Reactions of the Co-ordinatively Unsaturated μ_3-Alkylidyne Cluster $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ with PMe_2Ph†

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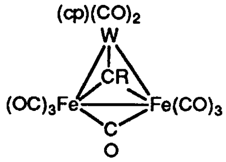
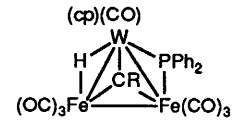
Treatment of the co-ordinatively unsaturated complex $[WFe_2H(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ (**3b**; R = C_6H_4Me-4) with 1 equivalent of PMe_2Ph at 20 °C affords the thermally unstable kinetic derivative $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(PMe_2Ph)(\eta\text{-}C_5H_5)]$ (**4**). N.m.r. spectroscopy reveals that at −40 °C compound (**4**) exists as an equilibrium mixture of two isomers [(**4a**) : (**4b**) = 4 : 3]. The core structures of all the PMe_2Ph derivatives described have features in common, and consist of a WFe_2 triangle of metal atoms which is capped by a μ_3-CR moiety. One W–Fe bond is bridged by a μ-PPh_2 ligand and the W atom carries a CO ligand and a cyclopentadienyl ring. In addition, for (**4a**) and (**4b**), the Fe–Fe bond is bridged by an hydride ligand and the iron atom remote from the μ-PPh_2 group carries three terminal CO ligands. The Fe atom which is ligated by the μ-PPh_2 group carries two CO ligands and the PMe_2Ph ligand. In isomer (**4a**) one of the latter CO ligands is pseudo *trans* to the μ-PPh_2 group, whereas the PMe_2Ph ligand adopts this site in (**4b**). At ambient temperature rotation of the $Fe(CO)_2(PMe_2Ph)$ group leads to interconversion of (**4a**) and (**4b**), but at this temperature (**4**) also isomerises to the thermodynamically favoured isomer $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)]$ (**5**). In compound (**5**) the hydride ligand bridges a W–Fe bond and the Fe–Fe bond is bridged by a CO ligand. The iron atom ligated by the μ-PPh_2 group carries two terminal CO ligands, whilst the remaining iron centre now carries the PMe_2Ph ligand and two terminal CO ligands. Thermal decarbonylation of (**5**) gives two new co-ordinatively unsaturated isomers $[WFe_2H(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)]$ (**7**) and (**8**) which do not interconvert at room temperature. The structure of (**7**) is closely related to that of compound (**4**) except that an $FeH(CO)(PMe_2Ph)$ group is now ligated by the μ-PPh_2 ligand. The structure of (**8**) is similarly related to that of (**5**), but the Fe–Fe bond is no longer bridged by a CO ligand and the hydride occupies a terminal site on the Fe atom remote from the μ-PPh_2 group. Compound (**7**) does not react with CO, but (**8**) with CO readily gives the saturated precursor (**5**). Compounds (**7**) and (**8**) do not react with PMe_2Ph at ambient temperatures but both react with this ligand in refluxing toluene to give good yields of the co-ordinatively unsaturated bis-PMe_2Ph complex $[WFe_2H(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (**9**). In compound (**9**) the iron centre remote from the μ-PPh_2 group carries two CO ligands and a PMe_2Ph ligand, whilst an $FeH(CO)(PMe_2Ph)$ group is ligated by the μ-PPh_2 ligand.

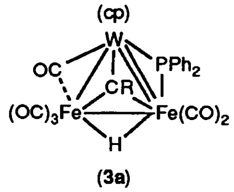
We have previously reported that treatment of the complex $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**1**; R = C_6H_4Me-4) with 1 equivalent of PPh_2H gives good yields of the complex $[WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7(\eta\text{-}C_5H_5)]$ (**2**).[1] Thermal decarbonylation of (**2**) (toluene, 111 °C) affords the co-ordinatively unsaturated, 46 c.v.e. (cluster valence electron) complex (**3**). A single-crystal *X*-ray diffraction study revealed that in the solid state the hydride ligand in (**3**) bridges the Fe–Fe bond. In contrast, solution n.m.r. data suggest a slightly different structure (**3b**) with a terminal hydride ligand attached to the iron centre which is remote from the bridging PPh_2 ligand.[2] Such clusters are comparatively scarce,[3] and often show enhanced reactivity towards a variety of donor ligands. Thus, treatment of (**3**) with alkynes ($R'C{\equiv}CR'$; R′ = Me, Et, or Ph) gives the novel vinylacyl complexes $[WFe_2(\mu_3\text{-}CR)\{\mu\text{-}C(O)C(R')CHR'\}(\mu\text{-}PPh_2)(CO)_5(\eta\text{-}C_5H_5)]$, which were structurally characterised by a single-crystal *X*-ray diffraction study on the but-2-yne derivative.[2] In this paper we report the reactions of complex (**3**) with PMe_2Ph which lead to a surprising variety of new saturated and co-ordinatively unsaturated PMe_2Ph derivatives.



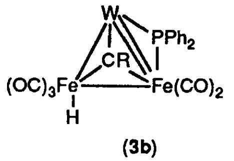
(**1**)



(**2**)



(**3a**)



(**3b**)

R = C_6H_4Me-4, cp = η - C_5H_5

Results and Discussion

Treatment of the co-ordinatively unsaturated complex $[WFe_2H(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ (**3b**) with 1 equivalent of PMe_2Ph at 20 °C results in an immediate colour change from dark green-brown to dark red-brown. However, over a period of *ca.* 12 h the colour of the solution continues to change,

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† *Non-S.I. unit employed:* atm = 101 325 Pa.

