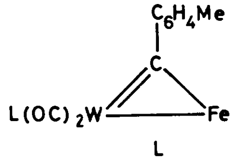
Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 65.[1] Reactions of the Complexes $[\mathrm{FeW(\mu\text{-}CR)(CO)_5(\eta\text{-}C_5Me_5)}]$ and $[\mathrm{Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)}]$ ($\mathrm{R = C_6H_4Me\text{-}4}$) with Alkynes $\mathrm{R'C_2R'}$ (R' = Me or Ph); Crystal Structures of $[\mathrm{FeW\{\mu\text{-}C(R)C(O)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)}]\cdot\mathrm{CH_2Cl_2}$ and $[\mathrm{FeW\{\mu\text{-}C(R)C(Et)C(H)C(Me)C(Me)\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)}]$ [*]

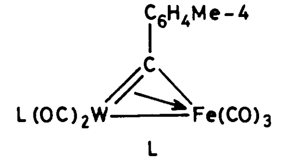
Joachim Hein, John C. Jeffery, Paul Sherwood, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The compounds $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)}]$ and $[\mathrm{Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)}]$ react with PhC≡CPh in toluene at *ca.* 85 °C to afford the complex $[\mathrm{FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Ph)C(Ph)\}(CO)_5(\eta\text{-}C_5Me_5)}]$. Similarly, the di-iron–tungsten compound and MeC≡CMe afford the related species $[\mathrm{FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)}]$. In contrast, the dimetal compound $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)}]$ and MeC≡CMe under mild conditions (*ca.* 0 °C, in $\mathrm{Et_2O}$) yield a mixture of the two complexes $[\mathrm{FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)}]$ (*ca.* 50—60%) and $[\mathrm{FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(H)C(Me)C(Me)\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)}]$ (*ca.* 5—10%). The structures of both these products have been established by *X*-ray diffraction studies. In the former the Fe–W bond [2.722(1) Å] is transversely bridged by a $\mathrm{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)C(Me)C(Me)}$ group, with the end carbon atoms of the chain σ-bonded to the tungsten, and the iron attached to the three carbon atoms carrying the two methyl and the tolyl substituents. The ketonic carbonyl group is at a non-bonding distance from both metal centres. The minor reaction product has an Fe–W bond [2.729(1) Å] bridged by a carbonyl group, the other three carbonyl groups being terminally bound to the iron. The iron atom is part of a $\overline{\mathrm{FeC(C_6H_4Me\text{-}4)C(Et)C(H)C(Me)C}}\mathrm{(Me)}$ metallacycle, with all the atoms of this six-membered ring being attached to the tungsten atom which is also ligated by the $\eta\text{-}\mathrm{C_5Me_5}$ group. The ^{1}H and ^{13}C-{^{1}H} n.m.r. data of the new compounds are reported and discussed.

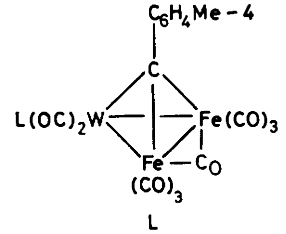
We have recently described[2] the synthesis of the iron–tungsten complexes $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_n(\eta\text{-}C_5Me_5)}]$ [n = 6 (**1a**), n = 5 (**2a**)] and $[\mathrm{Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)}]$ (**3a**). Earlier we reported[3,4] the preparation of their cyclopentadienyl analogues $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_n(\eta\text{-}C_5H_5)}]$ [n = 6 (**1b**), n = 5 (**2b**)] and $[\mathrm{Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)}]$ (**3b**). Although the pairs of dimetal compounds (**1**) and (**2**) have similar formulations their relative stabilities and reactivities towards substrate molecules are very different. Thus whereas (**2a**) can be isolated and fully characterised, although with CO it readily gives (**1a**), compound (**2b**) has only a fleeting existence at low temperatures (*ca.* −20 °C). Moreover, (**1b**) readily decomposes at room temperature, a product of this decomposition being (**3b**). In contrast with the behaviour of the dimetal species the trimetal compounds (**3**) are both robust. This has allowed studies to be made of several reactions of (**3b**),[5] including those with alkynes.[6] In order to compare further the reactivity of the (pentamethylcyclopentadienyl)tungsten–iron complexes with those of their cyclopentadienyl analogues, we describe herein reactions of (**2a**) and (**3a**) with alkynes. Reactions of the former with alkynes are of particular interest, since the instability of (**1b**) and (**2b**) precluded similar studies with these dimetal compounds.



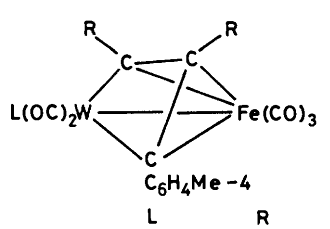
(**1a**) η-$\mathrm{C_5Me_5}$
(**1b**) η-$\mathrm{C_5H_5}$



(**2a**) η-$\mathrm{C_5Me_5}$
(**2b**) η-$\mathrm{C_5H_5}$



L
(**3a**) η-$\mathrm{C_5Me_5}$
(**3b**) η-$\mathrm{C_5H_5}$



	L	R
(**4a**)	η-$\mathrm{C_5Me_5}$	Ph
(**4b**)	η-$\mathrm{C_5H_5}$	Ph
(**4c**)	η-$\mathrm{C_5Me_5}$	Me
(**4d**)	η-$\mathrm{C_5H_5}$	Me

Results and Discussion

Compound (**3a**) with PhC≡CPh in toluene at *ca.* 85 °C affords the dimetal compound $[\mathrm{FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Ph)C(Ph)\}}$-

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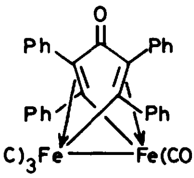
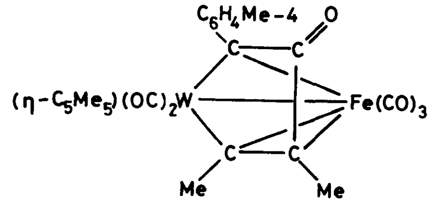
[*] 1,1,1,2,2-Pentacarbonyl-μ-[3-methyl-4-oxo-5-(*p*-tolyl)pent-2-en-2-yl-5-ylidene-C^2(Fe^1,W^2),C^3(Fe^1),C^5(Fe^1,W^2)]-2-(η-pentamethylcyclopentadienyl)irontungsten(*Fe-W*)–dichloromethane (1/1) and μ-carbonyl-1,1,1-tricarbonyl-μ-[2-ethyl-4-methyl-1-(*p*-tolyl)hexa-1,3-dien-1-yl-5-ylidene-C^1(Fe^1,W^2),C^2(W^2),C^3(W^2),C^4(W^2),C^5(Fe^1,W^2)]-2-(η-pentamethylcyclopentadienyl)irontungsten(*Fe-W*) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

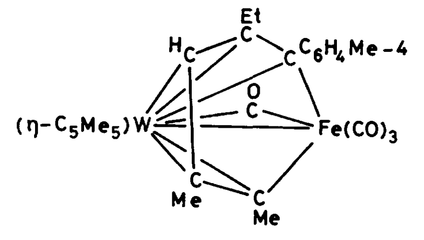
$(CO)_5(\eta\text{-}C_5Me_5)]$ (**4a**) in yields of *ca.* 80%, together with small amounts of the known compound $[Fe_2\{\mu\text{-}\sigma,\eta^2:\sigma',\eta^{2'}\text{-}C(Ph)C(Ph)C(O)C(Ph)C(Ph)\}(CO)_6]$ (**5**).[7] We showed previously that under similar conditions (**3b**) and PhC≡CPh give (**4b**).[6] Formation of the complexes (**4**) from (**3**) involves loss of an iron carbonyl fragment from the trimetal compounds. Evidently in the reaction of (**3a**) reported herein, the released iron carbonyl groups react with PhC≡CPh to give (**5**). The latter was originally prepared from $[Fe_2(CO)_9]$ and diphenylacetylene.



