Reactions of Alkynes with Bridging Alkylidyne Ligands in Metal Complexes: *X*-Ray Crystal Structures of $[FeW\{\mu_2\text{-}C(C_6H_4Me\text{-}4)\cdot C(Me)\cdot C(Me)\}(CO)_5\text{-}(\eta\text{-}C_5H_5)]$ and $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_2\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)\text{-}(CO)_6(\eta\text{-}C_5H_5)]$

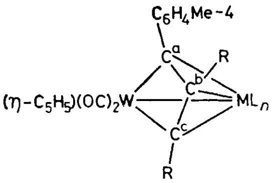
By JOHN C. JEFFERY, KEVIN A. MEAD, HAYAT RAZAY, F. GORDON A. STONE,
MICHAEL J. WENT, and PETER WOODWARD
(*Department of Inorganic Chemistry, University of Bristol, Bristol* BS8 1TS)

Summary Carbon–carbon bond formation *via* reactions of alkynes with di- or tri-metal complexes having bridging tolylidyne ligands is described, and the structures of the complexes $[FeW\{\mu_2\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)\}(CO)_5(\eta\text{-}C_5H_5)]$ and $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_2\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$ are established by *X*-ray diffraction studies.

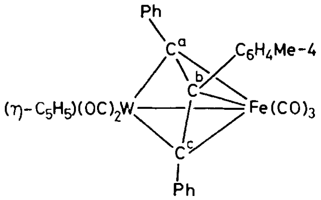
WE have previously shown[1,2] that di- and tri-metal complexes with bridging CR ligands can be synthesised in a step-wise manner from mononuclear metal carbyne complexes and low-valent compounds of other metals. Herein we report the reactivity of these species towards alkynes, leading to carbon–carbon bond formation and the isolation of metal complexes of interest in the context of isolobal relationships,[3] and of alkyne metathesis.

The dimetal compound[2] $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ reacts with PhC≡CPh (toluene, 110 °C, 2 d) to give purple crystals (80% yield) of complex (**1**). The ^{13}C n.m.r. spectrum $(CH_2Cl_2\text{–}CD_2Cl_2)$ is in accord with the structure proposed. The resonance for the ligated μ-*C* atom in the ^{13}C n.m.r. spectrum of the reactant at δ 312 p.p.m. is replaced in the spectrum of (**1**) by signals due to the $\mu_2\text{-}C^a(C_6H_4Me)\cdot C^b(Ph)\cdot C^c(Ph)$ group at δ 120·4 [C^b, *J*(RhC) 5 Hz], 104·8, and 104·4 p.p.m. [C^a and C^c, *J*(RhC) 10 Hz]. The compound $[CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ similarly reacts with PhC≡CPh and with MeC≡CMe to afford, respectively, dark green crystals of (**2**) {30% yield, ν_{CO}(hexane) 1 941s and 1 881s cm^{-1}; ^{13}C n.m.r. $(CDCl_3)$, δ 121 (C^b), 94 and 93 p.p.m. (C^a and C^c)}, and of (**3**) {40% yield; ν_{CO}(hexane) 1 937s and 1 875s cm^{-1}; ^{13}C n.m.r. $(CH_2Cl_2\text{–}CD_2Cl_2)$, δ 117 (C^b) and 92·5 and 89 p.p.m. (C^a and C^c)}.

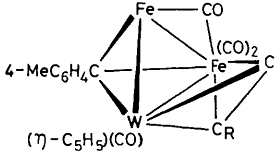
The structurally related iron–tungsten compounds (**4**)—(**7**)† were prepared by allowing the tri-metal complex $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ to react with the appropriate alkyne in toluene at 40—60 °C for several hours. In order to establish the structure of this new class of complex a single-crystal *X*-ray diffraction study of (**4**) was carried out.‡



	R	MLn
(1)	Ph	$Rh(\eta\text{-}C_9H_7)$
(2)	Ph	$Co(\eta\text{-}C_5Me_5)$
(3)	Me	$Co(\eta\text{-}C_5Me_5)$
(4)	Me	$Fe(CO)_3$
(5a)	Ph	$Fe(CO)_3$
(6)	CF_3	$Fe(CO)_3$
(7)	$C_6H_4Me\text{-}4$	$Fe(CO)_3$



(5b)



