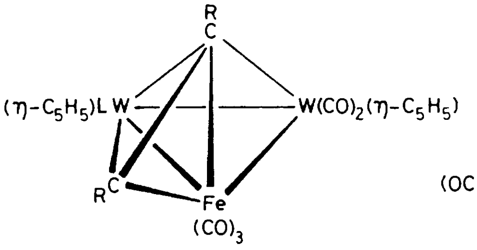
(1)



L

(2) CO

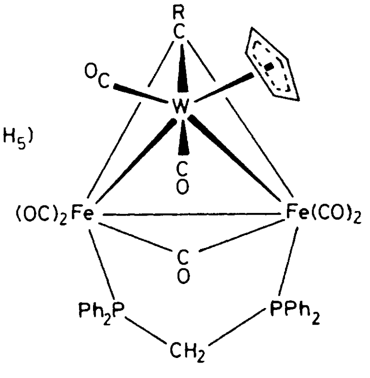
(4) PMe₂Ph



L

(3) CO

(6) O



(5)

R = C_6H_4Me-4

(1), but it is obtained in low yield (10%) because it readily undergoes further reaction. Complex (1) was fully identified spectroscopically, particularly by its ^{13}C-{^1H} n.m.r. spectrum. The latter had a resonance at δ 331.3 p.p.m. with ^{183}W satellites [J(WC) 137 Hz]. This signal is characteristic for the presence of a bridging alkylidyne carbon atom in (1). A similar resonance is observed at 336 p.p.m. for the μ-C nucleus in [$PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)$].[11] These signals for the μ-C ligated atoms are more deshielded than that for the carbyne-carbon atom in [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] (δ 300 p.p.m. for *C*R).[5] The ^{13}C-{^1H} n.m.r. spectrum of (1) also shows resonances for the other groups present, including signals for the WCO (216.1 p.p.m.) and FeCO (210.8 p.p.m.) carbonyl ligands.

Compound (1) with [$Fe_2(CO)_9$] affords the cluster compound (2), while with [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] it gives the trimetal species (3). Optimum conditions for preparing (2) and (3) directly from [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] and [$Fe_2(CO)_9$] are described in the Experimental section.

The i.r. spectrum of (2) shows a band at 1 785 cm^{-1} due to a bridging CO group, and a band at 1 845 cm^{-1} suggesting a semi-bridging carbonyl ligand. In addition, there are 11 bands in the terminal CO stretching region, indicating the presence in solution of an equilibrium between rotational isomers. A similar property is shown by the closely related compound [$Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)$] and is discussed elsewhere.[2] The isomers of (2) could arise through the $W(CO)_2(\eta\text{-}C_5H_5)$ group adopting different configurations about an axis through the tungsten atom and a triangular face formed by the μ_3-CFe_2 atoms.

The ^{13}C-{^1H} n.m.r. spectrum of (2) showed the expected resonance for the μ_3-C nucleus at δ 282.6 p.p.m. The corresponding signals in the spectra of [$Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)$] and [$Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3$] are seen at 257 and 275.7 p.p.m., respectively.[1,2] In the ^{13}C-{^1H} n.m.r. spectrum of (2) the CO ligands give rise to only one signal, indicating dynamic behaviour, as found with [$Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)$].

We have previously observed [2] that one CO group on each cobalt atom in [$Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)$] is readily substituted by $P(OMe)_3$, PMe_2Ph, or $Ph_2PCH_2PPh_2$ (dppm), the latter affording the dicobalt-bridged dppm species [$Co_2W(\mu_3\text{-}CR)(\mu\text{-dppm})(CO)_6(\eta\text{-}C_5H_5)$]. Compound (2) reacts similarly with PMe_2Ph and dppm, giving compounds (4) and (5), respectively.

The ^{31}P-{^1H} n.m.r. spectrum of (4) had only one resonance (δ 23.3 p.p.m.), indicating that the PMe_2Ph ligands are in equivalent environments. No ^{183}W satellite peaks were observed, strongly suggesting that the two tertiary phosphine groups are attached to the iron atoms. The ^1H and ^{13}C n.m.r. spectra were as expected (Experimental section). The ^{31}P-{^1H} n.m.r. spectrum of (5) also showed only one resonance (46.7 p.p.m.), again with no ^{183}W satellite peaks, in accord with a structure in which the dppm ligand bridges the Fe–Fe bond. At room temperature the ^{13}C-{^1H} n.m.r. spectrum of (5) showed a resonance for the μ_3-C nucleus at 272.1 p.p.m., with tungsten satellites [J(WC) 99 Hz], and a broad signal for the CO ligands. At −35 °C, however, the latter resonance resolved into four peaks (δ 269.8, 222.4, 217.8, and 216.0 p.p.m.). At the lower temperature the μ_3-C signal was not shifted from its position in the room-temperature spectrum. Based on the chemical shifts for the CO ligands observed at −35 °C, a reasonable assignment [2] is as follows: 269.8 (μ-Fe_2CO), 222.4 (WCO), 217.8 and 216.0 (FeCO). The i.r. spectrum of (5) showed a band due to a bridging CO group at 1 737 cm^{-1}, and although the lowest-frequency carbonyl band

Table 1. Selected interatomic distances (Å) and angles (°) for $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (2) with estimated standard deviations in parentheses

Fe(1)–W	2.805(2)	Fe(2)–W	2.756(2)	Fe(1)–C(3)	1.800(5)	Fe(2)–C(4)	1.798(5)
Fe(1)–Fe(2)	2.538(2)	Fe(1)–C(10)	1.969(5)	Fe(2)–C(5)	1.796(5)	Fe(2)–C(6)	1.792(5)
Fe(2)–C(10)	2.036(5)	W–C(10)	2.093(5)	Fe(1)–C(7)	2.051(5)	Fe(2)–C(7)	1.929(5)
Fe(1)–C(1)	1.822(5)	Fe(1)–C(2)	1.813(5)	W–C(8)	1.994(5)	W–C(9)	1.987(5)
		W–C(η-C_5H_5)	2.297(5)—2.368(6)				

