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Synthesis and crystal structure of $(\eta^5\text{-}C_5H_5)NiFe_3(CO)_7\text{-}(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}HC{\equiv}CPr^i)$: a butterfly cluster with an unprecedented metal core stoichiometry

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Abstract

The reaction of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with $(\eta^5\text{-}C_5H_5)_2Ni_2(Ph_2PC{\equiv}CR)$ ($R = Pr^i$, Ph) leads to several heterometallic clusters with known or unprecedented structures. The complexes $(\eta^5\text{-}C_5H_5)NiFe_2(CO)_6(\mu_3,\eta^2\text{-}C_2R)$, $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_4,\eta^2\text{-}HC{\equiv}CR)$, $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}C_2R)$, $(\eta^5\text{-}C_5H_5)_2NiFe_2(CO)_3(\mu\text{-}PPh_2)(C_2R)$ and $(\eta^5\text{-}C_5H_5)NiFe_3(CO)_7(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}HC{\equiv}CR)$ (**4**) have been identified in the reaction mixtures. The identities of the complexes have been established by elemental and spectroscopic analyses and by comparison with known derivatives. The structure of the Pr^i derivative of **4** has been determined by an X-ray diffraction study. Crystals are triclinic, space group $P\bar{1}$, with *a* 10.586(7), *b* 15.322(9), *c* 9.417(5) Å, α 101.32(2), β 78.22(2), γ 94.62(2)°, and $Z = 2$. The structure has been solved from diffractometer data by direct and Fourier methods, and refined by full-matrix least-squares to $R = 0.059$ for 2324 observed reflections. In the heteronuclear cluster, which has an unprecedented $NiFe_3$ stoichiometry, the Ni atom occupies an hinge position and a wing-side is bridged by the phosphido ligand.

Introduction

Syntheses of phosphido-bridged metal clusters have grown rapidly in number in recent years, and general preparative methods are now available for these derivatives. Some of these are: (i) thermal or photochemical reactions of phosphine-substituted metal clusters [1] and of clusters with coordinated diphosphines [2]; (ii) reactions of hydrogen- or halogen-containing phosphines with metal carbonyls or

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metal carbonyl hydrides [3]; (iii) reactions of coordinated chlorophosphines with carbonyl-metallates [4]; (iv) metal-fragment condensation [5] and cluster expansion reactions facilitated by phosphido- or phosphinidene ligands; (v) reductive elimination reactions [6]; reactions of free or terminally coordinated phosphino-alkynes with P–C bond cleavage [7].

We are investigating new methods for synthesis of phosphido- and phosphinidene-bridged heterometallic clusters containing nickel and iron or ruthenium or osmium [8]. We previously found that, among other, the reactions of $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$ with hydrocarbyl substituted Fe, Ru or Os clusters [9] and those of $M_3(CO)_{12}$ (M = Fe, Ru, Os) with $(\eta^5\text{-}C_5H_5)_2Ni_2(RC{\equiv}CR')$ under N_2 or H_2 [10] yield nickel containing heterometallic clusters, with some degree of selectivity.

As an extension of this method, we report here the reactions of phosphino-alkynes coordinated to nickel, namely $(\eta^5\text{-}C_5H_5)_2Ni_2(Ph_2PC{\equiv}CR)$ (R = Ph, Pr^i) with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. Several heterometallic derivatives were obtained and we identified $(\eta^5\text{-}C_5H_5)NiFe_2(CO)_6(\mu_3,\eta^2\text{-}C_2R)$ (R = Pr^i, **1b**), $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_4,\eta^2\text{-}HC{\equiv}CR)$ (R = Ph, **2a**; R = Pr^i, **2b**), $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}C_2R)$ (R = Ph, **3a**, previously reported [8b]; R = Pr^i, **3b**) and $(\eta^5\text{-}C_5H_5)NiFe_3(CO)_7(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}HC{\equiv}CR)$ (R = Ph, **4a**; R = Pr^i, **4b**). The X-ray structure of **4b** has been determined.

Two incompletely characterized phosphido-bridged derivatives (complexes **5a**, **6a** with R = Ph; **5b**, **6b** with R = Pr^i) have also been obtained.

