Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 48.[1] Reactions of the Cluster Complex $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4); Crystal Structures of $[FeW_2(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ and $[FeW_2(\mu_3\text{-}MeC_2C_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$[*]

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In toluene at 80 °C the compounds $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ react to give the ditungsten complex $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ as the major product. In contrast, the corresponding reaction with $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ yields a separable mixture of three cluster complexes: $[FeW_2(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(CO)_7(\eta\text{-}C_5H_5)_2]$, $[FeW_2(\mu_3\text{-}MeC_2C_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$, and $[FeW_2(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_2]$ with the last formed in trace amounts. The structures of $[FeW_2(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ and $[FeW_2(\mu_3\text{-}MeC_2C_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$ have been established by *X*-ray diffraction. In the vinylidene complex an ironditungsten triangle [mean Fe–W 2.854, W–W 3.030(1) Å] is bridged by the $C{=}CH_2$ ligand in such a manner that the latter is σ-bonded to the tungsten atoms (mean μ-C–W 2.06 Å) and η^2-co-ordinated to the iron [C–Fe 1.96(2) and 2.21(2) Å]. The iron atom is bonded by three terminal CO ligands, while the tungsten atoms are each ligated by a C_5H_5 and two CO groups. Three of the latter weakly semi-bridge the metal–metal bonds. The structure of the alkyne complex $[FeW_2(\mu_3\text{-}MeC_2C_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$ is based on a triangle of metal atoms [W–W 2.949(1), Fe–W 2.730(1) and 2.992(1) Å]. The $MeC_2C_6H_4Me$-4 ligand lies on the face of the triangle with its C_2 axis parallel to a Fe–W bond. The iron atom carries three CO groups and the tungsten atoms two such groups and a C_5H_5 ligand. Three of the tungsten-ligated CO groups semi-bridge the three edges of the metal triangle [W–C–O 164.5(9), 167.7(9), and 169.2(9)°]. The n.m.r. data for the compounds are reported, and possible pathways for formation of the three cluster complexes are discussed.

The di-irontungsten compounds $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**1a**, R = C_6H_4Me-4; **1b**, R = Me) are products[2,3] of reactions between $[Fe_2(CO)_9]$ and the mononuclear tungsten alkylidyne complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$. We are currently investigating the reactivity of these cluster compounds,[3,4] and the results described in this paper are relevant to earlier work with alkynes.[5] Reactions between (**1a**) and the species $Me_3SiC_2SiMe_3$ and $Bu^tC_2SiMe_3$ afford the trimetal compounds $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}alkyne)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$ (**2**) in which the $\mu_3\text{-}CFe_2W$ core structure found in (**1a**) is retained. In contrast, with the alkynes RC_2R (R = Me, Ph, C_6H_4Me-4, or CF_3), compound (**1a**) yields the dimetal compounds $[FeW\{\mu\text{-}CRCRC(C_6H_4Me\text{-}4)\}(CO)_5(\eta\text{-}C_5H_5)]$, the formation of which involves loss of an iron carbonyl fragment from the di-irontungsten precursors. In view of these results, and the isolobal relationship[6] existing between alkynes and the compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$, we have studied reactions between the latter and (**1a**). It was of interest to establish whether it would be possible to prepare tetranuclear metal complexes structurally similar to (**2**), but with the μ-$R^1C_2R^2$ groups replaced by a $RC{\equiv}W(CO)_2(\eta\text{-}C_5H_5)$ fragment, or whether in the reactions loss of an iron carbonyl fragment from (**1a**) would occur, as found on treatment of the latter with RC_2R (R = Me, Ph, C_6H_4Me-4, or CF_3).

Results and Discussion

Reaction between compound (**1a**) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in toluene at 80 °C resulted in complete degradation of the trimetal complex, and formation of the known species $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$[7] as the main product. In the light of other results described below, it seems likely that the μ-$C_2(C_6H_4Me\text{-}4)_2$ ditungsten compound forms in a stepwise manner under the reaction conditions. Initially a tetranuclear Fe_2W_2 metal compound, structurally akin to (**2**), might be produced, which subsequently releases iron carbonyl groups so as to yield $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ as the thermodynamically most stable product.

Under conditions similar to those employed in the reaction between the tolylmethylidyne tungsten compound and (**1a**), the ethylidyne analogue $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ afforded a separable mixture of three ironditungsten cluster compounds. These species were identified on the basis of microanalysis and spectroscopic data as complexes $[FeW_2(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ (**3**), $[FeW_2(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_2]$ (**4**), and $[FeW_2(\mu_3\text{-}MeC_2C_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$ (**5**). Compounds (**3**) and (**5**) were structurally characterised by single-crystal *X*-ray diffraction studies. The structure of (**4**) is based on n.m.r. data since suitable crystals of this compound, formed in only *ca.* 2% yield, were not obtained.

The *X*-ray diffraction results for (**3**) are summarised in Table 1, and the structure is shown in Figure 1. It is evident that an FeW_2 triangle of metal atoms is μ_3-bridged by a vinylidene

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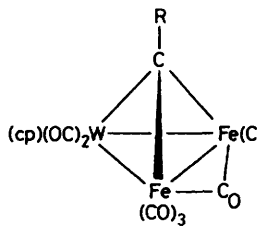
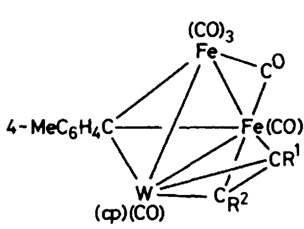
[*] 1,1,1,2,2,3,3-Heptacarbonyl-2,3-bis(η-cyclopentadienyl)-μ_3-[vinylidene-$C^1(Fe^1,W^2,W^3)C^2(Fe^1)$]-*triangulo*-ironditungsten and 1,1,1,2,2,3,3-heptacarbonyl-2,3-bis(η-cyclopentadienyl)-μ_3-[1-*p*-tolylpropene-1,2-diyl-$C^1(Fe^1,W^2)C^2(W^2,W^3)$]-*triangulo*-ironditungsten respectively.

