Perpendicular to parallel reorientation of a terminal alkyne on a mixed-metal triangle; synthesis and structural characterisation

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Reaction of $[Fe_2(CO)_6(\mu-\eta^2-CCPh)(\mu-PPh_2)]$ **1** with $[W_2(CO)_4(\eta^5-C_5H_5)_2]$ affords the coordinatively unsaturated 46-electron trinuclear Fe_2W cluster $[Fe_2W(CO)_5(\eta^5-C_5H_5)\{\mu_3-\eta^2-(\perp)-HCCPh\}(\mu-CO)(\mu-PPh_2)]$ **2**, in which an Fe–W edge is perpendicularly-bridged by a terminal alkyne molecule. Treatment of **1** with $[Mo_2(CO)_4(\eta^5-C_5H_5)_2]$ also gives a 46-electron cluster, $[Fe_2Mo(CO)_5(\eta^5-C_5H_5)\{\mu_3-\eta^2-(\perp)-HCCPh\}(\mu-CO)(\mu-PPh_2)]$ **3**, the molybdenum analogue of **2** and, in addition, the saturated 48-electron $FeMo_2$ trinuclear cluster $[FeMo_2(CO)_5(\eta^5-C_5H_5)_2\{\mu_3-\eta^2-(\perp)-CCPh\}$-$(\mu-PPh_2)]$ **4**, in which an acetylide ligand perpendicularly bridges an Fe–Mo bond. The trimetallic FeWCo acetylide-bridged species, $[FeWCo(CO)_6(\eta^5-C_5H_5)\{\mu_3-\eta^2-(\perp)-CCPh\}(\mu-PPh_2)]$ **5**, is the unique product when **1** is treated with the WCo heterobimetallic complex $[CoW(\eta^5-C_5H_5)(CO)_7]$, while the corresponding reaction of **1** with $[CoMo(\eta^5-C_5H_5)(CO)_7]$, leads to **3** and the molybdenum analogue of **5**, $[FeMoCo(CO)_6(\eta^5-C_5H_5)\{\mu_3-\eta^2-(\perp)-CCPh\}(\mu-PPh_2)]$ **6**. Carbonylation of **3** at elevated pressure (80 atm CO) results in a $\perp$–$\parallel$ alkyne reorientation to give the 48-electron cluster, $[Fe_2Mo(CO)_6(\eta^5-C_5H_5)\{\mu_3-\eta^2-(\parallel)-HCCPh\}(\mu-CO)(\mu-PPh_2)]$ **7**, as the sole product. Conversion of **7** back to **3** has been shown to occur in solution at room temperature. Single crystal X-ray diffraction studies have been performed on **2**, **3**, **4**, **6** and **7**.

1   Introduction

The facility of internal alkynes ($RC\equiv CR$ or $R'C\equiv CR$, $R = R' =$ hydrocarbyl) to bind to trinuclear transition metal centres has been well documented and indeed two different bonding modes predominate namely, $\mu_3-\eta^2-(\perp)$ and $\mu_3-\eta^2-(\parallel)$ modes,[1,2] the latter of which is considerably more common. In the main, the perpendicular bonding mode is exhibited for unsaturated 46-electron counts[2,3] and the parallel mode for saturated 48-electron counts.[1,4] One important exception to this pattern is the 46-electron cluster $[Rh_3(\eta^5-C_5H_5)(acac)(CO)(CF_3C_2CF_3)]$ (acac = acetylacetonate), in which the alkyne adopts an $\mu_3-\eta^2-(\parallel)$ coordination mode.[5]

Conversely, the synthesis of trimetallic complexes containing coordinated terminal alkynes ($RC\equiv CH$) are rare,[6] due in part to the ready transfer of the H-substituent of the alkyne to the metal framework.[1,2,7] Moreover, to the knowledge of the authors, only one example of a trimetallic cluster containing a perpendicularly-bridged terminal alkyne has been reported, namely $[Fe_3(CO)_9\{\mu_3-\eta^2-(\perp)-HCCOC(O)Me\}]$, this species being isolable only below $-70\,°C$.[8]

Recently, Carty and our group independently reported that the thermolysis of $[Fe_2(CO)_6(\mu-\eta^2-CCPh)(\mu-PPh_2)]$ **1** leads to regioselective dimerisation and carbonyl loss to give the tetra-iron cluster $[Fe_4(CO)_8(\mu_4-PhCCCCPh)(\mu-PPh_2)_2]$, in which the two phenylacetylide fragments have coupled through the centre of the Fe_4 plane (Fig. 1).[9,10] In this paper we investigate the thermolytic reactivity of **1** in the presence of bimetallic carbonyl species including the homobimetallic group 6 complexes $[M_2(CO)_4(\eta^5-C_5H_5)_2]$ (M = W, Mo) and the heterobimetallic group 6–group 9 complexes $[CoM(\eta^5-C_5H_5)(CO)_7]$ (M = W, Mo).

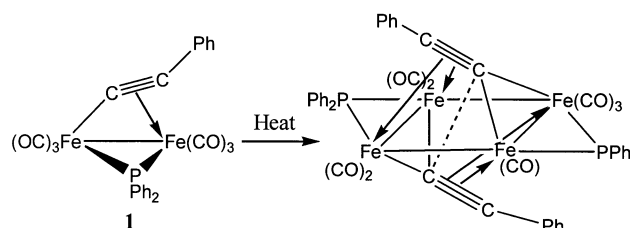**Fig. 1** Thermolysis of **1** to give $[Fe_4(CO)_8(\mu-PPh_2)_2(\mu_4-PhCCCCPh)]$.[9,10]

2   Results and discussion

2.1   Reaction of 1 with $[M_2(CO)_4(\eta^5-C_5H_5)_2]$ (M = W, Mo)

Treatment of **1** with the triply bonded ditungsten complex $[W_2(CO)_4(\eta^5-C_5H_5)_2]$ (generated *in situ*) in xylene at 363 K gave $[Fe_2W(CO)_5(\eta^5-C_5H_5)\{\mu_3-\eta^2-(\perp)-HCCPh\}(\mu-CO)(\mu-PPh_2)]$ **2** as the sole product in 23% yield. Similar treatment of $[Fe_2(CO)_6$-$(\mu-\eta^2-CCPh)(\mu-PPh_2)]$ with $[Mo_2(CO)_4(\eta^5-C_5H_5)_2]$ in toluene at 353 K afforded $[Fe_2Mo(CO)_5(\eta^5-C_5H_5)\{\mu_3-\eta^2-(\perp)-HCCPh\}$-$(\mu-CO)(\mu-PPh_2)]$ **3** and $[FeMo_2(CO)_5(\eta^5-C_5H_5)_2\{\mu_3-\eta^2-(\perp)$-$CCPh\}(\mu-PPh_2)]$ **4**, in a combined yield of 42% (Scheme 1). Complexes **2**, **3** and **4** have been characterised by ^1H, ^{31}P-$\{^1H\}$, ^{13}C-$\{^1H\}$ NMR and IR spectroscopy and by mass spectrometry and microanalysis (Table 1 and Experimental Section). In addition, all these complexes have been the subjects of single crystal X-ray diffraction studies.