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

Compound[b]	Colour	Yield %	ν(CO)[c]/cm⁻¹	Analysis/% C	Analysis/% H
(4a), **(4b)** $[\mathrm{WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(PMe_2Ph)(\eta\text{-}C_5H_5)}]$[d]	Brown	81	2 027s, 1 998s, 1 954s (br), 1 800w (br)		
(5) $[\mathrm{WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)}]\cdot\mathrm{CH_2Cl_2}$	Black	83	2 010m, 1 987s, 1 948s, 1 887w, 1 804w (br)	46.4 (46.1)	3.5 (3.5)
(7) $[\mathrm{WFe_2H(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)}]\cdot\mathrm{CH_2Cl_2}$	Purple	57	2 026s, 1 960s, 1 950s (sh), 1 907m, 1 808w (br)	46.0 (46.2)	3.7 (3.6)
(**8**) $[\mathrm{WFe_2H(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)}]\cdot\mathrm{CH_2Cl_2}$	Green-brown	29	1 995s, 1 968s, 1 931m, 1 920m (sh), 1 820w (br)	49.3 (49.2)	3.8 (3.7)
(9) $[\mathrm{WFe_2H(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)}]\cdot 1.5\mathrm{CH_2Cl_2}$	Black	86	1 959s, 1 901s, 1 890m (sh), 1 778w (br)	47.9 (47.9)	4.3 (4.1)

[a] Calculated values are given in parentheses. [b] R = $\mathrm{C_6H_4Me}$-4. [c] In $\mathrm{CH_2Cl_2}$. [d] Unstable isomers see text.

