

Activation of methanol in the reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with 1-phenylprop-2-yn-1-ol; crystal structures of and chemical relationships between $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\{\text{C}=\text{C}=\text{C}(\text{H})\text{Ph}\}]$ and $[\text{Fe}_2(\text{CO})_6\{\text{Ph}(\text{H})\text{CCCHC}(\text{OMe})\text{O}\}]$

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The complexes $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\{\text{C}=\text{C}=\text{C}(\text{H})\text{Ph}\}]$ and $[\text{Fe}_2(\text{CO})_6\{\text{Ph}(\text{H})\text{CCCHC}(\text{OMe})\text{O}\}]$ have been obtained in low yields from reaction of 1-phenylprop-2-yn-1-ol with $[\text{Fe}_3(\text{CO})_{12}]$ ('stabilized' with methanol), together with other oily derivatives, difficult to characterize. Their solid-state structures have been determined using X-ray diffraction techniques. The first reacts with excess of methanol to form the second. However, the yields of the latter are always low irrespective of the amount of methanol used. Experiments showed that this reaction also occurs on the TLC plates used for the chromatographic separation of the complexes. This behaviour is discussed.

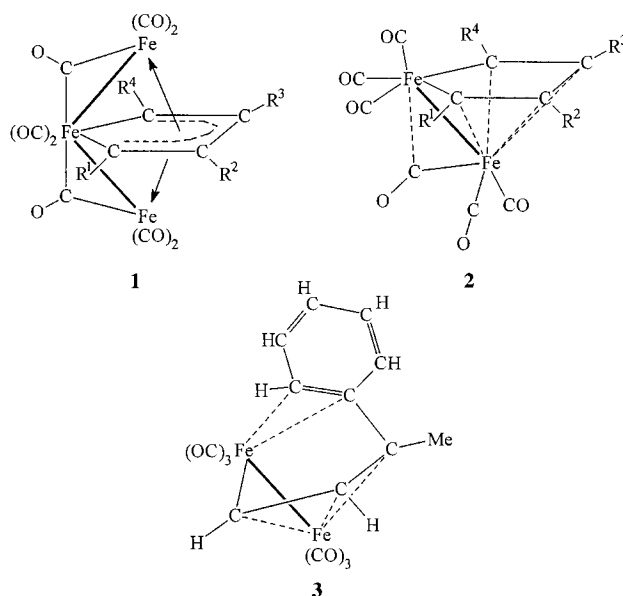
Propargyl (prop-2-ynyl) alcohols are used as synthons in, or may form organometallic intermediates for, organic syntheses leading to interesting commodity or speciality products.^{1,2} Reactions of these alcohols with the $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Ru}$ or Os) clusters have been reported (see below); however, their reactivity towards $[\text{Fe}_3(\text{CO})_{12}]$ has been relatively little studied.

We have recently undertaken a study of the behaviour of $[\text{Fe}_3(\text{CO})_{12}]$ towards the methyl-substituted propargyl alcohols $\text{HC}_2\text{CMe}_2(\text{OH})$ (2-methylbut-3-yn-2-ol) and $\text{HC}_2\text{C}(\text{Ph})\text{Me}(\text{OH})$ (2-phenylbut-3-yn-2-ol). For $\text{HC}_2\text{CMe}_2(\text{OH})$ we found two different dehydration processes. The major process, leading to tri- and di-nuclear metallacyclic derivatives (complexes **1** and **2** respectively), requires dimerization of two alkyne units, one of which has lost water from a methyl group and the OH, whereas the minor process involves loss of terminal alkyne hydrogen and the OH group to form the allenylidene species $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-C}=\text{C}=\text{CMe}_2)]$ **4b**.³ In contrast, $\text{HC}_2\text{C}(\text{Ph})\text{Me}(\text{OH})$ gives partially dehydrated tri- and di-nuclear metallacycles along with a moderate yield of an unusual binuclear 'deoxygenated' product **3** containing a phenylallenyl ligand.⁴ The structures of complexes **1–3** are shown in Scheme 1.

In an attempt at gaining a better understanding of the effect of the substituents upon the reactivity of propargyl alcohols, and at increasing the yields of the allenylidene complexes of type **4**, we have extended our study to include acetylenic alcohols not bearing methyl substituents. Here we report on the reactions of $\text{HC}_2\text{C}(\text{H})\text{Ph}(\text{OH})$ (1-phenylprop-2-yn-1-ol) with $[\text{Fe}_3(\text{CO})_{12}]$ in toluene or benzene both of which lead to medium yields of cluster **4** and surprisingly small yields of the metallacyclic complex **5** (Scheme 2). The latter displays an unprecedented ferrole structure having a methoxy substituent on one of the bridgehead carbons. The presence of the one group was intriguing for a while, until it was realised that the triiron dodecacarbonyl used in the syntheses was 'stabilized' with a considerable amount of methanol. The structures and chemical relationships of complexes **4** and **5** are discussed in this paper.