The molecular structure of **2** is depicted in Fig. 2 while selected bond distances and angles are, for both **2** and the isostructural **3**, listed in Table 2. The core of **2** consists of one tungsten atom, two iron atoms and two carbon atoms in a *closo*-trigonal bipyramidal arrangement. The alkyne carbon

Table 1 Infrared, ^{1}H and ^{31}P NMR data for the new complexes **2**–**7**

Compound	$\nu(CO)^a/cm^{-1}$	^{1}H NMR $(\delta)^b$	^{31}P NMR $(\delta)^c$
2	2024vs, 1990vs, 1959vs, 1784w	7.5–7.1 [m, 15H, Ph], 5.30 [s, 5H, Cp], 1.30 [d, [3]J(PH) 5, 1H, CH]	160.7 [s, J(PW) 134, μ-PPh$_2$]
3	2027vs, 1992vs, 1962s, 1790w	7.5–7.2 [m, 15H, Ph], 5.28 [s, 5H, Cp], 1.27 [d, [3]J(PH) 6, 1H, CH]	194.7 [s, μ-PPh$_2$]
4	2028vs, 1989s, 1961m	7.8–6.6 [m, 15H, Ph], 5.26 [s, 10H, Cp]	173.3 [s, μ-PPh$_2$]
5	2054vs, 2010s, 1995s, 1952sh	7.7–6.8 [m, 15H, Ph], 5.30 [s, 5H, Cp]	145.8 [s, μ-PPh$_2$]
6	2037m, 2010vs, 1978s, 1989sh	7.7–6.8 [m, 15H, Ph], 5.40 [s, 5H, Cp]	220.1 [s, μ-PPh$_2$]
7	2046s, 2011s, 1983s, 1949m, 1893w	7.7–7.1 [m, 15H, Ph], 4.80 [s, 5H, Cp]	218.9 [s, μ-PPh$_2$]

^{a} Recorded in *n*-hexane solution. ^{b} [1]H chemical shifts (δ) in ppm relative to SiMe$_4$ (0.0 ppm), coupling constants in Hz in CDCl$_3$ at 293 K. ^{c} [31]P chemical shifts (δ) in ppm relative to 85% external H$_3$PO$_4$ (0.0 ppm) (upfield shifts negative). Spectra were {[1]H}-gated decoupled and measured in CDCl$_3$ at 293 K.
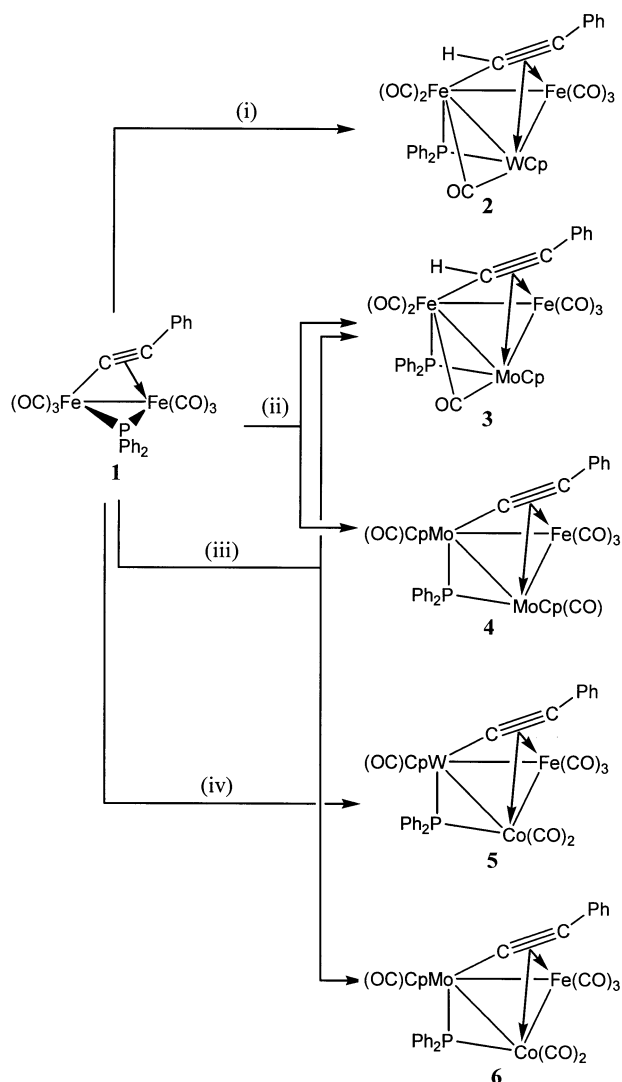
Scheme 1 *Reagents and conditions*: (i) [W$_2$(CO)$_4$(η^5-C$_5$H$_5$)$_2$], C$_6$H$_4$(CH$_3$)$_2$, 363 K; (ii) [Mo$_2$(CO)$_4$(η^5-C$_5$H$_5$)$_2$], C$_6$H$_5$CH$_3$, 363 K; (iii) [MoCo(CO)$_7$-(η^5-C$_5$H$_5$)], C$_6$H$_5$CH$_3$, 373 K; (iv) [WCo(CO)$_7$(η^5-C$_5$H$_5$)], C$_6$H$_5$CH$_3$, 373 K.

