Synthesis of Heterotrimetallic (Fe–Co–Ni)–Acetylene Clusters and *X*-Ray Crystal Structure of (η^5-C_5H_5)NiCoFe$(CO)_5(PPh_3)(C_2Ph_2)$

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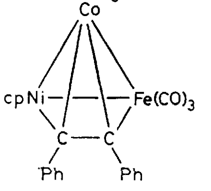
The heterobimetallic complexes (η^5-C_5H_5)NiCo$(CO)_3(C_2R^1R^2)$ [R^1 = Ph; R^2 = Ph or Me] react with $Fe_2(CO)_9$ to yield the heterotrimetallic clusters (η^5-C_5H_5)NiCoFe$(CO)_6(C_2R^1R^2)$; the stereochemistry of a triphenylphosphine derivative, the title compound, has been established by a single-crystal *X*-ray structure analysis.

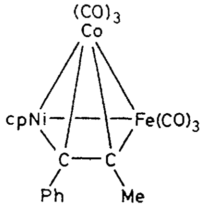
There is considerable current interest in the synthesis of transition metal clusters with co-ordinated acetylenes as potential models for the chemisorption of unsaturated hydrocarbons on metallic surfaces.[1] Additionally, there has been much recent activity in the synthesis of mixed-metal clusters in anticipation of unique reactivity and catalytic properties.[2] Hetero-*triangulo*-metallic clusters with two different metals forming the framework are now quite common, but those comprising three different metals are still quite rare.[2] We know of only one other example of a triangular cluster formed by three different 3d metals,[3] and none involving acetylene co-ordination. One approach to their synthesis is the addition of a third metal unit to an existing heterobimetallic-acetylene framework. The complexes (cp)NiCo$(CO)_3(C_2R^1R^2)$ (cp = η^5-cyclopentadienyl) (**1a, b**) have been recently synthesized[4,5]

(cp)NiCo$(CO)_3(C_2R^1R^2)$
(**1**) a; $R^1 = R^2 = $ Ph
b; R^1 = Ph, R^2 = Me

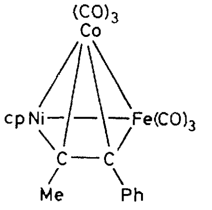
[and the structure of (**1a**) determined][4] and are analogous to the well known iso-electronic homometallic complexes[6,7] $Co_2(CO)_6(C_2R^1R^2)$ and $(cp)_2Ni_2(C_2R^1R^2)$.



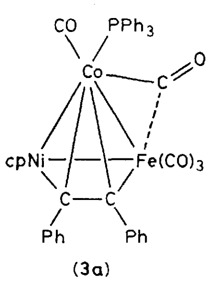
(**2a**)



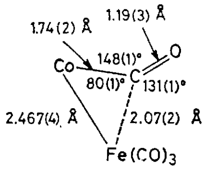
(**2b**)



(**2b′**)



(**3a**)



Stirring (**1a**) or (**1b**) overnight in hexanes with a large excess of $Fe_2(CO)_9$ gave after chromatography on Florisil [yield 30% based on (**1**) consumed] the dark-brown complexes (cp)NiCoFe$(CO)_6(C_2R^1R^2)$ (**2**; **a**, $R^1 = R^2 = $ Ph; **b**, R^1 = Ph, R^2 = Me), with i.r. spectra (hexane) ν(CO) 2078s, 2033s, 2020s, 2014s, 1975s, and 1961m cm^{-1} for (**2a**) and 2073s, 2028s, 2012s, 2002s, and 1969s, br cm^{-1} for (**2b**). The mass spectra exhibited the predicted isotopic pattern for an FeCoNi cluster and gave accurate mass values for the parent ions: (**2a**) *M* 583.8903 (calc.) and 583.8899 (found); (**2b**) *M* 521.8747 (calc.) and 521.8742 (found). The ^1H n.m.r. spectrum ($CDCl_3$) of (**2a**) displayed a single resonance for the cp protons (δ 4.92) and a phenyl multiplet at δ 7.06; however, (**2b**) exhibited two cp resonances (δ 4.89 and 5.16), two methyl resonances (δ 2.63 and 2.70) and phenyl peaks at δ 7.04 and 7.22. The most probable interpretation is that (**2b**) consists of two structural isomers (**2b** and **2b′**) arising from the two possible orientations of an unsymmetrical acetylene in a structure otherwise identical with that of (**2a**), and that all are rigid with regard to possible acetylene rotation on the face of the triangle at ambient temperature. However, the data do not allow a determination of the orientation of the acetylene ligand in the cluster. The tentative structures illustrated for (**2a**), (**2b**), and (**2b′**) are based upon a comparison with the recently determined structure[8] of the isoelectronic anion $[cpNiFe_2(CO)_6(C_2Ph_2)]^-$.