Experimental

Triiron dodecacarbonyl (Strem Chemicals) and $\text{HC}_2\text{C}(\text{H})\text{Ph}(\text{OH})$ (Lancaster Syntheses) were used as supplied. Reactions and general manipulations were performed under a dry



Scheme 1

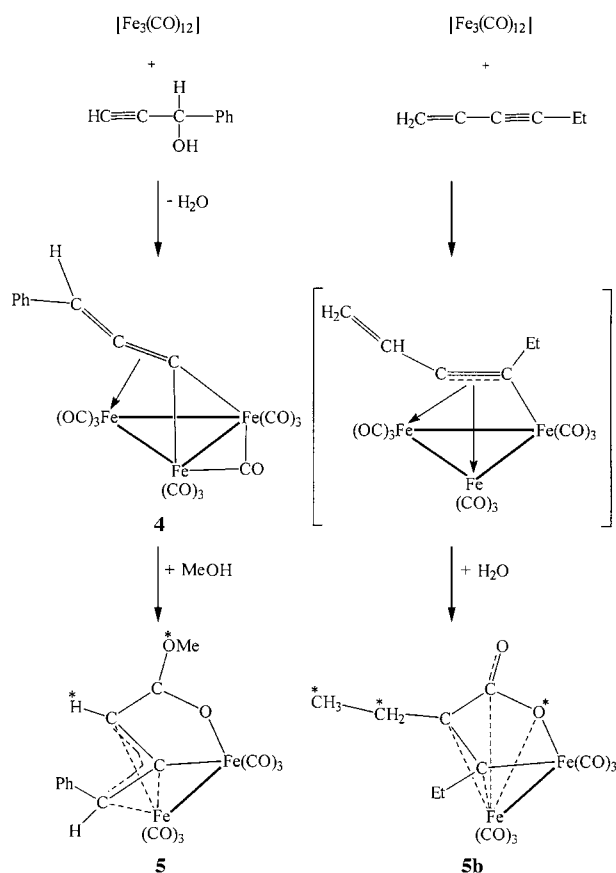
nitrogen atmosphere and the solvents benzene and toluene were dried by distillation over sodium prior to use. All reactions were performed in conventional glass vessels equipped with gas inlet, reflux condenser and mercury check valve. The reaction mixtures were filtered under N_2 and brought to small volume, under reduced pressure, prior to purification on preparative TLC plates [Merck Kieselgel PF, mixtures of light petroleum (b.p. 40–70 °C) and diethyl ether as eluent]. Where possible, the products were purified by recrystallization prior to analyses.

Solution IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer, proton and carbon-13 NMR spectra (in CDCl_3 and referenced externally to SiMe_4) on a JEOL GX 270 FT spectrometer and electron-impact (EI) mass spectra using a quadrupolar Finnigan-Mat TSQ-700 instrument. Elemental analyses were performed in the F. Pascher Laboratories (Germany).

Reactions of $[\text{Fe}_3(\text{CO})_{12}]$ with $\text{HC}_2\text{C}(\text{H})\text{Ph}(\text{OH})$

In toluene. A toluene solution (50 cm^3) of $[\text{Fe}_3(\text{CO})_{12}]$ (1.0 g, 1.98 mmol) and $\text{HC}_2\text{C}(\text{H})\text{Ph}(\text{OH})$ (0.5 cm^3 , ca. 4.0 mmol) was heated at reflux for 2 min. Upon reaching the boiling point

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foaming was observed along with a change from dark green to dark brown. Filtration of the reaction mixture removed the large amount of insoluble material formed during the reaction. Purification by TLC separated unchanged $[\text{Fe}_3(\text{CO})_{12}]$ along with dark brown complex **4** (about 1%), orange-red complex **5** (about 5%) and two orange-red products (complexes **6**, **7**) each in about 5% yield.

Complex 4 [Found (Calc.): C, 40.7 (40.6); H, 1.2 (1.1); Fe, 29.6 (29.8)%]. IR $[\nu(\text{CO}), \text{C}_7\text{H}_{16}]$: 2093ms, 2058vs, 2036vs, 2015ms, 1989ms and 1879m cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 7.70 (d), 7.49 (t), 7.33 (t, 5 H, Ph), 6.42 (s, 1 H, CH). EI mass spectrum: m/z 534 (P^+ - CO) followed by peaks corresponding to the loss of two to nine CO.

