Reactions of $[Ni_2(\eta\text{-}C_5H_5)_2\{HC_2C(=CH_2)CH_3\}]$ with $[M_3(CO)_{12}]$ (M = Ru or Os) in the Presence of Hydrogen. Synthesis and Crystal Structure of the New Heterotetrametallic Complex $[Ni_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_6\{C_2(H)C(=CH_2)CH_3\}]$ † and Spectroscopic Characterization of a Planar Isomer

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The influence of molecular hydrogen on the title reactions has been studied; different products (and yields) are obtained when this gas is used, instead of nitrogen, as reaction atmosphere. From the reactions of $[Fe_3(CO)_{12}]$ with $[Ni_2(\eta\text{-}C_5H_5)_2\{HC_2C(=CH_2)CH_3\}]$ the new heterometallic complex $[Ni_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_6\{C_2(H)C(=CH_2)CH_3\}]$ is obtained, whose structure has been determined by *X*-ray methods. Crystals are triclinic, space group $P\bar{1}$, with a unit cell of dimensions a = 8.881(7), b = 17.224(12), c = 7.912(7) Å, α = 78.87(4), β = 114.95(6), γ = 91.60(4)°, and Z = 2. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.046 for 2 965 observed reflections. The complex shows a 'spiked-triangular' metal atom frame and the alkyne ligand interacts with all four metals through both triple and double bonds. An isomeric complex has been also characterized and a square-planar structure has been assigned to it on the basis of spectroscopy and by comparison with known compounds. From the reactions of $[Ru_3(CO)_{12}]$ with the same alkyne, instead of the expected $[NiRu_3(\eta\text{-}C_5H_5)(\mu\text{-}H)(CO)_9\{C=C(H)C(=CH_2)CH_3\}]$, the already known $[NiRu_3(\eta\text{-}C_5H_5)(\mu\text{-}H)(CO)_9\{C=C(H)C(H)(CH_3)_2\}]$ complex has been obtained, by consequence of the hydrogenation of the reactant double bond.

The potential utility of heterometallic clusters for the activation of small molecules is currently recognised.[1,2] However, few examples of *cluster-based* catalytic reactions have been reported.[3–5]

We found that some heterohexa- and heterotetra-metallic ruthenium- and osmium–nickel clusters selectively hydrogenate the triple and double bonds under homogeneous conditions,[6] and that 'butterfly' complexes such as $[NiM_3(\eta\text{-}C_5H_5)(\mu\text{-}H)(CO)_9(C=CHR)]$ (M = Ru, R = Bu^t or Pr^i;[7] M = Os, R = Bu^t [8]) (1) were probably intermediates (or side products) of the above reactions.[8]

Following the discovery that molecular hydrogen flow increases considerably the yields of complexes (1) with respect to those obtained under nitrogen, we investigated the effect of this gas on the reactions leading to other heterometallic clusters which could be involved in the hydrogenation of multiple bonds.

By reaction of $[Ni_2(\eta\text{-}C_5H_5)_2(C_2Ph_2)]$ with $[Ru_3(CO)_{12}]$ in the presence of H_2, we could isolate the new complex $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_6(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)]$ (2),[9] not obtained in the presence of N_2; we proposed that the effect of H_2, amongst other things, was that of favouring the Ni–Ni bond breaking, hence giving higher yields of complexes containing $Ni(\eta\text{-}C_5H_5)$ 'fragments' not bonded to each other.

We then investigated the reactions of the nickel-co-ordinated isopropenylalkyne ligand; this ligand is of interest for a study of the selective hydrogenation of conjugated double and triple bonds, in the presence of clusters. In an attempt to obtain the 2-methylbut-1-en-3-yne homologue of the chiral cluster $[NiRu_2(\eta\text{-}C_5H_5)_2(CO)_3(\mu_3\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)]$ (3) [10] (by operating under N_2), we obtained the complex $[Ni_2Ru_2(\eta\text{-}C_5H_5)_2\{C_2(H)C(=CH_2)CH_3\}]$ (4), as main reaction product; this complex shows an uncommon 'spiked-triangular' metal atom frame and its structure has been determined by *X*-ray methods.[11]

Here we report the reactions of $[Fe_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ with $[Ni_2(\eta\text{-}C_5H_5)_2\{HC_2C(=CH_2)CH_3\}]$ (5) under hydrogen; among other derivatives, we have obtained the complex $[Ni_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_6\{C_2(H)C(=CH_2)CH_3\}]$ (6) and the isomeric complex $[Ni_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_6\{HC_2C(=CH_2)CH_3\}]$ (7).