Experimental

General experimental details. Materials. Purification and analysis of the products

$(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$ (Pressure Chemicals) and $Fe_2(CO)_9$ (Strem Chemicals) were commercial products; $Fe_3(CO)_{12}$ [11] and Ph_2PC_2R alkynes (R = Ph, Pr^i) [12] were prepared by published methods. Reactions were performed in conventional glassware, in n-heptane previously distilled and kept over sodium, pure and dry N_2 or H_2 (S.I.A.D.) atmospheres were maintained above the reaction mixtures.

The reaction solutions were filtered under N_2 and evaporated to dryness under reduced pressure; the residuals were redissolved in $CHCl_3$ and purified on preparative TLC plates (Kieselgel P.F. Merck; eluant, mixtures of light petroleum and diethyl ether). Whenever possible the products were crystallized from hexane, heptane, or heptane/$CHCl_3$. Elemental analyses were obtained by Pascher Laboratories (Bonn, W.Germany); the IR spectra were recorded on a Perkin Elmer 580 B instrument. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL JNM GX 270 FT. The EI mass spectra were obtained with a Kratos MS 50 instrument: the FAB spectra were recorded by Dr. J.M. Miller (Brock University, Canada).

Reactions of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with $(\eta^5\text{-}C_5H_5)_2Ni_2(Ph_2PC_2R)$

The dinickel complexes $(\eta^5\text{-}C_5H_5)_2Ni_2(Ph_2PC_2R)$ (R = Ph, Pr^i) were obtained by a method similar to that employed for $(\eta^5\text{-}C_5H_5)_2Ni_2(RC_2R')$ [10]. A mixture of $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$ with a 1.5 to 1 molar excess of phosphino-alkyne in heptane under N_2 was refluxed until the initially dark red solution had become green-brown. Evolution of CO occurred, and the disappearance of the CO stretchings typical of $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$ indicated the completion of the reaction. The solutions containing $(\eta^5\text{-}C_5H_5)_2Ni_2(Ph_2PC_2R)$ were treated with a two-fold molar proportion of the iron carbonyl and refluxed under N_2 or H_2 for 15–25 min. Very dark reaction solutions and considerable amounts of insoluble material were formed.

$Fe_2(CO)_9$, $R = Ph$. After 20 min reflux, low yields of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu,\eta\text{-}C_2Ph)$ [7] and of **2a** were obtained, together with about 20% (on nickel) of **3a** and five unidentified trace products.

$Fe_2(CO)_9$, $R = Pr^i$. After 15 min reflux, about 15% of **2b**, 5% of **1b**, 30% of **3b** and small amounts of $(\eta^5\text{-}C_5H_5)_2NiFe(CO)_3$ and **6b** were obtained, together with about 10% of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$.

$Fe_3(CO)_{12}$, $R = Ph$. After 25 min reflux, about 20% of **3a**, 10% of **2a**, about 10% each of **5a** and **6a** and 35–40% of **4a** were observed, together with small amounts of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and nickelocene.

$Fe_3(CO)_{12}$, $R = Pr^i$. After 25 min reflux, about 10% of **2b**, 5% of **1b**, 30% of **4b**, 15% of **5b**, 20% of **6b**, and 15% of **3b** were found, together with small amounts of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and nickelocene. No significant changes in type or yields of the products were noticed when a H_2 rather than N_2 stream was maintained in the vessel.

*Crystal structure determination of **4b***

Crystals of **4b** were obtained by slowly cooling a saturated heptane/$CHCl_3$ solution under N_2; after several days at $-20\,°C$ dark green-black crystals were obtained, together with some decomposition materials. Repeated attempts to obtain crystals of **5** and **6** were unsuccessful, and only microcrystalline powders were obtained.

Crystal data. $C_{29}H_{23}Fe_3NiO_7P$, $M = 740.72$, triclinic, space group $P\bar{1}$, a 10.586(7), b 15.322(9), c 9.417(5) Å, α 101.32(2), β 78.22(2), γ 94.62(2)°, V 1465(2) Å^3 (by least-squares refinement of the 2θ values of 26 reflections accurately measured reflections), $Z = 2$, $\lambda = 0.71069$ Å, $D_c = 1.679$ g cm^{-3}, $F(000) = 748$, $\mu(\text{Mo-}K_\alpha) = 21.91$ cm^{-1}. A crystal of approximate dimensions $0.09 \times 0.15 \times 0.45$ mm was used for the structure analysis. No absorption correction was made.

