Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 81.[1] Reactions of the Compound $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ with Alkylidyne–Molybdenum and –Tungsten Complexes. Reactivity of the Product $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)]$, and Crystal Structures of the Species $[W_2Fe(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}\sigma:\eta\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ and $[WFe\{\mu\text{-}C(Et)C(Et)C(H)CH(C_6H_4Me\text{-}4)\}(\mu\text{-}CO)(CO)_4(\eta\text{-}C_5H_5)]$ *

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Treatment of the compound $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ in thf (tetrahydrofuran) at room temperature with the reagents $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W, R = C_6H_4Me-4) affords the complexes $[MFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(R)\}(CO)_6(\eta\text{-}C_5H_5)]$ and $[W_2Fe(\mu_3\text{-}CR)\{\mu\text{-}\sigma:\eta\text{-}C(R){=}CH_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$. In a similar reaction, the ethylidyne–tungsten compound $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ affords a mixture of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(Me)\}(CO)_6(\eta\text{-}C_5H_5)]$, $[WFe_2(\mu_3\text{-}CEt)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$, and $[W_2Fe(\mu_3\text{-}MeC_2Me)(CO)_6(\eta\text{-}C_5H_5)_2]$. The structure of the species $[W_2Fe(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}\sigma:\eta\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ has been established by *X*-ray crystallography. The core of the molecule consists of a W_2Fe fragment [W(1)–W(2) 2.895(1), W(1)–Fe 2.738(1), W(2)–Fe 2.827(1) Å], capped by a CC_6H_4Me-4 ligand [W–μ_3-C 2.157(7) and 2.118(6) Å, Fe–μ_3-C 1.998(6) Å], and with the shorter W–Fe vector bridged by a $C(C_6H_4Me\text{-}4){=}CH_2$ group. The latter is σ bonded to the iron and is η^2-co-ordinated to the tungsten. Each tungsten is ligated by a C_5H_5 ligand. Three CO groups are attached to the iron, one to the tungsten bonded by the vinyl group, and two to the remaining tungsten atom. Some reactions of the complex $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(R)\}(CO)_6(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) with tertiary phosphines, alkynes, and the platinum reagent $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ have been studied. The products characterised include $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(R)\}(CO)_5(L)(\eta\text{-}C_5H_5)]$ [L = PPh_3, PMe_3, or dppm ($Ph_2PCH_2PPh_2$)], $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(R)\}(\mu\text{-}L_2)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)]$ [L_2 = dppm or dmpm ($Me_2PCH_2PMe_2$)], $[WFe\{\mu\text{-}C(R')C(R')C(H)CH(R)\}(\mu\text{-}CO)(CO)_4(\eta\text{-}C_5H_5)]$ (R′ = Et or Me), $[WFePt(\mu_3\text{-}CCH_2R)(CO)_6\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]$, and $[WPt\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(R)\}(CO)_3\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]$. N.m.r. data are reported and are discussed in relation to the structures proposed. An *X*-ray diffraction study established the structure of the product $[WFe\{\mu\text{-}C(Et)C(Et)C(H)CH(C_6H_4Me\text{-}4)\}(\mu\text{-}CO)(CO)_4(\eta\text{-}C_5H_5)]$ obtained from hex-3-yne. The W–Fe bond [2.798(1) Å] is asymmetrically bridged by a CO ligand [W–C–O 157.5(6)°]. The iron atom carries three terminal CO groups, and the tungsten one such group and the C_5H_5 ring. The metal–metal bond is spanned by a $C(Et)C(Et)C(H)CH(C_6H_4Me\text{-}4)$ moiety, the two ends of which are σ bonded to the iron atom, while the C(Et)C(Et)C(H) fragment is η^3-co-ordinated to the tungsten centre.

Our interest in polynuclear metal complexes with bridging alkylidene or alkylidyne ligands has been stimulated by a desire to establish rational synthetic routes to cluster compounds containing bonds between dissimilar transition elements, and also to explore the reactivity of the bridging C_1 fragments present in these species.[2] In the latter context the coupling of methylene and alkylidyne groups at di- or tri-metal centres is of particular interest in the light of stoicheiometric and catalytic processes occurring on surfaces. Previous work with molecular complexes in this area falls into two categories. In the first, a variety of C–C and metal–metal bond forming reactions take place when complexes containing ligated alkylidyne fragments are treated with metal compounds which can act as CH_2 transfer reagents, *e.g.* $[Ti\{Cl(AlMe_2)CH_2\}(\eta\text{-}C_5H_5)_2]$[3] or $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)(\eta\text{-}C_5H_5)_2]$.[4] In the second, coupling of alkylidyne and methylene fragments occurs when di- or tri-metal compounds containing μ-alkylidyne groups, *e.g.* $[MoFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$,[5] $[WFe(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)]$,[6] or $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$,[7] are treated with diazomethane. Also relevant is the observation that carbon–carbon bond formation takes place between cluster-bound COMe and CH_2 fragments.[8]

In order to extend our work in this area we have studied reactions between the alkylidyne–metal compounds $[M(\equiv CR)(CO)_2(\eta\text{-}C_5R'_5)]$ [(**1**), M = Mo, R = C_6H_4Me-4, R′ = H; M = W, R = C_6H_4Me-4 or Me, R′ = H; M = W, R = C_6H_4-Me-4, R′ = Me] and the di-iron complex $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ (**2**).[8] The investigation was stimulated by the results obtained previously with the compound $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)(\eta\text{-}C_5H_5)_2]$.[4] Moreover, it is known that compound (**2**)

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* 1,1,1,2,2,3-Hexacarbonyl-2,3-bis(η-cyclopentadienyl)-μ_3-(*p*-tolylmethylidyne)-μ-[$\sigma:\eta^2$-1′-tolylvinyl-$C^{1'2'}(W^2)$,$C^{1'}(Fe')$]iron-ditungsten(2*Fe–W*)(*W–W*) and μ-carbonyl-1,1,1,2-tetracarbonyl-2-(η-cyclopentadienyl)-μ-[3′-diethyl-1′-(*p*-tolyl)hex-3′-ene-1′,2′,4′-triyl-$C^{1',4'}$(Fe),$C^{2'-4'}$(W)]ironmolybdenum (*Fe–W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

reacts with alkynes to afford a variety of products resulting from coupling of $\mathrm{CH_2}$ and alkyne moieties.[9,10] In view of the isolobal relationship between the compounds (**1**) and alkynes,[11] it therefore seemed likely that reactions of the former species with (**2**) would yield interesting heteropolynuclear metal complexes.

Results and Discussion

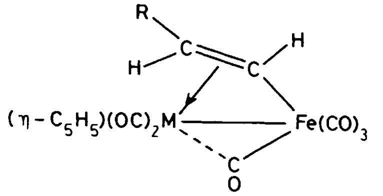
The reaction between (**1a**) and (**2**) in thf (tetrahydrofuran) at room temperature affords the dimetal compound $[\mathrm{MoFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)}]$ (**3a**). Although treatment of (**1b**) with (**2**) yields the related compound $[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)}]$ (**3b**), a further product of this reaction is the trimetal complex $[\mathrm{W_2Fe(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}\sigma:\eta\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_6(\eta\text{-}C_5H_5)_2}]$ (**4**).

$[\mathrm{M(\equiv CR)(CO)_2(\eta\text{-}C_5R'_5)}]$

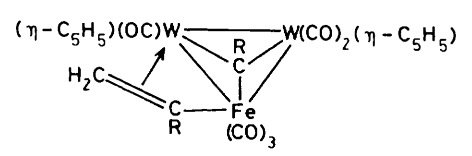
	M	R	R'
(**1a**)	Mo	$\mathrm{C_6H_4Me\text{-}4}$	H
(**1b**)	W	$\mathrm{C_6H_4Me\text{-}4}$	H
(**1c**)	W	Me	H
(**1d**)	W	$\mathrm{C_6H_4Me\text{-}4}$	Me

$[\mathrm{Fe_2(\mu\text{-}CH_2)(CO)_8}]$

(**2**)



	M	R
(**3a**)	Mo	$\mathrm{C_6H_4Me\text{-}4}$
(**3b**)	W	$\mathrm{C_6H_4Me\text{-}4}$
(**3c**)	W	Me



(**4**) R = $\mathrm{C_6H_4Me\text{-}4}$

Table 1. Analytical[a] and physical data for the new compounds

	Compound	Colour	Yield (%)	$\nu_{max.}(\mathrm{CO})$[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
(**3a**)	$[\mathrm{MoFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)}]$	Orange	27	[c] 2 077s, 2 019m, 2 006vs, 1 997vs, 1 937s, 1 882s	48.0 (47.8)	3.1 (2.8)
(**3b**)	$[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)}]$	Orange	41	[c] 2 077s, 2 018m, 2 006vs, 1 996vs, 1 932s, 1 874s	40.7 (40.7)	2.5 (2.4)
(**3c**)	$[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(Me)\}(CO)_6(\eta\text{-}C_5H_5)}]$[d]	Orange	34	[c] 2 077s, 2 017m, 2 003vs, 1 994vs, 1 933s, 1 873m	31.2 (31.3)	1.9 (2.0)
(**4**)	$[\mathrm{W_2Fe(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}\sigma:\eta\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_6(\eta\text{-}C_5H_5)_2}]$	Red	14	2 006m, 1 954vs, 1 906s, 1 846w	41.5 (42.0)	2.8 (2.8)
(**5a**)	$[\mathrm{WFe_2(\mu_3\text{-}CEt)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)}]$	Green	10	[c] 2 064s, 2 023vs, 2 008vs, 1 986s, 1 797w (br)	30.3 (29.9)	1.5 (1.6)
(**8a**)	$[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_5(PPh_3)(\eta\text{-}C_5H_5)}]$	Orange	77	[c] 2 034s, 1 975s, 1 958vs, 1 915vs, 1 858s	53.7 (53.9)	3.8 (3.5)
(**8b**)	$[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_5(PMe_3)(\eta\text{-}C_5H_5)}]$	Orange	84	2 030m, 1 957s, 1 889vs, 1 821m	41.9 (41.4)	4.7 (3.6)
(**8c**)	$[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_5(dppm)(\eta\text{-}C_5H_5)}]$	Orange	68	[c] 2 033s, 1 973s, 1 961vs, 1 914vs, 1 857s	55.5 (55.8)	4.2 (3.8)
(**8d**)	$[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_5(dmpm)(\eta\text{-}C_5H_5)}]$[e]	Orange		2 030s, 1 957s, 1 892m, 1 823m		
(**9**)	$[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_4(PMe_3)_2(\eta\text{-}C_5H_5)}]$	Red	92	1 971w, 1 896vs, 1 880 (sh), 1 787m	42.0 (42.0)	4.7 (4.7)
(**10a**)	$[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}dmpm)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)}]$	Green	66	1 961s, 1 905vs, 1 868w, 1 662m	41.4 (41.2)	4.2 (4.2)
(**10b**)	$[\mathrm{WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)}]$[f]	Green	36	1 967s, 1 914vs, 1 874 (sh), 1 667m		
(**11a**)	$[\mathrm{WFe\{\mu\text{-}C(Et)C(Et)C(H)CH(C_6H_4Me\text{-}4)\}(\mu\text{-}CO)(CO)_4(\eta\text{-}C_5H_5)}]$	Yellow	24	2 041vs, 1 974s, 1 965 (sh), 1 943 (sh), 1 781m,br	46.4 (46.6)	3.8 (3.7)
(**11b**)	$[\mathrm{WFe\{\mu\text{-}C(Me)C(Me)C(H)CH(C_6H_4Me\text{-}4)\}(\mu\text{-}CO)(CO)_4(\eta\text{-}C_5H_5)}]$	Yellow	32	2 042vs, 1 977s, 1 966 (sh), 1 943m, 1 780w,br	44.5 (44.8)	3.4 (3.2)
(**12**)	$[\mathrm{WFe\{\mu\text{-}C(Et){=}C(Et)CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)}]$[e]	Brown		2 051w, 2 023vs, 1 981s, 1 950s, 1 920 (sh)		
(**13**)	$[\mathrm{WFePt(\mu_3\text{-}CCH_2C_6H_4Me\text{-}4)(CO)_6\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)}]$	Green	56	2 028m, 2 011s, 1 986s, 1 941vs, 1 935 (sh), 1 855m,br	42.6 (42.8)	4.6 (4.4)
(**14**)	$[\mathrm{WPt\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_3\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)}]$[f]	Yellow		2 020s, 1 883s, 1 788m		

[a] Calculated values are given in parentheses. [b] In $\mathrm{CH_2Cl_2}$ unless otherwise stated. [c] In light petroleum. [d] Contains 0.5 $\mathrm{CH_2Cl_2}$ molecules of crystallisation. [e] Complex unstable, see text. [f] Complex not isolated in a pure state, see text.