The structure of the 64-electron 'spiked-triangular' complex (6) has been determined by *X*-ray diffraction; this structure is comparable with that of the homologue (4) but some significant differences have been found for the presence of an unsymmetrically bridging carbonyl on the metal triangle.

The structure of the 62-electron complex (7) is proposed on the basis of spectroscopy and for comparison with the established structure of $[Ni_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_6(C_2Et_2)]$.[12] The formation of these isomers is discussed, together with the influence of hydrogen on their yields, and on the other products containing iron or ruthenium. A comparison of the structural parameters of the 'spiked-triangular' clusters (4) and (6) with those of some other similar complexes is also made.

Experimental

Conventional glass apparatus was used for the syntheses of the complexes. The iron and ruthenium carbonyls were prepared by established procedures; $HC{\equiv}CC(=CH_2)CH_3$ (Fluka)

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† 3,3,3,4,4,4-Hexacarbonyl-1,2-bis(η-cyclopentadienyl)-μ_4-[1′–4′-η-3′-methylbutenyl-1′-ylidyne-$C^{1'}$(Ni^{1,2}, Fe^3), $C^{1'-4'}$(Fe^4)]-dinickeldiiron(*Ni–Ni*)(2 *Ni–Fe*^{3})(*Fe–Fe*).

Supplementary data available (No. SUP 23886, 22 pp.): H-atom coordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses, for the non-hydrogen atoms

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni(1)	5 278(1)	3 004(1)	12 504(1)	C(7)	3 493(9)	2 363(4)	11 616(10)
Ni(2)	2 552(1)	3 409(1)	10 291(2)	C(8)	2 872(9)	1 809(5)	12 689(12)
Fe(1)	4 157(1)	2 543(1)	9 583(2)	C(9)	1 467(10)	1 377(5)	11 761(13)
Fe(2)	3 435(1)	1 098(1)	11 184(2)	C(10)	858(10)	1 460(6)	9 777(13)
O(1)	4 882(10)	4 178(4)	8 713(11)	C(11)	738(12)	828(6)	12 906(15)
O(2)	1 920(9)	2 643(6)	5 600(10)	C(12)	6 830(13)	2 603(6)	15 377(12)
O(3)	7 339(8)	2 048(5)	9 807(11)	C(13)	7 799(10)	2 726(7)	14 336(15)
O(4)	3 103(11)	−571(4)	12 379(14)	C(14)	7 600(11)	3 529(7)	13 478(15)
O(5)	3 443(12)	815(6)	7 730(12)	C(15)	6 510(12)	3 906(7)	13 922(13)
O(6)	7 024(8)	872(4)	13 603(11)	C(16)	6 029(12)	3 333(6)	15 118(14)
C(1)	4 498(13)	3 559(6)	9 272(14)	C(17)	12(10)	3 728(7)	8 684(20)
C(2)	2 791(11)	2 572(6)	7 180(12)	C(18)	351(14)	3 567(7)	10 573(22)
C(3)	6 063(11)	2 228(6)	9 675(12)	C(19)	1 461(15)	4 091(8)	11 414(18)
C(4)	3 203(12)	100(6)	11 897(15)	C(20)	1 854(13)	4 574(6)	10 081(22)
C(5)	3 455(12)	994(6)	9 041(15)	C(21)	969(16)	4 367(7)	8 360(19)
C(6)	5 647(11)	975(5)	12 669(14)				

and nitrogen and hydrogen (SIAD) were commercial products. The purity of the alkyne was checked by ^1H n.m.r. spectroscopy. The gases and hydrocarbon solvents were dried before use.