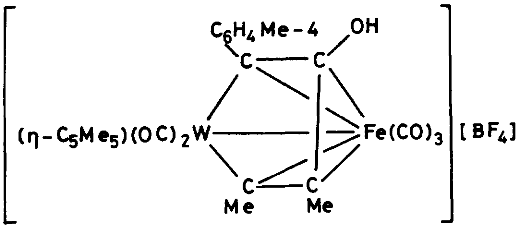
(**5**)



(**6**)



(**7**)



(**8**)

Compound (**4a**) was characterised by the analytical and spectroscopic data given in Tables 1 and 2. The mass spectrum shows a parent molecular ion. It is likely that formation of the compounds (**4a**) and (**4b**) involves intermediates in which a PhC≡CPh group edge-bridges an Fe–W bond in a trimetal species $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PhC_2Ph)(\mu\text{-}CO)(CO)_6(L)]$ (L = $\eta\text{-}C_5Me_5$ or $\eta\text{-}C_5H_5$). Coupling of the *p*-tolylmethylidyne group with the alkyne with concomitant loss of an $Fe(CO)_2$ fragment would afford (**4a**) or (**4b**). In agreement with this proposal, we isolated a stable complex $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$ from the reaction between (**3b**) and Me$_3$SiC≡CSiMe$_3$.[6]

The reaction between (**3a**) and MeC≡CMe also results in loss of an iron carbonyl fragment, and the dimetal compound $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)]$ (**4c**) is formed in yields of *ca.* 80%. The reaction occurs readily in toluene at *ca.* 85 °C, or more slowly at room temperature in light petroleum. Compound (**4d**), the cyclopentadienyl analogue of (**4c**), was obtained previously from the reaction between (**3b**) and MeC≡CMe, but in yields of only 10—30%. Data for (**4c**) are given in Tables 1 and 2, and are in accord with the formulation proposed. It may be noted that the molecular structure of (**4d**) has been established by *X*-ray diffraction,[6] and hence there is no ambiguity about the structure of species of this type.

As expected, the unsaturated compound (**2a**) reacts with PhC≡CPh to give (**4a**) in essentially quantitative yield. Surprisingly, however, the corresponding reaction between (**2a**) and MeC≡CMe did not afford (**4c**). Under mild conditions the major product is the complex $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)]$ (**6**) (*ca.* 60%), with small amounts of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(H)C(Me)C(Me)\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)]$ (**7**) (*ca.* 5—10%) also being formed. The nature of the complexes (**6**) and (**7**) was only established after *X*-ray diffraction studies had been carried out on both species, and hence discussion of their n.m.r. data (Table 2) is deferred until the structural studies have been presented.

The structure of (**6**) is shown in Figure 1, and selected bond distances and angles are given in Table 3. The Fe–W bond [2.722(1) Å] is the same length as that found in (**4d**) [2.720(1) Å],[6] and is spanned by a $\mu\text{-}C(C_6H_4Me\text{-}4)C(O)C(Me)C(Me)$ fragment. The latter is σ-bonded to the tungsten atom at C(1) and C(5), and linked to the iron atom at C(1), C(4), and C(5). The carbon atom C(2) is at a non-bonding distance from the iron [Fe–C(2) 2.49 Å] and tungsten [W–C(2) 3.04 Å] centres, and thus the C(2)O(2) group is ketonic in nature, thereby

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

Compound[b]	Colour	Yield (%)	$\nu_{max.}(CO)^c/cm^{-1}$	Analysis (%) C	H
(**4a**) $[FeW\{\mu\text{-}C(R)C(Ph)C(Ph)\}(CO)_5(\eta\text{-}C_5Me_5)]$	Deep red	79[d]	2 042s, 1 984m, 1 974m, 1 911w	[e]54.7 (55.8)	4.2 (4.1)
(**4c**) $[FeW\{\mu\text{-}C(R)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)]$	Orange	93	2 099s, 1 977s, 1 972s, 1 908w	[f]46.7 (48.2)	4.3 (4.2)
(**6**) $[FeW\{\mu\text{-}C(R)C(O)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)]$	Orange	58	[g]2 049s, 1 996m, 1 986m, 1 931w, 1 585wbr	[h]44.6 (44.4)	3.8 (3.8)
(**7**) $[FeW\{\mu\text{-}C(R)C(Et)C(H)C(Me)C(Me)\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)]$	Red	7	2 034s, 1 974m, 1 964m, 1 751w	51.6 (51.6)	5.0 (4.9)
(**8**) $[FeW\{\mu\text{-}C(R)C(OH)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)][BF_4]$	Pale orange	81	[g]2 077vs, 2 035s, 1 972m	41.5 (42.7)	3.9 (3.7)

[a] Calculated values are given in parentheses. [b] R = $C_6H_4Me\text{-}4$. [c] Measured in light petroleum unless otherwise stated. [d] From compound (**3a**). [e] *M* (mass spectrum), 796 (calc. 796). [f] *M*, 672 (672). [g] In CH_2Cl_2. [h] Crystallises with a molecule of CH_2Cl_2.

