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FULL PAPER

Oligomerisation of isopropenylacetylene in the presence of $Fe_3(CO)_{12}$. Crystal and molecular structure of the open-cluster isomers $Fe_3(CO)_{10}[H_2CC(CH_3)CC(H)C(H)C(CO)C(CH_3)CH_2]$, $Fe_3(CO)_{10}[HCC(CH_3)C(H)C(H)C(H)C(CO)C(CH_3)CH_2]$ and of the binuclear complex $Fe_2(CO)_5[C_{15}H_{18}(CO)]$

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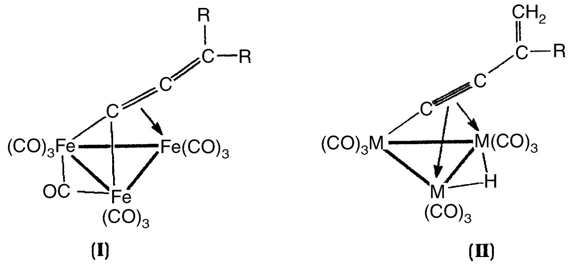
The reaction of 2-methyl-1-buten-3-yne (isopropenylacetylene, IPA) with triiron dodecacarbonyl in refluxing benzene leads to medium yields of four main derivatives. Two of them are the trinuclear open-cluster isomers $Fe_3(CO)_{10}[H_2CC(CH_3)CC(H)C(H)C(CO)C(CH_3)CH_2]$ (complex **1a**) and $Fe_3(CO)_{10}[HCC(CH_3)C(H)C(H)C(H)C(CO)C(CH_3)CH_2]$ (complex **1b**) containing an organic ligand formed upon tail-to-tail dimerization of the alkyne. In both complexes one isolated iron atom is part of a metallacyclic five-membered ring formed by three carbon atoms of one alkyne molecule and a carbon belonging to a CO. The other two iron atoms are linked together; however their bonding to the organic moiety is different in complexes **1a** and **1b**. This type of isomerism and the coordination mode of the unique iron atom are unprecedented in alkyne-cluster chemistry. The other two complexes are binuclear and have been identified, respectively, as $Fe_2(CO)_5[C_{15}H_{18}(CO)]$ (**2**) and $Fe_2(CO)_6L_3$ [L = IPA] (**3**). Complex **2** contains an unprecedented organic ligand formed by three alkyne molecules and one CO; this is different from other L_3CO (*troponic*) ligands found in the literature. The structures of complexes **1a**, **1b** and **2** have been studied by X-ray crystallography. Complex **3** did not give crystals suitable for X-ray analysis. Reaction pathways leading to new complexes are hypothesized.

Introduction

Propargyl alcohols, HC≡CC(OH)RR′, react with $M_3(CO)_{12}$ carbonyls (M = Fe, Ru) undergoing *dehydration* through two main pathways; one of them (more common when M = Fe) requires loss of the terminal alkynic hydrogen and of the alcoholic OH to give the *allenylidene* clusters $Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C{=}C{=}CRR')$ (type **I**). The second process (more common when M = Ru, in acidic conditions) occurs through the loss of the OH and of one hydrogen of an alkylic substituent (eg. R′ = Me); it leads to *vinyl-acetylide* clusters, such as $(\mu\text{-}H)Ru_3(CO)_9[C{\equiv}CC({=}CH_2)R]$ (type **II**).[1,2] The structures of complexes of type **I** and **II** are shown in Scheme 1.



Scheme 1

Free or coordinated *ene-yne* (or vinyl-acetylene) ligands are important as synthons in metal-mediated organic syntheses,[3] in reaction mechanisms related to anticancer drugs[4] and as potential NLO materials.[5] The interest in these ligands led us to explore reaction pathways to obtain iron carbonyl clusters containing ene-ynes.

As previously pointed out, triiron clusters of type **II** are difficult to obtain. The more simple approach would be the direct reaction of $Fe_3(CO)_{12}$ with ene-yne ligands. One such reaction was attempted using hex-1-en-3-yne (EtC≡CCH=CH_2).[6] The products, however, were formed upon *hydration* of the coordinated alkyne; the splitting of water into its components being favoured by the silica used for TLC purifications. No clusters of type **II** were observed. A comparable reaction sequence, starting from $Fe_3(CO)_{12}$ and 1-phenylprop-2-yn-1-ol [HC≡CC(H)(OH)Ph] led to a type **I** triiron allenyl cluster which underwent reaction with methanol to form an oxygenated metallacycle.[7]

We have now investigated the reaction of $Fe_3(CO)_{12}$ with 2-methylbut-1-en-3-yne, $HC{\equiv}CC({=}CH_2)CH_3$ (isopropenylacetylene, IPA).[8] Again, we could not isolate complexes of type **II**; however, we could obtain some clusters showing structural features not reported until now. The structures of the trinuclear isomers $Fe_3(CO)_{10}[H_2CC(CH_3)CC(H)C(H)C(CO)C(CH_3)CH_2]$ (**1a**) and $Fe_3(CO)_{10}[HCC(CH_3)C(H)C(H)C(H)C(CO)C(CH_3)CH_2]$ (**1b**) have been deduced from an X-ray diffraction study. The complexes show an unprecedented open cluster structure and some interesting metal-ligand interaction modes. $Fe_2(CO)_5[C_{15}H_{18}(CO)]$ (**2**) was initially hypothesized to belong to a known class of *troponic* derivatives; the X-ray analysis showed instead that it belongs to a new and unprecedented type of derivative. The oligomerization pathways of IPA in the presence of $Fe_3(CO)_{12}$ are discussed and compared with those observed in the presence of $Ru_3(CO)_{12}$.

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Experimental

General details, materials, analysis of the products

Triiron dodecacarbonyl (Strem Chemicals, stabilized with MeOH) and the alkyne (Lancaster Synthesis) were commercial products and were used as received. Solvents (benzene, heptane) were dehydrated over sodium. All the reactions were performed under a dry nitrogen atmosphere in conventional three necked flasks equipped with gas inlet, cooler, mercury check valve and magnetic stirring.