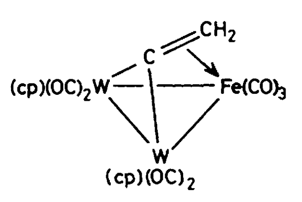
Supplementary data available (No. SUP 56569, 7 pp.): H-atom co-ordinates and thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



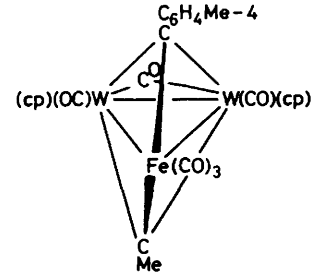
	R
(1a)	C$_6$H$_4$Me-4
(1b)	Me



	R^1	R^2
(2a)	SiMe$_3$	SiMe$_3$
(2b)	Bu^t	SiMe$_3$
(2c)	SiMe$_3$	Bu^t



(3)



cp = η-C$_5$H$_5$ (4)

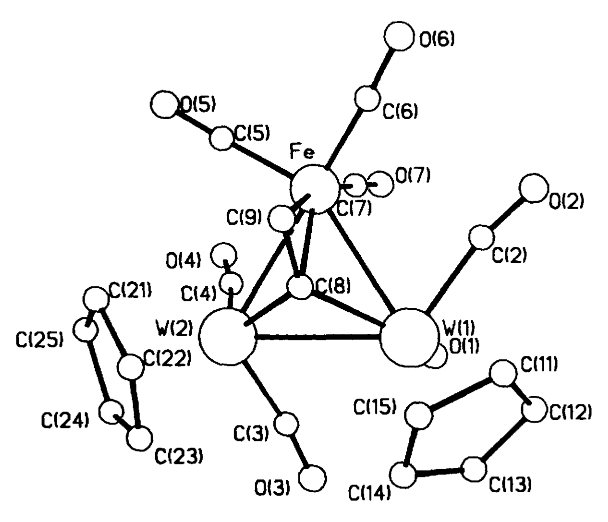


Figure 1. The molecular structure of [FeW$_2$(μ_3-σ:σ′:η^2-C=CH$_2$)(CO)$_7$(η-C$_5$H$_5$)$_2$] (3) showing the atom labelling scheme

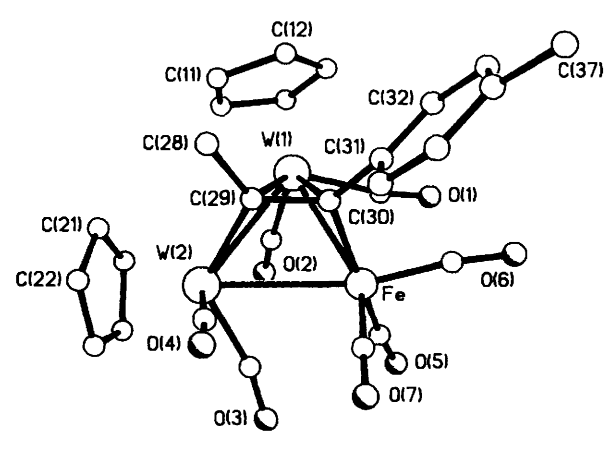


Figure 2. The molecular structure of [FeW$_2$(μ_3-MeC$_2$C$_6$H$_4$Me-4)(CO)$_7$(η-C$_5$H$_5$)$_2$] (5) showing the atom labelling scheme

ligand derived from the CMe group present in the reactant [W(≡CMe)(CO)$_2$(η-C$_5$H$_5$)]. The iron atom is bonded by three terminal CO ligands which are essentially orthogonal (mean OC–Fe–CO 96, mean Fe–C–O 177°), while the two tungsten atoms are each ligated by a C$_5$H$_5$ and two CO groups. Three of the latter weakly semi-bridge either a W–Fe [W(1)–C(2)–O(2) 169(1) and W(2)–C(4)–O(4) 171(1)°] or a W–W bond [W(2)–C(3)–O(3) 173(2)°].

In the crystal, the tungsten atoms are inequivalent but in solution the observation of a single resonance for the C$_5$H$_5$ ligands in the n.m.r. spectra (^{1}H and ^{13}C-{^{1}H}) shows that a dynamic process occurs. The latter probably involves rotation of the W(CO)$_2$(η-C$_5$H$_5$) groups.

Interest centres on the μ_3-C=CH$_2$ ligand which is attached to the FeW$_2$ triangle [W–W 3.030(1), mean W–Fe 2.854 Å] in such a manner that it forms σ bonds with the tungsten atoms and has an η^2-bonding mode *via* C(8)–C(9) with the iron atom. The μ_3-C–metal distances [C(8)–W(1) 2.04(1), C(8)–W(2) 2.07(2), and C(8)–Fe 1.96(2) Å] are comparable with those found[2] in (**1a**) [μ_3-C–W 2.093(5) and μ_3-C–Fe 1.969(5) and 2.036(5) Å]. The C(9)–Fe separation [2.21(2) Å] is somewhat longer than C(8)–Fe.

A variety of dimetal compounds are known in which the metal–metal bonds are spanned by vinylidene ligands.[8] *X*-Ray diffraction studies on several of these complexes have been carried out, and the carbon–carbon separations within the μ-C=CH$_2$ group are shorter by *ca.* 0.12 Å than that found for C(8)–C(9) [1.43(3) Å] in (3): *e.g.* [Mn$_2$(μ-C=CH$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] [1.31(1) Å],[9] [Ru$_2$(μ-C=CH$_2$)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)$_2$] [1.33(1) Å],[10] and [Rh$_2$(μ-C=CH$_2$)(CO)$_2$(η-C$_9$H$_7$)$_2$] [1.304(5) Å].[11] This is as expected, since co-ordination of the W$_2$(μ-C=CH$_2$) group in (3) to the iron centre would lengthen C(8)–C(9). It is noteworthy that in the compound [Os$_3$H$_2$(μ_3-C=CH$_2$)(CO)$_9$][12] the C=CH$_2$ distance (1.38 Å) is also significantly longer than the corresponding separations in the dimetal species. Moreover, the σ:σ′:η^2-C=CH$_2$ bridge system present in (3) and in the triosmium compound is similar to that which probably exists in the cation [Co$_3$(μ_3-C=CH$_2$)(CO)$_9$]$^+$, in agreement with extended-Huckel calculations for the tricobalt species.[13] Compound (3) appears to be the first example of a heteronuclear trimetal species with a μ_3-C=CH$_2$ ligand.

Selected *X*-ray diffraction data for compound (5) are given in Table 2, and the molecule is shown in Figure 2. The compound was thus structurally characterised as an ironditungsten alkyne-bridged complex [FeW$_2$(μ_3-MeC$_2$C$_6$H$_4$Me-4)(CO)$_7$(η-C$_5$H$_5$)$_2$]. This product has evidently formed *via* a coupling of the CMe and CC$_6$H$_4$Me-4 groups present in the reactants. In (5) the alkyne ligand adopts a μ_3-(η^2-∥) bonding mode[14] to the FeW$_2$ triangle. The ligated carbon atoms [C(29)–C(30)] lie parallel to the Fe–W(2) vector forming σ bonds to these metal atoms, while being η^2-co-ordinated to W(1). Atom C(29) carries the Me group, and C(30) the C$_6$H$_4$Me-4 moiety. Other isomers of (5) are possible with the alkyne retaining the μ_3-(η^2-∥) bonding mode. Thus the co-ordination sites C(29)Me and C(30)C$_6$H$_4$Me-4 might be interchanged, or alternatively C(29)–C(30) might be parallel to W(1)–W(2) on the face of the triangle. These possibilities are discussed further below.