Table 2 Selected bond distances (Å) and angles (°) for **2** and **3**

	2 (M = W)	**3** (M = Mo)
M(1)–Fe(1)	2.786(1)	2.777(1)
M(1)–Fe(2)	2.627(1)	2.625(1)
M(1)–Cp(centroid)	2.025(9)	2.027(6)
M(1)–C(5)	1.972(8)	1.960(6)
M(1)–C(24)	2.307(8)	2.294(6)
M(1)–C(25)	2.058(7)	2.087(5)
M(1)–P(1)	2.417(2)	2.426(1)
Fe(1)–Fe(2)	2.567(2)	2.568(1)
Fe(2)–C(5)	2.413(8)	2.394(6)
Fe(2)–P(1)	2.178(2)	2.179(2)
Fe(2)–C(24)	2.053(7)	2.045(5)
Fe(1)–C(24)	2.008(7)	2.025(6)
Fe(1)–C(25)	1.981(7)	1.978(5)
C(24)–C(25)	1.410(10)	1.414(7)
C(25)–C(26)	1.501(10)	1.476(7)
Mean Fe–C(carbonyl)	1.786	1.784
Fe(1)–Fe(2)–M(1)	64.85(4)	64.65(3)
Fe(2)–Fe(1)–M(1)	58.62(4)	58.65(3)
Fe(1)–M(1)–Fe(2)	56.53(4)	56.69(3)
Fe(2)–P(1)–M(1)	69.52(7)	69.25(4)
Fe(2)–C(5)–M(1)	72.8(3)	73.4(2)
C(25)–C(24)–Fe(2)	127.6(6)	128.8(4)
C(25)–C(24)–Fe(1)	68.3(4)	67.6(3)
C(24)–M(1)–Fe(2)	48.7(2)	48.6(1)
C(25)–M(1)–Fe(1)	45.3(2)	45.3(1)
C(25)–Fe(1)–M(1)	47.5(2)	48.6(2)
C(24)–Fe(1)–M(1)	54.7(2)	54.4(2)
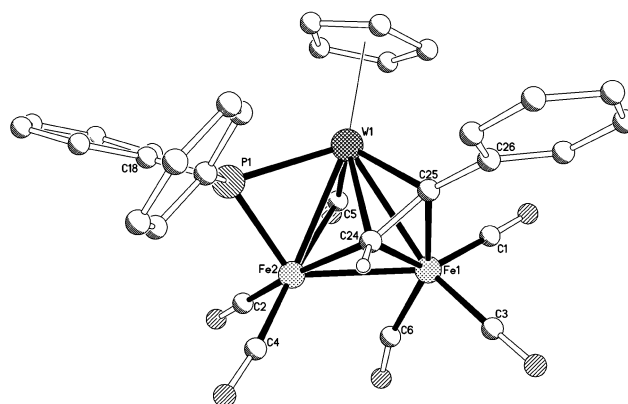
Fig. 2 Molecular structure of [Fe$_2$W(CO)$_5$(η^5-C$_5$H$_5$){μ$_3$-η^2-(⊥)-HCCPh}(μ-CO)(μ-PPh$_2$)] **2** including the atom numbering scheme. All hydrogen atoms except for H24 have been omitted for clarity.

atom C(24) occupies a five-connected equatorial vertex of the trigonal bipyramid while the other alkyne carbon atom C(25) occupies a four-connected apical position. The W(1)–Fe(2) edge of the polyhedron is bridged unsymmetrically by a diphenylphosphido group [W(1)–P(1) 2.417(2), Fe(2)–P(1) 2.178(2) Å] and by a semi-bridging carbonyl group [W(1)–C(5) 1.972(8), Fe(2)–C(5) 2.413(8) Å]. The Fe(2)–W(1) bond distance of 2.627(1) Å is significantly shorter than the Fe(1)–W(1) bond distance 2.786(1) Å, this presumably being the consequence of the constraints imposed by the two bridging ligands. The orientation of the alkyne carbon–carbon bond with respect to the Fe$_2$W triangle is perpendicular to the Fe(1)–

W(1) vector [*i.e.*, μ$_3$-η^2-(⊥)], a bonding mode that has been observed for several other crystallographically characterised 46-electron alkyne-bridged trimetallic clusters.[3] The carbon–carbon bond distance [C(24)–C(25) 1.410(10) Å] of the coordinated alkyne falls in the mid-range for other reported alkyne-bridged trimetallic complexes.[11]

The coordination spheres are completed at Fe(1) by three terminal carbonyl groups, Fe(2) by two terminal groups and W(1) by an η^5-cyclopentadienyl group. The molecular structure

of **3** is essentially the same as **2** with a molybdenum atom occupying the tungsten site in **2**. For both **2** and **3** the alkynic hydrogen atoms (H24) were located in the final difference maps and refined successfully.

The spectroscopic properties of **2** and **3** are in accord with their solid state structures being maintained in solution. The IR spectra of **2** and **3** show, in addition to three bands in the terminal carbonyl region, single bands at 1784 cm^{-1} (**2**) and 1790 cm^{-1} (**3**) due to the stretching vibration of the semi-bridging carbonyl groups. In the room temperature ^{1}H NMR spectra, signals for the cyclopentadienyl protons [δ 5.30 (**2**) and 5.28 (**3**)] and phenyl groups are seen as singlets and multiplets respectively, while the alkynic hydrogen atoms can be seen upfield as doublets at δ 1.30 [^3J(PH) 5 Hz] for **2** and δ 1.27 [^3J(PH) 6 Hz] for **3**. A similar chemical shift for the alkynic hydrogen atom has been observed at low temperature for [Fe$_3$(CO)$_9${μ_3-η^2-($\perp$)-HCCOC(O)Me}], in which a singlet is seen at δ 1.55.[8]

The ^{13}C-{^{1}H} NMR spectra at room temperature for **2** and **3** exhibit, in addition to phenyl and cyclopentadienyl peaks, two signals for the α- and β-carbon atoms of the phenylacetylene molecule. The downfield signals [δ 152.0 (**2**), 151.8 (**3**)] take the form of singlets and are attributed to the β-carbon atoms (*C*Ph) while the upfield signals [δ 60.1 (**2**) and 61.8 (**3**)] are seen as doublets [^3J(PC) 14 Hz (**2** and **3**)] and are assigned to the α-carbon atoms (*C*H). In [Fe$_3$(CO)$_9${μ_3-η^2-($\perp$)-HCCOC(O)Me}],[8] a similar upfield chemical shift for the α-carbon is seen at δ 70.2. Furthermore, the ^{13}C DEPT90 NMR spectrum for **3** is consistent with this assignment, with a proton being located on the α-carbon atom. In **2**, four peaks in the typical region for iron bound carbonyl groups are observed along with a single resonance at δ 195.0, for the bridging carbonyl group. The ^{31}P-{^{1}H} NMR spectra exhibit singlet resonances at δ 160.7 (**2**) and 194.7 (**3**), the former of which is flanked by ^{183}W satellites [J(WP) 134 Hz].

