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Reactions of $[Fe_3(CO)_{12}]$ with asymmetrically substituted alkynes [☆] I. Chemical relationships between the $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2RR')]$ and the carboxylato complexes $[Fe_2(CO)_6\{RC_2R'(COO)\}]$. The splitting of a water molecule into its components favoured by TLC materials

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Abstract

The reactions of $[Fe_3(CO)_{12}]$ with RC_2R' asymmetric alkynes lead to a variety of tri- an di-nuclear derivatives, each in two or three isomeric forms. Complexes $[Fe_3(CO)_9(RC_2R')]$ (**1**) are among the first formed, with two isomers for each structure expected. The carboxylato complexes $[Fe_2(CO)_6\{RC_2R'(COO)\}]$ (**2**) are formed upon reaction of complexes **1** with moisture during the purification on silica TLC plates. In particular, the reaction of (hex-1-en-3-yne) leads to the diethylcarboxylato complex $[Fe_2(CO)_6\{EtC_2Et(COO)\}]$. This process is probably promoted by the silica in the presence of moisture from the air or from the solvents used in the elution. The relationships between the isomers of complexes **1** and **2** are discussed. The formation of the carboxylato complexes presumably involves nucleophilic attack at a metal-coordinated carbonyl.

Keywords: Iron; Carbonyls; Cluster; Reactions with unsymmetric acetylenes; Effects of TLC

1. Introduction

The reactions of $[Fe_3(CO)_{12}]$ with alkynes have long been known and a variety of alkyne-substituted clusters and of di- and mono-nuclear derivatives have been reported and structurally characterized [1,2]. The best known reactions are those of C_2Ph_2 [1], which lead to the clusters $[Fe_3(CO)_9(C_2Ph_2)]$ (complex **1a**) [3], $[Fe_3(CO)_8(C_2Ph_2)_2]$ "violet isomer" (complex **3a**) and $[Fe_3(CO)_6(\mu\text{-}CO)_2(C_2Ph_2)_2]$ "green isomer" (complex **4a**) [4], binuclear derivatives [5] including the ferrole $[Fe_2(CO)_6(C_2Ph_2)_2]$ (complex **5a**) [6], $[Fe_2(CO)_6\{(C_2Ph_2)_2CO\}]$ (complex **6a**) [7] and the tropone precursor $[Fe_2(CO)_5\{(C_2Ph_2)_3CO\}]$ (complex **7a**) [8]. The reaction of $[Fe_3(CO)_{12}]$ with diethylacetylene (C_2Et_2) led to similar products (**1b–7b**) and, in addition, to the sawhorse hydroxyferrole $[Fe_2(CO)_6\{C_2(OH)(Et)\}_2]$ (complex **8b**) the maleoyl $[Fe(CO)_4\{(CO)_2\text{-}C_2Et_2\}]$ (complex **9b**) [9] and to the carboxylate $[Fe_2(CO)_6\{C_2Et_2(COO)\}]$ (complex **2b**) [10].

In spite of these studies, the formation of some of the above complexes are still poorly understood. Another aspect which has been relatively little explored is the formation of isomers, their relationships, and the effect of substituents on the alkyne on the products and yields. New reactions trends have also been found recently. For example, treatment of complex **5b** with dppm and Me_3NO or with RC_2R' and Me_3NO leads to the dppm-substituted complex **6b** [11] or to complexes **7** [12], respectively.

As part of a study of reactions leading to "models of intermediates" [12,13] or to organic products [14], starting from alkynes and metal carbonyls, we decided to investigate the reactions of $[Fe_3(CO)_{12}]$ with asymmetric alkynes RC_2R' ($R = Et$; $R' = Et$, Me, Ph or $CH = CH_2$), and also with PhC_2Me and C_2Ph_2 already reported. We expected that asymmetric alkynes could provide a deeper insight in the reaction mechanisms.

[☆] RC_2R': $R = Ph$, $R' = Me$, Et; $R = Et$, $R' = Me$, $CH = CH_2$.

This work is dedicated to the memory of Marisa Tiripicchio Camellini, a distinguished scientist and a dear friend.

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Unexpectedly, from $EtC_2CH=CH_2$ (hex-1-en-3-yne) we obtained the diethyl derivatives **1b** and **2b** together with complex $[Fe_3(CO)_8L_2]$, (**4c**; L = hex-1-en-3-yne) in two isomeric forms. We showed that complexes **2** are formed from **1** on TLC plates in the presence of moisture in a "surface-mediated organometallic reaction" [15]. Complexes **2** can be considered as models of intermediates for the formation of substituted acrylates via the industrially important Reppe carbonylation process [16]:

$$RC{\equiv}CR' + CO + H_2O \rightarrow RHC=CR'COOH$$

2. Experimental

2.1. General experimental details. Materials. Purification and analysis of the products

$[Fe_3(CO)_{12}]$ (Strem Chemicals) and the alkynes (Aldrich, Janssen, K & K) were commercial products and were used as received, after purity checks. Toluene was dried over sodium and the reactions were performed under dry dinitrogen in conventional glassware consisting of three-necked flasks equipped with a reflux condenser, mercury check valve and magnetic stirrer. The reaction mixtures were taken to small volume under reduced pressure and purified under air on preparative TLC plates (Kieselgel PF, Merck; eluents mixtures of light petroleum (b.p. 40–70°C) and diethyl ether) [17]. When possible, the products were crystallized from suitable solvents prior to the analyses.