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

	^{1}H (δ)[b]	^{13}C (δ)[c]
(**4a**)	1.86 (s, 15 H, C_5Me_5), 2.20 (s, 3 H, Me-4), 6.84—7.19 (m, 10 H, Ph), 7.30, 7.31 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 2]	225.3 [WCO, *J*(WC) 139], 214.2 (FeCO), 144.4—125.3 [C_6H_4, Ph, and μ-C(C_6H_4Me-4)*C*(Ph)C(Ph)], 104.4, 103.5 [μ-*C*(C_6H_4Me-4)C(Ph)*C*(Ph)], 100.5 (*C*$_5$Me$_5$), 21.8 (Me-4), 10.6 (C$_5$*Me*$_5$)
(**4c**)	1.83 (s, 15 H, C_5Me_5), 2.08, 2.10 (s × 2, 6 H, Me), 2.25 (s, 3 H, Me-4), 6.98, 7.22 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8]	[d]226.1 [WCO, *J*(WC) 144], 224.8 [WCO, *J*(WC) 138], 214.6 (FeCO), 142.4 [C^1(C_6H_4)], 133.9, 128.5, 128.1 (C_6H_4), 127.7 [μ-C(C_6H_4Me-4)*C*(Me)C(Me)], 105.5 [μ-*C*(C_6H_4Me-4), *J*(WC) 51], 101.1 [μ-C(C_6H_4Me-4)C(Me)*C*(Me), *J*(WC) 55], 99.2 (*C*$_5$Me$_5$), 22.0, 21.5, 21.2 (Me-4 and μ-C*Me*), 10.4 (C$_5$*Me*$_5$)
(**6**)	1.96 (s, 15 H, C_5Me_5), 1.98 (s, 3 H, Me), 2.28 (s, 3 H, Me-4), 2.48 (s, 3 H, Me), 6.98, 7.14 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8]	221.5 [WCO, *J*(WC) 139], 220.5 [WCO, *J*(WC) 132], 211.8 (FeCO), 194.9 (C=O), 157.2 [μ-*C*(C_6H_4Me-4), *J*(WC) 64], 146.9 [C^1(C_6H_4)], 135.1, 131.2, 127.9 (C_6H_4), 119.9 [μ-*C*(Me)FeW, *J*(WC) 73], 119.7 [C(O)*C*(Me)C(Me)], 100.6 (*C*$_5$Me$_5$), 33.2 [μ-C(*Me*)FeW], 21.0 (Me-4), 16.7 [C(O)C(*Me*)C(Me)], 10.3 (C$_5$*Me*$_5$)
(**7**)	1.52 [t, 3 H, *J*(HH) 7, CH$_2$*Me*], 1.88 (s, 15 H, C_5Me_5), 2.31, 2.50, 2.65 [s × 3, 9 H, Me-4, C(Me)C(Me)], 4.69 (s, 1 H, CH), 6.92–7.14 (m, 4 H, C_6H_4)	[e]259.2 (μ-CO), 211.6, 208.9, 207.9 (CO), 150.2 [C^1(C_6H_4)], 134.6 (C_6H_4), 130.7 [μ-*C*(C_6H_4Me-4)], 130.0, 129.1, 128.8, 128.0 (C_6H_4), 118.9 [*C*(Me)Fe] 109.0, 108.6 [*C*(Et),*C*(Me)], 103.2 (*C*$_5$Me$_5$), 90.2 (*C*H), 31.7 (*C*Me), 27.9 (*C*H$_2$Me), 21.2, 20.2, 19.4 (CH$_2$*Me*, Me-4, C*Me*), 9.5 (C$_5$*Me*$_5$)
(**8**)	1.98 (s, 15 H, C_5Me_5), 2.29 (s, 3 H, Me-4), 2.36 [s, 3 H, C(*Me*)C(OH)], 2.52 [s, 3 H, C(*Me*)W], 7.10, 7.24 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8], 7.48 [s br, 1 H, C(OH)]	213.7 [WCO, *J*(WC) 138], 211.5 [WCO, *J*(WC) 132], 207.1 (FeCO), 168.3 [μ-*C*(C_6H_4Me-4), *J*(WC) 64], 161.9 [C^1(C_6H_4)], 140.7, 139.0 [*C*(OH)*C*(Me)], 136.3, 130.1, 128.4 (C_6H_4), 117.2 [*C*(Me)C(Me)C(OH)], 102.8 (*C*$_5$Me$_5$), 32.8 (C*Me*), 21.2 (Me-4), 16.2 (C*Me*), 10.6 (C$_5$*Me*$_5$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures unless otherwise stated. [b] Measured in CD_2Cl_2. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2 unless otherwise stated. [d] In $CDCl_3$ at −40 °C. [e] At −10 °C.

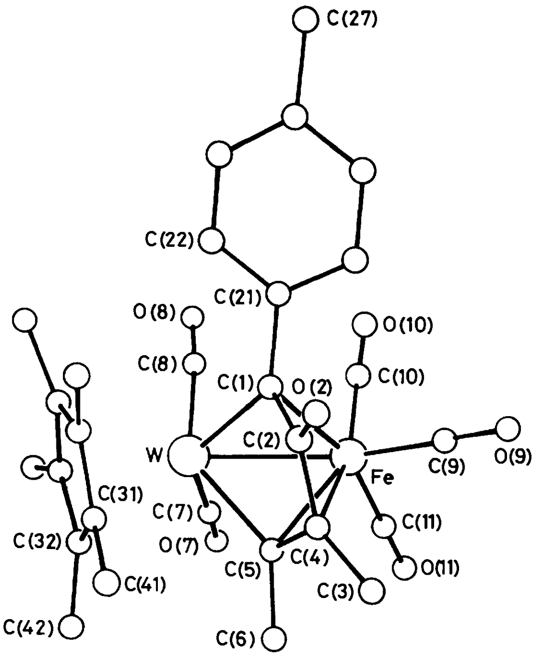


Figure 1. The molecular structure of [FeW{μ-C(C_6H_4Me-4)C(O)-C(Me)C(Me)}(CO)$_5$(η-C_5Me_5)]·CH_2Cl_2 (**6**), showing the crystallographic numbering scheme

accounting for the band observed in the i.r. spectrum of (**6**) at 1 585 cm^{-1}. The formation of (**6**) has evidently resulted from a linking of the *p*-tolylmethylidyne group, a carbonyl ligand, and a molecule of but-2-yne at the dimetal centre. We have recently isolated a related iron–molybdenum complex [FeMo{μ-C-(C_6H_4Me-4)C(O)C(Et)C(Et)}(CO)$_5$(η-C_5H_5)] from the reaction between [FeMo(μ-CC_6H_4Me-4)(CO)$_6$(η-C_5H_5)] and EtC≡CEt.[8]

In discussion[6] of the structure of (**4d**) attention was drawn to the fact that the isolobal model[9] allows this species to be regarded as an Fe(CO)$_3$ complex of a tungstacyclobutadiene moiety, since the W(CO)$_2$(η-C_5H_5) fragment is isolobal with CH. Similar considerations allow the C(1)C(2)C(4)C(5)W ring in (**6**) to be treated as a tungstacyclopentadienone 'ligand' to which an Fe(CO)$_3$ fragment is attached at C(1), W, C(5), and C(4) [Fe–C(1) 2.103(6), Fe–C(4) 2.215(6), Fe–C(5) 2.098(7) Å]. However, this view of the structure must not be over emphasised since the C(1)WC(5)C(4) fragment is distinctly non-planar. The W–C(1) and W–C(5) separations are 2.193(5) and 2.184(7) Å, respectively. The corresponding distances in (**4d**) are 2.194(6) and 2.164(7) Å.

In (**6**), the iron atom carries three carbonyl groups, and the tungsten two such groups, as well as the pentamethylcyclopentadienyl ligand. The five carbonyl groups are terminally bound to their respective metal centres with W–C(8)–O(8) [173.6(6)°] showing a slight deviation from linearity.

