Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 23.[1] Alkyne Insertion into Heteronuclear Dimetal Compounds with Bridging Tolylmethylidyne Ligands; Crystal Structures of $[\mathrm{FeW}\{\mu\text{-C}(\mathrm{C_6H_4Me}\text{-}4)\mathrm{C(Me)C(Me)}\}(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})]$ and $[\mathrm{Fe_2W}(\mu_3\text{-}\mathrm{CC_6H_4Me}\text{-}4)(\mu\text{-}\mathrm{Me_3SiC_2SiMe_3})(\mu\text{-CO})(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})]$ *

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Cobalt–tungsten complexes $[\mathrm{CoW}(\mu\text{-}\mathrm{CRCR^1CR^2})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})]$ ($\mathrm{R = C_6H_4Me}$-4; $\mathrm{R^1 = R^2}$ = Ph or Me; $\mathrm{R^1}$ = Ph or Me, $\mathrm{R^2}$ = Me or Ph; $\mathrm{R^1 = Bu^t}$, $\mathrm{R^2 = H}$), with allyl groups bridging the Co–W bonds, have been prepared by heating the alkynes PhC≡CPh, MeC≡CMe, MeC≡CPh, and $\mathrm{Bu^tC{\equiv}CH}$ with the compound $[\mathrm{CoW}(\mu\text{-CR})(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})]$. Related iron–tungsten compounds $[\mathrm{FeW}(\mu\text{-}\mathrm{CRCR^1CR^2})(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})]$ ($\mathrm{R^1 = R^2}$ = Me, Ph, $\mathrm{C_6H_4Me}$-4, or $\mathrm{CF_3}$) have been prepared by heating the appropriate alkyne $\mathrm{R^1C{\equiv}CR^2}$ with the cluster complex $[\mathrm{Fe_2W}(\mu_3\text{-CR})(\mu\text{-CO})(\mathrm{CO})_8(\eta\text{-}\mathrm{C_5H_5})]$ in toluene. In contrast, the diiron–tungsten species reacts with $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ and with $\mathrm{Bu^tC{\equiv}CSiMe_3}$ to afford compounds $[\mathrm{Fe_2W}(\mu_3\text{-CR})(\mu\text{-alkyne})(\mu\text{-CO})(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})]$ which retain the $\mu_3\text{-}\mathrm{CFe_2W}$ structural core, the product from $\mathrm{Bu^tC{\equiv}CSiMe_3}$ being formed as a mixture of isomers. The ^{1}H and ^{13}C-{^{1}H} n.m.r. data for all the compounds are reported and discussed, and the molecular structures of $[\mathrm{FeW}\{\mu\text{-C}(\mathrm{C_6H_4Me}\text{-}4)\mathrm{C(Me)C(Me)}\}(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})]$ and $[\mathrm{Fe_2W}(\mu_3\text{-}\mathrm{CC_6H_4Me}\text{-}4)(\mu\text{-}\mathrm{Me_3SiC_2SiMe_3})(\mu\text{-CO})(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})]$ have been established by *X*-ray diffraction. In the dimetal compound the Fe–W bond [2.720(1) Å] is bridged by a three-carbon chain [mean C–C 1.438(8) Å]. Whereas all the atoms of the chain are bound to the iron [2.047(6), 2.103(6), and 2.083(6) Å], only the two end carbons are attached to the tungsten [2.194(6) and 2.164(7) Å]. The iron atom carries three essentially orthogonal terminal carbonyl groups, and the tungsten is ligated by the cyclopentadienyl ring and two carbonyl groups. Crystals of $[\mathrm{FeW}\{\mu\text{-C}(\mathrm{C_6H_4Me}\text{-}4)\mathrm{C(Me)C(Me)}\}(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})]$ are monoclinic (space group *C*2/*c*); the structure has been refined to *R* 0.039 for 3 334 reflections measured to $2\theta = 55°$ at 220 K. In the diiron–tungsten compound the metal atoms form a triangle which is bridged asymmetrically by the $\mu_3\text{-}\mathrm{CC_6H_4Me}$-4 ligand; one of the Fe–W edges is bridged transversely on the opposite face of the triangle by the $\mu\text{-}\mathrm{Me_3SiC{\equiv}CSiMe_3}$ ligand. The iron atoms each carry three terminal carbonyl groups, but one of those on the iron atom associated with the acetylenic bridge is strongly semi-bridging to the other iron atom. The tungsten atom carries one terminal carbonyl group (oriented approximately parallel to the acetylene fragment) and the cyclopentadienyl ligand. The unbridged Fe–W bond (*ca.* 2.77 Å) is significantly longer than the other two (W–Fe 2.66, Fe–Fe 2.64 Å). Crystals of $[\mathrm{Fe_2W}(\mu_3\text{-}\mathrm{CC_6H_4Me}\text{-}4)(\mu\text{-}\mathrm{Me_3SiC_2SiMe_3})(\mu\text{-CO})(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})]$ are monoclinic (space group $P2_1$), and are unusual in that the crystallographic asymmetric unit comprises two enantiomorphous molecules of the complex related by a non-crystallographic centre of inversion. The structure has been refined to *R* 0.051 for 7 443 reflections measured to $2\theta = 60°$ at 293 K.

The compound $[\mathrm{W}({\equiv}\mathrm{CR})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$ ($\mathrm{R = C_6H_4Me}$-4) readily combines with a variety of metal–ligand fragments ML_n $[\mathrm{Pt(PR_3)_2}$, $\mathrm{M(CO)}(\eta\text{-}\mathrm{C_9H_7})$ (M = Rh or Ir), M(acac)(CO) (M = Rh or Ir, acac = acetylacetonate), $\mathrm{M(CO)}(\eta\text{-}\mathrm{C_5Me_5})$ (M = Co or Rh), $\mathrm{Fe(CO)_4}$, $\mathrm{Mn(CO)_2}(\eta\text{-}\mathrm{C_5H_4Me})$, $\mathrm{Re(CO)_2}(\eta\text{-}\mathrm{C_5H_5})$, and $\mathrm{Cr(CO)_2}(\eta\text{-}\mathrm{C_6Me_6})]$ to afford complexes containing the ring systems $\overline{\mathrm{W}(\mu\text{-CR})\mathrm{M}}$.[2–6] The latter are very reactive; for example, several of the dimetal compounds afford trimetal clusters with capping μ_3-CR ligands on treatment with mononuclear metal–ligand species.[5–9] In another type of behaviour, some of the dimetal compounds react with excess of the tolylmethylidynetungsten compound from which they are prepared. In this event two different reaction pathways may be followed; both, however, involve C–C bond formation. Either dimerisation of the tolylmethylidynetungsten complex occurs to give $[\mathrm{W_2}(\mu\text{-}\mathrm{RC_2R})(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_5})_2]$, or more usefully trimetal clusters are produced with $\mathrm{MW_2}$ triangles bridged by the alkyne $\mathrm{C_2(C_6H_4Me\text{-}4)_2}$.[5,9,10] The chemistry of carbyne groups when bridging metal–metal bonds is currently of interest, and this prompted us to study reactions of alkynes with some of the di- and trimetal compounds containing μ-CR ligands. It was expected that C–C bond-forming processes would be observed, as found with some of the reactions of $[\mathrm{W}({\equiv}\mathrm{CR})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$ mentioned above. In this paper we describe reactions of the species $[\mathrm{CoW}(\mu\text{-CR})(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})]$ and $[\mathrm{Fe_2W}(\mu_3\text{-CR})(\mu\text{-CO})(\mathrm{CO})_8(\eta\text{-}\mathrm{C_5H_5})]$ with alkynes. A preliminary report has been given.[11]

Results and Discussion

The compound $[\mathrm{CoW}(\mu\text{-CR})(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})]$ proved to be relatively inert towards alkynes, and no significant reaction occurred unless the reactants were heated in toluene

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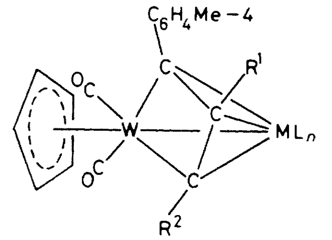
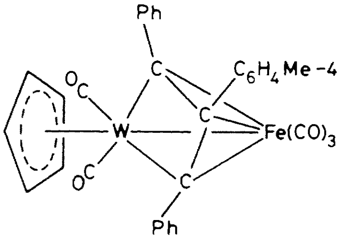
Supplementary data available (No. SUP 23906, 89 pp.): H-atom co-ordinates, thermal parameters, complete bond parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

* 1,1,1,2,2-Pentacarbonyl-2-η-cyclopentadienyl-μ-[1′,2′-dimethyl-3′-*p*-tolylpropen-1′-yl-3′-ylidene-C^{1-3}(Fe)$C^{1,3}$(W)]-irontungsten (*Fe–W*) and 1,3-μ-bis(trimethylsilyl)acetylene-1,2-μ-carbonyl-1,1,2,2,2,3-hexacarbonyl-3-η-cyclopentadienyl-μ_3-*p*-tolylmethylidyne-*triangulo*-di-irontungsten.