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

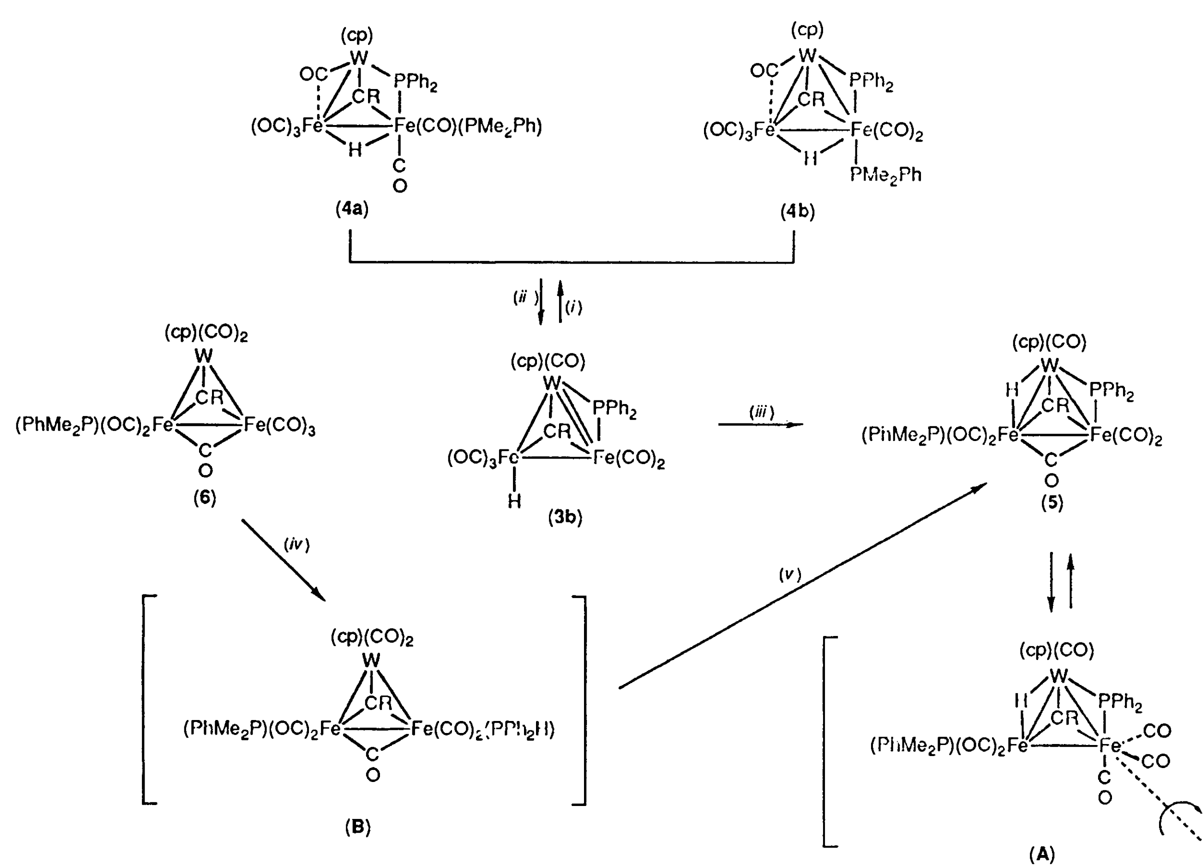
Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(4)[d]	(**4a**), −24.57 [dd, 1 H, $\mathrm{Fe_2(\mu\text{-}H)}$, J(PH) 28, 17]; (**4b**), −24.38 [dd, 1 H, $\mathrm{Fe_2(\mu\text{-}H)}$, J(PH) 28, 10]	
(5)	−18.18 [dd, 1 H, WFe(μ-H), J(PH) 31, 11, J(WH) 50], 1.93 [d, 3 H, P*Me*$_2$Ph, J(PH) 8], 2.12 (s, 3 H, Me-4), 2.16 [d, 3 H, P*Me*$_2$Ph, J(PH) 7], 5.20 [d, 5 H, $\mathrm{C_5H_5}$, J(PH) 1], 6.47, 6.74 [(AB)$_2$, 4 H, $\mathrm{C_6H_4}$, J(HH) 8], 6.8—7.5 (m, 15 H, Ph)	[e] 226.2 [dd, μ$_3$-*C*R, J(PC) 34, 7], 225.9 [d, WCO, J(PC) 10, J(WC) 142], 211.2 (FeCO), 207.2 [d, FeCO, J(PC) 10], 158.8 [C^1($\mathrm{C_6H_4}$)], 143.6 [d, C^1(Ph), J(PC) 35], 140.5 [d, C^1(Ph), J(PC) 42], 139.5 [d, C^1(Ph), J(PC) 37], 134—127 ($\mathrm{C_6H_4}$, Ph), 86.8 ($\mathrm{C_5H_5}$), 20.9 (Me-4), 15.9 [d, P*Me*$_2$Ph, J(PC) 27]
(7)	−11.75 [dd, 1 H, FeH, J(PH) 41, 5], 1.57 [d, 6 H, P*Me*$_2$Ph, J(PH) 9], 2.14 (s, 3 H, Me-4), 5.50 (s, 5 H, $\mathrm{C_5H_5}$), 6.38, 6.73 [(AB)$_2$, 4 H, $\mathrm{C_6H_4}$, J(HH) 8], 6.9—7.6 (m, 15 H, Ph)	[f] 328.9 [d, μ$_3$-*C*R, J(PC), 5, J(WC) 112], 221.2 [WCO, J(WC) 178], 215.6 [d, FeCO, J(PC) 32], 215.4 (FeCO), 212.9 (FeCO), 211.3 (FeCO), 163.8 [C^1($\mathrm{C_6H_4}$)], 146.2 [d, C^1(Ph), J(PC) 39], 145.1 [d, C^1(Ph), J(PC) 39], 141.1 [d, C^1(Ph), J(PC) 44], 135.9 [C^4($\mathrm{C_6H_4}$)], 134—127 ($\mathrm{C_6H_4}$, Ph), 94.8 ($\mathrm{C_5H_5}$), 21.1 (Me-4), 19.6 [d, P*Me*$_2$Ph, J(PC) 29], 16.4 [d, P*Me*$_2$Ph, J(PC) 27]
(**8**)	−9.63 [d, 1 H, FeH, J(PH) 31], 1.57 [d, 3 H, P*Me*$_2$Ph, J(PH) 9], 1.75 [d, 3 H, P*Me*$_2$Ph, J(PH) 9], 2.18 (s, 3 H, Me-4), 5.59 [d, 5 H, $\mathrm{C_5H_5}$, J(PH) 1], 6.24, 6.75 [(AB)$_2$, 4 H, $\mathrm{C_6H_4}$, J(HH) 8], 7.3—7.8 (m, 15 H, Ph)	331.8 [μ$_3$-*C*R, J(WC) 103], 218.7 [d, WCO, J(PC) 5, J(WC) 178], 216.9 [d, FeCO, J(PC) 17], 216.1 [d, FeCO, J(PC) 8], 215.3 [d, FeCO, J(PC) 12], 213.6 (FeCO), 165.0 [C^1($\mathrm{C_6H_4}$)], 146.5 [d, C^1(Ph), J(PC) 39], 143.3 [d, C^1($\mathrm{C_6H_5}$), J(PC) 49], 141.7 [d, C^1(Ph), J(PC) 42], 135.1 [C^4($\mathrm{C_6H_4}$)], 134—124 ($\mathrm{C_6H_4}$, Ph), 95.2 ($\mathrm{C_5H_5}$), 21.0 (Me-4), 20.7 [d, P*Me*$_2$Ph, J(PC) 29], 16.1 [d, P*Me*$_2$Ph, J(PC) 25]
(9)	−11.32 [ddd, 1 H, FeH, J(PH) 40, 28, 5], 0.93 [d, 3 H, P*Me*$_2$Ph, J(PH) 9], 1.24 [d, 3 H, P*Me*$_2$Ph, J(PH) 9], 1.38 [d, 3 H, P*Me*$_2$Ph, J(PH) 9], 1.73 [d, 3 H, P*Me*$_2$Ph, J(PH) 9], 2.14 (s, 3 H, Me-4), 5.38 (s, 5 H, $\mathrm{C_5H_5}$), 6.05, 6.59 [(AB)$_2$, 4 H, $\mathrm{C_6H_4}$, J(HH) 8], 7.1—7.8 (m, 20 H, Ph)	328.1 [μ$_3$-*C*R, J(WC) 107], 224.7 [WCO, J(WC) 181], 219.0 [dd, FeCO, J(PC) 29, 5], 218.2 [d, FeCO, J(PC) 5], 218.1 [d, FeCO, J(PC) 10], 166.0 [C^1($\mathrm{C_6H_4}$)], 147.9 [d, C^1(Ph), J(PC) 39], 146.7 [d, C^1(Ph), J(PC) 37], 145.1 [d, C^1(Ph), J(PC) 42], 142.6 [d, C^1(Ph), J(PC) 37], 135—125 ($\mathrm{C_6H_4}$, Ph), 95.0 ($\mathrm{C_5H_5}$), 22.5 [d, P*Me*$_2$Ph, J(PC) 30], 20.9 (Me-4), 18.8 [d, P*Me*$_2$Ph), J(PC) 27], 17.3 [d, P*Me*$_2$Ph, J(PC) 24], 16.4 [d, P*Me*$_2$Ph, J(PC) 24]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in $\mathrm{CD_2Cl_2}$ at room temperature unless otherwise noted. [c] Hydrogen-1 decoupled, measured in $\mathrm{CD_2Cl_2}$–$\mathrm{CH_2Cl_2}$ at room temperature unless otherwise noted; chemical shifts are positive to high frequency of $\mathrm{SiMe_4}$. [d] Mixture of thermally unstable isomers, see text, measured at −40 °C. [e] The ^{13}C-{^{1}H} n.m.r. spectrum at −40 °C showed FeCO resonances at δ 251.0 [s, br, $\mathrm{Fe_2(\mu\text{-}CO)}$], 214.0 (s, br, FeCO), 212.0 (s, br, FeCO), 211.0 (s, FeCO), and 206.9 p.p.m. [d, FeCO, J(PC) 10]. [f] Measured at −40 °C.

eventually becoming yellow-brown. The initial red-brown intermediate involved in this reaction may be isolated by treating compound (**3b**) with 1 equivalent of $\mathrm{PMe_2Ph}$ at 20 °C and then cooling the resultant red-brown solution to −40 °C to prevent further reaction. Following low-temperature chromatography, brown crystals of the thermally unstable complex $[\mathrm{WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(PMe_2Ph)(\eta\text{-}C_5H_5)}]$ (**4**) were obtained. Spectroscopic studies confirm that solutions of (**4**) cleanly rearrange at ambient temperature, affording yellow-brown solutions of the thermodynamically favoured isomer $[\mathrm{WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)}]$ (**5**).