In several previously reported reactions of the compounds [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] we have observed coupling of alkylidyne ligands, thereby yielding trimetal clusters with bridging alkynes.[2,15,16] Relevant to the structure of (5) are those of the compounds [RuW$_2$(μ_3-C$_2$Me$_2$)(CO)$_7$(η-C$_5$H$_5$)$_2$] and [OsW$_2$-

Table 1. Selected internuclear distances (Å) and angles (°) for $[FeW_2(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ (**3**)

W(1)–W(2)	3.030(1)	W(1)–Fe	2.864(2)	W(1)–C(1)	1.99(2)	W(1)–C(2)	1.99(2)
W(1)–C(8)	2.04(1)	W(2)–Fe	2.844(3)	W(2)–C(3)	1.93(2)	W(2)–C(4)	2.00(2)
W(2)–C(8)	2.07(2)	Fe–C(5)	1.78(2)	Fe–C(6)	1.76(3)	Fe–C(7)	1.76(2)
Fe–C(8)	1.96(2)	Fe–C(9)	2.21(2)	C(1)–O(1)	1.14(2)	C(2)–O(2)	1.16(2)
C(3)–O(3)	1.19(2)	C(4)–O(4)	1.14(2)	C(5)–O(5)	1.16(3)	C(6)–O(6)	1.17(4)
C(7)–O(7)	1.18(3)	C(8)–C(9)	1.43(3)				

W(2)–W(1)–Fe	57.6(1)	W(2)–W(1)–C(1)	85.7(4)	Fe–W(1)–C(1)	92.7(4)	W(2)–W(1)–C(2)	124.4(5)
Fe–W(1)–C(2)	67.6(5)	C(1)–W(1)–C(2)	88.4(7)	W(2)–W(1)–C(8)	42.9(6)	Fe–W(1)–C(8)	43.2(5)
C(1)–W(1)–C(8)	122.3(7)	C(2)–W(1)–C(8)	100.2(6)	W(1)–W(2)–Fe	58.2(1)	W(1)–W(2)–C(3)	68.9(7)
Fe–W(2)–C(3)	117.7(5)	W(1)–W(2)–C(4)	103.8(5)	Fe–W(2)–C(4)	75.1(6)	C(3)–W(2)–C(4)	88.8(7)
W(1)–W(2)–C(8)	42.0(4)	Fe–W(2)–C(8)	43.6(4)	C(3)–W(2)–C(8)	108.6(8)	C(4)–W(2)–C(8)	117.9(7)
W(1)–Fe–W(2)	64.1(1)	W(1)–Fe–C(5)	151.3(7)	W(2)–Fe–C(5)	87.3(7)	W(1)–Fe–C(6)	111.4(8)
W(2)–Fe–C(6)	164.4(9)	C(5)–Fe–C(6)	95.7(11)	W(1)–Fe–C(7)	90.1(5)	W(2)–Fe–C(7)	99.4(7)
C(5)–Fe–C(7)	96.5(9)	C(6)–Fe–C(7)	95.4(11)	W(1)–Fe–C(8)	45.3(4)	W(2)–Fe–C(8)	46.8(6)
C(5)–Fe–C(8)	113.6(7)	C(6)–Fe–C(8)	118.9(11)	C(7)–Fe–C(7)	129.9(7)	W(1)–Fe–C(9)	76.3(5)
W(2)–Fe–C(9)	77.3(7)	C(5)–Fe–C(9)	96.9(8)	C(6)–Fe–C(9)	87.1(11)	C(7)–Fe–C(9)	166.1(8)
C(8)–Fe–C(9)	39.4(7)	W(1)–C(1)–O(1)	176(1)	W(1)–C(2)–O(2)	169(1)	W(2)–C(3)–O(3)	173(2)
W(2)–C(4)–O(4)	171(1)	Fe–C(5)–O(5)	177(1)	Fe–C(6)–O(6)	175(2)	Fe–C(7)–O(7)	179(1)
W(1)–C(8)–W(2)	95.1(7)	W(1)–C(8)–Fe	91.5(6)	W(2)–C(8)–Fe	89.6(8)	W(1)–C(8)–C(9)	132(2)
W(2)–C(8)–C(9)	131(1)	Fe–C(8)–C(9)	80(1)	Fe–C(9)–C(8)	61(1)		

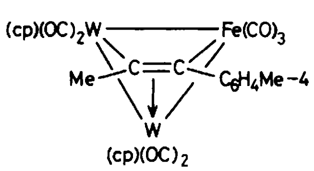
Table 2. Selected internuclear distances (Å) and angles (°) for $[FeW_2(\mu_3\text{-}MeC_2C_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$ (**5**)

W(1)–W(2)	2.949(1)	W(1)–Fe	2.730(1)	W(1)–C(29)	2.281(8)	W(1)–C(30)	2.232(7)
W(1)–C(1)	1.94(1)	W(1)–C(2)	1.98(8)	W(2)–Fe	2.992(1)	W(2)–C(29)	2.169(8)
W(2)–C(3)	1.939(8)	W(2)–C(4)	1.959(9)	Fe–C(30)	1.990(7)	Fe–C(1)	2.47(1)
Fe–C(5)	1.811(8)	Fe–C(6)	1.79(1)	Fe–C(7)	1.79(1)	C(29)–C(28)	1.52(1)
C(29)–C(30)	1.40(1)	C(30)–C(31)	1.49(1)	C(1)–O(1)	1.19(2)	C(2)–O(2)	1.15(1)
C(3)–O(3)	1.16(1)	C(4)–O(4)	1.15(1)	C(5)–O(5)	1.14(1)	C(6)–O(6)	1.14(1)
C(7)–O(7)	1.14(1)						