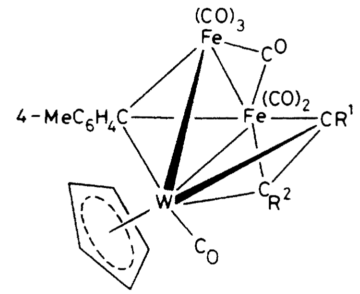
	R^1	R^2	ML_n
(1)	Ph	Ph	$Co(\eta-C_5Me_5)$
(2)	Me	Me	$Co(\eta-C_5Me_5)$
(3a)	Ph	Me	$Co(\eta-C_5Me_5)$
(3b)	Me	Ph	$Co(\eta-C_5Me_5)$
(4)	Bu^t	H	$Co(\eta-C_5Me_5)$
(5)	Me	Me	$Fe(CO)_3$
(6a)	Ph	Ph	$Fe(CO)_3$
(7)	CF_3	CF_3	$Fe(CO)_3$
(8)	C_6H_4Me-4	C_6H_4Me-4	$Fe(CO)_3$



(6b)

for *ca.* 1 d. Under these conditions compounds (1)—(4) were isolated as green crystals using the alkynes PhC_2Ph, MeC_2Me, MeC_2Ph, and Bu^tC_2H, respectively. The forcing conditions required can be understood in terms of kinetic factors, since in the cobalt–tungsten compound both metal atoms have closed 18-electron shells, and the CO ligands at the cobalt and tungsten centres are evidently not readily lost to provide sites for alkyne co-ordination as a preliminary step in reaction. In contrast, the cationic species $[CoW\{\mu-\sigma,\eta^3-CH(R)\}(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]^+$ reacts with but-2-yne at room temperature or even below to give the insertion product $[CoW\{\mu-\sigma,\eta^3-C(R)C(Me)C(Me)H\}(\mu-CO)(CO)(\eta-C_5H_5)(\eta-C_5Me_5)]^+$. In the cation $[CoW\{\mu-\sigma,\eta^3-CH(R)\}(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]^+$ the tungsten atom can readily adopt a 16-electron configuration, allowing reactions with phosphines or alkynes to proceed under mild conditions.[12]

The compounds (1)—(4) were characterised in the usual manner by microanalysis and by the spectroscopic data (Tables 1 and 2). The structures shown, with $\mu-CR–CR^1–CR^2$ groups bridging the metal–metal bond, are in accord with the n.m.r. data (Table 2). The $^{13}C-\{^1H\}$ n.m.r. spectrum of the compound $[CoW(\mu-CR)(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]$ shows a resonance for the ligated *C*R group at δ 341.0 p.p.m.[2] This signal is not present in the spectra of compounds (1)—(4). Instead, peaks are observed which may be assigned to the $\mu-C_3$ nuclei. In the spectrum of (1) these occur at δ 120.7, 93.5, and 92.7 p.p.m. The first signal is assigned to the central $\mu-CR^1$ carbon of the bridged allyl system. In mononuclear metal–allyl complexes the central carbon nucleus is also the most deshielded.[13] Moreover, compound (1) has an essentially symmetrical bridge structure with respect to the remainder of the molecule, leading one to expect a pattern of chemical shifts for the $\mu-C_3$ nuclei wherein one signal is separated from



	R^1	R^2
(9)	$SiMe_3$	$SiMe_3$
(10a)	$SiMe_3$	Bu^t
(10b)	Bu^t	$SiMe_3$

two others which are similar. It is not possible in the spectrum of (1), however, to distinguish between the resonances due to the $\mu-CC_6H_4Me-4$ and $\mu-CR^2$ groups at 93.5 and 92.7 p.p.m. However, in the spectrum of (4), a compound isolated as one isomer in low yield, it is possible to make a complete assignment for the peaks in the $^{13}C-\{^1H\}$ n.m.r. spectrum, since the resonance at δ 97.9 ($\mu-CH$) is of relatively high intensity due to the nuclear Overhauser effect.

Examination of the ^1H n.m.r. spectrum of the product (3) of the reaction between $MeC{\equiv}CPh$ and $[CoW(\mu-CR)(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]$ revealed peaks due to the presence of two isomers (3a) and (3b) formed in *ca.* 2 : 1 ratio, and which could be separated (Experimental section). The n.m.r. assignments (Table 2) for the two isomers are based on the premise that the isomer (3a) with the less symmetrical bridging $\mu-C(C_6H_4Me-4)–C(Ph)–C(Me)$ group is the species likely to give rise in the $^{13}C-\{^1H\}$ n.m.r. spectrum to two CO resonances. In contrast the isomer (3b), with the more symmetrical $\mu-C(C_6H_4Me-4)–C(Me)–C(Ph)$ bridge, will have near *pseudo*-mirror symmetry and hence would be expected to show only one CO resonance, as is observed (Table 2).

Since the groups $Co(CO)(\eta-C_5Me_5)$ and $Fe(CO)_4$ are isolobal[14] it would have been of interest to follow up the work on the reactions of $[CoW(\mu-CR)(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]$ with alkynes with a study of the reactions of the latter with $[FeW(\mu-CR)(CO)_6(\eta-C_5H_5)]$. However, the iron–tungsten compound is difficult to work with, since in the presence of either iron carbonyls or $[W({\equiv}CR)(CO)_2(\eta-C_5H_5)]$ it reacts rapidly to give the cluster compounds $[Fe_2W(\mu_3-CR)(\mu-CO)(CO)_8(\eta-C_5H_5)]$ and $[FeW_2(\mu_3-RC_2R)(CO)_6(\eta-C_5H_5)_2]$, respectively.[5] Consequently, it was thought useful to study reactions of the tricapped tolylmethylidyne species $[Fe_2W(\mu_3-CR)(\mu-CO)(CO)_8(\eta-C_5H_5)]$ with alkynes, to establish whether the latter would combine with the carbyne group.

Reactions occurred between $[Fe_2W(\mu_3-CR)(\mu-CO)(CO)_8(\eta-C_5H_5)]$ and alkynes in toluene under somewhat milder conditions than those required for $[CoW(\mu-CR)(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]$. With the alkynes $MeC{\equiv}CMe$, $PhC{\equiv}CPh$, $CF_3C{\equiv}CCF_3$, and $4-MeC_6H_4C{\equiv}CC_6H_4Me-4$, however, the diiron–tungsten cluster lost an $Fe(CO)_4$ fragment and afforded the dimetal complexes (5)—(8), which are structurally analogous to the cobalt species (1)—(4). In contrast, the alkynes $Me_3SiC{\equiv}CSiMe_3$ and $Bu^tC{\equiv}CSiMe_3$ gave products (9) and (10) in which the μ_3-CFe_2W core structure of the precursor is preserved. Data for the new compounds are given in Tables 1 and 2.

As with the cobalt–tungsten species, the iron–tungsten compounds (5)—(8) have n.m.r. spectra in accord with the structures illustrated. Certain features observed in the spectra merit comment. In the $^{13}C-\{^1H\}$ spectra of (5) and (7) two

Table 1. Analytical [a] and physical data for the cobalt– and iron–tungsten complexes

Complex [b]	M.p. [c] (θ_c/°C)	Colour	Yield (%)	ν(CO) [d]/cm^{-1}	Analysis (%)	
					C	H
(1) $[(\eta\text{-}C_5Me_5)Co(\mu\text{-}CRCPhCPh)W(CO)_2(\eta\text{-}C_5H_5)]$	240—244	Green	27	1 941s, 1 881s	59.8 (60.0)	4.8 (4.8)
(2) $[(\eta\text{-}C_5Me_5)Co(\mu\text{-}CRCMeCMe)W(CO)_2(\eta\text{-}C_5H_5)]$	190—195	Green	42	1 937s, 1 875s	53.3 (53.1)	5.4 (5.1)
(3) $[(\eta\text{-}C_5Me_5)Co(\mu\text{-}CRCPhCMe)W(CO)_2(\eta\text{-}C_5H_5)]$ [e]		Green	80	1 941s, 1 881s [f]	57.3 (56.9)	4.8 (4.9)
(4) $[(\eta\text{-}C_5Me_5)Co(\mu\text{-}CRCBu^tCH)W(CO)_2(\eta\text{-}C_5H_5)]$		Green	5	1 945s, 1 881s	51.8 (53.5)	5.7 (5.6)
(5) $[(OC)_3Fe(\mu\text{-}CRCMeCMe)W(CO)_2(\eta\text{-}C_5H_5)]$		Red	20 [g]	2 041s, 1 981s, 1 961w, 1 925w	44.1 (43.9)	3.2 (3.0)
(6) $[(OC)_3Fe(\mu\text{-}CRCPhCPh)W(CO)_2(\eta\text{-}C_5H_5)]$	210—220	Red	28	2 049s, 1 991s, 1 965w, 1 929m	53.0 (52.9)	3.4 (3.1)
(7) $[(OC)_3Fe\{\mu\text{-}CRC(CF_3)C(CF_3)\}W(CO)_2(\eta\text{-}C_5H_5)]$	138—140	Red	20 [g]	2 067s, 2 015s, 2 006m, 1 952w	37.7 (37.2)	1.7 (1.7)
(8) $[(OC)_3Fe(\mu\text{-}CRCRCR)W(CO)_2(\eta\text{-}C_5H_5)]$	210—215	Red	25	2 047s, 1 987s, 1 961w, 1 929m	52.7 (54.1)	3.3 (3.5)
(9) $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$	172—176	Green	78	2 057s, 2 015s, 1 999s, 1 977m, 1 967m, 1 879w, 1 861w	40.2 (40.5)	3.7 (3.6)
(10) $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}Bu^tC_2SiMe_3)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$		Green	8	2 055s, 2 045w, 2 009s, 1 997s, 1 973m, 1 965m, 1 877w, 1 861w	42.0 (42.8)	4.0 (3.7)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] With decomposition. [d] In hexane. [e] Isomers (see text). [f] For (3b), $\nu_{max.}$(CO) 1 991s and 1 921s cm^{-1}. [g] Yields are variable (10—30%).