W–Fe(1)–Fe(2)	61.9(1)	W–Fe(1)–C(10)	48.2(1)	C(10)–Fe(2)–C(4)	79.3(2)	C(10)–Fe(2)–C(5)	135.1(2)
W–Fe(1)–C(1)	101.9(2)	W–Fe(1)–C(2)	101.5(2)	C(10)–Fe(2)–C(6)	120.2(2)	C(10)–Fe(2)–C(7)	100.5(2)
W–Fe(1)–C(3)	154.5(2)	W–Fe(1)–C(7)	82.1(1)	C(4)–Fe(2)–C(5)	95.1(2)	C(4)–Fe(2)–C(6)	90.4(2)
Fe(2)–Fe(1)–C(10)	51.9(1)	Fe(2)–Fe(1)–C(1)	129.4(2)	C(4)–Fe(2)–C(7)	178.5(2)	C(5)–Fe(2)–C(6)	104.3(3)
Fe(2)–Fe(1)–C(2)	135.1(2)	Fe(2)–Fe(1)–C(3)	94.0(2)	C(5)–Fe(2)–C(7)	84.0(2)	C(6)–Fe(2)–C(7)	90.9(2)
Fe(2)–Fe(1)–C(7)	48.3(1)	C(10)–Fe(1)–C(1)	148.6(2)	Fe(1)–W–Fe(2)	54.3(1)	Fe(1)–W–C(10)	44.5(1)
C(10)–Fe(1)–C(2)	85.2(2)	C(10)–Fe(1)–C(3)	111.4(2)	Fe(1)–W–C(8)	80.5(1)	Fe(1)–W–C(9)	75.8(1)
C(10)–Fe(1)–C(7)	98.6(2)	C(1)–Fe(1)–C(2)	93.6(2)	Fe(2)–W–C(10)	47.2(1)	Fe(2)–W–C(8)	90.4(1)
C(1)–Fe(1)–C(3)	100.0(2)	C(1)–Fe(1)–C(7)	83.8(2)	Fe(2)–W–C(9)	129.7(1)	C(10)–W–C(8)	122.1(2)
C(2)–Fe(1)–C(3)	89.9(2)	C(2)–Fe(1)–C(3)	176.0(2)	C(10)–W–C(9)	93.9(2)	C(8)–W–C(9)	86.8(2)
C(3)–Fe(1)–C(7)	87.6(2)	W–Fe(2)–Fe(1)	63.8(1)	W–C(10)–Fe(1)	87.3(2)	W–C(10)–Fe(2)	83.7(2)
W–Fe(2)–C(10)	49.0(1)	W–Fe(2)–C(4)	93.3(2)	W–C(10)–C(11)	133.9(3)	Fe(1)–C(10)–Fe(2)	78.6(2)
W–Fe(2)–C(5)	87.5(2)	W–Fe(2)–C(6)	167.3(2)	Fe(1)–C(10)–C(11)	124.9(3)	Fe(2)–C(10)–C(11)	130.1(3)
W–Fe(2)–C(7)	85.5(1)	Fe(1)–Fe(2)–C(10)	49.5(1)	Fe(1)–C(7)–Fe(2)	79.2(2)	Fe(1)–C(7)–O(7)	136.3(4)
Fe(1)–Fe(2)–C(4)	127.6(2)	Fe(1)–Fe(2)–C(5)	127.4(2)	Fe(2)–C(7)–O(7)	144.4(4)		
Fe(1)–Fe(2)–C(6)	104.5(2)	Fe(1)–Fe(2)–C(7)	52.5(1)				

in the i.r. spectrum of (4) was at 1 873 cm^{-1} implying a semi- rather than a fully-bridging ligand, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum had a resonance assignable to a μ-CO group at δ 269.0 p.p.m.

The spectroscopic data for compound (3) were insufficient for structural characterisation of the compound. However, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum showed no resonance at *ca.* 270 p.p.m. ascribable to a μ_3-*C*R group, and hence the structure was not one in which a FeW_2 triangle of metal atoms is capped by an alkylidyne ligand. Thus to establish the structure of (3) a single-crystal *X*-ray diffraction study was undertaken. A similar study was also carried out on (2). Although the gross structural features of the latter species were evident from the spectroscopic data, it was important to carry out the *X*-ray diffraction study since this class of heteronuclear trimetal compound, in which a $RC{\equiv}W(CO)_2(\eta\text{-}C_5H_5)$ fragment bridges a homonuclear metal–metal bond, in this case Fe–Fe, is rare. The molecular parameters for compounds (2) and (3), as determined by the *X*-ray diffraction data, are summarised in Tables 1 and 2; the molecular structures are illustrated in Figures 1 and 2.

In (2) the triangular Fe_2W arrangement with a capping μ_3-CC_6H_4Me-4 ligand is confirmed (Figure 1). The Fe–Fe bond is bridged, slightly asymmetrically, by a CO ligand [Fe(1)–C(7)–Fe(2) 79.2(2)°; C(7)–Fe(1) 2.051(5), C(7)–Fe(2) 1.929(5) Å]. If the bridging carbonyl is notionally removed the basic structure is similar to that of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$,[2] and not surprisingly, as described above, the two clusters have similar chemical and spectroscopic properties. The remaining eight CO ligands occupy approximately orthogonal positions within the $Fe(CO)_3$ and $W(CO)_2$ moieties, with similar orientations to those observed in $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$.[1]

Although from the n.m.r. studies in solution the $Fe(CO)_3$ groups appear chemically equivalent, the molecule is chiral in the solid state by reason of the orientation of the $W(CO)_2(\eta\text{-}C_5H_5)$ and of the tolyl moieties. Perhaps as a result of this asymmetry the Fe–W distances [2.805(2) and 2.756(2) Å] differ by *ca.* 0.05 Å, as also do the two μ_3-C–Fe separations [2.036(5) and 1.969(5) Å]. However, in the pseudo mirror symmetric complex $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$ (acac = acetylacetonate)[2] the Rh–W distances are also significantly inequivalent (*ca.* 0.05 Å), suggesting that crystal-packing forces may be at least partially responsible for such effects. Notwithstanding such variations, the Fe–W distances in (2) are similar to those in $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ [2.772 (1) Å] and in $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ [2.784(3) Å],[12] while the Fe–Fe distance [2.538(2) Å] is comparable with those observed for the two CO-bridged Fe–Fe bonds in $[Fe_3(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}CMe)(\eta\text{-}C_5H_5)]$ [2.509(1) and 2.519(1) Å].[13]

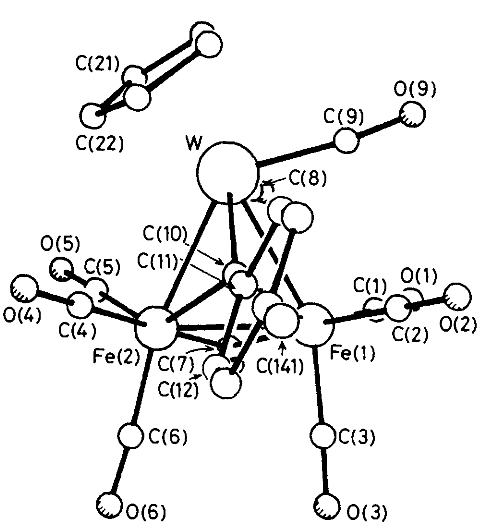


Figure 1. Molecular structure of $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (2) showing the atom-numbering scheme

We have previously discussed the bonding of the tolylidyne ligand in the related complexes $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$, $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$, and $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$.[1,2] Since the bonding of this ligand in (2) closely resembles that in the latter complex it requires no further comment here.

The molecular structure of (3) is shown in Figure 2. It is immediately evident that in the formation of (3) two [W(≡CR)-

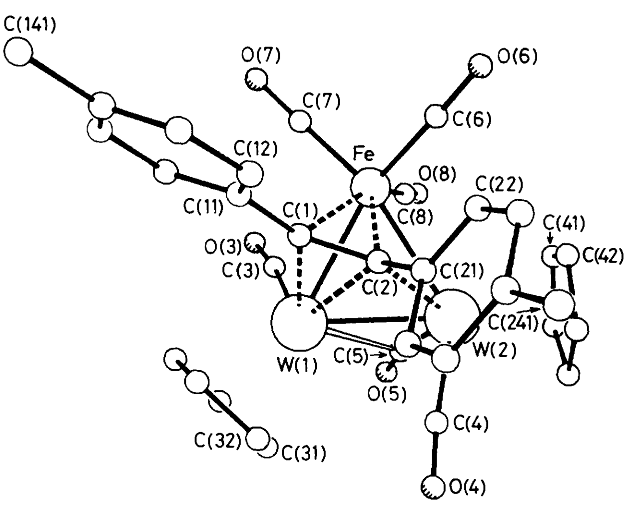


Figure 2. Molecular structure of [FeW$_2${μ$_3$-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_6$(η-C$_5$H$_5$)$_2$] (3) showing the atom-numbering scheme