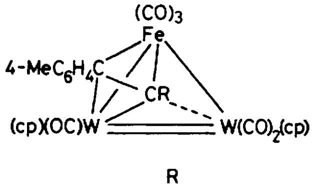
W(2)–W(1)–Fe	63.4(1)	W(2)–W(1)–C(29)	46.9(2)	Fe–W(1)–C(29)	67.5(2)	W(2)–W(1)–C(30)	69.9(2)
Fe–W(1)–C(30)	46.0(2)	W(2)–W(1)–C(1)	119.2(3)	Fe–W(1)–C(1)	61.0(3)	C(29)–W(1)–C(1)	122.8(4)
C(30)–W(1)–C(1)	88.1(4)	W(2)–W(1)–C(2)	65.8(3)	Fe–W(1)–C(2)	78.9(3)	C(29)–W(1)–C(2)	112.3(4)
C(30)–W(1)–C(2)	120.4(3)	C(1)–W(1)–C(2)	81.0(4)	W(1)–W(2)–Fe	54.7(1)	W(1)–W(2)–C(29)	50.1(2)
Fe–W(2)–C(29)	63.6(2)	W(1)–W(2)–C(3)	105.5(3)	Fe–W(2)–C(3)	63.1(3)	C(29)–W(2)–C(3)	124.9(3)
W(1)–W(2)–C(4)	120.2(3)	Fe–W(2)–C(4)	85.5(3)	C(29)–W(2)–C(4)	73.7(3)	C(3)–W(2)–C(4)	89.0(4)
W(1)–Fe–W(2)	61.9(1)	W(1)–Fe–C(30)	53.7(2)	W(2)–Fe–C(30)	71.6(2)	W(1)–Fe–C(1)	43.5(3)
W(2)–Fe–C(1)	101.8(3)	C(30)–Fe–C(1)	80.6(3)	W(1)–Fe–C(5)	108.1(3)	W(2)–Fe–C(5)	104.0(3)
C(30)–Fe–C(5)	161.5(4)	C(1)–Fe–C(5)	82.8(4)	W(1)–Fe–C(6)	110.1(3)	W(2)–Fe–C(6)	164.1(3)
C(30)–Fe–C(6)	92.6(4)	C(1)–Fe–C(6)	76.2(4)	C(5)–Fe–C(6)	91.5(4)	W(1)–Fe–C(7)	142.0(3)
W(2)–Fe–C(7)	88.1(3)	C(30)–Fe–C(7)	96.7(4)	C(1)–Fe–C(7)	168.2(4)	C(5)–Fe–C(7)	101.2(4)
C(6)–Fe–C(7)	92.5(4)	W(1)–C(29)–W(2)	83.0(3)	W(1)–C(29)–C(28)	127.5(6)	W(2)–C(29)–C(28)	122.4(6)
W(1)–C(29)–C(30)	70.0(5)	W(2)–C(29)–C(30)	114.2(5)	C(28)–C(29)–C(30)	121.7(7)	W(1)–C(30)–Fe	80.4(3)
W(1)–C(30)–C(29)	73.9(4)	Fe–C(30)–C(29)	110.7(5)	W(1)–C(30)–C(31)	132.9(6)	Fe–C(30)–C(31)	121.8(6)
C(29)–C(30)–C(31)	122.9(7)	W(1)–C(1)–Fe	75.5(4)	W(1)–C(1)–O(1)	164.5(9)	Fe–C(1)–O(1)	119.8(7)
W(1)–C(2)–O(2)	169.2(9)	W(2)–C(3)–O(3)	167.7(9)	W(2)–C(4)–O(4)	177.5(8)	Fe–C(5)–O(5)	175.9(9)
Fe–C(6)–O(6)	174.7(9)	Fe–C(7)–O(7)	177.4(8)				

$\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$.[15–17] In the rutheniumditungsten species the $\mu_3\text{-}C_2Me_2$ ligand lies parallel to a Ru–W bond in the crystal, although in solution the isomer with the axis of the alkyne parallel to the W–W vector is present to a small extent, as revealed by n.m.r. studies. The complex $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ exists both in the solid state and in solution as a 1:1 mixture of two isomers, differing only in orientation of the alkyne on the face of the OsW_2 triangle, lying parallel to a W–W vector in one and parallel to an Os–W vector in the other. The structure of (**5**) is in all important respects essentially identical with that of the latter isomer, and with that of $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ in the solid state.

In marked contrast with the structure of (**5**) is that of the co-ordinatively unsaturated complex $[FeW_2\{\mu_3\text{-}C_2(C_6H_4\text{-}Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (**6a**), which has one less CO ligand and is formed in the reaction between excess of $[W(\equiv CC_6H_4\text{-}Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Fe_2(CO)_9]$.[2] In this ironditungsten compound the $C_2(C_6H_4Me\text{-}4)_2$ ligand adopts the $\mu_3\text{-}(\eta^2\text{-}\perp)$ bonding mode,[14] and the tungsten–tungsten separation [2.747(1) Å] corresponds to a W=W bond. In (**5**) the W–W distance at 2.949(1) Å is significantly longer, although it is marginally shorter than that found [3.017(2) Å] in the equivalent isomer of $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$. The Fe–W separations in (**5**) are appreciably different with that bridged by C(30) [Fe–W(1) 2.730(1) Å] being *ca.* 0.26 Å shorter than that bridged by C(29) and C(30) [Fe–W(2) 2.992(1) Å]. A similar but less pronounced difference (*ca.* 0.1 Å) is found for the Os–W bonds in the isomer of $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ structurally analogous to (**5**), and it may well be that in the OsW_2 species the inherently longer Os–W bonds can more readily accommodate the $\mu_3\text{-}(\eta^2\text{-}\|)$ mode of alkyne bonding. The Fe–W distances in (**5**) lie at the extremes of the range of values found in the complexes (**3**)



(5)



R
(6a) C_6H_4Me-4
(6b) Me

cp = η-C_5H_5

[2.844(3) and 2.864(2) Å], $[Fe_2W(\mu_3$-CC_6H_4Me-4)(μ-CO)-$(CO)_8(\eta$-$C_5H_5)]$ [2.805(2) and 2.756(2) Å], and (**6a**) [2.731(1) and 2.747(2) Å].[2]

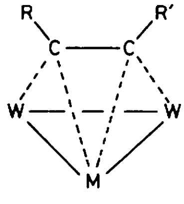
The W–C(alkyne) separations in (**5**) [W(1)–C(29) 2.281(8), W(1)–C(30) 2.232(7), and W(2)–C(29) 2.169(8) Å] are comparable with the range of values found in the two isomers of $[OsW_2\{\mu_3$-$C_2(C_6H_4Me$-$4)_2\}(CO)_7(\eta$-$C_5H_5)_2]$ (2.11—2.30 Å)[16,17] whilst the Fe–C(30) distance [1.990(7) Å] is similar to the related distances found in (**6a**) [2.011(5) and 2.052(5) Å].[2] The C(29)–C(30) bond length [1.40(1) Å], and the *cis* bent geometry of the alkyne are characteristic of alkynes bound to trimetal centres, and require no further comment.

The iron atom in (**5**) carries three terminally bound CO groups. However, three of the four carbonyl groups on the tungsten atoms semi-bridge the edges of the metal triangle [W(1)–C(1)–O(1) 164.5(9), W(1)–C(2)–O(2) 169.2(9), and W(2)–C(3)–O(3) 167.7(9)°]. Only W(2)–C(4)–O(4) is essentially linear [177.5(8)°]. The bonding of the C_5H_5 groups to the tungsten atoms is normal.