resonances due to WCO ligands are seen. This is as expected, in view of the lack of symmetry of the μ-CR–CR^1–CR^2 bridge systems. In contrast, the substituents on the μ-C_3 groups in (6) and (8) are either very similar or identical, leading to the appearance in the ^{13}C-{^{1}H} spectra of these compounds of only one peak due to the two CO ligands on tungsten. The single resonance due to the $Fe(CO)_3$ groups in the spectra of the compounds reflects the customary dynamic behaviour of this fragment. The spectrum of (5) shows three peaks due to the non-equivalent μ-C nuclei, the most deshielded signal (δ 130.1 p.p.m.) being assigned to the central carbon of the chain, the two resonances at 101.1 and 98.9 p.p.m. being due to the terminal carbons of the μ-C_3 group (see below). The spectrum of compound (7) was weak, and only the resonance due to the *C*C_6H_4Me-4 nucleus of the μ-C_3 group was observed. The ^{19}F n.m.r. spectrum, however, revealed two non-equivalent CF_3 groups {δ 32.88 [q, *J*(FF) 8] and 21.86 p.p.m. [q, *J*(FF) 8 Hz]; shifts relative to CCl_3F (external), positive values to high frequency}. In the ^{13}C-{^{1}H} spectrum of (8), as expected, there is only a single resonance for the two terminal μ-C nuclei of the bridge system, since in this species the substituents are identical.

Both the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra of (6), the product of the reaction between $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ and PhC≡CPh, revealed the presence of two isomers. This is most clearly seen from the ^{1}H spectrum (Table 2), the relative intensities of the peaks indicating that the proportion of (6a): (6b) is *ca.* 2 : 1. The ^{13}C-{^{1}H} spectra of the two isomers are very similar. Nevertheless, two environments for Me-4 groups are observed, and three resonances are seen for the μ-C nuclei. The fourth signal expected for the μ-C_3 group undoubtedly lies among the many peaks in the aromatic region (δ 146.7—125.5), and could not be positively identified. These data suggest that the two isomers have the structures (6a) and (6b) shown, differing in the arrangement of the Ph and C_6H_4Me-4 substituents in the bridge system. The existence of (6b), the minor isomer, implies a C≡C cleavage at some stage in the reaction. Since (6) is produced *via* a complicated reaction involving loss of an $Fe(CO)_4$ fragment from a μ_3-CFe_2W cluster, it is probably unwise to speculate in detail on the mechanism. However, in view of the existence of compounds (9) and (10), discussed below, it seems probable that the reactions leading to (5)—(9) proceed *via* the intermediacy of cluster species $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}alkyne)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$, which subsequently release $Fe(CO)_2$ groups and form the μ-C_3 ligands found in the dimetal species. With PhC≡CPh there is evidently a pathway for both carbon–carbon bond cleavage and bond formation *via* carbyne fragments and these processes are accompanied by a molecular rearrangement. Recently Vollhardt and co-workers [15] have observed cleavage of alkynes and coupling of carbyne fragments in certain tricobalt cluster systems.

In order to establish the molecular structures of the dimetal compounds (1)—(8) unequivocally, an *X*-ray diffraction study was carried out on (5) for which a suitable crystal was available. The molecular structure with the atom numbering scheme is shown in Figure 1, and selected distances and angles are given in Table 3.

The Fe–W bond [2.720(1) Å] is bridged by a three-carbon chain as expected. However, whereas all the atoms of the chain are bonded to the iron, only the two terminal atoms are attached to the tungsten. The iron atom is bonded by three approximately orthogonal and terminal carbonyl ligands, whilst the tungsten is ligated by the cyclopentadienyl ring and two terminal carbonyl groups.

Interest centres on the μ-C(C_6H_4Me-4)–C(Me)–C(Me) group which may be regarded as an allyl ligand η^3-bonded to iron and linked to tungsten *via* two σ bonds. However, the

Table 2. Hydrogen-1 and carbon-13 n.m.r. data [a] for the cobalt– and iron–tungsten complexes