The thermal instability of complex (**4**) precluded a complete characterisation (Table 1), but low-temperature ^{1}H and ^{31}P-{^{1}H} n.m.r. spectroscopy (Table 2) reveals that at −40 °C (**4**) exists as two major isomers (**4a**) and (**4b**). Tentative structures for them are shown in Scheme 1. The ^{1}H n.m.r. spectrum at −40 °C showed high-field resonances at δ −24.57 [dd, 1 H, $\mathrm{Fe_2(\mu\text{-}H)}$, J(PH) 28, 17 Hz] (**4a**) and −24.38 [dd, 1 H, $\mathrm{Fe_2(\mu\text{-}H)}$, J(PH) 28, 10 Hz] (**4b**). Integration of these resonances gives an isomer ratio of (**4a**):(**4b**) = 4:3. The chemical shift and coupling-constant data for the μ-H ligands in (**4a**) and (**4b**) are similar to that observed at δ −25.38 [dd, J(PH) 24, 11 Hz] for the μ-H ligand in the complex $[\mathrm{WFe_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}PEt_2)(CO)_6(PEt_2H)(\eta\text{-}C_5H_5)}]$.[1] The structure of the latter complex has been confirmed by a single-crystal *X*-ray study and is essentially identical to that proposed for isomer (**4b**).

The ^{31}P-{^{1}H} n.m.r. spectrum of complex (**4**) at −40 °C provides additional support for the presence of two isomers. Sharp resonances for the $\mathrm{PMe_2Ph}$ and μ-$\mathrm{PPh_2}$ ligands were observed at δ 14.3 [d, $\mathrm{Fe(PMe_2Ph)}$, J(PP) 39 Hz] and 143.5 [d, WFe(μ-P), J(PP) 39, J(WP) 363 Hz] (**4a**), and at δ 17.9 [d,



Scheme 1. R = C_6H_4Me-4. (*i*) Fast, $+PMe_2Ph$; (*ii*) $-PMe_2Ph$; (*iii*) slow, $+PMe_2Ph$; (*iv*) $+PPh_2H$, $-CO$; (*v*) $-CO$

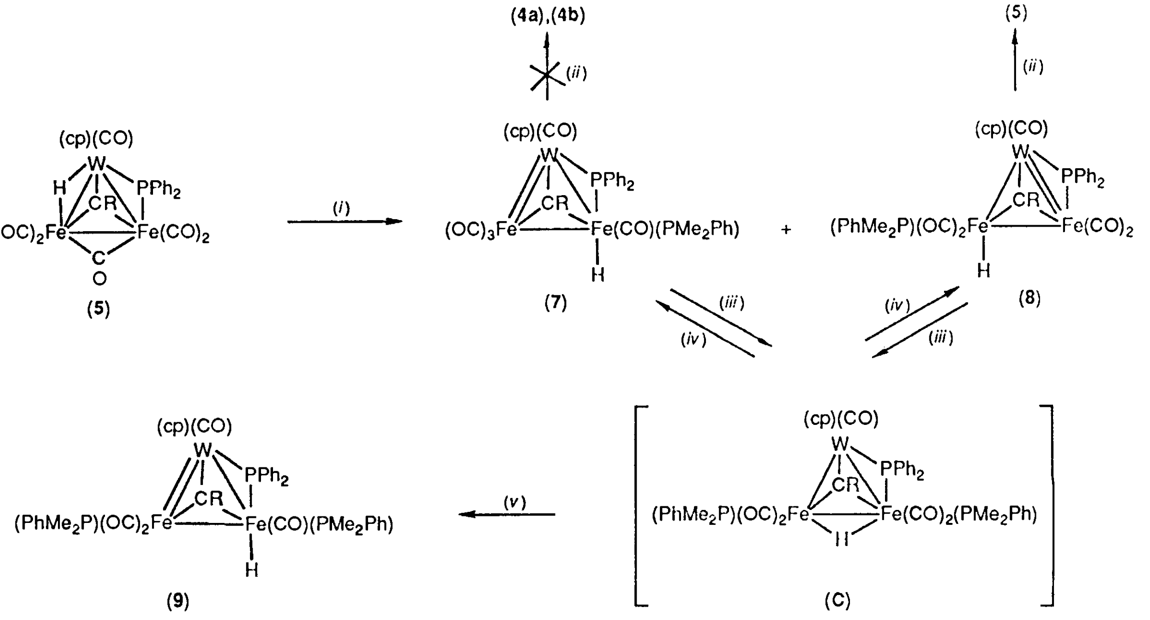
Table 3. Phosphorus-31 n.m.r. data for the complexes[a]