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the new compounds

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]
(3a)	2.30 (s, 3 H, Me-4), 4.28 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 12], 5.07 (s, 5 H, C_5H_5), 7.04, 7.18 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7], 8.26 [d, 1 H, μ-CH, *J*(HH) 12]	241.1, 234.1 (MoCO), 211.6 (FeCO), 209.3 (br, FeCO), 140.5 [$C^1(C_6H_4)$], 137.2 (C_6H_4), 130.8 (μ-C), 129.5, 125.3 (C_6H_4), 94.9 (C_5H_5), 77.6 [*C*H(C_6H_4Me-4)], 21.2 (Me-4)
(3b)	2.30 (s, 3 H, Me-4), 4.23 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 11], 5.22 (s, 5 H, C_5H_5), 7.11 (s, br, 4 H, C_6H_4), 7.86 [d, 1 H, μ-CH, *J*(HH) 11]	[d]228.9 [WCO, *J*(WC) 174], 221.0 [WCO, *J*(WC) 168], 212.6 (br, FeCO), 210.9 (FeCO), 209.0, 204.7 (br, FeCO), 141.2 [$C^1(C_6H_4)$], 136.9, 129.4, 125.0 (C_6H_4), 118.3 [μ-C, *J*(WC) 40], 93.6 (C_5H_5), 68.9 [*C*H(C_6H_4Me-4)], 21.3 (Me-4)
(3c)	1.70 [d, 3 H, Me, *J*(HH) 5], 3.38 [d of q, 1 H, C*H*Me, *J*(HH) 10, 5], 5.43 (s, 5 H, C_5H_5), 7.04 [d, 1 H, μ-CH, *J*(HH) 10]	227.9 [WCO, *J*(WC) 174], 221.6 [WCO, *J*(WC) 159], 211.3, 209.1 (FeCO), 126.5 [μ-C, *J*(WC) 40], 92.3 (C_5H_5), 70.5 (*C*HMe), 28.1 (Me)
(4)	[e]1.21 [d, 1 H, CH_2, *J*(HH) 3], 2.34 (s, 6 H, Me-4), 2.48 [d, 1 H, CH_2, *J*(HH) 3], 5.17 (s, 5 H, C_5H_5), 5.30 (s, 5 H, C_5H_5), 7.13 (m, 8 H, C_6H_4)	222.9, 214.9, 208.7 (CO), 158.5—125.3 (C_6H_4), 98.4, 91.8 (C_5H_5), 89.0 [μ-*C*(C_6H_4Me-4)=CH_2], 39.3 (CH_2), 21.3, 21.2 (Me-4)
(5a)	1.86 [t, 3 H, Me, *J*(HH) 7], 4.20 [q, 2 H, CH_2, *J*(HH) 7], 5.25 (s, 5 H, C_5H_5)	302.5 [μ_3-C, *J*(WC) 64], 252.8 (br, μ-CO), 212.7 (FeCO), 210.3 [WCO, *J*(WC) 166], 89.4 (C_5H_5), 50.6 (CH_2), 24.3 (Me)
(8a)	2.29 (s, 3 H, Me-4), 4.07 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 12], 5.11 (s, 5 H, C_5H_5), 6.95—7.58 (m, 20 H, C_6H_4, Ph, μ-CH)	[d]232.1 [WCO, *J*(WC) 171], 224.3 [WCO, *J*(WC) 171], 218.3 [d, FeCO, *J*(PC) 15], 215.4 [d, FeCO, *J*(PC) 15], 214.4 (FeCO), 142.6—123.6 (C_6H_4, Ph, μ-CH), 93.0 (C_5H_5), 68.6 [*C*H(C_6H_4Me-4)], 21.2 (Me-4)
(8b)	1.62 [d, 9 H, PMe_3, *J*(PH) 9], 2.28 (s, 3 H, Me-4), 3.92 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 11], 5.14 (s, 5 H, C_5H_5), 7.00, 7.14 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.32 [d of d, 1 H, μ-CH, *J*(HH) 11, *J*(PH) 4]	[d]232.6 [WCO, *J*(WC) 176], 224.1 [WCO, *J*(WC) 168], 217.2 (br, FeCO), 215.2 [d, FeCO, *J*(PC) 20], 213.3 (br, FeCO), 142.9 [$C^1(C_6H_4)$], 135.8, 129.2, 124.6 (C_6H_4), 118.2 [d, μ-CH, *J*(PC) 10], 92.8 (C_5H_5), 67.3 [*C*H(C_6H_4Me-4)], 21.5 [d, PMe_3, *J*(PC) 32], 21.2 (Me-4)
(8c)	2.28 (s, 3 H, Me-4), 3.36 [d of d, 2 H, CH_2, *J*(PH) 6, 6], 3.95 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 11], 5.08 (s, 5 H, C_5H_5), 6.89—7.59 (m, 25 H, C_6H_4, Ph, μ-CH)	[d]232.1, 223.8 (WCO), 217.2 [d, FeCO, *J*(PC) 15], 214.5 [d, FeCO, *J*(PC) 15], 214.0 (FeCO), 142.4—121.7 (C_6H_4, Ph, μ-CH), 93.1 (C_5H_5), 68.1 [*C*H(C_6H_4Me-4)], 34.9 [d of d, CH_2, *J*(PC) 28, 24], 21.2 (Me-4)
(8d)	1.16 [d, 3 H, PMe, *J*(PH) 4], 1.15 [d, 3 H, PMe, *J*(PH) 4], 1.63 [d, 3 H, PMe, *J*(PH) 9], 1.70 [d, 3 H, PMe, *J*(PH) 9], 1.97 [d of d, 2 H, CH_2, *J*(PH) 2, 8], 2.28 (s, 3 H, Me-4), 3.94 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 11], 5.14 (s, 5 H, C_5H_5), 7.00, 7.14 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.39 [d of d, 1 H, μ-CH, *J*(HH) 11, *J*(PH) 4]	
(9)	1.50 (m, 18 H, PMe_3), 2.27 (s, 3 H, Me-4), 3.39 [d, 1 H, C*H*(C_6H_4-Me-4), *J*(HH) 11], 5.12 (s, 5 H, C_5H_5), 6.98, 7.07 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7], 7.21 [d, 1 H, μ-CH, *J*(HH) 11]	[d]234.4 [WCO, *J*(WC) 171], 229.0 [WCO, *J*(WC) 178], 221.8 [d of d, FeCO, *J*(PC) 33, 22], 221.2 [d of d, FeCO, *J*(PC) 26, 24], 144.0 [$C^1(C_6H_4)$], 134.8, 129.0, 124.6 (C_6H_4), 121.4 [d of d, μ-CH, *J*(PC) 12, 5], 91.2 (C_5H_5), 69.7 [*C*H(C_6H_4Me-4)], 22.8 [d, PMe_3, *J*(PC) 29], 21.2 (Me-4), 20.5 [d, PMe_3, *J*(PC) 27]
(10a)	1.40 [d, 3 H, PMe, *J*(PH) 8], 1.47 [d, 3 H, PMe, *J*(PH) 9], 1.59 [d, 3 H, PMe, *J*(PH) 9], 1.69 [d, 3 H, PMe, *J*(PH) 9], 2.24 (s, 3 H, Me-4), 2.90 [d of d, 1 H, CH_2, *J*(PH) 10, 10], 3.05 [d of d, 1 H, CH_2, *J*(PH) 11, 11], 3.93 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 13], 4.79 [d, 5 H, C_5H_5, *J*(PH) 2], 6.94, 7.18 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 11], 8.32 [d of d, 1 H, μ-CH, *J*(HH) 13, *J*(PH) 2]	305.0 [d of d, μ-CO, *J*(PC) 17, 8], 245.0 [d, WCO, *J*(PC) 9], 221.9 [d, FeCO, *J*(PC) 21], 217.0 [d, FeCO, *J*(PC) 21], 142.6, 135.6, 129.2, 125.7 (C_6H_4), 116.1 [μ-CH, *J*(WC) 64], 94.2 [d, *C*H(C_6H_4Me-4), *J*(PC) 6], 87.5 (C_5H_5), 49.6 [d of d, CH_2, *J*(PC) 31, 18], 22.7—15.6 (PMe, Me-4)
(10b)	2.21 (s, 3 H, Me-4), 3.79 (m, 2 H, CH_2), 4.12 [d, 1 H, C*H*(C_6H_4-Me-4), *J*(HH) 13], 4.68 [d, 5 H, C_5H_5, *J*(PH) 1], 6.92—7.70 (m, 24 H, C_6H_4, Ph), 8.22 [d of d, 1 H, μ-CH, *J*(HH) 13, *J*(PH) 2]	
(11a)	[e]1.18 [t, 3 H, CH_2CH_3, *J*(HH) 7], 1.60 [t, 3 H, CH_2CH_3, *J*(HH) 7], 2.19 (s, 3 H, Me-4), 2.91—3.23 (m, 4 H, CH_2), 3.42 [d, 1 H, CH, *J*(HH) 3], 4.71 [d, 1 H, CH, *J*(HH) 3], 5.21 (s, 5 H, C_5H_5), 6.74, 6.92 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[e]237.3 [WCO, *J*(WC) 173], 223.6 [WCO, *J*(WC) 161], 212.7 212.1, 204.9 (FeCO), 176.0 (*C*Et), 153.7 [$C^1(C_6H_4)$], 132.5, 128.3, 123.3 (C_6H_4), 120.7 (*C*Et), 92.1 (C_5H_5), 82.9 (CH), 44.1 (CH), 40.0 (CH_2), 26.8 (CH_2), 20.8, 20.2, 14.7 (Me)
(11b)	2.21, 2.37, 3.08 (s × 3, 9 H, Me), 3.42 [d, 1 H, CH, *J*(HH) 2], 4.61 [d, 1 H, CH, *J*(HH) 2], 5.20 (s, 5 H, C_5H_5), 6.72, 6.94 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	238.4 [WCO, *J*(WC) 171], 225.2 [WCO, *J*(WC) 161], 213.6, 213.4, 206.0 (FeCO), 166.6 (*C*Me), 154.9 [$C^1(C_6H_4)$], 133.2, 129.1, 123.6 (C_6H_4), 115.5 (*C*Me), 92.5 (C_5H_5), 85.1 (CH), 44.8 (CH), 31.6 (C*Me*), 21.0, 20.1 (C*Me*, Me-4)
(12)	1.02—1.59 (m, 7 H, 2 × Me, C*H*), 2.06 (m, 1 H, CH_2), 2.33 (s, 3 H, Me-4), 2.59, 3.76 (m, 2 H, CH_2), 5.53 (s, 5 H, C_5H_5), 6.53, 6.80 [(AB), 2 H, CH=CH, *J*(AB) 15], 7.13, 7.33 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 6]	233.8, 217.6 (WCO), 215.7 (FeCO), 167.8, 158.2, 139.3 [*C*Et, $C^1(C_6H_4)$], 136.4 (CH), 134.1, 129.8, 127.5 (C_6H_4), 122.6 (CH), 92.7 (C_5H_5), 39.0, 26.7 (CH_2), 21.5, 19.6, 16.9 (Me)
(13)	1.26—1.93 (m, 33 H, C_6H_{11}), 2.28 (s, 3 H, Me-4), 4.31, 4.43 [(AB), 2 H, CH_2, *J*(AB) 16], 5.71 (s, 5 H, C_5H_5), 7.05 (s, 4 H, C_6H_4)	[d]318.2 (μ_3-C), 221.2, 215.2, 186.8 (br, CO), 137.3 [$C^1(C_6H_4)$], 133.9, 128.5, 127.4 (C_6H_4), 92.0 (C_5H_5), 66.8 (CH_2), 35.9 [br, $C^1(C_6H_{11})$], 28.1 [d, C_6H_{11}, *J*(PC) 20], 26.2 [d, C_6H_{11}, *J*(PC) 10], 24.9 (C_6H_{11}), 19.6 (Me-4)
(14)	1.13—2.16 (m, 33 H, C_6H_{11}), 2.27 (s, 3 H, Me-4), 3.92 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 10, *J*(PtH) 12], 5.18 (s, 5 H, C_5H_5), 6.96, 6.99 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 9], 7.21 [d of d, 1 H, μ-CH, *J*(HH) 10, *J*(PH) 6]	229.6, 228.2 (WCO), 195.6 [d, PtCO, *J*(PC) 5], 144.1 [$C^1(C_6H_4)$], 133.5, 128.1 (C_6H_4), 127.4 [d, μ-CH, *J*(PC) 3], 123.9 (C_6H_4), 89.2 (C_5H_5), 39.2—19.6 [C_6H_{11}, *C*H(C_6H_4Me-4), Me-4]

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

Data characterising the products (**3a**), (**3b**), and (**4**) are listed in Tables 1 and 2.