Compound	^{1}H (δ) [b]	^{13}C (δ) [c]
(1)	1.56 (s, 15 H, $\mathrm{C_5Me_5}$), 2.24 (s, 3 H, Me-4), 4.86 (s, 5 H, $\mathrm{C_5H_5}$), 7.10 (m, 4 H, $\mathrm{C_6H_4}$), 7.08 (m, 10 H, Ph)	[d] 229.6 [CO, *J*(WC) 144], 149.4—123.6 ($\mathrm{C_6H_4}$, Ph), 120.7 (μ-$C\mathrm{R}^1$), 93.5, 92.7 (μ-*C*R, μ-$C\mathrm{R}^2$), 89.7 ($C_5\mathrm{Me_5}$), 89.0 ($\mathrm{C_5H_5}$), 20.7 (Me-4), 8.3 ($\mathrm{C_5}Me_5$)
(2)	[e] 1.56 (s, 15 H, $\mathrm{C_5Me_5}$), 1.62, 2.00, 2.20 (3 s, 9 H, Me), 4.70 (s, 5 H, $\mathrm{C_5H_5}$), 7.20 (m, 4 H, $\mathrm{C_6H_4}$)	231.8 [CO, *J*(WC) 150], 230.3 [CO, *J*(WC) 147], 149.3—128.0 ($\mathrm{C_6H_4}$), 116.9 (μ-$C\mathrm{R}^1$), 92.5, 88.8 (μ-*C*R, μ-$C\mathrm{R}^2$), 88.8 ($C_5\mathrm{Me_5}$), 88.3 ($\mathrm{C_5H_5}$), 24.0 (μ-C*Me*), 21.4 (Me-4), 16.0 (μ-C*Me*), 8.4 ($\mathrm{C_5}Me_5$)
(3a)	[e] 1.58 (s, 15 H, $\mathrm{C_5Me_5}$), 2.22, 2.28 (2 s, 6 H, Me), 4.76 (s, 5 H, $\mathrm{C_5H_5}$), 7.01 (m, 4 H, $\mathrm{C_6H_4}$), 7.18 (m, 5 H, Ph)	230.2 [CO, *J*(WC) 143], 229.3 [CO, *J*(WC) 149], 149.0—126.2 ($\mathrm{C_6H_4}$, Ph), 117.7 (μ-*C*Ph), 93.8, 89.8 (μ-*C*R, μ-*C*Me), 89.8 ($C_5\mathrm{Me_5}$), 89.2 ($\mathrm{C_5H_5}$), 27.7 (μ-C*Me*), 21.4 (Me-4), 8.8 ($\mathrm{C_5}Me_5$)
(3b)	[e] 1.51 (s, 15 H, $\mathrm{C_5Me_5}$), 1.92, 2.20 (2 s, 6 H, Me), 4.63 (s, 5 H, $\mathrm{C_5H_5}$), 7.26 (m, 5 H, Ph), 7.42 (m, 4 H, $\mathrm{C_6H_4}$)	232.2 [CO, *J*(WC) 143], 151.8—124.0 ($\mathrm{C_6H_4}$, Ph), 112.5 (μ-*C*Me), 91.8, 91.0 (μ-*C*R, μ-*C*Ph), 89.5 ($C_5\mathrm{Me_5}$), 89.4 ($\mathrm{C_5H_5}$), 30.0 (μ-C*Me*), 19.7 (Me-4), 8.6 ($\mathrm{C_5}Me_5$)
(4)	[e] 1.13 (s, 9 H, $\mathrm{Bu^t}$), 1.46 (s, 15 H, $\mathrm{C_5Me_5}$), 2.16 (s, 3 H, Me-4), 2.28 (s, 1 H, μ-CH), 4.86 (s, 5 H, $\mathrm{C_5H_5}$), 7.06 (m, 4 H, $\mathrm{C_6H_4}$)	230.5 [CO, *J*(WC) 140], 230.2 [CO, *J*(WC) 138], 148.4—128.7 ($\mathrm{C_6H_4}$), 116.4 (μ-$C\mathrm{Bu^t}$), 97.9 (μ-CH), 89.7 ($C_5\mathrm{Me_5}$), 88.7 (μ-*C*R), 88.2 ($\mathrm{C_5H_5}$), 41.7 ($C\mathrm{Me_3}$), 32.7 ($\mathrm{C}Me_3$), 21.5 (Me-4), 9.5 ($\mathrm{C_5}Me_5$)
(5)	1.88, 2.17, 2.28 (3 s, 9 H, Me), 5.04 (s, 5 H, $\mathrm{C_5H_5}$), 7.06 (m, 4 H, $\mathrm{C_6H_4}$)	220.5, 220.4 [WCO, *J*(WC) 142 and 142], 214.5 (FeCO), 145.1—128.6 ($\mathrm{C_6H_4}$), 130.1 (μ-$C\mathrm{R}^1$), 101.1, 98.9 (μ-*C*R, μ-$C\mathrm{R}^2$), 87.9 ($\mathrm{C_5H_5}$), 25.1 (μ-C*Me*), 21.1 (Me-4), 18.2 (μ-C*Me*)
(6) [f]	2.24 {2.30} (s, 3 H, Me-4), 5.12 {5.12} (s, 5 H, $\mathrm{C_5H_5}$), 6.85 {6.96} (m, 4 H, $\mathrm{C_6H_4}$), 7.02 {7.02} (br, 10 H, Ph)	219.7 [WCO, *J*(WC) 140], 213.3 (FeCO), 146.7—125.5 ($\mathrm{C_6H_4}$, Ph, μ-$C\mathrm{R}^1$), 100.0, 99.3, 99.0 (μ-*C*R, μ-$C\mathrm{R}^2$), 88.8 ($\mathrm{C_5H_5}$), 21.0 {21.3} (Me-4)
(7)	2.32 (s, 3 H, Me-4), 5.24 (s, 5 H, $\mathrm{C_5H_5}$), 7.12 (m, br, 4 H, $\mathrm{C_6H_4}$)	[g] 216.0, 213.9 (WCO), 211.4 (FeCO), 141.6—128.2 ($\mathrm{C_6H_4}$), 128.8 [q, $\mathrm{CF_3}$, *J* (FC) 314], 123.4 [q, $\mathrm{CF_3}$, *J*(FC) 343], 109.1 (μ-*C*R), 88.4 ($\mathrm{C_5H_5}$), 21.3 (Me-4)
(8)	2.24 (s, 6 H, Me-4), 2.32 (s, 3 H, Me-4), 5.12 (s, 5 H, $\mathrm{C_5H_5}$), 6.86—6.96 (m br, 12 H, $\mathrm{C_6H_4}$)	[d] 220.1 [WCO, *J*(WC) 141], 213.3 (FeCO), 143.7—128.3 ($\mathrm{C_6H_4}$), 131.7 (μ-$C\mathrm{R}^1$), 99.2 [μ-*C*R, μ-$C\mathrm{R}^2$, *J*(WC) 50], 88.7 ($\mathrm{C_5H_5}$), 21.3 (Me-4), 21.0 (2 Me-4)
(9)	0.30 (s, 9 H, $\mathrm{SiMe_3}$), 0.44 (s, 9 H, $\mathrm{SiMe_3}$), 2.36 (s, 3 H, Me-4), 5.46 (s, 5 H, $\mathrm{C_5H_5}$), 6.9—7.3 (m br, 4 H, $\mathrm{C_6H_4}$)	257.7 (μ_3-C), 233.7 (μ-CO), 219.0, 211.1, 209.6, 208.3 (CO), 159.5—127.9 ($\mathrm{C_6H_4}$), 107.8 ($C\mathrm{SiMe_3}$), 97.1 ($\mathrm{C_5H_5}$), 75.7 ($C\mathrm{SiMe_3}$), 21.0 (Me-4), 3.3, 2.1 ($\mathrm{SiMe_3}$)
(10) [h]	0.49 {0.34} (s, 9 H, $\mathrm{SiMe_3}$), 1.30 {1.38} (s, 9 H, $\mathrm{Bu^t}$), 2.37 {2.40} (s, 3 H, Me-4), 5.46 {5.54} (s, 5 H, $\mathrm{C_5H_5}$), 6.8—7.3 {6.8—7.3} (m, 4 H, $\mathrm{C_6H_4}$)	[d] 257.2 {251.4} (μ_3-C), 239.7 {236.1} (μ-CO), 219.2 {220.9} (CO), 210.6 {209.9} (CO), 209.1 {208.3} (CO), 207.7 {207.7} (CO), 159.2—127.6 ($\mathrm{C_6H_4}$), 97.2 {97.2} ($\mathrm{C_5H_5}$), 38.8 {41.0} ($C\mathrm{Me_3}$), 33.4 {34.2} ($\mathrm{C}Me_3$), 20.9 {20.9} (Me-4), 3.7 {2.4} ($\mathrm{SiMe_3}$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in $\mathrm{CDCl_3}$ unless otherwise stated. [c] Measured in $\mathrm{CD_2Cl_2}$–$\mathrm{CH_2Cl_2}$ unless otherwise stated. [d] In $\mathrm{CDCl_3}$. [e] In $\mathrm{CD_2Cl_2}$. [f] Two isomers (2 : 1), see text; shifts given in braces are for minor isomer. [g] Measured at −50 °C, μ-$C\mathrm{CF_3}$ signals not located. [h] Two isomers formed (3 : 2), see text; shifts given in braces are for the second isomer. Signals for ligated carbons of the alkyne are seen at δ 149.5 ($C\mathrm{Bu^t}$), 112.0 ($C\mathrm{SiMe_3}$), and 81.5 p.p.m. ($C\mathrm{SiMe_3}$) with the fourth resonance ($C\mathrm{Bu^t}$) obscured under aromatic resonances at δ *ca.* 128 p.p.m.

isolobal model [14] suggests an attractive alternative description involving bonding of the $\mathrm{Fe(CO)_3}$ group in (5) to a tungstacyclobutadiene ring [compare (A) and (B) in the Scheme], which follows from the relationship $(\eta\text{-}\mathrm{C_5H_5})(\mathrm{OC})_2\mathrm{W} \leftarrow\!\circ\!\rightarrow \mathrm{CH}$ or CR. We have previously described [16] osmium- and ruthenium-ditungsten compounds which may be formulated as having $\mathrm{M(CO)_3}$ groups attached to a ditungstacyclobutadiene ring system [(C) in Scheme]. However, an $\mathrm{FeW_2}$ species structurally analogous to the $\mathrm{MW_2}$ (M = Ru or Os) compounds, and with 48 cluster valence electrons, is not known. Instead, a species (D) has been characterised which, with 46 cluster valence electrons, is formally unsaturated.[5]

Although these relationships are of interest, the presence of the metal-metal bond in (5), which is necessarily longer than the Fe-μ-C distances, results in the W, C(6), C(7), C(8) ring being non-planar, and slightly folded along the diagonal defined by C(6) and C(8). The interplanar angle between the planes W, C(6), C(8) and C(6), C(7), C(8) is 161.5°. The C(6)–C(7) [1.440(8) Å] and C(7)–C(8) [1.435(8) Å] separations are between those expected for carbon–carbon single and double bonds, which is consistent with an 'allylic' or 'tungstacyclobutadiene' description. Moreover, the C(6)–W [2.194(6) Å] and C(8)–W [2.164(7) Å] distances are comparable with that [2.14(2) Å] found in $[\mathrm{W(=CPh_2)(CO)_5}]$[17] and just within the range [2.10(2)—2.49(3) Å] of those measured in tungsten compounds with C–W single bonds.[1,18] This suggests that the delocalisation observed in the μ-$\mathrm{C_3}$ chain may partially encompass the tungsten atom.

As mentioned above, the alkynes $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ and $\mathrm{Bu^tC{\equiv}CSiMe_3}$ react with $[\mathrm{Fe_2W}(\mu_3\text{-CR})(\mu\text{-CO})(\mathrm{CO})_8(\eta\text{-}\mathrm{C_5H_5})]$ to afford the trimetal species (9) and (10). The $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum of (9) (Table 2) showed the characteristic resonance for a μ_3-*C*R group (δ 257.7 p.p.m.) and signals typical for the ligated carbon nuclei of an alkyne (δ 107.8 and 75.7 p.p.m.), thus establishing that in this compound a bridging allyl group had not been formed. In order to establish the structure of (9) an *X*-ray diffraction study was carried out. The results are summarised in Table 4.

