Synthesis and Reactions of Co-ordinatively Unsaturated μ_3-Alkylidyne Clusters; *X*-Ray Crystal Structures of the Phosphido Bridged Complexes $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ and $[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(O)C(Me)CHMe\}(\mu\text{-}PEt_2)(CO)_5(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$)†

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Thermal decarbonylation (toluene, 111 °C) of the complexes $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PR'_2)(CO)_7(\eta\text{-}C_5H_5)]$ [$R = C_6H_4Me\text{-}4, R' = Ph$ (**2**) or Et (**3**)] gives good yields of the co-ordinatively unsaturated, 46 cluster valence electron derivatives $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PR'_2)(CO)_6(\eta\text{-}C_5H_5)]$ [$R' = Ph$ (**4**) or Et (**5**)]. The structure of the μ-PPh_2 complex (**4**) was established by a single-crystal *X*-ray diffraction study and consists of a WFe_2 triangle of metal atoms [W–Fe(1) 2.817(1), W–Fe(2) 2.523(1), and Fe(1)–Fe(2) 2.569(1) Å] capped by a μ_3-CC_6H_4Me-4 group. The W–Fe(2) bond is bridged by a μ-PPh_2 ligand [W–μ–P 2.357(1), Fe(2)–μ–P 2.219(1) Å] whilst a hydride ligand, which was located and refined, bridges the homonuclear Fe–Fe bond [Fe(1)–H(1) 1.73(4), Fe(2)–H(1) 1.54(6) Å]. The tungsten atom carries a cyclopentadienyl ring and a terminal CO ligand. The Fe(2) centre bound to phosphorus has two terminal CO ligands, whilst the remaining Fe(1) atom has three approximately orthogonal terminal CO groups. The μ-PPh_2 bridged W–Fe(2) separation of 2.523(1) Å is extremely short. This suggests the presence of appreciable multiple-bond character in the W–Fe(2) bond which is consistent with the formulation of (**4**) as a co-ordinatively unsaturated complex. Spectroscopic data for complexes (**4**) and (**5**) reveal that in solution the hydride ligand adopts a terminal site on the Fe(1) atom. This contrasts with the bridging Fe(μ-H)Fe interaction observed in the solid state for (**4**). Solutions of (**4**) and (**5**) react with CO (15 min, 20 °C) to regenerate their saturated precursors (**2**) and (**3**) respectively. Dichloromethane solutions of (**4**) and (**5**) also react with alkynes ($R''C{\equiv}CR''$, R'' = Me, Et, or Ph) to give the vinylacyl complexes $[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(O)C(R'')CHR''\}(\mu\text{-}PR'_2)(CO)_5(\eta\text{-}C_5H_5)]$ [$R' = Ph$, R'' = Me (**6a**), Et (**6b**), or Ph (**6c**); R' = Et, R'' = Me (**7**)]. The molecular structure of the but-2-yne derivative (**7**) was established by a single crystal *X*-ray diffraction study. The structure consists of a WFe_2 triangle of metal atoms [W–Fe(1) 2.808(1), W–Fe(2) 2.679(1), and Fe(1)–Fe(2) 2.673(1) Å] capped by a μ_3-alkylidyne ligand. One W–Fe bond is bridged by a μ-PEt_2 ligand whilst the remaining W–Fe bond is bridged by a μ-C(O)C(Me)CHMe group which has been formed by coupling of hydride, but-2-yne, and CO ligands. The *cis*-{μ-C(O)C(Me)CHMe} ligand adopts a π-allyl η^3-bonding mode to Fe(2) [Fe(2)–C(O) 2.083(5), Fe(2)–C(Me) 2.173(6), and Fe(2)–CHMe 2.186(6) Å], and the C(O) end of the chain uses an orthogonal set of orbitals to η^2 bond to the W atom [W–C(O) 2.011(5), W–O 2.281(4) Å]. Protonation of the complexes (**6a**) and (**7**) (CH_2Cl_2, $HBF_4{\cdot}Et_2O$) occurs at the oxygen atom of the *cis*-{μ-C(O)C(Me)CHMe} ligand affording the unsaturated μ-allylidene derivatives $[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(OH)C(Me)CHMe\}(\mu\text{-}PR'_2)(CO)_5(\eta\text{-}C_5H_5)][BF_4]$ [R' = Ph (**8**) or Et (**9**)]. The spectroscopic data (i.r. and ^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$ n.m.r.) for the new WFe_2 complexes are discussed and mechanisms are proposed to account for their formation.

Heteronuclear di- or tri-metal complexes with alkylidene or alkylidyne ligands undergo a remarkably diverse range of reactions with alkynes,[1] and these together with related studies on homonuclear species reflect a widespread interest in the reactions of C^1 fragments bridging metal–metal bonds.[2] In previous papers we have examined the reactions of the heterotrimetal alkylidyne complexes $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8L]$ [$R = C_6H_4Me\text{-}4$, $L = \eta\text{-}C_5H_5$) (**1a**) or $\eta\text{-}C_5Me_5$ (**1b**)] and $[MoFe_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**1c**) with alkynes.[3,4] With diphenylacetylene the principal products of these reactions are the dimetal species $[WFe\{\mu\text{-}C(R)C(Ph)C(Ph)\}(CO)_5L]$ and $[MoFe\{\mu\text{-}C(R)C(Ph)C(Ph)\}(CO)_5(\eta\text{-}C_5H_5)]$. For (**1a**) and (**1b**) similar products are obtained with but-2-yne,[3] but a more complex reaction occurs for (**1c**) affording the complex $[MoFe\{\mu\text{-}C(R)C(CHMe)CH_2C(Me)C(Me)\}(CO)_4(\eta\text{-}C_5H_5)]$.[4] These reactions are characterised by the coupling of one or more molecules of the incoming alkyne with a μ_3-CR moiety and fragmentation of the parent trimetal cluster to a dimetal species. If cluster fragmentation could be prevented related reactions could be studied at trimetal centres. We have previously shown that reaction of the complex (**1a**) with 1 equivalent of the secondary phosphines PR'_2H(R' = Ph or Et) affords the phosphido-bridged derivatives $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PR'_2)(CO)_7(\eta\text{-}C_5H_5)]$ [R' = Ph (**2**) or Et (**3**)].[5–7] These μ-PR'_2 bridged complexes are more resistant to cluster fragmentation reactions than is (**1**). In this paper we describe the synthesis of co-

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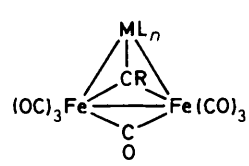
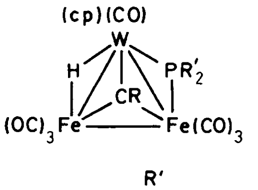
† 1,1,1,2,2,3-Hexacarbonyl-3-η-cyclopentadienyl-2,3-μ-diphenylphosphido-1,2-μ-hydrido-μ_3-*p*-tolylmethylidyne-*triangulo*-1,2-di-iron-3-tungsten, and 1,1,1,2,2-pentacarbonyl-3-η-cyclopenta-dienyl-1,3-μ-diethylphosphido-2,3-μ-[1-oxobut-2-en-1-yl-$C^1O(W)C^{1-3}(Fe^2)$]-μ_3-*p*-tolyl-methylidyne-*triangulo*-1,2-di-iron-3-tungsten.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

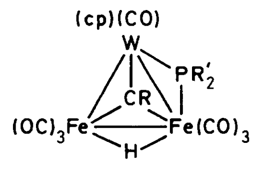


ML_n

(1a) $W(CO)_2(cp)$
(1b) $W(CO)_2(\eta\text{-}C_5Me_5)$
(1c) $Mo(CO)_2(cp)$



R′
(2) Ph
(3a) Et



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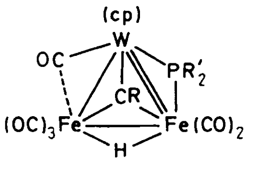
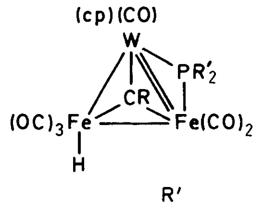
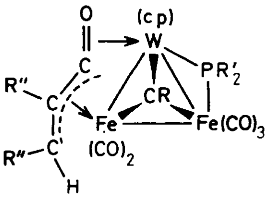