(CO)$_2$(η-C$_5$H$_5$)] molecules have coupled to form a 4-MeC$_6$H$_4$C≡CC$_6$H$_4$Me-4 ligand which is asymmetrically bound to an FeW$_2$ triangle of metal atoms. The alkyne RC(1)≡C(2)R fragment transversely bridges the Fe–W(1) bond, such that C(2) is μ$_3$-co-ordinated to all three metal atoms, whilst C(1) is μ-bonded to W(1) and Fe. This is a relatively rare example of a μ$_3$(η^2-⊥) alkyne bonding mode; [14,15] a very similar μ$_3$-C$_2$M$_3$ framework of this type has been structurally characterised previously in [Fe$_3$(μ$_3$-C$_2$Ph$_2$)(CO)$_9$].[16]

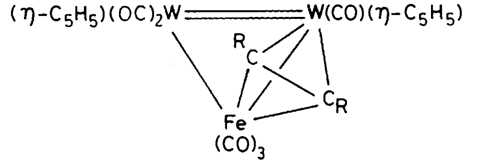
The Fe atom carries three terminal carbonyl groups, and the W atoms each carry one terminal carbonyl group, with a second CO on W(2) being semi-bridging to W(1). Complexes (3) and [Fe$_3$(μ$_3$-C$_2$Ph$_2$)(CO)$_9$] are electronically unsaturated, having only 46 c.v.e. (cluster valence electrons). In the related 48 c.v.e. species [MW$_2$(μ$_3$-C$_2$R$_2$)(CO)$_7$(η-C$_5$H$_5$)$_2$] (M = Ru or Os) [6] the alkyne ligands adopt the more common μ$_3$(η^2-||) bonding mode.

Despite the molecular asymmetry the Fe–W distances are fairly similar, with the bridged-bond Fe–W(1) [2.731(1) Å] being marginally shorter than Fe–W(2) [2.745(1) Å]. These values are in the middle of the range (2.81 —2.64 Å) observed in a number of clusters [1,12] having a μ$_3$-CM^{1}M^{2}M^3 trimetalla-

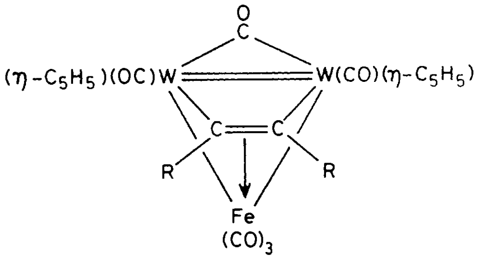
Table 2. Comparison of selected interatomic distances (Å) and angles (°) for [FeW$_2${μ$_3$-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_6$(η-C$_5$H$_5$)$_2$] (3) and for [FeW$_2$(O){μ$_3$-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_5$(η-C$_5$H$_5$)$_2$] (6), with estimated standard deviations in parentheses

Complex (3)		Complex (6)		Complex (3)		Complex (6)	
Fe–W(1)	2.731(1)	Fe–W(2)	2.747(2)	Fe–C(8)	1.781(7)	Fe–C(5)	1.774(10)
Fe–W(2)	2.745(1)	Fe–W(1)	2.677(1)	W(1)–C(3)	1.946(6)	W(2)–O	1.726(7)
W(1)–W(2)	2.747(1)	W(1)–W(2)	2.848(1)	W(1)–C(5)	2.564(8)	W(2)–C(2)	2.517(10)
Fe–C(1)	2.052(5)	Fe–C(9)	2.017(9)	W(1)–C(η-C$_5$H$_5$)	2.300(7)—	W(2)–C(η-C$_5$H$_5$)	2.407(7)—
Fe–C(2)	2.011(5)	Fe–C(10)	2.027(9)		2.335(7)		2.448(9)
W(1)–C(1)	2.040(6)	W(2)–C(9)	2.046(10)	W(2)–C(4)	1.963(6)	W(1)–C(1)	1.951(11)
W(1)–C(2)	2.289(5)	W(2)–C(10)	2.480(10)	W(2)–C(5)	1.963(7)	W(1)–C(2)	1.983(12)
W(2)–C(2)	2.264(7)	W(1)–C(10)	2.259(8)	W(2)–C(η-C$_5$H$_5$)	2.277(8)—	W(1)–C(η-C$_5$H$_5$)	2.330(12)—
Fe–C(6)	1.766(6)	Fe–C(4)	1.783(12)		2.372(9)		2.382(9)
Fe–C(7)	1.790(8)	Fe–C(3)	1.783(9)	C(1)–C(2)	1.399(9)	C(9)–C(10)	1.441(11)