Complexes were analysed using a Perkin-Elmer atomic absorption spectrometer and an F & M C,H,N analyser. Some analyses were performed by F. Pascher Laboratories (Bonn, Germany). The IR spectra were measured on a Perkin-Elmer 580 spectrometer and ^1H and ^{13}C NMR spectra on a JEOL GX 270 or EX 400 spectrometer [18]. Electron impact (EI) mass spectra were obtained on a Finnigan-Mat TSQ-700 quadrupolar mass spectrometer [19].

2.2. Reactions of the alkynes with $[Fe_3(CO)_{12}]$

2.2.1. Hex-1-en-3-yne

$[Fe_3(CO)_{12}]$ (2.0 g, ca. 4.0 mmol) was suspended in toluene (150 ml) under dinitrogen, an excess of the alkyne was added and the mixture was heated under reflux for 5–10 min. After TLC, the following products were collected: brown **1b** (10%), green **4c** (5%), green **4c**′ (5%) and pink **2b** (5%).

Complex 1b [20]. $C_{15}H_{10}Fe_3O_9$, M.W. 502. Elemental analysis (calculated values in parentheses): C 36.04 (36.0), H 2.07 (1.6), Fe 32.7 (33.6)%. EI-MS: $P^+ = m/z$ 502, loss of nine CO groups. IR: 2079 s, 2048 vs(sh), 2037 vs, 2020 vs(b) cm^{-1}. ^1H NMR: 3.64–3.62 s(b) (CH_2, C_α), 1.73 s(b) (CH_3, C_α), 1.65 s(b) (CH_2, C_β), 0.48 s(b) (CH_3, C_β). ^{13}C NMR: 15.2 s, 16.4 s, 22.2 s, 39.8 s; 207.6 s, 211.7 s.

Complex 4c. $C_{20}H_{20}Fe_3O_8$, M.W. 552. C 43.8 (43.53), H 3.0 (2.92), Fe 31.1 (30.36)%. EI-MS: $P^+ = m/z$ 552, loss of eight CO groups. IR: 2069 s, 2032-2024 vs(b), 2000 s(b), 1982 s(b), 1878 m-s, 1865 m-s cm^{-1}. ^1H NMR: 7.07 t(b) (1H, =CH), 5.42 t(b) (1H, =CH), 4.86 d (2H, $=CH_2$), 4.44 d (2H, $=CH_2$), 3.28 d, 1.61 s (CH_3, Et), 1.30 s(b) (CH_2, Et), 0.50 s (CH_2, CH_3, Et).

Complex 4c′. C 43.3, H 2.84%. EI-MS: as for **4c**. IR: 2075 s, 2036 vs(sh), 2032 vs, 2018 s(b), 1986 s(b), 1880 m-s, 1868 m-s cm^{-1}. ^1H NMR: 5.34 t (2H, =CH), 4.82 d (4H, $=CH_2$), 3.23 s(b) (4H, CH_2, Et), 1.62 s (6H, CH_3, Et).

Complex 2b [20]. $C_{13}Fe_2H_{10}O_8$. C 38.8 (38.47), H 2.6 (2.48), Fe 27.2 (27.51)%. EI-MS: $P^+ = m/z$ 406. IR: 2090 m-s, 2059 vs, 2024 vs(sh), 2018 vs, 1994 s(b), 1739 m(b) cm^{-1}.

2.2.2. Reactions with pent-2-yne

Treatment of a toluene suspension of 5.0 g (ca. 10 mmol) of $[Fe_3(CO)_{12}]$ with 2.0 ml (ca. 25 mmol) of the alkyne under N_2 for 3 min under reflux yields a dark-brown suspension. Filtration allows the recovery of a considerable amount of rubber-like brown solid (not investigated). TLC of the filtrate showed the presence of some unreacted $[Fe_3(CO)_{12}]$ and of yellow **5d** (20%), brown **1d** (3%), pink **2d** (10%), green **4d** (3%), orange **6d** (20%), purple **7d**, purple **7d**′ (10%) and some decomposition products.

Complex 5d. $C_{16}H_{16}Fe_2O_6$, M.W. 416. C 46.5 (46.20), H 4.0 (3.88), Fe 27.1 (26.85)%. EI-MS: $P^+ = m/z$ 416, loss of six CO groups. IR: 2068 s, 2048 vs, 1960 vs(b), 1940 w(b) cm^{-1}. ^1H NMR: 2.63 m (CH_2, Et), 1.21 t (CH_3, Et), 2.37 s (Me) (minor isomer); 2.20 s (Me), 2.56 m (CH_2, Et), 1.12 t (CH_3, Et) (major isomer); ratio 0.6 to 1. ^{13}C NMR: 13.5 s, 13.9 s, 14.6 s, 16.2 d (CH_3, Et); 22.4 s, 28.6 s, 35.9 s, 36.0 s (CH_2, Et, CH_3); 127.5 s, 128.5 s, 133.3 s, 170.0 s, 176.4 s, 176.8 s (C_{ring}); 206.5 s, 206.6 s, 206.8 s, (3 CO), 211.4 s, 214.1 s (2 CO), 214.2 s (2 CO).