The crystal structure of compound (9) is unusual: the monoclinic unit cell, of symmetry $P2_1$, has $Z = 4$, but the two molecules which comprise the crystallographic asymmetric unit are themselves related by a non-crystallographic centre of inversion, and hence form an enantiomorphous pair. The molecular structure of (9) is illustrated in Figure 2 which also

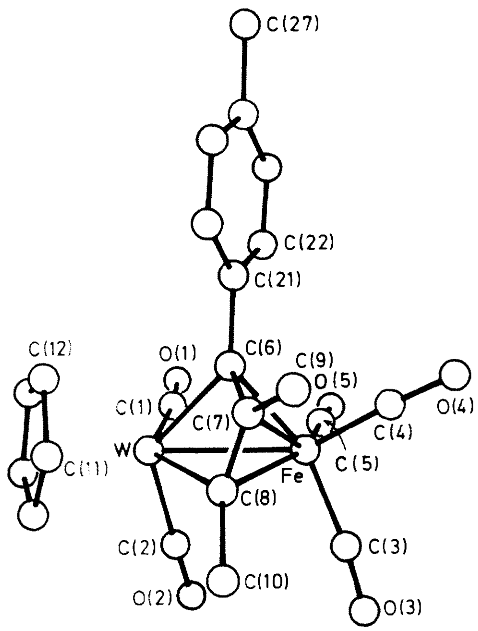
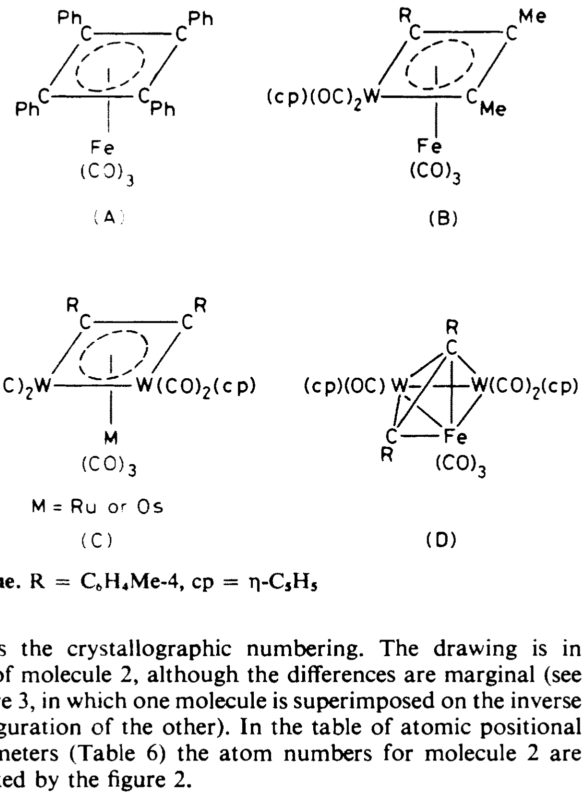


Figure 1. The molecular structure of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5H_5)]$ (5) showing the atom-numbering scheme



Scheme. R = $C_6H_4Me\text{-}4$, cp = $\eta\text{-}C_5H_5$

shows the crystallographic numbering. The drawing is in fact of molecule 2, although the differences are marginal (see Figure 3, in which one molecule is superimposed on the inverse configuration of the other). In the table of atomic positional parameters (Table 6) the atom numbers for molecule 2 are prefixed by the figure 2.

The molecule consists of a triangle of metal atoms with a μ_3-tolylmethylidyne ligand capping one face of the triangle. One of the iron–tungsten bonds [W–Fe(2)] is bridged transversely by a bis(trimethylsilyl)acetylene ligand, and this ligand tips towards the opposite face of the metal-atom triangle. Atoms C(3), C(6), and C(7) are at distances 1.33, −0.40, and −1.46 Å, respectively, from the plane through the metal atoms. This arrangement of the $Me_3SiC{\equiv}CSiMe_3$ ligand accounts for the appearance of resonances in the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of compound (9) corresponding to two non-equivalent $CSiMe_3$ groups.

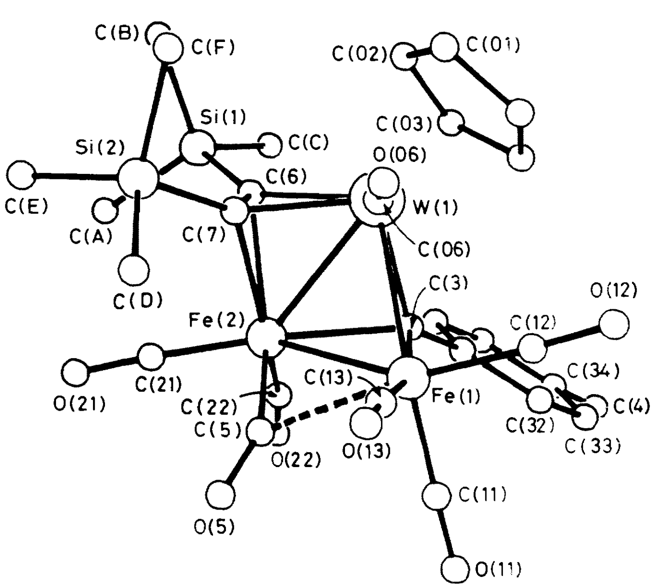


Figure 2. The molecular structure of $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$ (9) showing the atom-numbering scheme. For molecule 2 the atom numbers are prefixed by the figure 2 in Tables 4 and 6, but the simple numbering of molecule 1 has been used throughout the text, even though figures quoted are those for molecule 2

The W–Fe(1) bond distance [2.775(2) Å] is similar to the tungsten-iron separations [2.756(2) and 2.805(2) Å] in the parent compound $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$,[5] and is appreciably longer than either W–Fe(2) [2.648(2) Å] or Fe(1)–Fe(2) [2.640(3) Å]. The acetylenic bridge is not markedly asymmetric [W–C(6) 2.053(14), W–C(7) 2.107(12), Fe(2)–C(6) 2.184(12), and Fe(2)–C(7) 2.126(13) Å] although the longer bonds are, perhaps surprisingly, to the iron atom. The plane defined by the atoms Si(1), C(6), C(7), and Si(2) is approximately normal (83°) to the plane of the metal triangle.

The C(6)—C(7) separation of 1.34(2) Å is in the range [1.27(4)—1.44(1) Å] previously observed[5,19-21] in trimetal compounds with $\mu(\eta^2\text{-}\perp)$ alkyne ligands. The μ_3-C(3) atom asymmetrically bridges the metal triangle [C(3)–Fe(1) 1.941(11), C(3)–Fe(2) 2.154(12), and C(3)–W 2.075(12) Å]; however, the non-bonded distance (3.10 Å) between C(3) and the alkyne carbon atom C(6) is relatively small, and only a minor topological change would be required to bring these atoms into proximity for bonding. This provides some evidence that compound (9) represents a model for an intermediate in the pathway by which the species (5)—(8) are formed. It is interesting that (9) does not readily decompose to a complex structurally analogous to (5)—(8), since its stability is not readily rationalised on either steric or electronic grounds.

The tungsten atom carries one cyclopentadienyl group and one terminal carbonyl ligand, while the iron atoms each carry three carbonyl ligands. One of those attached to Fe(2), however, is strongly semi-bridging to Fe(1) [Fe(2)–C(5) 1.832(12), Fe(1)–C(5) 2.25(2) Å, and Fe(2)–C(5)–O(5) 152.6(14)°], and has, therefore, been delineated in the molecular formula as a bridging species (μ-CO).

Figure 4 shows a stereoscopic view of the packing of complex (9). The molecules are stacked along *b* in an almost linear mode, hence producing an unusually extended unit cell. The two crystallographically independent molecules are related

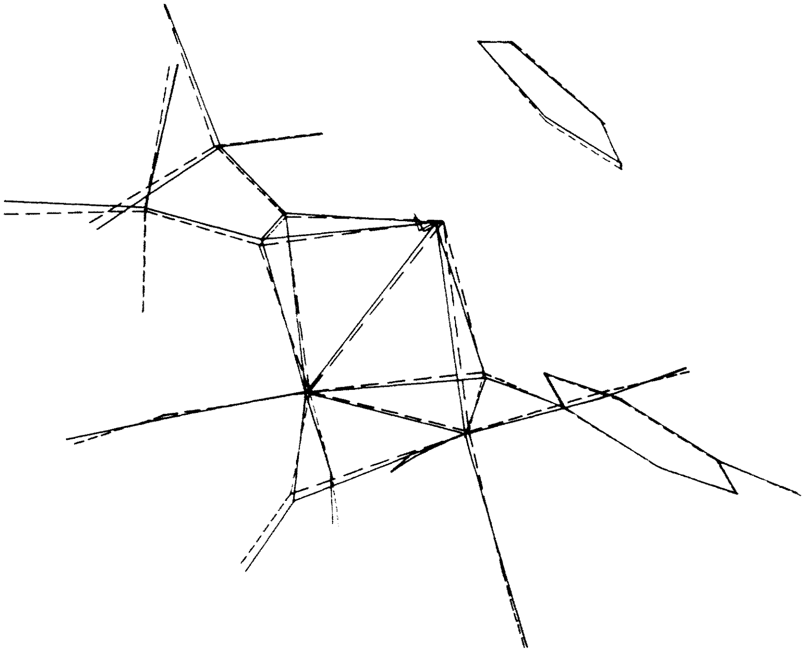


Figure 3. Superposition of the two crystallographically independent molecules of (9), after inversion of configuration for one molecule

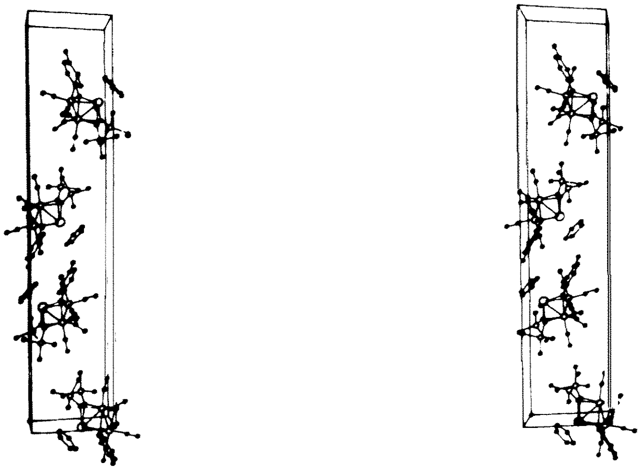


Figure 4. A stereoscopic view of the contents of the unit cell of (9) showing the novel packing arrangement

by a *pseudo*-(non-crystallographic) centre of inversion,* small deviations being evident, as shown in Figure 3. Close inspection of the relevant parameters reveals that the major difference between the two molecules lies in the length of the W–Fe(2) bonds which are, for molecules 2 and 1, respectively, 2.648(2) and 2.682(2) Å; a difference of seventeen times σ(Fe–W). Another major difference involves the W–C(alkyne) separations [five and ten times σ(W–C)]. These changes necessitate some angular differences, particularly within the Fe_2W triangle, the remainder of the molecule being otherwise largely unaltered.

