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Preliminary communication

Ligand exchange between metals: synthesis and characterisation of binuclear and trinuclear iron-alkyne complexes. Crystal structures of $[(\eta^5\text{-}C_5H_5)_2Fe_3(CO)_3(\mu_3\text{-}CO)(\mu\text{-}CO)(CF_3C_2CF_3)]$ and $[\{\mu\text{-}CF_3CC(CF_3)S\}\{Fe(CO)_3\}_2]$

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Abstract

Reaction of $[(\eta^5\text{-}C_5H_5)(CO)Fe\{\mu\text{-}C(CF_3){=}C(CF_3)SMe\}_2Fe(CO)(\eta^5\text{-}C_5H_5)]$ with $Fe_3(CO)_{12}$ leads to an exchange of ligands (hexafluorobut-2-yne, cyclopentadienyl or sulphur) between the metal centres and the formation of several new complexes. Two of these, $[(\eta^5\text{-}C_5H_5)_2Fe_3(CO)_3(\mu_3\text{-}CO)(\mu\text{-}CO)(CF_3C_2CF_3)]$ and $[\{\mu\text{-}CF_3CC(CF_3)S\}\{Fe(CO)_3\}_2]$, have been shown by X-ray diffraction to contain $\mu_3\text{-}\eta^2\text{-}\|$ $CF_3C_2CF_3$ units bridging Fe_3 and Fe_2S triangles, respectively.

The chemistry of alkyne-substituted carbonyl cluster complexes is of current interest as a potential model for the chemisorption of unsaturated hydrocarbons on metallic surfaces [1]. Of the various preparative methods available for bimetallic and cluster compounds containing alkynes that involving ligand exchange between different metal atoms has been little used [2]. Recently we showed that this method can be employed to obtain a novel tetracobalt-alkyne complex [3]. We now report new reactions in which Fe_2 and Fe_3 alkyne complexes are formed by ligand exchange between metal atoms.

By treating $Fe_3(CO)_{12}$ with the thio-alkenyl dimer $[Cp(CO)Fe\{\mu\text{-}C(CF_3){=}C(CF_3)\text{-}SMe\}_2Fe(CO)Cp]$ (I) ($Cp = \eta^5\text{-}C_5H_5$) [4] in refluxing toluene we obtained the complexes II–VIII (see Scheme 1).

Complexes II–VIII * have been identified by NMR (^1H, ^{13}C, ^{19}F), infrared and

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* All compounds gave satisfactory elemental analyses.

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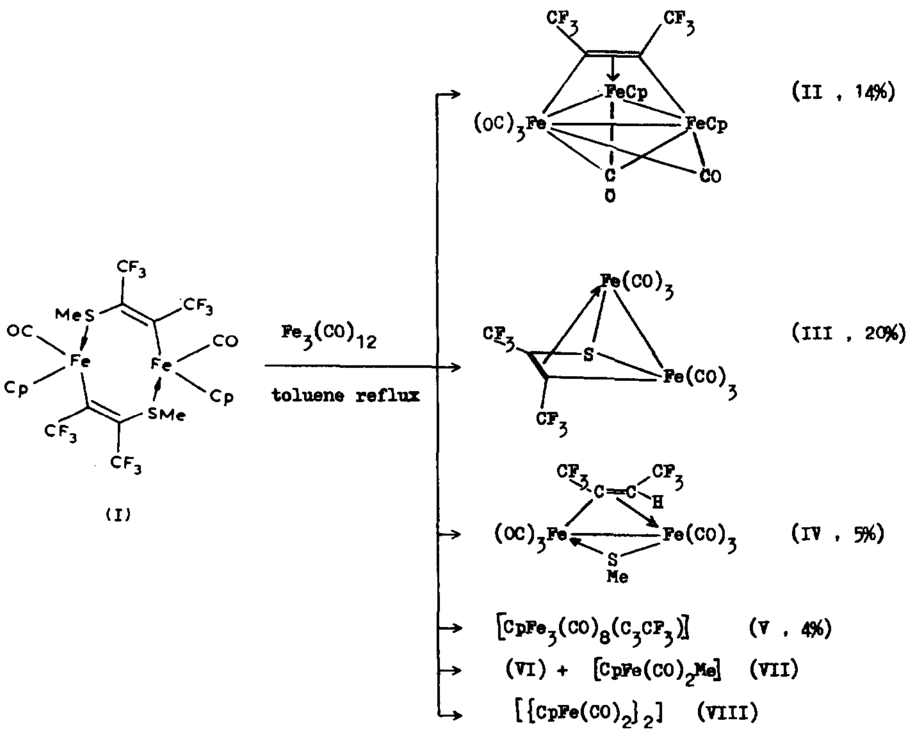

Scheme 1.