The reaction mixtures were filtered under N_2, brought to small volume under reduced pressure and separated on preparative TLC plates (Merck Kieselgel P.F.; eluent mixtures of light petroleum (bp 40–70 °C) and diethyl ether in variable v/v ratios). The products were crystallized and analyzed by means of a Bruker Equinox 55 spectrophotometer (KBr cells); the ^1H NMR spectra were obtained on a JEOL GX 270/89 instrument[9] and electron-impact mass spectra with a Finnigan-Mat TSQ-700 quadrupolar mass spectrometer.[10]

The ^1H NMR spectrum of IPA, registered for comparison with those of the complexes, shows signals at: 5.30 m, 5.21 m (2H, CH_2), 2.81 s (1H, HC≡), 1.82 t (3H, CH_3).

Reaction of $Fe_3(CO)_{12}$ with IPA

In a typical reaction, to a suspension of the iron carbonyl (*ca.* 2.0 g, 4 mmol) in benzene (100 cm^3) 0.5 cm^3 of liquid IPA (*ca.* 7 mmol) was added; the mixture was refluxed for 6 min, then allowed to cool and filtered under N_2. TLC purification showed the presence of unreacted parent carbonyl (*ca.* 10%) and of the following bands: yellow and pink (trace amounts, not collected), red (**1a**, *ca.* 15%), red–brown (**1b**, *ca.* 10%), red–orange (**2**, *ca.* 20%) and dark red (**3**, *ca.* 20%). The bands corresponding to **1b** and **2** were partly superposed, so that the complexes could not be collected as pure specimens. Longer reaction times resulted in lower yields of **1a** and **1b** and increased yields of the other complexes, in particular of **2**.

Complex 1a. C 41.8 (41.4), H 2.01 (1.97)% (Calc. values in parentheses). IR: 2107 w, 2058 m, 2048 m(sh), 2031 vs, 2020 s(sh), 1992 m, 1985 m, cm^{-1}. ^1H NMR(C_6D_6, −40 °C): 7.05–7.03 d (HC≡, C_{10}), 2.35 d (HC≡, C_6, C_7), 1.71 s (CH_3, C_4 or C_{14}), 1.25 m (CH_2), 0.84 t (CH_3, C_5). EI MS: P^+ = 608 *m*/*z* (very low intensity) and 580 *m*/*z* (first very intense peak), loss of 10 CO's; very intense peaks at 300 *m*/*z* (Fe_3L_2) and 272 *m*/*z* ($Fe_2L_2(CO)$) (L = IPA).

Complex 1b. C 41.9, H 2.02% (see **1a**). IR: 2054 vs, 2048 s(sh), 2023 s, 1996 vs, 1989 s(sh), 1974 m, 1953 m. ^1H NMR: 6.03 s (≡CH, C_{10}), 5.74 dd (≡CH, C_7, C_8), 5.39 dd (≡C, C_6), 4.83 d (CH_2), 1.96 s, 0.89 t (CH_3). EI MS: P^+ = 580 *m*/*z*, loss of 10 CO's (see **1a**).

Complex 2. C 54.6 (54.4), H 3.4 (3.2)%. IR: 2071 s, 2039 vs, 2005 vs, 2001 vs(sh), 1988 m, cm^{-1}. ^1H NMR: 5.73 d (CH, C_5,C_6), 5.38 s (CH, C_8), 5.09 s (1H), 4.83 s (CH_2, C_1 or C_{15}), 2.39 d (CH_2, C_1 or C_{15}), 2.31 d (CH_2, C_{11}), 2.27 s, 2.23 s (CH_3, C_1,C_{15}), 1.57–1.50 m (CH_3, C_{12}). EI MS: P^+ = 478 *m*/*z*, loss of 5 CO; intense peak at 304 *m*/*z*.

Complex 3. C 52.5 (52.7), H 3.9 (3.76)%. IR: 2051 vs, 2021 vs, 1988 m, cm^{-1}. ^1H NMR: 6.21 s (1H), 5.41 s (1H), 5.02 d (2H,CH_2), 3.83 s (1H), 2.17–2.09 m (4H,CH_2), 1.56 s, 1.28 t, 0.90 t (9H, CH_3). EI MS: P^+ = 478 *m*/*z*, loss of 6 CO; very intense peaks at 338 *m*/*z* ($Fe_2(CO)L_3$) (L = IPA), 310 and 272/270 *m*/*z*.

The attributions of the NMR spectra are not unequivocal because of the complex structures of the derivatives and, in some instances, can be reversed.

Behaviour of complex 1a on the TLC plates and in solvents

The complex forms a red band during TLC elution, from which deep red crystals used for the X-ray analysis were obtained. It gives red solutions when dissolved in benzene, toluene, hexane and heptane. It immediately turns deep green when dissolved in $CHCl_3$ or CH_2Cl_2; from these solutions a deep green solid could be recovered. This green material showed the following spectroscopic data. IR ($CHCl_3$): 2109 w, 2071 m–s, 2057 s(sh), 2039 vs(b), 2002 s(vb). EI MS: 504 *m*/*z* (low intensity, $Fe_3(CO)_{12}$), 448 *m*/*z* (medium intensity, $Fe_3(CO)_{10}$); intense peak at 364 *m*/*z* [$Fe_3(CO)_7$?, $Fe_2(CO)_9$?], loss of 7 CO's (very intense peaks): very intense peak at 112 *m*/*z* (Fe_2, $Fe(CO)_2$).

Behaviour of complexes 1a and 1b under thermal conditions

Complex **1a** was dissolved in benzene, under N_2 and heated to reflux for 10 min. TLC purification showed the presence of unreacted **1a** (*ca.* 50%), of complex **2** (*ca.* 30%) of trace amounts of complex **1b** and of **3** together with some other trace products and decomposition.