Compound (10) would be expected to have a structure similar to that of (9). However, the former is produced as a mixture (3 : 2) of isomers (10a) and (10b), as evidenced by the ^{1}H and ^{13}C-{^{1}H} n.m.r. data (Table 2). In both spectra, peaks due to the two isomers are seen, which can be understood if it is assumed that the species differ in the orientation of the $\mathrm{Bu^tC{\equiv}CSiMe_3}$ group with respect to the μ_3-$\mathrm{CC_6H_4Me}$-4 ligand.

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. The instrumentation used to obtain spectroscopic information has been listed previously.[1] The compounds [CoW(μ-$\mathrm{CC_6H_4Me}$-4)$\mathrm{(CO)_3}$(η-$\mathrm{C_5H_5}$)(η-$\mathrm{C_5Me_5}$)] [2] and [$\mathrm{Fe_2W}$(μ_3-$\mathrm{CC_6H_4Me}$-4)(μ-CO)$\mathrm{(CO)_8}$(η-$\mathrm{C_5H_5}$)] [5] were prepared by methods reported earlier. Analytical and spectroscopic data for the new compounds are given in Tables 1 and 2.

Synthesis of the Cobalt–Tungsten Complexes (1)—(4).—A mixture of [CoW(μ-$\mathrm{CC_6H_4Me}$-4)$\mathrm{(CO)_3}$(η-$\mathrm{C_5H_5}$)(η-$\mathrm{C_5Me_5}$)] (0.36 g, 0.58 mmol) and $\mathrm{PhC{\equiv}CPh}$ (0.21 g, 1.16 mmol) in toluene (20 cm^3) was placed in a Schlenk tube fitted with a high-pressure stopcock. The reaction vessel was evacuated, sealed, and then heated at 120 °C for 3 d. After cooling to room temperature, the resulting green mixture was evaporated *in vacuo*, thereby affording an oil. The latter was dissolved (*ca.* 10 cm^3) in dichloromethane–light petroleum (1 : 3), and chromatographed on alumina. Elution with the same solvent mixture afforded a single green eluate. Removal of solvent *in vacuo* yielded a residue which was recrystallised from dichloromethane–light petroleum (1 : 5) to give dark green *crystals* of [CoW{μ-C($\mathrm{C_6H_4Me}$-4)C(Ph)C(Ph)}$\mathrm{(CO)_2}$(η-$\mathrm{C_5H_5}$)(η-$\mathrm{C_5Me_5}$)] (1) (0.12 g, 27%).

Compounds (2)—(4) were prepared in a similar fashion. Compound (3) was formed as a mixture of isomers, and it was possible to separate (3a) (*ca.* 70%) from (3b) (*ca.* 30%) by fractional crystallisation, the former isomer being the less soluble in dichloromethane–light petroleum. Complexes (2) and (3) were isolated after reaction times of *ca.* 24 h, but (4)

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* This effect is not particularly common; one recent example is given in ref. 22.

Table 3. Selected internuclear distances (Å) and angles (°) for [FeW{μ-C(C_6H_4Me-4)C(Me)C(Me)}$(CO)_5$(η-C_5H_5)] (5)

Fe-W	2.720(1)	W-C(1)	2.025(6)	C(1)-O(1)	1.129(9)	C(2)-O(2)	1.134(7)
W-C(2)	2.008(6)	W-C(6)	2.194(6)	C(3)-O(3)	1.147(7)	C(4)-O(4)	1.136(9)
W-C(8)	2.164(7)	W-C(11)	2.317(4)	C(5)-O(5)	1.150(8)	C(6)-C(7)	1.440(8)
W-C(12)	2.355(4)	W-C(13)	2.346(5)	C(6)-C(21)	1.494(6)	C(7)-C(9)	1.506(9)
W-C(14)	2.303(5)	W-C(15)	2.285(4)	C(8)-C(7)	1.435(8)	C(8)-C(10)	1.483(8)
Fe-C(3)	1.788(6)	Fe-C(4)	1.773(7)	C(24)-C(27)	1.529(7)	C-C(C_5H_5)	1.420 *
Fe-C(5)	1.770(7)	Fe-C(6)	2.047(6)	C-C(C_6H_4Me-4)	1.395 *		
Fe-C(7)	2.103(6)	Fe-C(8)	2.083(6)				
C(1)-W-C(2)	84.0(2)	Fe-W-C(6)	47.8(2)	W-C(6)-Fe	79.7(2)	W-C(6)-C(7)	95.9(3)
Fe-W-C(8)	48.9(2)	C(6)-W-C(8)	61.6(2)	Fe-C(6)-C(7)	71.8(3)	W-C(6)-C(21)	133.3(4)
C(3)-Fe-C(4)	97.3(3)	C(3)-Fe-C(5)	93.9(3)	Fe-C(6)-C(21)	129.5(4)	C(7)-C(6)-C(21)	125.3(5)
C(4)-Fe-C(5)	93.9(3)	W-Fe-C(6)	52.5(2)	Fe-C(7)-C(6)	67.6(3)	Fe-C(7)-C(8)	69.2(3)
W-Fe-C(7)	68.0(2)	C(6)-Fe-C(7)	40.6(2)	C(6)-C(7)-C(8)	101.9(5)	Fe-C(7)-C(9)	128.0(5)
W-Fe-C(8)	51.5(2)	C(6)-Fe-C(8)	65.4(2)	C(6)-C(7)-C(9)	130.2(5)	C(8)-C(7)-C(9)	127.8(5)
C(7)-Fe-C(8)	40.1(2)	W-C(1)-O(1)	174.6(6)	W-C(8)-Fe	79.6(2)	W-C(8)-C(7)	97.3(4)
W-C(2)-O(2)	176.9(6)	Fe-C(3)-O(3)	178.9(6)	Fe-C(8)-C(7)	70.7(3)	W-C(8)-C(10)	133.1(4)
Fe-C(4)-O(4)	178.2(7)	Fe-C(5)-O(5)	176.3(7)	Fe-C(8)-C(10)	126.9(5)	C(7)-C(8)-C(10)	126.3(6)

* Rigid group.

Table 4. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses for [Fe_2W(μ_3-CC_6H_4Me-4)(μ-$Me_3SiC_2SiMe_3$)(μ-CO)$(CO)_6$(η-C_5H_5)] (9)