The ^{1}H n.m.r. spectra of (**3a**) and (**3b**) contain peaks characteristic of C_6H_4Me-4 and C_5H_5 groups, but of most significance is the appearance of doublet signals for (**3a**) at δ 4.28 and 8.26 [*J*(HH) 12 Hz], and for (**3b**) at δ 4.23 and 7.86 [*J*(HH) 11 Hz]. These resonances may be assigned to a CH=CH fragment, the magnitude of the ^{1}H–^{1}H coupling firmly establishing a *trans* arrangement for the two protons.[4,12,13] In the ^{1}H n.m.r. spectrum of [WFe{μ-σ:η-CH=CH(C_6H_4Me-4)}(μ-CO)$(CO)_5$(η-C_5Me_5)], having the CH=CH(C_6H_4Me-4) moiety η-co-ordinated to the iron atom, coupling between the protons of the *trans* CH=CH group is 13 Hz.[6] The relatively low-field shift of the μ-CH protons in the spectra of (**3a**) (δ 8.26) and (**3b**) (δ 7.86) reflects the μ-carbene-like nature of these μ-C groups, a feature also observed in the ^{1}H n.m.r. spectra of homonuclear di-iron and diruthenium species with bridging vinyl groups.[13] In the ^{13}C-{^{1}H} n.m.r. spectra (Table 2) of (**3a**) and (**3b**) characteristic signals are observed for the vinyl groups {μ-CH, δ 130.8 (**3a**) and 118.3 p.p.m. [*J*(WC) 40 Hz] (**3b**); *C*H(C_6H_4Me-4), δ 77.6 (**3a**) and 68.9 p.p.m. (**3b**)}. In a ^{13}C spectrum of (**3b**) these peaks appear as doublets with *J*(HC) 154 and 165 Hz, respectively. The magnitude of the ^{183}W–^{13}C coupling on the resonance at δ 118.3 p.p.m. in the spectrum of (**3b**) provides strong evidence that the vinyl ligand is η-co-ordinated and not σ bound to the tungsten atom. Compounds containing bridging vinyl ligands σ bonded to tungsten generally have larger *J*(WC) couplings for the μ-CH group, *e.g.* [WRu_2{μ-σ:η-CH=CH(C_6H_4Me-4)}(μ-CO)$(CO)_3$(η-C_5H_5)$_3$] [*J*(WC) 96 Hz][4] and [WFe{μ-σ:η-CH=CH(C_6H_4Me-4)}(μ-CO)$(CO)_5$(η-C_5Me_5)] [*J*(WC) 58 Hz].[6]

The i.r. spectra of (**3a**) and (**3b**) show six absorptions in the carbonyl stretching region (Table 1), and the bands at 1 882 [(**3a**)] and 1 874 cm^{-1} [(**3b**)] suggest the presence of a semi-bridging CO group. Examination of the ^{13}C-{^{1}H} n.m.r. spectra reveals that the carbonyl groups undergo dynamic behaviour. The spectrum of (**3a**), measured at room temperature, exhibits signals at δ 241.1 and 234.1 p.p.m. diagnostic for carbonyls attached to molybdenum.[14] There is also a sharp peak at δ 211.6, as well as a broad resonance at 209.3 p.p.m. attributable to carbonyl ligands bonded to iron. Cooling the sample to −40 °C led to no changes in the signals due to the Mo$(CO)_2$ group or in the resonance at 211.6 p.p.m. However, the broad signal divided into three broad peaks at δ 212.1, 208.6, and 207.0 p.p.m. Similarly, the carbonyl region of the ^{13}C-{^{1}H} n.m.r. spectrum of (**3b**), measured at −40 °C, has signals due to the W$(CO)_2$ moiety at δ 228.9 [*J*(WC) 174] and 221.0 p.p.m. [*J*(WC) 168 Hz], and three broad and one sharp peak in the region associated with carbonyls bound to iron at δ 212.6 (br), 210.9, 209.0 (br), and 204.7 (br) p.p.m. Cooling the sample of (**3b**) to −80 °C gives rise to a spectrum having four sharp signals at δ 212.4, 211.1, 209.0, and 204.8 p.p.m., with little other significant change. Conversely, the ^{13}C-{^{1}H} n.m.r. spectrum, measured at ambient temperatures, has a sharp signal at 209.6 p.p.m. and a broad resonance at 207.6 p.p.m. in the region for carbonyl groups ligating an iron atom. At 80 °C (in $C_6D_5CD_3$–PhMe solvent) the spectrum shows only one resonance for the W$(CO)_2$ fragment (δ 219.4) and one signal for the carbonyls bonded to iron (δ 209.1 p.p.m.). Surprisingly, although the peak due to the μ-C nucleus remains sharp that for the *C*H(C_6H_4-Me-4) nucleus collapses, being only just visible in the spectrum at 80 °C.

The above results can be rationalised in terms of (**3a**) and (**3b**) having the structures shown and with the CO ligands at the respective metal centres being rigid on the n.m.r. time-scale at −80 °C. As the temperature is raised the pseudo-Fe$(CO)_3$ group begins to rotate slowly, leading to broadening of the three signals associated with this moiety. At higher temperatures these three carbonyl ligands display an equivalence, leading to collapse of the three broad signals to one broad resonance. At 80 °C rapid site-exchange takes place between all the iron-bound carbonyl groups leading to the appearance of one resonance due to these ligands. The apparent observation of only one signal for the tungsten-ligated carbonyl groups in the spectrum of (**3b**) at 80 °C implies that there is a mirror plane rendering the two carbonyls equivalent on the n.m.r. time-scale. Thus the μ-vinyl group must undergo a dynamic process resulting in collapse of the μ-CH resonance and the introduction of a mirror plane. The archetypal dynamic process for such ligands involves a pivoting mechanism with interchange of the σ and π bonds between the two metal centres.[12,13,15] However, for (**3a**) and (**3b**) the pivoting mechanism would not introduce a mirror plane. Moreover, it is difficult to devise a tenable mechanism without either lifting the η-co-ordination of the vinyl group to molybdenum or tungsten or invoking a more drastic rearrangement. Although a rocking motion of the W$(CO)_2$(η-C_5H_5) fragment could lead to an accidental coincidence of the signals for the tungsten-bound CO ligands, this would not explain the peculiar behaviour of the μ-C=C resonances.

The identity of compound (**4**), the second product from the reaction between (**1b**) and (**2**), did not become evident until an *X*-ray diffraction study was carried out. The important structural parameters obtained from this study are presented in Table 3, and the structure is shown in Figure 1. The core of the molecule consists of a W_2Fe fragment [W(1)–W(2) 2.895(1),

Table 3. Selected internuclear distances (Å) and angles (°) for [W_2Fe(μ_3-CC_6H_4Me-4){μ-σ:η-C(C_6H_4Me-4)=CH_2}$(CO)_6$(η-C_5H_5)$_2$] (**4**)

W(1)–W(2)	2.895(1)	W(1)–Fe	2.738(1)	W(1)–C(1)	1.964(7)	W(1)–C(7)	2.132(6)
W(1)–C(8)	2.283(6)	W(1)–C(9)	2.157(7)	W(2)–Fe	2.827(1)	W(2)–C(2)	1.968(7)
W(2)–C(3)	1.941(7)	W(2)–C(9)	2.118(6)	Fe–C(4)	1.813(7)	Fe–C(5)	1.779(7)
Fe–C(6)	1.758(7)	Fe–C(7)	2.074(7)	Fe–C(9)	1.998(6)	C(1)–O(1)	1.137(8)
C(2)–O(2)	1.152(9)	C(3)–O(3)	1.174(9)	C(4)–O(4)	1.143(8)	C(5)–O(5)	1.147(9)
C(6)–O(6)	1.159(9)	C(7)–C(8)	1.448(9)				
W(2)–W(1)–Fe	60.2(1)	Fe–W(1)–C(7)	48.5(2)	Fe–W(1)–C(8)	72.0(2)	C(7)–W(1)–C(8)	38.1(2)
W(2)–W(1)–C(9)	46.8(2)	Fe–W(1)–C(9)	46.3(2)	W(1)–W(2)–Fe	57.2(1)	C(2)–W(2)–C(3)	92.7(3)
W(1)–W(2)–C(9)	47.9(2)	Fe–W(2)–C(9)	44.9(2)	W(1)–Fe–W(2)	62.7(1)	C(4)–Fe–C(5)	92.0(3)
C(4)–Fc–C(6)	107.0(3)	C(5)–Fe–C(6)	86.5(3)	W(1)–Fe–C(7)	50.3(2)	W(1)–Fe–C(9)	51.3(2)
W(2)–Fe–C(9)	48.4(2)	W(1)–C(1)–O(1)	176.2(6)	W(2)–C(2)–O(2)	174.1(6)	W(2)–C(3)–O(3)	171.5(7)
Fe–C(4)–O(4)	174.5(7)	Fe–C(5)–O(5)	170.6(6)	Fe–C(6)–O(6)	177.8(7)	W(1)–C(7)–Fe	81.2(2)
W(1)–C(7)–C(8)	76.6(4)	Fe–C(7)–C(8)	114.0(5)	W(1)–C(7)–C(31)	133.9(4)	Fe–C(7)–C(31)	120.5(4)
C(8)–C(7)–C(31)	119.5(6)	W(1)–C(8)–C(7)	65.3(3)	W(1)–C(9)–W(2)	85.2(2)	W(1)–C(9)–Fe	82.4(2)
W(2)–C(9)–Fe	86.7(2)	W(1)–C(9)–C(41)	134.1(4)	W(2)–C(9)–C(41)	123.7(4)	Fe–C(9)–C(41)	128.8(4)

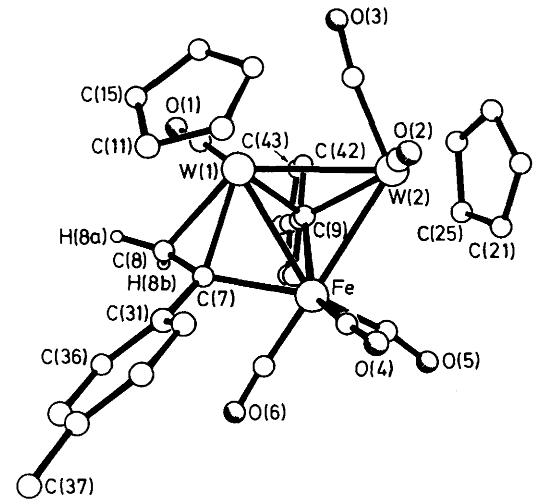


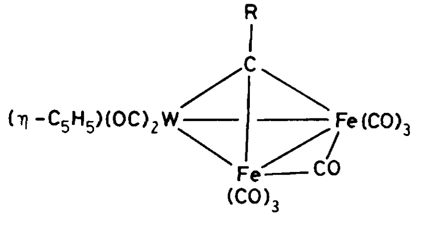
Figure 1. The molecular structure of $[W_2Fe(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(C_6H_4Me\text{-}4)\text{=}CH_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (**4**) showing the atom labelling

W(1)–Fe 2.738(1), W(2)–Fe 2.827(1) Å], capped by a *p*-tolylmethylidyne ligand [W(1)–C(9) 2.157(7), W(2)–C(9) 2.118(6), Fe–C(9) 1.998(6) Å], with the shorter tungsten–iron vector [W(1)–Fe] bridged by a $C(C_6H_4Me\text{-}4)\text{=}CH_2$ group. The latter is σ-bonded to the iron and is η^2-co-ordinated to W(1) [C(7)–C(8) 1.448(9), Fe–C(7) 2.074(7), W(1)–C(7) 2.132(6), W(1)–C(8) 2.283(6) Å].

Each tungsten atom is ligated by a C_5H_5 ring, with W(1) carrying one CO ligand and W(2) two such groups. The iron atom is bonded by three CO groups, which occupy approximately orthogonal positions. The W(2)–C(3)–O(3) and Fe–C(5)–O(5) moieties show a slight deviation from linearity with angles of 171.5(7) and 170.6(6)°, respectively. The i.r. spectrum of (**4**) (Table 1) shows a band at 1 846 cm^{-1}, suggesting that in solution a semi-bridging carbonyl group may be present; presumably resulting from a further bending of one or other of the above groups.

Having established the structure of (**4**) by *X*-ray diffraction, the n.m.r. data (Table 2) may be readily interpreted. The ^1H n.m.r. spectrum shows the presence of two non-equivalent η-C_5H_5 ligands, but only one peak for the Me-4 substituents. The latter feature is not surprising since the Me-4 fragments are relatively isolated from the remainder of the molecule. The CH_2 fragment gives rise to doublet signals at δ 1.21 and 2.48, the magnitude (3 Hz) of the ^1H–^1H coupling being as expected.[12,13] Due to the poor solubility of (**4**), the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum was not of good quality. Hence the resonance for the μ_3-C nucleus was not observed. However, peaks ascribable to the two C_5H_5 and the two Me-4 groups were seen, and resonances at δ 89.0 and 39.3 p.p.m. can be assigned to the μ-*C*$(C_6H_4Me\text{-}4)\text{=}CH_2$ and CH_2 groups, respectively. These assignments were confirmed by measurement of the proton-coupled carbon-13 spectrum. In the latter the resonance for the CH_2 unit appeared as a doublet of doublets [*J*(HC) 151 and 171 Hz], while that for the μ-*C*$(C_6H_4Me\text{-}4)$ nucleus was a doublet [*J*(HC) 5 Hz]. The latter value is characteristic of a two-bond C–H coupling,[16] presumably *trans*-*C*$(C_6H_4Me\text{-}4)\text{=}C$*H*.