Complex 1d. $C_{14}H_8Fe_3O_9$, M.W. 488. C 34.6 (34.48), H 1.8 (1.65), Fe 35.0 (34.35)%. EI-MS: $P^+ = m/z$ 488, loss of nine CO groups. IR: 2080 m, 2035 vs(sh), 2030 vs, 2010 s, 1996 m, 1994 m cm^{-1}. ^1H NMR: 3.59 m (CH_3, Et), 1.25 s (Me) (minor isomer); 3.40 s (Me), 1.60 m (CH_2, Et), 0.43 t (CH_3, Et) (major isomer); ratio 0.3 to 1.

*Complex **2d***. $C_{12}H_8Fe_2O_8$, M.W. 392. C 36.4 (36.78), H 2.1 (2.06), Fe 28.2 (28.50)%. EI-MS: $P^+ = m/z$ 392. IR: 2083 m-s, 2050 vs, 2015 s, 2007 s(sh), 1986 m-w, 1754 m-w(b) cm^{-1}. ^1H NMR: 2.77 q (CH_2, Et), 2.68 s (Me), 1.41 dt (CH_3, Et) (major isomer); 2.29 s (Me), 1.41 dt (minor isomer); ratio 0.4 to 1.

*Complex **4d***. $C_{18}H_{16}Fe_3O_8$. C 41.0 (40.96), H 3.7 (3.56), Fe 31.9 (31.74)%. EI-MS: $P^+ = m/z$ 528. IR: 2055 m, 2021 vs, 1990 s, 1975 s, 1874 m, 1860 m cm^{-1}. ^1H NMR: 3.45 q, 3.33 q, (CH_2, Et), 2.99 s (Me), 1.75 t, 1.67 t, 1.18 s (Me) (one isomer); 1.25 q (CH_2, Et), 1.04 s (Me), 0.48 t (CH_3, Et) (other isomer); ratio 1 : 1.

*Complex **6d***. $C_{17}H_{16}Fe_2O_7$. C 46.2 (46.0), H 3.9 (3.63), Fe 25.7 (25.16)%. EI-MS: $P^+ = m/z$ 444, loss of seven CO groups. IR: 2075 s, 2042 vs, 2010 (sh), 2008 vs, 1990 m, 1682 m-s cm^{-1}. ^1H NMR: 3.08 m, 2.99 m (CH_2, Et), 2.87 s (Me), 2.09 m, 1.69 m (CH_2, Et), 1.31 t, 1.12 t (CH_3, Et) (major isomer); 2.83 s (Me), 1.89 m (CH_2, Et), 1.11 dt (CH_3, Et) (minor isomer); ratio 1 : 0.5. ^{13}C NMR: 13.3 s, 13.4 s, 16.6 s, 17.7 s (Et, CH_3); 25.3 s, 25.8 s, 33.4 s, 33.8 s, 41.1 s (CH_2, Et; Me): 95.9 s, 101.7 s, 102.9 s (C_{ring}); 193.2 s, 193.9 s, 196.6 s, 197.6 s, 198.0 s (CO/C_{ring}).

*Complex **7d***. $C_{21}H_{24}Fe_2O_6$. C 52.5 (52.10), 5.3 (5.0), Fe 22.9 (23.07)%. EI-MS: $P^+ = m/z$ 484. IR: 2074 s, 2028 s(sh), 2021 vs, 2004 s, 1968 s, 1675 m-s(b) cm^{-1}. ^1H NMR: 3.62 q (CH_2Et), 3.17 s (Me), 2.47 q (CH_2Et), 2.26 q (CH_2Et), 2.19 s (Me), 1.72 s (Me), 1.57 t (CH_3, Et), 1.35 t (CH_3Et), 0.69 t (CH_3Et). ^{13}C NMR: 12.0 d, 16.0 s, 17.0 s, 18.2 s, 27.1 s, 30.0 s, 33.6 s, 39.2 s (Et, Me); 65.8 s, 88.5 s, 101.6 s, 111.4 s (C_{ring}); 201.1 s, 205.2 s, 205.4 s, 208.9 s, 209.2 s, 210.4 s, 210.7 s, 211.6 s (CO terminal and ketonic, C_{ring}).

*Complex **7d'***. C 52.3, H 4.9%. EI-MS: see **7d**. IR: 2074 s, 2025 vs, 2004 s, 1968 s, 1675 m-s cm^{-1}. ^1H NMR: 3.58 m (CH_2Et), 3.43 m (CH_2Et), 2.16 s (Me), 2.07 s (Me), 1.69 s (Me), 1.56 t (CH_3Et), 1.48 t (CH_3Et), 1.22 q (CH_2Et), 0.68 t (CH_3Et). ^{13}C NMR: 11.3 s, 12.2 s, 15.1 s, 1.9 d, 18.2 s, 18.3 d, 18.4 s, 27.1 d, 27.5 s, 30.0 s, 34.1 s, 39.5 s, 42.4 s (Me, Et); 65.2 s, 79.0 s, 111.8 s (C_{ring}); 201.3 s, 206.6 s, 209.3 s, 210.4 s, 210.6 s, 210.7 s, 210.8 s, 211.7 s (CO, terminal, ketonic, C_{ring}).