Data collection and processing. A Siemens AED diffractometer was used in the $\theta/2\theta$ scan mode, with niobium-filtered Mo-K_α radiation; all the reflections for θ 3–24° were measured. Of 4489 independent reflections, 2324 with $I \geq 2\sigma(I)$ were considered observed and used in the analysis.

Structure solution and refinement. Direct and Fourier methods were used with full-matrix least-squares and anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. The hydrogen atoms were placed at geometrically calculated positions and introduced in the final structure factor calculations. Final R and R_w values were 0.0592 and 0.0770, respectively. The SHELX system of computer programs was used [13]. Atomic scattering factors, corrected for anomalous dispersion of Ni, Fe and P, were taken from ref. 14. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna. Final atomic coordinates for the non-hydrogen atoms are given in Table 1. Coordinates for the hydrogen atoms and a list of structure factors are available from the authors.

Results and discussion

The reactions described provide a non-selective route to heterometallic compounds of known or unprecedented structures; the elemental analyses, IR and mass

Table 1

Fractional coordinates ($\times 10^4$) with e.s.d.'s in parentheses for the non-hydrogen atoms of the complex **4b**

Atom	*x*	*y*	*z*
Ni	6669(1)	2201(1)	3630(2)
Fe(1)	9015(2)	2378(1)	3659(2)
Fe(2)	8360(2)	2305(1)	1293(2)
Fe(3)	7000(2)	931(1)	1603(2)
P	9450(3)	3419(2)	2386(3)
O(1)	6869(11)	3411(9)	103(13)
O(2)	10118(11)	1909(9)	−1497(12)
O(3)	8631(11)	3279(7)	6708(11)
O(4)	11610(9)	1960(7)	3806(11)
O(5)	8066(13)	−502(9)	−689(14)
O(6)	4882(16)	−162(12)	2829(17)
O(7)	5620(14)	1576(9)	−338(16)
C(1)	7452(14)	2978(11)	588(16)
C(2)	9452(14)	2052(10)	−427(17)
C(3)	8764(13)	2927(9)	5495(16)
C(4)	10577(14)	2146(9)	3733(15)
C(5)	7639(14)	52(10)	191(18)
C(6)	5745(18)	272(13)	2319(21)
C(7)	6226(18)	1368(13)	462(20)
C(8)	8738(12)	1283(8)	2208(14)
C(9)	7780(11)	1240(8)	3517(14)
C(10)	7605(13)	583(9)	4544(15)
C(11)	7990(15)	960(10)	6022(17)
C(12)	8370(17)	−273(12)	3778(19)
C(13)	5503(14)	2596(10)	5743(17)
C(14)	5934(15)	3350(11)	5144(18)
C(15)	5504(17)	3276(13)	3897(20)
C(16)	4765(16)	2519(11)	3622(18)
C(17)	4759(16)	2052(11)	4737(19)
C(18)	11134(11)	3664(8)	1632(13)
C(19)	11658(12)	4537(9)	1787(14)
C(20)	12992(13)	4708(9)	1316(16)
C(21)	13753(15)	3995(11)	676(17)
C(22)	13276(14)	3133(10)	465(16)
C(23)	11911(12)	2957(9)	971(14)
C(24)	8786(11)	4518(8)	2912(13)
C(25)	8428(12)	4935(8)	4360(14)
C(26)	7909(13)	5773(9)	4743(15)
C(27)	7775(13)	6208(9)	3662(15)
C(28)	8160(14)	5811(10)	2154(16)
C(29)	8656(13)	4955(9)	1792(15)

spectra of the complexes **1**–**6** are given in Table 2, the NMR spectra in Table 3. The spectroscopic data for **1b** are consistent with the formulation $(\eta^5\text{-}C_5H_5)NiFe_2(CO)_6\text{-}(\mu_3,\eta^2\text{-}C_2Pr^i)$ and with a structure closely comparable to that of $(\eta^5\text{-}C_5H_5)NiFe_2\text{-}(CO)_6(C_2Bu^t)$ [15], in which the acetylide interacts with one Fe atom through a σ-bond and with the second Fe atom and the Ni atom through two π-bonds.