The reaction between compounds (**1c**) and (**2**) was also studied. A chromatographically separable mixture of the three complexes $[WFe\{\mu\text{-}\sigma\text{:}\eta\text{-}CH\text{=}CH(Me)\}(CO)_6(\eta\text{-}C_5H_5)]$ (**3c**), $[WFe_2(\mu_3\text{-}CEt)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**5a**), and $[W_2Fe(\mu_3\text{-}MeC_2Me)(CO)_6(\eta\text{-}C_5H_5)_2]$ was obtained. The latter species has been characterised previously[17] as a product of the reaction between (**1c**) and $[Fe_2(CO)_9]$. Formation of $[W_2Fe(\mu_3\text{-}MeC_2\text{-}Me)(CO)_6(\eta\text{-}C_6H_5)_2]$ probably arises from a combination of (**1c**) with carbonyl–iron fragments present in the reaction mixture which do not contain methylene groups. Coupling of alkylidyne ligands to produce μ_3-alkyne trimetal complexes is well established.[2]



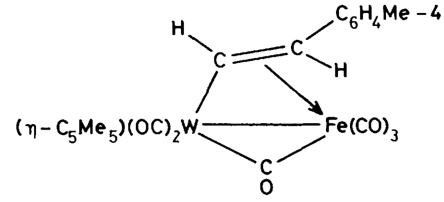
	R
(**5a**)	Et
(**5b**)	Me
(**5c**)	$C_6H_4Me\text{-}4$

The spectroscopic data for (**3c**) (Tables 1 and 2) clearly showed that it is an analogue of (**3a**) and (**3b**). Interestingly, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**3c**) measured at room temperature shows two sharp signals (δ 209.1 and 211.3 p.p.m.) due to the carbonyl groups attached to the iron. This contrasts with the one sharp and one broad resonance observed in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**3a**) and (**3b**) when recorded at room temperature. The data for (**3c**) presumably imply fast rotation of the pseudo-$Fe(CO)_3$ group at room temperature, but complete site-exchange between all carbonyl–iron sites is not taking place.

Compound (**5a**) is readily characterised by the data given in Tables 1 and 2. In particular, the spectroscopic properties are very similar to those reported for the previously characterised species $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ [R = Me (**5b**) or $C_6H_4Me\text{-}4$ (**5c**)], prepared by treating (**1b**) or (**1c**) with an excess of $[Fe_2(CO)_9]$.[17,18] In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**5a**), measured at −40 °C, the resonance at δ 302.5 p.p.m., showing ^{183}W–^{13}C coupling (64 Hz), is assigned to the μ_3-C nucleus. The signal at δ 252.8 is due to the μ-CO ligand, and the peaks at δ 212.7 and 210.3 p.p.m. [*J*(WC) 166 Hz] are attributable to the $Fe(CO)_3$ and $W(CO)_2$ groups, respectively. It is interesting to note that the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of both (**5b**) and (**5c**) measured at room temperature exhibit only one resonance for the CO ligands, indicating that site-exchange of these groups is rapid on the n.m.r. time-scale over the whole cluster.[17,18] However, the spectrum of (**5b**) when measured at −50 °C shows three signals at δ 256.8 (μ-CO), 212.8 [Fe(CO)], and 209.6 p.p.m. [W(CO)], an almost identical pattern to that shown by (**5a**) at −40 °C.

Treatment of compound (**1d**) with (**2**) in thf at room temperature afforded the complex $[WFe\{\mu\text{-}\sigma\text{:}\eta\text{-}CH\text{=}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5Me_5)]$ (**6**), previously prepared by the addition of CH_2N_2 to the dimetal compound $[WFe(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)]$.[6] Complex (**6**) is structurally related to the compounds (**3**), but differs in having the vinyl group σ-bonded to the tungsten and η^2-co-ordinated to the iron. Moreover, (**6**) contains a bridging carbonyl group. Thus, the bulky η-C_5Me_5 ligand present in (**1d**) leads to a product having the $C_6H_4Me\text{-}4$ fragment removed from proximity to the $W(\eta\text{-}C_5Me_5)$ group. The nature of the supporting ligands in the various products appears to play a critical role in the orientation of the vinyl unit, as discussed below.

An alternative preparation of an iron–tungsten complex with a bridging vinyl group has been reported. Treatment of $[W\{\sigma\text{-}CH\text{=}C(H)C(O)Ph\}(CO)_3(\eta\text{-}C_5H_5)]$ with $[Fe_2(CO)_9]$ gives a



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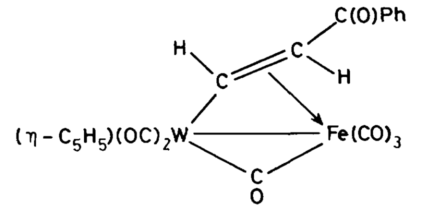
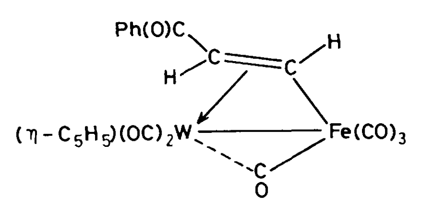


(7a)



(7b)

mixture of products including a species formulated as [WFe{μ-σ:η-CH=C(H)C(O)Ph}(μ-CO)(CO)$_5$(η-C$_5$H$_5$)] (**7**).[19] The latter was assigned a structure (**7a**) similar to (**6**) in having the vinyl group σ bonded to tungsten and η^2-co-ordinated to iron. Formulation of (**7a**) was based on ^{1}H n.m.r. spectroscopy and a partial *X*-ray diffraction study which demonstrated the presence of the Fe–W bond but failed to identify the ligands. The reported[19] i.r. spectrum of (**7**) in the metal carbonyl region is very similar to the spectra of the complexes (**3**), and is different from that of (**6**).[6] In particular, the metal carbonyl stretching band at lowest frequency for (**7**) is at 1 881 cm^{-1}, and was assigned to the μ-CO ligand. This contrasts markedly with the spectrum of (**6**) where the μ-CO absorption is seen at 1 742 cm^{-1}. It seems likely, therefore, that (**7**) has structure (**7b**) with the vinyl ligand η^2-co-ordinated to tungsten, and is thus related to the species (**3b**).

Possible routes to compounds (**3**)—(**6**) are shown in the accompanying Scheme. Formation of the intermediate (**A**), having the alkylidyne–tungsten molecule formally acting as a two-electron donor to the iron centre, has ample precedent,[2] as does coupling of the CR and CH$_2$ fragments to yield (**B**).[3,4] Loss of an iron–carbonyl group from a trimetal species MFe$_2$ (M = Mo or W) is well known,[20] and in this case yields the unsaturated species (**C**). Rearrangement of the latter to (**C′**) could readily occur *via* the well established pivoting mechanism.[12,13,15] Reaction of (**C′**) (M = W, R = C$_6$H$_4$Me-4, η-C$_5$R$'_5$ = η-C$_5$H$_5$) with (**1b**) would yield complex (**4**). Rearrangement of (**C**) to the μ-alkyne–μ-hydrido intermediate (**D**), followed by migration of hydride to the CR group of the alkyne would lead to the observed products (**3**) and (**6**). A similar reaction has been observed in the protonation of [Mo$_2$(μ-HC$_2$H)(CO)$_4$(η-C$_5$H$_5$)$_2$] to give the salt [Mo$_2$(μ-σ:η-CH=CH$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$][BF$_4$].[21]

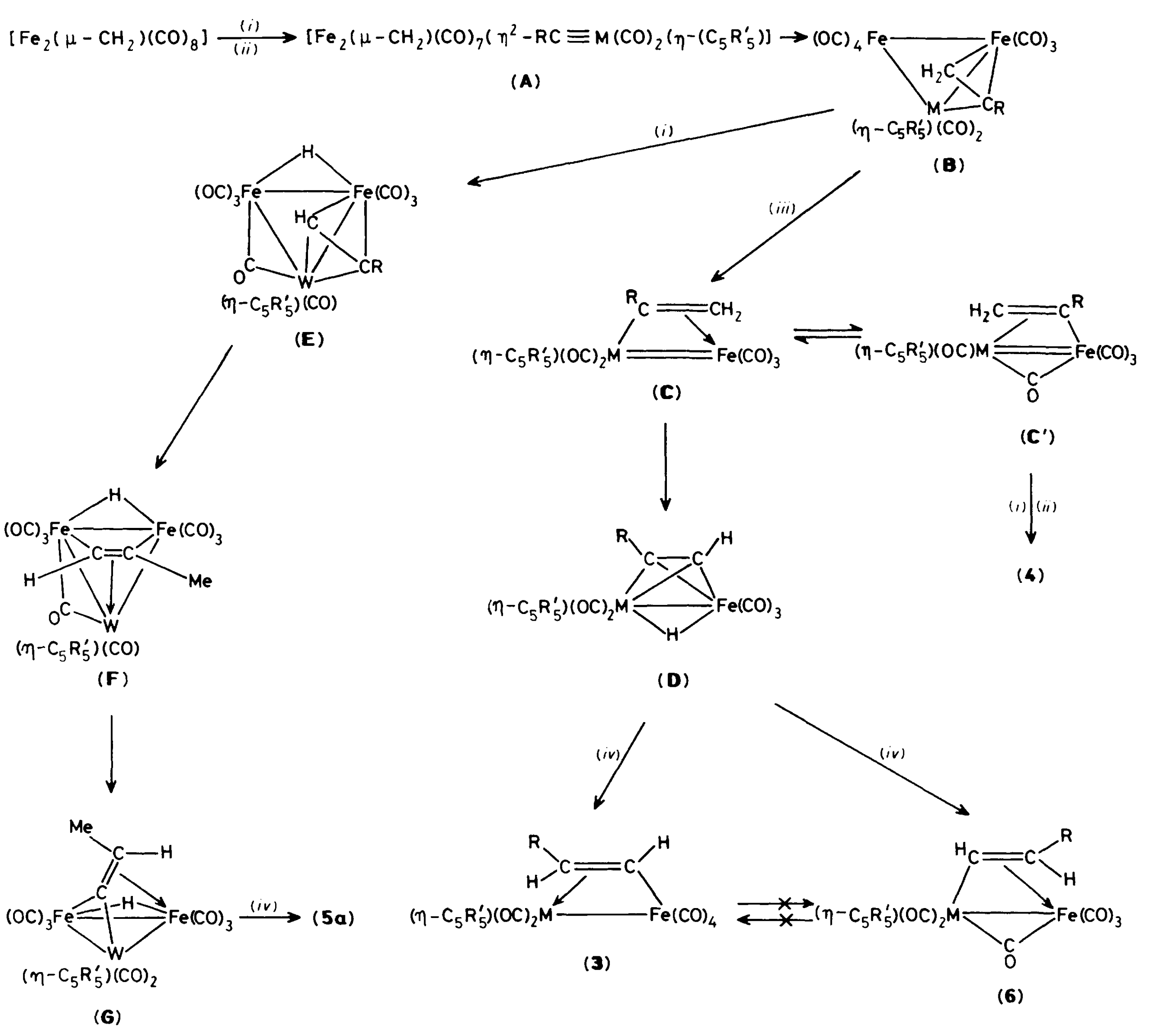
Alternatively, loss of CO from (**B**) with migration of hydrogen could afford the μ_3-(η^2-$\perp$) trimetal–alkyne complex (**E**). The shift from the alkyne bonding mode in (**E**) to that [μ_3-(η^2-$\parallel$)] in (**F**) has ample precedent,[22] as does the further transformation to (**5a**) *via* the μ_3-vinylidene intermediate (**G**).[23–26] Interestingly, treatment of (**3c**) with [Fe$_2$(CO)$_9$] did not yield (**5a**). Hence the former species is not an intermediate in the formation of the latter.