Having established the structure of (**6**) by *X*-ray crystallography, it became possible to assign the peaks observed in the ^{13}C-{^{1}H} n.m.r. spectrum (Table 2), although some of the assignments must remain tentative. Resonances at δ 221.5 and 220.5 p.p.m. of equal intensity show ^{183}W–^{13}C coupling and are thus attributable to the two CO ligands attached to the tungsten atom. A peak at δ 211.8 p.p.m. (three times as intense as those at 221.5 and 220.5 p.p.m.) is assigned to the Fe(CO)$_3$ fragment, the CO groups undergoing site exchange, leading to the appearance of only one signal. A resonance at 194.9 p.p.m. may be attributed to the ketonic carbonyl group. In the spectrum of the compound [FeMo{μ-C(C_6H_4Me-4)C(O)C(Et)-C(Et)}(CO)$_5$(η-C_5H_5)], which contains a similar group, the corresponding signal is at δ 186.2 p.p.m.[8] Resonances in the spectrum of (**6**) at 157.2 and 119.9 p.p.m. are assigned to the μ-*C*C_6H_4Me-4 and μ-*C*Me nuclei, respectively, since both signals show ^{183}W–^{13}C coupling, as expected for carbon atoms attached directly to tungsten. The peak at δ 119.7 which shows no ^{183}W–^{13}C coupling then remains to be assigned to the *C*(Me)C(O) nucleus. The resonances at 100.6 and 10.3 p.p.m. are due to the *C*$_5$Me$_5$ and C$_5$*Me*$_5$ groups, respectively. The signal at 21.0 p.p.m. is probably due to the Me-4 group, leaving the signals at 33.2 and 16.7 p.p.m. to be attributed to one or

Table 3. Selected internuclear distances (Å) and angles (°) for $[\mathrm{FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)]\cdot CH_2Cl_2}$ (**6**) with estimated standard deviations in parentheses

W–Fe	2.722(1)	W–C(1)	2.193(5)	W • • • C(2)	3.04	W–C(5)	2.184(7)
W–C(7)	1.999(6)	W–C(8)	2.018(7)	Fe–C(1)	2.103(6)	Fe • • • C(2)	2.49
Fe–C(4)	2.215(6)	Fe–C(5)	2.098(7)	Fe–C(9)	1.774(7)	Fe–C(10)	1.772(7)
Fe–C(11)	1.804(7)	C(1)–C(2)	1.458(8)	C(1)–C(21)	1.504(8)	C(2)–O(2)	1.246(6)
C(2)–C(4)	1.474(8)	C(4)–C(3)	1.514(10)	C(4)–C(5)	1.385(8)	C(5)–C(6)	1.519(9)
C(7)–O(7)	1.140(7)	C(8)–O(8)	1.143(9)	C(9)–O(9)	1.141(9)	C(10)–O(10)	1.147(9)
C(11)–O(11)	1.142(9)	W–C(C_5Me_5) (mean)	2.350				
Fe–W–C(1)	49.2(2)	Fe–W–C(5)	49.2(2)	C(1)–W–C(5)	73.6(2)	Fe–W–C(7)	83.6(2)
Fe–W–C(8)	89.6(2)	C(7)–W–C(8)	81.8(3)	W–Fe–C(1)	52.2(2)	C(1)–Fe–C(4)	67.2(2)
W–Fe–C(5)	51.9(2)	C(1)–Fe–C(5)	77.3(2)	C(4)–Fe–C(5)	37.3(2)	C(9)–Fe–C(10)	94.0(4)
C(9)–Fe–C(11)	96.4(3)	C(10)–Fe–C(11)	94.9(3)	W–C(1)–Fe	78.6(2)	W–C(1)–C(2)	111.3(4)
Fe–C(1)–C(2)	86.6(4)	W–C(1)–C(21)	129.2(4)	Fe–C(1)–C(21)	122.0(4)	C(2)–C(1)–C(21)	115.5(4)
C(1)–C(2)–O(2)	126.9(5)	C(1)–C(2)–C(4)	109.4(4)	O(2)–C(2)–C(4)	123.4(6)	Fe–C(4)–C(2)	82.1(3)
Fe–C(4)–C(3)	128.7(5)	C(2)–C(4)–C(3)	117.6(5)	C(2)–C(4)–C(5)	115.5(6)	C(3)–C(4)–C(5)	126.1(5)
W–C(5)–Fe	78.9(2)	W–C(5)–C(4)	115.9(4)	W–C(5)–C(6)	124.5(4)	Fe–C(5)–C(6)	124.7(5)
C(4)–C(5)–C(6)	118.3(6)	W–C(7)–O(7)	176.6(7)	W–C(8)–O(8)	173.6(6)	Fe–C(9)–O(9)	178.9(6)
Fe–C(10)–O(10)	176.5(6)	Fe–C(11)–O(11)	179.4(5)				

Table 4. Selected internuclear distances (Å) and angles (°) for $[\mathrm{FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(H)C(Me)C(Me)\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)]}$ (**7**) with estimated standard deviations in parentheses

W–Fe	2.729(1)	W–C(1)	2.147(4)	W–C(4)	2.286(4)	W–C(5)	2.335(5)
W–C(7)	2.315(5)	W–C(8)	2.134(5)	W–C(10)	2.072(5)	Fe–C(1)	2.072(5)
Fe–C(8)	2.051(5)	Fe–C(10)	2.120(5)	Fe–C(11)	1.782(6)	Fe–C(12)	1.809(5)
Fe–C(13)	1.814(5)	C(1)–C(4)	1.426(6)	C(1)–C(21)	1.499(6)	C(3)–C(2)	1.508(9)
C(3)–C(4)	1.519(7)	C(4)–C(5)	1.430(6)	C(5)–C(7)	1.423(7)	C(7)–C(6)	1.524(7)
C(7)–C(8)	1.418(7)	C(8)–C(9)	1.520(7)	C(10)–O(10)	1.170(6)	C(11)–O(11)	1.141(8)
C(12)–O(12)	1.139(7)	C(13)–O(13)	1.137(7)	W–C(C_5Me_5) (mean)	2.350		
Fe–W–C(1)	48.5(1)	C(1)–W–C(4)	37.4(2)	C(4)–W–C(5)	36.0(2)	C(5)–W–C(7)	35.6(2)
C(7)–W–C(8)	36.9(2)	C(8)–W–Fe	48.0(1)	C(1)–W–C(10)	78.0(2)	C(8)–W–C(10)	77.4(2)
C(1)–Fe–C(8)	91.9(2)	C(10)–Fe–C(12)	165.5(2)	C(11)–Fe–C(12)	99.4(3)	C(11)–Fe–C(13)	86.6(2)
C(12)–Fe–C(13)	98.9(2)	W–C(1)–Fe	80.6(2)	Fe–C(1)–C(4)	119.8(3)	W–C(1)–C(21)	137.9(3)
Fe–C(1)–C(21)	115.3(2)	C(4)–C(1)–C(21)	119.0(4)	W–C(4)–C(3)	131.6(3)	C(1)–C(4)–C(3)	122.5(4)
C(1)–C(4)–C(5)	121.1(4)	C(3)–C(4)–C(5)	116.3(4)	C(4)–C(5)–C(7)	131.1(4)	W–C(7)–C(6)	135.6(3)
C(5)–C(7)–C(6)	115.1(4)	C(5)–C(7)–C(8)	122.3(4)	C(6)–C(7)–C(8)	122.5(4)	W–C(8)–Fe	81.4(2)
Fe–C(8)–C(7)	118.5(3)	W–C(8)–C(9)	130.1(3)	Fe–C(8)–C(9)	118.7(4)	C(7)–C(8)–C(9)	118.6(4)
W–C(10)–Fe	81.2(2)	W–C(10)–O(10)	150.1(4)	Fe–C(10)–O(10)	128.4(4)	Fe–C(11)–O(11)	175.3(5)
Fe–C(12)–O(12)	178.9(5)	Fe–C(13)–O(13)	174.4(5)				

other of the methyl substitutents of the C(Me)C(Me) fragment.