mass spectroscopy. The structures of V and VI are not yet fully established but X-ray diffraction studies are in progress. Analysis of the mass spectrum of II indicated that three iron atoms were present in the molecule. X-ray diffraction studies have been carried out on II and III in order to establish their structures unequivocally [*]. II is monoclinic, space group $P2_1/n$, with four $C_{19}H_{10}F_6Fe_3O_5$ molecules in a cell of dimensions a 14.549(2), b 9.079(3), c 15.977(3) Å, β 107.08(1)°. Refinement of 300 parameters using 1480 absorption-corrected intensities [$I \geqslant 2.5\sigma(I)$, θ(Mo-K_α) < 22°] gave $R = 0.035$ and $R_w = 0.043$. III is also monoclinic, space group $P2_1/n$, with four $C_{10}F_6Fe_2O_6S$ molecules in a cell of dimensions a 9.194(2), b 13.261(1), c 12.937(2) Å, β 105.35(2)°. Refinement of 227 parameters using 2862 absorption-corrected intensities [$I \geqslant 3\sigma(I)$, θ(Mo-K_α) < 30°] gave $R = 0.031$ and $R_w = 0.033$. An Enraf–Nonius CAD4F diffractometer with a graphite monochromator and Mo X-rays were used for both analyses and calculations were carried out with the GX system [5] on a GOULD 3227 computer.

In II (Fig. 1) the alkyne is σ-bonded to Fe(1) and Fe(3) and π-bonded to Fe(2) so that the C(7)–C(8) and Fe(1)–Fe(3) vectors are nearly parallel. The alkyne is therefore attached to the Fe_3 triangle in μ_3-η^2-$\|$ fashion: this is the most common form of attachment of an alkyne to a M_3 triangle [2]. The resulting *nido*-Fe_3C_2 unit thereby has a slightly distorted square-pyramidal geometry [with Fe(2) at the apex],

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[*] Atomic coordinates for this work can be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW. Any request should include the full literature citation for this communication.

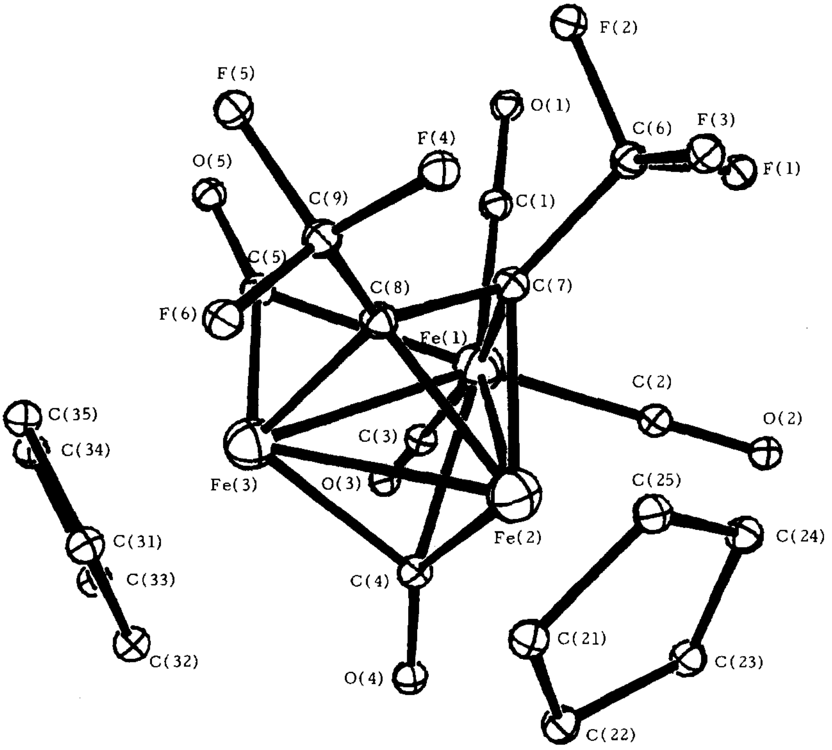

Fig. 1. A perspective view of a molecule of II. Selected bond lengths (Å) are: Fe(1)–Fe(2) 2.540(2), Fe(1)–Fe(3) 2.614(2), Fe(2)–Fe(3) 2.503(2), Fe(1)–C(1) 1.79(1), Fe(1)–C(2) 1.78(1), Fe(1)–C(3) 1.79(1), Fe(1)–C(4) 2.17(1), Fe(1)–C(5) 2.23(1), Fe(1)–C(7) 1.98(1), Fe(2)–C(4) 1.86(1), Fe(2)–C(7) 1.93(1), Fe(2)–C(8) 1.96(1), Fe(2)–C(Cp) 2.04(1)–2.08(1), Fe(3)–C(4) 2.02(1), Fe(3)–C(5) 1.79(1), Fe(3)–C(8) 1.96(1), Fe(3)–C(Cp) 2.08(1)–2.13(1), C(7)–C(8) 1.42(1).