Complex 5 [Found (Calc.): C, 45.0 (45.0); H, 2.3 (2.2); Fe, 24.4 (24.6)%]. IR $[\nu(\text{CO}), \text{C}_7\text{H}_{16}]$: 2077m, 2035vs, 2008s, 1996s, 1980m and 1581m cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 7.20 (m, 5 H, Ph), 6.30 (s, 1 H, C^1H), 3.77 (s, 1 H, C^3H) (for labelling scheme see Fig. 2; these assignments may be reversed) and 3.72 (s, 3 H, CH_3). $^{13}\text{C NMR}$ (CDCl_3): δ 54.3 (s, CH_3), 57.9 (s, CH), 90.9 (s, CH), 125.5, 128.0, 128.3 (Ph), 142.3 (s, C^2 or C^4), two broad signals at about 190 (CO). EI mass spectrum: m/z 454 (P^+), with subsequent peaks corresponding to loss of up to six CO.

Complex 6: oily, tentative identification $[\text{Fe}_2(\text{CO})_6\text{L}_2]$ (M 532). IR $[\nu(\text{CO}), \text{C}_7\text{H}_{16}]$: 2073s, 2040vs, 1999vs (br) and 1950mw cm^{-1} . EI mass spectrum: m/z 526 (P^+) and subsequent peaks corresponding to loss of one to six CO. $^1\text{H NMR}$ (CDCl_3) (broad peaks): δ 7.47–6.87 (mm, Ph), 6.07–5.98 (d), 5.52–5.38 (d), 3.83 (m), 1.28 (s) and 0.89 (s).

Complex 7: oily, tentative identification $[\text{Fe}_2(\text{CO})_6\text{L}_2] \cdot 2\text{H}_2\text{O}$ (M 498). IR $[\nu(\text{CO}), \text{C}_7\text{H}_{16}]$: 2074m, 2043vs, 2004–1996vs (vbr) and 1954mw cm^{-1} . $^1\text{H NMR}$ (CDCl_3) (very broad peaks): δ 7.28 (Ph), 1.29 (s) and 0.90 (s). EI mass spectrum: m/z 526 (P^+).

In benzene. To a benzene suspension (50 cm^3) of $[\text{Fe}_3(\text{CO})_{12}]$ (1.0 g, 1.98 mmol) was added excess of $\text{HC}_2\text{C}(\text{H})\text{Ph}(\text{OH})$ (0.5

cm^3 , ca. 4.0 mmol) and the mixture heated at reflux for 6 min. A change from dark green to grey was observed along with a large amount of foaming. Complexes **4** (10%), **5** (5%) and **6** (10%) and several decomposition products (not identified) were separated by TLC.

In the presence of methanol. The compound $[\text{Fe}_3(\text{CO})_{12}]$ (1.0 g, 1.98 mmol) was suspended in a mixture of toluene (50 cm^3) and methanol (5.0 cm^3). The compound $\text{HC}_2\text{C}(\text{H})\text{Ph}(\text{OH})$ (0.5 cm^3 , 4.0 mmol) was added and the mixture heated at reflux for 3 min. A change from dark green to grey was observed. Complexes **4** and **5**, both in yields of 10%, were separated by TLC and **6** and **7** in a combined yield of 10%.

Reaction of complex 4 with methanol in benzene

Complex **4** (50 mg, ca. 0.10 mmol) was dissolved in a mixture of benzene (25 cm^3) and methanol (5.0 cm^3) and the mixture heated at reflux. The reaction was monitored at intervals of 3 min, using IR spectroscopy. A decrease in the intensity of the bands due to complex **4** was noted together with the appearance, increase and stabilization (after 6 min) of bands characteristic of **5**. Thin-layer chromatography of the remaining solution allowed isolation of **4** and **5** in a ratio of ca. 9:1.

Behaviour of complex 4 on the TLC plates in the presence of methanol

Crystals of complex **4** (50 mg) were dissolved in MeOH (10 cm^3), the dissolution occurring slowly and leading to a purple solution. A fraction of the solution (5 cm^3) was deposited on a dry TLC plate as a purple band and exposed to air. After 15 min elution (light petroleum and 10% diethyl ether) separated an orange band and a purple band, which IR spectroscopy showed to be complexes **4** and **5** respectively, in a ratio of ca. 1:9. To the remainder of the solution was added water (0.5 cm^3) and the suspension thus obtained deposited on a TLC plate as an irregular purple band. Exposure to the air for 15 min followed by elution with light petroleum and 10% diethyl ether allowed isolation of complex **4** and a trace amount of **5**. Some decomposition products were also observed.

Crystallography

Crystal data. Complex **4**, $\text{C}_{19}\text{H}_6\text{Fe}_3\text{O}_{10}$, M = 561.8, monoclinic, space group $P2_1/c$ (no. 14), a = 15.140(5), b = 12.478(6), c = 11.928(6) Å, β = 107.55(2)°, U = 2147.3(10) Å³. Cell data were based upon the setting angles of 30 reflections with $20 < 2\theta < 35^\circ$, Z = 4, D_c = 1.738 g cm^{-3} , $F(000)$ = 1112. Prismatic black crystal of dimensions 0.12 × 0.32 × 0.34 mm, $\mu(\text{Mo-K}\alpha)$ = 20.5 cm^{-1} .