Attempts at purifying and crystallizing complex **1b** always resulted in the deposition of crystals of **1b** and of **2** together. The crystals of **1b** used for the X-ray analysis were separated by hand. This behaviour did not allow us to investigate the thermal reactivity of **1b**.

X-Ray analyses

The crystal data and the refinement parameters of X-ray analyses are collected in Table 1. The reflection intensities were collected on a four circle automatic diffractometer Siemens P4.

For complexes **1a**, **1b** and **2** the Fe, C and O atoms were anisotropically refined, while the hydrogen atoms were treated in different ways. In complex **1a** all H atoms were localized in the final Fourier difference maps and refined with fixed U_{iso} values. For complex **1b** all H atoms were localized on the Fourier difference maps; for three of them it was necessary to fix the C–H distance and all were refined with fixed U_{iso} values. In complex **2** the H atoms of CH_3 groups were put in calculated positions and refined riding on the corresponding C atoms. The other H atoms were found on the final maps; for some of them the coordinates were free during refinement and for others the C–H distances were fixed. For all H atoms the U_{iso} value was fixed during refinement. Any statement regarding the hydrogen atoms must be considered, obviously, with caution.

CCDC reference numbers 175533–175535.

See http://www.rsc.org/suppdata/dt/b1/b111070p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Spectroscopic characterization and reactivity of the new complexes

The reaction of $Fe_3(CO)_{12}$ with IPA leads to four main organometallic products, all containing oligomeric alkyne ligands. These were characterized by means of IR and ^1H NMR spectroscopies and by mass spectrometry. However, in some instances, in the mass spectra parent ion signals of very low intensity were obtained; the complexity of the NMR spectra, also, did not always allow unequivocal attributions. Therefore, when possible, the structure of the complexes was determined by X-ray diffraction. Complexes **1a**, **1b** and **2** gave crystals suitable for X-ray analyses; in contrast, **3** did not give good quality crystals. Thus, for this complex we can only propose a tentative structure in accordance with the NMR and mass spectrometric results; on these bases **3** could be a flyover complex (type **VI**) as discussed below.

The behaviour of **1a** on the TLC plates indicates that it is not sensitive to moisture. In previous work we had observed,

Table 1 Crystal data and refinement parameters for complexes **1a**, **1b** and **2**

Complex	**1a**	**1b**	**2**
Empirical formula	$C_{21}H_{12}Fe_3O_{11}$	$C_{21}H_{12}Fe_3O_{11}$	$C_{21}H_{18}Fe_2O_6$
M	607.86	607.86	478.05
T/K	293(2)	293(2)	293(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
a/Å	12.9293(15)	14.354(5)	8.549(5)
b/Å	14.5344(13)	8.028(3)	14.799(7)
c/Å	13.0375(13)	21.089(8)	16.467(8)
α/°	90	90	85.11(3)
β/°	105.376(8)	100.43(2)	85.46(4)
γ/°	90	90	83.57(3)
V/Å^3	2362.3(4)	2390.0(15)	2057.5(19)
Z, Calculated density/g cm^{-3}	4, 1.709	4, 1.689	4, 1.543
μ/mm^{-1}	1.876	1.854	1.444
F(000)	1216	1216	976
Crystal size/mm	0.30 × 0.40 × 0.76	0.08 × 0.24 × 0.60	0.02 × 0.34 × 0.40
θ range data collection/°	1.97 to 27.50	1.96 to 36.08	1.24 to 25.00
Limiting indices	$-16 \leqslant h \leqslant 1, -1 \leqslant k \leqslant 18, -16 \leqslant l \leqslant 16$	$-1 \leqslant h \leqslant 20, -11 \leqslant k \leqslant 1, -29 \leqslant l \leqslant 29$	$-10 \leqslant h \leqslant 1, -17 \leqslant k \leqslant 17, -19 \leqslant l \leqslant 19$
Refl. collected/unique	6545/5389 [R(int) = 0.0330]	8862/6981 [R(int) = 0.0302]	8903/7248 [R(int) = 0.0504]
Completeness to θ (%)	99.3	99.8	100.0
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5389/0/352	6981/3/352	7248/17/576
Goodness-of-fit on F^2	1.028	1.010	0.942
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0449$, $wR2 = 0.1064$ [4021 refl.]	$R1 = 0.0476$, $wR2 = 0.0857$ [3673 refl.]	$R1 = 0.0605$, $wR2 = 0.1459$ [3712 refl.]
R indices (all data)	$R1 = 0.0663$, $wR2 = 0.1179$	$R1 = 0.1185$, $wR2 = 0.1087$	$R1 = 0.1417$, $wR2 = 0.1855$
Largest diff. peak and hole/e Å^{-3}	0.520 and −0.642	0.427 and −0.599	0.510 and −0.475

indeed, that TLC materials may contain traces of water which is responsible for several *surface organometallic reactions* including hydration or dehydration of cluster-bound alkyne ligands.[1,2,6,7] Hydration of IPA would lead to 2-methyl-3-butyn-1-ol [HC≡C(Me)$_2$OH, MBO, see ref. 8]. The reactions of MBO with $Fe_3(CO)_{12}$ had already been investigated; small yields of a type **I** allenyl complex and higher yields of partially dehydrated (isomeric) metallacyclic complexes were obtained.[11] None of these complexes could be detected after the reactions reported here.

It is worthy to note, also, that **1a** is unaffected by the diethyl ether used in the TLC elution and by hydrocarbon solvents (*e.g.* heptane, benzene, toluene). In contrast, it is very sensitive to chlorinated solvents; the deep green solutions obtained deposited a deep green solid which was identified as $Fe_3(CO)_{12}$.

We could also observe that upon thermal treatment **1a** gives mainly **2** and that **1b** and **2** co-crystallize; this could indicate that both **1a** and (mostly) **1b** are precursors of **2**. We could also observe (reactions not reported) that **2** and **3** do not interconvert. They are presumably formed through different mechanisms.