The reactivity of dimetal complexes containing bridging vinyl ligands is of interest,[12,13,19,24] and accordingly we have studied some reactions of compound (**3b**). Treatment of the latter with PPh$_3$ gives the complex [WFe{μ-σ:η-CH=CH-(C$_6$H$_4$Me-4)}(CO)$_5$(PPh$_3$)(η-C$_5$H$_5$)] (**8a**). Similarly, treatment of (**3b**) with one equivalent of PMe$_3$ afforded the complex [WFe{μ-σ:η-CH=CH(C$_6$H$_4$Me-4)}(CO)$_5$(PMe$_3$)(η-C$_5$H$_5$)] (**8b**), as well as a small amount of the bis(trimethylphosphine) species [WFe{μ-σ:η-CH=CH(C$_6$H$_4$Me-4)}(CO)$_4$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (**9**). The spectroscopic data for (**8a**) and (**8b**) indicate that they have similar structures (Tables 1, 2, and 4). Moreover, the ^{31}P-{^{1}H} n.m.r. resonances for (**8a**) [δ 57.2 p.p.m., *J*(WP) 44 Hz] and (**8b**) (δ 15.5 p.p.m.) show only small or zero ^{183}W–^{31}P coupling, respectively, in accord with the phosphine ligands being bonded to iron and not to the tungsten centre.[18,27] In the ^{1}H n.m.r. spectrum of (**8a**) a doublet resonance at δ 4.07 [*J*(HH) 12 Hz] reveals that the vinyl ligand is *trans* in nature, as in the precursor. The resonance due to the μ-CH proton was not observed, presumably being obscured under signals for the PPh$_3$ group. In the spectrum of (**8b**), however, the presence of the *trans*-CH=CH(C$_6$H$_4$Me-4) fragment was clearly revealed with a doublet resonance at δ 3.92 [*J*(HH) 11 Hz] due to the C*H*(C$_6$H$_4$Me-4) proton, and a doublet of doublets signal at δ 7.32 [*J*(HH) 11, *J*(PH) 4 Hz] due to the μ-C*H* proton. The ^{13}C-{^{1}H} n.m.r. spectra of (**8a**) and (**8b**) are also in agreement with the formulations proposed. In particular, the spectrum of (**8b**) shows a doublet resonance at δ 118.2 p.p.m. [*J*(PC) 10 Hz] and a singlet at δ 67.3 p.p.m. These peaks may be assigned to the μ-*C*H and *C*H(C$_6$H$_4$Me-4) nuclei, respectively. The ^{31}P–^{13}C coupling on the former signal, and the absence of such coupling on the latter resonance, are again in agreement with the formulation of the μ-vinyl group being σ bonded to the iron atom. The peak for the μ-*C*H group in the ^{13}C-{^{1}H} n.m.r. spectrum of (**8a**) was obscured by resonances for the PPh$_3$ ligand. The FeCO region of the spectra of (**8a**) and (**8b**) exhibit three sharp resonances for the former and three broad signals for the latter (Table 2), suggesting that the bulky PPh$_3$ ligand in (**8a**) prevents the carbonyl ligands attached to iron from undergoing site-exchange.

Treatment of (**3b**) with an excess of PMe$_3$ affords the complex [WFe{μ-σ:η-CH=CH(C$_6$H$_4$Me-4)}(CO)$_4$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (**9**), which was obtained as a by-product in the synthesis of (**8b**). Data characterising (**9**) are given in Tables 1, 2, and 4. The absence of ^{31}P–^{31}P coupling on the two ^{31}P-{^{1}H} n.m.r. peaks for (**9**) suggests that the PMe$_3$ ligands are *cis* to one another.

Treatment of (**3b**) with the bidentate phosphines dppm (Ph$_2$PCH$_2$PPh$_2$) and dmpm (Me$_2$PCH$_2$PMe$_2$) was also studied. Compound (**3b**) with dppm affords [WFe{μ-σ:η-CH=CH(C$_6$H$_4$Me-4)}(CO)$_5$(dppm)(η-C$_5$H$_5$)] (**8c**). Examination of the ^{31}P-{^{1}H} n.m.r. spectrum of (**8c**) reveals that only one phosphorus atom of the dppm ligand is co-ordinated to a metal centre. The doublet resonance (Table 4) at δ 50.1 p.p.m. [*J*(PP) 85 Hz] is characteristic for this ligand bound to iron,[18,27a] while the doublet signal at δ −27.1 p.p.m. [*J*(PP) 85 Hz] is close to the resonance observed [δ −27.7 p.p.m., *J*(PP) 42 Hz] for the non-metal ligating PPh$_2$ group in [WFe(μ-CC$_6$H$_4$Me-4)(CO)$_4$(dppm){HB(pz)$_3$}] [HB(pz)$_3$ = hydrotris(pyrazol-1-yl)borate].[27a]

Treatment of (**3b**) with dmpm afforded a trace of [WFe{μ-σ:η-CH=CH(C$_6$H$_4$Me-4)}(CO)$_5$(dmpm)(η-C$_5$H$_5$)] (**8d**), but the main product was the complex [WFe{μ-σ:η-CH=CH(C$_6$H$_4$-

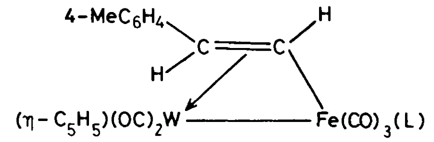


Scheme. M = Mo or W, R = C_6H_4Me-4 or Me, R′ = H or Me for (**6**). (*i*) −CO, (*ii*) +[$M(\equiv CR)(CO)_2(\eta$-$C_5R'_5)$], (*iii*) −$Fe(CO)_4$, (*iv*) +CO

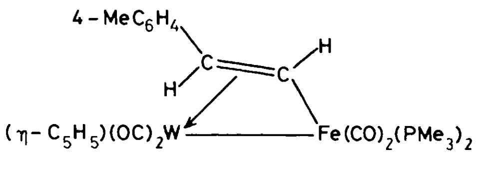
Me-4)}(μ-dmpm)(μ-CO)$(CO)_3(\eta$-$C_5H_5)$] (**10a**); the two species being readily separable by column chromatography. Compound (**8d**) is unstable, and in solution yields (**10a**). However, the i.r. and ^1H n.m.r. spectra of (**8d**) could be measured (Tables 1 and 2), and the data indicate that it is analogous to (**8c**).

The ^{31}P-{^1H} n.m.r. spectrum of (**10a**) (Table 4) revealed doublet resonances at δ 52.8 [*J*(PP) 81] and −14.9 p.p.m. [*J*(PP) 81, *J*(WP) 247 Hz] which may be attributed to the phosphorus atoms bound to the iron and tungsten atoms, respectively. The ^1H n.m.r. spectrum has signals at δ 3.93 [*J*(HH) 13] and 8.32 p.p.m. [*J*(PH) 2, *J*(HH) 13 Hz] which establishes the *trans* nature of the CH=CH(C_6H_4Me-4) ligand. The ^{13}C-{^1H} n.m.r. spectrum is very informative (Table 2). In addition to resonances attributable to the C_6H_4Me-4, η-C_5H_5, and dmpm units, signals at δ 116.1 [*J*(WC) 64] and 94.2 p.p.m. [*J*(PC) 6 Hz] may be assigned to the μ-C and *C*H(C_6H_4Me-4) nuclei of the vinyl ligand. The value of the ^{183}W–^{13}C coupling suggests that the vinyl group is now σ bound to the tungsten and η^2-co-ordinated to iron. The carbonyl region of the spectrum has two doublet resonances at δ 217.0 [*J*(PC) 21] and 221.9 p.p.m. [*J*(PC) 21 Hz] attributable to iron-ligated CO groups, and a doublet peak at δ 245.0 p.p.m. [*J*(PC) 9 Hz] for a WCO group. In addition a signal which appears as a doublet of doublets at δ 305.0 p.p.m. [*J*(PC) 17 and 8 Hz] can be assigned to a bridging carbonyl, since the carbon nucleus couples to both phosphorus atoms which are ligating different metals. The i.r. spectrum of (**10a**) has an absorption at 1 662 cm^{-1} which may be attributed to the bridging carbonyl group. The very deshielded resonance in the ^{13}C-{^1H} n.m.r. spectrum, accompanied by the low frequency i.r. stretch for this ligand, is not unusual in these systems. For example, the related molecule [WFe{μ-σ:η-CH=CH(C_6H_4Me-4)}(μ-CO)$(CO)_5(\eta$-$C_5Me_5)$] (**6**) has a peak in its ^{13}C-{^1H} n.m.r. spectrum at δ 281.6 p.p.m. attributable to the bridging carbonyl group, and an absorption in the i.r. spectrum at 1 742 cm^{-1}. Similarly, the electronically unsaturated compounds [WFe(μ-CC_6H_4Me-4)(μ-L)(μ-CO)$(CO)_2${$HB(pz)_3$}] (L = dppm or dmpm) have resonances in their ^{13}C-{^1H} n.m.r. spectra at δ 266.1 and 271.0 p.p.m. respectively, and i.r. absorptions at 1 718 and 1 668 cm^{-1}, respectively, for the μ-CO groups.[27a]

Attempts to convert compound (**8c**), which contains a pendant dppm ligand, into a complex with a μ-dppm group were only partially successful. The best method proved to be ultra-violet irradiation of thf solutions of (**8c**) which afforded



	L
(8a)	PPh_3
(8b)	PMe_3
(8c)	dppm
(8d)	dmpm



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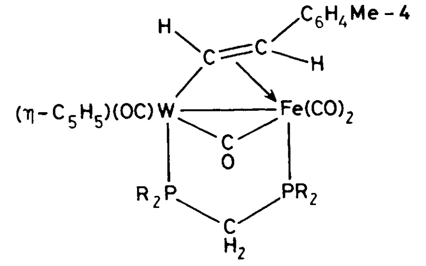
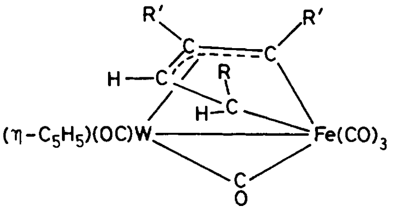


	R
(10a)	Me
(10b)	Ph

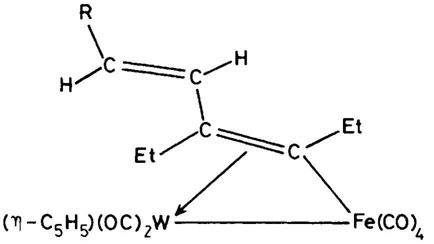
Table 4. Phosphorus-31 n.m.r. data for the new compounds

Compound	$^{31}P(\delta)$[a]
(8a)	57.2 [s, FeP, J(WP) 44]
(8b)	15.5 (s, FeP)
(8c)	50.1 [d, FeP, J(PP) 85], −27.1 [d, P, J(PP) 85]
(9)	19.5 (s, FeP), 18.8 (s, FeP)
(10a)	52.8 [d, FeP, J(PP) 81], −14.9 [d, WP, J(PP) 81, J(WP) 247]
(10b)	69.4 [d, FeP, J(PP) 93], 7.1 [d, WP, J(PP) 93, J(WP) 254]
(13)	[b]46.8 [s, PtP, J(PtP) 3 545]
(14)	36.5 [s, PtP, J(PtP) 3 030, J(WP) 15]

[a] Hydrogen-1 decoupled, chemical shifts (δ) are in p.p.m. and are positive to high frequency of 85% H_3PO_4 (external). Coupling constants are in Hz, with measurements in $CDCl_3$, unless otherwise stated. [b] Measured in CD_2Cl_2–CH_2Cl_2.



	R	R'
(11a)	C_6H_4Me-4	Et
(11b)	C_6H_4Me-4	Me



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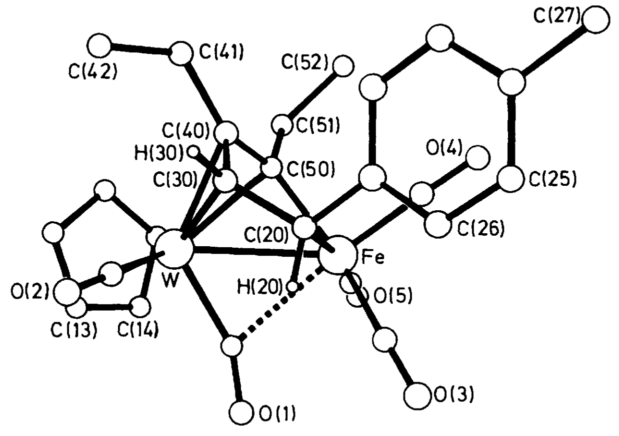


Figure 2. The molecular structure of $[WFe\{\mu\text{-}C(Et)C(Et)C(H)CH(C_6H_4\text{-}Me\text{-}4)\}(\mu\text{-}CO)(CO)_4(\eta\text{-}C_5H_5)]$ (**11a**) showing the atom labelling

$[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)]$ (**10b**). However, compound (**10b**) was not obtained pure, as evidenced by the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum. As well as peaks clearly due to (**10b**) (Table 4), there were other unidentified resonances. Furthermore, compound (**10b**) is very insoluble, and attempts to obtain good quality $^{13}C\text{-}\{^1H\}$ n.m.r. spectra were unsuccessful. However, the ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. data (Tables 2 and 4), and the similarity of the i.r. spectra of (**10a**) and (**10b**), leaves no doubt as to the nature of this compound.