The structure of the minor reaction product (**7**) was unexpected and novel, and is shown in Figure 2, with selected bond distances and angles summarised in Table 4. In (**7**) two molecules of but-2-yne have combined with the *p*-tolylmethylidyne group at the dimetal centre in a process involving not only carbon–carbon bond formation but also hydrogen shifts between carbon centres.

The Fe–W bond [2.729(1) Å], of similar length to that in (**6**), is bridged by a carbonyl group C(10)O(10) [Fe–C(10) 2.120(5), W–C(10) 2.072(5) Å, W–C(10)–O(10) 150.1(4), Fe–C(10)–O(10) 128.4(4)°]. This ligand accounts for the appearance of a band in the i.r. spectrum at 1 751 cm^{-1} (Table 1). The remaining three carbonyl groups are all terminally bound to the iron, and are orthogonal to one another.

The ends of the five-carbon chain at C(1) and C(8) are attached to the iron atom [Fe–C(1) 2.072(5), Fe–C(8) 2.051(5) Å] by σ bonds of essentially similar length. These linkages, together with the Fe–W and Fe–C(10) bonds, allow the iron atom to attain an 18-electron closed-shell configuration. The tungsten atom also attains this configuration, being ligated by the C_5Me_5 group, the bridging carbonyl group C(10)O(10), and by formally receiving six electrons from the metallacycle incorporating the six atoms $\overline{\mathrm{FeC(1)C(4)C(5)C(7)C(8)}}$. The C–C bond lengths within this ring [C(1)–C(4) 1.426(6), C(4)–C(5) 1.430(6), C(5)–C(7) 1.423(7), C(7)–C(8) 1.418(7) Å] show no significant difference indicating considerable electron delocalisation. It is tempting to view the $\overline{\mathrm{FeC(1)C(4)C(5)C(7)C(8)}}$ system as a 'ferrabenzene' fragment ligating a W(η-C_5Me_5) group, with the bridging carbonyl being present to give each metal a closed-shell configuration. The C–C distances in the metallacycle are very similar to those found in an 'osmabenzene' complex.[10] However, the presence of the metal–metal bond in (**7**) results in the $Fe(CO)_3$ group lying out of the plane defined by C(1)C(4)C(5)C(7)C(8) by 0.80 Å.

Establishment of the structure of (**7**) allows discussion of the ^1H and ^{13}C-{^1H} n.m.r. spectra of the compound (Table 2). However, not all signals could be definitively assigned. Moreover, in the ^1H spectrum, the resonance for the C*H*$_2$Me group, expected to occur as a double doublet of quartets, was not observed, probably due to the effect of a poor signal-to-noise ratio. The resonance for the CH$_2$*Me* group is seen as an apparent triplet at δ 1.52. Peaks for the other three methyl groups occur as singlets at δ 2.31, 2.50, and 2.65, but it is not possible to correlate these resonances with specific methyl substituents. A singlet peak at δ 4.69 may be assigned to the CH group in the C_5Fe metallacycle.

In the ^{13}C-{^1H} n.m.r. spectrum, the resonance at δ 259.2

p.p.m. is in the expected chemical shift region for a bridging CO group. The Fe(CO)$_3$ moiety gives rise to three peaks at a δ 211.6, 208.9, and 207.9 p.p.m., and hence these carbonyl ligands are not undergoing site-exchange on the n.m.r. time-scale. The C_6H_4 group displays six resonances, implying restricted rotation about the C(1)–C(21) bond (Figure 2). A signal at δ 27.9 p.p.m. is assigned to the CH_2 group, since in a fully coupled ^{13}C spectrum it occurs as an apparent triplet [*J*(HC) 129 Hz]. Similarly, the resonance at δ 90.2 p.p.m. is assigned to the CH group in the C_5Fe ring, since in a fully coupled spectrum it appears as a doublet [*J*(HC) 151 Hz]. The peaks at 130.7 and 118.9 p.p.m. are attributed to the *C*C_6H_4Me-4 and *C*(Me)Fe groups, respectively, since these nuclei would be expected to be somewhat deshielded, on account of their being σ-bonded to iron. The assignments made in Table 2 for the resonances at δ 109.0, 108.6, and 31.7 p.p.m. must be regarded as tentative.

