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Preliminary communication

Alkyne coordination and scission by a tetrametallic framework. Crystal structure of $[(\eta^5\text{-}C_5H_5)_2Fe_2Co_2(\mu\text{-}CO)(CO)_4\text{-}\{\mu_3\text{-}C(CF_3)\}_2]$

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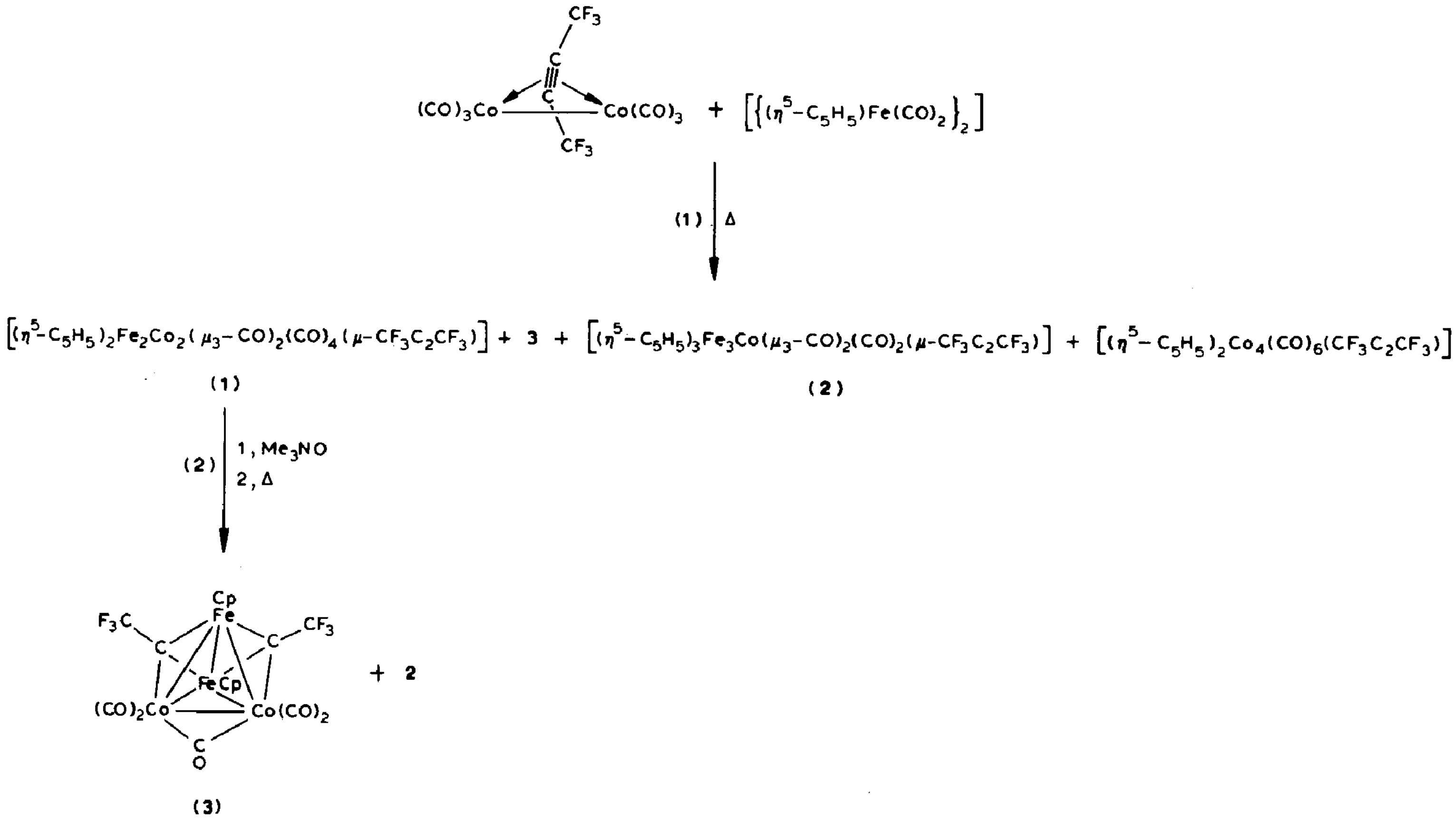
Abstract