X-Ray structure of complexes 1a and 1b

The two molecules of complexes **1a** and **1b** (Fig. 1 and 2) are formed by a mononuclear moiety $Fe(CO)_4$ and by a binuclear moiety $Fe_2(CO)_6$ connected *via* an organic ligand formed by a tail-to-tail dimerization of two IPA molecules and by one inserted CO whose origin is discussed below. The mononuclear moiety (Fe(3)) is identical in the two complexes while in the binuclear fragments Fe(1) and Fe(2) are enveloped in a different way by the organic moiety. As discussed below, the isomerism of the complexes is due to differences in the organic chain and in its coordination to the metals. Relevant bond distances and angles are listed in Tables 2 and 3 for complexes **1a** and **1b**, respectively.

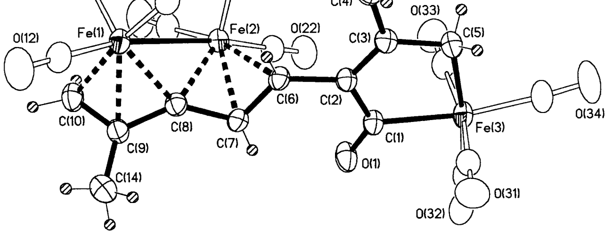


Fig. 1 An ORTEP plot of $Fe_3(CO)_{10}[H_2CC(CH_3)CC(H)C(H)C(CO)$-$C(CH_3)CH_2]$ **1a**, with 30% thermal ellipsoids.

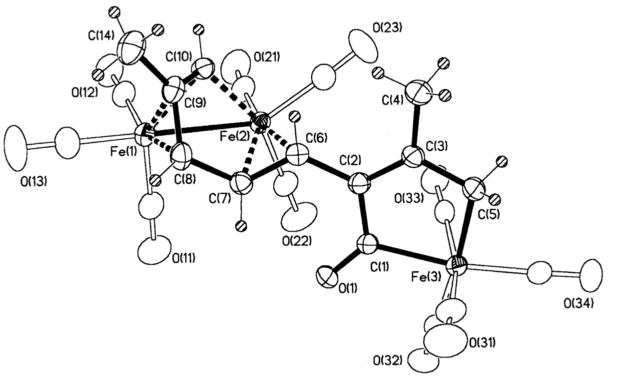


Fig. 2 An ORTEP plot of $Fe_3(CO)_{10}[HCC(CH_3)C(H)C(H)C(H)C$-$(CO)C(CH_3)CH_2]$ **1b**, with 30% thermal elliposids.

In the *mononuclear fragment* Fe(3) has a distorted octahedral environment. It forms a penta-atomic planar ring (mean deviation from planarity 0.02 and 0.07 Å for **1a** and **1b**, respectively) with the organic moiety; the organic moiety behaves as a two-electron donor, in agreement with the Fe(3)–C(1) and Fe(3)–C(5) bond distances and with the distances inside the ring. The C(1)–O(1) distance corresponds to a double bond and in the ring a double bond is also localized between C(2) and C(3) (1.347(4) Å av.). The similarity of the mononuclear fragments of **1a** and **1b** includes the C(6)H(6) atoms; the C(2)C(6) fragment corresponds to one former IPA unit with a triple bond between C(2) and C(6) and a double bond between C(3) and C(5).

Table 2 Some relevant bond distances [Å] and angles [°] for complex **1a**

Fe(1)–Fe(2)	2.7565(6)	C(1)–C(2)	1.471(4)
Fe(1)–C(8)	1.993(3)	C(2)–C(3)	1.347(4)
Fe(1)–C(9)	2.105(3)	C(2)–C(6)	1.487(4)
Fe(1)–C(10)	2.126(4)	C(3)–C(4)	1.485(4)
Fe(2)–C(8)	1.970(3)	C(3)–C(5)	1.490(4)
Fe(2)–C(7)	2.102(3)	C(6)–C(7)	1.402(4)
Fe(2)–C(6)	2.207(3)	C(7)–C(8)	1.407(4)
Fe(3)–C(1)	2.050(3)	C(8)–C(9)	1.402(4)
Fe(3)–C(5)	2.069(3)	C(9)–C(10)	1.412(5)
C(1)–O(1)	1.203(4)	C(9)–C(14)	1.501(6)
C(1)–Fe(3)–C(5)	81.77(12)	C(3)–C(5)–Fe(3)	110.6(2)
C(2)–C(1)–Fe(3)	113.4(2)	C(4)–C(3)–C(5)	116.6(3)
C(3)–C(2)–C(1)	115.7(3)	C(7)–C(6)–C(2)	126.2(3)
C(3)–C(2)–C(6)	122.7(3)	C(6)–C(7)–C(8)	117.2(3)
C(1)–C(2)–C(6)	121.6(3)	C(9)–C(8)–C(7)	140.4(3)
C(2)–C(3)–C(4)	124.9(3)	C(8)–C(9)–C(10)	115.7(3)
C(2)–C(3)–C(5)	118.5(3)	C(9)–C(10)–Fe(1)	69.7(2)