The pathway by which the formation of the phenylacetylene ligands in **2** and **3**, from the reaction of **1** with [M$_2$(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (M = W, Mo), takes place is uncertain. By analogy with the low temperature reaction of the anionic triiron cluster [Fe$_3$(CO)$_9${μ_3-η^2-($\perp$)-CCOC(O)Me}]$^-$ with protonic acids, which affords [Fe$_3$(CO)$_9${μ_3-η^2-($\perp$)-HCCOC(O)Me}],[8] it would seem likely that the anionic species [Fe$_2$M(CO)$_5$(η^5-C$_5$H$_5$){μ_3-η^2-($\perp$)-CCPh}(μ-CO)(μ-PPh$_2$)]$^-$ (M = W, Mo) are generated initially followed by protonation to give **2** or **3**. This protonation may occur, for example, during the chromatographic work-up.

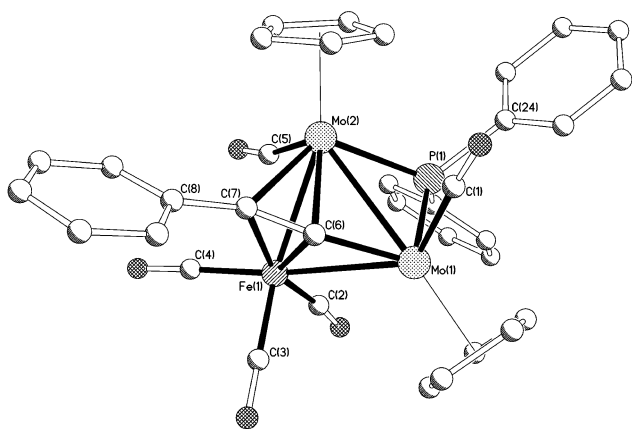The molecular structure of **4** is depicted in Fig. 3 while

Fig. 3 Molecular structure of [FeMo$_2$(CO)$_5$(η^5-C$_5$H$_5$)$_2${μ_3-η^2-($\perp$)-CCPh}(μ-PPh$_2$)] **4** including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

selected bond distances and angles are listed in Table 3. Crystals suitable for the X-ray structure determination were obtained by slow evaporation from a dichloromethane–hexane solution at 273 K.

The structure of **4** consists of a Mo$_2$Fe triangle in which a phenylacetylide unit σ-bonds to Mo(1) and perpendicularly bridges the Mo(1)–Fe(2) metal–metal bond *via* its π-orbitals to form a *closo*-trigonal-bipyramidal arrangement. The Mo(1)–Mo(2) vector [2.987(2) Å] is, in addition, unsymmetrically bridged by a diphenylphosphido group [Mo(1)–P(1) 2.400(4) Å, Mo(2)–P(1) 2.450(3) Å], with each molybdenum centre bound by a η^5-cyclopentadienyl ligand and by a terminal carbonyl ligand. At iron three terminal carbonyl ligands complete the coordination sphere. The acetylide C–C bond distance is 1.33(2) Å and falls in the range observed for a number of other acetylide-bridged heterotrimetallic complexes.[12] A formal electron count shows that the –CCPh unit functions as a five-electron donor to furnish a saturated 48-electron cluster giving rise to a *closo*-trigonal bipyramidal, six skeletal electron pair structure.

The spectroscopic and analytical data for **4** are consistent with the above formulation. In the IR spectrum, carbonyl absorptions are observed for terminal carbonyl groups only. The ^{1}H NMR spectrum shows a multiplet for the phenyl protons and one broad signal for the cyclopentadienyl ligands integrating to ten protons despite the inequivalent chemical environments. In the ^{31}P-{^{1}H} NMR spectrum a sharp singlet at δ 173.3 is seen for the bridging phosphido group. The ^{13}C-{^{1}H} NMR spectrum shows, in addition to phenyl and cyclopentadienyl resonances, peaks due to the terminal carbonyl groups and acetylide carbon atoms. The acetylide signals are seen as singlets at δ 161.5 and 146.4, the more downfield signal being assigned to the α-carbon and the more upfield signal to the β-carbon atom (*C*Ph). A similar assignment for the acetylide α- and β-carbon atoms was made previously for [Mo$_3$(CO)$_5$-(η^5-C$_5$H$_5$)$_3${μ_3-η^2-($\perp$)-CCPh}].[13]

2.2 Reaction of 1 with [CoM(CO)$_7$(η^5-C$_5$H$_5$)] (M = W, Mo)

Reaction of **1** with [CoW(CO)$_7$(η^5-C$_5$H$_5$)] in toluene at 363–373 K for 24 h affords the heterotrimetallic acetylide cluster [FeWCo(CO)$_6$(η^5-C$_5$H$_5$){μ_3-η^2-($\perp$)-CCPh}(μ-PPh$_2$)] **5** as the sole product in moderate yield. Similar treatment of **1** with [CoMo(CO)$_7$(η^5-C$_5$H$_5$)] gives [FeMoCo(CO)$_6$(η^5-C$_5$H$_5$){μ_3-η^2-($\perp$)-CCPh}(μ-PPh$_2$)] **6**, along with [Fe$_2$Mo(CO)$_5$(η^5-C$_5$H$_5$)-{μ_3-η^2-($\perp$)-HCCPh}(μ-CO)(μ-PPh$_2$)] **3**, in good overall yield (Scheme 1). Complexes **5** and **6** have been characterised by ^{1}H, ^{31}P-{^{1}H}, ^{13}C-{^{1}H} NMR and IR spectroscopy along with mass spectrometry and microanalysis (Table 1 and Experimental section). In addition, **6** has been the subject of a single crystal X-ray diffraction study.

A view of **6** is shown in Fig. 4 and selected bond distances and angles are collected in Table 4. The molecule consists of core atoms Mo(1), Fe(1), Co(1), C(8) and C(7) which adopt a *closo*-
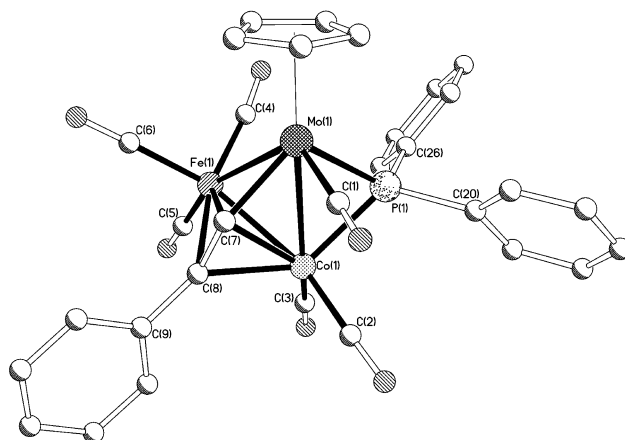

Fig. 4 Molecular structure of [FeMoCo(CO)$_6$(η^5-C$_5$H$_5$){μ_3-η^2-($\perp$)-CCPh}(μ-PPh$_2$)] **6** including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