Reaction of $[(CO)_3Co(\mu\text{-}CF_3C_2CF_3)Co(CO)_3]$ with $[\{(C_5H_5)Fe(CO)_2\}_2]$ leads to the new heterometallic clusters $[(C_5H_5)_2Fe_2Co_2(\mu_3\text{-}CO)_2(CO)_4(\mu\text{-}CF_3C_2CF_3)]$ (1), $[(C_5H_5)_3Fe_3Co(\mu_3\text{-}CO)_2(CO)_2(\mu\text{-}CF_3C_2CF_3)]$ (2) and product 3. Complex 3 is also obtained upon thermolysis of 1. Spectroscopic studies and single crystal X-ray analysis establish that 3 is the bis-carbyne complex $[(C_5H_5)_2Fe_2Co_2(\mu\text{-}CO)(CO)_4\{\mu_3\text{-}C(CF_3)\}_2]$, and is therefore derived by cleavage of the C≡C bond of the alkyne.

Processes involving formation and scission of carbon–carbon bonds coordinated to transition metal clusters are of current interest as potential models for the chemisorption of unsaturated hydrocarbons on metallic surfaces [1]. Most of the cleavages of alkyne ligands involve trinuclear complexes [2]. Examples involving tetranuclear clusters are scarce, and to our knowledge only one so far has been described [3]. We now report a new example of a carbon–carbon triple bond scission on a tetrametallic cluster.

Treatment of $[(CO)_3Co(\mu\text{-}CF_3C_2CF_3)Co(CO)_3]$ [4] with the dimeric iron complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ in refluxing octane gave the heterometallic clusters **1** (ca. 60% yield) and **2** (ca. 7% yield, relative to Co), together with the known complex $[(C_5H_5)_2Co_4(\mu\text{-}CO)(CO)_4(\mu\text{-}CF_3C_2CF_3)]$ [5] (ca. 8% yield), and a further product **3** (see below) (ca. 14% yield).

The formulations proposed for complexes **1** and **2** are based on microanalysis and spectroscopic data. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of **1**, obtained at −40 °C, was especially informative in the CO ligand region, showing one resonance for the


CF3
(CO)3Co
Co(CO)3
CF3
+ [{(η5-C5H5)Fe(CO)2}2]
(1) Δ
[(η5-C5H5)2Fe2Co2(μ3-CO)2(CO)4(μ-CF3C2CF3)] + 3 + [(η5-C5H5)3Fe3Co(μ3-CO)2(CO)2(μ-CF3C2CF3)] + [(η5-C5H5)2Co4(CO)6(CF3C2CF3)]
(1)
(2)
(2) 1, Me3NO 2, Δ
Cp Fe
F3C
CF3
FeCp
(CO)2Co
Co(CO)2
C O
+ 2
(3)

Scheme 1.