Table 3 Some relevant bond distances [Å] and angles [°] of complex **1b**

Fe(1)–Fe(2)	2.636(1)	C(1)–C(2)	1.474(4)
Fe(1)–C(10)	2.047(3)	C(2)–C(3)	1.348(4)
Fe(1)–C(8)	2.072(3)	C(2)–C(6)	1.479(4)
Fe(1)–C(9)	2.086(3)	C(3)–C(5)	1.485(5)
Fe(2)–C(10)	1.970(3)	C(3)–C(4)	1.496(5)
Fe(2)–C(7)	2.240(3)	C(6)–C(7)	1.383(4)
Fe(2)–C(6)	2.275(3)	C(7)–C(8)	1.466(5)
Fe(3)–C(1)	2.051(3)	C(8)–C(9)	1.423(5)
Fe(3)–C(5)	2.074(3)	C(9)–C(10)	1.391(5)
C(1)–O(1)	1.206(4)	C(9)–C(14)	1.508(5)
C(1)–Fe(3)–C(5)	81.58(13)	C(2)–C(3)–C(4)	125.5(3)
O(1)–C(1)–C(2)	124.9(3)	C(5)–C(3)–C(4)	114.9(3)
O(1)–C(1)–Fe(3)	121.9(2)	C(3)–C(5)–Fe(3)	109.8(2)
C(2)–C(1)–Fe(3)	113.2(2)	C(7)–C(6)–C(2)	127.3(3)
C(3)–C(2)–C(1)	114.6(3)	C(6)–C(7)–C(8)	121.7(3)
C(3)–C(2)–C(6)	123.4(3)	C(9)–C(8)–C(7)	118.3(3)
C(1)–C(2)–C(6)	122.0(3)	C(10)–C(9)–C(8)	111.8(3)
C(2)–C(3)–C(5)	119.6(3)	C(9)–C(10)–Fe(2)	116.9(2)

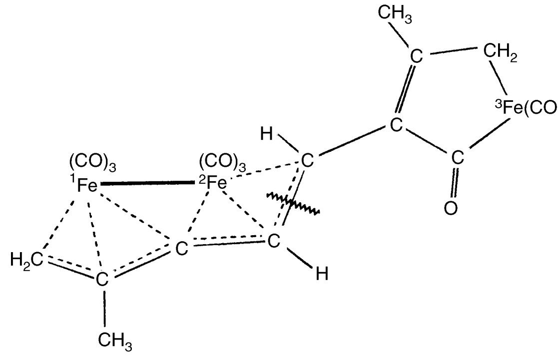
The presence of "isolated" Fe(CO)$_4$ fragments in polymetallic derivatives is rare: there are, however, some literature examples of clusters containing Fe(CO)$_4$ units linked to tri- and bi-nuclear iron fragments through a bridging diphosphine.[13] It is worthy of note that these clusters undergo degradation to binuclear fragments; this is helpful when considering the behaviour of **1a** in solution and as a possible precursor of compound **2**.

It is difficult to hypothesize the origin of C(1)–O(1); a reasonable hypothesis could be that a *Fe(CO)$_5$* fragment (formed from alkyne-assisted fragmentation of Fe$_3$(CO)$_{12}$) is coordinated to the three alkynic carbons and that C(1)–O(1) is in an "agostic" situation between the iron and the carbon atom chain. This hypothesis would be in accordance with the observed retro-formation of Fe$_3$(CO)$_{12}$ [through recombination of Fe(CO)$_5$ fragments].

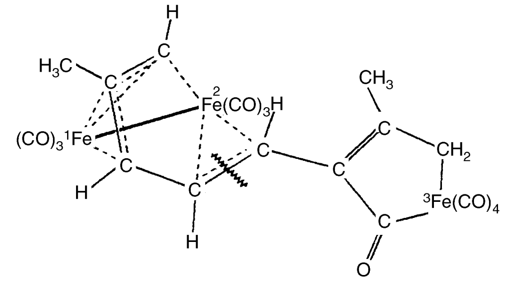
In the *binuclear fragment* of **1a** the two iron atoms (Fe(1)–Fe(2) 2.7565(6) Å) are coordinated to five carbon atoms of the organic chain (C(10)H$_2$–C(9)Me–C(8)–C(7)H–C(6)H) acting as bis π-allylic ligands; each iron atom interacts with three allylic carbon atoms (Fe(1)–C(10) 2.126(4), Fe(1)–C(9) 2.105(3), Fe(1)–C(8) 1.993(3); Fe(2)–C(8) 1.970(3), Fe(2)–C(7) 2.102(3), Fe(2)–C(6) 2.207(3) Å). The Fe(1,2)–C(8) distances are significantly shorter than the other ones. The carbon–carbon bond distances are very similar (1.406(4) Å av.) in agreement with a delocalization in the C(6)∸C(10) chain and with a bis-allylic ligand; therefore, considering the chain as a six-electron-donor, the 18-electron rule is observed. The C(6)–C(7) and C(9)–C(10) bonds were originally a triple and a double bond in the IPA molecules. This coordination mode of five carbon atoms to two iron atoms has not been previously observed, to our knowledge. The three carbonyl ligands on each iron atom are staggered.

In complex **1b** the binuclear fragment of the molecule is formed by two iron atoms (Fe(1)–Fe(2) 2.636(1) Å) around which a five carbon atom chain of the organic moiety (C(10)H–C(9)Me–C(8)H–C(7)H–C(6)H) is wrapped. Each iron atom is coordinated to three carbon atoms (Fe(1)–C(10) 2.047(3), Fe(1)–C(9) 2.086(3), Fe(1)–C(8) 2.072(3); Fe(2)–C(10) 1.970(3), Fe(2)–C(7) 2.240(3), Fe(2)–C(6) 2.275(3) Å). While in complex **1a** the organic moiety begins on Fe(2) with C(6) and ends on Fe(1) with C(10), in complex **1b** the organic ligand begins and ends on the same atom Fe(2). The carbon–carbon distances are also different to each other, (C(6)–C(7) 1.383(4), C(7)–C(8) 1.466(5), C(8)–C(9) 1.423(5), C(9)–C(10) 1.391(5) Å), and suggest a greater double bond character of C(6)–C(7) and of C(9)–C(10); this lower degree of electron delocalization may suggest the incipient formation of a metallacyclic (ferrole-like) system.[12] Only two pairs of carbonyls are eclipsed (CO(11) and CO(22), CO(21) and CO(12)).

The carbon chain of **1b** is *isomeric* with that of **1a**; in fact, its formation requires a hydrogen shift from the IPA terminal C(10) of **1a** to the C(8) atom of **1b**. The unprecedented open structures of the clusters and the interactions within the organic moieties and the metals in **1a** and **1b** are compared in Scheme 2.