Compound	^{31}P (δ)
(**4**)[b]	(**4a**), 14.3 [d, Fe(PMe_2Ph), *J*(PP) 39], 143.5 [d, WFe(μ-P), *J*(PP) 39, *J*(WP) 363]; (**4b**), 17.9 [d, Fe(PMe_2Ph), *J*(PP) 46], 154.6 [d, WFe(μ-P), *J*(PP) 46, *J*(WP) 397]
(**5**)	24.7 [d, Fe(PMe_2Ph), *J*(PP) 5], 113.5 [d, WFe(μ-P), *J*(PP) 5, *J*(WP) 281]
(**7**)	39.5 [d, Fe(PMe_2Ph), *J*(PP) 34], 159.8 [d, WFe(μ-P), *J*(PP) 34, *J*(WP) 360]
(**8**)	32.0 [s, Fe(PMe_2Ph)], 164.6 [s, WFe(μ-P), *J*(WP) 374]
(**9**)	30.7 [s, Fe(PMe_2Ph)], 37.9 [d, Fe(PMe_2Ph), *J*(PP) 30], 153.1 [d, WFe(μ-P), *J*(PP) 30, *J*(WP) 371]

[a] Chemical shifts in p.p.m., coupling constants in Hz, hydrogen-1 decoupled; chemical shifts are positive to high frequency of 85% H_3PO_4 (external), measured in CD_2Cl_2 at room temperature unless otherwise noted. [b] Measured at −40 °C.

Fe(PMe_2Ph), *J*(PP) 46 Hz] and 154.6 p.p.m. [d, WFe(μ-P), *J*(PP) 46, *J*(WP) 397 Hz] (**4b**). The large *J*(PP) couplings observed for the isomers of (**4**) are consistent with the PMe_2Ph ligands being bound to the Fe atoms attached to the μ-PPh_2 centres, as established in the structure of the related complex [$WFe_2(\mu_3\text{-CR})(\mu\text{-H})(\mu\text{-PEt}_2)(CO)_6(PEt_2H)(\eta\text{-}C_5H_5)$] [*J*(PP) 42 Hz].[1] The ^{31}P-{^1H} and ^1H n.m.r. data for (**4a**) and (**4b**) are very similar which is to be expected since these isomers differ only by virtue of the orientation of the $Fe(CO)_2(PMe_2Ph)$ group. At 20 °C the ^{31}P-{^1H} n.m.r. spectrum showed broad doublet signals due to (**4a**) and (**4b**) (ratio 2:1). Evidently at this temperature interconversion of the isomers begins to occur and this dynamic behaviour can be readily explained by rotation of the $Fe(CO)_2(PMe_2Ph)$ group.

The structure of the thermodynamically favoured isomer [$WFe_2(\mu_3\text{-CR})(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-CO})(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)$] (**5**) was firmly established by its spectroscopic and physical data. The i.r. spectrum in CH_2Cl_2 shows absorptions due to terminal CO ligands and a broad peak at 1 804 cm^{-1} is assigned to a bridging CO ligand. The ^1H n.m.r. spectrum showed a μ-H resonance at δ −18.18 [dd, *J*(PH) 31, 11, *J*(WH) 50 Hz] and the presence of ^{183}W satellites on this signal confirms that the hydride ligand bridges a W–Fe bond. Two resonances at δ 1.93 [d, *J*(PH) 8 Hz] and 2.16 [d, *J*(PH) 7 Hz] were also observed for the diastereotopic methyl groups of the PMe_2Ph ligand. The ^{31}P-{^1H} n.m.r. spectrum showed resonances at δ 24.7 [d, *J*(PP) 5 Hz] and 113.5 p.p.m. [d, *J*(PP) 5, *J*(WP) 281 Hz] due to the PMe_2Ph and μ-PPh_2 moieties respectively. The small *J*(PP) coupling between these atoms is consistent with these groups being bound to different iron centres. The ^{13}C-{^1H} n.m.r. spectrum at −40 °C showed peaks as expected. The signal assigned to the μ_3-*C*R atom at δ 226.2 p.p.m. [dd, *J*(PC) 34, 7 Hz] is comparable with that found at δ 217.0 p.p.m. [dt, *J*(PC) 40, 12 Hz] for the μ_3-*C*R ligand in the complex [$WFe_2H(\mu_3\text{-CR})(\mu\text{-PPh}_2)_3(CO)_4(\eta\text{-}C_5H_5)$].[4] In contrast, the chemical shift for the μ_3-*C*R atom in the complex [$WFe_2(\mu_3\text{-CR})(\mu\text{-H})(\mu\text{-PEt}_2)(CO)_6(PEt_2H)(\eta\text{-}C_5H_5)$] at δ 256.6 p.p.m. [*J*(WC) 100 Hz], is *ca.* 30—40 p.p.m. more deshielded than found in the latter complexes.[2] This difference may be related to the relative orientation of the μ_3-CR moiety and the phosphorus ligands. In the compounds (**5**) and [$WFe_2H(\mu_3\text{-CR})(\mu\text{-PPh}_2)_3(CO)_4(\eta\text{-}C_5H_5)$] the μ_3-*C*R resonances show appreciable coupling to the ^{31}P atoms which suggests that the phosphorus ligands are transoid to the μ_3-CR groups. This ligand arrangement has been confirmed by a single-crystal *X*-ray diffraction study on the latter complex, which showed that the μ_3-CR and μ-PPh_2 ligands lie on opposite sides of the WFe_2 triangle of metal atoms. In contrast, the structure of



Scheme 2. R = C_6H_4Me-4. (*i*) Toluene, 111 °C, −CO; (*ii*) +CO, (*iii*) toluene, 111 °C, +PMe_2Ph; (*iv*) −PMe_2Ph; (*v*) −CO

[$WFe_2(\mu_3$-CR)(μ-H)(μ-PEt_2)$(CO)_6(PEt_2H)(\eta$-$C_5H_5)$] shows that the phosphorus ligands are approximately coplanar with the metal atoms, and this orientation appears to be associated with a more deshielded μ_3-CR resonance and an absence of detectable *J*(PC) coupling. The carbonyl region of the ^{13}C-{^1H} n.m.r. spectrum of (**5**) at −40 °C was particularly informative. Signals at δ 251.0 and 226.6 p.p.m. were assigned to a Fe(μ-CO)Fe moiety and a WCO ligand respectively. In addition, resonances at δ 214.0, 212.0, 211.0, and 206.9 p.p.m. were observed for the terminal CO ligands attached to the two iron centres. The ^{13}C-{^1H} n.m.r. spectrum measured at 20 °C is similar to that at −40 °C, except that the resonances at δ 251.0, 214.0, and 212.0 p.p.m. become so broad that they are no longer detectable above the baseline noise. This is consistent with slow exchange of three carbonyl ligands *via* an intermediate such as (**A**) shown in Scheme 1.