Complex (5) was obtained as already reported for its homologues,[13] by refluxing $[\{Ni(\eta-C_5H_5)(CO)\}_2]$ with a 1.5 molar excess of $HC\equiv CC(=CH_2)CH_3$ in heptane, or octane, under an inert atmosphere (N_2 or H_2) until the disappearance of ν(CO) of the $[\{Ni(\eta-C_5H_5)(CO)\}_2]$ (i.r. monitoring). In the presence of H_2 as reaction atmosphere we did not obtain hydrogenated products, nor decomposition, and the yields and reaction times were comparable with those observed under nitrogen; instead, under hydrogen *flow*, hydrogenation and decomposition occur to an appreciable extent.

The reaction mixtures containing (5) were allowed to cool in the inert atmosphere; then the iron or ruthenium carbonyl was added, and the solutions allowed to reflux either under a nitrogen atmosphere, or a hydrogen *flow*.

Treatment of (5) with equimolar amounts of $[Fe_3(CO)_{12}]$ {the amount of $[Fe_3(CO)_{12}]$ was calculated by assuming a 100% yield of complex (5)} in refluxing heptane, under N_2 for 40 min, leads to the formation of the following products (averaged yields, calculated on iron, in parentheses): unreacted $[Fe_3(CO)_{12}]$ (5%), $[\{Fe(\eta-C_5H_5)(CO)_2\}_2]$ (10%), $[Fe_2(CO)_6(C_5H_6)_2]$ (10%), complex (6) (15%), complex (7) (20%), and three trace products, still under investigation. The same reaction, under hydrogen flow, led to the deposition of a thick nickel mirror on the glass vessel and to the products $[\{Fe(\eta-C_5H_5)(CO)_2\}_2]$ (10%), $[Fe_2(CO)_6(C_5H_6)_2]$ (3%), complex (6) (10—15%), complex (7) (40%) and to a still unidentified trace product.

Reflux of a 3 : 1 molar excess of $HC\equiv CC(=CH_2)CH_3$ with $[Ni_2Fe_2(\eta-C_5H_5)_2(CO)_6(\mu_3-CO)]$[12] in benzene, for 15 min under N_2, leads to 30% of unaltered starting cluster, *ca.* 25% of complex (7), and to some decomposition.

Treatment of (5) with equimolar amounts of $[Ru_3(CO)_{12}]$ in refluxing octane, for 20 min under N_2 leads to $[\{Ru(\eta-C_5H_5)(CO)_2\}_2]$ (5%), complex (4) (40%), and trace amounts of other derivatives.[11] Under the same conditions, with hydrogen flow, we obtained $[NiRu_3(\eta-C_5H_5)(\mu-H)_3(CO)_9]$[6] (20%), $[NiRu_3(\eta-C_5H_5)(\mu-H)(CO)_9\{C=C(H)C(H)(CH_3)_2\}]$[7] (1b) (10%), complex (4) (15%), and two still unidentified products in small amounts; on increase of the reaction time to 40 min, another dark blue cluster in *ca.* 5% yield was obtained; this complex is still under investigation.

The reaction mixtures were filtered under nitrogen and evaporated under reduced pressure, dissolved in $CHCl_3$, and fractionated on preparative t.l.c. plates [Kieselgel G, Merck; light petroleum (b.p. 40–70 °C) and diethyl ether mixtures (90 : 10) as eluants].

The complexes were crystallized from saturated heptane–chloroform solutions and kept for days at −10 °C under nitrogen. Satisfactory elemental analyses were obtained for all the complexes on an F & M 185 (C, H, N) analyser and on a Perkin-Elmer 303 AAS.

Physical Measurements.—The i.r. spectra were recorded on a Perkin-Elmer 580 B instrument (KBr optics); the ^1H n.m.r. spectra were obtained on JEOL C 60 HL and on Varian XL 100 instruments; the ^{13}C n.m.r. spectra were recorded either on Varian XL-100 and Bruker 200-MHz machines (the latter from the University of Strasbourg). The e.s.r. spectra were obtained on a Varian E 109.