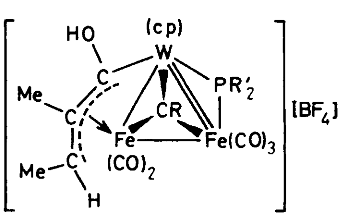
(4a) R′ = Ph



R′
(4b) Ph
(5) Et



	R′	R″
(6a)	Ph	Me
(6b)	Ph	Et
(6c)	Ph	Ph
(7)	Et	Me



R′
(8) Ph
(9) Et

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

ordinatively unsaturated derivatives of (2) and (3), which undergo facile reactions with alkynes, affording products in which the $WFe_2(\mu_3\text{-}CR)$ core is retained. A preliminary account of some of the work described herein has been given.[7]

Results and Discussion

Solutions of the μ-PPh_2 bridged complex $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7(\eta\text{-}C_5H_5)]$ (2) are stable at room temperature, but readily undergo thermal decarbonylation in toluene (111 °C, 30 min) to give the co-ordinatively unsaturated, 46 c.v.e. (cluster valence electron) complex (4). Solutions of (4) decompose rapidly on chromatography at room temperature, but following chromatography on alumina at −40 °C good yields of (4) may be obtained. A single crystal *X*-ray diffraction study was carried out on (4). In the solid state the Fe–Fe bond is bridged by a hydride ligand [isomer (4a)], but in solution spectroscopic data (Tables 1 and 2) suggest an alternative structure [isomer (4b)] with the hydride occupying a terminal site on Fe(1).

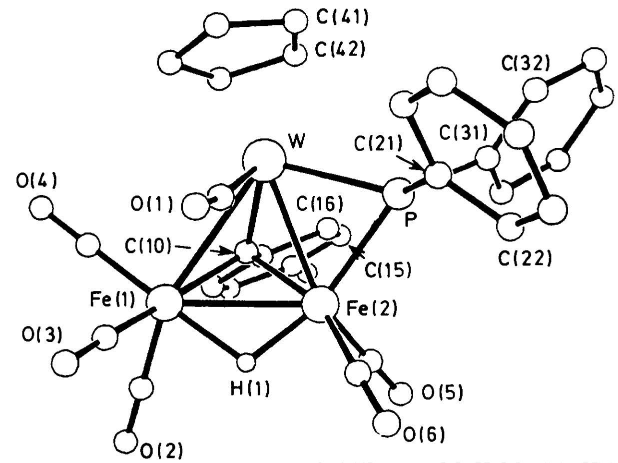


Figure 1. Molecular structure of $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ (4) showing the atom numbering scheme

The molecular structure of complex (4) is shown in Figure 1 and selected bond lengths and angles are in Table 3. The structure consists of the expected WFe_2 triangle of metal atoms capped by a μ_3-CC_6H_4Me-4 group. The W–Fe(2) bond is bridged by a μ-PPh_2 ligand [W–μ-P 2.357(1), Fe(2)–μ-P 2.219(1) Å], whilst a hydride ligand, which was located and refined, bridges the homonuclear Fe–Fe bond [Fe(1)–H(1) 1.73(4), Fe(2)–H(1) 1.54(6) Å]. The tungsten atom carries a cyclopentadienyl ring and a terminal CO ligand which shows a weak semi-bridging interaction with Fe(1) [W–C(1)–O(1) 168.7(4)°]. The Fe(2) centre bound to phosphorus has two terminal CO ligands and the remaining Fe(1) atom has three approximately orthogonal terminal CO groups. Comparison of the W–μ-C and Fe–μ-C separations [W-C(10) 2.018(4), Fe(1)–C(10) 1.916(5), Fe(2)–C(10) 2.132(3) Å] with those observed in a series of related WFe_2 alkylidyne clusters (range W–μ-C 1.981—2.093, range Fe–μ-C 1.960—2.130 Å)[5] reveals a rather long Fe(2)–μ-C separation of 2.132(3) Å, and correspondingly short Fe(1)–μ-C and W–μ-C separations of 1.916(5) and 2.018(4) Å respectively. It therefore appears that the somewhat weak interaction between Fe(2) and the μ_3-CR moiety is offset by a proportional increase in multiple-bond character within the W(μ-CR)Fe(1) framework. The unbridged W–Fe(1) separation of 2.817(1) Å is the longest observed in complexes of this type (range W–Fe 2.679—2.805 Å).[5] In contrast, the μ-PPh_2 bridged W–Fe(2) separation of 2.523(1) Å is extremely short (range μ-PR_2 bridged W–Fe, 2.712—2.940 Å).[5] This suggests the presence of appreciable multiple-bond character in the W–Fe(2) bond which is consistent with the formulation of (4) as a co-ordinatively unsaturated 46 c.v.e. complex. The W–Fe bond lengths in the unsaturated (32 c.v.e.) dimetal complexes $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ [$HB(pz)_3$ = tris(pyrazol-1-yl)-borate] [2.612(2) Å][8] and $[WFe(\mu\text{-}PPh_2)(CO)_5\{HB(pz)_3\}]$ [2.658(2) Å][9] provide additional support for this suggestion. The Fe–Fe separation of 2.569(1) Å is marginally longer than that found in the parent cluster (1a) [2.538(2) Å] and this is typical of the behaviour expected for a metal–metal bond bridged by a μ-H ligand.[10] Unlike the co-ordinatively unsaturated compound $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$[11] in which an interaction between a ruthenium centre and a P-C(phenyl) bond exists, and the compound $[Fe_3(\mu\text{-}H)\{\mu\text{-}P(C_6H_4OMe\text{-}$

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

Compound[b]		Colour	Yield	$\nu(CO)^c/cm^{-1}$	Analysis/%	
					C	H
(4)	$[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]^d$	Black	88	2 045s, 1 997s, 1 981s, 1 961m, 1 840(br)	45.4 (45.5)	2.9 (2.8)
(5)	$[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PEt_2)(CO)_6(\eta\text{-}C_5H_5)]^{d,e}$	Black	81	2 041s, 1 990s, 1 977s, 1 957m, 1 841w (br)	36.9 (36.9)	3.1 (3.1)
(6a)	$[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(O)C(Me)CHMe\}(\mu\text{-}PPh_2)(CO)_5(\eta\text{-}C_5H_5)]$	Dark green	44	2 020s, 1 972s, 1 954s, 1 938m (sh), 1 921m	47.9 (48.2)	3.4 (3.3)
(6b)	$[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(O)C(Et)CHEt\}(\mu\text{-}PPh_2)(CO)_5(\eta\text{-}C_5H_5)]$	Dark green	47	2 019s, 1 971s, 1 953s, 1 934m (sh), 1 921m	48.8 (49.4)	3.7 (3.7)
(6c)	$[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(O)C(Ph)CHPh\}(\mu\text{-}PPh_2)(CO)_5(\eta\text{-}C_5H_5)]^f$	Dark green	40	2 022s, 1 979s, 1 959m, 1 946m (sh), 1 929m (sh)	51.2 (51.1)	3.4 (3.2)
(7)	$[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(O)C(Me)CHMe\}(\mu\text{-}PEt_2)(CO)_5(\eta\text{-}C_5H_5)]$	Dark brown	51	2 023s, 1 956s, 1 937m, 1 912m	41.4 (41.8)	3.7 (3.8)
(8)	$[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(OH)C(Me)CHMe\}(\mu\text{-}PPh_2)(CO)_5(\eta\text{-}C_5H_5)][BF_4]$	Brown	92	2 057s, 2 007s, 1 973m	43.7 (43.8)	3.2 (3.1)
(9)	$[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(OH)C(Me)CHMe\}(\mu\text{-}PEt_2)(CO)_5(\eta\text{-}C_5H_5)][BF_4]$	Brown	80	2 057s, 2 004s, 1 979m	37.2 (37.5)	3.8 (3.5)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] In CH_2Cl_2. [d] Complexes have terminal hydride ligands in solution. [e] Crystallised with 0.5 CH_2Cl_2. [f] Crystallised with 1.0 CH_2Cl_2.

4)R}(CO)$_9$],[12] in which an Fe atom is ligated by a double bond of the C_6H_4OMe-4 aromatic ring system, the electron deficiency of (4) is compensated by the presence of multiple-bond character in the W–Fe(2) bond. Such clusters are comparatively scarce,[13] and as discussed for (4) in subsequent sections of this paper, often show enhanced reactivity towards a variety of donor ligands.