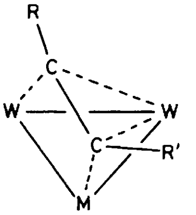
Having established the molecular structures of (**3**) and (**5**), the n.m.r. data for these complexes are readily interpretable. The ^1H n.m.r. spectrum of (**3**) shows resonances at δ 5.14 (2 H) and 5.29 (10 H), and these peaks are characteristic for CH_2 and C_5H_5 groups, respectively. The ^{13}C-$\{^1H\}$ n.m.r. spectrum has signals for the μ-C=CH_2 group at δ 264.8 [μ-C, *J*(WC) 86 Hz] and 80.7 p.p.m. (CH_2). In the ^{13}C-$\{^1H\}$ n.m.r. spectrum of $[Co_3Fe(\mu_4$-$C{=}CH_2)(\mu$-$CO)_2(CO)_7(\eta$-$C_5H_5)]$ the μ_4-C=CH_2 resonances occur at δ 304.3 and 63.0 p.p.m.[18]

As mentioned above, with compound (**5**) there is the possibility of isomerism. Although in the solid state only one isomer is present, the n.m.r. data reveal that in solution dynamic behaviour occurs involving an equilibrium between two isomers, these being present in a ratio of *ca.* 4:1 based on peak intensities. Thus at room temperature the ^1H n.m.r. spectrum of (**5**) shows only a broad resonance for the η-C_5H_5 group at δ 5.19, and a broad signal at δ 2.56 for a MeC≡ group. However, on measuring the spectrum at −60 °C, signals are seen for two sets of non-equivalent η-C_5H_5 groups. These occur at δ 5.26 and 5.42 for the major isomer, and at δ 4.87 and 5.24 for the minor. Similarly, there are signals for the MeC≡ groups of the major and minor isomers at δ 2.57 and 2.63, respectively. Although only one Me-4 resonance is observed, this is not unexpected since the environments for this group could be very similar in either isomer. The ^{13}C-$\{^1H\}$ n.m.r. spectrum is in accord with the ^1H spectrum showing at −50 °C resonances for inequivalent C_5H_5 groups at δ 92.2 and 91.9 p.p.m. for the major isomer, and at δ 94.8 and 92.5 p.p.m. for the minor. Correspondingly, there are two MeC≡ group signals, one for each isomer at δ 38.4 (minor) and 38.0 p.p.m. (major).

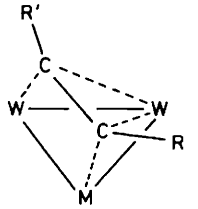
We referred above to the existence of two isomeric forms of the compounds $[RuW_2(\mu_3$-$C_2Me_2)(CO)_7(\eta$-$C_5H_5)_2]$[15] and $[MW_2\{\mu_3$-$C_2(C_6H_4Me$-$4)_2\}(CO)_7(\eta$-$C_5H_5)_2]$ (M = Ru or Os).[16,17] In these species isomerism is a consequence of the existence of two possible rotamers for μ_3-(η^2-∥) alkyne bonding to the metal triangle [(**a**) and (**b**), M = Ru, R = R′ = Me; M = Ru or Os, R = R′ = C_6H_4Me-4]. These isomers interconvert



(a)



(b)



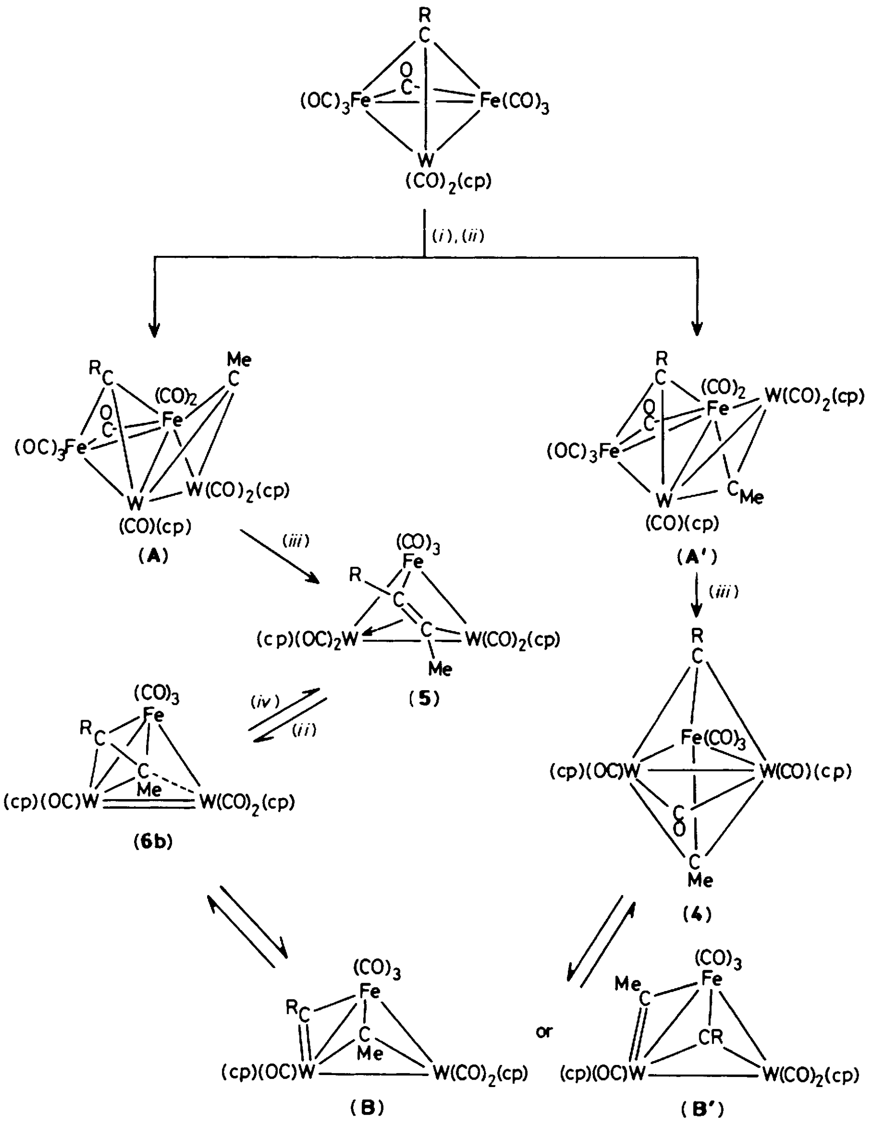
(c)

rapidly at ambient temperatures on the n.m.r. time-scale *via* rotation of the alkyne, but at low temperatures (*ca.* −80 °C) the dynamic process ceases. With (**5**), the presence of an asymmetrically substituted alkyne leads to a third possible isomer [(**c**), M = Fe, R = Me, R′ = C_6H_4Me-4]. The detection by n.m.r. spectroscopy of only two isomers for (**5**) in solution does not rule out the existence of a third, which might be present in concentrations too low to be observed. The dominant isomer in solution may well be that observed in the crystal (Figure 2), corresponding to (**b**) above. The available data do not allow a distinction between (**a**) and (**c**) for the minor isomer.