The mass spectra were obtained on a Hitachi–Perkin-Elmer RMU 6H single-focusing instrument, operating at 70 eV and equipped with a direct inlet system. The analyses were performed at the lowest temperature compatible with the volatility of the samples; however, in some instances, decomposition was observed.

Crystallographic Data Collection for (6).—A black irregularly shaped crystal of (6), having approximate dimensions 0.22 × 0.25 × 0.30 mm, was used for the data collection. The cell parameters were obtained from a least-squares procedure applied to the θ values of 30 reflections accurately measured on a Siemens AED single-crystal diffractometer.

Crystal data. $C_{21}H_{16}Fe_2Ni_2O_6$, $M = 593.47$, triclinic, $a = 8.881(7)$, $b = 17.224(12)$, $c = 7.912(7)$ Å, $\alpha = 78.87(4)$, $\beta = 114.95(6)$, $\gamma = 91.60(4)°$, $U = 1\,075(2)$ Å^3, $Z = 2$, $D_c = 1.834$ g cm^{-3}, $F(000) = 596$, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 30.94$ cm^{-1}, space group $P\bar{1}$ from structure determination.

A complete set of intensity data was collected, with θ in the range 3—27°, on the same diffractometer using Nb-filtered Mo-K_α radiation and the θ/2θ scan technique. Of a total of 4 347 independent reflections, 2 965 having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis. One reflection was remeasured after 50 reflections as a check on crystal and instrument stability; no significant change in the measured intensity of this reflection was observed during the data collection.

The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established by Wilson's method. No correction for absorption effects was applied in view of the low absorbance of the sample.

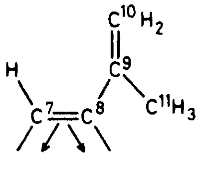
The structure was solved by Patterson and Fourier methods and the refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs[14] with first isotropic and then anisotropic thermal parameters for all non-hydrogen atoms. A difference-Fourier map revealed clearly the positions of all the hydrogen atoms excepting those of the two cyclopentadienyl ligands which were placed in their geometrically calculated positions and included in the final structure factor calculations. The function minimized in the least-squares was $\Sigma w|\Delta F|^2$; unit weights were used at each stage of the refinement by analysing the variation of $|\Delta F|$ as a function of $|F_o|$. The atomic scattering factors (corrected for anomalous dispersion of Fe and Ni) were taken from ref. 15. The final R value was 0.046 (observed reflections only). The atomic fractional co-ordinates for the non-hydrogen atoms are given in Table 1. Calculations were performed on the CYBER 7600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Results and Discussion

Spectroscopic Characterization.—*Complex* (6). The i.r. spectrum of (6) (hexane solution) shows ν(CO) at 2 047vs, 1 999vs, 1 954m br, and 1 785w cm^{-1}. The H n.m.r. spectrum (CDCl$_3$) shows signals at δ 6.80 (s, H^8), 5.20 (s, C_5H_5), 5.10 (s, C_5H_5), 2.40 (s, CH_3), and 2.0—1.40 (s, $H^{101,102}$), integrated intensities 1 : 5 : 5 : 3 : 1 : 1. The ^{13}C n.m.r. of the complex [CDCl$_3$ solution, tris(acetylacetonato)chromium(III) as shift relaxation reagent, downfield positive with respect to SiMe$_4$] shows signals at 25.4 (C^{11}), 48.1 (C^{10}), 89.7 and 91.2 (slightly inequivalent C_5H_5 groups), 141.1 (C^9), 236.0 and 237.1 (two inequivalent sets of CO groups), 267.0 and 287.3; these two latter signals are attributed to the μ_3-CO and C^7. The data for complex (4), for comparison, are as follows. I.r. spectrum (C_6H_{14} solution): 2 068vs, 2 020vs, 2 008s, 1 995s, and 1 960vs cm^{-1}. This is well comparable with that of (6), but for the band at 1 785 cm^{-1}, attributed to a bridging CO. ^{1}H N.m.r. (CDCl$_3$): δ 6.5 (s, H^8), 4.96 (s, C_5H_5), 4.92 (s, C_5H_5), 2.35 (s, CH_3), 2.15—1.40 (s, $H^{101,102}$). In the ^{13}C n.m.r. (previously not reported) only the following signals, downfield positive with respect to SiMe$_4$, were observed (CDCl$_3$): δ 23.76 (CH_3), 46.71 (CH_2), 82.21 (C^8), 89.01 (C_5H_5), 114.73 (C^9). The CO and C^7 signals were not observed, probably because of their very low intensity.