The analytical data for complex (4) (Table 1) are in accord with the structure (**4a**) established by *X*-ray diffraction. In the solid state the hydride ligand bridges the Fe–Fe bond but n.m.r. spectroscopic data reveal that in solution an alternative structure (**4b**) is adopted. Thus, the ^1H n.m.r. spectrum of (4) (Table 2) shows a sharp high-field resonance at δ −10.55. This chemical shift is similar to that observed for the terminal hydride ligands in the complex $[FeIrH_4(\mu\text{-}PPh_2)(CO)_3(PPh_3)_2]$ (δ −9.8 and −12.3)[14] and is substantially more deshielded than the values observed for the μ-H ligands in the complexes $[Fe_3(\mu\text{-}H)\{\mu\text{-}P(C_6H_4OMe\text{-}4)Me\}(CO)_9]$ [δ(μ-H) −19.41][12] and (**3b**) (δ −24.72). These data suggest that in solution the hydride ligand adopts a terminal site on Fe(1) and the absence of either ^{183}W satellites or coupling to the μ-P ligand provides additional support for this assignment.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of complex (4) shows a singlet at δ 175.4 p.p.m. [*J*(WP) 374 Hz], the observation of ^{183}W satellite peaks confirming that this ligand bridges a W–Fe bond. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum showed the expected signals including a resonance at δ 332.1 p.p.m. [s, *J*(WC) 108 Hz] ascribed to the μ_3-*C*R atom. This signal is *ca.* 62 p.p.m. more deshielded than that found for the co-ordinatively saturated precursor (2) [δ 270.5 p.p.m., *J*(WC) 110 Hz], and a similar relationship has previously been established for the chemical shifts of the μ-*C*R carbon centres in the pair of dimetal complexes $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_n(\eta\text{-}C_5H_5)]$ [*n* = 5, 32 c.v.e., δ 392.5; *n* = 6, 34 c.v.e., δ 331.3 p.p.m.].[8] Resonances due to the tungsten carbonyl ligand at δ 217.7 p.p.m. [*J*(WC) 176 Hz], two iron carbonyl ligands at δ 214.5 [d, *J*(PC) 10 Hz] and 210.8 p.p.m., and an $Fe(CO)_3$ group at δ 211.7 p.p.m., were also observed in accord with the solution structure of (**4b**) shown.

Decarbonylation of the μ-PEt_2 complex $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PEt_2)(CO)_7(\eta\text{-}C_5H_5)]$ (3) was also investigated to allow comparison with the results obtained for (2). Whereas (2) exists as a single isomer, in solution (3) exists as an equilibrium mixture of two isomers in which the hydride ligand bridges either a W–Fe (**3a**) or the Fe–Fe (**3b**) bond. Notwithstanding this difference, thermal decarbonylation of (3) proceeded smoothly to give good yields of the co-ordinatively unsaturated complex $[WFe_2(\mu_3\text{-}CR)H(\mu\text{-}PEt_2)(CO)_6(\eta\text{-}C_5H_5)]$ (5). Spectroscopic and analytical data for (5) suggest a structure in solution identical to that observed for (**4b**) with a terminal hydride ligand attached to iron. The unsubstituted parent cluster (**1a**) does not undergo thermal, photochemical, or chemical (Me_3NO) decarbonylation. The facile elimination of carbonyl ligands from the iron centres ligated by the μ-PR'_2 groups in (2) and (3) demonstrates that phosphido groups exert a labilising effect on CO ligands, and this effect has been noted in related systems.[15]

Solutions of complexes (4) and (5) readily react with CO (15 min, 20 °C) to regenerate their saturated precursors (2) and (3) respectively. Attempts to carry out reactions with hydrogen, ethene, or diazomethane were less successful. With hydrogen no reaction was observed [20 atm (*ca.* 2 × 10^6 Pa), 20 °C], and treatment with either ethene or diazomethane resulted in rapid reactions affording large numbers of products (> 5) which could not be isolated in sufficient yields to allow their identification. In contrast, (4) and (5) react cleanly with alkynes (R″C≡CR″, R″ = Me, Et, or Ph; 42 °C, CH_2Cl_2) to give good yields of the vinylacyl complexes $[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(O)C(R'')CHR''\}(\mu\text{-}PR'_2)(CO)_5(\eta\text{-}C_5H_5)]$ [R′ = Ph, R″ = Me (**6a**), Et (**6b**), or Ph (**6c**); R′ = Et, R″ = Me (7)]. Discussion of the spectroscopic data for these complexes is deferred until the results of a single-crystal *X*-ray diffraction study on the but-2-yne derivative (7) have been described.

The molecular structure of (7) is shown in Figure 2 and selected bond lengths and angles are in Table 4. The structure consists of a WFe_2 triangle of metal atoms capped by a μ_3-CR ligand. One W–Fe bond is bridged by a μ-PEt_2 ligand whilst the remaining W–Fe bond is bridged by a μ-C(O)C(Me)CHMe group which has been formed *via* coupling of hydride, but-2-yne, and CO ligands. Comparison of the W–μ-C and Fe–μ-C separations [W–C(10) 1.992(5), Fe(1)–C(10) 2.130(5), Fe(2)–C(10) 2.025(5) Å] with those observed in a series of related WFe_2 alkylidyne clusters (range W–μ-C 1.981—2.093, range Fe–μ-C 1.960—2.130 Å)[5] reveals somewhat long Fe–μ-C separations and a correspondingly short W–μ-C separation. The W–Fe [2.679(1) and 2.808(1) Å] and Fe–Fe [2.673(1) Å] separations are as expected for co-ordinatively saturated

Table 2. Hydrogen-1, carbon-13, and phosphorus-31 n.m.r. data[a] for the complexes