The transformation of (**8c**) into (**10b**), and (**8d**) into (**10a**) is of interest. In addition to CO being eliminated, the vinyl ligand changes its orientation across the metal–metal bond, and a carbonyl ligand bridges between the two metals, so that each metal continues to obey the eighteen-electron rule. As mentioned earlier, interchange of the σ and π bonds between the two metal centres in bridging vinyl–dimetal complexes is well known.[12,13,15] However, in all previous cases the compounds are symmetric species and are either charged or contain a bridging hydrido group. Thus, in the transformation the eighteen-electron rule is maintained by formally localising the hydrido unit or charge onto one metal centre. A similar dynamic process cannot occur for the parent compound (**3b**), and any pivoting of the $\mu\text{-}CH{=}CH(C_6H_4Me\text{-}4)$ ligand if it occurred

Table 5. Selected internuclear distances (Å) and angles (°) for [WFe{μ-C(Et)C(Et)C(H)CH(C_6H_4Me-4)}(μ-CO)$(CO)_4$(η-C_5H_5)] (**11a**)

W–Fe	2.798(1)	W–C(30)	2.356(8)	W–C(40)	2.295(7)	W–C(50)	2.237(6)
W–C(1)	1.984(6)	W–C(2)	1.973(6)	Fe–C(20)	2.115(5)	Fe–C(50)	2.013(6)
Fe • • • C(1)	2.410(7)	Fe–C(3)	1.799(7)	Fe–C(4)	1.776(7)	Fe–C(5)	1.792(9)
C(20)–C(30)	1.490(7)	C(20)–C(21)	1.499(9)	C(30)–C(40)	1.411(9)	C(40)–C(50)	1.432(10)
C(40)–C(41)	1.532(9)	C(50)–C(51)	1.493(10)	C(41)–C(42)	1.501(13)	C(51)–C(52)	1.522(15)
C(1)–O(1)	1.166(8)	C(2)–O(2)	1.144(7)	C(3)–O(3)	1.146(10)	C(4)–O(4)	1.138(9)
C(5)–O(5)	1.153(12)						
Fe–W–C(30)	64.5(1)	Fe–W–C(40)	68.1(1)	C(30)–W–C(40)	35.3(2)	Fe–W–C(50)	45.4(2)
C(30)–W–C(50)	61.3(2)	C(40)–W–C(50)	36.8(2)	C(1)–W–C(2)	87.7(3)	W–Fe–C(20)	76.6(1)
W–Fe–C(50)	52.4(2)	C(20)–Fe–C(50)	85.0(2)	C(3)–Fe–C(4)	96.6(3)	C(3)–Fe–C(5)	97.4(1)
C(4)–Fe–C(5)	96.4(4)	Fe–C(20)–C(30)	99.3(4)	Fe–C(20)–C(21)	116.4(3)	C(30)–C(20)–C(21)	114.5(5)
C(20)–C(30)–C(40)	119.9(5)	C(30)–C(40)–C(50)	111.1(5)	C(30)–C(40)–C(41)	122.1(6)	C(50)–C(40)–C(41)	126.8(6)
Fe–C(50)–C(40)	112.4(4)	Fe–C(50)–C(51)	126.7(6)	C(40)–C(50)–C(51)	117.8(6)	C(40)–C(41)–C(42)	115.6(7)
C(50)–C(51)–C(52)	116.9(8)	W(1)–C(1)–O(1)	157.5(6)	Fe–C(1)–O(1)	123.3(5)	W–C(2)–O(2)	177.0(6)
Fe–C(3)–O(3)	178.0(10)	Fe–C(4)–O(4)	178.1(6)	Fe–C(5)–O(5)	178.4(8)		

would correspond to an isomerisation between two distinct structures. The orientation of the vinyl fragment in these heteronuclear dimetal systems is very dependent on the ligands present. Thus in compound (**6**), which is related to (**3b**) having the η-C_5H_5 group in the latter replaced by the η-C_5Me_5 ligand in the former, the vinyl moiety is σ bonded to the tungsten and η^2-co-ordinated to the iron.[6] In the formation of (**10a**) and (**10b**) it may be that the steric demands of the η-C_5H_5 and the μ-dmpm and μ-dppm groups force a configuration where the *p*-tolylmethyl substituent points away from the tungsten atom.

The reaction of (**3b**) with alkynes was also studied. Treatment of (**3b**) with hex-3-yne afforded a mixture of the two complexes [WFe{μ-C(Et)C(Et)C(H)CH(C_6H_4Me-4)}(μ-CO)$(CO)_4$(η-C_5H_5)] (**11a**) and [WFe{μ-C(Et)=C(Et)CH=CH(C_6H_4Me-4)}$(CO)_6$(η-C_5H_5)] (**12**), separated by chromatography. The reaction between (**3b**) and but-2-yne gave [WFe{μ-C(Me)C(Me)C(H)CH(C_6H_4Me-4)}(μ-CO)$(CO)_4$(η-C_5H_5)] (**11b**). Examination of the spectroscopic data for (**11a**) and (**11b**) (Tables 1 and 2) suggests that the compounds are closely related. An *X*-ray diffraction study was carried out on (**11a**) to establish the structure. The molecule is shown in Figure 2 and structural parameters are given in Table 5. The W–Fe separation [2.798(1) Å] is somewhat longer than those in the complexes [WFe{μ-C(C_6H_4Me-4)C(Me)C(Me)}$(CO)_5$(η-C_5H_5)] [2.720(1) Å],[20a] [WFe{μ-C(C_6H_4Me-4)C(O)C(Me)C(Me)}$(CO)_6$(η-C_5Me_5)] [2.772(1) Å],[28] and [WFe{μ-C(C_6H_4Me-4)C(Et)C(H)C(Me)C(Me)}(μ-CO)$(CO)_3$(η-C_5Me_5)] [2.729(1) Å].[28] The metal–metal bond in (**11a**) is strongly semi-bridged by a CO ligand [W–C(1)–O(1) 157.5(6)°, W–C(1) 1.98(1), Fe • • • C(1) 2.41 Å]. The iron atom is ligated by three essentially orthogonally disposed carbonyl groups, and the tungsten atom carries a terminal CO group and the C_5H_5 ring. Of most interest is the μ-C(Et)C(Et)C(H)CH(C_6H_4Me-4) fragment which is derived by coupling of the vinyl moiety with the alkyne. The two ends of this ligand [C(20) and C(50)] are σ bound to the iron atom [Fe–C(20) 2.115(5), Fe–C(50) 2.013(6) Å]. In addition C(30), C(40), and C(50) are η^3 bound to the tungsten atom [W–C(30) 2.356(8), W–C(40) 2.295(7), W–C(50) 2.237(6) Å]. The bond between C(20) and C(30) [1.490(7) Å] is only slightly shorter than that expected for a single carbon–carbon bond, whilst the other carbon–carbon separations in the ligand [C(30)–C(40) 1.411(9), C(40)–C(50) 1.432(10) Å] are intermediate between those expected for single and double bonds. The hydrogen atoms H(30) and H(40) were located in the difference map and were thus included in the least-squares refinement in fixed positions. This type of ring system has also been found in the compounds [PPh_4][Fe_2{μ-C(Ph)C(Ph)C(CF_3)CH(CF_3)}$(CO)_6$][29] and in [Co_2{μ-C(Ph)C(CO_2Me)C(Ph)CH(CO_2Me)}(μ-CO)$(CO)_2$(η-C_5H_5)].[30] In these related systems the hydrogen of the CH(R) group occupies an *exo* position. However, in (**11a**) the hydrogen occupies an *endo* position relative to the W–Fe bond, presumably to minimise steric interaction between the C_6H_4Me-4 group and the rest of the molecule.

Having established the structure of (**11a**), and by implication that of (**11b**) also, the spectroscopic data are readily interpretable. The ^1H n.m.r. spectra of (**11a**) and (**11b**) (Table 2) have peaks due to the η-C_5H_5 and C_6H_4Me-4 groups and the Et or Me substituents on the bridging ligand. In addition, doublet resonances at δ 3.42 and 4.71 [*J*(HH) 3 Hz] for (**11a**), and at δ 3.42 and 4.61 [*J*(HH) 2 Hz] for (**11b**) can be assigned to the CH and C*H*(C_6H_4Me-4) groups. The size of the coupling between the protons is of the correct magnitude[31] for the dihedral angle between the CH bonds, as found in the crystal structure (*ca.* 77°). The ^{13}C-{^1H} n.m.r. spectra of the compounds exhibit three signals characteristic of iron-ligated carbonyl groups, and a peak assignable to a terminal carbonyl on tungsten. A peak at δ 237.3 [*J*(WC) 173] for (**11a**), and at δ 238.4 p.p.m. [*J*(WC) 171 Hz] for (**11b**), are attributed to the semi-bridging CO ligand. In accord with this observation the i.r. spectra have absorptions at 1 781 (**11a**) and 1 780 cm^{-1} (**11b**) due to either a bridging or a semi-bridging CO group. The spectra obtained as Nujol mulls showed no significant differences from the solution spectra, implying that the solution and solid-state structures are the same, and thus contain a semi-bridging CO ligand. Nevertheless, formal electron counting at each metal centre would require a fully bridging carbonyl group for the eighteen-electron rule to be obeyed. In addition to signals in the ^{13}C-{^1H} n.m.r. spectra due to the η-C_5H_5, C_6H_4Me-4, and the Et or Me groups derived from the alkyne, there are four resonances which can be assigned to the four contact carbons of the *C*(R)*C*(R)*C*(H)*C*(C_6H_4Me-4)H fragment. The signals at δ 44.1 [(**11a**)] and 44.8 p.p.m. [(**11b**)] appear as doublets in the proton-coupled ^{13}C spectrum with *J*(HC) 141 and 142 Hz, respectively. The position[14] of the resonances, and to a lesser extent the magnitude of *J*(HC),[16] suggests a metal–alkyl type carbon, and thus these peaks are assigned to the *C*(H)C_6H_4Me-4 carbon. By implication, the signals at δ 82.9 [(**11a**)] and 85.1 p.p.m. [(**11b**)], which also appear as a doublet in the ^1H-coupled ^{13}C spectrum [with *J*(HC) 154 and 156 Hz, respectively] can be assigned to the CH group. The remaining resonances at δ 120.7 and 176.0 [(**11a**)], and at δ 115.5 and 166.6 p.p.m. [(**11b**)], are attributed to the two *C*Et [(**11a**)] or *C*Me[(**11b**)] nuclei. These signals are broadened in the proton-coupled ^{13}C n.m.r. spectrum due to long range ^1H–^{13}C coupling. In view of the 'alkylidene-like' nature of the

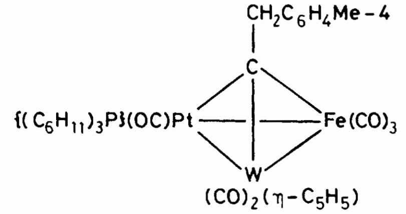
Fe*C*R′ (R′ = Me or Et) nuclei [*i.e.* C(50) in Figure 2] it is likely that this carbon atom gives rise to the more deshielded of the two resonances.

Compound (**12**), the other product of the reaction of (**3b**) with hex-3-yne, is unstable. Furthermore, repeated attempts to obtain a crystalline sample for microanalysis were unsuccessful. Nevertheless, reasonable n.m.r. spectra were recorded, and the formulation of this compound is based solely on these data. The ^{1}H n.m.r. spectrum of (**12**) is informative. There are peaks due to the η-C_5H_5 and C_6H_4Me-4 groups and also resonances which integrate for two ethyl groups. Of most significance is an AB pattern at δ 6.53 and 6.80 [*J*(AB) 15 Hz]. The closeness of the two resonances indicates that the vinyl group no longer bridges the two metals, as in this case the signals are always well separated (see above). Furthermore, the chemical shifts are typical for 'free alkenes', suggesting that the carbon–carbon double bond is not co-ordinated to a metal. The ^{13}C-{^{1}H} n.m.r. spectrum is also informative. In the carbonyl region there are two signals at δ 233.8 and 217.6 p.p.m. assigned to WCO groups. The latter is rather shielded for these systems but within the normal range observed for tungsten-ligated CO units.[14] A peak at δ 215.7 p.p.m. is attributed to an $Fe(CO)_3$ or to an $Fe(CO)_4$ group. Cooling the sample to −60 °C results in no appreciable change in the spectrum. In addition to resonances for the C_6H_4Me-4, η-C_5H_5, and Et group, there are five other peaks of interest. Resonances at δ 122.6 and 136.4 p.p.m. are assigned to the CH and *C*(H)C_6H_4Me-4 nuclei. In the proton-coupled ^{13}C spectrum these signals appear as a doublet of doublets [*J*(HC) 158, 5] and a doublet [*J*(HC) 159 Hz], respectively. The large coupling is consistent with a ^1J(HC) value for an approximately *sp*^{2} hybridised carbon, while the smaller coupling is as expected for a ^2J(HC) coupling across a carbon–carbon double bond.[16] Finally, in the ^{13}C-{^{1}H} n.m.r. spectrum there are resonances at δ 167.8, 158.2, and 139.3 p.p.m. which may be assigned to the two *C*Et and the $C^1(C_6H_4)$ nuclei. The data described above are consistent with the formulation shown for (**12**), but in the absence of an *X*-ray structure determination this assignment must be regarded as tentative.