Compound (**5**) can be prepared by an alternative route, *via* treatment of the PMe_2Ph complex [$WFe_2(\mu_3$-CR)(μ-CO)$(CO)_7(PMe_2Ph)(\eta$-$C_5H_5)$] (**6**)[1] with 1 equivalent of PPh_2H at 20 °C in CH_2Cl_2. This reaction presumably proceeds *via* an intermediate such as [$WFe_2(\mu_3$-CR)(μ-CO)$(CO)_6(PPh_2H)(PMe_2Ph)(\eta$-$C_5H_5)$] (**B**) (Scheme 1) analogous to the previously characterised compound [$WFe_2(\mu_3$-CR)(μ-CO)$(CO)_6(PMe_2Ph)_2(\eta$-$C_5H_5)$].[5]

A mechanism which accounts for the products observed in the reaction of complex (**3b**) with PMe_2Ph is shown in Scheme 1. Rapid reversible addition of PMe_2Ph to (**3b**) gives the kinetically favoured product (**4**), whilst the thermodynamically stable isomer (**5**) arises *via* a much slower attack of PMe_2Ph at the iron centre remote from the μ-PPh_2 ligand. This proposal is supported by the observation that the ^{31}P-{^1H} n.m.r. spectrum of (**4**) shows traces (*ca.* 5%) of the co-ordinatively unsaturated compound (**3b**) and a resonance due to free PMe_2Ph. This confirms that the kinetically favoured product (**4**) is actually in equilibrium with (**3b**) and free PMe_2Ph as shown in Scheme 1. The migration of phosphine ligands between metal centres has previously been observed in the isomerisation of [$MoMn(\mu$-H)(μ-$PPh_2)(CO)_4$(dppm)$(\eta$-$C_5H_5)$] to [$MoMn(\mu$-H)(μ-PPh_2)(μ-dppm)$(CO)_4(\eta$-$C_5H_5)$],[6] and in the isomerisation of [$RuCo(\mu$-$PPh_2)(CO)_5$(dppm)] to [$RuCo(\mu$-PPh_2)(μ-dppm)$(CO)_5$] (dppm = $Ph_2PCH_2PPh_2$).[7]

The co-ordinatively unsaturated complex (**3b**) used in these studies was obtained *via* thermal elimination of a CO ligand from the Fe atom ligated to the μ-PPh_2 ligand in the saturated precursor (**2**). A similar iron centre exists in complex (**5**) because the PMe_2Ph ligand is co-ordinated to the iron centre remote from the μ-PPh_2 bridge. It therefore seemed probable that an analogous decarbonylation reaction might take place for (**5**). Thermal decarbonylation of (**5**) was found to proceed smoothly in refluxing toluene (111 °C, *ca.* 1 h) and following chromatography on alumina two isomeric, co-ordinatively unsaturated complexes [$WFe_2H(\mu_3$-CR)(μ-$PPh_2)(CO)_5(PMe_2Ph)(\eta$-$C_5H_5)$] (**7**) and (**8**) were isolated (Scheme 2). The major dark purple isomer (**7**) was obtained in *ca.* 60% yield, whilst the minor dark green-brown isomer (**8**) was obtained in *ca.* 30% yield. Analytical and spectroscopic data are in accord with the structures shown.

The ^1H n.m.r. spectrum of (**7**) has a resonance at δ −11.75 [dd, *J*(PH) 41, 5 Hz] which is assigned to a terminal hydride ligand bound to the Fe atom which is attached to both phosphorus ligands. The ^{31}P-{^1H} n.m.r. spectrum has signals at 39.5 [d, Fe(PMe_2Ph), *J*(PP) 34 Hz], and 159.8 p.p.m. [d, WFe(μ-P), *J*(PP) 34, *J*(WP) 360 Hz] and the comparatively large magnitude of the *J*(PP) coupling is consistent with a structure having both phosphorus ligands bound to the same Fe atom. The ^{13}C-{^1H} n.m.r. spectrum measured at −40 °C showed a μ_3-*C*R resonance at δ 328.9 p.p.m. [d, *J*(PC) 5, *J*(WC) 112 Hz]. The deshielded chemical shift of the μ_3-*C*R atom is characteristic of a co-ordinatively unsaturated species and similar values are observed for the unsaturated complex (**3b**) [δ(μ_3-*C*R) 332.1 p.p.m.], and the related μ-PEt_2 complex [$WFe_2H(\mu_3$-CR)(μ-$PEt_2)(CO)_6(\eta$-$C_5H_5)$] [δ(μ_3-*C*R) 331.0 p.p.m.].[2] The ^{13}C-{^1H} n.m.r. spectrum of complex (**7**) in the carbonyl region showed sharp resonances for each of the CO ligands and this confirms a static structure of the type shown in Scheme 2.