The complexes **2a** and **2b** were identified as $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(HC{\equiv}CR)$ (R = Ph, Pr^i), having a quasi-square planar metal core (4 M–M); the structures of

Table 2

Elemental analyses, physical and spectroscopic properties of complexes **1**–**6**

Complex	Physical properties	Elemental analysis (%)	IR (ν(CO); C_6H_{14}) (cm^{-1})	Mass spectrum	Ref.
1b[a]	Dark brown crystals	C 41.0(40.83)[b], Fe 24.0(23.73), H 2.8(2.57), Ni 13.1 (12.47)	2062s, 2021vs, 1994vs 1987s(sh), 1973m	$P^+ = 470$ *m/e*[c]	this work
2a	Dark blue solid	C 46.2(45.79), Fe 18.0(17.74), H 2.7(2.56) Ni 18.9(18.65)	2021m(b), 2012vs, 1965vs(b)	–	this work
2b[d]	Dark blue crystals	C 43.1(42.36), Fe 18.2(18.76), H 3.2(3.05), Ni 17.2(19.72)	2014m(b), 2008vs, 1963vs(b)	$P^+ = 538$ *m/e*[c] (calc. 596)	this work
3a	Dark brown violet crystals	see ref. 8b	2019vs, 1975vs, 1953vs, 1927w	$P^+ = 782$ *m/e*[e]	8b
3b	Dark brown violet crystals	C 52.15(51.13), Fe 14.4(14.36), H 3.60(3.62) Ni 15.0(15.62), P 3.95(3.97)	2022vs, 1977vs, 1956vs, 1930w	$P^+ = 610$ *m/e*[e] (calc. 752)	this work
4a	Dark green solid	C 48.6(49.61), Fe 21.8(21.63), H 2.81(2.73) Ni 7.8(7.58), P 3.8(3.97)	2039s, 1995s, 1985vs(vb), 1944w(b)	–	this work
4b	Dark green crystals	C 47.1(47.02), Fe 21.9(22.62), H 3.3(3.13), Ni 7.46(7.93), P 4.07(4.18)	2036vs(b), 1992vs(sh), 1983vs(b)	$P^+ = 656$ *m/e*[e] (calc. 742)	this work
5b	Dark brown solid	C 47.0, Fe 18.8, H 3.60, Ni 12.9, P 3.53	2086vs, 2046vs, 2032s(sh), 2015s, 1993vs, 1978vs(b), 1962vs(b)	Decomposes[e]	this work
6b	Dark green solid	C 57.1, Fe 17.8, H 4.3, Ni 7.09, P 3.30	2064vs(b), 1974–1945vs(vb)	$P^+ = 612$[e] (calc. 636)	this work

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[a] ^{1}H NMR (δ, $CDCl_3$: 5.24 s (5H, CP), 3.25 m (1H, C*H*Me_2), 1.25 t,b(6H, Me).
[b] Calculated values in parentheses.
[c] EI Mass spectrum.
[d] ^{1}H NMR (δ, $CDCl_3$): 8.62 s (1H, HC alkyne), 5.39 s(5H, Cp), 5.30 s (5H, Cp), 2.90 m (1H, C*H*Me_2), 0.97 d (6H, Me).
[e] FAB mass spectrum.
[f] ^{1}H NMR (δ, $CDCl_3$): 10.30 d (1H, HC alkyne), 8.20–7.10 m (15H, Ph), 4.60 s (5H, Cp).

the homologues with RC≡CR (R = Et, Ph) have already been reported [9a,9d]. Noteworthy is the presence in complexes **2** of a coordinated alkyne and the absence in **1** and **2** of phosphido-bridges.