Complex (4) decomposes in the mass spectrometer, whereas (6) gives the parent ion at m/e 592, then loss of six carbonyls and two cyclopentadienyl groups, then complex fragmentation of the organic moiety, and loss of CH$_4$.

Complex (7). In the i.r. spectrum (C_6H_{14} solution) ν(CO) is observed at 2 010vs and 1 968vs br cm^{-1}; in the ^{1}H n.m.r. (CDCl$_3$) signals at δ 6.80 (s, 1 H), 5.30 (s, 5 H), 5.25 (s, 5 H), 2.40 (d, 2 H), and 2.0 (s, br, 3 H), in integrated intensities 1 : 5 : 5 : 2 : 3 are observed. In the ^{13}C n.m.r. [registered under the same conditions as (6); complex (7) slightly decomposes when left in solution] a lower number of signals than for (6) was observed, as expected; these are at 26.0 (C^{11}) (see diagram below), 59.8 (C^{10}), 91.4 (equivalent C_5H_5 ligands), 137.6 (C^9), 231.0 and 236.2 (slightly inequivalent CO groups, probably axially and equatorially bound), 267.8 and 287.5 (inequivalent acetylenic carbons bearing different substituents; C^7 and C^8).



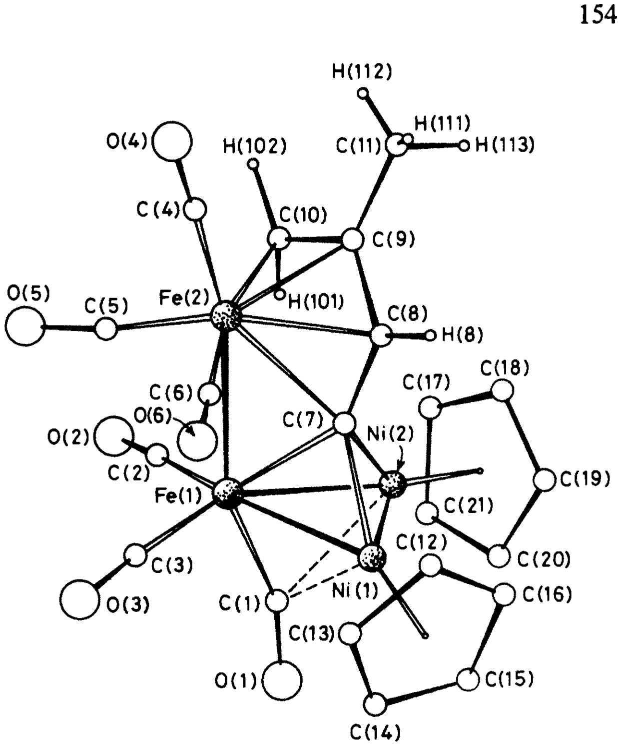


Figure 1. View of the molecular structure of the complex [Ni$_2$Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_6${C$_2$(H)C(=CH$_2$)CH$_3$}] showing the atomic numbering scheme

In the mass spectrum of complex (7) the highest signal is observed at m/e 538, corresponding to [Ni$_2$Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4${HC$_2$C(=CH$_2$)CH$_3$}] with an isotopic pattern of Fe$_2$Ni$_2$; then release of 4 CO groups is observed, and finally complex decomposition involving release of C$_5$H$_5$ units and organic fragments. This behaviour is consistent with the reported spectra of complexes homologous to (7).[12b]

The dark blue colour and the spectroscopic properties of (7) correspond to those found for [Ni$_2$Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_6$(C$_2$R$_2$)] [R = C(=CH$_2$)CH$_3$] [12] complexes; on this basis we propose for (7) a square-planar structure with the non-isomerized alkyne co-ordinated to two nickel atoms *via* σ bonds, and to two iron atoms *via* π bonds. The effective atomic number (e.a.n.) count for these complexes, when considering the alkyne as a formal four-electron donor is 62 electrons; the skeletal electron count (s.e.c.) gives a six-vertices, eight-electron-pair ' *nido* ' structure.