2.2.3. Reactions with 1-phenylbut-1-yne

Treatment of 5.0 g (ca. 10 mmol) of $[Fe_3(CO)_{12}]$ with 2.5 ml (ca. 17 mmol) of alkyne in refluxing toluene gives a carmine-brown suspension. After TLC purification [21], the following products were identified: unreacted $[Fe_3(CO)_{12}]$, brown **1e** (2%), light-yellow **5e** (5%), orange **5e'** (10%), green **4e** (2%), carmine **6e** (40%), orange **6e'** (30%) and a yellow complex (complex A) still to be identified (10%).

The reaction was repeated with the same stoichiometric amounts but in refluxing cyclohexane for 4 min. The same products and yields were observed except that the yield of **1e** were increased to 4–5% and small amounts of pink **2e** were observed.

*Complex **1e***. $C_{19}H_{10}Fe_3O_9$. C 41.2(41.50), H 1.9(1.83), Fe 31.0(30.47)%. EI-MS: $P^+ = m/z$ 550, loss of nine CO groups. IR: 2066 m-s, 2029 vs, 2011 m-s, 1997 s(sh), 1993 s, 1985 m-s cm^{-1}. ^1H NMR: 7.80–7.00 mm (Ph), 6.00 d (Ph), 3.37 q (CH_2Et), 1.19 q (CH_2Et) (major isomer); 2.42 q, 0.25 t (Minor isomer); ratio 0.1 to 1.

*Complex **2e***. $C_{17}H_{10}Fe_2O_8$. C 45.1(44.98), H 2.3(2.22), Fe 26.0(25.75)%. EI-MS: $P^+ = m/z$ 454. IR: 2091 m, 2066 vs, 2058 s(sh), 2044 vs, 2011 vs, 1990 s, 1662 m-s cm^{-1}. ^1H NMR: 7.41–7.20 m (Ph), 2.44 q (CH_2Et), 0.89 t (CH_3, Et).

*Complex **5e***. $C_{26}H_{20}Fe_2O_6$. C 57.6(57.81), H 3.8 (3.73), Fe 21.0 (20.68)%. EI-MS: $P^+ = m/z$ 540. IR: 2064 s, 2027 s, 1991 vs(b), 1928 m cm^{-1}. ^1H NMR: 7.15 s(b) (Ph), 2.30 q (CH_2Et), 1.06 t (CH_3Et).

*Complex **4e***. $C_{28}H_{20}Fe_3O_8$. C 51.7(51.58), H 3.2 (3.09), Fe 25.8 (25.69)%. EI-MS: $P^+ = m/z$ 652. IR: 2058 s, 2018 vs, 2011 vs, 1998 s, 1973 m-s(b), 1869 m, 1858 m cm^{-1}. ^1H NMR: 8.17–6.55 m (Ph), 2.89 q (CH_2, Et), 1.23 t/q (CH_2, CH_3, Et), 0.49 t (CH_3, Et).

*Complex **5e'***. $C_{27}H_{20}Fe_2O_7$. EI-MS: see **5e**. IR: 2058 s, 2019 s, 1994 vs(b), 1970 s cm^{-1}. ^1H NMR: 7.27–7.17 m (Ph), 4.83 d (CH_2, Et), 2.92 d (CH_2, Et), 2.21 s (CH_3, Et), 0.73 s (CH_3, Et). ^{13}C NMR: 13.7 s, 23.7–24.0 d, 67.3 s, 69.3 s: 81.3 s, 104.3 s; 125.8–128.1 m (Ph); 136.5 s, 148.2 s, 167.6 s; 210.6 s (CO).

*Complex **6e***. $C_{36}H_{30}Fe_2O_6$. C 57.2(57.08), H 3.6(3.55), Fe 20.0(19.66)%. EI-MS: $P^+ = m/z$ 568, loss of eight fragments with $m/z = 0.28$. IR: 2071 m, 2044 vs, 2013 vs, 1999 m, 1989 m, 1722 m-s, 1674 m cm^{-1}. ^1H NMR: 7.34–7.16 m (Ph), 2.58 qq (CH_2, Et), 1.07 qq (CH_2, Et), 0.86 tt (CH_3, Et). ^{13}C NMR: 13.9 s, 26.2 s,; 99.6 s (C_{ring}); 127.9–128.1 m (Ph); 147.8 s (C_{ring}); 197.0 s, 198.1 s, 206.6 s, 208.2 s, 211.4 s, 211.8 s.