Complex **5**, $\text{C}_{17}\text{H}_{10}\text{Fe}_2\text{O}_8$, M = 454.0, triclinic, space group $P\bar{1}$ (no. 2), a = 6.843(3), b = 10.695(4), c = 13.130(6) Å, α = 87.30(2), β = 83.16(2), γ = 73.36(2)°. Cell data were based upon the setting angles of 30 reflections with $20 < 2\theta < 35^\circ$, Z = 2, D_c = 1.649 g cm^{-3} , $F(000)$ = 456. Prismatic brown crystal of dimensions 0.36 × 0.48 × 0.50 mm, $\mu(\text{Mo-K}\alpha)$ = 16.3 cm^{-1} .

Data collection and processing. The data were collected at room temperature on a Siemens P4 diffractometer with graphite-monochromatized Mo-K α radiation (λ = 0.710 73 Å); θ - 2θ (complex **4**) and ω (**5**) mode with scan range 2.00 (**4**) and 2.40° (**5**), 2θ range 2.0–55.0° ($-19 \leq h \leq 19$, $0 \leq k \leq 15$, $0 \leq l \leq 15$) (**4**) and 2.0–50.0° ($-9 \leq h \leq 9$, $-13 \leq k \leq 13$, $0 \leq l \leq 16$) (**5**). Two standard reflections measured every 50 showed no decay; 7978 (**4**) and 4481 (**5**) reflections measured, 4759 (**4**) and 3182 (**5**) unique [R_{int} = 0.022 (**4**), 0.063 (**5**) after absorption correction (maximum, minimum transmission factors = 0.53–0.36 (**4**), 0.35–0.23 (**5**), giving 2942 (**4**) and 2418 (**5**) with $F > 4.0\sigma(F)$]. Empirical absorption correction applied according to the method of ref. 5.

Structure analysis and refinement. The structures were solved by direct methods and Fourier-difference syntheses using the Siemens SHELXTL IRIS package,⁶ used also for refinement (full-matrix least squares). The non-hydrogen atoms were anisotropically refined. The last Fourier-difference maps showed peaks corresponding to the H atoms of the ligands; the H atoms of the phenyl rings were, however, calculated and refined riding on the corresponding carbon atoms with $U_{\text{iso}} = 0.080 \text{ \AA}^2$. The atoms H(1) of complex **4** and H(1) and H(3) of **5** were located on the corresponding experimental peaks found in the Fourier-difference maps and a refinement was tried. The satisfactory results, obviously with high estimated standard derivations (e.s.d.s), of the distances and of the isotropic thermal parameters verified this approach. These H atoms were also confirmed by NMR data. The weighting scheme was $w = [\sigma^2(F_o) + aF_o^2]^{-1}$ with $a = 0.0003$ (**4**) and 0.002 (**5**). The final $R = \Sigma|F_o - F_c|/\Sigma F_o$ and $R' = [\Sigma w^2|F_o - F_c|^2/\Sigma w^2 F_o^2]^{1/2}$ indices were 0.037 and 0.036 (**4**) and 0.043 and 0.059 (**5**); goodness of fit = 1.14 (**4**) and 1.04 (**5**). The maximum and minimum peaks in the final Fourier-difference map were 0.49 , -0.31 (**4**) and 0.46 , -0.35 e \AA^{-3} (**5**).

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/469.

Results and Discussion

Under the conditions used, the reactions of $[\text{Fe}_3(\text{CO})_{12}]$ with $\text{HC}_2\text{C}(\text{H})\text{Ph}(\text{OH})$ led mostly to formation of insoluble decomposition products or to other unidentifiable species (presumed to be polymeric organic derivatives). Among the soluble products, complexes **6** and **7** were tentatively characterized as the partially dehydrated metallacyclic complexes $[\text{Fe}_2(\text{CO})_6\text{L}_2]$ or $[\text{Fe}_2(\text{CO})_6\text{L}_2] \cdot 2\text{H}_2\text{O}$ comparable with the known compounds **1** and **2** (Scheme 1).

The allenylidene complex **4** was also obtained in low to medium yields. Its formation requires dehydration of $\text{HC}_2\text{C}(\text{H})\text{Ph}(\text{OH})$ with loss of the terminal alkyne hydrogen and of the OH group. To our knowledge, there are only two examples for this type of dehydration on metal clusters of the iron triad. The first was reported by Aime *et al.*⁷ who trapped, as an intermediate in the dehydration of $\text{HC}_2\text{CPh}_2(\text{OH})$ on $[\text{Os}_3(\text{CO})_{12}]$, the open cluster $[\text{Os}_3(\mu\text{-H})(\mu\text{-OH})(\text{CO})_9(\text{C}=\text{C}=\text{CPh}_2)]$ **4c**. The second is the previously mentioned reaction of $\text{HC}_2\text{CMe}_2(\text{OH})$ with $[\text{Fe}_3(\text{CO})_{12}]$ ³ forming complex **4b** in low yield. Other triiron allenylidene derivatives (*e.g.* complex **4d**,⁸ Table 2) have been obtained through reaction routes not involving clusters and/or dehydration of propargyl alcohols.^{8,9} Little is known of the chemistry of the allenylidene complexes of type **4**,¹⁰ the formation of **5** represents a new example of their reactivity.