The structure proposed for compound (**4**) is based on spectroscopic data since, as mentioned earlier, crystals for an *X*-ray diffraction study were not available. Nevertheless, the spectroscopic evidence is convincing. The ^{13}C-$\{^1H\}$ n.m.r. spectrum has resonances at δ 286.6 and 293.7 p.p.m. which are characteristic for μ_3-C ligands present in different environments. Peaks for the Me-4 and C*Me* groups are also observed at 19.8 and 51.2 p.p.m., respectively. Other signals in the ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra are in accord with the formulation proposed, although the observation of only three CO resonances in the ^{13}C-$\{^1H\}$ spectrum indicates that site exchange of the carbonyl groups occurs. A broad band at 1 827 cm^{-1} in the i.r. spectrum of (**4**) is assigned to a bridging CO ligand, and bands at 2 035, 2 002, 1 967, and 1 946 cm^{-1} are assigned to terminal CO groups. Interestingly, this band pattern closely resembles that of a compound obtained in trace quantities from the reaction between (**1a**) and $[W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)]$. It is possible that this very minor product is the species $[FeW_2(\mu_3$-CC_6H_4Me-$4)_2(CO)_6(\eta$-$C_5H_5)_2]$.

Vollhardt and co-workers[19] have reported some tricobalt complexes in which both sides of a Co_3 triangle are capped by alkylidyne groups. These species are formed by alkyne cleavage reactions, and are evidently related to (**4**). Also related structurally is the tri-iron compound $[Fe_3(\mu_3$-$CMe)(\mu_3$-$COEt)$-$(CO)_9]$ in which CMe and COEt ligands triply bridge a Fe_3 triangle.[20] Interestingly, this iron compound reacts with carbon monoxide to give the bridged alkyne complex $[Fe_3(\mu_3$-$MeC_2OEt)(CO)_{10}]$, a product formed by coupling of two alkylidyne ligands, as observed in the synthesis of (**5**).

It is of interest to speculate on the reaction pathways followed in the formation of compounds (**3**)—(**5**). The syntheses of (**4**) and (**5**) might occur according to the routes indicated in the Scheme. Intermediates (**A**) and (**A′**) are analogous to compounds (**2b**) and (**2c**) characterised previously,[5] and the isolobal relationship existing between MeC≡$W(CO)_2(\eta$-$C_5H_5)$ and alkynes makes the initial formation of (**A**) and (**A′**)



Scheme. R = C_6H_4Me-4, cp = η-C_5H_5. (*i*) + [W(≡CMe)$(CO)_2$(cp)]; (*ii*) − CO; (*iii*) − $Fe(CO)_n$, *n* = 2 or 3; (*iv*) + CO

plausible. Formation of (**5**) from (**A**) could occur by coupling of the triply-bridging carbyne groups, and with concomitant or sequential release of a carbonyliron fragment, in a process similar to that reported earlier.[5] Formation of (**4**) from (**A′**), the isomer of (**A**) might occur directly, also with loss of a carbonyliron fragment. However, an alternative pathway for the formation of (**4**) might be *via* (**6b**) (or its isomer with the Me and C_6H_4Me-4 sites reversed), and the intermediates (**B**) or (**B′**). As mentioned above, we have previously characterised compound (**6a**) and established the structure by *X*-ray diffraction,[2] thus making the existence of (**6b**) plausible. Moreover, trimetal compounds with edge- and triply-bridging carbyne ligands, as postulated for (**B**) and (**B′**), are known.[21,22] Particularly interesting in this context is the observation[22] that the compound $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$, one isomer of which is structurally similar to (**5**), releases CO on heating and forms $[OsW_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)_2]$, a species akin to (**B**) or (**B′**). This process is thought to occur *via* an intermediate with a structure similar to (**6a**). Although it is an attractive hypothesis to suggest that (**4**) is formed *via* C–C scission of an alkyne complex[23] we have no evidence at present to prefer a route to (**4**) *via* (**5**), as compared with the more direct pathway *via* (**A′**). An experiment in which (**5**) was refluxed in methylcyclohexane for several hours in an attempt to isolate (**4**) was inconclusive. Infrared spectroscopy showed no evidence for (**4**) although some decomposition of (**5**) was observed. Finally, the above mentioned conversion of $[Fe_3(\mu_3\text{-}CMe)(\mu_3\text{-}COEt)(CO)_9]$ into the alkyne complex $[Fe_3(\mu_3\text{-}MeC_2OEt)(CO)_{10}]$ makes it just possible that (**4**) is an intermediate in the formation of (**5**). However, since the former was obtained in such small amounts it was not possible to test this idea by experiment.

The major product of the reaction between (**1a**) and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ is compound (**3**) and none of our previous work suggests how the latter is formed. It is possible that intermediate (**A**) or (**A′**) (Scheme) undergoes hydrogen transfer to give a cluster species with μ-H and μ-C=CH_2 groups. The hydrido ligand could then migrate to the ligated carbon atom of an edge- or triply-bridging CC_6H_4Me-4 group. Loss of an $Fe\{=CH(C_6H_4Me\text{-}4)\}(CO)_n$ fragment might then occur,

Table 3. Atomic positional parameters (fractional co-ordinates; × 10^4) for complex (**3**), with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
W(1)	775(1)	1 647(1)	1 538(1)	C(7)	212(29)	3 486(9)	2 234(11)
W(2)	2 136(1)	1 620(1)	3 387(1)	O(7)	−1 390(21)	3 775(8)	1 987(10)
Fe	2 590(4)	3 042(1)	2 594(2)	C(8)	3 344(22)	1 885(10)	2 621(11)
C(1)	−1 929(24)	1 914(9)	1 385(9)	C(9)	5 181(29)	2 275(12)	2 793(14)
O(1)	−3 525(17)	2 034(8)	1 259(8)	C(11)	1 817(15)	1 077(6)	650(7)
C(2)	598(25)	2 655(9)	895(12)	C(12)	−292	976	289
O(2)	302(22)	3 165(7)	409(9)	C(13)	−660	451	817
C(3)	−242(29)	962(9)	2 770(11)	C(14)	1 222	229	1 504
O(3)	−1 675(18)	526(8)	2 475(8)	C(15)	2 752	615	1 401
C(4)	440(24)	2 479(8)	3 519(11)	C(21)	5 353(19)	1 646(7)	4 616(10)
O(4)	−352(18)	2 964(7)	3 698(9)	C(22)	5 256	934	4 151
C(5)	3 759(28)	3 522(10)	3 593(14)	C(23)	3 699	422	4 105
O(5)	4 463(22)	3 865(9)	4 224(10)	C(24)	2 834	818	4 542
C(6)	3 418(38)	3 769(11)	2 115(17)	C(25)	3 856	1 574	4 858
O(6)	4 121(29)	4 222(10)	1 837(13)				