(1a)



(1b)

Scheme 2

The Fe(1)–Fe(2) bond is longer in **1a** than in **1b**, owing to the different disposition of the organic ligand.

No relevant intermolecular interaction was found from packing analysis.

X-Ray structure of complex 2

The structure of complex **2** is shown in Fig. 3 and significant bond distances and angles are listed in Table 4; the asymmetric unit contains two independent molecules (A and B).

In compound **2**, two iron atoms (Fe(1)–Fe(2) 2.705(2) Å mean value between the two molecules of the asymmetric unit) link three [Fe(1)] and two [Fe(2)] carbonyl ligands and are coordinated to an alkyne trimer; two IPA alkynes are joined tail[C(5)]-to-tail[C(6)] from C(1) to C(7) and the third alkyne moiety is joined head[C(7)]-to-tail[C(8)]. In the middle of the

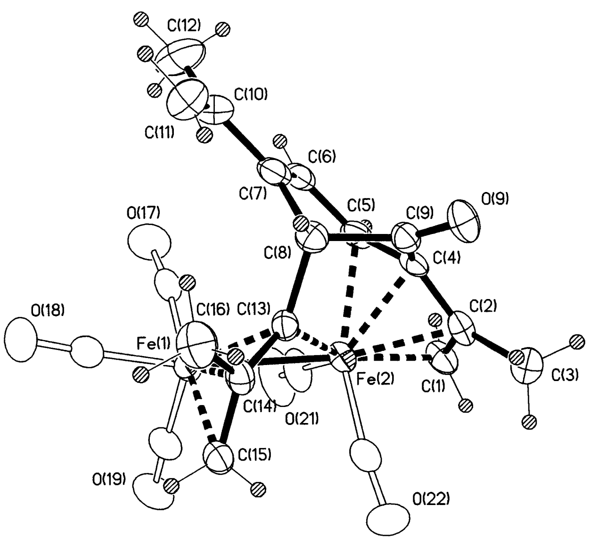


Fig. 3 An ORTEP plot of $Fe_2(CO)_5[C_{15}H_{18}(CO)]$ **2**, with 30% thermal ellipsoids.

chain, one CO is bonded to the tail of one unit [C(8)] and to the head of another [C(4)] thus forming a six-membered carbon ring. The ring is not planar. Inside the organic chain three types of C–C bond distance may be found: (i) 1.33(1) Å av., (ii) a range from 1.40(1) Å to 1.47(1) Å, (iii) 1.52(1) Å av. The first value corresponds to a double bond character and this value is associated with the C(6)–C(7) and C(10)–C(11) bonds. The second range of values (ii) are bonds which display, to a greater or lesser extent, a delocalized double bond character. These refer to the double bonds involved in a π-interaction with Fe(1) (C(13)–C(14) and C(14)–C(15)) or with Fe(2) (C(1)–C(2), C(2)–C(4), C(4)–C(5)) or to a delocalization in C(5)–C(6) and C(7)–C(10) due to two conjugated double bonds. The remaining bonds (iii) (1.52(1) Å av.) have a more pronounced single bond character.

The Fe–C bonds linking the organic moiety to the bimetallic fragment range between the values of 2.022(7) and 2.218(8) Å, with the shorter values corresponding to the bridge C(13), while the other values correspond to π-coordination to the iron atoms.

The organic moiety acts, according to the 18-electron rule, as an eight-electron donor.

No relevant intermolecular interaction exists.

Oligomerisation pathways of IPA

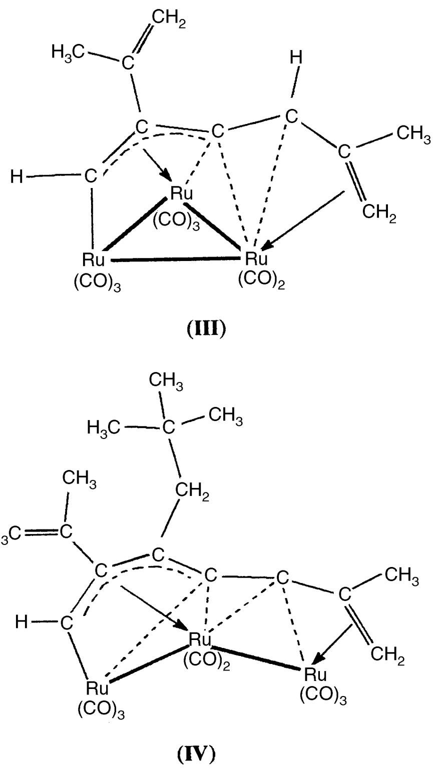
(a) Trinuclear complexes. Oligomerisation reactions of IPA in the presence of $Ru_3(CO)_{12}$ have been reported: this allows a comparison with the results of this work. In the presence of $Ru_3(CO)_{12}$ formation of a type **II** ene-yne complex occurs as the first step.[14] This is followed by head-to-tail dimerization and shift of an alkynic hydrogen in the carbon atom chain to form the closed cluster **III** (Scheme 3, below).[15] Addition of IPA to the acetylide complex (μ-H)$Ru_3(CO)_9[C{\equiv}CC(Me)_3]$ (a type **II** structure) results in the formation of a ramified ligand containing the acetylide in the middle of a seven-carbon atom chain; two IPA molecules are linked (one head-to-tail, the other tail-to-tail) to the acetylide α-carbon; again, hydrogen shift in the carbon chain is observed. Opening of the cluster and hydride shift to the organic moiety also occur, to form cluster **IV**.[16] In **IV**, however, two M–M bonds are still present, contrasting with complexes **1**. No CO insertion in the organic moiety was observed in the reactions involving ruthenium. The structures of clusters **III** and **IV** are shown in Scheme 3.