Complex **5**, having a new type of ferrole structure, results from the presence of methanol as a stabilizer in the parent iron carbonyl. Examples of new products being formed because of the presence of unsuspected reagents have been reported.¹¹⁻¹³ The experimental evidence suggests the formation of **5** from **4** either in solution or on the TLC plates.

Owing to the fact that reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with $\text{HC}_2\text{C}(\text{H})\text{Ph}(\text{OH})$ leads to several products and to decomposition, a reaction mechanism is difficult to establish. Formation of **5** from **4** would involve loss of $[\text{Fe}(\text{CO})_x]$, insertion of an already co-ordinated CO into an iron-allenylidene bond and oxidative addition of methanol. Reversible insertion of CO has previously been observed during the reaction of diruthenium allenyl complexes with alkynes.¹⁴ Carboxylato complexes related to **5** have been synthesized through reaction of alkyne-substituted triiron clusters. One such example, the formation of

Table 1 Bond lengths (Å) and angles (°) for complex **4**

Fe(1)–Fe(2)	2.611(1)	Fe(1)–Fe(3)	2.569(1)
Fe(1)–C(3)	1.897(3)	Fe(1)–C(41)	2.034(4)
Fe(2)–Fe(3)	2.619(1)	Fe(2)–C(2)	2.096(4)
Fe(2)–C(3)	2.007(4)	Fe(3)–C(3)	1.922(4)
Fe(3)–C(41)	1.984(4)	C(1)–H(1)	0.914(37)
C(1)–C(2)	1.329(6)	C(1)–C(6)	1.464(6)
C(2)–C(3)	1.346(5)	C(41)–O(41)	1.153(6)
Fe(2)–Fe(1)–Fe(3)	60.7(1)	Fe(1)–Fe(2)–Fe(3)	58.8(1)
Fe(1)–Fe(3)–Fe(2)	60.4(1)	H(1)–C(1)–C(2)	114.7(26)
H(1)–C(1)–C(6)	119.5(26)	C(2)–C(1)–C(6)	125.8(4)
C(1)–C(2)–C(3)	153.8(4)	Fe(1)–C(3)–Fe(2)	83.9(1)
Fe(1)–C(3)–Fe(3)	84.5(2)	Fe(2)–C(3)–Fe(3)	83.6(1)
Fe(1)–C(3)–C(2)	134.3(2)	Fe(2)–C(3)–C(2)	74.5(2)
Fe(3)–C(3)–C(2)	130.8(2)	Fe(1)–C(41)–Fe(3)	79.5(2)
Fe(1)–C(41)–O(41)	138.3(3)	Fe(3)–C(41)–O(41)	142.1(3)

the diiron complex $[\text{Fe}_2(\text{CO})_6\{(\text{C}_2\text{Et}_2)(\text{CO}_2)\}]$ **5b** in the reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with C_2Et_2 ,¹⁵ was explained by the presence of water.¹⁶ More recently, we have demonstrated that complex **5b** can be obtained from addition of hex-1-en-3-yne ‡ to $[\text{Fe}_3(\text{CO})_{12}]$ and that its formation was due to the splitting of a molecule of water by the TLC silica.¹⁷ We therefore propose that **5** is formed upon activation of methanol, in a way comparable to the formation of **5b**, as shown in Scheme 2. The behaviour of **4** on the TLC plates may suggest that, like that of water, the activation of methanol is also favoured by the silica used for the chromatographic separations.¹⁷

Mononuclear complexes¹⁸⁻²⁰ undergo reactions comparable with those observed for the formation of **4** and **5**. Thus, the alcohols $\text{HC}_2\text{CR}_2(\text{OH})$ undergo dehydration in the presence of cationic ruthenium complexes to form $\text{M}=\text{C}=\text{CR}_2$ allenylidene systems. Further, the alcohol $\text{HC}_2\text{CH}_2\text{OH}$ reacts with MeOH to form a complex of the type $\text{M}=\text{C}=\text{C}(\text{H})(\text{CH}_2\text{OMe})$.¹⁸ Uptake of R'OH may also occur at the α -carbon of the ligand allenylidene to give the derivatives $\text{M}-\text{C}(\text{OR}')(\text{CH}=\text{CR}_2)$. Dehydration involving the terminal alkyne hydrogen seems therefore to be general for prop-2-yn-1-ols on mononuclear ruthenium complexes.¹⁹ In addition, prop-2-ynyl alcohol undergoes dehydration to give allenylidene on a mononuclear metallacyclic palladium complex. Addition of water to the α -carbon of the allenylidene affords $\text{Pd}-\text{C}(\text{OH})=\text{C}=\text{CH}_2$ system which can then tautomerize to give $\text{Pd}-\text{C}(=\text{O})\text{CH}=\text{CH}_2$.²⁰