Complex (1b). Finally, the spectroscopic properties, mass spectral behaviour, and colour of (1b) were found to be the same as for [NiRu$_3$(η-C$_5$H$_5$)(μ-H)(CO)$_9$(C=CHPr^i)].[7b] Also the cell parameters of a crystal of this complex were identical to those obtained for the isopropyl derivative; hence the identity of the complexes has been confirmed.

Crystal Structure of Complex (6).—The structure of (6) is shown in Figure 1 together with the atomic numbering scheme. Bond distances and angles are given in Table 2.

The complex consists of a ' spiked-triangular ' metal cluster where an isosceles triangle is formed by two nickel and one iron atom, Fe(1), with another iron atom, Fe(2), apically bound to Fe(1). Each Ni atom η-co-ordinates a cyclopentadienyl ligand; of the six carbonyl groups, five [three on Fe(2) and two on Fe(1)] are terminal, the sixth asymmetrically

Table 2. Bond distances (Å) and angles (°)

(*a*) In the co-ordination sphere of the metal atoms

Ni(1)–Ni(2)	2.337(3)	Ni(1)–C(7)	1.868(8)	Fe(1)–C(3)	1.760(10)	Fe(2)–C(7)	2.266(8)
Ni(1)–Fe(1)	2.384(2)	Ni(2)–C(1)	2.184(13)	Fe(1)–C(7)	1.905(8)	Fe(2)–C(8)	2.066(9)
Ni(2)–Fe(1)	2.384(3)	Ni(2)–C(7)	1.913(7)	Fe(2)–C(4)	1.738(11)	Fe(2)–C(9)	2.073(10)
Fe(1)–Fe(2)	2.755(3)	Fe(1)–C(1)	1.755(11)	Fe(2)–C(5)	1.747(11)	Fe(2)–C(10)	2.128(10)
		Fe(1)–C(2)	1.763(9)	Fe(2)–C(6)	1.807(11)		