*Complex **6e'***. C 57.4, H 3.7%. EI-MS: see **6e**. IR: 2073 s, 2044 vs, 2009 vs, 1990 m-s, 1728 w, 1680 m-s cm^{-1}. ^1H NMR: 7.37–7.05 m (Ph); 2.97–2.89 m, 2.71–2.66 q, 2.59–2.48 m (CH_2, Et); 1.22 s, 0.83 t (CH_3, Et). ^{13}C NMR: 13.5 s, 13.7 s, 18.8 s, 19.0 s, 22.6 s, 26.7 s, 28.9 s, 31.7 s, 42.5 s; 98.1 s, 106.9 s, 107.9 s (C_{ring}); 127.5–128.9 m (Ph); 130.7 s, 131.0 s, 148.0 s (C_{ring});

196.6 s, 204.7 s, 205.1 s, 205.6 s, 206.4 s, 207.2, 207.7 s, 208.9 s, 209.1 s, 210.4 s, 211.4 s.

2.2.4. Reactions of 1-phenylprop-1-yne

The reaction in hexane has already been reported [22] to give **1f** (yield not reported) and **4f–7f**. The reaction was repeated in cyclohexane. Treatment of 5.0 g (ca. 10 mmol) of $[Fe_3(CO)_{12}]$ with 2.5 ml of liquid alkyne for 4 min under reflux yielded $[Fe_3(CO)_9(PhC_2Me)]$ (**1f**, 2–5%) and complexes **4f–7f** in low yields [21].

Complex 1f. EI-MS: $P^+ = m/z$ 536, loss of nine CO groups. ^1H NMR: 7.70–6.99 mm, 5.93 d (Ph); 3.01 s (Me), 1.05 s (Me); isomer ratio 10 : 9.

2.3. Behaviour of complexes 1 on the TLC plates

When the reaction solutions of $[Fe_3(CO)_{12}]$ and hex-1-en-3-yne were purified on Kieselgel PF (Merck) preparative TLC plates previously dried for 2 h at 120°C, using light petroleum (b.p. 40–70°C)–diethyl ether (90 : 10, v/v) [17], the brown band corresponding to "**1b**" moved close to the front, followed by complexes **4c** and **4c′**. Small amounts of pink **2b** were left at the bottom of the plates.

Pure crystals of **1b** obtained from hex-1-en-3-yne were dissolved in $CHCl_3$ and the solutions were deposited on TLC plates and left in air for some time before elution. After elution, increased amounts of **2b** were collected, the maximum yield approaching 20% of **1b** after 15 min, exposure, after which a decrease was observed (10% after 30 min.) and decomposition products were formed. Very similar behaviour was observed when pure crystals of **1b** obtained from hex-3-yne [10] were treated as above.

The reaction of $[Fe_3(CO)_{12}]$ with hex-1-en-3-yne was repeated in dry toluene, together with D_2O. After elution, non-deuterated complexes **1b** and **2b** were collected (^1H NMR identification). The IR spectrum of the reaction mixture showed a complex pattern of ν(CO) bands including signals in the 1880–1860 cm^{-1} region. However, no signals were observed in the 1800–1600 cm^{-1} region (typical of **2b**). This shows that **2b** is not formed from the solvent moisture.

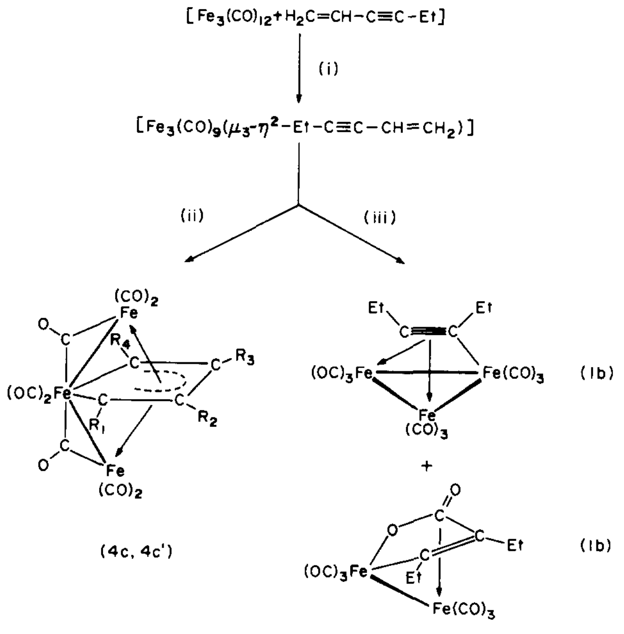
The $CDCl_3$ solutions of **1d** and **1e** from the NMR runs were left for 2 d at room temperature under N_2 and then purified by TLC. Neither **2d** nor **2e** was observed. In contrast, when left for some time on the TLC plates before elution, the complexes gave **2d** or **2e** (maximum yields ca. 15% and 5%, respectively, after 20 min).

Treatment of $[Fe_3(CO)_9(PhC_2Me)]$ (**1f**) for different times on the TLC plates did not give any complex **2f** but isomers of **5f** were observed instead. Treatment of pure crystals of $[Fe_3(CO)_9(C_2Ph_2)]$ on TLC plates for 20 min before elution led to the parent complex (45%), 45% of $[Fe_2(CO)_6(C_2Ph_2)_2]$, **5a**, and some decomposition. No **2a** could be detected.