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
W(1)-Fe(1)	2.773(2)	W(2)-Fe(21)	2.775(2)	Fe(1)-C(5)	2.298(14)	Fe(21)-C(25)	2.25(2)
W(1)-Fe(2)	2.682(2)	W(2)-Fe(22)	2.648(2)	Fe(2)-C(5)	1.823(11)	Fe(22)-C(25)	1.832(12)
Fe(1)-Fe(2)	2.645(3)	Fe(21)-Fe(22)	2.640(3)	C(5)-O(5)	1.17(2)	C(25)-O(25)	1.16(2)
W(1)-C(6)	2.128(12)	W(2)-C(26)	2.053(14)	Fe(1)-C(11)	1.80(2)	Fe(21)-C(211)	1.79(2)
W(1)-C(7)	2.234(11)	W(2)-C(27)	2.107(12)	Fe(1)-C(12)	1.75(2)	Fe(21)-C(212)	1.77(2)
Fe(2)-C(6)	2.137(11)	Fe(22)-C(26)	2.184(12)	Fe(1)-C(13)	1.86(2)	Fe(21)-C(213)	1.831(14)
Fe(2)-C(7)	2.111(15)	Fe(22)-C(27)	2.126(13)	C(11)-O(11)	1.13(2)	C(211)-O(211)	1.15(3)
C(6)-C(7)	1.43(2)	C(26)-C(27)	1.34(2)	C(12)-O(12)	1.13(3)	C(212)-O(212)	1.16(3)
C(6)-Si(1)	1.865(11)	C(26)-Si(21)	1.873(13)	C(13)-O(13)	1.12(3)	C(213)-O(213)	1.13(2)
C(7)-Si(2)	1.849(14)	C(27)-Si(22)	1.883(14)	Fe(2)-C(21)	1.80(2)	Fe(22)-C(221)	1.75(2)
W(1)-C(3)	2.01(2)	W(2)-C(23)	2.075(12)	Fe(2)-C(22)	1.78(2)	Fe(22)-C(222)	1.78(2)
Fe(1)-C(3)	1.961(14)	Fe(21)-C(23)	1.941(11)	C(21)-O(21)	1.11(3)	C(221)-O(221)	1.16(2)
Fe(2)-C(3)	2.090(14)	Fe(22)-C(23)	2.154(12)	C(22)-O(22)	1.13(3)	C(222)-O(222)	1.14(3)
C(3)-C(31)	1.51(2)	C(23)-C(231)	1.50(2)	Mean W-C(cp)	2.334(13)		2.402(12)
C(34)-C(4)	1.55(3)	C(234)-C(24)	1.51(4)	Mean C-C(cp)	1.420		1.420
W(1)-C(06)	2.00(2)	W(2)-C(206)	1.95(2)	Mean Si-C(Me)	1.88(3)		1.87(2)
C(06)-O(06)	1.15(3)	C(206)-O(206)	1.18(3)	Mean C-C(Ph)	1.395		1.395
W(1)-Fe(1)-Fe(2)	59.3(1)	W(2)-Fe(21)-Fe(22)	58.5(1)	Fe(1)-C(12)-O(12)	177(2)	Fe(21)-C(212)-O(212)	174(2)
W(1)-Fe(2)-Fe(1)	62.7(1)	W(2)-Fe(22)-Fe(21)	63.3(1)	Fe(1)-C(13)-O(13)	172(2)	Fe(21)-C(213)-O(213)	176.6(14)
Fe(1)-W(1)-Fe(2)	58.0(1)	Fe(21)-W(2)-Fe(22)	58.2(1)	Fe(2)-C(21)-O(21)	171.6(15)	Fe(22)-C(221)-O(221)	175.9(13)
C(6)-C(7)-Si(2)	136.8(9)	C(26)-C(27)-Si(22)	137.1(9)	Fe(2)-C(22)-O(22)	176.1(14)	Fe(22)-C(222)-O(222)	171.5(14)
C(7)-C(6)-Si(1)	137.6(10)	C(27)-C(26)-Si(21)	140.7(11)	Fe(1)-C(5)-O(5)	126.7(10)	Fe(21)-C(25)-O(25)	127.5(11)
W(1)-C(06)-O(06)	165.5(13)	W(2)-C(206)-O(206)	168.7(12)	Fe(2)-C(5)-O(5)	154.2(13)	Fe(22)-C(25)-O(25)	152.6(14)
Fe(1)-C(11)-O(11)	177(2)	Fe(21)-C(211)-O(211)	179(2)	Fe(1)-C(5)-Fe(2)	78.9(5)	Fe(21)-C(25)-Fe(22)	79.8(5)

was obtained only in low yield after heating the reactants for 5 d at 120 °C.

Synthesis of the Iron–Tungsten Compounds (5)—(8).—In a representative reaction, a mixture of [Fe_2W(μ_3-CC_6H_4Me-4)(μ-CO)$(CO)_8$(η-C_5H_5)] (0.72 g, 1 mmol) and PhC≡CPh (0.18 g, 1 mmol) in toluene (30 cm^3) was heated at 80 °C for 3—4 h in an evacuated Schlenk tube fitted with a high-pressure stopcock. After cooling to ambient temperature, insoluble brown material was removed by filtration. The solvent was then removed *in vacuo* and the residue, dissolved in the minimum amount of dichloromethane–light petroleum (1 : 1), was chromatographed on an alumina column (40 × 2 cm). Elution with the same solvent mixture gave, after removal of solvent *in vacuo*, a red residue. Recrystallisation from dichloromethane–light petroleum (1 : 10) afforded red *crystals* of [FeW{μ-C(C_6H_4Me-4)C(Ph)C(Ph)}$(CO)_5$(η-C_5H_5)] (6) (0.20 g, 28%).

The related compound (8) was obtained similarly, and in comparable yield. In the synthesis of compounds (5) and (7) a *ca.* 20-fold excess of the gaseous alkyne was used. The products, however, were obtained in variable yield although reaction conditions and isolation procedures were similar to those for complexes (6) and (8).

Synthesis of the Diiron–Tungsten Compounds (9) *and* (10).—A light petroleum (20 cm^3) solution of [Fe_2W(μ_3-CC_6H_4Me-4)(μ-CO)$(CO)_8$(η-C_5H_5)] (0.73 g, 1.01 mmol) and Me_3SiC≡CSiMe_3 (0.19 g, 1.10 mmol) was refluxed for 23 h, after which time solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (20 cm^3) and filtered through a 3-cm alumina pad. Solvent was removed *in vacuo* and the residue crystallised from dichloromethane–light petroleum (1 : 4) to give green *crystals* of [Fe_2W(μ_3-CC_6H_4Me-4)(μ-$Me_3SiC_2SiMe_3$)(μ-CO)$(CO)_6$(η-C_5H_5)] (9) (0.74 g, 78%).

Table 5. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for [FeW{μ-C(C_6H_4Me-4)-C(Me)C(Me)}$(CO)_5$(η-C_5H_5)] (5)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.133 58(1)	0.227 89(2)	−0.196 83(2)	C(9)	0.174 4(3)	0.398 8(6)	−0.449 6(6)
Fe	0.178 69(3)	0.161 85(6)	−0.357 44(6)	C(10)	0.248 8(3)	0.338 8(5)	−0.208 2(5)
C(1)	0.087 4(3)	0.099 2(5)	−0.230 2(6)	C(11)	0.131 4(2)	0.398 8(3)	−0.140 6(4)
O(1)	0.061 5(3)	0.027 7(5)	−0.240 5(5)	C(12)	0.077 9(2)	0.371 3(3)	−0.192 8(4)
C(2)	0.189 1(3)	0.129 1(5)	−0.112 3(5)	C(13)	0.062 8(2)	0.289 9(3)	−0.130 8(4)
O(2)	0.219 8(2)	0.074 6(4)	−0.060 2(4)	C(14)	0.107 0(2)	0.267 3(3)	−0.040 3(4)
C(3)	0.246 1(3)	0.124 0(5)	−0.296 2(5)	C(15)	0.149 4(2)	0.334 6(3)	−0.046 4(4)
O(3)	0.289 5(2)	0.101 4(4)	−0.256 7(5)	C(21)	0.064 91(13)	0.267 1(3)	−0.463 6(3)
C(4)	0.183 3(3)	0.169 1(6)	−0.495 7(6)	C(22)	0.037 59(31)	0.177 9(3)	−0.509 8(3)
O(4)	0.185 0(3)	0.175 2(6)	−0.585 0(5)	C(23)	−0.009 25(13)	0.186 5(3)	−0.594 2(3)
C(5)	0.148 4(3)	0.037 8(6)	−0.374 9(6)	C(24)	−0.028 77(13)	0.284 2(3)	−0.632 4(3)
O(5)	0.130 8(2)	−0.044 6(4)	−0.389 1(5)	C(25)	−0.001 45(13)	0.373 4(3)	−0.586 2(3)
C(6)	0.115 6(3)	0.261 0(5)	−0.374 1(5)	C(26)	0.045 40(13)	0.364 9(3)	−0.501 8(3)
C(7)	0.162 6(3)	0.322 1(5)	−0.368 6(5)	C(27)	−0.080 0(3)	0.292 2(8)	−0.725 3(6)
C(8)	0.195 4(3)	0.295 6(5)	−0.261 3(5)				