Table 3

^{1}H, ^{13}C and ^{31}P NMR spectra of the complexes **3–6**

Complex	^{1}H NMR (δ, $CDCl_3$)	^{13}C NMR (ppm, $CDCl_3$) [a]	^{31}P NMR ($CDCl_3$, H_3PO_4)	reference
3a	8.10 m, 7.75–7.50 m (15 H, Ph) [b], 5.27 s (5H, Cp), 4.29 s (5H, Cp).	90.3 s(Cp), 94.70 s(Cp), 127.8 – 128.2 m. 128.8–129.4 m (Ph carbons); 133.2–133.3 d (C acetylide); 133.4–133.5 d (C, acetylide); 215.4 s, 224.1–224.3 d (CO's)	+186.4 s	8b
3b	9.0 m, 7.20 m (10H, Ph), 5.50 s (5H, Cp), 4.30 s (5H, Cp), 3.70 m($CHMe_2$), 2.20 d, 1.50 d (6H, Me)	14.07, 22.6–26.5 d, 31.5, 37.8 (i-Pr); 91.50 s (Cp); 93.1 s (C, acetylide), 93.9 s(Cp); 127.7–128.6 dd, 129.4–130.3 dd, 132.7–133.2 dd, 140.6–143.3 dd (Ph, carbons); 163.0 d (C, acetylide); 214.3 s, 215.0 d, 229.3 d (CO's)	+199.0 s	this work
4b	9.28 s (1H, CH alkyne), 8.17– –7.56 mm (10H, Ph); 4.39 s (5H, Cp), 3.62 m (1H, $CHMe_2$), 1.50 d, 126 d (6H, Me)	14.08, 22.6, 27.6, 31.5–32.3 d (i-Pr); 93.39 s(Cp); 127.9–128.5 dd, 129.9–130.2 dd, 132.0–133.2 dd (Ph carbons); 140.4 d (C alkyne); 147.2 d (C, alkyne); 184.1 s, 206.8–210.8 m, 214.2–222.6 m (CO's).	+231.0 s	this work
5b	7.26–7.20 m (10H, Ph), 5.47 s (5H, Cp), 5.03 s(1H), 3.75 m (1H), 2.50–0.50 many broad signals (12H ca., Me)	14.07, 22.61, 25.74, 26.0 d, 31.55, 37.97, 47.79 s(i-Pr); 93.03 s (Cp); 127.8–127.9 dd, 128.5 d, 133.0 d, 142.2 d, 143.9 d (Ph carbons; alkyne carbons); 211.5 d, 216.1 s, 219.9 d, 228.8 s, 229.5 d (CO's)	+248.7 s	this work
6b	8.00, 7.82, 7.48, 7.28 m (10 H, Ph), 4.55 s (5H, Cp), 4.34 s (5H, Cp), 4.07 m (1H, $CHMe_2$), 1.88–1.78 q (6H, Me)	25.79, 37.94 (i-Pr); 82.25 s(Cp), 49.47 s(Cp); 127.7 d, 128.5 d, 129.2 d, 132.5 d, 142.1 d, 145.2 d (Ph carbons); 157.8 s (C acetylide), 176.4 s (C, acetylide); 213.9 s, 216.2 dd, 229.5 d (CO's)	+245.5 s	this work

[a] At room temperature (see text); C–H decoupled. [b] Integration and tentative attribution in parentheses.

For the complex **3b**, the spectroscopic data indicate a structure similar to that of **3a** [8b], with a spiked triangular metal core and the phosphido ligand bridging the Ni–Fe "spike". The homologue **3a** can be obtained in better yield by treating $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu,\eta\text{-}C_2Ph)$ with $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$ under H_2.

For complex **4a** a structure similar to that of **4b** (see below) is proposed on the basis of the spectroscopic data. However the ^{1}H NMR spectrum shows a doublet for the H–C (alkyne) hydrogen; if long-range coupling with phosphorus is ruled out, this could indicate the presence of isomers in solution. Two isomers can be envisaged, arising from the different orientation of the Ph and H substituents of the alkyne with respect to the Ni–Fe hinge atoms; similar behaviour has been noted for $(\eta^5\text{-}C_5H_5)NiRu_3(MeCCHCEt)$ [16].

The analytical and spectroscopic data do not allow a firm identification of complexes **5**; the analysis of **5b** indicates a Fe/Ni/P ratio of 3/2/1. Only one cyclopentadienyl and a μ-PPh_2 bridge must be present, together with at least two C_2Pr^i ligands, but the very broad NMR signals do not allow any reliable attributions. Moreover, in view of our failure to obtain good FAB spectra we cannot be sure of the number of carbonyls (all terminal).