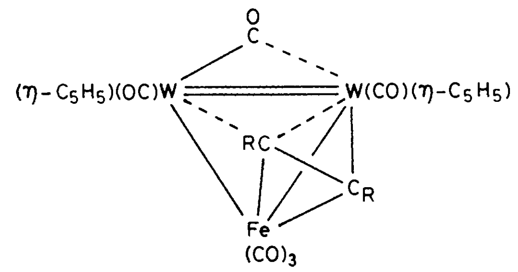
Complex (3)		Complex (6)		Complex (3)		Complex (6)	
W(1)–Fe–W(2)	60.2(1)	W(2)–Fe–W(1)	63.3(1)	C(1)–W(1)–C(3)	99.7(3)	C(9)–W(2)–O	110.0(4)
W(1)–Fe–C(1)	47.9(2)	W(2)–Fe–C(9)	47.9(3)	C(1)–W(1)–C(5)	125.6(2)	C(9)–W(2)–C(2)	125.0(4)
W(1)–Fe–C(2)	55.3(2)	W(2)–Fe–C(10)	60.4(3)	C(2)–W(1)–C(3)	116.4(2)	C(10)–W(2)–O	131.3(4)
W(1)–Fe–C(6)	152.6(2)	W(2)–Fe–C(4)	161.3(3)	C(2)–W(1)–C(5)	94.9(2)	C(10)–W(2)–C(2)	92.3(3)
W(1)–Fe–C(7)	105.6(2)	W(2)–Fe–C(3)	98.0(4)	C(3)–W(1)–C(5)	77.8(3)	O–W(2)–C(2)	—
W(1)–Fe–C(8)	100.2(2)	W(2)–Fe–C(5)	91.9(4)	W(1)–W(2)–Fe	59.6(1)	W(2)–W(1)–Fe	59.5(1)
W(2)–Fe–C(1)	87.3(2)	W(1)–Fe–C(9)	87.9(2)	W(1)–W(2)–C(2)	53.3(1)	W(2)–W(1)–C(10)	56.7(2)
W(2)–Fe–C(2)	54.2(2)	W(1)–Fe–C(10)	55.3(2)	W(1)–W(2)–C(4)	77.9(2)	W(2)–W(1)–C(1)	86.1(3)
W(2)–Fe–C(6)	103.2(3)	W(1)–Fe–C(4)	106.3(3)	W(1)–W(2)–C(5)	63.4(2)	W(2)–W(1)–C(2)	59.6(3)
W(2)–Fe–C(7)	162.1(2)	W(1)–Fe–C(3)	156.9(4)	Fe–W(2)–C(2)	46.1(1)	Fe–W(1)–C(10)	47.6(2)
W(2)–Fe–C(8)	77.4(3)	W(1)–Fe–C(5)	77.1(3)	Fe–W(2)–C(4)	132.4(3)	Fe–W(1)–C(1)	129.8(3)
C(1)–Fe–C(2)	40.3(2)	C(9)–Fe–C(10)	41.7(3)	Fe–W(2)–C(5)	93.4(2)	Fe–W(1)–C(2)	101.6(3)
C(1)–Fe–C(6)	114.5(3)	C(9)–Fe–C(4)	119.7(4)	C(2)–W(2)–C(4)	92.2(3)	C(10)–W(1)–C(1)	83.7(4)
C(1)–Fe–C(7)	90.0(3)	C(9)–Fe–C(3)	88.8(4)	C(2)–W(2)–C(5)	115.6(3)	C(10)–W(1)–C(2)	116.2(4)
C(1)–Fe–C(8)	147.8(3)	C(9)–Fe–C(5)	139.2(5)	C(4)–W(2)–C(5)	85.2(3)	C(1)–W(1)–C(2)	88.3(5)
C(2)–Fe–C(6)	97.5(2)	C(10)–Fe–C(4)	101.0(4)	W(1)–C(1)–Fe	83.7(2)	W(2)–C(9)–Fe	85.1(3)
C(2)–Fe–C(7)	128.9(3)	C(10)–Fe–C(3)	129.3(4)	W(1)–C(1)–C(2)	81.2(4)	W(2)–C(9)–C(10)	88.9(6)
C(2)–Fe–C(8)	131.5(3)	C(10)–Fe–C(5)	131.4(4)	W(1)–C(1)–C(11)	136.9(4)	W(2)–C(9)–C(41)	134.3(6)
C(6)–Fe–C(7)	93.9(3)	C(4)–Fe–C(3)	95.2(5)	Fe–C(1)–C(2)	68.3(3)	Fe–C(9)–C(10)	69.5(5)
C(6)–Fe–C(8)	96.6(3)	C(4)–Fe–C(5)	101.0(5)	Fe–C(1)–C(11)	128.6(4)	Fe–C(9)–C(41)	125.3(6)
C(7)–Fe–C(8)	96.0(3)	C(3)–Fe–C(5)	90.8(4)	C(2)–C(1)–C(11)	133.1(5)	C(10)–C(9)–C(41)	131.0(8)
W(2)–W(1)–Fe	60.1(1)	W(1)–W(2)–Fe	57.1(1)	W(1)–C(2)–W(2)	74.2(2)	W(2)–C(10)–W(1)	73.7(3)
W(2)–W(1)–C(1)	87.5(2)	W(1)–W(2)–C(9)	82.8(2)	W(1)–C(2)–Fe	78.6(2)	W(2)–C(10)–Fe	74.3(3)
W(2)–W(1)–C(2)	52.5(2)	W(1)–W(2)–C(10)	49.6(2)	W(1)–C(2)–C(1)	61.7(3)	W(2)–C(10)–C(9)	55.6(5)
W(2)–W(1)–C(3)	103.9(2)	W(1)–W(2)–O	116.5(3)	W(1)–C(2)–C(21)	142.6(4)	W(2)–C(10)–C(31)	147.4(6)
W(2)–W(1)–C(5)	43.2(1)	W(1)–W(2)–C(2)	42.8(3)	W(2)–C(2)–Fe	79.6(2)	W(1)–C(10)–Fe	77.1(3)
Fe–W(1)–C(1)	48.3(1)	Fe–W(2)–C(9)	47.0(2)	W(2)–C(2)–C(1)	130.7(4)	W(1)–C(10)–C(9)	124.2(6)
Fe–W(1)–C(2)	46.2(1)	Fe–W(2)–C(10)	45.3(2)	W(2)–C(2)–C(21)	106.1(4)	W(1)–C(10)–C(31)	114.4(5)
Fe–W(1)–C(3)	70.4(2)	Fe–W(2)–O	86.5(3)	Fe–C(2)–C(1)	71.5(3)	Fe–C(10)–C(9)	68.7(5)
Fe–W(1)–C(5)	81.8(2)	Fe–W(2)–C(2)	87.3(3)	Fe–C(2)–C(21)	138.8(4)	Fe–C(10)–C(31)	137.5(7)
C(1)–W(1)–C(2)	37.2(2)	C(9)–W(2)–C(10)	35.5(3)	C(1)–C(2)–C(21)	122.0(6)	C(9)–C(10)–C(31)	120.8(7)



(3a)



(3b)



(3c)

tetrahedrane core and containing iron and tungsten, and as such show no unusual features. In marked contrast, the W(1)–W(2) separation [2.747(1) Å] is unusually short. Typical W–W single bonds are significantly longer, *e.g.* $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ [3.222(1) Å],[17] $[OsW_2(\mu_3\text{-}C_2R_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ [two isomers: 3.159(2) and 3.017(2) Å],[6] and $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ [2.991(1) Å].[18] It has been estimated that the W≡W distance in $[W_2(CO)_4(\eta\text{-}C_5H_5)_2]$ would be *ca.* 2.45 ± 0.01 Å.[19] These data suggest that a W=W bond in a low-valent metal complex might be *ca.* 2.72—2.84 Å in length. It is, therefore, tentatively suggested that the W(1)–W(2) separation in (3) is consistent with W=W character.

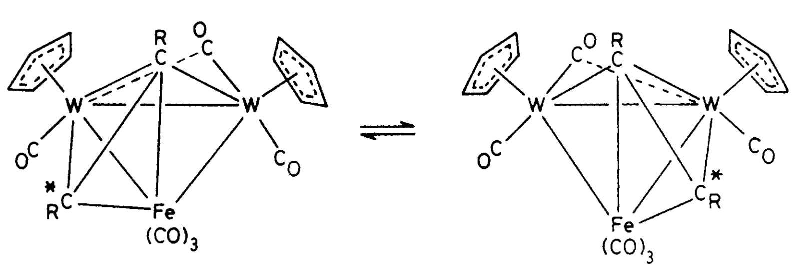
The alkyne ligand has a C(1)–C(2) distance of 1.399(9) Å, and a *cis*-bent geometry which closely resembles that found for the similarly co-ordinated alkyne in $[Fe_3(\mu_3\text{-}C_2Ph_2)(CO)_9]$ [C–C(alkyne) 1.41(2) Å].[16] The η^2-bonding of this ligand to the $Fe(CO)_3$ moiety is relatively symmetrical [Fe–C(1) 2.052(5), Fe–C(2) 2.011(5) Å], and comparable Fe–C(alkyne) distances are observed in $[Fe_3(\mu_3\text{-}C_2Ph_2)(CO)_9]$ (range 1.95—2.10 Å). The corresponding $W(1)(\eta^2\text{-}C_2R_2)$ separations differ by 0.25 Å, with W(1)–C(1) [2.040(6) Å] shorter than W(1)–C(2) [2.289(5) Å]. The W(2)–C(2) distance is similar to W(1)–C(2), and these values are close to those found for the W–C (alkyne) bonds in the two isomers of $[OsW_2(\mu_3\text{-}C_2R_2)(CO)_7\text{-}(\eta\text{-}C_5H_5)_2]$ (range 2.18—2.37 Å).[6]

The nature of the bonding in (3) is evidently complicated, but the major structural features can be rationalised by considering the molecule in terms of the two electron-pair structures (3a) and (3b). In (3a) the ditolylalkyne ligand transversely bridges the Fe–W(1) vector in a manner similar to that observed for the $Me_3SiC{\equiv}CSiMe_3$ ligand in $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$.[20] In (3b) the alkyne adopts the common $\mu_3(\eta^2\text{-}\|)$ bonding mode. The W(1)–C(2)–W(2) interaction in (3) can be considered as a three-centre two-electron bond leading to a situation (3c) in the solid, intermediate between (3a) and (3b). The presence of the semi-bridging carbonyl C(5)O(5) [W(2)–C(5)–O(5) 164.9(7)°] would serve to delocalise electron density between the tungsten atoms.