Table 6. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for [Fe_2W($μ_3$-CC_6H_4Me-4)-(μ-$Me_3SiC_2SiMe_3$)(μ-CO)$(CO)_6$(η-C_5H_5)] (9)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	−0.080 6(3)	−0.006 46(5)	−0.022 4(2)	Fe(21)	0.484 1(3)	0.295 39(5)	0.300 6(2)
Fe(2)	−0.148 0(2)	0.042 46(4)	−0.222 1(2)	Fe(22)	0.418 6(2)	0.246 57(4)	0.101 5(2)
W(1)	−0.393 88(5)	−0.000 00	−0.242 73(5)	W(2)	0.172 19(6)	0.287 68(1)	0.0788 0(5)
C(11)	0.129(3)	−0.015 8(5)	0.008 3(2)	C(211)	0.691(2)	0.306 6(8)	0.333(2)
C(12)	−0.133(3)	−0.047 7(5)	0.013 8(15)	C(212)	0.434(3)	0.337 7(5)	0.334(2)
C(13)	−0.049(3)	0.010 9(6)	0.160(2)	C(213)	0.515(2)	0.280 3(4)	0.482 6(13)
C(21)	−0.119(2)	0.087 8(5)	−0.242(2)	C(221)	0.452(2)	0.202 2(4)	0.092(2)
C(22)	−0.029(2)	0.036 6(4)	−0.325 4(15)	C(222)	0.532(2)	0.253 5(4)	−0.006 2(15)
C(01)	−0.653 5(14)	−0.022 7(4)	−0.291 3(13)	C(201)	−0.088 9(13)	0.311 7(3)	0.028 0(14)
C(02)	−0.656 0(13)	−0.012 0(4)	−0.427 3(13)	C(202)	−0.093 0(13)	0.301 3(3)	−0.108 9(14)
C(03)	−0.539 2(13)	−0.032 1(4)	−0.455 4(13)	C(203)	0.020 6(13)	0.322 1(31)	−0.138 8(14)
C(04)	−0.464 4(13)	−0.055 2(4)	−0.336 7(13)	C(204)	0.095 0(13)	0.345 3(3)	−0.020 5(14)
C(05)	−0.535 0(13)	−0.049 4(4)	−0.235 3(13)	C(205)	0.027 3(13)	0.338 9(3)	0.082 6(14)
C(06)	−0.376(2)	0.005 8(5)	−0.039(2)	C(206)	0.184(2)	0.282 5(4)	0.276 1(2)
C(3)	−0.171(2)	−0.011 2(4)	−0.235 3(15)	C(23)	0.401 6(13)	0.302 0(4)	0.091 2(11)
C(4)	0.014(4)	−0.107 9(7)	−0.589(3)	C(24)	0.580(4)	0.397 4(6)	−0.265(3)
C(5)	0.003(2)	0.049 1(4)	−0.035 3(14)	C(25)	0.578(2)	0.242 1(4)	0.287 3(15)
C(6)	−0.406 5(14)	0.048 3(4)	−0.347 1(12)	C(26)	0.154 1(2)	0.241 6(4)	−0.027 6(14)
C(7)	−0.364(2)	0.056 6(3)	−0.197 6(12)	C(27)	0.192 2(14)	0.233 9(4)	0.112 7(13)
C(31)	−0.118 9(11)	−0.035 6(2)	−0.325 6(8)	C(231)	0.448 3(12)	0.326 5(3)	−0.001 3(8)
C(32)	−0.171 6(11)	−0.029 7(2)	−0.474 8(8)	C(232)	0.540 8(12)	0.355 8(3)	0.062 5(8)
C(33)	−0.131 7(11)	−0.053 0(2)	−0.560 8(8)	C(233)	0.581 2(12)	0.379 2(3)	−0.022 9(8)
C(34)	−0.039 2(11)	−0.082 3(2)	−0.497 6(8)	C(234)	0.529 2(12)	0.373 3(3)	−0.172 2(8)
C(35)	0.013 4(11)	−0.088 3(2)	−0.348 3(8)	C(235)	0.436 8(12)	0.344 0(3)	−0.236 0(8)
C(36)	−0.026 4(11)	−0.065 0(2)	−0.262 3(8)	C(236)	0.396 3(12)	0.320 6(3)	−0.150 5(8)
C(A)	−0.407(3)	0.108 5(6)	−0.554(2)	C(2A)	0.173(3)	0.183 8(5)	−0.235(3)
C(B)	−0.727(2)	0.082 7(5)	−0.548(2)	C(2B)	−0.151(2)	0.207 0(5)	−0.239(2)
C(C)	−0.532(4)	0.036 9(6)	−0.675(2)	C(2C)	0.039(3)	0.253 5(5)	−0.360 4(15)
C(D)	−0.625(3)	0.082 2(5)	−0.109(3)	C(2D)	0.299(3)	0.197 1(5)	0.412(2)
C(E)	−0.416(3)	0.134 0(5)	−0.181(3)	C(2E)	0.130(3)	0.155 9(4)	0.125(2)
C(F)	−0.266(3)	0.092 4(6)	0.099(2)	C(2F)	−0.066(3)	0.209 7(6)	0.206(3)
O(11)	0.258(2)	−0.023 2(4)	0.028(2)	O(211)	0.823(2)	0.314 3(5)	0.353(2)
O(12)	−0.160(3)	−0.075 0(4)	0.038(2)	O(212)	0.394(3)	0.364 2(4)	0.362(2)
O(13)	−0.021(2)	0.017 8(4)	0.276 4(12)	O(213)	0.539(2)	0.272 3(4)	0.598 2(12)
O(21)	−0.082(2)	0.114 9(3)	−0.250(2)	O(221)	0.480(2)	0.172 9(3)	0.094(2)
O(22)	0.049(2)	0.034 8(4)	−0.390 0(14)	O(222)	0.613(2)	0.254 0(4)	−0.070(2)
O(06)	−0.401 3(15)	0.008 5(4)	0.064 1(12)	O(206)	0.164(2)	0.281 0(4)	0.384 4(12)
O(5)	0.103 9(14)	0.064 6(4)	0.058 3(12)	O(25)	0.679 9(15)	0.226 7(4)	0.379 9(12)
Si(1)	−0.514 2(5)	0.069 49(11)	−0.528 4(4)	Si(21)	0.055 5(5)	0.222 06(10)	−0.214 1(4)
Si(2)	−0.414 8(5)	0.090 78(10)	−0.094 8(5)	Si(22)	0.142 8(5)	0.198 69(10)	0.217 2(4)

A diethyl ether (20 cm^3) solution of [Fe_2W($μ_3$-CC_6H_4Me-4)-(μ-CO)$(CO)_8$(η-C_5H_5)] (0.60 g, 0.84 mmol) and $Bu^tC\equiv CSiMe_3$ (0.14 g, 0.84 mmol) was refluxed for 2 d until all the reactants had been consumed. Solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane (20 cm^3) and filtered through a 4-cm alumina pad. The solution was then chromatographed on alumina. Elution with light petroleum–dichloromethane (4 : 1) afforded, after removal of solvent, green *crystals* of [Fe_2W($μ_3$-CC_6H_4Me-4)(μ-$Bu^tC_2SiMe_3$)(μ-CO)-$(CO)_6$(η-C_5H_5)] (10) (0.05 g, 8%).

Crystal Structure Determinations.—(*a*) [FeW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_5$(η-C$_5$H$_5$)] (5). Crystals of compound (5) grow as red prisms. Diffracted intensities were recorded at 220 K from a crystal of dimensions *ca.* 0.40 × 0.40 × 0.24 mm. Of the total 3 946 independent reflections ($2\theta \leqslant 55°$), measured on a Nicolet *P*3*m* four-circle diffractometer, 3 334 satisfied the criterion $I \geqslant 2.5\sigma(I)$, and these were used in the solution and refinement of the structure. Intensity data were corrected for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data. $C_{22}H_{18}FeO_5W$, $M = 601.9$, monoclinic, $a = 26.01(1)$, $b = 12.880(4)$, $c = 12.554(5)$ Å, $\beta = 105.10(3)°$, $U = 4\,060(3)$ Å^3, $Z = 8$, $D_c = 1.97$ g cm^{-3}, $F(000) = 2\,320$, space group $C2$ c (no. 15), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 61.8 cm^{-1}.

The solution and refinement of the structure were similar to those for (9), described below, except in the following respects: chemically related methyl, cyclopentadienyl, and aryl hydrogen atoms were given common refined isotropic thermal parameters. Refinement with the weighting scheme $w = [\sigma^2(F) + 0.001\,|F|^2]^{-1}$ converged at *R* 0.039 (*R'* 0.044). Atom co-ordinates are listed in Table 5.

(*b*) [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-Me$_3$SiC$_2$SiMe$_3$)(μ-CO)(CO)$_6$(η-C$_5$H$_5$)] (9). Crystals grow as emerald green rectangular prisms; that chosen for data collection had dimensions *ca.* 0.30 × 0.22 × 0.42 mm. Data were collected at room temperature. Of the total 9 051 reflections ($2\theta \leqslant 60°$) only those 7 443 which satisfied the criterion $I \geqslant 2\sigma(I)$ were used in the structure solution and refinement. Check reflections 4 $\bar{7}$ $\bar{3}$ and 1 2 3 were measured every 50 reflections and showed no evidence of decay throughout the 140 h of data collection. Correction was made for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data. $C_{28}H_{30}Fe_2O_7Si_2W$, $M = 830.3$, monoclinic, $a = 8.922(5)$, $b = 38.765(15)$, $c = 10.055(4)$ Å, $\beta = 114.30(4)°$, $U = 3\,170(3)$ Å^3, $Z = 4$, $D_c = 1.74$ g cm^{-3}, $F(000) = 1\,632$, space group $P2_1$ (no. 4), μ(Mo-K_α) = 47.2 cm^{-1}.

A Patterson function enabled two independent tungsten atoms to be located, strongly suggesting $P2_1$ symmetry rather than $P2_1/m$. The remaining non-hydrogen atoms were located by successive electron-density difference syntheses. Blocked-cascade least-squares refinement was performed, with anisotropic thermal parameters for all non-hydrogen atoms. The tolyl and cyclopentadienyl rings were constrained to regular hexagonal and pentagonal geometry, respectively. Hydrogen atoms were included at calculated positions, the methyl groups being allowed to refine as rigid groups (H–C–H 109.5°). All hydrogen atoms were given a fixed isotropic thermal parameter 1.2 times U_{equiv} of the carbon atom to which they were attached. Individual weights were apportioned according to the scheme $w = [\sigma^2(F) + 0.000\,8|F|^2]^{-1}$, and refinement converged at *R* 0.051 (*R'* 0.051). Scattering factors, with corrections for the effects of anomalous dispersion for all atoms, were from ref. 23. All calculations were carried out within the Laboratory on a Data General 'Eclipse' minicomputer with the SHELXTL[24] system of programs. Atom co-ordinates are listed in Table 6.

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