	R	R′
(8)	$SiMe_3$	$SiMe_3$
(9a)	$SiMe_3$	Bu^t
(9b)	Bu^t	$SiMe_3$

Crystal data: $C_{22}H_{18}FeO_5W$, M = 601·9, monoclinic, space group $C2/c$, a = 26·01(1), b = 12·880(4), c = 12·554(5) Å, β = 105·10(3)°, U = 4 060(3) Å^3, Z = 8, D_c = 1·97 g cm^{-3}, $F(000)$ = 2 320, $\mu(\text{Mo-}K_\alpha)$ = 61·8 cm^{-1}. Current R 0·039 (R' = 0·044) for 3 334 absorption-corrected intensities [220 K, $2\theta \leqslant 55°$, $I \geqslant 2·5\,\sigma(I)$, Nicolet *P*3*m* diffractometer, Mo-K_α ($\bar{\lambda}$ = 0·710 69 Å)].

The molecular structure (Figure 1) shows an Fe–W bond bridged by a three-carbon chain, with the tungsten atom bonded to the two terminal carbon atoms and the iron attached to all three carbon atoms. Although the bridging ligand may be regarded as an allyl group, η^3-bonded to iron and linked to tungsten by two σ bonds, an alternative description of an $Fe(CO)_3$ group η^4-bonded to a tungstacyclobutadiene ring is more attractive in view of the isolobal relation between $W(CO)_2(\eta\text{-}C_5H_5)$ and CR. However, owing to the presence of the metal–metal bond [2·720(1) Å],

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† Selected spectroscopic data (i.r. measured in methylcyclohexane, ^1H n.m.r. in $CDCl_3$, ^{13}C {^1H}-decoupled in $CDCl_3\text{–}CH_2Cl_2$): (**4**), ν_{CO} 2 041s, 1 981s, 1 961w, and 1 925w cm^{-1}; n.m.r.: ^1H, δ 1·88, 2·17, and 2·28 (3 × s, 9 H, Me), 5·04 (s, 5 H, C_5H_5), and 7·06 (m, 4 H, C_6H_4); ^{13}C, δ 220·5 and 220·4 [W*C*O, *J*(WC) 142 Hz], 214·5 (Fe*C*O), 145·1 (C^1 of C_6H_4Me-4), 135 (C^4 of C_6H_4Me-4), 130·1 (μ-C^b), 128·9 and 128·6 (C^2, C^3, C^5, and C^6 of C_6H_4Me-4), 101·1 and 99·0 [μ-C^a and μ-C^c, *J*(WC) 47 and 51 Hz], 87·9 (C_5H_5), 25·1 (μ-C^b*Me*), 21·1 (C_6H_4*Me*), and 18·2 p.p.m. (μ-C^c*Me*); (**5**), ν_{CO}, 2 049s, 1 991s, 1 965w, and 1 929m cm^{-1}; n.m.r.: measured on 2 : 1 mixture of isomers (**5a**) and (**5b**), ^1H, (**5a**) δ 2·24 (s, 3 H, Me-4), 5·12 (s, 5 H, C_5H_5), 6·85 (m, 4 H, C_6H_4), and 7·02 (m, 10 H, Ph); (**5b**), δ 2·30 (s, 3 H, Me-4), 5·12 (s, 5 H, C_5H_5), 6·96 (m, 4 H, C_6H_4), and 7·02 (m, 10 H, Ph); ^{13}C, δ 219·7 [W*C*O, *J*(WC) 140 Hz], 213·3 (Fe*C*O), 146·7—125·5 (Ph, C_6H_4, and μ-C^b), 100·0, 99·3, and 99·0 (μ-C^a and μ-C^c), 88·8 (C_5H_5), 21·0 (Me-4), and 21·3 p.p.m. (Me-4); (**6**), ^{19}F n.m.r. ($CDCl_3$, rel. CCl_3F external, positive shifts to high frequency), δ 32·88 [q, 3 F, CF_3, *J*(FF) 8 Hz] and 21·86 p.p.m. [q, 3 F, CF_3, *J*(FF) 8 Hz].