3. Results and discussion

The reactions of $[Fe_3(CO)_{12}]$ with EtC_2Me, EtC_2Ph and MeC_2Ph led, as expected, to complexes **1** and **4–7**. In general, these were obtained as mixtures of isomers which (with some exceptions) could not be separated on the TLC plates. However, the isomers of complexes **4–7** and their ratios could be identified by ^1H NMR spectroscopy. The analytical and spectroscopic data for these complexes are consistent with the proposed structures. Because these have been reported already [1–8], we shall not discuss these derivatives in detail. A full account of their isomerism and of their role in the formation of organic products will be given in a subsequent paper.

Here we consider in particular complexes **1** and **2**. The reactions of EtC_2Ph and MeC_2Ph in toluene are very fast and give mostly binuclear complexes. Only in cyclohexane could small yields of complexes **1** and **4** be obtained. Unexpectedly, the reaction of $[Fe_3(CO)_{12}]$ with hex-1-en-3-yne led to the diethyl derivatives **1b**, **2b**, with apparent hydrogenation of the alkyne. The isomeric complexes **4c** and **4c′** (containing the original alkyne) were also formed as minor products, presumably in a competitive reaction as shown in Scheme 1. The identity of the products obtained from hex-1-en-3-yne with those formed by C_2Et_2 was confirmed by



Scheme 1. Reaction conditions: (i) heat, dry toluene; (ii) excess of hex-l-en-3-yne; (iii) on silica TLC plates in the presence of moisture. **4c**: $R_1 = R_3 = Et$, $R_2 = R_4 = CH{=}CH_2$. **4c′**: $R_1 = R_4 = Et$, $R_2 = R_3 = CH{=}CH_2$.

measuring the cell parameters of **1b** obtained from hex-2-en-3-yne and comparing them with those found for **1b** obtained from hex-3-yne [23]. An accurate X-ray analysis of a crystal of **2b** obtained from hex-1-en-3-yne was performed [24] and a sketch is given in Scheme 2. This excluded the presence of $-CH=CH_2$ groups in the complex and confirmed its identity with the complex in Ref. [10].

3.1. Some comments on the formation and role of complexes 1

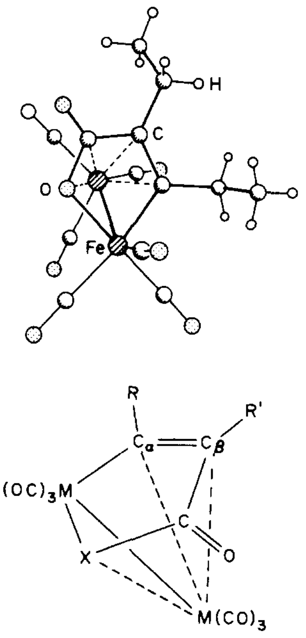
Complexes **1** belong to the well established family of trigonal bipyramidal $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-alkyne})]$ derivatives [25] and are precursors of all other complexes mentioned in this paper. Their isomerism is therefore of considerable interest. There are at present only three examples of asymmetrically substituted complexes **1**, **1d**, **1e** and **1f** [22], all obtained as two isomers. The isomers could not be separated by TLC, but ^1H NMR spectroscopy allowed their identification and the evaluation of their relative proportions (Table 1). The resonances of the substituents on the alkyne $C(\alpha)$ or $C(\beta)$ were assigned on the basis of literature data [22]. The major isomers of complexes **1d** and **1e** are those with the Et group on $C(\beta)$ and $C(\alpha)$, respectively. For **1d** this is consistent with previous reports indicating that $C(\alpha)$ is more positive and therefore the thermodynamically stable isomer is the one with the stronger electron donor (Me) on this carbon atom. For **1e** the major isomer is that with Et rather than Ph on $C(\alpha)$.

Complexes **1** react further, presumably by reorientation of the alkyne in parallel fashion along an edge, as shown indirectly by a two-electron electrochemical reduction [22]. In the presence of excess of alkyne, complexes **3**–**7** are formed, whereas in the presence of water, complexes **2** were obtained (Scheme 1).

Table 1
^1H NMR chemical shifts of complexes **1**

Complex		^1H NMR		Ref.
		$C(\alpha)$	$C(\beta)$	
$[Fe_3(CO)_9C_2Ph_2]$	**1a**	7.35 m, 5.88 m		[22]
$[Fe_3(CO)_9C_2Et_2]$	**1b**	3.60q, 1.72t	1.63q, 0.48t	[22]
		3.60q, 1.72t	1.63q, 0.49t	[38]
$[Fe_3(CO)_9C_2Me_2]$		3.36s	1.18s	[22]
$[Fe_3(CO)_9EtC_2Me]$	**1d**	3.59m	1.25s	t.w. [b]
$[Fe_3(CO)_9MeC_2Et]$ [a]	**1d**	3.40s	1.60m, 0.43t	t.w.
$[Fe_3(CO)_9EtC_2Ph]$ [a]	**1e**	3.37q, 1.19t	7.40m, 6.00d	t.w.
$[Fe_3(CO)_9PhC_2Et]$	**1e**	7.40m, 6.00d	2.42q, 0.25t	t.w.
$[Fe_3(CO)_9PhC_2Me]$	**1f**	7.65m, 5.90m	1.10s	[22]
		7.60m, 5.93d	1.05s	t.w.
$[Fe_3(CO)_9MeC_2Ph]$ [a]	**1f**	3.05s	7.65m, 5.90m	[22]
		3.01s	7.60m, 5.93d	t.w.