Crystal structures of complexes **4** and **5**

The structure of **4**, which is the only known unsymmetrically substituted triiron allenylidene derivative, is given in Fig. 1 and selected bond distances and angles are presented in Table 1. The allenylidene moiety is held almost perpendicular (96°) to the Fe_3 plane while the phenyl ring is coplanar with atoms C(1), C(2) and C(3), having a mean deviation from planarity of 0.05 \AA . The atoms C(3), Fe(1), Fe(3), C(41), O(41) form a plane, having a mean deviation from planarity of 0.013 \AA , oriented at 60° with respect to the Fe_3 cluster. As a consequence, the slight asymmetry (8σ) of the C(3) bridge [Fe(1)–C(3), $1.897(3)$, Fe(3)–C(3) $1.922(4) \text{ \AA}$] has a counterbalance on the parallel slight (12σ) asymmetry of the CO(41) bridge [Fe(1)–C(41) $2.034(4)$, Fe(3)–C(41) $1.984(4) \text{ \AA}$]. Such a behaviour is observed also in $[\text{Fe}_3(\text{CO})_{10}(\text{C}=\text{C}=\text{CPh}_2)]$ **8**; for $[\text{Fe}_3(\text{CO})_{10}(\text{C}=\text{C}=\text{CMe}_2)]$ ^{1b} and $[\text{Os}_3\text{H}(\text{OH})(\text{CO})_9(\text{C}=\text{C}=\text{CPh}_2)]$ **4c**, the high e.s.d.s do not allow a similar analysis.

A comparison with the structural parameters of the other two triiron allenylidene derivatives (Table 2) shows that the cluster edge doubly bridged by the μ -CO and by C(3) is always the shortest and that complex **4** shows the longest Fe–Fe

‡ Hex-1-en-3-yne, $\text{EtC}_2\text{CH}=\text{CH}_2$, could be considered as either the dehydration product of $\text{EtC}_2\text{C}(\text{H})\text{Me}(\text{OH})$ or of $\text{EtC}_2\text{CH}_2\text{CH}_2\text{OH}$.

Table 2 Comparison of the structural parameters (bond lengths in Å, angles in °) of the allenylidene complexes **4**, **4b** and **4d** [$\text{Fe}_3(\text{CO})_{10}\{\text{C}=\text{C}=\text{C}(\text{R})\text{R}'\}$]

	4b (R,R' = Me) ³	4d (R,R' = Ph) ⁸	4 (R = H, R' = Ph)
M(1)–M(2)	2.600(2)	2.603(1)	2.611(1)
M(1)–M(3)	2.559(2)	2.559(2)	2.569(1)
M(2)–M(3)	2.601(2)	2.613(1)	2.619(1)
M(1)–C(3)	1.905(8)	1.899(3)	1.897(3)
M(2)–C(2)	2.182(7)	2.199(3)	2.096(4)
M(2)–C(3)	2.010(7)	2.004(3)	2.007(4)
M(3)–C(3)	1.921(8)	1.917(3)	1.922(4)
C(1)–C(2)	1.309(12)	1.331(3)	1.329(6)
C(2)–C(3)	1.351(11)	1.338(1)	1.346(5)
C(1)–C(2)–C(3)	148.8(8)	151.5(2)	153.8(4)

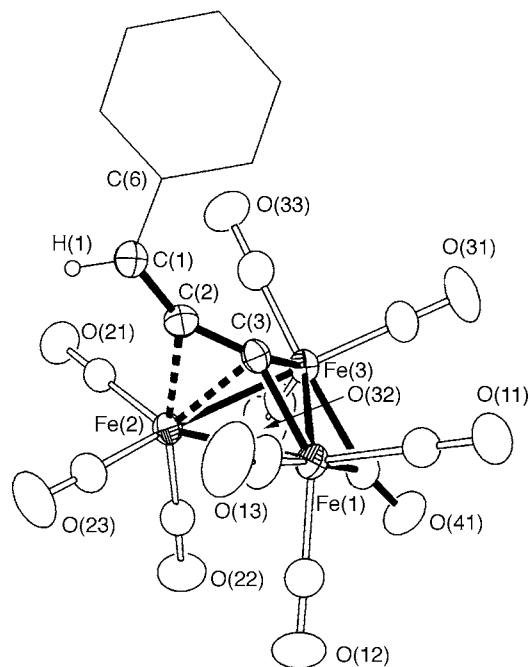


Fig. 1 An ORTEP²¹ plot (30% probability) of [$\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\{\text{C}=\text{C}=\text{C}(\text{H})\text{Ph}\}$] **4**