Table 3 Selected bond distances (Å) and angles (°) for **4**

Fe(1)–Mo(1)	2.845(2)	Mo(1)–Mo(2)	2.987(2)
Fe(1)–Mo(2)	2.738(2)	Mo(2)–Cp(centroid)	1.993(7)
Mo(2)–C(5)	1.947(15)	Mo(2)–P(1)	2.450(3)
Mo(2)–C(6)	2.266(13)	Mo(2)–C(7)	2.248(12)
Mo(1)–P(1)	2.400(4)	Mo(1)–Cp(centroid)	2.018(8)
Mo(1)–C(1)	1.98(2)	Fe(1)–C(6)	2.065(12)
Mo(1)–C(6)	1.992(12)	C(6)–C(7)	1.33(2)
Fe(1)–C(7)	2.089(11)	Mean Fe–C(carbonyl)	1.79
C(7)–C(8)	1.47(2)		
Mo(1)–Mo(2)–Fe(1)	59.42(5)	Fe(1)–Mo(1)–Mo(2)	55.94(5)
Mo(1)–Fe(1)–Mo(2)	64.64(5)	Mo(1)–P(1)–Mo(2)	76.02(10)
Mo(1)–C(6)–C(7)	155.5(10)	C(6)–Mo(2)–C(7)	34.2(4)
C(6)–Fe(1)–C(7)	37.2(5)	Mo(1)–C(6)–Mo(2)	88.8(5)
Fe(1)–C(7)–Mo(2)	78.2(4)	C(6)–C(7)–C(8)	140.9(12)

**Table 4** Selected bond distances (Å) and angles (°) for **6**

Mo(1)–Fe(1)	2.819(1)	Fe(1)–C(7)	2.032(6)
Mo(1)–Co(1)	2.749(1)	Fe(1)–C(8)	2.086(7)
Mo(1)–Cp(centroid)	2.010(8)	Co(1)–C(7)	2.065(6)
Mo(1)–C(7)	1.997(6)	Co(1)–C(8)	2.056(7)
Mo(1)–P(1)	2.375(2)	Co(1)–P(1)	2.207(2)
Mo(1)–C(1)	1.980(8)	C(7)–C(8)	1.314(9)
Fe(1)–Co(1)	2.501(1)	Mean Fe–C(carbonyl)	1.790
Mean Co–C(carbonyl)	1.785		
Fe(1)–Co(1)–Mo(1)	64.75(3)	Fe(1)–C(7)–Co(1)	75.2(2)
Fe(1)–Mo(1)–Co(1)	53.36(3)	Fe(1)–C(8)–Co(1)	74.3(2)
Mo(1)–Fe(1)–Co(1)	61.90(3)	Co(1)–C(7)–Mo(1)	85.2(2)
Co(1)–P(1)–Mo(1)	73.64(6)	Fe(1)–C(7)–Mo(1)	88.8(3)
Mo(1)–C(7)–C(8)	153.2(5)	C(7)–C(8)–C(9)	144.0(6)

trigonal bipyramidal arrangement with C(7) sitting in an equatorial site and C(8) an axial site. The acetylide ligand is σ-bonded to the molybdenum atom and at the same time forms a transverse bridge across the Co(1)–Fe(1) bond. The molybdenum–cobalt bond is bridged unsymmetrically by the diphenylphosphido group [Co(1)–P(1) 2.207(2) Å, Mo(1)–P(1) 2.375(2) Å]. The acetylide moiety is coordinated to the FeCoMo triangular face with its α-carbon bound to all three metal atoms with bond distances Mo(1)–C(7) 1.997(6) Å, Fe(1)–C(7) 2.032(6) Å and Co(1)–C(7) 2.065(6) Å. The β-carbon atom is linked to the Fe(1) and Co(1) atoms with bond distances Fe(1)–C(8) 2.086(7) Å and Co(1)–C(8) 2.056(7) Å. The acetylide carbon–carbon bond distance of 1.314(9) Å compares well with **4** [1.33(2) Å] and is within the range reported for other known acetylide-bridged trimetallic complexes.[12] The majority of known crystallographically characterised heterotrimetallic acetylide clusters contain either one or two different kinds of metal atoms, whereas examples containing three unique metal atoms are, to the knowledge of the authors, unknown.[14]

The spectroscopic properties of **5** and **6** are entirely in accord with expectation and correlate with those observed for the acetylide analogue **4**. The IR spectra display three absorption bands in the terminal carbonyl region. The ^{31}P-{^{1}H} NMR spectra shows for each complex a singlet [δ 145.8 (**5**), 220.1 (**6**)] with the chemical shifts varying on replacement of tungsten by molybdenum. In the ^{13}C-{^{1}H} NMR spectra at room temperature, peaks are seen for the α-carbon atoms [δ 188.9 (**5**), 174.6 (**6**)] and the β-carbon atoms [δ 147.5 (**5**), 155.0 (**6**)] of the acetylide ligand in addition to resonances for the carbonyl, phenyl and cyclopentadienyl groups.

2.3 Carbonylation of [Fe₂Mo(CO)₅(η⁵-C₅H₅){μ₃-η²-(⊥)-HCCPh}(μ-CO)(μ-PPh₂)] 3

To further support the coordinative unsaturation in the 46-electron complexes **2** and **3**, complex **3** has been reduced by addition of a molecule of carbon monoxide. On treatment of **3** at room temperature in toluene under a pressure of 80 atm.,
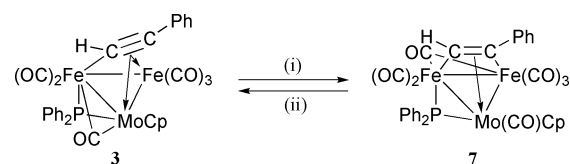
Scheme 2 *Reagents and conditions*: (i) CO (80 atm.), $C_6H_5CH_3$, 293 K; (ii) CDCl₃, 293 K.

complex [Fe₂Mo(CO)₆(η⁵-C₅H₅){μ₃-η²-(||)-HCCPh}(μ-CO)-(μ-PPh₂)] **7** is isolated as the sole product (Scheme 2). Complex **7** has been characterised by ^{1}H, ^{31}P-{^{1}H}, ^{13}C-{^{1}H} NMR and IR spectroscopy and by mass spectrometry (Table 1 and Experimental section). Furthermore, **7** has been the subject of a single crystal X-ray diffraction study.