Complex **6b** has a Fe/Ni/P ratio of 2/1/1, two different cyclopentadienyls, one PPh_2 bridge, one C_2Pr^i ligand, and all terminal CO's; for this complex several 48 electron structures, with either μ-PPh_2 or with M–P–C bonds, can be suggested. Unfortunately it is not possible to distinguish between the two types of structures on the basis of the ^{31}P chemical shifts alone [17].

Crystal structure of the complex 4b

A view of the structure of **4b** is shown in the Fig. 1; selected bond distances and angles are given in Table 4. The complex contains a tetranuclear cluster of three Fe and one Ni atoms coordinated by seven terminal carbonyls, a bridging phosphido ligand, a cyclopentadienyl ligand, and an isopropylacetylene ligand. The cluster has a butterfly arrangement of the metal atoms with the heteroatom on the hinge side, which is the longest one [Ni–Fe(2) 2.561(3) Å, the other sides varying between 2.436(2) to 2.484(3) Å]. The non-bonding Fe(1)–Fe(3) distance between the wing-tips is 3.529(3) Å and the dihedral angle between the two triangular wings is 114.1(1)°. The phosphido ligand bridges a wing side in a quasi-symmetrical way, and the

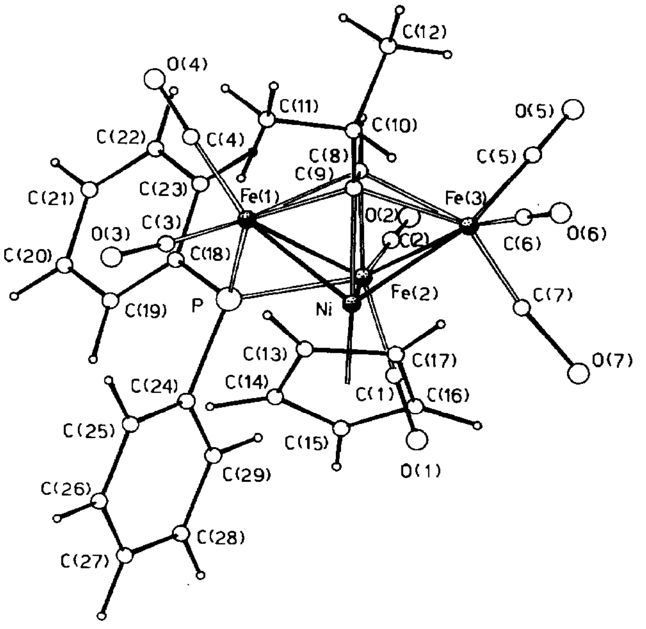

Fig. 1. Perspective view of the structure of the complex $(\eta^5\text{-}C_5H_5)NiFe_3(CO)_7(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}CH{\equiv}CPr^i)$ (**4b**) with the atomic numbering scheme.

Table 4

Selected bond distances (Å) and angles (°)