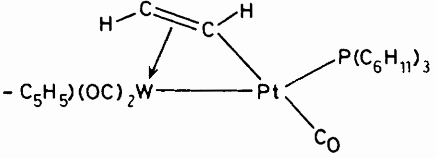
Carbon–carbon bond forming reactions between bridging vinyl ligands and alkynes, as in the formation of the compounds (**11**), are relatively rare. These syntheses are subtly different from those previously described by Mathieu and co-workers[29] in that in the present work CO is not incorporated into the hydrocarbon fragment formed by combination of the vinyl and alkyne groups, and moreover in the species (**11**) the CHCH(R) moiety retains its identity and has not rearranged.

Because the complex $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ readily attacks cluster complexes, incorporating $Pt\{P(cyclo\text{-}C_6H_{11})_3\}$ fragments in the resulting products,[32] compound (**3b**) was treated with the platinum reagent in an attempt to obtain a trimetal species having a WFePt core. The reaction proceeded readily in Et_2O at room temperature to afford a chromatographically separable mixture of the compounds $[WFePt(\mu_3\text{-}CCH_2C_6H_4Me\text{-}4)(CO)_6\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]$ (**13**) and $[WPt\{\mu\text{-}\sigma{:}\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_3\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]$ (**14**). The latter species was obtained as an oil, and repeated attempts at crystallisation failed. The available data for both products are given in Tables 1, 2, and 4.

Compounds structurally similar to (**13**) and (**14**) have been prepared previously by different routes.[33,34] In the ^{1}H n.m.r. spectrum of (**13**) the $CCH_2C_6H_4$Me-4 group gives rise to an AB pattern with resonances at δ 4.31 and 4.43 [*J*(AB) 16 Hz]. This arises as the protons of the CH_2 unit are magnetically inequivalent, due to the absence of a plane of symmetry in the molecule. Alternatively, restricted rotation about the C–CH_2-C_6H_4Me-4 bond would render the CH_2 protons chemically inequivalent. However, restricted rotation in these systems is normally associated with conjugation of a bonding orbital on the μ_3-C atom with the aromatic ring, or to steric effects.[35] Both of these situations seem unlikely in compound (**13**). The ^{13}C-{^{1}H} n.m.r. spectrum has a signal at δ 66.8 p.p.m. attributed to the $CCH_2C_6H_4$Me-4 carbon. In the proton-coupled ^{13}C n.m.r. spectrum the peak is a pseudo-triplet [*J*(HC) 127 Hz]. The magnitude of *J*(HC) is consistent with the formulation proposed. In addition, a resonance at δ 318.2 p.p.m. is attributed to the μ_3-alkylidyne carbon, while broad peaks at δ 221.2, 215.2, and 186.8 p.p.m. are assigned to the $W(CO)_2$, $Fe(CO)_3$, and Pt(CO) groups, respectively. The observation of only one resonance for the $Fe(CO)_3$ group is usual for these compounds,[34] while the appearance of one resonance for the tungsten-ligated carbonyl groups implies accidental equivalence of these ligands. The ^{31}P-{^{1}H} n.m.r. spectrum shows a single resonance at δ 46.8 p.p.m. [*J*(PtP) 3 545 Hz].



(**13**)



(**14**)

Formation of (**13**) involves conversion of the vinyl ligand in (**3b**) into an alkylidyne group, a transformation having precedent.[4,24] Moreover, the synthesis of (**13**) provides a further example of the use of the complexes $[Pt(C_2H_4)_2(PR_3)]$ (R = alkyl or aryl) in the preparation of mixed-metal compounds and in the activation of ligated organic groups.[36]

Compound (**14**), the other product of the reaction of (**3b**) with $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ is related to the previously reported[34] species $[WPt\{\mu\text{-}\sigma{:}\eta\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_3(PMe_3)(\eta\text{-}C_5H_5)]$. The formulation proposed for (**14**) is consistent with the spectroscopic data (Tables 1, 2, and 4). In particular, the ^{1}H n.m.r. spectrum unequivocally demonstrates the presence of the bridging *trans*-CH=CH(C_6H_4Me-4) ligand. The ^{13}C-{^{1}H} n.m.r. spectrum has resonances at δ 229.6 and 228.2 p.p.m. for tungsten-ligated carbonyl groups, and a signal at δ 195.6 p.p.m. [*J*(PC) 5 Hz] for the PtCO unit. The poor quality of this spectrum prevented the observation of ^{195}Pt satellite peaks. The μ-C nucleus resonates at δ 127.4 p.p.m. [*J*(PC) 3 Hz], while the peak for the *C*(H)C_6H_4Me-4 nucleus is obscured by signals for the *cyclo*-C_6H_{11} groups. The ^{31}P-{^{1}H} n.m.r. spectrum has a singlet at δ 36.5 p.p.m. [*J*(PtP) 3 030, *J*(WP) 15 Hz]. The orientation of the $Pt(CO)\{P(C_6H_{11})_3\}$ group is not known, but the similarity in the values of *J*(PtP) and *J*(WP) with those for $[WPt\{\mu\text{-}\sigma{:}\eta\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_3(PMe_3)(\eta\text{-}C_5H_5)]$ suggests that the $P(C_6H_{11})_3$ ligand is *trans* to the metal–metal bond.[34] It follows from the formulation of (**14**) that compound (**12**) is best envisaged as formed by an exchange reaction between the isolobal $Fe(CO)_4$ and $Pt(CO)\{P(C_6H_{11})_3\}$ fragments.

Experimental

All reactions were carried out under oxygen-free nitrogen, using Schlenk tube techniques. Solvents were dried before use, and light petroleum refers to that fraction of b.p. 40—60 °C. The i.r. spectra were measured with Nicolet 10-MX and 5Z-DX spectrophotometers, and n.m.r. spectra with JNM JEOL FX 90Q, GX 270, and GX 400 instruments. Alumina (B.D.H. aluminium oxide, Brockman activity II) was used for chromatography unless otherwise stated. Chromatography columns were generally *ca.* 20 cm in length and 3 cm in diameter. The compounds $[M(\equiv CR)(CO)_2(\eta\text{-}C_5R'_5)]$ (**1**),[6,37] $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ (**2**),[9] and $[Pt(C_2H_4)_2\{P(\textit{cyclo}\text{-}C_6H_{11})_3\}]$[38] were prepared by methods described previously. Analytical and spectroscopic data for the new compounds are given in Tables 1 and 2.

Reactions of $[Fe_2(\mu\text{-}CH_2)(CO)_8]$.—(*i*) A mixture of (**1a**) (0.28 g, 0.88 mmol) and (**2**) (0.34 g, 0.97 mmol) was stirred in thf (25 cm^3) at room temperature for 16 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 3:7) and chromatographed. Elution with the same solvent mixture removed initially traces of (**2**), followed by a major brown eluate. Removal of solvent *in vacuo* gave orange *microcrystals* of $[MoFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)]$ (**3a**) (0.12 g). Other minor fractions removed from the column were obtained in insufficient quantity for characterisation.

(*ii*) Similarly, a mixture of (**1b**) (0.67 g, 1.64 mmol) and (**2**) (0.75 g, 2.13 mmol) in thf (30 cm^3) was stirred for 16 h, after which time solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (3 × 10 cm^3), and the extracts were combined and added to alumina (*ca.* 2.5 g) which was dried *in vacuo*. The alumina was added to the top of a chromatography column. Elution with CH_2Cl_2–light petroleum (1:9) removed a yellow fraction, identified by i.r. as containing (**2**). Further elution with CH_2Cl_2–light petroleum (1:4) gave a light brown eluate, which after removal of solvent *in vacuo* yielded orange *microcrystals* of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)]$ (**3b**) (0.40 g). Elution with CH_2Cl_2–light petroleum (3:2) gave a brown eluate, which after removal of solvent *in vacuo*, and crystallisation of the residue from the same solvent (10 cm^3, 1:9), afforded red *microcrystals* of $[W_2Fe(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}\sigma:\eta\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (**4**) (0.11 g).

(*iii*) Similarly, a mixture of (**1c**) (0.40 g, 1.20 mmol) and (**2**) (0.43 g, 1.23 mmol) was stirred in thf (30 cm^3) for 16 h. Solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 3:7) and chromatographed. Elution with the same solvent mixture removed traces of (**2**) (identified by i.r.), followed by a green eluate. Removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (10 cm^3, 1:9), yielded green *crystals* of $[WFe_2(\mu_3\text{-}CEt)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**5a**) (0.08 g). Further elution of the column gave a brown-orange eluate, which after removal of solvent *in vacuo* and crystallisation of the residue from light petroleum (10 cm^3) at −20 °C afforded orange *crystals* of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(Me)\}(CO)_6(\eta\text{-}C_5H_5)]$ (**3c**) (0.21 g). Final elution with CH_2Cl_2–thf (9:1) gave a purple eluate which after removal of solvent *in vacuo* gave a solid identified by i.r. and ^1H n.m.r. spectroscopy[17] as $[W_2Fe(\mu_3\text{-}MeC_2Me)(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.11 g, 24%).

Reactions of the Compound $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)]$ (**3b**).—(*i*) A mixture of (**3b**) (0.11 g, 0.19 mmol) and PPh_3 (0.05 g, 0.19 mmol) was stirred in Et_2O (20 cm^3) for 16 h. Solvent was removed *in vacuo*, and the residue, dissolved in CH_2Cl_2–light petroleum (5 cm^3, 3:7), was chromatographed (2 × 15 cm column). Elution with the same solvent mixture yielded an orange eluate, which after removal of solvent *in vacuo* gave orange *microcrystals* of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_5(PPh_3)(\eta\text{-}C_5H_5)]$ (**8a**) (0.12 g).

(*ii*) A solution of (**3b**) (0.09 g, 0.15 mmol) in Et_2O (20 cm^3) was treated with PMe_3 (15 μl, *ca.* 0.15 mmol). After stirring for 24 h, the solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 3:7), and chromatographed (2 × 15 cm column). Elution with the same solvent mixture gave a trace of compound (**3b**) (identified by i.r.). Elution with CH_2Cl_2–light petroleum (2:3) gave an orange eluate which after removal of solvent *in vacuo* yielded orange *crystals* of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_5(PMe_3)(\eta\text{-}C_5H_5)]$ (**8b**) (0.08 g). Further elution of the column with the same solvent mixture gave a trace of the red compound (**9**) (see below).

(*iii*) A solution of (**3b**) (0.16 g, 0.27 mmol) in Et_2O (20 cm^3) was treated with PMe_3 (0.2 cm^3, 1.97 mmol). After stirring for 16 h, solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1), and chromatographed (2 × 15 cm column). Elution with the same solvent mixture gave an intense red eluate as the major product. Removal of solvent *in vacuo* yielded red *crystals* of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_4(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**9**) (0.17 g).

(*iv*) The compound $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_5(dppm)(\eta\text{-}C_5H_5)]$ (**8c**) (0.11 g) was prepared from (**3b**) (0.10 g, 0.17 mmol) and dppm (0.07 g, 0.18 mmol) in a similar manner to that described for (**8a**).

(*v*) A solution of (**3b**) (0.36 g, 0.61 mmol) in Et_2O (40 cm^3) was treated with dmpm (1.3 cm^3 of a 0.47 mol dm^{-3} solution in light petroleum, *ca.* 0.6 mmol). The mixture was stirred for 16 h, after which period solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1), and chromatographed. Elution with the same solvent mixture gave an orange eluate, which after removal of solvent *in vacuo* afforded small amounts of the unstable compound $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_5(dmpm)(\eta\text{-}C_5H_5)]$ (**8d**). Elution of the column with neat CH_2Cl_2 gave a green-brown eluate which after removal of solvent *in vacuo* yielded green *crystals* of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}dmpm)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)]$ (**10a**) (0.27 g).

Photolysis of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_5(dppm)(\eta\text{-}C_5H_5)]$ (**8c**).—A thf solution (20 cm^3) of compound (**8c**) (0.11 g, 0.12 mmol) in a water-jacketed quartz vessel was irradiated for 1 h (500 W medium pressure Hanovia mercury vapour lamp). Solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (3 cm^3) and chromatographed (2 × 15 cm column). Elution with CH_2Cl_2–thf (9:1) yielded a single green eluate which after removal of solvent *in vacuo* and washing with light petroleum (3 × 10 cm^3) gave green *microcrystals* of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)]$ (**10b**) (0.04 g). The compound could only be obtained contaminated with traces of another complex.