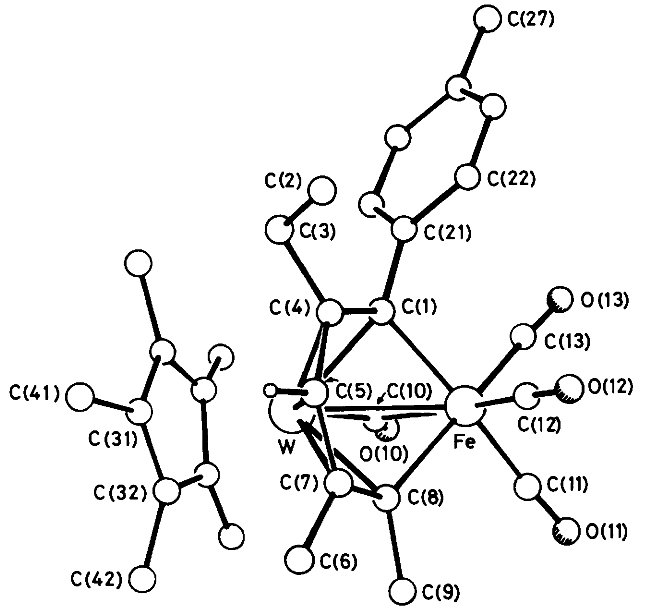
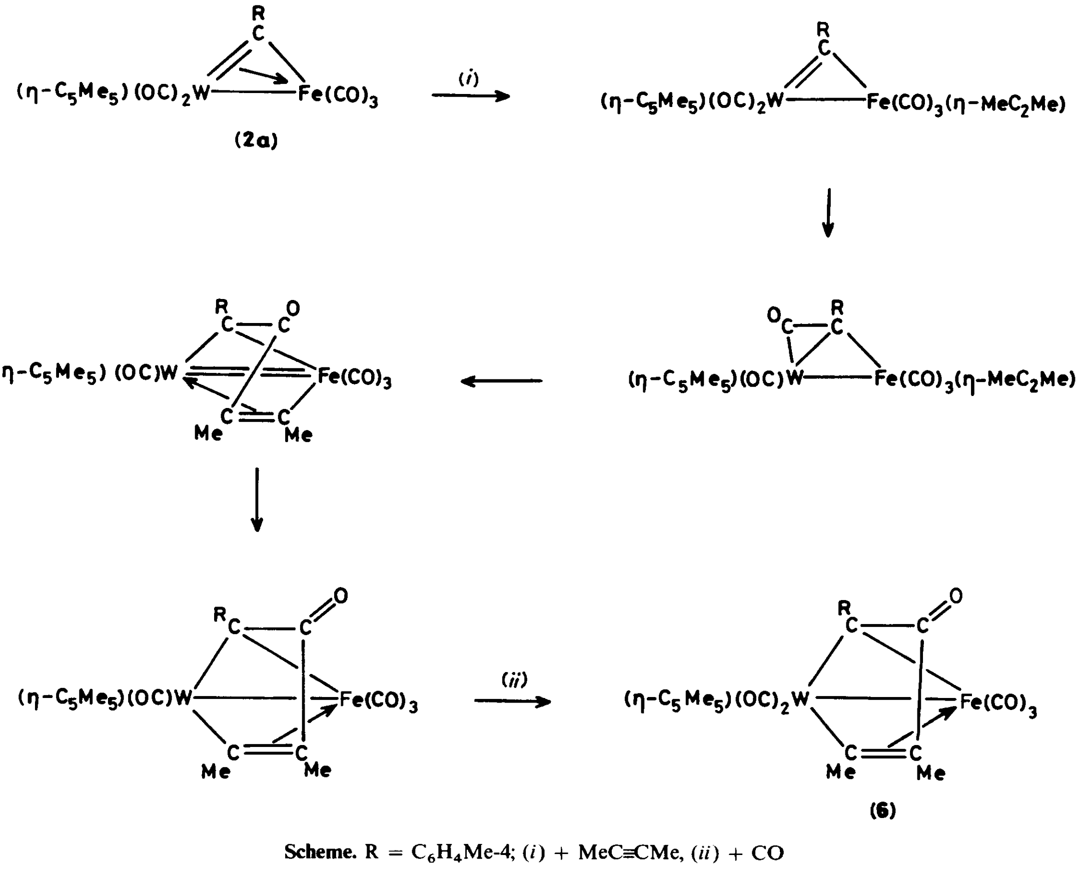


Figure 2. The molecular structure of [FeW{μ-C(C_6H_4Me-4)C(Et)C(H)-C(Me)C(Me)}(μ-CO)(CO)$_3$(η-C_5Me_5)] (**7**) showing the crystallographic numbering scheme

As mentioned earlier, formation of compounds (**6**) and (**7**) from the reaction between (**2a**) and MeC≡CMe was unexpected, because (**2a**) with PhC≡CPh had given (**4a**), a product formed by coupling of the μ-CC_6H_4Me-4 ligand with the alkyne. It is easy to visualise that this might occur *via* an intermediate in which PhC≡CPh is co-ordinated to the iron centre in an electronically saturated species [FeW(μ-CC_6H_4Me-4)(CO)$_5$-(η-PhC_2Ph)(η-C_5Me_5)]. Carbon–carbon bond formation between the μ-CC_6H_4Me-4 and PhC_2Ph ligands would then produce (**4a**). The electronic unsaturation of (**2a**) would facilitate the process which occurs in high yield. The pathways by which (**6**) and (**7**) are formed, however, are obscure at present. Complex (**6**) is produced in very good yield (*ca.* 60%), a somewhat surprising result as it contains one more carbonyl group than its precursor (**2a**). Evidently a reactive intermediate is produced which effectively scavenges a CO molecule from other species present. One of several possible pathways is depicted in the Scheme. As indicated, migration of a CO group terminally bound to tungsten to the alkylidyne fragment is invoked, thereby generating a ketenyl ligand. This is now a well established process,[11] and relevant also is the recently observed photo-induced carbonylation of [W(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)]



Scheme. R = C_6H_4Me-4; (*i*) + MeC≡CMe, (*ii*) + CO

Table 5. Fractional atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses, for (**6**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1 895(1)	1 688(1)	1 006(1)	C(23)	3 581(4)	−2 216(8)	2 637(3)
Fe	921(1)	1 465(1)	1 825(1)	C(24)	3 454(4)	−2 637(8)	3 236(3)
C(1)	2 199(4)	1 191(7)	2 090(3)	C(25)	2 905(5)	−1 785(8)	3 452(4)
C(2)	2 259(4)	2 549(7)	2 488(3)	C(26)	2 497(4)	−562(8)	3 083(3)
O(2)	2 735(3)	2 789(5)	3 065(2)	C(27)	3 882(6)	−3 960(9)	3 637(4)
C(3)	1 404(5)	4 851(9)	2 541(4)	C(31)	2 801(4)	3 644(7)	985(3)
C(4)	1 597(4)	3 578(7)	2 135(3)	C(32)	2 278(4)	3 353(8)	306(3)
C(5)	1 300(4)	3 404(7)	1 440(3)	C(33)	2 471(4)	1 886(8)	131(3)
C(6)	726(5)	4 585(8)	1 030(3)	C(34)	3 099(4)	1 272(7)	688(3)
C(7)	830(4)	1 669(8)	265(3)	C(35)	3 298(4)	2 370(8)	1 210(3)
O(7)	243(3)	1 642(7)	−180(3)	C(41)	2 916(5)	5 105(8)	1 347(4)
C(8)	1 800(4)	−531(8)	849(3)	C(42)	1 774(5)	4 480(8)	−178(4)
O(8)	1 755(4)	−1 762(6)	702(3)	C(43)	2 143(6)	1 165(10)	−566(3)
C(9)	771(4)	1 504(9)	2 635(3)	C(44)	3 575(5)	−117(10)	658(4)
O(9)	687(3)	1 523(7)	3 161(3)	C(45)	4 002(4)	2 318(10)	1 870(4)
C(10)	792(5)	−490(8)	1 734(3)	C(50)	5 723(6)	6 181(12)	940(5)
O(10)	733(4)	−1 762(6)	1 709(3)	Cl(1)	4 812(9)	6 809(20)	1 001(8)
C(11)	−121(4)	1 902(9)	1 348(4)	Cl(1a)	4 971(8)	6 366(20)	1 322(6)
O(11)	−782(4)	2 168(8)	1 042(3)	Cl(2)	5 871(5)	6 426(9)	181(3)
C(21)	2 622(4)	−150(7)	2 475(3)	Cl(2a)	5 420(5)	7 343(9)	199(3)
C(22)	3 168(4)	−1 011(7)	2 257(3)				

