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Preliminary communication

SYNTHESIS OF MIXED METAL CLUSTERS FROM BINUCLEAR PRECURSORS: X-RAY STRUCTURE OF $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)$, A MOLECULE WITH A μ_4-ACETYLIDE ON A SPIKED TRIANGULAR METAL FRAMEWORK

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Summary

The tetranuclear mixed metal cluster $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)$ (1) has been synthesised in high yield via condensation of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)$ and $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$: X-ray analysis has revealed a novel structure for 1 with a μ_4-acetylide coordinated on a spiked triangular metal skeleton.

Key factors in the rapid growth of heterometallic transition metal cluster chemistry have been the development of rational synthetic routes to mixed metal systems [1] and the belief that cooperativity effects between metals may promote unique patterns of substrate activation [2]. Somewhat surprisingly, in view of the importance of iron and nickel as catalytic metals, relatively few mixed Fe/Ni clusters [2,3] have been synthesised and examples of Fe_2Ni_2 compounds are restricted mainly to $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_7$ [4] and to alkyne derivatives of the types $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(RC{\equiv}CR)$ [4] and $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(C_5H_6)$ [5]. Herein we report a high yield synthesis of the novel tetranuclear cluster $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)$ (1), which uses the condensation of a diiron precursor

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$Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)$ (2) [6] with $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$ (3). Unusual structural features of the new cluster 1 include (i) a rare spiked triangular metal framework; (ii) an unprecedented $\mu_4\text{-}\eta^2$-bonding mode for the acetylide and (iii) a phosphido bridge between the "spiked" nickel atom and an iron atom of the closed triangle.

Treatment of equimolar amounts of 2 and 3 in refluxing benzene under dinitrogen for 20 h, followed by column chromatography (Florisil; eluant hexane) afforded 1 (46%), unreacted 2 and 3 together with small amounts of an unidentified brown cluster. Previous work with 3 as a cluster synthon [7] suggested that better yields might be obtained under dihydrogen. Indeed in refluxing heptane under a slow dihydrogen flow for 40 min, 2 (1.5 mmol) and 3 (5.0 mmol) gave a 75% yield of 1, separated by TLC (silica gel, eluant petroleum ether/ethyl ether). Spectroscopic and analytical data for 1 (ν(CO), C_7H_{16}, 2019 vs, 1975 vs, 1953 vs, 1927 w cm^{-1}: ^1H NMR, CD_2Cl_2, δ 8.10 m, 7.75 m, 7.50 s (C_6H_5, 15H), 5.27 s (C_5H_5, 5H), 4.29 s (C_5H_5, 5H); ^{13}C NMR, $(CD_3)_2CO$, δ 92.17 s (C_5H_5), 94.47 s (C_5H_5), 128.89—134.10 m (C_6H_5), 141.59 d, J(P—C) 33Hz (C_α-acetylene) 142.61 d, J(P—C) 20 Hz (C_β-acetylene), 212.40 s, 215.64 s, 216.11 s, 222.72 s, 225.14 s (CO); ^{31}P NMR δ (wrt, H_3PO_4) CD_2Cl_2 + 186.4 ppm; mass spectrum (FAB) M^+ 782) established the molecular formula, the presence of a μ-PPh_2 bridge across a metal—metal bond [8] and two different C_5H_5 groups. Precise structural details were provided by an X-ray analysis[≠].

A perspective view of the molecule is shown in Fig. 1. The skeletal framework consists of an isosceles triangular arrangement of two iron atoms and a nickel atom with the remaining cyclopentadienyl nickel unit axially ligated with respect to the closed triangle at Fe(1) (Ni(1)—Fe(1)—Ni(2) 96.99(2)° Ni(1)—Fe(1)—Fe(2) 92.51(2)°). The alkyne unit is σ-bonded to Fe(1) and Ni(1) probably via a three centre interaction and is η^2-bound to Fe(2) and Ni(2), thus acting as a 5-electron donor to the cluster. The interaction of C(16) with all four metals in 1 is particularly noteworthy. Multisite bonding to a single carbon atom is a recurring structural feature of cluster carbides [9], vinylidenes [10] and acetylides [11]; $\mu^4\text{-}\eta^2$-bonding modes have been documented for acetylides and vinylidenes in butterfly clusters [10] and on squares faces of polymetallic derivatives [11]. However cluster 1 and the recently reported $(\eta^5\text{-}C_5H_5)FeRuCo_2(CO)_9(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)$ [12] are the only known examples of $\mu_4\text{-}\eta^2$-acetylide bonding in spiked tetrametallic systems.