‡ Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

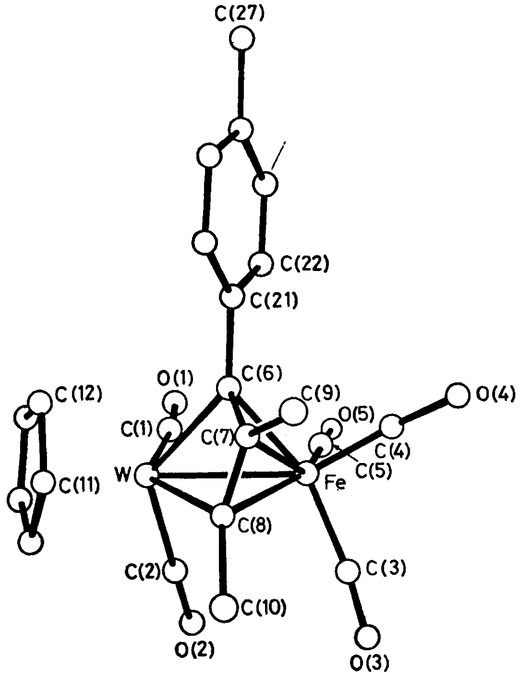

FIGURE 1. Molecular structure of [FeW{μ-C(C_6H_4Me-4)C(Me)-C(Me)}$(CO)_5(\eta$-$C_5H_5)$], (**4**). Fe–W 2·720(1), Fe–C(6) 2·047(6), Fe–C(7) 2·103(6), Fe–C(8) 2·083(6), W–C(6) 2·194(6), W–C(8) 2·154(7), C(6)–C(7) 1·440(8), C(7)–C(8) 1·435(8), Fe–CO mean 1·78(1), W–C(1) 2·03(1), W–C(2) 2·01(1) Å; ∠Fe–C(6)–W 79·7(2), Fe–C(8)–W 79·6(2), W–C(6)–C(7) 95·9(3), C(6)–C(7)–C(8) 101·9(5), C(7)–C(8)–W 97·3(4), C(8)–W–C(6) 61·6(2)°.

which is necessarily longer than the Fe–μ–C distances [mean 2·078 Å], the $\overline{\mathrm{W{\cdot}C(6){\cdot}C(7){\cdot}C(8)}}$ ring is not planar. The stability of the rings in (**1**)—(**7**) may be delicately balanced. Evidence for this was found with (**5**), the n.m.r. spectra† revealing the presence in solution of two isomers [(**5a**) and (**5b**), 2:1] corresponding to the bridge-forms C(C_6H_4Me-4)·C(Ph)·C(Ph) and C(Ph)·C(C_6H_4Me-4)·C(Ph). The statistical scrambling of the CPh and CC_6H_4Me-4 groups could proceed *via* an iron–tungsten intermediate with μ-CPh and μ-Ph$C_2C_6H_4$Me-4 ligands, rotation of the latter[4] with reformation of C–C bonds giving the mixture.

Formation of (**4**)—(**7**) involves loss of an $Fe(CO)_3$ group from [$Fe_2W(\mu$-CC_6H_4Me-4)$(CO)_9(\eta$-$C_5H_5)$]. Some understanding of the steps involved in cluster degradation was gained by studying reactions of the cluster with $Me_3SiC_2SiMe_3$ and $Bu^tC_2SiMe_3$ which afforded complexes (**8**) and (**9**), the latter as a mixture of isomers.¶ The ^{13}C n.m.r. spectrum of (**8**) showed a resonance at δ 257·7 p.p.m. for the μ_3-C atom and signals at 107·8 and 75·7 due to the alkyne-carbon atoms *C*$SiMe_3$. To establish the overall structure an *X*-ray diffraction study of (**8**) was carried out.‡

Crystal data: $C_{28}H_{30}Fe_2O_7Si_2W$, M = 830·3, monoclinic, space group $P2_1$, a = 8·922(5), b = 38·765(15), c = 10·055(4) Å, β = 114·30(4)°, U = 3 170(3) $Å^3$, D_m = 1·72 g cm^{-1}, Z = 4, D_c = 1·74 g cm^{-3}, $F(000)$ = 1 632, μ(Mo-K_α) = 47·2 cm^{-1}. Current R 0·051 (R' 0·051) for 7 443 absorption-corrected intensities [293 K, $2\theta \leqslant 60°$, $I \geqslant 4{\cdot}0\,\sigma(I)$].