Table 6. Fractional atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses, for (**7**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2 040(1)	1 488(1)	1 825(1)	O(13)	1 433(5)	−279(2)	4 295(3)
Fe	428(1)	612(1)	2 795(1)	C(21)	2 463(5)	1 266(2)	4 149(3)
C(1)	1 649(5)	1 405(2)	3 276(3)	C(22)	1 792(6)	1 299(3)	5 000(3)
C(2)	821(7)	3 019(4)	4 199(5)	C(23)	2 471(6)	1 116(3)	5 807(3)
C(3)	1 870(5)	2 687(3)	3 582(4)	C(24)	3 851(6)	899(3)	5 817(4)
C(4)	1 260(5)	2 084(2)	3 065(3)	C(25)	4 513(6)	879(3)	4 980(4)
C(5)	317(5)	2 233(3)	2 316(3)	C(26)	3 827(5)	1 062(2)	4 161(3)
C(6)	−1 093(6)	2 183(3)	859(4)	C(27)	4 579(8)	680(4)	6 702(4)
C(7)	−263(5)	1 813(3)	1 611(3)	C(31)	3 181(5)	2 377(3)	1 035(3)
C(8)	−16(5)	1 107(3)	1 581(3)	C(32)	2 702(5)	1 894(3)	368(3)
C(9)	−609(6)	705(3)	770(3)	C(33)	3 399(5)	1 271(2)	555(3)
C(10)	2 286(5)	461(3)	2 051(3)	C(34)	4323(5)	1 374(2)	1 343(3)
O(10)	2 872(4)	−46(2)	1 908(3)	C(35)	4 200(5)	2 057(3)	1 621(3)
C(11)	−308(6)	−142(3)	2 322(4)	C(41)	2 846(7)	3 117(3)	1 029(4)
O(11)	−724(6)	−648(2)	2 062(3)	C(42)	1 806(6)	2 048(4)	−478(4)
C(12)	−1 103(5)	958(3)	3 332(3)	C(43)	3 348(6)	652(3)	−55(3)
O(12)	−2 078(4)	1 177(3)	3 658(3)	C(44)	5 447(5)	889(3)	1 643(4)
C(13)	1 068(6)	92(3)	3 742(4)	C(45)	5 080(6)	2 391(3)	2 350(4)

which gives the ditungsten compound $[W_2\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)C(C_6H_4Me\text{-}4)\}(CO)_4(\eta\text{-}C_5H_5)_2]$.[12] Formation of the latter also requires capture of a CO molecule from other species present.

It is noteworthy that although (**7**) is produced in low yield, its formation requires loss of two CO molecules from the precursor (**2a**). Hydrogen migration steps, probably metal assisted, are necessary to produce the C(H)C(Et) fragment found in (**7**). Related rearrangements have been observed in the reaction between but-2-yne and the iron–molybdenum compound $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$,[8] and these processes will be discussed further in a subsequent paper in this series.

During the course of the work reported herein, compound (**6**) was protonated with $HBF_4{\cdot}Et_2O$, and the salt $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(OH)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)][BF_4]$ (**8**) was thus obtained. The compound was characterised by microanalysis and spectroscopic data (Tables 1 and 2). A broad signal in the ^1H n.m.r. spectrum of (**8**) at δ 7.48 can be assigned to the OH group, the remaining signals all being shifted to lower field than their counterparts in the spectrum of (**6**). Unequivocal assignment of certain signals in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum is not possible. However, resonances at δ 213.7 and 211.5 p.p.m. are due to the tungsten ligating carbonyl groups, on account of the appearance of ^{183}W satellite peaks on these signals. A broad resonance at δ 207.1 p.p.m. is due to the $Fe(CO)_3$ moiety, and signals at δ 168.3 and 161.9 p.p.m. may be assigned to the $\mathit{C}C_6H_4Me\text{-}4$ and $\mathit{C}^1(C_6H_4)$ nuclei, respectively, the former displaying $^{183}W\text{–}^{13}C$ coupling (64 Hz). Signals at δ 140.7, 139.0, and 117.2 p.p.m. are assigned to the three $\mathit{C}(OH)\mathit{C}(Me)\mathit{C}(Me)$ nuclei. That seen at δ 140.7 p.p.m. is probably due to the C(OH) group, and replaces the resonance observed at δ 194.9 p.p.m. (C=O) in the spectrum of (**6**).

The results described in this paper demonstrate that the electronically unsaturated 32-valence-electron heteronuclear dimetal compound (**2a**) undergoes a novel reaction with but-2-yne. One C–C bond-forming process produces the fragment $C(C_6H_4Me\text{-}4)C(O)C(Me)C(Me)$ at the dimetal centre *via* introduction of one molecule of but-2-yne. In the other process, which yields (**7**), two molecules of the alkyne are used to generate C–C bonds but this is accompanied by hydrogen migrations between the carbon atoms. Reactions between alkynes and homonuclear dimetal compounds bridged by alkylidyne groups do not appear to provide such a variety of pathways for product formation.

Experimental

All experiments were carried out using Schlenk-tube techniques under a dry, oxygen-free nitrogen atmosphere, and with all solvents dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction of b.p. 40—60 °C. Chromatographic separations were carried out at *ca.* 10 °C on columns of dimensions 3 × 20 cm, packed with Brockman Activity II alumina. Infrared spectra were measured with Nicolet MX5 and MX10 spectrometers, and n.m.r. spectra with JEOL JNM GX 400, GX 270, and FX 90Q instruments. Mass spectra were performed on an AEI MS902 instrument. The compounds (**2a**) and (**3a**) were prepared as previously described.[2] Analytical and other data for the new compounds are given in Table 2.

Reactions of $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)]$ *with Alkynes*.—(*i*) A mixture of (**3a**) (0.10 g, 0.13 mmol) and PhC≡CPh (0.036 g, 0.20 mmol) was heated in toluene at 85 °C for 5.5 h, in a Schlenk tube fitted with a high-pressure stopcock. After cooling to room temperature, solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1) and the solution chromatographed. Elution with CH_2Cl_2–light petroleum (3:2) developed a large orange band, followed by a small light red band. Recovery of the orange-red eluate followed by removal of solvent *in vacuo* afforded dark red *crystals* of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Ph)C(Ph)\}(CO)_5(\eta\text{-}C_5Me_5)]$ (**4a**) (0.084 g), after crystallisation from CH_2Cl_2–light petroleum (1:10) at −78 °C. The light red eluate, after removal of solvent *in vacuo*, yielded red *microcrystals* of $[Fe_2\{\mu\text{-}\sigma,\eta^2{:}\sigma',\eta^{2'}\text{-}C(Ph)C(Ph)C(O)C(Ph)C(Ph)\}(CO)_6]$ (**5**)[7] (0.01 g, 12%) (Found: C, 62.9; H, 3.1. Calc. for $C_{35}H_{20}Fe_2O_7$: C, 63.3; H, 3.0%); $\nu_{max.}$(CO) at 2 075w, 2 051s, 2 020m, and 1 680w cm^{-1} (in light petroleum). Carbon-13 n.m.r. (at −40 °C in CD_2Cl_2–CH_2Cl_2), δ 210.5, 207.4, 206.8 (CO), 196.7 (C=O), 193.6 (*C*Ph), 148.7 [C^1(Ph)], 137.8 [C^4(Ph)], 130.2—127.6 (Ph), and 95.3 p.p.m. [*C*(Ph)C(O)*C*Ph].