Having established the molecular structure of (3) by the *X*-ray diffraction study, it was possible to interpret many of the spectroscopic properties. The semi-bridging CO ligand reveals itself in the i.r. spectrum by a band at 1 838 cm^{-1}. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum, resonances at δ 168.5 and 153.8 p.p.m. may be ascribed to the carbon atoms C(1) and C(2). Surprisingly, in view of the *X*-ray diffraction results which show the $\eta\text{-}C_5H_5$ ligands in (3) in different environments, only one resonance is seen (92.0 p.p.m.) in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum. Similarly, the ^1H n.m.r. spectrum also shows a single resonance for a $\eta\text{-}C_5H_5$ group at δ 5.09 (10 H). Evidently (3) undergoes dynamic behaviour by a mechanism which renders the C_5H_5 rings equivalent, and the process shown in the Scheme is proposed. Unfortunately (3) has poor solubility, and hence it was not possible to measure spectra at low temperatures.

The reaction between $[Fe_3(CO)_{12}]$ and $[W({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]$ in thf at room temperature was also investigated. The products were compounds (2), (3), (6), and a small amount of the bridged alkyne complex $[W_2(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$. The latter is often observed in reactions between the alkylidynetungsten compound and transition-metal complexes.[1] The nature of the violet crystalline complex (6) was only resolved after a single-crystal *X*-ray diffraction study, described below. It was observed, however, that (6) was slowly formed from (3) by allowing samples of the latter to stand in air. The n.m.r. spectra [^1H and $^{13}C\text{-}\{^1H\}$] of (6) established that it contained $\eta\text{-}C_5H_5$ groups in two environments. The i.r. spectrum showed bands for terminal CO groups, while an absorption at 1 792 cm^{-1} suggested the presence of a bridging carbonyl group. Compound (6) appeared to be a polar compound since on chromatography it could only be eluted with acetone or tetrahydrofuran. Fortunately, suitable crystals were available and an *X*-ray diffraction study was carried out.

The molecular dimensions are summarised in Table 2 and the structure is illustrated in Figure 3. Compound (6) is found to be a derivative of (3) in which an oxygen atom has replaced the CO ligand on the tungsten atom bonded to iron and bridged by the alkyne group. The stereochemical features of (3) and (6) are virtually unaltered by this substitution, and are listed side-by-side for easy comparison in Table 2. The principal effect of oxygen substitution in (6) is to increase the length of all the bonds to the W(2)=O group. Thus the W(2)–C($\eta\text{-}C_5H_5$) separations in (6) are on average *ca.* 0.1 Å longer than in (3), and a similar increase is observed in the W(1)–



Scheme. Proposed dynamic behaviour of (3) in solution

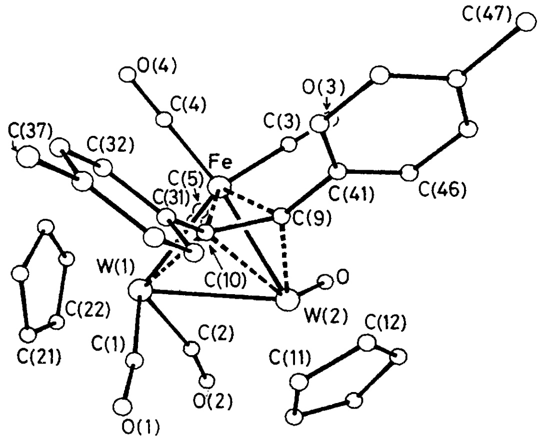


Figure 3. Molecular structure of [$FeW_2(O)\{\mu_3$-$C_2(C_6H_4Me$-$4)_2\}$-$(CO)_5(\eta$-$C_5H_5)_2$] (6) showing the atom-numbering scheme

W(2) distance. Although the bonding of the ditolylalkyne ligand to the FeW_2 triangle is evidently similar to that found in (3), the marked lengthening of the W(2)–C(10) bond (*ca.* 0.2 Å) and the concomitant shortening of the W(1)–C(10) bond suggest that for (6) a $\mu_3(\eta^2$-$\|)$ bonding mode for the alkyne ligand might be more dominant than in (3).

Experimental

The experimental techniques used, and the instrumentation employed, have been previously described.[1,2] For n.m.r. measurements, chemical shifts, δ (p.p.m.), are relative to $SiMe_4$ for the ^1H and ^{13}C-$\{^1H\}$ spectra and to 85% H_3PO_4 (external) for ^{31}P-$\{^1H\}$ spectra. Unless otherwise stated, ^1H spectra were measured in [$^2H_2$]dichloromethane, and ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ spectra in [$^2H_2$]dichloromethane–CH_2Cl_2. For ^{13}C-$\{^1H\}$ spectra [$Cr(acac)_3$] was added. Light petroleum refers to that fraction of b.p. 40—60 °C. The compound [$W(\equiv CC_6H_4$-Me-$4)(CO)_2(\eta$-$C_5H_5)$] was prepared by the literature method.[5]

Syntheses.—[$FeW(\mu$-CC_6H_4Me-$4)(CO)_6(\eta$-$C_5H_5)$]. A mixture of [$Fe_2(CO)_9$] (0.73 g, 2 mmol) and [$W(\equiv CC_6H_4Me$-$4)$-$(CO)_2(\eta$-$C_5H_5)$] (0.82 g, 2 mmol) in diethyl ether (15 cm^3) at room temperature was stirred for *ca.* 8 h. The resulting deep brown solution, containing some [$Fe(CO)_5$] (**CAUTION**), was evaporated to dryness, leaving a black residue. The latter was dissolved in dichloromethane–light petroleum (1 : 5) and chromatographed on Florisil (2 × 40 cm column). Elution with the same solvent mixture afforded a brown-red band. Solvent was removed *in vacuo* giving brown *microcrystals* of the compound [$FeW(\mu$-CC_6H_4Me-$4)(CO)_6(\eta$-$C_5H_5)$] (1) (0.12 g, 10%) (Found: C, 37.6; H, 2.4. $C_{19}H_{12}FeO_6W\cdot\frac{1}{4}CH_2Cl_2$ requires C, 39.9; H, 2.1%); $\nu_{max.}$ (CO) 2 073m, 2 025m, 1 993s, 1 929s, and 1 869w cm^{-1} (CH_2Cl_2). N.m.r.: ^1H, δ 2.17 (s, 3 H, Me-4), 5.34 (s, 5 H, η-C_5H_5), and 7.19 (m, 4 H, C_6H_4); ^{13}C, δ 331.3 [μ-C, *J*(WC) 137 Hz], 216.1 (WCO), 210.8 (FeCO), 158.7 [C(1)C(C_6H_4)], 137.5 [C(4)(C_6H_4)], 128.2 [C(2) and C(6)(C_6H_4)], 125.9 [C(3) and C(5)(C_6H_4)], 92.1 (η-C_5H_5), and 20.5 p.p.m. (Me-4). Further elution of the chromatography column with dichloromethane–light petroleum (1 : 1) gave compound (2), and finally, with dichloromethane, compound (3). However, optimum yields of the trimetal species are obtained as described below.