distances. The other structural parameters are in a narrow range of values and indicate a considerable 'rigidity' for C=C=C distances of this metal–ligand arrangement, while a greater flexibility of the C=C=C angle occurs, if we include also the complexes [$\text{Fe}_3(\text{CO})_8(\text{C}=\text{C}=\text{CPh}_2)_2$] [157.7(4) and 152.8(4)°] and [$\text{Os}_3\text{H}(\text{OH})(\text{CO})_9(\text{C}=\text{C}=\text{CPh}_2)_2$] [145(3)°]. In complexes where the allenylidene is η^1 bonded to two metals the angle is 174°. ²² It is worth noting that the C=C distances involved in π bonding with one iron and those apparently not bound to the metals are very close to each other, that is within the experimental error. Linear and folded allenylidene moieties with different coordinating patterns on diruthenium clusters are known. ²³

A double contact O(41a)⋯O(22b) and O(22a)⋯O(41b) (3.025 Å) giving rise to a dimer and an intermolecular weak hydrogen bond, C(11a)–H(11a)⋯O(33) (2.66 Å, 165°), C(11a)⋯O(33) 3.599 Å, should be mentioned.

The structure of compound **5** is shown in Fig. 2 and relevant distances and angles are in Table 3. Atoms C(1), C(2) and C(3) in complexes **4** and **5** comprise a moiety common to both. Complex **5** is characterized by a pentaatomic ferrole metallacycle [Fe(1)–C(2)–C(3)–C(4)–O(1)] which differs from the usual ferrole structures, and that of **5b**,§ in the following ways:

Table 3 Bond lengths (Å) and angles (°) for complex **5**

Fe(1)–Fe(2)	2.619(1)	Fe(1)–O(1)	2.016(3)
Fe(1)–C(2)	1.963(4)	Fe(2)–C(1)	2.217(5)
Fe(2)–C(2)	1.954(5)	Fe(2)–C(3)	2.120(4)
O(1)–C(4)	1.252(5)	O(2)–C(4)	1.309(5)
O(2)–C(5)	1.439(6)	C(1)–H(1)	1.112(43)
C(1)–C(2)	1.410(5)	C(1)–C(6)	1.496(6)
C(2)–C(3)	1.441(6)	C(3)–H(3)	1.028(37)
C(3)–C(4)	1.429(5)		
Fe(2)–Fe(1)–O(1)	87.7(1)	Fe(2)–Fe(1)–C(2)	47.9(1)
O(1)–Fe(1)–C(2)	84.3(1)	Fe(1)–Fe(2)–C(1)	77.1(1)
Fe(1)–Fe(2)–C(2)	48.2(1)	C(1)–Fe(2)–C(2)	38.9(1)
Fe(1)–Fe(2)–C(3)	69.8(1)	C(1)–Fe(2)–C(3)	68.5(2)
C(2)–Fe(2)–C(3)	41.2(2)	Fe(1)–O(1)–C(4)	110.2(2)
C(4)–O(2)–C(5)	117.6(3)	Fe(2)–C(1)–H(1)	118.2(26)
H(1)–C(1)–C(2)	122.5(22)	Fe(2)–C(1)–C(6)	114.6(3)
C(2)–C(1)–C(6)	124.8(3)	Fe(1)–C(2)–Fe(2)	83.9(2)
Fe(1)–C(2)–C(3)	106.4(3)	Fe(2)–C(2)–C(3)	75.6(3)
C(1)–C(2)–C(3)	117.8(3)	Fe(2)–C(3)–H(3)	117.4(21)
C(2)–C(3)–H(3)	123.4(22)	C(2)–C(3)–C(4)	114.3(3)
H(3)–C(3)–C(4)	116.5(19)	O(1)–C(4)–O(2)	121.7(3)
O(1)–C(4)–C(3)	120.0(3)	O(2)–C(4)–C(3)	118.2(3)

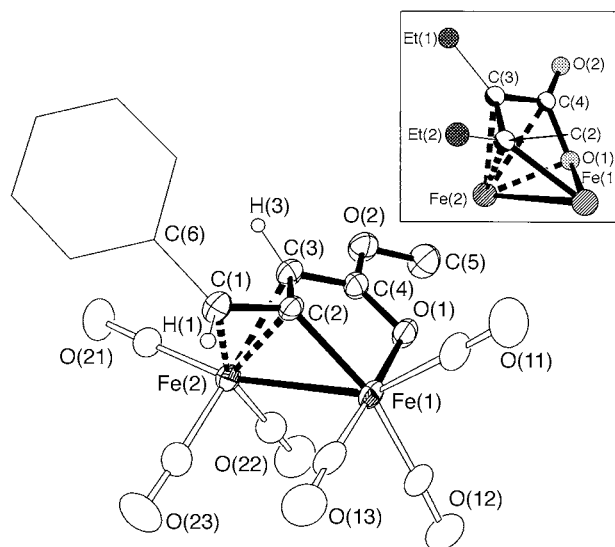


Fig. 2 An ORTEP plot (30% probability) of [$\text{Fe}_2(\text{CO})_6(\text{Ph})(\text{H})\text{C}-\text{CCHC}(\text{OMe})\text{O}$] **5**. In the inset the structure of complex **5b** is reported for comparison