[a] Major isomer. Isomer ratios: **1d** (1 : 0.3), **1e** (1 : 0.1).
[b] This work.



M = Fe, R = R′ = Et	this work
M = Fe, R = R′ = Ph	26
M = Fe, R = H, R′ = ^{t}Bu	26
M = Fe, R = Me, R′ = Et	this work
M = Fe, R = Ph, R′ = Et	this work
M = Fe; R = H, R′ = Ph, X = S	37a
M = Ru; R = R′ = Ph, X = NPh	37b
M = Fe; R = Me, R′ = NEt_2, X = NEt	39
M = Fe; R = Me, R′ = NEt_2, X = NPh	39
M = Fe; R = Me, R′ = NEt_2, X = SPh	39 [a]

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[a] C=S instead of C=O.

Scheme 2. Sketch of the structure of complex **2b** and schematic representation of the five-membered metallacyclic dinuclear structures of complexes **2**.

3.2. Role of water in the formation of complexes 2

Complex **2b** was originally obtained in low yield by reaction of $[Fe_3(CO)_{12}]$ and C_2Et_2 in heptane [10]. Later Milone et al. [26] proposed a new synthetic approach, involving the reaction of $[Fe_2(CO)_9]$ with C_2Et_2 in wet acetone or THF under N_2, O_2 or air, giving yields of up to 20%. In this way they also synthesized complex **2a** and the $HC_2{}^tBu$ derivative **2g** in 5–10% yields. The latter was obtained as a single isomer, with ^tBu on $C(\beta)$ as a consequence of a regiospecific process (see Table 2 and Scheme 2). Finally, by using ^{13}C- and ^{18}O-labelled (metal)carbonyl and water, they showed by NMR and mass spectrometry that the carbon of the COO group arises from a coordinated carbonyl, whereas the extra oxygen comes from water. A reaction sequence based on two intermediates of which the first, $[Fe_2(CO)_7(C_2Et_2)]$, had been isolated was proposed [1]. The structure of the second, $[Fe_2(CO)_6(\mu\text{-}C_2Et_2O)]$, was postulated to be similar to that of $[Fe_2(CO)_6(\mu\text{-}C_2Ph_2O)]$, characterized by X-ray diffraction [27]. The latter was obtained from $[Fe(CO)_4]^{2-}$ and PhC(O)Cl, along with CO_2 and PhC(O)O(Ph)C=C(Ph)OC(O)Ph in a reaction comparable to the formation of acrylates via the water-gas shift reaction. In the scheme, attack of "O" at coordinated CO was proposed. An alternative could be insertion of CO into the M–C bond of the alkyne ligand or attack of alkyne at a coordinated CO. This is discussed below.

The above scheme has been proposed for $[Fe_2(CO)_9]$ in wet solvents. The process occurring on TLC plates is presumably comparable. It would involve attack of OH^- and incorporation or elimination of H^+. Presumably stereospecific attack occurs (see below). In the light of the behaviour of complexes **1** on silica, we propose that the formation of complexes **2** does not occur directly in hydrocarbon solvent but is promoted by the TLC silica in the presence of moisture (from air or from the solvents) in a "surface-mediated organometallic reaction" [15]. We showed that **1b** and **2b** are not formed from hex-1-en-3-yne in toluene in the presence of added D_2O. The attack of water or of OH (from silica) at coordinated carbonyls should be accompanied by insertion/attack at the alkyne. The small yields observed on silica, due to the limited availability of water, implies that attack of OH^- is the rate-determining process. We could obtain neither complex **2a** nor **2g** [28] with the procedure described in this paper.

As pointed out previously, the reaction of hex-1-en-3-yne leads to the formation of the diethyl complex **2b** and to the separation of water. Few examples of such a reaction on surfaces have been reported [29]. A mononuclear butatrienylidene ruthenium cation reacts with atmospheric moisture to form an acetylethynyl derivative. This requires attack of water at the organic ligand and elimination of a proton [30].

Nucleophilic and electrophilic attack of the components of water on coordinated carbonyls are well documented on surfaces [15] and some examples are also known for alkyne-substituted clusters [31]. Several examples under homogeneous conditions in solution have also been reported. One is complex $[Fe_2(CO)_6\{C_2(OH)(Et)\}_2]$ (**8b**), obtained in the reaction of $[Fe_3(CO)_{12}]$ and C_2Et_2 [9]. "Activation" of water also occurs in the reaction of $[Co_2(CO)_8]$ with C_2Et_2 [32] and of $[Ru_3(CO)_{11}(PPh_2C{\equiv}C^iPr)]$ with THF–H_2O to form $[Ru_4(CO)_{10}(C{=}CH^iPr)(\mu_3\text{-}OH)(\mu\text{-}PPh_2)]$ [33].