[$Fe_2W(\mu_3$-CC_6H_4Me-$4)(\mu$-$CO)(CO)_8(\eta$-$C_5H_5)$]. A mixture of [$Fe_2(CO)_9$] (2.18 g, 6.0 mmol) and [$W(\equiv CC_6H_4Me$-$4)(CO)_2$-$(\eta$-$C_5H_5)$] (0.81 g, 2.0 mmol) in diethyl ether (20 cm^3) was stirred overnight at room temperature. The deep brown solution was evaporated to dryness. The black residue was redissolved in dichloromethane and filtered through an alumina pad (3 cm). The solution was concentrated (*ca.* 1 cm^3), and slow addition of light petroleum (*ca.* 15 cm^3) gave large black *crystals* of [$Fe_2W(\mu_3$-CC_6H_4Me-$4)(\mu$-$CO)(CO)_8(\eta$-$C_5H_5)$] (2) (0.98 g, 70%) (Found: C, 36.7; H, 1.7. $C_{22}H_{12}Fe_2O_9W$ requires C, 36.7; H, 1.7%); $\nu_{max.}$ (CO) 2 073m, 2 065w, 2 029s, 2 019m, 2 009s, 2 001s, 1 989m, 1 979m, 1 961w, 1 951w, 1 921w, 1 845w(br), and 1 785m(br) cm^{-1} (cyclohexane). N.m.r.: ^1H, δ 2.4 (s, 3 H, Me-4), 5.37 (s, 5 H, η-C_5H_5), and 7.29 (m, 4 H, C_6H_4); ^{13}C, δ 282.6 (μ_3-C), 212.9 (br, CO), 158.1 [C(1)(C_6H_4)], 136.8 [C(4)(C_6H_4)], 131.2 [C(2) and C(6) (C_6H_4)], 127.9 [C(3) and C(5) (C_6H_4)], 88.5 (C_5H_5), and 20.1 p.p.m. (Me-4).

[$FeW_2\{\mu_3$-$C_2(C_6H_4Me$-$4)_2\}(CO)_6(\eta$-$C_5H_5)_2$]. A mixture of [$Fe_2(CO)_9$] (0.36 g, 1 mmol) and [$W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)$] (1.63 g, 4 mmol) in diethyl ether (20 cm^3) was stirred at room temperature for 2 d. The deep purple-brown solution was evaporated to dryness *in vacuo*. The residue was re-dissolved in dichloromethane–light petroleum (1 : 1) and chromatographed on Florisil (2 × 30 cm column). Elution with the same solvent mixture gave some unreacted [$W(\equiv CC_6H_4$-Me-$4)(CO)_2(\eta$-$C_5H_5)$] followed by compound (3). Elution with 100% dichloromethane gave a deep purple band. The solution was evaporated *in vacuo* and the residue crystallised from dichloromethane–light petroleum (1 : 1) affording purple black *crystals* of [$FeW_2\{\mu_3$-$C_2(C_6H_4Me$-$4)_2\}(CO)_6(\eta$-$C_5H_5)_2$] (3) (0.66 g, 72%) (Found: C, 41.5; H, 2.6. $C_{32}H_{24}FeO_6W_2$ requires C, 41.5; H, 2.6%); $\nu_{max.}$ (CO) 2 024s, 1 983s, 1 962s, 1 919s, and 1 838m(br) cm^{-1} (cyclohexane). N.m.r.: ^1H, δ 2.19 (br, 6 H, Me-4), 5.09 (s, 10 H, C_5H_5), and 6.83 (br, 8 H, C_6H_4Me-4); ^{13}C, δ 225.6, 217.0, 215.0 (CO), 168.5 (CC_6H_4-Me-4), 154.5 [C(1)(C_6H_4)], 153.8 (CC_6H_4Me-4), 152.7 [C(1)-(C_6H_4)], 135.1, 133.8 [C(4)(C_6H_4)], 129.7, 128.3 [C(2) and C(6)(C_6H_4)], 127.5 [C(3) and C(5)(C_6H_4)], 92.0 (C_5H_5), and 21.0 p.p.m. (Me-4).

Reaction of [$Fe_3(CO)_{12}$] with [$W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)$].—A mixture of [$Fe_3(CO)_{12}$] (0.25 g, 0.5 mmol) and [$W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)$] (0.41 g, 1 mmol) in thf (30 cm^3) was stirred for 5 d at room temperature. Solvent was