(i) the O(1) atom is bonded only to Fe(1) and not to both iron atoms as in **5b**; (ii) attached to C(2) there is a small chain bonded to Fe(2) forming an 'allylic' ensemble not previously found in any of the known ferroles; a puckered plane consisting of atoms C(1), C(2), C(3), C(4), C(5), O(1) and O(2) [mean deviation from planarity 0.061 Å where C(2) is the atom with the greatest deviation, 0.15 Å] is thus formed; (iii) the axes of the $\text{Fe}(\text{CO})_3$ cones of the $\text{Fe}_2(\text{CO})_6$ unit make angles of 60° [around Fe(1)] and 47° [around Fe(2)] with respect to the Fe–Fe line ²⁴ and the carbonyl groups are staggered (average nearly 30°), while in complex **5b** the angles are 43° and 21° respectively and the carbonyl groups are also staggered. The wider angles of complex **5** are in keeping with the presence of bulkier substituents on the ligand and with the shift of the pentaatomic 'ferrole' ring towards Fe(1) with respect to **5b**. As with most of the ferroles, complex **5** seems to prefer the non-sawhorse arrangement of carbonyl groups. ²⁵ A comparison of some significant bonding distances and angles in **5** and in **5b** is given in Table 4 and in Fig. 2.

In complex **5**, where only one atom C(2) bridges the Fe–Fe bond, this Fe–Fe distance is considerably longer and the same happens for Fe(1)–O(1), while C(4)–O(1) is shorter; the

§ The data for complex **5b** correspond to a structural redetermination, the parameters of which are provided in the supplementary material.

Table 4 Comparison of bond lengths (Å) of complexes **5** and **5b**

	5	5b ¹⁷
Fe(1)–Fe(2)	2.619(1)	2.445(1)
Fe(1)–O(1)	2.016(3)	1.953(2)
Fe(2)–O(1)	—	1.988(1)
O(1)–C(4)	1.252(5)	1.373(3)
O(2)–C(4)	1.309(5)	1.196(3)
O(2)–C(5)	1.439(6)	—
C(1)–C(2)	1.410(5)	1.515(3) C(2)–Et
C(1)–C(6)	1.469(6)	—
C(2)–C(3)	1.441(6)	1.401(3)
C(3)–C(4)	1.429(5)	1.482(2)
C(1)–Fe(2)	2.217(5)	—
C(2)–Fe(2)	1.954(5)	2.110(1)
C(2)–Fe(1)	1.963(4)	1.961(2)
C(3)–Fe(2)	2.120(4)	2.166(2)
C(4)–Fe(2)	—	2.410(2)

C(1)–C(2), C(2)–C(3) and C(3)–C(4) distances in **5** indicate delocalization and the C(1)/C(2)/C(3)–Fe(2) distances are typical of an iron–allyl system. The C–C distances of this ensemble are considerably longer than the C–C distances of the allenylidene moiety found in **4**, presumably because of the different co-ordination to the metals. The C(4)–O(1) and C(4)–O(2) distances are equal and are typical of enolic moieties. The structural differences observed for **5** and **5b** are also reflected by the IR spectra. Thus for **5b** a 'ketonic' shift is observed at 1739 cm⁻¹ (*cf.* 1581 cm⁻¹ for **5**). Finally, the ¹H NMR spectrum confirms the presence of a CH₃ group (δ 3.72) in **5** and of hydrogens (δ 6.30, 3.77) on C(3) and C(1) but not on C(2).

Behaviour of different propargyl alcohols with [Fe₃(CO)₁₂]

Under comparable conditions, different behaviour has been observed for propargyl alcohols having different substituents. The alkyne HC₂C(OH)Me₂ undergoes terminal H/OH dehydration as a minor pathway with the major pathway involving partial Me/OH dehydration.³ The compound HC₂C(Me)Ph(OH) undergoes competitive deoxygenation and cyclization (with partial dehydration).⁴ Finally the reactions of HC₂C(H)–Ph(OH) lead to the formation of complex **4**, in moderate yield, indicating that, in the absence of methyl substituents, the H/OH dehydration pattern may become an important process. This is in keeping with the earlier observation that H/OH dehydration seems to be the main reaction pathway for HC₂CPh₂(OH) on [Os₃(CO)₁₂], presumably because an OH/Ph dehydration pathway would be exceedingly difficult. Comparable behaviour was reported under ionic or acidic conditions on mononuclear ruthenium complexes.²⁶

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