Spectroscopic data for the minor isomer (**8**) confirms that the PMe_2Ph ligand is attached to the Fe atom remote from the μ-PPh_2 bridging ligand. The ^1H n.m.r. spectrum has a resonance at δ −9.63 [d, *J*(PH) 31 Hz] assigned to a terminal hydride ligand. Resonances in the ^{31}P-{^1H} spectrum at δ 32.0 and 164.6 p.p.m. [*J*(WP) 374 Hz] are assigned to the Fe(PMe_2Ph) and

WFe(μ-PPh$_2$) moieties respectively. The lack of detectable ^{31}P–^{31}P coupling between these ligands shows that they ligate different iron centres; a similar feature was noted for compound (**5**) where only a small J(PP) coupling of 5 Hz is observed. When the ^{31}P n.m.r. spectrum of (**8**) was measured with selective decoupling of the methyl and aromatic protons the signal at δ 164.6 p.p.m. showed no change whilst that at δ 32.0 p.p.m. was split into a doublet. This confirms that the hydride ligand couples with the PMe$_2$Ph ligand. The ^{13}C-{^{1}H} n.m.r. spectrum has a signal at δ 331.8 p.p.m. [J(WC) 103 Hz] ascribed to the μ_3-CR nucleus. As noted for (**7**), the comparatively deshielded chemical shift for the μ_3-CR resonance is consistent with (**8**) being a 46 c.v.e. co-ordinatively unsaturated species. Other resonances were observed in the ^{13}C-{^{1}H} n.m.r. spectrum as expected for the structure shown.

The co-ordinatively unsaturated compound (**3**) readily reacts with CO to regenerate the saturated precursor (**2**). Similarly treatment of (**8**) with CO (1 atm) in CH$_2$Cl$_2$ rapidly (5 min) causes the quantitative regeneration of the co-ordinatively saturated complex (**5**). However, treatment of (**7**) with CO for >1 h caused no change, the i.r. spectrum of the solution showing absorptions due to (**7**) only. The lack of reactivity of complex (**7**) towards CO is in accord with the observation that complex (**4**), which would be the expected product of CO addition to (**7**), is thermodynamically less stable than the isomeric complex (**5**). The instability of (**4**) with respect to (**5**) presumably reflects unfavourable steric interactions between the PMe$_2$Ph and μ-PPh$_2$ ligands in (**4**), which do not occur in the isomeric complex (**5**).

The complexes (**7**) and (**8**) do not react with further PMe$_2$Ph at room temperature. However, addition of 1 equivalent of PMe$_2$Ph to either (**7**) or (**8**) in refluxing toluene (111 °C) afforded excellent yields of the co-ordinatively unsaturated complex [WFe$_2$H(μ_3-CR)(μ-PPh$_2$)(CO)$_4$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)] (**9**). Analytical data for dry crystalline samples of (**9**) were consistently in agreement with the presence of 1.5 molecules of CH$_2$Cl$_2$ of crystallisation. The spectroscopic data were in accord with the structure shown. The ^{1}H n.m.r. spectrum showed peaks as expected, including a resonance for the terminal hydride ligand at δ −11.32 [ddd, FeH, J(PH) 40, 28, 5 Hz]. The presence of three sets of ^{31}P–^{1}H couplings and the absence of detectable ^{183}W satellite peaks indicates that the hydride moiety is bound to the Fe atom ligated by the μ-PPh$_2$ group. The chemical shift of this signal is similar to those observed for the hydride ligands of (**7**) (δ −11.75) and (**8**) (δ −9.63), in accord with a terminal rather than a bridging hydride ligand in (**9**). The ^{1}H n.m.r. spectrum of a dry crystalline sample of complex (**9**) also exhibited a signal due to CH$_2$Cl$_2$, which was clearly resolved from that due to CHDCl$_2$. The integral of this solvent peak provided additional support for the formulation (**9**)·1.5CH$_2$Cl$_2$. The ^{31}P-{^{1}H} n.m.r. spectrum of (**9**) showed resonances at δ 30.7 [Fe(PMe$_2$Ph)], 37.9 [d, Fe(PMe$_2$Ph), J(PP) 30 Hz], and 153.1 p.p.m. [d, WFe(μ-PPh$_2$), J(PP) 30, J(WP) 371 Hz], which support the structure shown. The ^{13}C-{^{1}H} n.m.r. spectrum showed the expected resonances for the CO ligands and once more the presence of a comparatively deshielded μ_3-CR resonance supports the formation of (**9**) as a co-ordinatively unsaturated species.

The isomeric complexes (**7**) and (**8**) do not interconvert at room temperature. However thermolysis of either (**7**) or (**8**) in toluene at 111 °C leads to the formation of an equilibrium mixture of (**7**) and (**8**) which are present in the ratio *ca.* 2:1 respectively. In this isomerisation reaction traces (*ca.* 5%) of the unsaturated bis-PMe$_2$Ph complex (**9**) were also detected by ^{31}P-{^{1}H} n.m.r. spectroscopy. This suggests that the mechanism of thermal interconversion of the isomers (**7**) and (**8**) involves the formation of a saturated intermediate such as [WFe$_2$(μ_3-CR)(μ-H)(μ-PPh$_2$)(CO)$_5$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)] [(**C**) in Scheme 2]. A small amount of decomposition might well provide the free PMe$_2$Ph required for the formation of this intermediate. Subsequent elimination of a PMe$_2$Ph ligand from the appropriate iron centre would then give (**7**) or (**8**). A similar mechanism has been proposed to account for the isomerisation of [RuCo(μ-PPh$_2$)(CO)$_5$(dppm)] to [RuCo(μ-PPh$_2$)(μ-dppm)(CO)$_5$], which occurs in refluxing tetrahydrofuran when free dppm is present.[7] It also seems likely that the formation of complex (**9**) from treatment of either (**7**) or (**8**) with PMe$_2$Ph proceeds *via* elimination of a CO ligand from the same intermediate (**C**). Attempts to isolate the intermediate (**C**) by treating a CH$_2$Cl$_2$ solution of (**9**) with CO (1 atm) for 4 h resulted in no change. As discussed for the 46 c.v.e. complex (**7**), steric effects presumably make this reaction highly unfavourable.