Table 3. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (2)							
W	0.877 94(2)	0.618 79(1)	0.804 95(1)	O(7)	0.533 1(5)	0.766 9(3)	0.738 0(3)
Fe(1)	0.636 40(7)	0.552 31(5)	0.740 12(3)	C(8)	0.842 3(5)	0.733 8(4)	0.730 2(4)
Fe(2)	0.631 34(7)	0.644 18(5)	0.873 17(3)	O(8)	0.832 3(5)	0.801 0(4)	0.686 7(3)
C(10)	0.729 8(5)	0.515 8(4)	0.839 1(3)	C(9)	0.930 6(5)	0.538 3(4)	0.709 8(4)
C(1)	0.643 4(6)	0.605 0(4)	0.639 8(3)	O(9)	0.972 2(5)	0.492 5(4)	0.658 0(3)
O(1)	0.650 1(5)	0.636 6(4)	0.577 6(3)	C(11)	0.731 2(5)	0.413 5(4)	0.875 0(3)
C(2)	0.679 0(5)	0.424 6(4)	0.707 5(3)	C(12)	0.622 4(6)	0.374 5(4)	0.916 6(3)
O(2)	0.705 2(5)	0.345 9(4)	0.685 8(3)	C(13)	0.626 2(7)	0.276 1(4)	0.949 0(3)
C(3)	0.464 1(5)	0.516 4(4)	0.744 3(4)	C(14)	0.734 1(6)	0.213 0(4)	0.938 7(3)
O(3)	0.355 5(4)	0.497 6(4)	0.748 5(4)	C(15)	0.841 3(5)	0.250 4(4)	0.896 6(3)
C(4)	0.684 7(6)	0.596 3(4)	0.968 3(3)	C(16)	0.840 7(5)	0.349 6(4)	0.865 5(3)
O(4)	0.719 1(5)	0.569 8(4)	1.029 5(3)	C(141)	0.737 3(8)	0.107 7(5)	0.974 5(5)
C(5)	0.677 9(6)	0.773 9(4)	0.892 9(3)	C(21)	1.030 9(6)	0.728 4(5)	0.864 5(4)
O(5)	0.703 9(7)	0.856 7(4)	0.904 5(4)	C(22)	0.969 1(6)	0.674 2(5)	0.927 5(4)
C(6)	0.461 6(6)	0.636 7(5)	0.904 3(3)	C(23)	0.997 8(6)	0.568 6(5)	0.919 0(4)
O(6)	0.354 0(5)	0.635 2(4)	0.927 8(3)	C(24)	1.078 5(6)	0.556 0(5)	0.850 9(4)
C(7)	0.578 5(5)	0.697 1(4)	0.770 7(3)	C(25)	1.099 9(5)	0.655 4(5)	0.817 3(4)
(*b*) $[FeW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (3)							
W(1)	0.052 64(3)	0.184 67(2)	0.323 06(2)	C(15)	−0.264 3(10)	0.230 7(6)	0.584 6(6)
W(2)	−0.051 18(3)	0.237 22(2)	0.115 94(2)	C(16)	−0.209 2(9)	0.207 1(5)	0.501 5(6)
Fe	−0.269 65(10)	0.149 58(6)	0.206 59(7)	C(141)	−0.386 0(12)	0.354 1(8)	0.682 4(7)
C(1)	−0.154 3(7)	0.244 8(5)	0.336 0(5)	C(21)	−0.185 5(7)	0.405 7(5)	0.222 9(5)
C(2)	−0.151 1(7)	0.291 8(5)	0.243 2(5)	C(22)	−0.335 9(9)	0.438 1(5)	0.167 1(6)
C(3)	−0.011 0(9)	0.035 9(5)	0.319 1(6)	C(23)	−0.365 0(9)	0.543 9(5)	0.160 5(6)
O(3)	−0.032 0(8)	−0.051 2(4)	0.327 0(6)	C(24)	−0.244 7(8)	0.620 1(5)	0.209 0(6)
C(4)	0.151 0(9)	0.327 3(6)	0.172 7(6)	C(25)	−0.091 9(9)	0.586 4(5)	0.263 3(6)
O(4)	0.267 5(8)	0.381 2(5)	0.197 0(6)	C(26)	−0.064 4(8)	0.483 0(5)	0.270 9(6)
C(5)	0.092 9(9)	0.120 7(5)	0.151 9(6)	C(241)	−0.272 7(10)	0.735 5(5)	0.202 4(7)
O(5)	0.178 0(7)	0.054 5(4)	0.150 6(5)	C(31)	0.337 0(9)	0.211 5(6)	0.382 1(7)
C(6)	−0.459 7(8)	0.191 4(5)	0.127 2(6)	C(32)	0.274 1(10)	0.299 1(6)	0.414 8(7)
O(6)	−0.585 9(7)	0.214 4(4)	0.074 9(5)	C(33)	0.192 3(9)	0.262 6(7)	0.485 1(7)
C(7)	−0.359 3(8)	0.068 4(5)	0.284 1(6)	C(34)	0.202 9(11)	0.153 7(8)	0.493 9(7)
O(7)	−0.417 1(8)	0.013 4(5)	0.331 7(5)	C(35)	0.294 8(10)	0.125 0(7)	0.428 3(8)
C(8)	−0.255 0(9)	0.047 2(5)	0.119 7(6)	C(41)	−0.226 1(14)	0.191 0(8)	−0.054 3(7)
O(8)	−0.250 1(9)	−0.027 0(4)	0.072 4(5)	C(42)	−0.257 9(11)	0.289 1(7)	−0.027 9(7)
C(11)	−0.216 8(7)	0.277 1(5)	0.422 7(5)	C(43)	−0.123 7(12)	0.354 6(6)	−0.014 0(7)
C(12)	−0.281 0(9)	0.371 7(5)	0.429 4(6)	C(44)	−0.002 9(13)	0.296 4(8)	−0.034 6(8)
C(13)	−0.331 4(9)	0.394 6(6)	0.515 1(7)	C(45)	−0.068 7(14)	0.194 0(8)	−0.059 6(7)
C(14)	−0.327 1(9)	0.326 0(6)	0.591 7(6)				
(*c*) $[FeW_2(O)\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_5(\eta\text{-}C_5H_5)_2]$ (6)							
W(1)	0.305 62(4)	0.230 84(3)	0.387 23(3)	C(12)	0.190 0(10)	0.245 4(5)	0.020 3(6)
W(2)	0.186 66(4)	0.147 02(3)	0.177 55(3)	C(13)	0.205 0(10)	0.137 3(5)	0.000 7(6)
Fe	−0.010 3(2)	0.154 50(10)	0.301 72(10)	C(14)	0.356 9(10)	0.112 4(5)	0.070 2(6)
C(31)	0.092 7(9)	0.412 9(4)	0.265 8(6)	C(15)	0.435 9(10)	0.205 2(5)	0.132 6(6)
C(32)	0.043 8(9)	0.454 1(4)	0.344 9(6)	C(1)	0.442 8(13)	0.339 4(9)	0.334 6(8)
C(33)	0.034 1(9)	0.564 0(4)	0.348 9(6)	O(1)	0.530 4(13)	0.408 6(8)	0.313 0(8)
C(34)	0.073 3(9)	0.632 7(4)	0.273 8(6)	C(2)	0.414 3(13)	0.119 2(9)	0.344 1(9)
C(35)	0.122 2(9)	0.591 4(4)	0.194 6(6)	O(2)	0.493 8(11)	0.054 2(7)	0.340 4(8)
C(36)	0.131 9(9)	0.481 6(4)	0.190 7(6)	C(3)	−0.181 8(13)	0.066 0(9)	0.225 2(8)
C(37)	0.061(2)	0.753 5(9)	0.275 4(11)	O(3)	−0.288 9(11)	0.007 6(8)	0.178 4(8)
C(41)	−0.150 8(7)	0.257 7(6)	0.079 4(5)	C(4)	−0.115 6(13)	0.204 7(8)	0.381 4(8)
C(42)	−0.226 5(7)	0.348 8(6)	0.080 9(4)	O(4)	−0.183 8(12)	0.238 3(8)	0.432 1(8)
C(43)	−0.365 1(7)	0.367 4(6)	−0.002 0(4)	C(5)	0.071 9(14)	0.045 4(8)	0.379 2(9)
C(44)	−0.428 1(7)	0.294 9(6)	−0.086 3(4)	O(5)	0.112 4(14)	−0.030 4(7)	0.423 6(7)
C(45)	−0.352 4(7)	0.203 8(6)	−0.087 8(4)	O	0.118 4(10)	0.011 1(6)	0.163 7(6)
C(46)	−0.213 7(7)	0.185 2(6)	−0.004 9(4)	C(21)	0.514 8(14)	0.302 5(12)	0.537 9(8)
C(47)	−0.581(2)	0.321(2)	−0.174 2(11)	C(22)	0.489 1(14)	0.190 0(12)	0.554 3(8)
C(9)	−0.003 5(11)	0.231 4(7)	0.167 9(7)	C(23)	0.327 5(14)	0.163 4(12)	0.558 6(8)
C(10)	0.099 3(11)	0.293 4(7)	0.258 8(7)	C(24)	0.253 3(14)	0.259 6(12)	0.544 9(8)
C(11)	0.332 8(10)	0.287 4(5)	0.101 8(6)	C(25)	0.369 0(14)	0.345 5(12)	0.532 1(8)

removed *in vacuo*, the residue dissolved in the minimum of dichloromethane, and chromatographed on Florisil (40 × 2.5 cm column). Graded elution with dichloromethane–light petroleum (10—100% CH_2Cl_2) afforded in sequence $[Fe_3(CO)_{12}]$ (trace), $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (trace), compound (2) (0.1 g), $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.05 g) (identified spectroscopically [1]), and compound (3) (0.05 g). Elution of the column with acetone gave, after evaporation of solvent, *microcrystals* of $[FeW_2(O)\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_5(\eta\text{-}C_5H_5)_2]$ (6) (80 mg) (Found: C, 40.7; H, 2.7. $C_{31}H_{24}FeO_6W_2$ requires C, 40.7; H, 2.7%); $\nu_{max.}$ (CO) 2 039s, 1 979m, 1 954m, 1 918w, and 1 792w(br) cm^{-1} (CH_2Cl_2); $\nu_{max.}$ (WO) 890s cm^{-1} (Nujol). N.m.r.: ^1H, δ 2.33 (s, 3 H, Me-4), 2.35 (s, 3 H, Me-4), 5.35 (s, 5 H, C_5H_5), 6.01 (s, 5 H, C_5H_5), and 6.5—7.1 (m, 8 H, C_6H_4); ^{13}C, δ 210.6 (CO), 155—126 (CC_6H_4), 108.9 (C_5H_5), 96.8 (C_5H_5), 21.2 and 20.9 p.p.m. (Me-4).