The molecular structure of **7** is shown in Fig. 5 and selected bond distances and angles are given in Table 5. The core of the molecule consists of a triangle of two iron atoms and one
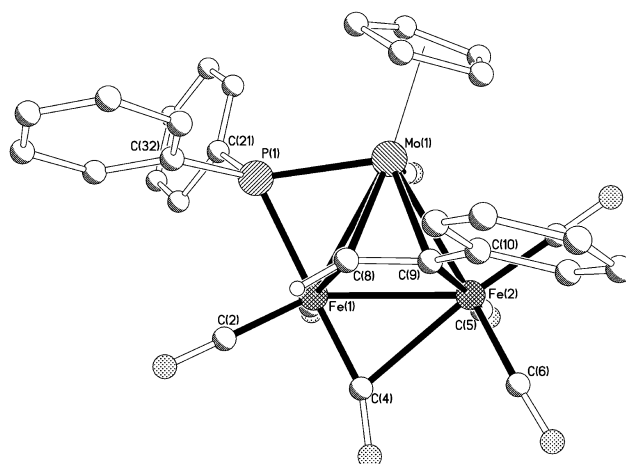

Fig. 5 Molecular structure of [Fe₂Mo(CO)₆(η⁵-C₅H₅){μ₃-η²-(||)-HCCPh}(μ-CO)(μ-PPh₂)] **7** including the atom numbering scheme. All hydrogen atoms except for H8 have been omitted for clarity.

Table 5 Selected bond distances (Å) and angles (°) for **7**

Mo(1)–Fe(1)	2.714(2)	Mo(1)–Fe(2)	2.715(2)
Fe(1)–Fe(2)	2.680(3)	Fe(1)–P(1)	2.248(4)
Mo(1)–P(1)	2.351(4)	Fe(1)–C(4)	1.789(16)
Fe(2)–C(4)	2.448(15)	Fe(1)–C(8)	1.991(13)
Mo(1)–C(8)	2.233(15)	Fe(2)–C(9)	1.971(13)
Mo(1)–C(9)	2.286(14)	C(8)–C(9)	1.352(19)
Mo(1)–Cp(centroid)	2.006(13)	Mean Fe–C(carbonyl)	1.785
Mo(1)–Fe(2)–Fe(1)	60.36(6)	Fe(2)–Fe(1)–Mo(1)	60.44(6)
Fe(1)–Mo(1)–Fe(2)	59.17(6)	Fe(1)–P(1)–Mo(1)	72.3(1)
Fe(1)–C(4)–Fe(2)	76.7(6)	Fe(1)–C(8)–C(9)	111.1(1)
C(8)–C(9)–Fe(2)	108.0(9)	C(8)–C(9)–Mo(1)	70.5(9)
C(9)–C(8)–Mo(1)	74.7(9)	C(8)–Mo(1)–C(9)	34.8(5)

molybdenum atom with a molecule of phenylacetylene adopting a parallel bonding mode and lying parallel to the Fe(1)–Fe(2) edge of the Fe$_2$Mo triangle. This observed geometry is consistent with σ-bonding to Fe(1) and Fe(2) [Fe(1)–C(8) 1.991(13) Å, Fe(2)–C(9) 1.971(13) Å] and π-bonding to the molybdenum atom [Mo(1)–C(9) 2.286(14) Å, Mo(1)–C(8) 2.233(15) Å]. The C(8)–C(9) bond distance of the alkyne is 1.352(19) Å and is similar to those found in other trimetallic 48-electron parallel-bonded alkyne-bridged clusters.[15] The iron–molybdenum bond lengths are almost symmetrical despite the Fe(2)–Mo(1) bond being spanned by a diphenylphosphido group [Fe(2)–Mo(1) 2.715(2) Å, Fe(1)–Mo(1) 2.714(2) Å]. The Fe(1)–Fe(2) bond [2.680(3) Å] is slightly longer than that in **3** [2.568(1) Å] and is additionally linked by a semibridging carbonyl group [Fe(1)–C(4) 1.789(16), Fe(2)–C(4) 2.448(15) Å]. Three terminal groups complete the coordination sphere at Fe(2), two at Fe(1) and one carbonyl and cyclopentadienyl group at Mo(1).

It is noteworthy that the ⊥–∥ alkyne reorientation during conversion of **3** to give **7** is in accord with polyhedral skeletal electron pair theory. Complex **3** is a six skeletal electron pair system and should therefore assume a *closo*-trigonal bipyramidal geometry. On the other hand the electron precise complex **7** has seven skeletal electron pairs and is thus consistent with the *nido*-octahedral structure observed. Similar ⊥–∥ reorientation of internal alkynes has been reported previously for a number of homotrimetallic group 8 clusters.[2,4c,16] To the knowledge of the authors this is the first report of the reorientation of an alkyne occurring on heterotrimetallic centres and, moreover, with a terminal alkyne molecule.

The infrared spectrum of **7** in the carbonyl region confirms that reduction has taken place in its formation from **3**. New bands appear in the carbonyl stretching region due to terminal carbonyl groups and an additional weak band at 1893 cm^{-1} suggests the presence of a semibridging carbonyl group. The ^{1}H NMR spectrum shows, in addition to phenyl resonances, a singlet at δ 4.8 which is assigned to the cyclopentadienyl ring. The peak due to the alkynic hydrogen atom could not be seen; it presumably overlaps with the phenyl group multiplets and is obscured by them. Notably, the alkynic hydrogen atom of the 48-electron cluster [Fe$_3$(CO)$_9$(μ-CO){μ$_3$-η^2-(∥)-HCC(C$_6$H$_{10}$-OH)}][5a] is observed as a downfield singlet at δ 6.93. The resonance for the phosphido bridge is seen as a singlet in the ^{31}P-{^{1}H} NMR spectrum at δ 218.9.

Interestingly complex **7**, on standing in solution at ambient temperature, converts, in the absence of CO, slowly back to **2** by the loss of a molecule of CO. A similar decarbonylation reaction has been observed for the triiron cluster [Fe$_3$(CO)$_9${μ$_3$-η^2-(∥)-MeOCH$_2$CCCH$_2$OMe}].[4c]

Conclusions

A series of phosphido-bridged triangular heterotrimetallic clusters (**2**–**7**) has been prepared incorporating phenylacetylene or phenylacetylide as the organic bridging ligand. All the clusters containing the phenylacetylide ligands (**4**–**6**) adopt perpendicular bonding modes, possess 48-electron configurations, and are σ-bonded to the group 6 metal centre. The unsaturated 46-electron clusters (**2** and **3**) contain phenylacetylene ligands perpendicularly bonding across an iron–group 6 metal edge. Conversion of **3** to the saturated 48-electron cluster **7** with concomitant carbonylation and ⊥–∥ reorientation of the terminal alkyne has been demonstrated as has the reconversion back to **3**.