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$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-H)(μ-PPh$_2$)(CO)$_7$(η-C$_5$H$_5$)] (**2**),[1] [WFe$_2$H(μ_3-CC$_6$H$_4$Me-4)(μ-PPh$_2$)(CO)$_6$(η-C$_5$H$_5$)] (**3b**),[2] and [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_7$(PMe$_2$Ph)(η-C$_5$H$_5$)] (**6**)[1] were prepared by the literature methods. Analytical and other data for the new compounds are listed in Tables 1—3.

Synthesis of the Compound [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-H)(μ-PPh$_2$)(CO)$_6$(PMe$_2$Ph)(η-C$_5$H$_5$)] (**4**).—A CH$_2$Cl$_2$ (20 cm^3) solution of [WFe$_2$H(μ_3-CC$_6$H$_4$Me-4)(μ-PPh$_2$)(CO)$_6$(η-C$_5$H$_5$)] (**3b**) (0.29 g, 0.35 mmol) was treated with PMe$_2$Ph (0.05 g, 0.36 mmol) at 20 °C. The resulting red-brown solution was immediately cooled to −40 °C and then the solvent was removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$–light petroleum (2:3) at −40 °C and chromatographed on alumina at the same temperature. Gradient elution with CH$_2$Cl$_2$–light petroleum (2:3 to 4:1) afforded a brown band which was collected at −40 °C. The solvent was removed *in vacuo* to afford brown *microcrystals* of [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-H)(μ-PPh$_2$)(CO)$_6$(PMe$_2$Ph)(η-C$_5$H$_5$)] (**4**) (0.27 g, 81%). Compound (**4**) rearranges in solution at 20 °C over a period of *ca.* 6 h to afford the isomeric compound (**5**).

Synthesis of the Compound [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-H)(μ-PPh$_2$)(μ-CO)(CO)$_5$(PMe$_2$Ph)(η-C$_5$H$_5$)] (**5**).—(*i*) A toluene (20 cm^3) solution of [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-H)(μ-PPh$_2$)(CO)$_7$(η-C$_5$H$_5$)] (**2**) (0.45 g, 0.53 mmol) was refluxed for 30 min (111 °C) to generate (**3b**) *in situ*. The solvent was removed *in vacuo* and replaced by CH$_2$Cl$_2$ (20 cm^3). To this solution was added PMe$_2$Ph (0.07 g, 0.51 mmol). The solution was stirred at 20 °C for 12 h, after which time the solvent was removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$–light petroleum (1:3) and chromatographed on alumina. Elution with the same solvent afforded a green-brown band which was collected. Removal of the solvent *in vacuo* and recrystallisation from CH$_2$Cl$_2$–light petroleum (1:8) yielded black crystals of [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-H)(μ-PPh$_2$)(μ-CO)(CO)$_5$(PMe$_2$Ph)(η-C$_5$H$_5$)]· CH$_2$Cl$_2$ (**5**) (0.46 g, 83%). *In vacuo*, black crystals of (**5**) readily lose the CH$_2$Cl$_2$ solvent of crystallisation and in the process a green powder is obtained.

(*ii*) A CH$_2$Cl$_2$ (20 cm^3) solution of [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_7$(PMe$_2$Ph)(η-C$_5$H$_5$)] (**6**) (0.38 g, 0.46 mmol) was treated with PPh$_2$H (0.085 g, 0.46 mmol) at 20 °C. The solution was stirred at this temperature for 48 h, after which time the solvent was removed *in vacuo*. Chromatography and recrystallisation as described in (*i*) afforded (**5**)$\cdot CH_2Cl_2$ (0.31 g, 65%).

Thermolysis of the Compound [$WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)$] (**5**).—A toluene (10 cm^3) solution of [$WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)$] (**5**) (0.47 g, 0.45 mmol) was refluxed (111 °C) for 1 h, after which time the solvent was removed *in vacuo*. The red-brown residue was dissolved in CH_2Cl_2–light petroleum (1:4) and chromatographed on alumina. Elution with the same solvent afforded two major bands. The first red-purple band was collected, and the solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2–hexane (1:6) afforded dark purple *microcrystals* of [$WFe_2H(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)$]$\cdot CH_2Cl_2$ (**7**) (0.26 g, 57%).

Further elution of the column with CH_2Cl_2–light petroleum (2:3) afforded a second green band, from which solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2–hexane (1:6) yielded dark green-brown crystals of [$WFe_2H(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)$]$\cdot CH_2Cl_2$ (**8**) (0.12 g, 29%).

Synthesis of the Compound [$WFe_2H(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)$] (**9**).—A toluene (10 cm^3) solution of [$WFe_2H(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_5(PMe_2Ph)(\eta\text{-}C_5H_5)$]$\cdot CH_2Cl_2$ (**7**) (0.30 g, 0.30 mmol) was treated with PMe_2Ph (0.04 g, 0.29 mmol) and the solution was refluxed (111 °C) for 2 h. After this time the solvent was removed *in vacuo*, and the residue was redissolved in CH_2Cl_2–light petroleum (1:1). Chromatography on alumina, eluting with the same solvent mixture, afforded a brown band which was collected. The solvent was removed *in vacuo*, and subsequent recrystallisation from CH_2Cl_2–light petroleum (1:8) yielded black crystals of [$WFe_2H(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)$]$\cdot 1.5CH_2Cl_2$ (**9**) (0.30 g, 86%). Similar yields (*ca.* 80%) of (**9**) were obtained from the reaction of (**8**) with 1 equivalent of PMe_2Ph in refluxing toluene, the reaction and work-up procedures being the same as described for the reaction of (**7**) with PMe_2Ph.

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