Ni(2)–Ni(1)–Fe(1)	60.7(1)	Fe(2)–Fe(1)–C(2)	99.2(3)	C(7)–Fe(1)–Ni(1)	50.1(2)	C(6)–Fe(2)–C(8)	96.5(4)
Fe(1)–Ni(2)–Ni(1)	60.7(1)	Fe(2)–Fe(1)–C(3)	97.0(3)	C(7)–Fe(1)–Ni(2)	51.5(2)	C(6)–Fe(2)–C(9)	131.0(4)
Fe(2)–Fe(1)–Ni(1)	93.7(1)	Fe(2)–Fe(1)–C(7)	54.6(2)	C(4)–Fe(2)–C(5)	94.9(5)	C(6)–Fe(2)–C(10)	166.6(4)
Fe(2)–Fe(1)–Ni(2)	100.1(1)	C(1)–Fe(1)–C(2)	95.2(5)	C(4)–Fe(2)–C(6)	91.1(5)	C(6)–Fe(2)–Fe(1)	84.7(3)
Ni(1)–Fe(1)–Ni(2)	58.7(1)	C(1)–Fe(1)–C(3)	95.9(5)	C(4)–Fe(2)–C(8)	112.7(4)	C(7)–Fe(2)–C(8)	37.6(3)
Ni(2)–Ni(1)–C(7)	52.7(2)	C(1)–Fe(1)–C(7)	103.7(4)	C(4)–Fe(2)–C(9)	88.9(5)	C(7)–Fe(2)–C(9)	69.0(3)
Fe(1)–Ni(1)–C(1)	43.5(3)	C(1)–Fe(1)–Ni(1)	67.3(3)	C(4)–Fe(2)–C(10)	97.0(5)	C(7)–Fe(2)–C(10)	78.9(3)
Fe(1)–Ni(1)–C(7)	51.5(2)	C(1)–Fe(1)–Ni(2)	61.5(4)	C(4)–Fe(2)–Fe(1)	166.3(4)	C(7)–Fe(2)–Fe(1)	43.2(2)
C(1)–Ni(1)–C(7)	85.3(4)	C(2)–Fe(1)–C(3)	102.0(4)	C(5)–Fe(2)–C(6)	98.8(5)	C(8)–Fe(2)–C(9)	40.3(3)
Fe(1)–Ni(2)–C(1)	44.9(3)	C(2)–Fe(1)–C(7)	124.2(4)	C(5)–Fe(2)–C(7)	114.8(4)	C(8)–Fe(2)–C(10)	70.5(4)
Fe(1)–Ni(2)–C(7)	51.2(2)	C(2)–Fe(1)–Ni(1)	155.4(3)	C(5)–Fe(2)–C(8)	148.0(4)	C(8)–Fe(2)–Fe(1)	80.7(3)
C(1)–Ni(2)–C(7)	89.1(4)	C(2)–Fe(1)–Ni(2)	98.3(3)	C(5)–Fe(2)–C(9)	130.0(5)	C(9)–Fe(2)–C(10)	39.1(4)
C(1)–Ni(2)–Ni(1)	62.6(3)	C(3)–Fe(1)–C(7)	126.8(4)	C(5)–Fe(2)–C(10)	91.1(5)	C(9)–Fe(2)–Fe(1)	103.6(3)
C(7)–Ni(2)–Ni(1)	50.9(2)	C(3)–Fe(1)–Ni(1)	97.0(3)	C(5)–Fe(2)–Fe(1)	72.9(4)	C(10)–Fe(2)–Fe(1)	89.7(3)
Fe(2)–Fe(1)–C(1)	158.2(4)	C(3)–Fe(1)–Ni(2)	150.9(3)	C(6)–Fe(2)–C(7)	88.7(3)		

(*b*) In the carbonyl groups

O(1)–C(1)	1.172(13)	O(3)–C(3)	1.140(13)	O(5)–C(5)	1.134(14)
O(2)–C(2)	1.143(11)	O(4)–C(4)	1.158(13)	O(6)–C(6)	1.128(13)

Ni(1)–C(1)–Ni(2)	61.9(3)	Ni(1)–C(1)–O(1)	124.4(8)	Fe(1)–C(2)–C(2)	175.5(10)	Fe(2)–C(5)–O(5)	170.2(10)
Ni(1)–C(1)–Fe(1)	69.2(3)	Ni(2)–C(1)–O(1)	123.6(9)	Fe(1)–C(3)–O(3)	176.3(9)	Fe(2)–C(6)–O(6)	177.7(8)
Ni(2)–C(1)–Fe(1)	73.6(4)	Fe(1)–C(1)–O(1)	160.9(10)	Fe(2)–C(4)–O(4)	177.6(11)		

(*c*) In the organic ligands

C(7)–C(8)	1.410(12)	C(12)–C(13)	1.409(15)	C(14)–C(15)	1.376(16)	C(18)–C(19)	1.363(19)
C(8)–C(9)	1.427(13)	C(12)–C(16)	1.399(15)	C(15)–C(16)	1.417(15)	C(19)–C(20)	1.372(20)
C(9)–C(10)	1.407(13)	C(13)–C(14)	1.398(17)	C(17)–C(18)	1.366(21)	C(20)–C(21)	1.367(20)
C(9)–C(11)	1.505(15)			C(17)–C(21)	1.422(18)		