Table 4. Atomic positional parameters (fractional co-ordinates; × 10^4) for complex (**5**), with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
W(1)	1 314(1)	6 393(1)	6 997(1)	C(34)	1 780(9)	4 157(3)	8 303(8)
W(2)	3 856(1)	6 501(1)	5 799(1)	C(35)	2 875(10)	4 282(3)	7 687(10)
Fe	3 838(1)	6 113(1)	8 621(1)	C(36)	3 082(9)	4 772(3)	7 341(9)
C(11)	−462(11)	6 316(4)	5 039(12)	C(37)	1 597(11)	3 618(3)	8 710(11)
C(12)	−838(11)	5 999(4)	6 008(13)	C(1)	1 519(11)	6 414(4)	8 980(11)
C(13)	−1 086(11)	6 273(5)	7 118(15)	O(1)	1 344(9)	6 482(4)	10 117(9)
C(14)	−830(12)	6 796(5)	6 807(15)	C(2)	2 276(11)	7 049(3)	7 361(10)
C(15)	−510(12)	6 808(4)	5 511(13)	O(2)	2 643(8)	7 452(2)	7 635(8)
C(21)	2 629(15)	6 790(5)	3 678(12)	C(3)	5 338(10)	6 744(3)	7 284(10)
C(22)	3 863(16)	6 603(5)	3 532(11)	O(3)	6 309(8)	6 935(3)	7 986(8)
C(23)	4 965(17)	6 901(5)	4 243(14)	C(4)	5 035(10)	5 915(3)	5 626(9)
C(24)	4 342(17)	7 274(5)	4 864(14)	O(4)	5 709(8)	5 572(3)	5 475(8)
C(25)	2 896(16)	7 213(4)	4 501(13)	C(5)	4 498(10)	6 634(3)	9 742(9)
C(28)	1 970(11)	5 521(3)	4 676(10)	O(5)	4 878(9)	6 949(3)	10 509(8)
C(29)	2 546(9)	5 847(3)	5 916(8)	C(6)	3 533(11)	5 747(3)	10 046(11)
C(30)	2 567(8)	5 683(3)	7 259(8)	O(6)	3 400(10)	5 541(3)	11 015(7)
C(31)	2 218(9)	5 157(3)	7 588(9)	C(7)	5 449(10)	5 787(3)	8 569(9)
C(32)	1 113(9)	5 033(3)	8 227(9)	O(7)	6 485(7)	5 578(3)	8 587(8)
C(33)	903(10)	4 532(3)	8 574(10)				

producing (**3**). Conversion of μ_3-CMe ligands into μ-H and μ-C=CH$_2$ groups is well established.[8,24]

Experimental

All reactions were carried out using Schlenk-tube techniques under an atmosphere of oxygen-free nitrogen. Light petroleum refers to that fraction of b.p. 40—60 °C. All solvents were rigorously dried before use. The instrumentation used has been described in previous parts of this Series.[1] Carbon-13 n.m.r. chemical shifts are to high frequency of SiMe$_4$ (0.0 p.p.m.), and were measured in CD$_2$Cl$_2$–CH$_2$Cl$_2$ solutions. N.m.r. measurements are at room temperature unless otherwise stated. Infrared spectra were recorded in CH$_2$Cl$_2$. The compounds [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)][2] and [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4 or Me)[25] were prepared by literature methods.

Reactions of the Compound [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)] (**1a**).—(*i*) A mixture of (**1a**) (0.80 g, 1.12 mmol) and [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.46 g, 1.12 mmol) in toluene (35 cm^3) was heated at 80 °C for 24 h in an evacuated Schlenk tube, fitted with a high-pressure stopcock. Solvent was removed *in vacuo*, and the residue dissolved in CH$_2$Cl$_2$–light petroleum (1 : 1, 12 cm^3) and chromatographed at −20 °C on an alumina column (2 × 40 cm^3). Elution with CH$_2$Cl$_2$–light petroleum (1 : 2) afforded at first a brown band from which unreacted (**1a**) (0.41 g) was recovered. Further elution gave a red-purple eluate which, after removal of solvent *in vacuo*, gave [W$_2${μ-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_4$(η-C$_5$H$_5$)$_2$] (0.29 g, 50%), identified spectroscopically.[7] Finally, a trace of a green-purple compound was recovered from the column. The i.r. spectrum of this complex [$\nu_{max.}$(CO) at 2 037s, 2 006vs, 1 973m (sh), 1 950m, and 1 815w cm^{-1}] was very similar to that of (**4**).

(*ii*) Similarly, a mixture of (**1a**) (0.77 g, 1.08 mmol) and [W(≡CMe)(CO)$_2$(η-C$_5$H$_5$)] (0.36 g, 1.08 mmol) was heated in toluene (20 cm^3) at 80 °C for 24 h. Solvent was removed *in vacuo* and the residue dissolved in CH$_2$Cl$_2$–light petroleum (4 : 1, 10 cm^3) and chromatographed at −20 °C on a Florisil column. Elution with CH$_2$Cl$_2$–light petroleum (1 : 1) developed in sequence on the column four bands which were brown, purple, green, and purple in colour. The brown eluate yielded, after removal of solvent *in vacuo*, a trace of unreacted (**1a**), identified by i.r. Removal of solvent from the first purple eluate afforded, after crystallisation of the residue from CH$_2$Cl$_2$–light petroleum (1 : 5, *ca.* 5 cm^3), purple *crystals* of [FeW$_2$(μ_3-σ:σ':η^2-C=CH$_2$)(CO)$_7$(η-C$_5$H$_5$)$_2$] (**3**) (0.15 g, 18%) (Found: C, 29.8; H, 1.5. C$_{19}$H$_{12}$FeO$_7$W$_2$ requires C, 29.4; H, 1.6%); $\nu_{max.}$(CO) at 2 035m, 2 023m (sh), 1 983vs, 1 956s, 1 917w (sh), and 1 850w br cm^{-1}. N.m.r.: ^{1}H (CD$_2$Cl$_2$), δ 5.14 (s, 2 H, CH$_2$) and 5.29 (s, 10 H, C$_5$H$_5$); ^{13}C-{^{1}H}, δ 264.8 [μ-*C*=CH$_2$, *J*(WC) 86], 217.0 [WCO, *J*(WC) 169], 213.2 (FeCO), 212.3 [WCO, *J*(WC) 168 Hz], 90.1 (C_5H_5), and 80.7 p.p.m. (μ-C=*C*H_2).