3 Experimental

3.1 General techniques

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.[17] Infrared spectra were recorded in hexane solution in 0.5 mm NaCl cells, using a Perkin-Elmer 1710 Fourier-transform spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS 890 instrument using 3-nitrobenzyl alcohol as a matrix. Proton (reference to SiMe$_4$), ^{31}P NMR and ^{13}C NMR spectra were recorded on either a Bruker WM250 or AM400 spectrometer, ^{31}P NMR chemical shifts are referenced to 85% H$_3$PO$_4$. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the Department of Chemistry, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing R_f values. Elemental analyses were performed at the Department of Chemistry, Cambridge.

Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The syntheses of **1**,[18] [M$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_6$] (M = W, Mo),[19] and [CoM(η^5-C$_5$H$_5$)(CO)$_7$] (M = W, Mo)[20] have been reported previously.

3.2 Synthesis of 2

[W$_2$(CO)$_6$(η^5-C$_5$H$_5$)$_2$] (0.90 g, 1.35 mmol) in xylene (60 cm^3) was refluxed vigorously at 433 K for 48 h whilst purging gently with nitrogen to remove evolved CO. After cooling to 363 K, **1** (0.76 g, 1.34 mmol) was added and the solution maintained at 363 K for 24 h. After the removal of solvent under reduced pressure the mixture was absorbed onto a minimum quantity of silica, added to the top of a chromatography column and eluted with hexane–dichloromethane (1 : 1). This gave in addition to a small amount of starting materials, the brown crystalline complex [Fe$_2$W(CO)$_5$(η^5-C$_5$H$_5$){μ$_3$-η^2-(⊥)-HCCPh}(μ-CO)(μ-PPh$_2$)] **2** (0.32 g, 23%). Complex **2**: FAB mass spectrum, m/z 813 (M$^+$) and M$^+$ − nCO (n = 1–5). NMR (CDCl$_3$, 293 K): ^{13}C (^{1}H composite pulse decoupled), δ 229.5 [s, W–CO], 215.8 [s, Fe–CO], 211.7 [d, ^2J(PC) 14, Fe–CO], 210.8 [d, ^2J(PC) 7, Fe–CO], 195.0 [s, μ-CO], 152.0 [s, C$_β$], 142–127 [m, Ph], 94.9 [s, C$_5$H$_5$], 60.1 [d, ^2J(PC) 14, C$_α$].

Table 6 Crystallographic and data processing parameters for complexes **2**, **3**, **4**, **6** and **7**

Complex	2	3	4	6	7
Formula	$C_{31}H_{21}Fe_2O_6PW$	$C_{31}H_{21}Fe_2MoO_6P$	$C_{35}H_{25}FeMo_2O_5P$	$C_{31}H_{20}CoFeMoO_6P$	$C_{32}H_{21}Fe_2MoO_7P \cdot CH_2Cl_2$
M	816.00	728.09	804.25	730.16	841.02
Crystal size/mm	$0.20 \times 0.15 \times 0.15$	$0.20 \times 0.20 \times 0.10$	$0.30 \times 0.25 \times 0.10$	$0.50 \times 0.30 \times 0.20$	$0.38 \times 0.31 \times 0.14$
Temperature/K	293(2)	293(2)	293(2)	293(2)	180(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Lattice parameters					
$a/\text{Å}$	11.122(3)	11.108(2)	10.505(4)	10.577(4)	9.403(1)
$b/\text{Å}$	13.160(4)	13.177(3)	19.905(5)	20.399(4)	12.500(4)
$c/\text{Å}$	10.756(2)	10.810(2)	9.282(2)	13.625(2)	14.208(2)
$a/°$	100.34(3)	100.85(2)	97.65(2)	90	93.07(1)
$\beta/°$	111.19(2)	111.25(1)	112.72(2)	93.51(2)	98.32(1)
$\gamma/°$	75.27(3)	74.77(2)	85.76(3)	90	104.59(2)
$U/\text{Å}^3$	1413(1)	1415(1)	1774(1)	2929(1)	1592(1)
Z	2	2	2	4	2
$D_c/\text{Mg m}^{-3}$	1.916	1.709	1.506	1.656	1.754
$F(000)$	2552	728	800	1456	840
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	5.174	1.548	1.506	1.567	1.554
Reflections collected	5681	5255	6794	5453	6691
Independent reflections	5348	4973	4617	5152	5571
R_{int}	0.0371	0.0294	0.0881	0.0459	0.1529
Parameters/restraints	371/0	373/0	409/0	370/0	381/0
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0431$, $wR_2 = 0.1100$	$R_1 = 0.0375$, $wR_2 = 0.0857$	$R_1 = 0.0592$, $wR_2 = 0.1704$	$R_1 = 0.0466$, $wR_2 = 0.1075$	$R_1 = 0.0938$, $wR_2 = 0.2173$
Final R indices (all data)	$R_1 = 0.0718$, $wR_2 = 0.1404$	$R_1 = 0.0796$ $wR_2 = 0.1617$	$R_1 = 0.1159$ $wR_2 = 0.3883$	$R_1 = 0.1227$ $wR_2 = 0.2186$	$R_1 = 0.1760$ $wR_2 = 0.2607$
Goodness of fit on F^2 (all data)	1.034	1.040	1.070	1.048	1.030

Data in common: graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o{}^2) + (aP)^2]$, $P = [\max(F_o{}^2, 0) + 2(F_c{}^2)]/3$, where a is a constant adjusted by the program; goodness of fit $= [\Sigma(F_o{}^2 - F_c{}^2)2/(n-p)]^{1/2}$ where n is the number of reflections and p the number of parameters.