as expected for a cluster with five vertices and seven skeletal electron pairs. Three terminal CO ligands are bonded to Fe(1). The C(4)–O(4) carbonyl is attached in an unsymmetrical μ_3 fashion to the Fe_3 triangle on the side opposite to the alkyne; respective Fe–C(4) bond lengths are 2.17(1), 1.86(1) and 2.02(1) Å. The C(5)–O(5) carbonyl lies on the same side of the Fe_3 plane as the alkyne and semi-bridges the Fe(1)–Fe(3) bond, the respective Fe–C(5) distances being 2.23(1) and 1.79(1) Å. The Fe(2)–C(Cp) distances (mean 2.066 Å) are on average slightly shorter than the Fe(3)–C(Cp) distances (mean 2.103 Å) and the Fe–Fe bond lengths involving Fe(2) [2.540(2) and 2.503(2) Å] are shorter than the Fe(1)–Fe(3) bond length of 2.614(2) Å.

III (Fig. 2) contains two $Fe(CO)_3$ units linked by both a Fe–Fe bond of 2.533(1) Å and a $C(CF_3)C(CF_3)S$ bridging unit. The sulphur atom is equidistant from the two iron atoms, CF_3-substituted C(1) is bonded to Fe(1) [Fe(1)–C(1) 2.027(4) Å] and also forms a single C(1)–S bond of 1.752(4) Å. C(2) is bonded to both iron atoms [Fe–C(2) 2.080(4) and 1.935(3) Å]. The coordination of C(1) and C(2) and the near parallelism of the C(1)–C(2) and Fe(2)–S vectors permit III to be described in terms of the μ_3–η^2-$\|$ attachment of hexafluorobut-2-yne to an Fe_2S triangle. The

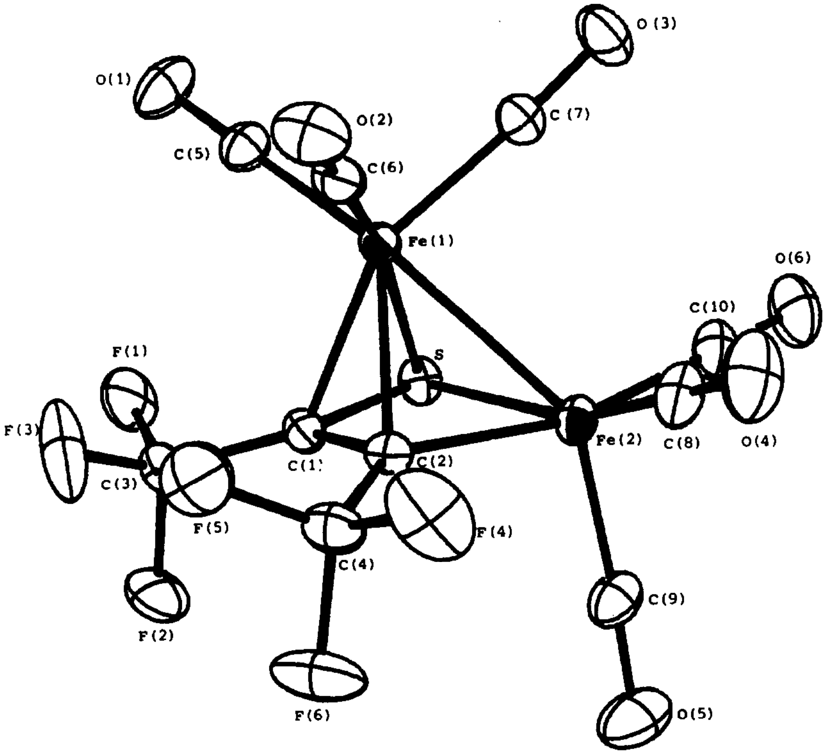

Fig. 2. A perspective view of a molecule of III. Selected bond lengths (Å) are: Fe(1)-Fe(2) 2.533(1), Fe(1)-S 2.260(2), Fe(1)-C(1) 2.027(4), Fe(1)-C(2) 2.080(4), Fe(1)-C(5) 1.803(4), Fe(1)-C(6) 1.790(4), Fe(1)-C(7) 1.799(4), Fe(2)-S(1) 2.273(2), Fe(2)-C(2) 1.935(4), Fe(2)-C(8) 1.789(5), Fe(2)-C(9) 1.772(5), Fe(2)-C(10) 1.834(5), C(1)-C(2) 1.406(5), C(1)-S 1.752(4).

nido-square pyramidal geometry of the $Fe_2SC(1)C(2)$ unit, with Fe(1) apical, is expected for a cluster with seven skeletal pairs and five vertices.

The reactions described here clearly involve ligand migration processes: for example, II contains the tri-iron unit of $Fe_3(CO)_{12}$ together with Cp and $CF_3C_2CF_3$ ligands originally present only in I, while III and IV contain $Fe(CO)_3$ units linked by $CF_3C_2CF_3$ and sulphur or SMe ligands. Our results thus indicate that ligand migration provides a convenient pathway to novel binuclear and cluster complexes of iron.

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