Reactions of $[WFe\{\mu\text{-}\sigma:\eta\text{-}CH{=}CH(C_6H_4Me\text{-}4)\}(CO)_6(\eta\text{-}C_5H_5)]$ (**3b**), *with Alkynes*.—(*i*) A solution of (**3b**) (0.20 g, 0.34 mmol) in Et_2O (25 cm^3) was treated with $EtC{\equiv}CEt$ (*ca.* 0.3 cm^3, 2.6 mmol). After stirring for 16 h, solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (10 cm^3) and added to Florisil (*ca.* 2.0 g). After pumping, the solid material was added to the top of a chromatography column (2 × 15 cm) packed with Florisil. Elution with light petroleum yielded small amounts of compound (**3b**) (identified by i.r.), and a trace of an unidentified pink compound. Elution of the column with

CH_2Cl_2–light petroleum (1:1) gave a yellow eluate which after removal of solvent *in vacuo* afforded yellow *microcrystals* of [$WFe\{\mu$-$C(Et)C(Et)C(H)CH(C_6H_4Me$-$4)\}(\mu$-$CO)(CO)_4(\eta$-$C_5H_5)$] (**11a**) (0.05 g). Elution with CH_2Cl_2 gave a brown eluate which after removal of solvent gave a brown unstable oil formulated as [$WFe\{\mu$-$C(Et)$=$C(Et)CH$=$CH(C_6H_4Me$-$4)\}$-$(CO)_6(\eta$-$C_5H_5)$] (**12**). Other minor fractions were not collected.

(*ii*) A solution of (**3b**) (0.11 g, 0.15 mmol) in Et_2O (15 cm^3) was treated with $MeC{\equiv}CMe$ (*ca.* 0.3 cm^3, 3.6 mmol) in a Schlenk tube fitted with a high-pressure stopcock. The mixture was stirred for 16 h, after which time a yellow precipitate had formed. Solvent was removed with a syringe, and the precipitate was washed with Et_2O (2 × 5 cm^3) to yield yellow *microcrystals* of [$WFe\{\mu$-$C(Me)C(Me)C(H)CH(C_6H_4Me$-$4)\}(\mu$-$CO)(CO)_4$-$(\eta$-$C_5H_5)$] (**11b**). The Et_2O washings were combined with the solvent from the reaction. Solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (10 cm^3) and added to Florisil (*ca.* 2.0 g). After pumping *in vacuo* the solid material obtained was added to the top of a Florisil chromatography column (2 × 15 cm). Elution with CH_2Cl_2–light petroleum (1:9) gave a trace of compound (**3b**) (identified by i.r.). Elution with CH_2Cl_2–light petroleum (1:1) gave a yellow eluate which after removal of solvent *in vacuo* afforded additional yellow *microcrystals* of (**11b**) (0.03 g). Other minor bands on the column were not collected.

Reaction of [$WFe\{\mu$-σ:η-CH=$CH(C_6H_4Me$-$4)\}(CO)_6(\eta$-$C_5H_5)$] *with* [$Pt(C_2H_4)_2\{P(C_6H_{11})_3\}$].—A mixture of compound (**3b**) (0.09 g, 0.15 mmol) and [$Pt(C_2H_4)_2\{P(C_6H_{11})_3\}$] (0.08 g, 0.15 mmol) was stirred in Et_2O for 16 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 3:7) and chromatographed (2 × 15 cm column). Elution with the same solvent mixture gave traces of an unidentified orange compound and (**3b**) (identified by i.r.). Further elution with CH_2Cl_2–light petroleum (1:4) gave a grey-green eluate which after removal of solvent afforded green *microcrystals* of [$WFePt(\mu_3$-$CCH_2C_6H_4Me$-$4)(CO)_6$-$\{P(C_6H_{11})_3\}(\eta$-$C_5H_5)$] (**13**) (0.09 g). Elution of the column with neat CH_2Cl_2 gave a yellow eluate which after removal of solvent *in vacuo* afforded a yellow oil identified as [$WPt\{\mu$-σ:η-CH=$CH(C_6H_4Me$-$4)\}(CO)_3\{P(C_6H_{11})_3\}(\eta$-$C_5H_5)$] (**14**). Attempts to recrystallise this oil were unsuccessful.

Crystal Structure Determinations.—(*a*) [$W_2Fe(\mu_3$-CC_6H_4-Me-$4)\{\mu$-σ:η-$C(C_6H_4Me$-$4)$=$CH_2\}(CO)_6(\eta$-$C_5H_5)_2$] (**4**). Red crystals of (**4**) were grown from CH_2Cl_2–light petroleum. Diffracted intensities were collected at 293 K on a Nicolet *R*3*m*/μ diffractometer from a crystal of dimensions *ca.* 0.25 × 0.40 × 0.50 mm. Of the 5 142 unique data collected (Wyckoff ω-scans, $2\theta \leqslant 50°$), 4 221 had $F \geqslant 5.0\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected empirically for *X*-ray absorption (using azimuthal scan data)[39] and extinction, and for Lorentz and polarisation effects.

Crystal data. $C_{33}H_{26}FeO_6W_2$, $M = 942.1$, monoclinic, $a = 10.501(6)$, $b = 16.783(9)$, $c = 16.601(7)$ Å, $\beta = 94.72(4)°$, $U = 2\,916(3)$ Å^3, $Z = 4$, $D_c = 2.15$ g cm^{-3}, $F(000) = 1\,784$, space group $P2_1/c$, Mo-K_α *X*-radiation (graphite monochromator $\bar{\lambda} = 0.710\,69$ Å), $\mu(\text{Mo-}K_\alpha) = 85.8$ cm^{-1}.

The structure was solved, and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included at calculated positions (C–H 0.96 Å) with a common refined isotropic thermal parameter for those belonging to methyl groups, and fixed isotropic thermal parameters (*ca.* 1.2 × U_{equiv} of the parent carbon atom) for the remaining aromatic hydrogen atoms. Approximate co-ordinates for the vinyl CH_2 hydrogen atoms [H(8a) 0.125, 0.780, 0.478 and H(8b) −0.003, 0.806, 0.488] were obtained from a final difference synthesis but these atoms were not included in the final model. Refinement by blocked-cascade least squares led to $R = 0.029$ ($R' = 0.028$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,12|F|^2]$ gave a satisfactory analysis of variance. The final electron density difference synthesis showed no peaks >0.90 or <-0.92 e Å^{-3}. Scattering factors with corrections for anomalous dispersion were taken from ref. 40. The later stages of refinement were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs.[39] Atomic co-ordinates are given in Table 6.

Table 6. Atomic positional (fractional co-ordinates) parameters (× 10^4), with estimated standard deviations (e.s.d.s) in parentheses, for compound (**4**)

Atom	*x*	*y*	*z*
W(1)	777(1)	6 780(1)	5 992(1)
W(2)	−982(1)	6 490(1)	7 215(1)
Fe	−145(1)	8 034(1)	6 825(1)
C(1)	−225(7)	6 563(4)	4 964(4)
O(1)	−748(5)	6 451(3)	4 347(3)
C(2)	663(7)	6 367(4)	7 862(4)
O(2)	1 566(5)	6 272(3)	8 294(3)
C(3)	−731(7)	5 524(4)	6 605(4)
O(3)	−718(6)	4 906(3)	6 275(4)
C(4)	938(7)	8 172(4)	7 722(4)
O(4)	1 538(6)	8 249(4)	8 323(3)
C(5)	−1 484(7)	8 334(4)	7 342(4)
O(5)	−2 316(6)	8 629(3)	7 635(3)
C(6)	−280(7)	8 959(4)	6 329(4)
O(6)	−373(6)	9 581(3)	6 026(4)
C(7)	1 220(6)	8 019(4)	5 991(4)
C(8)	706(7)	7 871(4)	5 168(4)
C(9)	−1 119(6)	7 208(3)	6 161(4)
C(11)	3 044(7)	6 690(4)	5 862(4)
C(12)	2 841(7)	6 371(4)	6 630(4)
C(13)	2 071(7)	5 682(4)	6 525(4)
C(14)	1 789(7)	5 580(4)	5 686(4)
C(15)	2 383(7)	6 205(4)	5 281(4)
C(21)	−2 342(8)	6 905(5)	8 216(5)
C(22)	−1 869(9)	6 155(5)	8 444(5)
C(23)	−2 291(9)	5 603(5)	7 846(5)
C(24)	−3 057(8)	6 019(5)	7 235(5)
C(25)	−3 071(7)	6 835(5)	7 460(5)
C(31)	2 433(7)	8 487(4)	6 141(4)
C(32)	3 314(7)	8 384(4)	6 812(4)
C(33)	4 372(7)	8 864(4)	6 933(4)
C(34)	4 618(7)	9 474(4)	6 401(5)
C(35)	3 760(7)	9 571(4)	5 733(4)
C(36)	2 695(7)	9 089(4)	5 605(4)
C(37)	5 764(8)	10 013(5)	6 562(6)
C(41)	−2 307(6)	7 301(4)	5 622(4)
C(42)	−2 964(7)	6 636(4)	5 266(4)
C(43)	−4 037(7)	6 714(5)	4 746(5)
C(44)	−4 575(7)	7 458(5)	4 560(4)
C(45)	−3 972(7)	8 105(4)	4 928(4)
C(46)	−2 871(7)	8 036(4)	5 445(4)
C(47)	−5 727(8)	7 548(6)	3 961(5)

(*b*) [$WFe\{\mu$-$C(Et)C(Et)C(H)CH(C_6H_4Me$-$4)\}(\mu$-$CO)(CO)_4$-$(\eta$-$C_5H_5)$] (**11a**). The structure solution and refinement were similar to that noted for (**4**) except in the following respects. Yellow crystals of (**11a**) were grown from CH_2Cl_2–light petroleum. Diffracted intensities were collected at 293 K on a Nicolet $P2_1$ diffractometer. Of the 3 813 unique data collected (Wyckoff ω-scans, $2\theta \leqslant 50°$), 3 152 had $F \geqslant 5.0\sigma(F)$, and only these were used for structure solution and refinement.

Crystal data. $C_{25}H_{24}FeO_5W$, $M = 644.2$, monoclinic, $a = 33.23(2)$, $b = 9.423(5)$, $c = 15.411(5)$ Å, $\beta = 103.58(4)°$, $U = 4\,690(4)$ Å^3, $Z = 8$, $D_c = 1.82$ g cm^{-3}, $F(000) = 2\,512$, space group $C2/c$, Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å), $\mu(\text{Mo-}K_\alpha) = 56.6$ cm^{-1}.

Table 7. Atomic positional (fractional co-ordinates) parameters ($\times 10^4$), with e.s.d.s in parentheses, for compound (**11a**)

Atom	*x*	*y*	*z*
W	1 829(1)	4 917(1)	8 509(1)
Fe	1 460(1)	7 599(1)	8 440(1)
C(11)	1 739(3)	3 091(9)	7 451(5)
C(12)	2 065(3)	2 733(7)	8 142(5)
C(13)	2 376(2)	3 721(7)	8 190(5)
C(14)	2 248(4)	4 710(9)	7 503(7)
C(15)	1 842(3)	4 326(11)	7 041(4)
C(20)	1 410(2)	6 793(5)	9 691(3)
C(30)	1 383(2)	5 248(5)	9 476(5)
C(40)	1 155(2)	4 784(6)	8 633(5)
C(50)	1 192(2)	5 763(7)	7 946(4)
C(41)	901(3)	3 411(7)	8 517(6)
C(42)	1 050(3)	2 286(8)	9 207(9)
C(51)	925(3)	5 525(11)	7 033(6)
C(52)	473(3)	5 968(15)	6 876(8)
C(21)	1 059(2)	7 353(5)	10 050(4)
C(22)	674(2)	6 721(7)	9 913(4)
C(23)	371(3)	7 268(8)	10 285(5)
C(24)	427(2)	8 468(7)	10 812(4)
C(25)	806(2)	9 127(7)	10 951(5)
C(26)	1 119(2)	8 577(6)	10 592(4)
C(27)	80(3)	9 065(11)	11 206(7)
C(1)	2 157(2)	6 683(6)	8 806(4)
O(1)	2 450(2)	7 406(5)	8 952(4)
C(2)	2 064(2)	4 284(6)	9 744(4)
O(2)	2 209(2)	3 868(6)	10 445(3)
C(3)	1 744(2)	9 011(7)	9 099(6)
O(3)	1 917(3)	9 904(5)	9 536(7)
C(4)	965(2)	8 410(7)	8 255(4)
O(4)	653(2)	8 963(6)	8 147(4)
C(5)	1 565(3)	8 097(10)	7 393(6)
O(5)	1 623(2)	8 435(9)	6 714(5)

Hydrogen atoms were included at calculated positions (C–H 0.96 Å) with a common refined isotropic thermal parameter for those belonging to methyl groups, and fixed isotropic thermal parameters (*ca.* 1.2 × U_{equiv} of the parent carbon atom) for the remaining aromatic and CH_2 hydrogen atoms. The hydrogen atoms H(30) and H(40) were located from a difference synthesis and were included in the final refinements in fixed positions with refined isotropic thermal parameters. Refinement by blocked-cascade least squares led to $R = 0.041$ ($R' = 0.043$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.004|F|^2]$ gave a satisfactory analysis of variance. The final electron density difference synthesis showed no peaks >0.83 or < -1.8 e Å^{-3}. Atomic co-ordinates are given in Table 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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