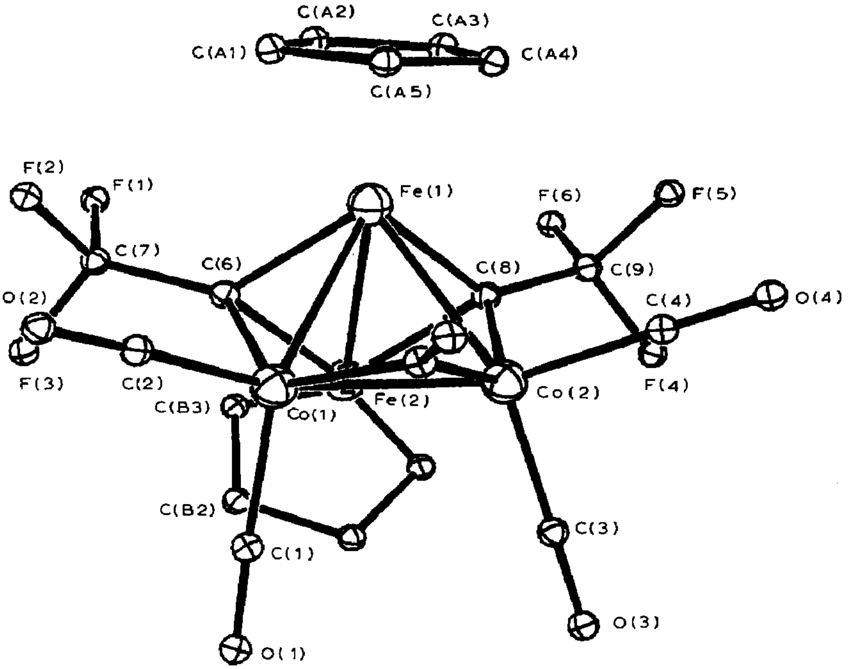


Fig. 1. A perspective view of a molecule of $[(\eta^5\text{-}C_5H_5)_2Fe_2Co_2(\mu\text{-}CO)(CO)_4\{\mu_3\text{-}C(CF_3)\}_2]$ (3). Hydrogen atoms are omitted for clarity. Selected distances (Å) are: Fe(1)–Fe(2) 2.418(1), Co(1)–Co(2) 2.381(1), Fe(1)–Co(1) 2.517(1), Fe(1)–Co(2) 2.501(1), Fe(2)–Co(1) 2.518(1), Fe(2)–Co(2) 2.550(1), Fe–C(CF_3) 1.851(3)–1.880(3), Fe–C(Cp) 2.092(5)–2.121(4), Co–C(CF_3) 1.907(3) and 1.900(3), Co–CO terminal 1.779(4)–1.791(4), Co–CO bridging 1.940(4) and 1.960(4), C(6)...C(8) 2.841(4).

μ_3-CO groups (δ 260.8 ppm), and only one signal for the $Co(CO)_2$ carbonyls (δ 198.1 ppm). The data favour a pseudo-octahedral M_4C_2 structure (seven framework bonding pairs) rather than a pseudo-tetrahedral M_4 configuration, but at present we cannot distinguish unambiguously between these two geometries by spectroscopy alone. X-ray diffraction studies are in progress for a more precise structural characterisation.

Thermolysis of $[(C_5H_5)_2Fe_2Co_2(\mu_3\text{-}CO)_2(CO)_4(\mu\text{-}CF_3C_2CF_3)]$ (1) in refluxing toluene in the presence of Me_3NO provided the dialkylidyne cluster 3 as the major product (ca. 48%) along with the cobalt tri-iron cluster 2 (ca. 2.8%) (see Scheme 1). The formulation of complex 3 was established by a combined spectroscopic and X-ray diffraction study *. 3 is triclinic, space group $P\bar{1}$, with 2 $C_{19}H_{10}Co_2Fe_2F_6O_5$ molecules in a cell, of dimensions a 9.229(1), b 9.246(1), c 14.257(2) Å, α 79.739(9), β 77.794(9), γ 61.857(9)°. Refinement of 308 parameters using 3343 absorption-corrected intensities gave $R = 0.026$ and $R_w = 0.033$. An Enraf–Nonius CAD4F diffractometer with a graphite monochromator and Mo-K rays were used and calculations were carried out with the GX system [6] on a GOULD 3227 computer. In 3 (Fig. 1) the Fe_2Co_2 system defines a tetrahedral cluster and is associated with 60 outer valence electrons as expected for a tetrahedral arrangement. Each cobalt atom

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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.

bears two terminal carbonyl ligands, and the Co–Co bond is bridged symmetrically by a fifth carbonyl group. Two $C(CF_3)$ groups cap two Fe_2Co triangular faces of the trigonal (*nido*) pyramid. Within the metal framework, the Co–Co and Fe–Fe bonds (respectively 2.381(1) and 2.418(1) Å) are appreciably shorter than the Co–Fe bonds (2.501(1)–2.550(1) Å). The molecule displays approximate $m(C_s)$ symmetry, with the mirror plane passing through Fe(1), Fe(2), C(5) and O(5). Although Fe(1) and Fe(2) display nearly identical coordinations their environments are not equivalent, since Fe(1) and C(5)–O(5) lie on the opposite side of the C(6), Co(1), Co(2), C(8) plane to Fe(2).

The structure of **3** clearly shows that a C≡C cleavage occurs in reaction 2. Weakening of the triple bond of the hexafluorobut-2-yne coordinated to iron and cobalt atoms in the complex **1** can be brought about both by removal of electron density from C–C bonding orbitals and by population of antibonding C–C orbitals through retrodative bonding. The presence of electron-attracting CF_3 substituents in the alkyne facilitates retrodative bonding and may also directly weaken the coordinated C≡C bond.

This work thus provides a new example of induction of the scission of an alkyne ligand by a tetranuclear cluster, with formation of a bis-carbyne complex which could be considered as an intermediate in the reported occurrence of products formally derived from alkyne cleavage and metathesis [1]. Extensive work in this area with a variety of alkynes containing electron-withdrawing substituents is now in progress.

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