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]	^{31}P(δ)[d]
(4)	−10.55 (s, 1 H, FeH), 2.17 (s, 3 H, Me-4), 5.69 (s, 5 H, C_5H_5), 6.34, 6.80 [(AB)$_2$, 4 H, C_6H_4, J(HH) 8], 7.3—7.8 (m, 10 H, Ph)	332.1 [μ_3-*C*R, J(WC) 108], 217.7 [WCO, J(WC) 176], 214.5 [d, FeCO, J(PC) 10], 211.7 [Fe(CO)$_3$], 210.8 (FeCO), 163.4 [C^1(C_6H_4)], 145.1 [d, C^1(Ph), J(PC) 39], 143.2 [d, C^1(Ph), J(PC) 49], 137.4 [C^4(C_6H_4)], 125—134 (Ph, C_6H_4), 95.6 (C_5H_5), 21.1 (Me-4)	175.4 [s, WFe(μ-P), J(WP) 374]
(5)	−10.09 (s, 1 H, FeH), 1.35 [ddd, 3 H, CH$_2$*Me*, J(PH) 18, J(HH), 8, 8], 1.45 [ddd, 3 H, CH$_2$*Me*, J(PH) 17, J(HH) 8, 8] 1.6—3.4 (m, 4 H, C*H*$_2$Me), 2.25 (s, 3 H, Me-4), 5.65 [d, 5 H, C_5H_5, J(PH) 1], 6.54, 7.02 [(AB)$_2$, 4 H, C_6H_4, J(HH) 8]	331.0 [μ_3-*C*R, J(WC) 108], 216.1 [d, WCO, J(PC) 5], 215.4 [d, FeCO, J(PC) 12], 212.1 [Fe(CO)$_3$], 210.9 (FeCO), 164.1 [C^1(C_6H_4)], 136.9 [C^4(C_6H_4)], 128.6 [C^2, C^6 (C_6H_4)], 125.9 [C^3, C^5(C_6H_4)], 95.0 (C_5H_5), 32.9 [d, *C*H$_2$Me, J(PC) 20], 27.5 [d, *C*H$_2$Me, J(PC) 29], 21.1 (Me-4), 12.0 [d, CH$_2$*Me*, J(PC) 5], 11.2 [d, CH$_2$*Me*, J(PC) 5]	181.9 [s, WFe(μ-P), J(WP) 347]
(6a)	1.76 [d, 3 H, CH*Me*, J(HH) 6], 2.19 (s, 3 H, C*Me*), 2.41 (s, 3 H, Me-4), 2.54 [q, 1 H, C*H*Me, J(HH) 6], 5.10 [d, 5 H, C$_5$*H*$_5$, J(PH) 1], 6.7—7.9 (m, 14 H, C_6H_4, Ph)	[e]246.9 [d, μ_3-*C*R, J(PC) 12, J(WC) 137], 224.8 (FeCO), 219.8 (FeCO), 215.0 [br, Fe(CO)$_3$], 197.5 [*C*(O)C(Me), J(WC) 71], 159.0 [C^1(C_6H_4)], 145—127 (m, Ph, C_6H_4), 95.3 (C_5H_5), 77.6 (*C*Me), 51.3 (*C*HMe), 21.0 (Me-4), 17.1 (Me), 16.8 (Me)	170.4 [s, WFe(μ-P), J(WP) 317]
(6b)	1.35 [t, 3 H, CH$_2$*Me*, J(HH) 7], 1.38 [t, 3 H, CH$_2$*Me*, J(HH) 7], 1.9—2.6 (m, 5 H, C*H*$_2$Me, C*H*Et), 2.41 (s, 3 H, Me-4), 5.09 [d, 5 H, C_5H_5, J(PH) 1], 6.82, 7.08 [(AB)$_2$, 4 H, C_6H_4, J(HH) 8], 6.8—7.9 (m, 10 H, Ph)	247.0 [d, μ_3-*C*R, J(PC) 10, J(WC) 123], 224.9 (FeCO), 219.8 (FeCO), 215.0 [br, Fe(CO)$_3$], 197.2 [*C*(O)C(Et), J(WC) 56], 159.0 [C^1(C_6H_4)], 145—127 (m, Ph, C_6H_4), 95.2 (C_5H_5), 80.9 (*C*Et), 58.0 (*C*HEt), 25.6 (*C*H$_2$Me), 24.9 (*C*H$_2$Me), 21.0 (Me-4), 16.0 (CH$_2$*Me*), 14.0 (CH$_2$*Me*)	169.3 [s, WFe(μ-P), J(WP) 320]
(6c)	2.40 (s, 3 H, Me-4), 3.24 (s, 1 H, C*H*Ph), 5.24 [d, 5 H, C_5H_5, J(PH) 1], 6.84, 7.10 [(AB)$_2$, 4 H, C_6H_4, J(HH) 8], 7.2—7.6 (m, 20 H, Ph)	249.8 [d, μ_3-*C*R, J(PC) 10, J(WC) 128], 222.2 (FeCO), 219.8 (FeCO), 215.0 [br, Fe(CO)$_2$], 209.0 (br, FeCO), 194.7 [*C*(O)C(Ph)], 157.7 [C^1(C_6H_4)], 144—125 (m, Ph, C_6H_4), 95.3 (C_5H_5), 81.6 (*C*Ph), 50.1 (*C*HPh), 20.9 (Me-4)	173.0 [s, WFe(μ-P), J(WP) 317]
(7)	1.35 [ddd, 3 H, CH$_2$*Me*, J(PH) 18, J(HH) 7, 7], 1.51 [ddd, 3 H, CH$_2$*Me*, J(PH) 17, J(HH) 7, 7], 1.81 [d, 3 H, CH*Me*, J(HH) 6], 1.9—2.8 (m, 4 H, C*H*$_2$Me), 2.08 (s, 3 H, C*Me*), 2.36 (s, 3 H, Me-4), 2.84 [q, 1 H, C*H*Me, J(HH) 6], 5.17 (s, 5 H, C_5H_5), 6.80, 7.01 [(AB)$_2$, 4 H, C_6H_4, J(HH) 8]	245.9 [d, μ_3-*C*R, J(PC) 7, J(WC) 114], 225.0 (FeCO), 219.4 (FeCO), 212.0 [br, Fe(CO)$_3$], 205.7 [*C*(O)C(Me), J(WC) 64], 160.5 [C^1(C_6H_4)], 134.7 [C^4(C_6H_4)], 129.0 [C^2, C^6(C_6H_4)], 127.7 [C^3, C^5(C_6H_4)], 95.2 (C_5H_5), 78.2 (*C*Me), 57.3 (*C*HMe), 27.4 [d, *C*H$_2$Me, J(PC) 25], 20.9 (Me-4), 17.1 [d, *C*H$_2$Me, J(PC) 27], 16.6 (Me), 15.8 (Me), 12.0 [d, CH$_2$*Me*, J(PC) 5], 11.4 [d, CH$_2$*Me*, J(PC) 7]	183.1 [s, WFe(μ-P), J(WP) 303]
(8)	2.01 [d, 3 H, CH*Me*, J(HH) 6], 2.16 (s, 3 H, CMe), 2.48 (s, 3 H, Me-4), 5.46 (s, 5 H, C_5H_5), 6.65, 7.22 [(AB)$_2$, 4 H, C_6H_4, J(HH) 8], 7.1 [s, br, 1 H, C(OH)], 7.3—7.8 (m, 10 H, Ph)	*f*	178.5 [s, WFe(μ-P), J(WP) 339]
(9)	1.3—2.9 (m, 10 H, C*H*$_2$Me, CH$_2$*Me*), 2.00 [d, 3 H, CH*Me*, J(HH) 6], 2.22 (s, 3 H, C*Me*), 2.43 (s, 3 H, Me-4), 3.50 [q, 1 H, C*H*Me, J(HH) 6], 5.61 (s, 5 H, C_5H_5), 6.30 [s, br, 1 H, C(OH)], 6.53, 7.18 [(AB)$_2$, 4 H, C_6H_4, J(HH) 8]	305.6 [d, μ_3-*C*R, J(PC) 5, J(WC) 134], 243.1 [C(OH), J(WC) 151], 217.7 (FeCO), 213.0 (br, FeCO), 208.0 (FeCO), 207.0 (br, FeCO), 204.0 (br, FeCO), 159.8 [C^1(C_6H_4)], 138.9 [C^4(C_6H_4)], 129.2 [C^2, C^6(C_6H_4)], 125.8 [C^3, C^5(C_6H_4)], 115.4 (*C*Me), 99.5 (C_5H_5), 85.0 (*C*HMe), 31.0 [d, *C*H$_2$Me, J(PC) 23], 30.4 [d, *C*H$_2$Me, J(PC) 31], 21.0 (Me-4), 17.9 (Me), 16.4 (Me), 11.9 [d, CH$_2$*Me*, J(PC) 8], 11.6 [d, CH$_2$*Me*, J(PC) 6]	180.8 [s, WFe(μ-P), J(WP) 333]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in CD_2Cl_2 at room temperature. [c] Hydrogen-1 decoupled, measured in CD_2Cl_2–CH_2Cl_2, chemical shifts are positive to high frequency of $SiMe_4$. [d] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H_3PO_4 (external), measured in CD_2Cl_2–CH_2Cl_2. [e] N.O.e. spectrum ($CDCl_3$–$CHCl_3$) showed δ 50.3 p.p.m. [d, *C*HMe, J(HC) 159 Hz]. [f] Not measured.

clusters of this type. Interest centres on the μ-C(O)C(Me)CHMe ligand which adopts an η^3-bonding mode to Fe(2), whilst the C(O) end of the chain uses an orthogonal set of orbitals to η^2 bond to the W atom. The allylic bonding of the μ-C(O)C(Me)CHMe chain to Fe(2) is very similar to that observed in the mononuclear complex [N(PPh$_3$)$_2$][Fe(CO)$_3${η^3-C(O)C(R)CHR}] (R = CO$_2$Me),[16] and the η^2-co-ordination of the C(O) moiety to W resembles that found in the acyl complex [WCl$_2${η^2-C(O)CH$_2$Me}(CO)(η-C$_5$H$_5$)].[17] A parallel may also be drawn with the complex [MoMn{μ-CH$_2$C(Me)CH-Me}(μ-PPh$_2$)(μ-CO)(CO)$_3$(η-C$_5$H$_5$)], in which the μ-CH$_2$C-(Me)CHMe moiety is η^3 bonded to the Mo centre with an orthogonal Mn··· C··· H interaction.[18]

The analytical and spectroscopic data for compounds (**6a**)—(**6c**) and (**7**) suggest that these compounds all have structures in solution which are consistent with those established in the solid state for (**7**). The data for the but-2-yne complex (**6a**) are typical of this series. In the ^{1}H n.m.r. spectrum signals for the CHMe fragment of the vinylacyl ligand were observed at δ 1.76 (Me) and 2.54 (H) and the expected resonances were observed for the μ_3-CC$_6$H$_4$Me-4 ligand. The ^{31}P-{^{1}H} n.m.r. spectrum has a singlet resonance at δ 170.4 p.p.m. and the observation of ^{183}W satellite peaks [J(WP) 317 Hz] confirms that the μ-PPh$_2$ ligand bridges a heteronuclear W–Fe bond. In the ^{13}C-{^{1}H} n.m.r. spectrum the μ_3-*C*R resonance occurs at δ 246.9 p.p.m. and resonances at δ 224.8, 219.8 [Fe(CO)], and 215.0 p.p.m. [Fe(CO)$_3$] correspond to the five iron carbonyl ligands. The ligated carbon atoms of the μ-C(O)C(Me)CHMe moiety gives rise to signals at δ 197.5 [C(O), J(WC) 71 Hz], 77.6 (*C*Me), and 51.3 p.p.m. (*C*HMe). The chemical shift of the signal assigned to