So far, (**2a**) and (**2b**) have resisted attempts to grow single crystals suitable for *X*-ray analysis. Reaction of (**2a**) with PPh_3 in hexane displaces a CO group to give (cp)NiCoFe$(CO)_5(PPh_3)(C_2Ph_2)$ (**3a**); i.r. (hexane) ν(CO) 2039s, 1974s, and 1969s cm^{-1}; (KBr) ν(CO) 2040s, 1965s, br, and 1827s cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 4.72 (cp). The structure of (**3a**)

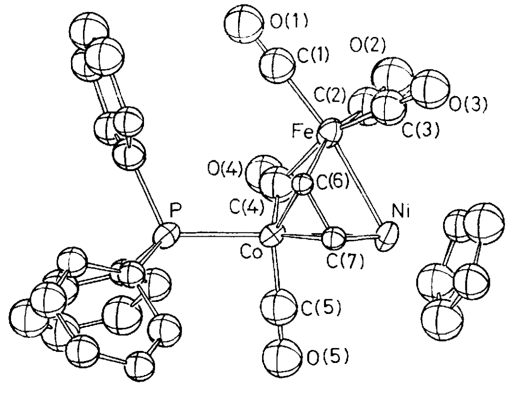


Figure 1. ORTEP plot (45% thermal ellipsoids) of (η^5-C_5H_5)-NiCoFe$(CO)_5(PPh_3)(C_2Ph_2)$. Phenyl groups of the acetylene are omitted for clarity. Bond distances (Å): Ni–Fe, 2.486(4); Ni–Co, 2.390(4); Co–Fe, 2.467(4); Co–P, 2.230(6); Ni–C(7), 1.93(2); Fe–C(6), 2.03(2). Bond angles (°): Ni–Co–Fe, 61.6(1); Ni–Fe–Co, 57.7(1); Fe–Ni–Co, 60.7(1); Ni–C(7)–Co, 74.1(6); Fe–C(6)–Co, 74.3(6).

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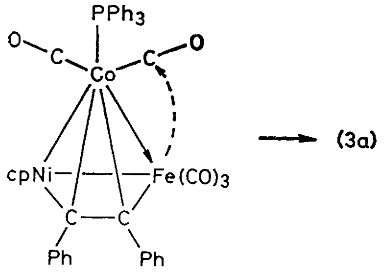
(crystallized from $CHCl_3$–hexane), determined by single-crystal *X*-ray diffraction, is shown in Figure 1.

Crystal data: $C_{42}H_{30}CoFeNiO_5P$, $M = 819.15$, monoclinic, space group $P2_1/c$, $a = 11.698(2)$, $b = 14.768(3)$, $c = 22.616(4)$ Å; $\beta = 111.82(1)°$, $U = 3627.1$ Å^3, $Z = 4$, $D_c = 1.48$ g cm^{-3}, μ(Mo-K_α) = 14.67 cm^{-1}. The intensities of 2316 independent reflections ($3 \leqslant 2\theta \leqslant 35°$) were measured on a Picker FACS-I automatic diffractometer using a crystal of dimensions $0.09 \times 0.15 \times 0.11$ mm. The metals and the phosphorus atom were located by direct methods. Successive difference Fourier syntheses revealed the remaining non-hydrogen atoms. All hydrogen atom co-ordinates were calculated geometrically. The structure has been refined by block-diagonal least-squares methods with anisotropic thermal parameters for Fe, Co, Ni, and P to current values of $R = 0.057$, $R_w = 0.070$ and goodness of fit = 1.32 for 1109 observed reflections [$I \geqslant 2.3\sigma(I)$].†

The structure corresponds to the valence-bond description shown for (**3a**), in which each metal atom achieves an 18 electron configuration and the cluster has 48 electrons. The acetylene is symmetrically bound to the cobalt with bond lengths of 2.05(2) and 2.04(2) Å. The phosphorus atom lies slightly out of the metallic plane [0.10(1) Å] and is close to being colinear with the Co–Ni bond [angle P–Co–Ni 177.2(2)°]. A notable feature is the unique carbonyl group bridging the Co–Fe bond in a grossly unsymmetrical manner, as shown. This kind of CO co-ordination has been termed 'semibridging'[9] and its occurrence in this structure may be understood in simple valence terms as a perturbation of the terminal CO group on cobalt in the hypothetical non-bridged structure as a result of the iron atom disposing of excess electron density (resulting from the Co→Fe 2e$^-$ donation) by attacking the carbonyl carbon atom (Scheme 1).

While it seems likely, it does not necessarily follow that the parent heterotrimetallic complexes (**2**) contain either the same orientation of the acetylene, or the unique semibridging carbonyl group featured in (**3a**), since various plausible structures may readily be drawn which satisfy the usual valence rules.



Scheme 1

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.