3.3 Synthesis of 3 and 4

$[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ (0.90 g, 1.83 mmol) in toluene (60 cm^3) was refluxed vigorously at 383 K for 24 h whilst purging gently with nitrogen to remove evolved CO. After cooling to 353 K, **1** (1.0 g, 1.76 mmol) was added and the solution maintained at 353 K for 24 h. After the removal of solvent under reduced pressure the residue was absorbed onto a minimum quantity of silica, added to the top of a chromatography column and eluted with hexane-dichloromethane (1 : 1). This gave in addition to small quantity of starting material, the brown complex $[Fe_2Mo(CO)_5(\eta^5\text{-}C_5H_5)\{\mu_3\text{-}\eta^2\text{-}(\perp)\text{-}HCCPh\}(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ **3** (0.31 g, 21%) and $[FeMo_2(CO)_5(\eta^5\text{-}C_5H_5)_2\{\mu_3\text{-}\eta^2\text{-}(\perp)\text{-}CCPh\}(\mu\text{-}PPh_2)]$ **4** (0.35 g, 21%). Complex **3**: (Found: C, 50.7; H, 2.9. $C_{31}H_{21}Fe_2MoO_6P$ requires C, 51.1; H, 2.9%). FAB mass spectrum, m/z 728 (M$^+$) and M$^+$ $- n$CO ($n = 1$–5). NMR (CDCl$_3$, 293 K): ^{13}C (^{1}H composite pulse decoupled), δ 151.8 [s, C$_\beta$], 132–127 [m, Ph], 96.8 [s, C$_5$H$_5$], 61.8 [d, ^2J(PC) 14, C$_\alpha$]. Complex **4**: (Found: C, 52.4; H, 3.1. $C_{35}H_{25}FeMo_2O_5P$ requires C, 52.3; H, 3.1%). FAB mass spectrum, m/z 728 (M$^+$) and M$^+$ $- n$CO ($n = 1$–5). NMR (CDCl$_3$, 293 K): ^{13}C (^{1}H composite pulse decoupled), δ 215.0 [s, FeCO], 211.5 [s, FeCO], 208.5 [s, FeCO], 161.5 [s, C$_\alpha$], 146.4 [s, C$_\beta$], 144–127 [m, Ph], 98.9 [s, C$_5$H$_5$], 95.2 [s, C$_5$H$_5$].

3.4 Synthesis of 5

To a solution of $[CoW(\eta^5\text{-}C_5H_5)(CO)_7]$ (0.97 g, 1.92 mmol) in toluene (60 cm^3) was added **1** (1.10 g, 1.94 mmol) and the solution heated to 373 K for 24 h. After the removal of solvent under reduced pressure, the mixture was absorbed onto a minimum quantity of silica, added to the top of a chromatography column and eluted with hexane-dichloromethane (3 : 1). This gave, in addition to a small amount of starting materials, the brown crystalline complex $[FeWCo(CO)_6(\eta^5\text{-}C_5H_5)\{\mu_3\text{-}\eta^2\text{-}(\perp)\text{-}CCPh\}(\mu\text{-}PPh_2)]$ **5** (0.60 g, 38%). Complex **5**: FAB mass spectrum, m/z 818 (M$^+$) and M$^+$ $- n$CO ($n = 1$–5). NMR (CDCl$_3$, 293 K): ^{13}C (^{1}H composite pulse decoupled),

δ 216.5 [s, Fe–CO], 216.0 [d, ^2J(PC) 16, W–CO], 215.0 [s, Fe–CO], 209.8 [s, Co–CO], 205.3 [s, Co–CO], 188.9 [s, C$_\alpha$], 147.5 [s, C$_\beta$], 145–128 [m, Ph], 89.7 [s, C$_5$H$_5$].

3.5 Synthesis of 6

To a solution of $[CoMo(\eta^5\text{-}C_5H_5)(CO)_7]$ (1.10 g, 2.64 mmol) in toluene (60 cm^3) was added **1** (1.49 g, 2.63 mmol) and the solution heated to 363 K for 24 h. After the removal of solvent under reduced pressure, the mixture was absorbed onto a minimum quantity of silica, added to the top of a chromatography column and eluted with hexane–dichloromethane (3 : 1). This gave in addition to a small amount of starting materials, the brown crystalline complexes $[Fe_2Mo(CO)_5(\eta^5\text{-}C_5H_5)\{\mu_3\text{-}\eta^2\text{-}(\perp)\text{-}HCCPh\}(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ **3** (0.40 g, 21%) and $[FeMoCo(CO)_6(\eta^5\text{-}C_5H_5)\{\mu_3\text{-}\eta^2\text{-}(\perp)\text{-}CCPh\}(\mu\text{-}PPh_2)]$ **6** (0.70 g, 36%). Complex **6**: FAB mass spectrum, m/z 732 (M$^+$) and M$^+$ $- n$CO ($n = 1$–6). NMR (CDCl$_3$, 293 K): ^{13}C (^{1}H composite pulse decoupled), δ 236.8 [s, Mo–CO], 213.2 [s, Fe–CO], 174.6 [s, C$_\alpha$], 155.0 [s, C$_\beta$], 146–128 [m, Ph], 89.5 [s, C$_5$H$_5$].

3.6 Carbonylation of 3 to give 7

A solution of $[Fe_2Mo(CO)_5(\eta^5\text{-}C_5H_5)\{\mu_3\text{-}\eta^2\text{-}(\perp)\text{-}HCCPh\}(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ **3** (0.70 g, 0.96 mmol) in toluene (60 cm^3) in a 100 cm^3 Roth autoclave was pressurised with 80 atmospheres of CO. The sealed system was stirred at room temperature for 24 h. After venting the gas, the solvent was removed under reduced pressure and the residue dissolved in the minimum quantity of dichloromethane. The solution was applied to base of preparative TLC plates and eluted with hexane–dichloromethane (4 : 1). This gave, in addition to a small amount of starting material, the brown crystalline complex $[Fe_2Mo(CO)_6(\eta^5\text{-}C_5H_5)\{\mu_3\text{-}\eta^2\text{-}(\parallel)\text{-}HCCPh\}(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ **7** (0.57 g, 70%). Complex **7**: (Found: C, 50.0; H, 3.1. $C_{32}H_{21}FeMo_2O_5P$ requires C, 50.8; H, 2.8%). FAB mass spectrum, m/z 756 (M$^+$) and M$^+$ $- n$CO ($n = 1$–7). NMR (CDCl$_3$, 293 K): ^{13}C (^{1}H composite pulse decoupled), not stable in solution.

3.7 Crystallography

X-Ray intensity data was collected using Rigaku AFC5R (**2**, **3**, **4** and **6**) and Stoe diffractometers (**7**). Both systems were equipped with an Oxford Cryosystems Cryostream. Details of data collection, refinement and crystal data are listed in Table 6. Semiempirical absorption corrections based on φ-scan data were applied[21] to the data. The structures were solved by direct methods [SHELXS86 (**3**, **6**);[22a] SHELXS97 (**2**, **4**, **7**)[22b]] and subsequent Fourier-difference syntheses and refined anisotropically on all ordered non-hydrogen atoms by full-matrix least squares on F^2 [SHELXL93 (**3**, **6**);[23a] SHELXL97 (**2**, **4**, **7**)[23b]]. Hydrogen atoms were placed in geometrically idealised positions and refined using a riding model. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance.

CCDC reference numbers 175751–175755.

See http://www.rsc.org/suppdata/dt/b1/b110874n/ for crystallographic data in CIF or other electronic format.

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