Table 3. Selected internuclear distances (Å) and angles (°) for [WFe$_2$(μ$_3$-CC$_6$H$_4$Me-4)(μ-H)(μ-PPh$_2$)(CO)$_6$(η-C$_5$H$_5$)] (4)

W–Fe(1)	2.817(1)	W–Fe(2)	2.523(1)	W–P	2.357(1)	W–C(1)	1.978(5)
W–C(10)	2.018(4)	Fe(1)–Fe(2)	2.569(1)	Fe(1)–H(1)	1.73(4)	Fe(1)–C(2)	1.772(6)
Fe(1)–C(3)	1.818(6)	Fe(1)–C(4)	1.765(4)	Fe(1)–C(10)	1.916(5)	Fe(2)–P	2.219(1)
Fe(2)–H(1)	1.54(6)	Fe(2)–C(5)	1.777(4)	Fe(2)–C(6)	1.773(4)	Fe(2)–C(10)	2.132(3)
P–C(21)	1.821(4)	P–C(31)	1.826(5)	C(1)–O(1)	1.158(6)	C(2)–O(2)	1.150(8)
C(3)–O(3)	1.135(7)	C(4)–O(4)	1.145(5)	C(5)–O(5)	1.136(5)	C(6)–O(6)	1.144(5)
Fe(1)–W–Fe(2)	57.2(1)	Fe(1)–W–P	110.0(1)	Fe(2)–W–P	54.0(1)	Fe(1)–W–C(10)	42.8(1)
Fe(2)–W–C(10)	54.6(1)	P–W–C(10)	100.1(1)	W–Fe(1)–Fe(2)	55.6(1)	W–Fe(1)–H(1)	90(2)
Fe(2)–Fe(1)–H(1)	36(2)	Fe(2)–Fe(1)–C(2)	107.7(2)	H(1)–Fe(1)–C(2)	82(2)	Fe(2)–Fe(1)–C(3)	108.1(2)
H(1)–Fe(1)–C(3)	87(2)	C(2)–Fe(1)–C(3)	95.5(3)	Fe(2)–Fe(1)–C(4)	143.8(2)	H(1)–Fe(1)–C(4)	175(1)
C(2)–Fe(1)–C(4)	94.9(2)	C(3)–Fe(1)–C(4)	97.1(2)	W–Fe(1)–C(10)	45.7(1)	Fe(2)–Fe(1)–C(10)	54.5(1)
H(1)–Fe(1)–C(10)	84(2)	W–Fe(2)–Fe(1)	67.2(1)	W–Fe(2)–P	59.2(1)	Fe(1)–Fe(2)–P	124.8(1)
W–Fe(2)–H(1)	107(1)	Fe(1)–Fe(2)–H(1)	41(1)	P–Fe(2)–H(1)	154(2)	Fe(1)–Fe(2)–C(5)	113.6(2)
P-Fe(2)–C(5)	111.0(2)	H(1)–Fe(2)–C(5)	95(2)	Fe(1)–Fe(2)–C(6)	115.6(2)	H(1)–Fe(2)–C(6)	81(1)
C(5)–Fe(2)–C(6)	90.4(2)	W–Fe(2)–C(10)	50.5(1)	Fe(1)–Fe(2)–C(10)	47.0(1)	P–Fe(2)–C(10)	101.1(1)
H(1)–Fe(2)–C(10)	81(1)	W–P–Fe(2)	66.8(1)	W–P–C(21)	121.5(1)	Fe(2)–P–C(21)	119.8(2)
W–P–C(31)	121.0(1)	Fe(2)–P–C(31)	125.7(1)	C(21)–P–C(31)	101.2(2)	Fe(1)–H(1)–Fe(2)	104(2)
W–C(1)–O(1)	168.7(4)	Fe(1)–C(2)–O(2)	178.2(5)	Fe(1)–C(3)–O(3)	178.4(5)	Fe(1)–C(4)–O(4)	179.0(5)
Fe(2)–C(5)–O(5)	178.0(4)	Fe(2)–C(6)–O(6)	177.7(4)	W–C(10)–Fe(1)	91.4(2)	W–C(10)–Fe(2)	74.8(1)
Fe(1)–C(10)–Fe(2)	78.6(1)	W–C(10)–C(11)	131.7(3)	Fe(1)–C(10)–C(11)	132.5(4)	Fe(2)–C(10)–C(11)	125.4(3)

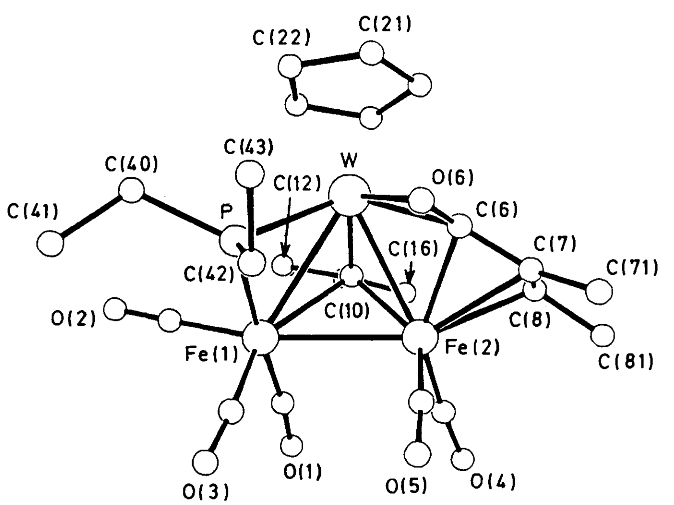


Figure 2. Molecular structure of [WFe$_2$(μ$_3$-CC$_6$H$_4$Me-4){μ-C(O)C(Me)CHMe}(μ-PEt$_2$)(CO)$_5$(η-C$_5$H$_5$)] (7) showing the atom numbering scheme

the acyl carbon atom is similar to the shift of δ 190.0 p.p.m. observed for the acyl carbon centre in the complex [WCo$_2${μ$_3$-C(C$_6$H$_4$Me-4)C(Et)C(Et)*C*(O)}(μ-CO)(CO)$_4${PPh$_2$C(Et)=CHEt}(η-C$_5$H$_5$)],[19] and the chemical shifts of the central *C*Me and outer *C*HMe carbon atoms are typical of those expected for π-allylic ligands.[20] In a proton-coupled nuclear Overhauser enhancement (n.O.e) ^{13}C n.m.r. spectrum of (**6a**) the resonance for the *C*HMe carbon atom appeared as a doublet [*J*(HC) 159 Hz)] providing additional confirmation of these assignments.

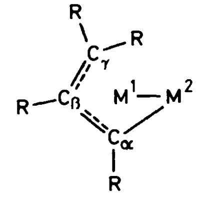
The formation of the complexes (**6a**)—(**6c**) and (**7**) may well involve alkyne addition to the unsaturated precursors (**4b**) or (**5**) followed by insertion of the alkyne into the Fe–H bond to yield *cis*-vinyl intermediates. Subsequent CO insertion would then afford the observed products (**6a**)—(**6c**) and (**7**). A very similar reaction occurs in the synthesis of the mononuclear complex [N(PPh$_3$)$_2$][Fe(CO)$_3${η^3-C(O)C(R)CHR}] (R = CO$_2$Me) from [N(PPh$_3$)$_2$][FeH(CO)$_4$] and RC≡CR (R = CO$_2$Me), but here the product contains a *trans*-vinylacyl moiety, in contrast to the *cis* stereochemistry observed for this fragment in complexes (**6a**)—(**6c**) and (**7**).[16] Several reactions of related transition-metal hydrides with alkynes provide examples of stable complexes analogous to the intermediates likely to be involved in the formation of (**6a**)—(**6c**) and (**7**). Thus, the co-ordinatively unsaturated complex [Ru$_3$(μ-H)(μ-PPh$_2$)(CO)$_9$] with PhC≡CPh affords the μ$_3$-alkyne derivative [Ru$_3$(μ$_3$-PhC≡CPh)(μ-H)(μ-PPh$_2$)(CO)$_9$].[21] In contrast, the dimetal species [Mn$_2$(μ-H)(μ-PPh$_2$)(CO)$_8$] reacts with alkynes under u.v. irradiation to afford the vinyl complexes [Mn$_2$(μ-CR=CHR)(μ-PPh$_2$)(CO)$_7$],[22] and in a similar manner the unsaturated complex [Os$_3$(μ-H)$_2$(CO)$_{10}$] reacts with PhC≡CPh to yield the vinyl species [Os$_3$(μ-H)(μ-CPh=CHPh)(CO)$_{10}$].[23]

Protonation of [N(PPh$_3$)$_2$][Fe(CO)$_3${η^3-C(O)C(R)CHR}] with CF$_3$CO$_2$H gives the neutral alkene complex [Fe(CO)$_4${η-C(R)H=CHR}] *via* de-insertion of the acyl carbonyl group. In contrast, methylation with [Me$_3$O][BF$_4$] or MeOSO$_2$F affords the complex [Fe{C(OMe)C(R)CHR}(CO)$_3$] *via* addition of Me$^+$ to the acyl oxygen atom.[24] It was therefore of interest to examine protonation of the related μ-C(O)C(Me)CHMe ligands bridging the W–Fe dimetal centres in complexes (**6a**) and (**7**).