Reactions of Compound (2) *with Phosphines*.—(*a*) A diethyl ether (30 cm^3) solution of (2) (0.52 g, 0.73 mmol) was treated with PMe_2Ph (0.20 g, 1.46 mmol) and the mixture stirred. After i.r. analysis had shown the total consumption of (2), solvent was removed *in vacuo* and the residue dissolved in dichloromethane (20 cm^3) and filtered through an alumina pad. Evaporation of solvent gave a residue which was crystallised from dichloromethane–light petroleum (1 : 1) to give black *crystals* of $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_6(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (4) (0.57 g, 84%) (Found: C, 45.7; H, 3.8; P, 4.7. $C_{36}H_{34}Fe_2O_7P_2W$ requires C, 46.2; H, 3.7; P, 6.6%); $\nu_{max.}$ (CO) 2 037m, 1 997s, 1 965s, 1 941s, and 1 873m cm^{-1} (dichloromethane). N.m.r.: ^1H ($[^2H_1]$chloroform), δ 1.68 [d, 12 H, MeP, *J*(PH) 9 Hz], 2.31 (s, 3 H, Me-4), 4.97 (s, 5 H, C_5H_5), 6.8—7.6 (m, 14 H, Ph and C_6H_4); ^{31}P, δ 23.3 p.p.m.; ^{13}C, δ 272.8 (μ_3-C), 269.0 (μ-CO), 222—216 (br, CO), 161.1 [C(1)(C_6H_4)], 140—126 (Ph and C_6H_4), 89.4 (C_5H_5), 19.9 (Me-4), and 14.2 p.p.m. [d, PMe, *J*(PC) 27 Hz].

(*b*) A diethyl ether (30 cm^3) solution of (2) (0.76 g, 1.07 mmol) and $Ph_2PCH_2PPh_2$ (0.41 g, 1.07 mmol) was stirred for 24 h. Solvent was removed *in vacuo* and the residue crystallised from dichloromethane–light petroleum (1 : 1) to afford black *crystals* of $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_6(Ph_2PCH_2PPh_2)(\eta\text{-}C_5H_5)]$ (5) (0.57 g, 52%) (Found: C, 51.6; H, 3.2; P, 6.5. $C_{45}H_{34}Fe_2O_7P_2W$ requires C, 51.8; H, 3.3; P, 5.9%); $\nu_{max.}$ (CO) 2 023m, 2 015s, 1 963s, 1 943s, 1 925m, 1 893m, and 1 737w cm^{-1} (methylcyclohexane). N.m.r.: ^1H ($[^2H_1]$chloroform), δ 2.40 (s, 3 H, Me-4), 3.34 [t of quartets 2 H, CH_2, *J*(PH) 10, *J*(HH) 5 Hz], 5.13 (s, 5 H, C_5H_5), and 6.8—7.7 (m, 24 H, Ph and C_6H_4); ^{31}P, δ 46.7 p.p.m.; ^{13}C ($[^2H_1]$chloroform–dichloromethane, −35 °C), δ 272.1 (μ_3-C), 269.8 (μ-CO), 222.4 (WCO), 217.8 (FeCO), 216.0 (FeCO), 159.8 [C(1)(C_6H_4)], 139—127 (Ph and C_6H_4), 89.5 (C_5H_5), 36.2 (CH_2), and 21.2 p.p.m. (Me-4).

Crystal-structure Determinations.—(*a*) $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (2). Crystals of (2) were grown from dichloromethane–light petroleum. Intensities were collected at 200 K from a wedge-shaped crystal of dimensions *ca.* 0.50 × 0.20 × 0.125 mm in the range $2.9 \leqslant 2\theta \leqslant 60°$. Data were collected on a Nicolet *P3m* four-circle diffractometer, according to methods described earlier.[21,22] Because of some initial doubts as to whether the space group was genuinely orthorhombic, and not monoclinic, two octants of data (*hkl* and $hk\bar{l}$) were collected. Of the total 6 881 intensities, 5 837 reflections ($hkl + hk\bar{l}$, not merged) had $F \geqslant 6.0\ \sigma(F)$, where σ(*F*) is the standard deviation based on counting statistics, and these were used in the solution and refinement of the structure, after the data had been corrected for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data. $C_{22}H_{12}Fe_2O_9W$, *M* = 715.5, Orthorhomibic, *a* = 10.078(8), *b* = 13.115(8), *c* = 16.785(8) Å, *Z* = 4, D_c = 2.12 g cm^{-3}, *U* = 2 218(3) $Å^3$, *F*(000) = 1 368, space group $P2_12_12_1$ (no. 19), Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 66.3 cm^{-1}.

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and electron-density difference methods. Hydrogen atoms were included at calculated positions, chemically related hydrogen atoms being given common refined isotropic thermal parameters. All remaining atoms were refined with anisotropic thermal parameters. Refinement by blocked-cascade least squares led to *R* 0.030 (*R′* 0.031) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.000\,65|F_o|^2]^{-1}$ giving a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >2.4 e $Å^{-3}$. Scattering factors were from ref. 23. All computations were carried out on an Eclipse (Data General) minicomputer with the SHELXTL system of programs.[24] Atom co-ordinates for all three structures are listed in Table 3.

(*b*) $[FeW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (3). A suitable purple-black crystal of dimensions *ca.* 0.45 × 0.35 × 0.175 mm was grown from dichloromethane–light petroleum solutions.

Crystal data. $C_{32}H_{24}FeO_6W_2$, *M* = 927.6, Triclinic, *a* = 8.622(2), *b* = 12.799(4), *c* = 13.443(8) Å, α = 90.72(4), β = 108.45(4), γ = 93.34(2)°, *Z* = 2, D_c = 2.209 g cm^{-3}, *U* = 1 404(1) $Å^3$, *F*(000) = 876, space group $P\bar{1}$ (no. 2), μ(Mo-K_α) = 89.1 cm^{-1}.

Conditions as for (2) except: 5 327 reflections to 2θ = 50° gave 4 337 independent intensities [$F \geqslant 6.0\sigma(F)$]. In refinement, hydrogen atoms were given isotropic thermal parameters which were 1.2 times the equivalent isotropic thermal parameter of the attached carbon atom. Weights $w = [\sigma^2(F_o) + 0.001\,2|F_o|^2]^{-1}$. Final electron density (max.) by difference = 1.9 e $Å^{-3}$. *R* 0.037, *R′* 0.039.

(*c*) $[FeW_2(O)\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_5(\eta\text{-}C_5H_5)_2]$ (6). Crystals were grown by diffusion from dichloromethane solution into a layer of light petroleum. The one used for data collection was prismatic and of dimensions *ca.* 0.10 × 0.26 × 0.28 mm, with well developed (001), (00$\bar{1}$), (010), (0$\bar{1}$0), (101), and ($\bar{1}$0$\bar{1}$) faces.

Crystal data. $C_{31}H_{24}FeO_6W_2$, *M* = 916.1, Triclinic, *a* = 8.694(2), *b* = 12.540(4), *c* = 13.365(7) Å, α = 88.03(4), β = 108.44(3), γ = 97.54(2) °, *Z* = 2, D_c = 2.22 g cm^{-3}, *U* = 1 370(1) $Å^3$, *F*(000) = 864, space group $P\bar{1}$ (no. 2), μ(Mo-K_α) = 86.1 cm^{-1}.

Conditions as for (2) except: 5 437 reflections to 2θ = 50° gave 3 916 independent intensities [$F \geqslant 5.0\ \sigma(F)$]. Cyclopentadienyl and tolyl rings were refined as rigid groups: C–C(C_5H_5) 1.420; C–C(C_6H_4Me) 1.395; C–H 0.960 Å. Weights $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$. Final electron density (max.) by difference = 1.5 e $Å^{-3}$ except near W (*ca.* 2.5 e $Å^{-3}$); *R* 0.049, *R′* 0.050.

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