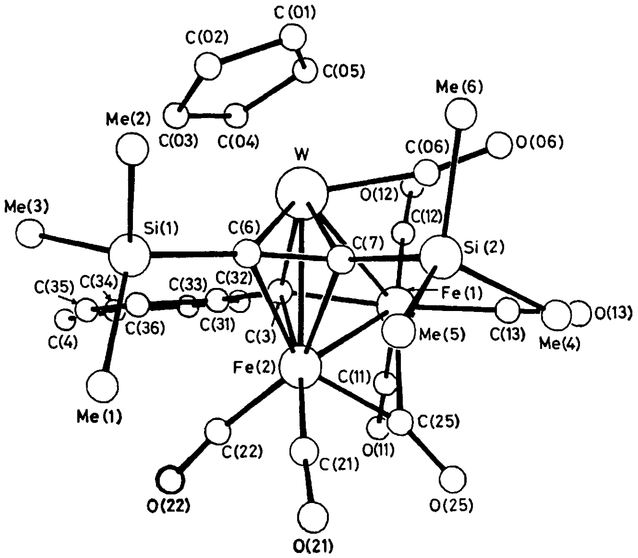

FIGURE 2. Molecular structure of [$Fe_2W(\mu_3$-CC_6H_4Me-4)(μ_2-$Me_3SiC_2SiMe_3$)(μ-CO)$(CO)_6(\eta$-$C_5H_5)$], (**8**). Dimensions of one of the two essentially equivalent molecules in the asymmetric unit are as follows. W–Fe(1) 2.775(2), W–Fe(2) 2·648(2), Fe(1)–Fe(2) 2·640(3), W–C(3) 2·075(12), Fe(1)–C(3) 1·941(11), Fe(2)–C(3) 2·154(12), W–C(6) 2·053(14), Fe(2)–C(6) 2·184(12), W–C(7) 2·107(12), Fe(2)–C(7) 2·126(13) Å; ∠W–Fe(1)–Fe(2) 58·5(1), W–Fe(2)–Fe(1) 63·3(1), Fe(1)–W–Fe(2) 58·2(1), Fe(1)–C(3)–Fe(2) 80·1(4), Fe(1)–C(3)–W 87·4(5), Fe(2)–C(3)–W 77·5(4), Fe(2)–C(6)–W 77·3(4), Fe(2)–C(7)–W 77·4(4), Si(1)–C(6)–C(7) 140·7(11), C(6)–C(7)–Si(2) 137·1(9).

The molecular structure (Figure 2) shows a near-isosceles triangle of metal atoms triply bridged by a tolylidyne ligand [though with the bridging carbon atom notably further from Fe(2) than from Fe(1)] and with the W–Fe(2) bond transversely bridged, on the opposite side of the triangle to the tolylidyne ligand, by the $Me_3SiC_2SiMe_3$ ligand. Each iron atom carries three carbonyl groups, of which one of those on Fe(2) is semibridging to Fe(1).

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¶ Selected spectroscopic data are as follows: (**8**), ν_{CO} 2 057s, 2 015s, 1 999s, 1 977m, 1 967m, 1 879w, and 1 861w cm^{-1}; n.m.r.: ^1H, δ 0·30 (s, 9 H, SiMe), 0·44 (s, 9 H, SiMe), 2·36 (s, 3 H, Me-4), 5·46 (s, 5 H, C_5H_5), and 7·3—6·9 (m, 4 H, C_6H_4); (**9a**, **b**), ν_{CO} 2 055s, 2 045w, 2 009s, 1 997s, 1 973m, 1 965m, 1 877w, and 1 861w cm^{-1}, ^{13}C n.m.r. ($CDCl_3$, {^1H}-decoupled), δ 257·2 (μ_3-C), 251·4 (μ_3-C), 239·7 (μ-CO), 236·1 (μ-CO), 220·9, 219·2, 210·6, 209·9, 209·1, 208·3, and 207·7 (7 × CO), 159·2 (C^1 of C_6H_4Me-4), 149·5 (Bu^t*C*$_2SiMe_3$), 135·9 (C^4 of C_6H_4Me-4), 129·6 (C^2, C^3, C^5, C^6 of C_6H_4Me-4), 127·6 (C^2, C^3, C^5, C^6 of C_6H_4Me-4), 112·0 (Bu^t*C*$_2SiMe_3$), 97·2 (C_5H_5), 41·0 (*C*Me_3), 38·8 (*C*Me_3), 34·2 [C(*C*$H_3)_3$], 33·4 [C(*C*$H_3)_3$], 20·9 (Me-4), 3·7 (SiMe), and 2·4 p.p.m. (SiMe).

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