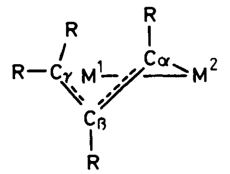
Protonation of complex (**6a**) or (**7**) (CH$_2$Cl$_2$, HBF$_4$·Et$_2$O) occurs at the oxygen atom of the *cis*-{μ-C(O)C(Me)CHMe} ligand affording the unsaturated (46 c.v.e.) μ-allylidene derivatives [WFe$_2$(μ$_3$-CC$_6$H$_4$Me-4){μ-C(OH)C(Me)CHMe}(μ-PR'$_2$)(CO)$_5$(η-C$_5$H$_5$)][BF$_4$] [R' = Ph (**8**) or Et (**9**)]. Solutions of the latter complexes decompose over a period of hours in CH$_2$Cl$_2$ and the spectroscopic data for these compounds are therefore of comparatively poor quality. Analytical data were however in excellent agreement with the proposed structures. Data for the two species are similar and only those for complex (**9**) are described here. The ^{1}H n.m.r. spectrum shows the expected resonances for the CHMe group at δ 3.50 [q, C*H*Me, *J*(HH) 6 Hz] and 2.00. [d, CH*Me*, *J*(HH) 6 Hz], and a broad signal at δ 6.3 may be assigned to the OH proton. The ^{31}P-{^{1}H} n.m.r. spectrum showed a singlet resonance at δ 180.8 p.p.m. and the observation of ^{183}W satellite peaks [*J*(WP) 333 Hz] confirms that this group bridges a W–Fe bond. In the ^{13}C-{^{1}H} n.m.r. spectrum the μ$_3$-*C*R resonance appears as a doublet at δ 305.6 p.p.m. [*J*(PC) 5, *J*(WC) 134 Hz] and resonances for the ligated carbon atoms of the μ-C(OH)C(Me)CHMe ligand are observed at δ 243.1 [C(OH), *J*(WC) 151 Hz], 115.4 (*C*Me), and 85.0 p.p.m. (*C*HMe). The μ$_3$-*C*R resonance is *ca.* 60 p.p.m. downfield of that observed for the precursor compound (**7**) [δ (μ$_3$-*C*R) 245.9 p.p.m.], and this is consistent with the formulation of (**9**) as a co-ordinatively unsaturated 46 c.v.e. complex.

Table 4. Selected internuclear distances (Å) and angles (°) for [$WFe_2(\mu_3$–CC_6H_4Me-4){μ-C(O)C(Me)CHMe}(μ-$PEt_2)(CO)_5(\eta$-$C_5H_5)$] (**7**)

W–Fe(1)	2.808(1)	W–Fe(2)	2.679(1)	W–P	2.374(2)	W–C(6)	2.011(5)
W–O(6)	2.281(4)	W–C(10)	1.992(5)	Fe(1)–Fe(2)	2.673(1)	Fe(1)–P	2.262(2)
Fe(1)–C(1)	1.785(7)	Fe(1)–C(2)	1.792(7)	Fe(1)–C(3)	1.782(7)	Fe(1)–C(10)	2.130(5)
Fe(2)–C(4)	1.770(7)	Fe(2)–C(5)	1.787(6)	Fe(2)–C(6)	2.083(5)	Fe(2)–C(7)	2.173(6)
Fe(2)–C(8)	2.186(6)	Fe(2)–C(10)	2.025(5)	P–C(40)	1.830(7)	P–C(42)	1.815(7)
C(1)–O(1)	1.145(8)	C(2)–O(2)	1.138(9)	C(3)–O(3)	1.148(9)	C(4)–O(4)	1.150(9)
C(5)–O(5)	1.144(8)	C(6)–O(6)	1.296(6)	C(6)–C(7)	1.408(8)	C(7)–C(71)	1.525(8)
C(7)–C(8)	1.379(8)	C(8)–H(8)	0.99(4)	C(8)–C(81)	1.500(9)		
Fe(1)–W–Fe(2)	58.3(1)	Fe(1)–W–P	50.9(1)	Fe(2)–W–P	93.9(1)	Fe(1)–W–C(6)	101.9(2)
Fe(1)–W–O(6)	104.6(1)	Fe(2)–W–O(6)	74.8(1)	P–W–O(6)	81.5(1)	C(6)–W–O(6)	34.3(2)
Fe(1)–W–C(10)	49.2(2)	Fe(2)–W–C(10)	48.7(1)	P–W–C(10)	99.8(2)	W–Fe(1)–Fe(2)	58.5(1)
W–Fe(1)–P	54.6(1)	Fe(2)–Fe(1)–P	96.8(1)	C(1)–Fe(1)–C(2)	90.7(3)	C(1)–Fe(1)–C(3)	95.6(3)
C(2)–Fe(1)–C(3)	101.9(3)	W–Fe(1)–C(10)	45.0(1)	Fe(2)–Fe(1)–C(10)	48.3(1)	P–Fe(1)–C(10)	99.3(2)
W–Fe(2)–Fe(1)	63.3(1)	C(4)–Fe(2)–C(5)	93.1(3)	W–Fe(2)–C(6)	48.0(1)	W–Fe(2)–C(7)	83.3(1)
C(6)–Fe(2)–C(7)	38.6(2)	W–Fe(2)–C(8)	95.3(2)	C(6)–Fe(2)–C(8)	67.2(2)	C(7)–Fe(2)–C(8)	36.9(2)
W–Fe(2)–C(10)	47.6(2)	Fe(1)–Fe(2)–C(10)	51.7(2)	W–P–Fe(1)	74.5(1)	W–P–C(40)	122.6(2)
Fe(1)–P–C(40)	116.8(2)	W–P–C(42)	117.8(2)	Fe(1)–P–C(42)	119.3(2)	C(40)–P–C(42)	104.5(3)
Fe(1)–C(1)–O(1)	176.6(6)	Fe(1)–C(2)–O(2)	176.4(7)	Fe(1)–C(3)–O(3)	117.0(6)	Fe(2)–C(4)–O(4)	176.1(6)
Fe(2)–C(5)–O(5)	176.7(6)	W–C(6)–Fe(2)	81.7(2)	W–C(6)–O(6)	84.3(3)	Fe(2)–C(6)–O(6)	125.8(4)
W–C(6)–C(7)	142.7(4)	Fe(2)–C(6)–C(7)	74.2(3)	O(6)–C(6)–C(7)	133.0(5)	W–O(6)–C(6)	61.3(3)
Fe(2)–C(7)–C(6)	67.3(3)	Fe(2)–C(7)–C(71)	126.5(4)	C(6)–C(7)–C(71)	119.2(5)	Fe(2)–C(7)–C(8)	72.1(3)
C(6)–C(7)–C(8)	115.9(5)	C(71)–C(7)–C(8)	124.7(5)	Fe(2)–C(8)–C(7)	71.1(3)	Fe(2)–C(8)–H(8)	98(3)
C(7)–C(8)–H(8)	113(3)	Fe(2)–C(8)–C(81)	126.0(5)	C(7)–C(8)–C(81)	123.0(5)	H(8)–C(8)–C(81)	116(3)



cis



trans

Complexes such as (**8**) or (**9**) in which an organic ligand of the general formula μ-σ:η^3-C(R)C(R)CR_2 bridges a metal–metal bond have been variously described as μ-allylidenes, vinylcarbenes, or σ,π-allyls. Two possible conformations of this C_3 fragment have been observed as shown below, and they are generally referred to as *cis* or *trans*, reflecting the relationship between M^2 and C_γ.