Removal of solvent from the green eluate gave a residue which was crystallised from CH_2Cl_2–light petroleum (1:2, *ca.* 5 cm^3) to give green-purple *crystals* of [$FeW_2(\mu_3$-CMe)(μ_3-CC_6H_4Me-4)$(CO)_6(\eta$-$C_5H_5)_2$] (**4**) (0.02 g, 2%) (Found: C, 35.5; H, 2.2. $C_{26}H_{20}FeO_6W_2$ requires C, 36.6; 2.4%); $\nu_{max.}$(CO) at 2 035s, 2 002vs, 1 967m, 1 946m, and 1 827w br cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$), δ 2.47 (s, 3 H, Me-4), 4.28 (s, 3 H, μ_3-CMe), 5.32 (s, 10 H, C_5H_5), and 7.15, 7.19 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8 Hz]; ^{13}C-{^{1}H} (−40 °C), δ 293.7, 286.6 (μ_3-C), 229.7, 212.3, 211.5 (CO), 164.0 [C^1 (C_6H_4)], 135.0, 127.0, 124.6 (C_6H_4), 96.6 (C_5H_5), 51.2 (μ-C*Me*), and 19.8 p.p.m. (Me-4).

Removal of solvent *in vacuo* from the purple eluate gave a residue which was crystallised from CH_2Cl_2–light petroleum (1:5, *ca.* 5 cm^3) to afford purple *crystals* of [$FeW_2(\mu_3$-$MeC_2C_6H_4$Me-4)$(CO)_7(\eta$-$C_5H_5)_2$] (**5**) (0.13 g, 13%) (Found: C, 36.7; H, 2.3. $C_{27}H_{20}FeO_7W_2$ requires C, 36.8; H, 2.3%); $\nu_{max.}$(CO) at 2 035s, 2 016m (sh), 1 966vs, 1 950s (sh), 1 931m (sh), and 1 881w br cm^{-1}. N.m.r.: ^{1}H (CD_2Cl_2), δ 2.31 (s, 3 H, Me-4), 2.56 (s, 3 H, Me), 5.19 (br, 10 H, C_5H_5), and 7.04, 7.08 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7 Hz]; at −60 °C (peaks due to minor isomer asterisked), δ 2.33 (s, 6 H, Me-4), 2.57 (s, 3 H, Me), 2.63* (s, 3 H, Me), 4.87* (s, 5 H, C_5H_5), 5.24* (s, 5 H, C_5H_5), 5.26 (s, 5 H, C_5H_5), 5.42 (s, 5 H, C_5H_5), and 6.59—7.50 (m br, 8 H, C_6H_4); ^{13}C-{^{1}H} (at −50 °C), δ 222.9, 222.4, 221.6, 220.1, 214.4, 210.1, 207.6 (CO), 155.7—127.0 (C_6H_4 and C_2), 94.8*, 92.5*, 92.2, 91.9 (C_5H_5), 38.4*, 38.0 (Me), 21.3, and 21.2* p.p.m. (Me-4).

Small quantities of the known compound [$W_2(CO)_6(\eta$-$C_5H_5)_2$] (*ca.* 0.04 g) were also identified in the reaction residues by i.r. and mass spectroscopy.

Crystal Structure Determinations.—(*a*) [$FeW_2(\mu$-σ:σ′:η^2-C=$CH_2)(CO)_7(\eta$-$C_5H_5)_2$] (**3**).—Crystals of (**3**) grow as black plates from dichloromethane–light petroleum. Diffracted intensities were collected on a Nicolet $P2_1$ diffractometer at 298 K using a crystal of dimensions *ca.* 0.60 × 0.35 × 0.20 mm. Of the 4 060 reflections measured (θ–2θ scans, $2\theta \leqslant 50°$), 2 780 had $F \geqslant 5\sigma(F)$, and only these were used in the solution and refinement of the structure. Intensity data were corrected for Lorentz, polarisation, and *X*-ray absorption effects. The last was by an analytical absorption procedure.[26]

Crystal data for (**3**). $C_{19}H_{12}FeO_7W_2$, M = 775.8, monoclinic, a = 7.640(8), b = 16.261(11), c = 18.389(19) Å, β = 119.31(6)°, U = 1 992(3) Å^3, Z = 4, D_c = 2.59 g cm^{-3}, $F(000)$ = 1 424, space group $P2_1/c$, μ(Mo-K_α) = 125.3 cm^{-1}, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å.

The solution and refinement of the structure was similar to that described for (**5**) below, except in the following respects. Hydrogen atoms were not included in the refinement and the cyclopentadienyl ring systems were treated as rigid groups (C–C 1.395 Å). Refinement converged at *R* 0.067 (*R′* 0.068) with the weighting scheme $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$. A final electron-density difference synthesis showed no peaks ⩾ 1 e Å^{-3} except in the vicinity of the metal atoms where peaks of *ca.* 3 e Å^{-3} were observed. The comparatively poor value for *R* and the large residual peaks near the metal atoms reflect our inability to correct completely for the severe absorption which arises from the large value of μ(Mo-K_α), and the plate-like nature of the crystals.

(*b*) [$FeW_2(\mu_3$-$MeC_2C_6H_4$Me-4)$(CO)_7(\eta$-$C_5H_5)_2$] (**5**). Crystals of compound (**5**) grow as black prisms from dichloromethane–light petroleum. That used for data collection had dimensions *ca.* 0.50 × 0.25 × 0.25 mm. Data were collected as for (**3**). Of the 4 401 intensities (ω scans, $2\theta \leqslant 50°$), 3 486 with $F \geqslant 5\sigma(F)$ were used in the refinement. An empirical absorption correction based upon azimuthal scan data was used.

Crystal data for (**5**). $C_{27}H_{20}FeO_7W_2$, M = 880.0, monoclinic, a = 9.633(5), b = 26.648(8), c = 9.933(5) Å, β = 101.92(4)°, U = 2 495(2) Å^3, Z = 4, D_c = 2.34 g cm^{-3}, $F(000)$ = 1 648, space group $P2_1/n$, μ(Mo-K_α) = 100.2 cm^{-1}.

The structure was solved, and all non-hydrogen atoms were located, by conventional heavy-atom and difference-Fourier methods. Hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters *ca.* 1.2 times $U_{equiv.}$ of their parent carbon atoms. All remaining atoms were given anisotropic thermal parameters. Refinement by blocked-cascade least-squares converged at *R* 0.034 (*R′* 0.036) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,8|F|^2]$. The final electron-density difference synthesis showed no peaks > 1 e Å^{-3}. Scattering factors were from ref. 27. All calculations were carried out on a Data General 'Eclipse' computer with the SHELXTL system of programs.[26] Atomic co-ordinates for (**3**) and (**5**) are listed in Tables 3 and 4, respectively.

Acknowledgements

We thank the Spanish Ministry of Education and Science for a Fellowship (to E. D.).

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Received 11*th November* 1985; *Paper* 5/1980