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The Synthesis and Crystal Structure of Two New Heterometallic Clusters: $(\eta\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_3\text{-}CO)$ and $(\eta\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(C_2Et_2)$

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By reacting cyclopentadienyl-nickel derivatives and iron-carbonyls, in hydrocarbons, we obtained the complex $(\eta\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_3\text{-}CO)$ (complex I) [1]. Reactions of the same nickel derivatives with alkyne–carbonyls of iron and ruthenium were previously reported [2–5]; the complex $(\eta\text{-}C_5H_5)_2$-$Ni_2Fe_2(CO)_6(C_2Et_2)$ (complex II) was obtained, together with other products. Its structure was proposed on the basis of instrumental results and E.A.N. formalism.

Complexes I and II contain the same Ni_2Fe_2 core; for I i.r. evidence was indicative of the presence of CO's bonded to more than two metals, in II the alkyne was expected to be bonded to four metals. Thus we considered the possibility of a structural relationship for these two derivatives.

We now report the crystal structures of I and II and some chemical evidence, which clearly indicates that no relationship exists for these complexes and that probably two different reaction mechanisms lead to them.

Complex I can be obtained by refluxing in heptane, under nitrogen, equimolecular amounts of nickelocene with $Fe_3(CO)_{12}$, or of $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ with either $Fe(CO)_5$ or $Fe_3(CO)_{12}$, for 20 min. The product was purified by t.l.c. plates (Kieselgel P. F. Merck, eluant mixtures of ethyl ether and light petroleum); it shows, in the mass spectrometer, the parent ion at 556 m/e and loss of seven CO's. The i.r. spectrum, in the CO stretching region (n-heptane solution) shows absorptions at 2041 s, 2014 vs and 1722 m–s cm^{-1}. The synthesis and the analytical data for II have been already reported [2].

The black-green crystals of I, crystallized at −10 °C from a heptane–$CHCl_3$ solution, are triclinic, a = 8.028(8), b = 14.561(12), c = 7.961(8) Å, α = 94.58(7), β = 97.26(11), γ = 92.23(9)°, $\underline{V}$ = 919 Å^3, Z = 2, d_{calc} = 2.01 g cm^{-3}, space group $P1$.

The blue-black crystals of II, crystallized at 0 °C from heptane solutions, are triclinic, a = 10.124(10), b = 14.676(12), c = 8.396(8) Å, α = 95.80(8), β = 111.20(10), γ = 72.89(9)°, V = 1111 Å^3, Z = 2, d_{calc} = 1.82 g cm^{-3}, space group $P\bar{1}$.

3586 (for I) and 2714 (for II) reflections in the range $3 < \theta < 26°$ (for I) and $3 < \theta < 22°$ (for II) were recorded on an AED single-crystal diffractometer using the Nb-filtered MoKα radiation; of them 2570 (for I) and 1338 (for II) were used in the structure analyses, having $I > 2\sigma(I)$. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares to an R value of 0.039 (for I) and of 0.045 (for II).

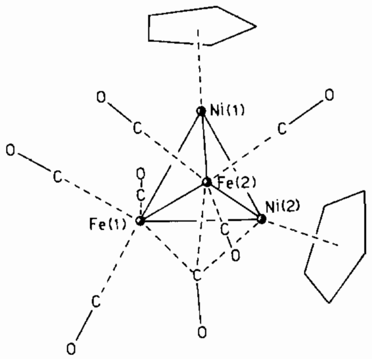

Fig. 1. The structure of $(\eta\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_3\text{-}CO)$.

The structure of I, represented in Fig. 1, is characterized by a tetrahedral metal atom core with five very close metal–metal bond distances (Fe(1)–Ni(1) = 2.432, Fe(1)–Ni(2) = 2.408, Fe(2)–Ni(1) = 2.438, Fe(2)–Ni(2) = 2.411 and Ni(1)–Ni(2) = 2.441 Å) and the sixth one (Fe(1)–Fe(2) = 2.530 Å) slightly longer. Two cyclopentadienylic ligands are coordinated to the nickel atoms and six terminal CO's are disposed three on each iron atom; however one of these is slightly distorted towards Ni(1), thus forming an 'incipient semi-bridging' group [6].

The seventh carbonyl is triply bridging Fe(1), Fe(2) and Ni(2) in an asymmetric way, the metal–carbon distances being Fe(1)–C = 1.981, Fe(2)–C = 1.961 and Ni(2)–C = 2.110 Å. Indeed, on the basis of the E.A.N. formalism, this carbonyl should bridge the iron atoms only; thus the behaviour of Ni(2) is not in accordance with the E.A.N. formalism, as it is bound to a cyclopentadienylic group and to four other atoms.

The structure of II is represented in Fig. 2. A butterfly arrangement of the metal atoms was expected [3, 4, 7], instead a tetrahedral distorted square arrangement was found. The metal–metal bond distances are very close and well comparable with those found in I (Fe(1)–Ni(1) = 2.426, Fe(1)–

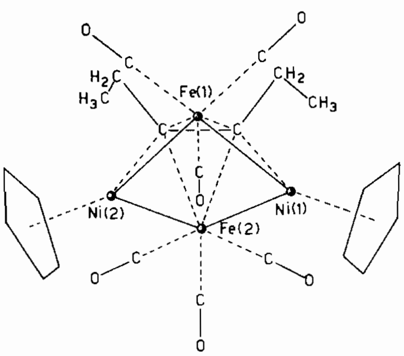

Fig. 2. The structure of (η-C_5H_5)$_2$$Ni_2Fe_2(CO)_6(C_2Et_2)$.

Ni(2) = 2.417, Fe(2)–Ni(1) = 2.422 and Fe(2)–Ni(2) = 2.414 Å); the non-bonding Fe(1)–Fe(2) and Ni(1)–Ni(2) distances are 3.204 and 3.454 Å respectively. In the metal square the bond angles are equal pairwise (Ni(1)–Fe(1)–Ni(2) = 91.0, Ni(1)–Fe(2)–Ni(2) = 91.2, Fe(1)–Ni(1)–Fe(2) = 82.7 and Fe(1)–Ni(2)–Fe(2) = 83.0°).

The E.A.N. formalism is fulfilled in the complex II, as each Ni atom is bonded to one cyclopentadienylic ligand, to two Fe atoms and σ to one alkynic carbon, whereas each Fe atom is bonded to three terminal CO's, to two Ni atoms and interacts π with the alkyne. In this cluster thus the alkyne behaves as a six-electron donor (the C–C alkynic bond distance is 1.431 Å). Few other examples of tetrametallic clusters characterized by a square metal arrangement were reported [8] and, to our knowledge, II is the first heterometallic example.

From the above results, one can observe that, in absence of alkynes, the 'classical' tetrahedral metal arrangement is preferred, whereas in presence of alkynes different arrangements can be observed either for homometallic [8e] and for heterometallic [3, 4] clusters and for the complex II, probably depending on the starting metallic reactants or on the bonding of the alkyne to the metals or on the alkyne substituents. A detailed study of the mechanisms of formation of these clusters is now in progress in our laboratories.

Chemical evidence has shown that the complexes I and II are not related; indeed, attempts of obtaining II by treating I in heptane or cyclohexane for few minutes with variable amounts of C_2Et_2 under inert atmosphere were unsuccessful; only demolition products of I could be observed.

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