If protonation of the C(O) group in (**6a**) and (**7**) occurs with retention of configuration the resulting complexes (**8**) and (**9**) would be expected to have the *cis*-μ-allylidene structures shown. Complexes with *trans*-μ-allylidene ligands are comparatively rare,[25,26] however *cis* species are well established and structurally characterised examples include the complexes [Mo_2{μ-C(H)C(H)CMe_2}$(CO)_4(\eta$-$C_5H_5)_2$],[27] [Fe_2{μ-C(CO_2Me)-C(CO_2Me)CHMe}$(CO)_2(\eta$-$C_5H_5)_2$],[28] [Ru_2{μ-C(Me)C(Me)-CH_2}$(CO)_2(\eta$-$C_5H_5)_2$],[29] and [WCo{μ-C(C_6H_4Me-4)C(Me)-CHMe}(μ-CO)(CO)$(\eta$-$C_5H_5)(\eta$-$C_5Me_5)$][BF_4].[30]

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. All solvents were dried and deoxygenated before use. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free atmosphere. The i.r. spectra were measured with Nicolet 10-MX and 5Z-DX spectrophotometers, and n.m.r. spectra with JNM FX 90Q, GX 270, and GX 400 instruments. Chromatography was carried out on Aldrich Florisil (100—200 mesh) or B.D.H. Alumina. The compounds [$WFe_2(\mu_3$-CC_6H_4Me-4)(μ-H)(μ-$PR'_2)(CO)_7(\eta$-$C_5H_5)$] [R′ = Ph (**2**) or Et (**3**)] were prepared by the literature method.[5] Analytical and other data for the new compounds are listed in Tables 1 and 2.

Thermolysis of the Complexes [$WFe_2(\mu_3$-CC_6H_4Me-4)(μ-H)(μ-$PR'_2)(CO)_7(\eta$-$C_5H_5)$] [R′ = Ph (**2**) or Et (**3**)].—A toluene (20 cm^3) solution of complex (**2**) (0.52 g, 0.61 mmol) was refluxed (111 °C) for 30 min, after which time the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (2:3) and chromatographed on alumina at −40 °C. Elution with the same solvent afforded two bands. The first olive-green band (*ca.* 5%) was identified as unchanged (**2**) by its i.r. spectrum. The second dark grey band was collected, and the solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2–light petroleum (1:10) afforded black *crystals* of [$WFe_2(\mu_3$-CC_6H_4Me-4)(μ-H)(μ-$PPh_2)(CO)_6(\eta$-$C_5H_5)$] (**4**) (0.44 g).

Similarly a solution of complex (**3**) (0.27 g, 0.36 mmol) in toluene (20 cm^3) was refluxed (111 °C) for 40 min, and then the solvent was removed *in vacuo*. The residue was chromatographed and recrystallised as for (**2**), to afford black *microcrystals* of [$WFe_2(\mu_3$-CC_6H_4Me-4)(μ-H)(μ-$PEt_2)(CO)_6(\eta$-$C_5H_5)$] (**5**) (0.21 g). Compound (**5**) decomposes slowly in air, and its solutions are very air sensitive.

Reactions of the Complexes [$WFe_2(\mu_3$-CC_6H_4Me-4)(μ-H)(μ-$PR'_2)(CO)_6(\eta$-$C_5H_5)$] [R′ = Ph (**4**) *or* Et (**5**)] *with Alkynes*.—(*i*) A toluene (15 cm^3) solution of [$WFe_2(\mu_3$-CC_6H_4Me-4)(μ-H)(μ-$PPh_2)(CO)_7(\eta$-$C_5H_5)$] (**2**) (0.40 g, 0.47 mmol) was refluxed for 30 min (111 °C) to generate (**4**) *in situ*. The solvent was removed *in vacuo* and replaced by CH_2Cl_2 (30 cm^3). An excess of but-2-yne (0.25 g, 4.6 mmol) was added to this solution of (**4**), which was then refluxed (42 °C). After 15 h the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (1:3) and chromatographed on alumina. Gradient elution with CH_2Cl_2–light petroleum (1:3 to 2:1) afforded a major green band, from which the solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2–light petroleum (1:8) afforded dark green *microcrystals* of [$WFe_2(\mu_3$-CC_6H_4Me-4) {μ-C(O)C-(Me)CHMe}(μ-$PPh_2)(CO)_5(\eta$-$C_5H_5)$] (**6a**) (0.18 g).

(*ii*) Using the above procedure the reaction of [$WFe_2(\mu_3$-CC_6H_4Me-4)(μ-H)(μ-$PPh_2)(CO)_7(\eta$-$C_5H_5)$] (**2**) (0.40 g, 0.47

Table 5. Atomic positional parameters (fractional co-ordinates) for compound (**4**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2 549(1)	1 137(1)	3 401(1)	C(15)	6 114(5)	2 547(4)	1 106(3)
Fe(1)	968(1)	2 242(1)	2 425(1)	C(16)	4 980(5)	2 007(4)	1 594(3)
Fe(2)	1 190(1)	16(1)	1 788(1)	C(17)	7 520(6)	4 254(5)	235(4)
P	2 006(1)	−1 075(1)	2 651(1)	C(21)	758(4)	−2 412(4)	3 093(3)
C(1)	528(5)	572(4)	3 644(3)	C(22)	33(5)	−3 617(5)	2 489(4)
O(1)	−578(3)	180(3)	3 913(2)	C(23)	−857(6)	−4 654(5)	2 834(4)
C(2)	733(5)	2 911(5)	1 442(3)	C(24)	−1 026(6)	−4 513(6)	3 782(5)
O(2)	549(5)	3 347(5)	813(3)	C(25)	−306(6)	−3 326(6)	4 380(4)
C(3)	−826(5)	1 933(5)	2 752(4)	C(26)	578(5)	−2 274(5)	4 046(3)
O(3)	−1 958(4)	1 732(5)	2 935(4)	C(31)	3 418(4)	−1 709(4)	2 372(3)
C(4)	1 802(5)	3 778(5)	3 209(3)	C(32)	3 778(5)	−2 431(4)	2 953(3)
O(4)	2 361(5)	4 773(4)	3 717(3)	C(33)	4 926(5)	−2 817(5)	2 818(4)
C(5)	1 768(4)	−133(4)	643(3)	C(34)	5 738(5)	−2 468(5)	2 106(4)
O(5)	2 177(4)	−206(4)	−77(2)	C(35)	5 399(5)	−1 767(5)	1 510(4)
C(6)	−436(5)	−1 312(5)	1 352(3)	C(36)	4 229(5)	−1 387(4)	1 642(3)
O(6)	−1 471(4)	−2 172(4)	1 041(3)	C(41)	3 989(7)	986(6)	4 638(4)
C(10)	2 718(4)	1 958(4)	2 262(3)	C(42)	4 880(6)	1 704(7)	4 066(4)
C(11)	3 944(4)	2 572(4)	1 783(3)	C(43)	4 622(6)	2 852(6)	4 127(4)
C(12)	4 173(5)	3 739(4)	1 478(3)	C(44)	3 574(6)	2 827(6)	4 727(4)
C(13)	5 334(5)	4 285(4)	1 015(3)	C(45)	3 221(6)	1 694(7)	5 044(3)
C(14)	6 306(5)	3 690(4)	794(3)				