The overall electron count of 64-electrons for 1, is appropriate for either a square planar or metalloligated triangular structure with four metal—metal bonds. Although examples of both equatorially [13] and axially [14] metallo-

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[≠] *Crystal data*: $Ni_2Fe_2PO_5C_{35}H_{25}$, black, orthorhombic crystals, space group, $P2_1\,2_1\,2_1$, a 11.110(2), b 15.635(2), c 18.570(2) Å, $Z = 4$, $U = 3225.7(7)$ Å^3, $D_c = 1.618$ gm cm^{-3}, $F(000) = 1592$, μ(Mo-K_α) 21.40 cm^{-1}. The structure solution (Patterson, Fourier methods) and refinement (full matrix least squares, all non-hydrogen atoms anisotropic) were based on 2430 observed ($I \geqslant 3\sigma(I)$) (3223 measured) reflections (Syntex $P2_1$ diffractometer, max 2θ 50°). Final R and R_W values are 0.029 and 0.031.

The atomic coordinates (Table 1), thermal parameters (Table 2), bond lengths and angles (Table 3) and Structure Factors (Table 4) 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.

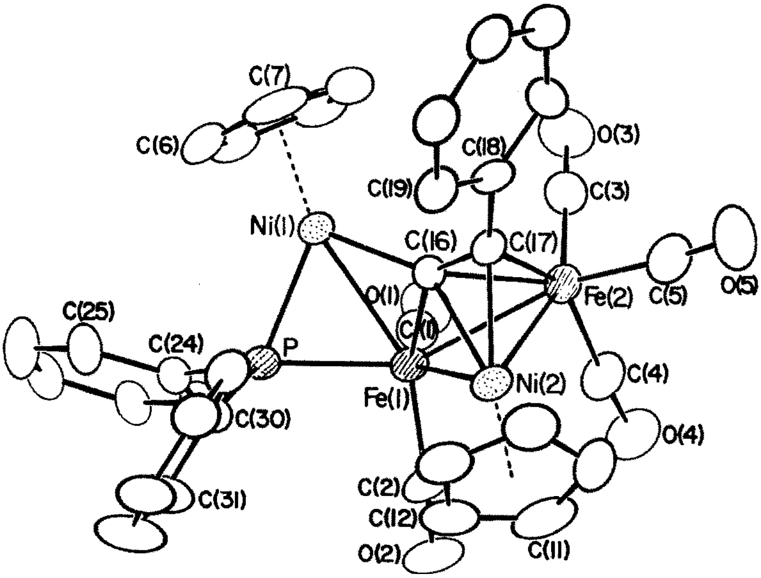

Fig. 1. The molecular structure of $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)$ (1). Important internuclear distances include: Ni(1)—Fe(1) 2.277(1), Fe(1)—Ni(2) 2.584(1), Fe(1)—Fe(2) 2.606(1), Ni(2)—Fe(2) 2.394(1), Ni(1)—P 2.130(2), Fe(1)—P 2.178(2), Ni(1)—C(16) 1.920(5), Fe(1)—C(16) 1.923(6), Ni(2)—C(16) 2.051(5), Fe(2)—C(16) 2.073(6), Ni(2)—C(17) 1.969(6), Fe(2)—C(17) 2007(6), C16—C(17) 1.313(8) Å.

ligated structures have recently been structurally characterised, spiked triangular clusters are uncommon and for Fe_2Ni_2 systems the only related compound is $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_5(\mu_3\text{-}CO)(C_5H_6)$ [5].

It is interesting that in the conversion of 2 to 1 via reaction with 3 the μ-PPh_2 group bridging the Fe—Fe bond in 2 moves to a position bridging Ni(1) and Fe(1) in 1 while the acetylide remains bound to both iron atoms. These observations and the high yield of 1 from 2 and 3 suggests that acetylide bridged compounds such as 2 may well be reactive two atom sources for heterometallic cluster synthesis.

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