Fe(1)-Fe(2)	2.445(3)	Fe(2)-C(8)	2.031(14)
Fe(2)-Fe(3)	2.484(3)	Ni-C(9)	1.931(13)
Fe(1)-Ni	2.482(3)	Fe(1)-C(8)	1.988(12)
Fe(2)-Ni	2.561(3)	Fe(1)-C(9)	2.093(12)
Fe(3)-Ni	2.436(2)	Fe(3)-C(8)	2.037(13)
Fe(1)-P	2.145(4)	Fe(3)-C(9)	2.089(14)
Fe(2)-P	2.187(4)	C(8)-C(9)	1.436(16)
Fe(1)-C(3)	1.745(14)	C(1)-O(1)	1.153(23)
Fe(1)-C(4)	1.737(16)	C(2)-O(2)	1.099(17)
Fe(2)-C(1)	1.766(18)	C(3)-O(3)	1.149(17)
Fe(2)-C(2)	1.781(14)	C(4)-O(4)	1.171(19)
Fe(3)-C(5)	1.765(14)	C(5)-O(5)	1.116(18)
Fe(3)-C(6)	1.710(19)	C(6)-O(6)	1.164(25)
Fe(3)-C(7)	1.733(22)	C(7)-O(7)	1.185(27)
Fe(2)-Fe(1)-Ni	62.6(1)	Ni-C(9)-C(8)	103.9(9)
Fe(1)-Fe(2)-Fe(3)	91.4(1)	Fe(2)-C(8)-C(9)	108.9(9)
Fe(1)-Fe(2)-Ni	59.4(1)	Fe(1)-C(3)-O(3)	178(1)
Fe(3)-Fe(2)-Ni	57.7(1)	Fe(1)-C(4)-O(4)	177(1)
Fe(2)-Fe(3)-Ni	62.7(1)	Fe(2)-C(1)-O(1)	179(1)
Fe(1)-Ni-Fe(3)	91.7(1)	Fe(2)-C(2)-O(2)	179(1)
Fe(1)-Ni-Fe(2)	58.0(1)	Fe(3)-C(5)-O(5)	179(1)
Fe(3)-Ni-Fe(2)	59.6(1)	Fe(3)-C(6)-O(6)	179(2)
Fe(1)-P-Fe(2)	68.7(1)	Fe(3)-C(7)-O(7)	172(2)

cyclopentadienyl ligand is η^5-bonded to the Ni atom. The isopropylacetylene molecule interacts in a μ_4,η^2-fashion with all four metal atoms, being σ-bonded to the hinge atoms and π-bonded to the wing-tip atoms through the multiple bond which lies almost parallel to the hinge of the cluster. The isopropyl substituent lies on the same side as the Ni atom, at least in the solid state. The possiblility of isomerism for the complexes **4** was considered above.

Although homometallic butterfly clusters with alkynes coordinated parallel to the hinge are relatively common [18], only a limited number of heterometallic examples has been reported [19–24]. In particular, only one example of phosphido-bridged heterometallic butterfly cluster is known, $RuCo_3(CO)_9(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}HC{\equiv}CBu^t)$ [19]; this also has the heterometal on the hinge, and the phosphido bridge in a position comparable to that found in **4b**.

Finally **4b** is, to our knowledge, the first example of tetra-heteronuclear cluster with Fe_3Ni stoichiometry. The previously reported tetranuclear Fe–Ni derivatives, namely the tetrahedral $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_7$ [9a], the square planar $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(RC_2R')$, including complexes **2** [9d], the spiked triangular complexes **3** [8b], and $(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(C_5H_6)$ [10c,d], all have Ni_2Fe_2 cores.

Some general remarks

The structures of the complexes discussed above can partly account for the low selectivity observed in the reactions described. Thus, the clusters **1–6** are formed via several competitive or concomitant processes such as: (i) C–P bond cleavage in the phosphino-alkynes; (ii) Ni–Ni and Fe–Fe bond cleavage and condensation of the fragments formed; (iii) reductive coupling of hydrogen and acetylides; and (iv) transfer of cyclopentadienyl and CO from nickel to iron with formation of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and nickelocene.

C–P bond cleavage in coordinated phosphino-alkynes is well known [7]; reductive coupling of hydrocarbyl fragments with (coordinated) hydrogen has been recently observed for other homo- and hetero-metallic phosphido-bridged clusters [6d,25], and is apparently a general feature of the chemistry of these species.

The question of the origin of the hydrogen necessary to form the acetylene ligands of the complexes **2** and **4** merits consideration. It cannot come from moisture in the $Fe_3(CO)_{12}$, present as a consequence of the preparative procedure used [11], since the complexes are also obtained when dried $Fe_2(CO)_9$ is used. We have observed, however, that nickel-containing clusters such as $(\eta^5\text{-}C_5H_5)NiM_3H_3(CO)_9$ (M = Ru, Os) can dehydrogenate saturated and unsaturated hydrocarbons under heterogeneous conditions [26], and nickel alloys are commonly used for hydrogen storage purposes [27]. Thus the most probable origin of the hydrogen is the partial dehydrogenation of the solvent by the considerable amount of nickel powder deposited during the reactions. This could thus be an example of a reaction whose products are formed, in part, because of the presence of heterogeneous material with specific catalytic properties.

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