Table 4 Bond lengths [Å] and angles [°] for complex **2**

	Molecule A	Molecule B
Fe(1)–Fe(2)	2.711(2)	2.701(2)
Fe(1)–C(13)	2.033(7)	2.032(6)
Fe(1)–C(14)	2.100(7)	2.097(7)
Fe(1)–C(15)	2.126(8)	2.118(9)
Fe(2)–C(13)	2.039(7)	2.022(6)
Fe(2)–C(4)	2.055(7)	2.044(7)
Fe(2)–C(2)	2.097(7)	2.100(8)
Fe(2)–C(1)	2.151(8)	2.160(9)
Fe(2)–C(5)	2.190(7)	2.218(8)
C(1)–C(2)	1.426(10)	1.422(11)
C(2)–C(4)	1.431(10)	1.413(10)
C(2)–C(3)	1.503(10)	1.507(10)
C(4)–C(5)	1.414(9)	1.399(10)
C(4)–C(9)	1.507(9)	1.500(10)
C(5)–C(6)	1.469(10)	1.448(11)
C(6)–C(7)	1.365(10)	1.346(10)
C(7)–C(10)	1.464(11)	1.471(11)
C(7)–C(8)	1.512(10)	1.518(10)
C(8)–C(9)	1.526(10)	1.511(10)
C(8)–C(13)	1.559(9)	1.553(9)
C(9)–O(9)	1.201(8)	1.201(8)
C(10)–C(11)	1.302(13)	1.321(14)
C(10)–C(12)	1.508(12)	1.507(12)
C(13)–C(14)	1.400(9)	1.419(9)
C(14)–C(15)	1.415(10)	1.416(11)
C(14)–C(16)	1.519(9)	1.511(10)
C(2)–C(1)–Fe(2)	68.3(4)	68.2(4)
C(1)–C(2)–C(4)	115.1(7)	114.7(7)
C(1)–C(2)–C(3)	121.8(7)	121.5(8)
C(3)–C(2)–C(4)	123.0(7)	123.5(7)
C(2)–C(4)–C(5)	120.2(7)	122.1(7)
C(2)–C(4)–C(9)	121.8(6)	121.9(7)
C(5)–C(4)–C(9)	115.8(6)	114.4(7)
C(4)–C(5)–C(6)	117.9(7)	118.7(7)
C(5)–C(6)–C(7)	121.3(7)	121.7(7)
C(6)–C(7)–C(8)	113.6(7)	113.5(7)
C(6)–C(7)–C(10)	122.8(8)	124.8(8)
C(8)–C(7)–C(10)	123.6(7)	121.7(8)
C(7)–C(8)–C(9)	108.1(6)	107.1(6)
C(7)–C(8)–C(13)	113.5(6)	111.9(6)
C(9)–C(8)–C(13)	102.9(5)	104.1(6)
C(4)–C(9)–C(8)	107.5(6)	107.8(6)
O(9)–C(9)–C(4)	125.5(6)	123.8(7)
O(9)–C(9)–C(8)	127.0(7)	128.4(7)
C(7)–C(10)–C(11)	123.0(9)	123.4(9)
C(7)–C(10)–C(12)	117.7(9)	116.9(9)
C(11)–C(10)–C(12)	119.3(9)	119.8(9)
C(8)–C(13)–C(14)	118.5(6)	117.7(6)
C(8)–C(13)–Fe(1)	132.4(5)	131.9(5)
C(8)–C(13)–Fe(2)	111.5(4)	112.1(4)
Fe(1)–C(13)–Fe(2)	83.5(3)	83.6(2)
C(13)–C(14)–C(15)	118.3(7)	115.9(7)
C(13)–C(14)–C(16)	123.2(7)	123.3(7)
C(15)–C(14)–C(16)	117.6(7)	120.5(7)

In this work we provide evidence that oligomerization and co-oligomerization of IPA also occurs in the presence of $Fe_3(CO)_{12}$ but that different products are obtained. The "incipient" opening of cluster **IV** (2 M–M bonds) should be compared with the open structures of **1a** and **1b** (1 M–M bond only). This could indicate that: (i) opening of clusters of type **II** (not isolated for iron) can be induced by entering IPA molecules and (ii) that this process can continue, for iron, until separate metal fragments are obtained.

(b) Binuclear complexes. In accordance with literature data[13] and our experimental results, complex **2** and, in far lesser extent, complex **3** are formed from **1a** or **1b**. Release of iron, transfer and shift of C(1)–O(1) to the organic chain, favoured (or competing) with the entering of a third IPA molecule could easily explain the formation of **2** and, in lesser extent, that of **3**. A remote possibility is that the binuclear complexes are formed first and that they undergo addition of $Fe(CO)_x$ (x = 4,5) fragments to form complexes **1**.



(III)

(IV)

Scheme 3

Cyclotrimerization of alkynes (and/or CO) on iron complexes is not unknown; *flyover* derivatives and *tropone precursors* (see below) are obtained. The mass spectrum of complex **2** showed a parent ion and a fragmentation corresponding to $Fe_2(CO)_5[L_3(CO)]$; this led us to think that the structure of **2** could be compared to the not very common *troponic* complexes **V**[17] shown in Scheme 4. However, the X-ray analysis showed that **2** belongs to a structural family containing a new organic moiety.