Nucleophilic attack at coordinated CO is common. For example, the cluster $[FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2Me_2)]$ in which the alkyne is parallel to an Fe–Co edge, undergoes addition of MeI at a CO coordinated to the σ-bound cobalt, followed by protonation. Loss of $Co(CO)_2$ follows and the ferrole-like $[FeCo(CO)_6\{CMe.CMe.CMe.O\}]$ is formed [34]. Attack of PPh_2Cl at $[HFe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}MeC_2Ph]^-$ forms the dinuclear $[Fe_2(CO)_6\{PhCCMeCHOPPh_2\}]$ with a structure comparable to that of complexes **2** [35]. This reaction requires shift of the cluster hydride to the carbon and attack of PPh_2 at the oxygen of a coordinated CO.

The above reactions indicate that trinuclear complexes with "parallel" alkynes are prone to nucleophilic attack at CO followed by protonations and insertions into M–C (alkyne) bonds to give dinuclear products. Attack of alkynes to coordinated CO or insertion of CO into coordinated alkynes is known in solution, as

Table 2
^1H NMR chemical shifts for complexes **2** and related structures

Complex		^1H NMR		Ref.
		R(C, α)	R′(C, β)	
$[Fe_2(CO)_6\{C_2Ph_2]COO\}]$	**2a**	7.33, 7.19m		[26]
$[Fe_2(CO)_6\{(C_2Et_2)COO\}]$	**2b**	2.85q, 1.36t	1.33q, 0.95t	[10]
$[Fe_2(CO)_6\{(HC_2{}^tBu)COO\}]$	**2g**	8.62s [a]	1.46s [b]	[26]
$[Fe_2(CO)_6\{(MeC_2Et)COO\}]$ [c]	**2d**	2.68s	1.41dt	t.w. [f]
$[Fe_2(CO)_6\{(EtC_2Me)COO\}]$	**2d**	1.41dt	2.29s	t.w.
$[Fe_2(CO)_6\{(PhC_2Et)COO\}]$	**2e**	7.41, 7.20m	2.44q, 0.89t	t.w.
$[Fe_2(CO)_6\{MeC_2(NEt_2)(CO)(NEt)\}]$		2.5s [d]	3.25q, 1.25t [e]	[39]
$[Fe_2(CO)_6\{MeC_2(NEt_2)(CO(NPh)\}]$		2.6s [d]	3.4m, 1.2m [e]	[39]
$[Fe_2(CO)_6\{MeC_2(NEt_2)(CS)(NPh)\}]$		2.2s [d]	3.25q, 1.25t [e]	[39]
$[Fe_2(CO)_6(PhCCMeHCOPPh_2)]$		7.5m	1.64s [d]	[35]

[a] R = H.
[b] R′ = ^{t}Bu.
[c] Major isomer (ratio 1 : 0.4).
[d] R = Me.
[e] R′ = NEt_2.
[f] This work.

for complexes **6** and **7** and for some cluster derivatives [36]. However, such a reaction has not been reported on surfaces.

3.3. Some comments on complexes 2

There are only a few examples of the same type as complexes **2**. These belong to the isoelectronic and isostructural family characterized by a five membered metallacyclic ring also containing a heteroelement [37] as shown in Scheme 2.

Our investigation showed that on the TLC plates the yields of complexes **2** decrease in the order $C_2Et_2 > MeC_2Et > PhC_2Et$ and that the derivatives with PhC_2Me (not reported in the literature) and with C_2Ph_2 (**2a**) or $HC_2{}^tBu$ (**2g**) [27] are not formed under the conditions adopted in this work. As mentioned previously, complex **2b** can be considered as an intermediate (or as a "model of an intermediate") [13,14] in the hydrocarboxylation of C_2Et_2 to diethylacrylates. The results reported here indicate that complexes **2** may be formed in wet solvents or on silica, as a consequence of the water-gas shift reaction, the main difference being that CO_2 is not released but is inserted into a metal–alkyne bond:

$$M{-}CO + H_2O \rightarrow M{-}C(=O)O + H_2$$

Unfortunately, only three examples of asymmetrically substituted complexes **2** are known, **2d**, **2e** and **2g**. Again, the isomerism may be detected by ^1H NMR spectroscopy as shown in Table 2. The assignment of the resonances to the substituents on $C(\alpha)$ or $C(\beta)$ is supported by literature data [22,26,39].

Comparison with Table 1 shows that the major isomers of complexes **1d** and **1e** are characterized by the Et groups on the alkyne $C(\beta)$ or $C(\alpha)$, respectively, whereas the major isomers of **2d** and **2e** show the Et substituents on $C(\beta)$ and $C(\alpha)$, respectively. This indicates that the major isomers of both complexes correspond. A tempting hypothesis is that this is a consequence of the stereospecific interaction of $C(\beta)$ of complex **1** with the carbon (positively polarized) of the COO group. Complex **2g** (not obtained under our conditions) shows the ^{t}Bu group on $C(\beta)$ rather than on $C(\alpha)$. The few examples available make a generalization of this observation only tentative. Regioselective carbonylation of alkynes coordinated to cobalt carbonyls has been reported, but in that case was believed to be controlled by the bulk of the alkyne substituents [40].

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