(*ii*) Using a similar procedure to that employed in the synthesis of (**4a**), a mixture of (**3a**) (0.19 g, 0.24 mmol) and an excess of MeC≡CMe (*ca.* 4 cm^3) in toluene (30 cm^3) at 85 °C for 5.5 h gave orange *microcrystals* of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)]$ (**4c**) (0.15 g).

Compound (**4c**) (0.08 g) was also obtained from (**3a**) (0.38 g, 0.48 mmol) and an excess of MeC≡CMe (*ca.* 4 cm^3) in light petroleum (40 cm^3) at 10 °C for *ca.* 1 d. The crude reaction mixture was filtered through a Celite pad (*ca.* 5 cm), and solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 2:3) and chromatographed. Elution with CH_2Cl_2–light petroleum (3:2), removal of solvent *in vacuo*, and crystallisation at −78 °C from CH_2Cl_2–light petroleum (1:3), gave *crystals* of (**4c**).

Reactions of $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)]$ *with Alkynes*.—(*i*) A CH_2Cl_2 (20 cm^3) solution of (**2a**) (0.34 g, 0.55 mmol) and PhC≡CPh (0.10 g, 0.56 mmol) was stirred at room temperature for 1 h, and the reactants subsequently refluxed for 5 h to consume all of (**2a**). After removal of solvent *in vacuo*, the residue was dissolved in the minimum quantity of light petroleum–CH_2Cl_2 (3:2), and chromatographed using the same solvent mixture. Solvent was removed *in vacuo* from the red eluate, and the residue crystallised at −20 °C from CH_2Cl_2–light petroleum (1:5) to give deep red *crystals* of (**4a**) (0.34 g).

(*ii*) An Et_2O (40 cm^3) solution of (**2a**) (0.75 g, 1.21 mmol) was treated with an excess of MeC≡CMe (*ca.* 4 cm^3), and the mixture stirred for 48 h at 0 °C. Solvent was removed *in vacuo*, and the brown residue dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1) and chromatographed. Elution with the same solvent mixture afforded brown, red, and orange bands. The brown eluate was shown by i.r. spectroscopy to contain an inseparable mixture of products. Solvent was removed *in vacuo* from the red and orange eluates and the respective residues were crystallised from CH_2Cl_2–light petroleum (1:5) giving orange-red *crystals* of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)]$ (**6**) (0.49 g), and red *crystals* of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(H)C(Me)C(Me)\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)]$ (**7**) (0.06 g).

Protonation of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)]$.—Compound (**6**) (0.21 g, 0.31 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and treated with an excess of $HBF_4{\cdot}Et_2O$ (*ca.* 1.0 mmol) at 0 °C. After stirring for 0.5 h, solvent was removed *in vacuo*, and the residue washed with Et_2O (3 × 10 cm^3) and dried *in vacuo* to give pale orange *microcrystals* of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(OH)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)][BF_4]$ (**8**) (0.20 g).

Crystal Structure Determinations.—(*a*) $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5Me_5)]{\cdot}CH_2Cl_2$ (**6**). Crystals grow from a mixture of CH_2Cl_2 and light petroleum (1:5) as orange plates. Diffracted intensities were collected at 293 K on a Nicolet *P*3*m* diffractometer, from a crystal of dimensions *ca.* 0.25 × 0.35 × 0.10 mm. Of the 4 805 unique data collected [ω–2θ scans, $2\theta \leqslant 50°$, weak data with $40 \leqslant 2\theta \leqslant 50°$ being skipped if a prescan indicated that $I \lesssim 2.0\sigma(I)$], 4 012 had $I \geqslant 2.0\sigma(I)$ and only these were used in structure solution and refinement. The data were corrected for *X*-ray absorption (by an empirical method based on azimuthal scan data[13]), Lorentz, and polarisation effects.

Crystal data. $C_{28}H_{28}FeO_6W{\cdot}CH_2Cl_2$, *M* = 785.16 (including solvent), monoclinic, space group $P2_1/c$ (no. 14), *a* = 17.130(3), *b* = 8.980(1), *c* = 20.719(3) Å, β = 107.58(1)°, *U* = 3 038(1) Å^3, *Z* = 4, D_c = 1.72 g cm^{-3}, *F*(000) = 1 544, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 45.6 cm^{-1}.

The structure was solved by conventional heavy-atom methods, and successive difference Fourier syntheses were used to locate all non-hydrogen atoms, these being refined with anisotropic thermal parameters. The asymmetric unit was found to contain a disordered molecule of CH_2Cl_2, which was modelled in the final stages of refinement by four chlorine positions (site occupation = 0.5) and one carbon atom (site occupation = 1.0), each refining with anisotropic thermal parameters. All hydrogen atoms, with the exception of those in the solvent molecule, were included at calculated positions (C–H 0.96 Å) with a common refined thermal parameter for all methyl hydrogen atoms, and fixed isotropic thermal parameters (*ca.* 1.2 × $U_{equiv.}$ of the parent carbon atoms) for the phenyl hydrogen atoms. Refinement by blocked-cascade least squares led to *R* 0.033 (*R'* 0.032), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\ 35|F|^2]$ gave a satisfactory analysis of variance. An empirical isotropic extinction correction was applied.[13] The final electron-density difference synthesis showed no peaks >0.86 or < −0.65 e Å^{-3}.

(*b*) $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(H)C(Me)C(Me)\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)]$ (**7**). Crystals grow from a mixture of CH_2Cl_2 and light petroleum (1:5) as red plates. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.15 × 0.50 × 0.40 mm. Of the 4 882 unique data collected (ω–2θ scans, $2\theta \leqslant 50°$), 3 996 had $I \geqslant 2.0\sigma(I)$, and only these were used in structure solution and refinement. The data were corrected for *X*-ray absorption (by an empirical method based on azimuthal scan data[13]), Lorentz, and polarisation effects.

Crystal data. $C_{30}H_{34}FeO_4W$, *M* = 698.28, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), a = 9.589(1), b = 19.794(5), c = 14.484(2) Å, β = 91.04(1)°, U = 2 749(1) Å^3, Z = 4, D_c = 1.69 g cm^{-3}, F(000) = 1 384, μ(Mo-K_α) = 48.3 cm^{-1}.

The structure was solved as for (**6**) and thereby all non-hydrogen atoms and H(3a), H(3b), and H(5) were located. All non-hydrogen atoms were refined with anisotropic thermal parameters. Atoms H(3a), H(3b), and H(5) were refined with isotropic thermal parameters, the distances C(3)–H(3a) and C(3)–H(3b) being constrained to 0.96 Å. All other hydrogen atoms were included at calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (*ca.* 1.2 × $U_{\text{equiv.}}$ of the parent carbon atoms) for the aromatic hydrogen atoms, and common refined isotropic thermal parameters for chemically related groups of methyl hydrogen atoms. Refinement by blocked-cascade least squares converged at R 0.027 (R' 0.026), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,25|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >0.81 or < −0.53 e Å^{-3}. All calculations were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs.[13] Scattering factors and corrections for anomalous dispersion were taken from ref. 14. The atomic co-ordinates for (**6**) and (**7**) are given in Tables 5 and 6, respectively.

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