As previously pointed out, we could not obtain crystals of **3** suitable for an X-ray analysis. On the basis of the analytic, mass spectrometric and spectroscopic data, this complex could belong to the family of the $Fe_2(CO)_6[L(X)L]$ flyover derivatives (**VI**) (X = L or CO, Scheme 2). Several iron, cobalt and ruthenium complexes with X = CO have been reported and characterized.[18,19] In contrast, only a few complexes where X = alkyne are known.[20] The formation of complexes **VI** requires trimerization of the alkynes and shift of the terminal hydrogen of the "central" alkyne molecule. In our opinion, complex **3** belongs to this structural type of derivatives. We cannot exclude, however, that **3** is the result of another cyclotrimerization mode found, till now, for only one compound (**VII**, a potential precursor of the troponic **VI**, also shown in Scheme 4).[21]

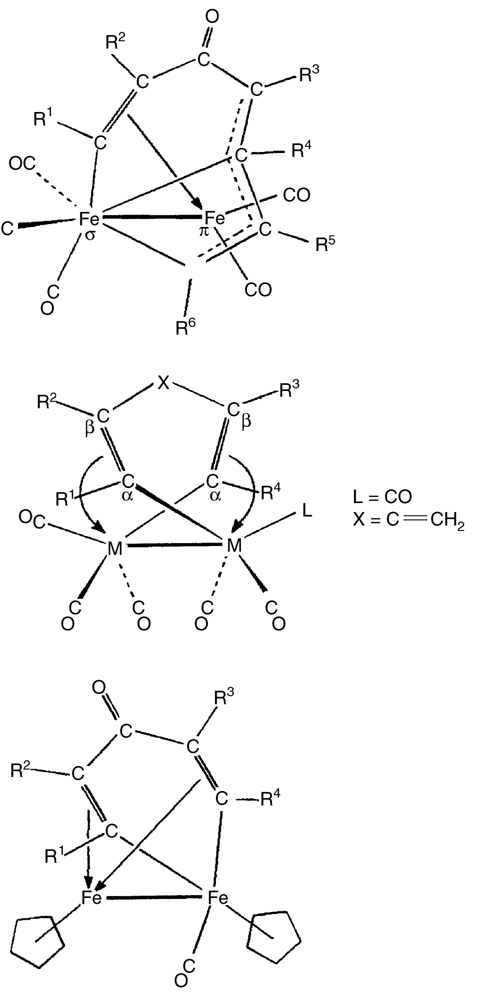
A comparison of the organic moieties of complexes **2**, **V** and **VI** could be helpful for understanding the cyclo-oligomerization pattern of alkynes. These are shown in Scheme 5 (the zigzag lines separate the acetylenic moieties).

In the tropone complexes **V**, two alkyne molecules are linked tail-to-tail and the third one head-to-tail. This also occurs in **2**. However, the position and linking of the CO is different in the two types of structures. In particular, in the troponic complexes a "linear" carbon chain (with the possibility of forming several isomers) is present, whereas in **2** the CO is part of a carbon atom cycle sitting in the middle of the chain. To our knowledge, this oligomerisation pattern for alkynes (and ene-ynes) has not been previously evidenced.

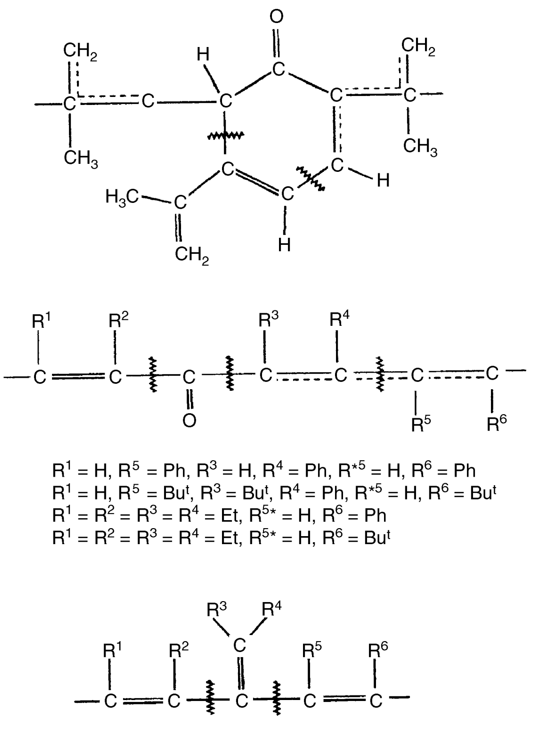
(V)

(VI)

(VII)



Scheme 4



(2)

(V)

$R^1 = H, R^5 = Ph, R^3 = H, R^4 = Ph, R^{*5} = H, R^6 = Ph$
$R^1 = H, R^5 = Bu^t, R^3 = Bu^t, R^4 = Ph, R^{*5} = H, R^6 = Bu^t$
$R^1 = R^2 = R^3 = R^4 = Et, R^{5*} = H, R^6 = Ph$
$R^1 = R^2 = R^3 = R^4 = Et, R^{5*} = H, R^6 = Bu^t$

(VI)

R^3 or R^4 = H

Scheme 5

Finally, in the flyover complexes **VI** (where X = alkyne) the central alkyne molecule behaves in a comparable way to the acetylide in cluster **IV** and no CO's are inserted into the organic chain. This behaviour is a further example of the great versatility of alkyne-clusters interactions.

Concluding remarks

Alkyne-cluster chemistry is a quite old research field.[22] Even old trees, however, can produce flowers and fruits. In this work we report on new complexes obtained upon oligomerisation of an ene-yne molecule in the presence of $Fe_3(CO)_{12}$. New open-cluster structures have been obtained and new co-oligomerisation patterns have been evidenced. We also produce evidence for the formation of metal-carbonyl fragments during the reactions of trinuclear carbonyls with alkynes; and for the recondensation of fragments to give retrosynthesis to the parent carbonyl.

We have also found an unprecedented example of isomerism in the organic moiety linking open cluster complexes and we have indirect evidence for the role of these complexes as precursors of bimetallic compounds. The bonding situation of C(1)–O(1) in complexes **1a** or **1b** could also be considered a model for the transfer of a terminal CO from a metal carbonyl fragment to an organic moiety.[23] Complexes **1** could represent "molecular models" for the interaction between metals and polymers (IPA and isoprene are closely related) or of corrosion inhibitors.[8] Last but not least, the behaviour of **1a** in solution led us to think that it can act as an efficient chemical sensor for chlorinated solvents.

Acknowledgements

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