Table 6. Atomic positional parameters (fractional co-ordinates) for compound (**7**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1 124(1)	5 617(1)	6 256(1)	C(81)	−38(5)	3 444(4)	7 574(4)
Fe(1)	2 868(1)	5 291(1)	6 598(1)	C(10)	1 658(4)	5 417(3)	7 091(3)
Fe(2)	1 556(1)	4 328(1)	6 826(1)	C(11)	1 604(4)	5 768(3)	7 723(3)
P	2 416(1)	5 641(1)	5 631(1)	C(12)	2 010(4)	6 448(3)	7 851(3)
C(1)	3 174(4)	4 999(4)	7 367(3)	C(13)	1 942(5)	6 785(4)	8 444(3)
O(1)	3 402(3)	4 839(3)	7 861(2)	C(14)	1 451(5)	6 461(3)	8 916(3)
C(2)	3 468(5)	6 150(4)	6 692(3)	C(15)	1 016(4)	5 786(4)	8 787(3)
O(2)	3 878(4)	6 677(3)	6 773(3)	C(16)	1 107(4)	5 445(3)	8 203(3)
C(3)	3 647(4)	4 715(4)	6 199(3)	C(17)	1 388(6)	6 821(4)	9 564(3)
O(3)	4 178(4)	4 358(3)	5 958(3)	C(21)	−8(4)	6 285(4)	5 746(3)
C(4)	1 860(5)	3 895(3)	7 541(3)	C(22)	686(5)	6 785(3)	5 823(3)
O(4)	2 023(4)	3 584(3)	7 999(3)	C(23)	823(4)	6 885(3)	6 469(4)
C(5)	2 105(5)	3 633(3)	6 365(3)	C(24)	211(4)	6 445(3)	6 783(3)
O(5)	2 486(4)	3 186(3)	6 091(3)	C(25)	−308(4)	6 077(4)	6 338(3)
C(6)	608(4)	4 583(3)	6 154(2)	C(40)	2 879(5)	6 512(4)	5 317(3)
O(6)	755(3)	4 692(2)	5 563(2)	C(41)	3 849(5)	6 472(5)	5 093(4)
C(7)	270(4)	3 970(3)	6 495(3)	C(42)	2 494(4)	4 976(4)	4 989(3)
C(71)	60(5)	3 241(3)	6 151(3)	C(43)	2 005(5)	5 220(5)	4 395(3)
C(8)	219(4)	4 064(3)	7 135(3)				

mmol) with a large excess of hex-3-yne (*ca.* 0.5 cm^3) gave dark olive-green *microcrystals* of $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}C(O)C(Et)CHEt\}(\mu\text{-}PPh_2)(CO)_5(\eta\text{-}C_5H_5)]$ (**6b**) (0.20 g).

(*iii*) A toluene (15 cm^3) solution of $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7(\eta\text{-}C_5H_5)]$ (**2**) (0.40 g, 0.47 mmol) was refluxed for 30 min (111 °C) to generate complex (**4**) *in situ*. The solvent was removed *in vacuo* and replaced by CH_2Cl_2 (30 cm^3). An excess of diphenylacetylene (0.42 g, 2.35 mmol) was added to this solution of (**4**), which was then refluxed (42 °C). After 48 h, the solvent was removed *in vacuo*. Isolation and purification as described in (*i*) gave dark green *microcrystals* of $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}C(O)C(Ph)CHPh\}(\mu\text{-}PPh_2)(CO)_5(\eta\text{-}C_5H_5)]\cdot CH_2Cl_2$ (**6c**) (0.21 g).

(*iv*) A toluene (15 cm^3) solution of $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PEt_2)(CO)_7(\eta\text{-}C_5H_5)]$ (**3**) (0.30 g, 0.40 mmol) was refluxed for 40 min (111 °C) to generate complex (**5**) *in situ*. The solvent was removed *in vacuo* and replaced by CH_2Cl_2 (30 cm^3). An excess of but-2-yne (0.25 g, 4.6 mmol) was added to this solution of (**5**), which was then refluxed (42 °C). After 15 h the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (1:3) and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (2:3) afforded a major brown band, from which the solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2–light petroleum (1:8) afforded large dark brown *crystals* of $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}C(O)C(Me)CHMe\}(\mu\text{-}PEt_2)(CO)_5(\eta\text{-}C_5H_5)]$ (**7**) (0.16 g).

Protonation of the Complexes $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}C(O)C(Me)CHMe\}(\mu\text{-}PR'_2)(CO)_5(\eta\text{-}C_5H_5)]$ $[R' = Ph$ (**6a**) *or* Et (**7**)] *with* $HBF_4\cdot Et_2O$.—(*i*) A CH_2Cl_2 (5 cm^3) solution of complex (**6a**) (0.22 g, 0.25 mmol) was treated with $HBF_4\cdot Et_2O$ (0.25 mmol) at 20 °C. After 5 min the volume of the solution was reduced to *ca.* 2 cm^3 *in vacuo*. Slow addition of diethyl ether (5 cm^3) afforded $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}C(OH)C(Me)CHMe\}(\mu\text{-}PPh_2)(CO)_5(\eta\text{-}C_5H_5)][BF_4]$ (**8**) (0.22 g) as a brown powder.

(*ii*) A CH_2Cl_2 (5 cm^3) solution of complex (**7**) (0.30 g, 0.39 mmol) was similarly treated with *ca.* 1 equivalent of $HBF_4\cdot Et_2O$ (0.39 mmol) at 20 °C. Crystallisation as above afforded $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}C(OH)C(Me)CHMe\}(\mu\text{-}PEt_2)(CO)_5(\eta\text{-}C_5H_5)][BF_4]$ (**9**) (0.27 g) as a very air-sensitive brown powder.

Crystal Structure Determinations.—Data were collected using Nicolet $P2_1$ or $P3$ diffractometers (293 K, Mo-K_α X-radiation, graphite monochromator, $\bar{\lambda} = 0.710\ 69$ Å). The data were corrected for Lorentz, polarisation and X-ray absorption effects.[31] The structures were solved by conventional heavy-atom or direct methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. Final refinements by blocked-cascade least squares were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs.[31] Scattering factors with corrections for anomalous dispersion were taken from ref. 32. Atom coordinates are given in Tables 5 and 6.

Crystals of $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ were grown from CH_2Cl_2–light petroleum (1:10) as black prisms (crystal dimensions *ca.* 0.45 × 0.42 × 0.34 mm). Of the 5 868 data collected (θ—2θ scans, $2\theta \leqslant 50°$), 4 775 unique data had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement. An empirical absorption correction was applied using a method based upon azimuthal scan data.

Crystal data for (**4**). $C_{31}H_{23}Fe_2O_6PW$, $M = 818.0$, triclinic, space group $P\bar{1}$, $a = 10.089(4)$, $b = 11.145(6)$, $c = 14.501(7)$ Å, $\alpha = 100.87(4)$, $\beta = 92.01(4)$, $\gamma = 110.62(4)°$, $U = 1\ 489(1)$ Å^3, $Z = 2$, $D_c = 1.82$ g cm^{-3}, $F(000) = 796$, $\mu(\text{Mo-}K_\alpha) = 49.9$ cm^{-1}.

All non-hydrogen atoms were refined with anisotropic thermal parameters. The position of the μ-H(1) hydrogen atom was refined with an isotropic thermal parameter. All other hydrogen atoms were included in calculated positions (C–H 0.96 Å) with either fixed isotropic thermal parameters *ca.* 1.2 $U_{\text{equiv.}}$ of the parent carbon atoms (C_6H_5, C_6H_4, and η-C_5H_5), or a common refined isotropic thermal parameter (Me-4). Final $R = 0.027$ ($R' = 0.028$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0003|F|^2]$. The final electron-density difference synthesis showed no peaks >0.9 or <-0.5 e Å^{-3}.

Crystals of $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}C(O)C(Me)CHMe\}(\mu\text{-}PEt_2)(CO)_5(\eta\text{-}C_5H_5)]$ (**7**) were grown from CH_2Cl_2–light petroleum (1:8). A dark brown block-shaped fragment (crystal dimensions *ca.* 0.45 × 0.35 × 0.20 mm) was cut from the corner of a much larger plate-like crystal. Of the 6 254 data collected (θ—2θ scans, $2\theta \leqslant 55°$), 4 188 unique data had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement. An empirical absorption correction was applied using a method based upon azimuthal scan data.

Crystal data for (**7**). $C_{27}H_{29}Fe_2O_6PW$, $M = 776.1$, orthorhombic, space group $Pbca$, $a = 15.192(4)$, $b = 17.797(6)$, $c = 21.351(7)$ Å, $U = 5\ 772(3)$ Å^3, $Z = 8$, $D_c = 1.79$ g cm^{-3}, $F(000) = 3\ 040$, $\mu(\text{Mo-}K_\alpha) = 51.5$ cm^{-1}.

All non-hydrogen atoms were refined with anisotropic thermal parameters. The position of the vinyl hydrogen H(8) was refined with an isotropic thermal parameter. All other hydrogen atoms were included in calculated positions (C–H 0.96 Å) with either fixed isotropic thermal parameters *ca.* $1.2U_{\text{equiv.}}$ of the parent carbon atoms (C_6H_4 and η-C_5H_5), or common refined isotropic thermal parameters (Me-4, Me, and CH_2). Final $R = 0.032$ ($R' = 0.032$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0003|F|^2]$. The final electron-density difference synthesis showed no peaks >1.1 or <-1.0 e Å^{-3}.

Acknowledgements

We thank the S.E.R.C. for support *via* a research studentship (to J. G. L-S.).

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Received 16*th August* 1989; *Paper* 9/03516H