Ni(1)–C(7)–Ni(2)	76.3(3)	Fe(1)–C(7)–Fe(2)	82.2(3)	C(9)–C(8)–Fe(2)	70.1(5)	C(11)–C(9)–Fe(2)	126.3(7)
Ni(1)–C(7)–Fe(1)	78.4(3)	C(8)–C(7)–Ni(1)	128.1(6)	C(9)–C(8)–C(7)	120.4(8)	C(11)–C(9)–C(8)	120.2(8)
Ni(1)–C(7)–Fe(2)	130.6(4)	C(8)–C(7)–Ni(2)	126.4(6)	C(10)–C(9)–C(11)	122.2(9)	Fe(2)–C(9)–C(8)	69.5(5)
Ni(2)–C(7)–Fe(1)	77.3(3)	C(8)–C(7)–Fe(1)	145.2(6)	C(10)–C(9)–Fe(2)	72.5(6)	Fe(2)–C(10)–C(9)	68.4(5)
Ni(2)–C(7)–Fe(2)	141.5(4)	C(8)–C(7)–Fe(2)	63.5(4)	C(10)–C(9)–C(8)	117.5(8)		

triply bridges the metal triangle. In the similar complex (4) all the carbonyl groups were terminal. Finally, an isomerized 2-methylbut-1-en-3-yne ligand, with the hydrogen shifted from C(7) to C(8), interacts with all the metals.

The spiked-triangular arrangement of metal atoms is rather rare in cluster chemistry and only in recent years has an increasing number of examples been reported, among them the homometallic $[ReH_4(CO)_{15}]^{2-}$ [16] and $[Fe_4(CO)_{12}(CS)S]$ (8) [17] and the heterometallic $[Mo_2Co_2(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)]$ (9).[18]

Two kinds of spiked-triangular complex are found; those in which the ' spike ' lies in the same plane of the clusters, and those in which it is perpendicular to the triangle. The above mentioned examples, as well as complexes (4) and (6), present spikes ' out-of-plane '. A comparison of the more significant structural parameters for the related clusters (4), (6), (8), and (9) is given in Table 3.

All the complexes except (9), in which a double Mo–Mo bond is proposed, show short metal–metal distances in the triangle and long or very long metal–metal distances in the ' spike '. In particular, for (6) an Fe–Fe distance of 2.755(3) Å is found in the spike whereas the Fe–Ni and Ni–Ni distances are 2.384(3) and 2.337(3) Å respectively in the triangle.

The co-ordination of the alkyne-derived ligand is noteworthy and is similar to that found in (4). The four adjacent carbon atoms C(7),C(8),C(9),C(10) are involved in extensive η-bonding with Fe(2) (distances ranging from 2.066 to 2.266 Å), and C(7) also caps the metal triangle interacting with Fe(1), Ni(1), and Ni(2) through three σ bonds [distances 1.905(8), 1.868(8), and 1.913(7) Å respectively]. The M–C(7)–M angles are comparable to those found for apically bound CR (R = alkyl or aryl) ligands on triangular clusters.[19]

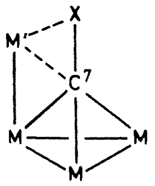
The bonding of C(7) and C(8) in (6) is strictly comparable with that of the thiocarbonyl CS in (8) and of the carbonyl in (9), both these ligands capping a triangular frame and interacting with the ' spike '.

Extensive delocalization of the former triple and double bonds of the alkyne is observed in the tetra-atomic carbon chain C(7)—C(10), as shown by the C–C bond distances in the range 1.407—1.427 Å.

The complexes (4) and (6) are 64-electron species when considering the alkyne as a six-electron donor (both double and triple bonds being involved in metal–carbon interactions). Indeed, they are diamagnetic both in the solid state and in solution.

The C(1)–O(1) carbonyl in (6) is not terminal. The distances Fe(1)–C(1), Ni(2)–C(1), and Ni(1)–C(1) are 1.755(11), 2.184(13), and 2.352(10) Å respectively, with an angle Fe(1)–

Table 3. Significant bond distances (Å) and angles (°) in (6) and in structurally related compounds



Complex	M–M (cluster)	M–M′ (spike)	M–M–M′	M–C^7	M′–C^7	M–C^7–M	C^7–X	Ref.
(4) [a]	2.515(6) [b]	2.960(5) [c]	91.4(1)	2.06(2) [d]	2.46(3) [d]	79(1)	1.45(4) [e]	11
	2.495(5) [b]		94.7(1)	1.83(3) [f]		80(1)		
	2.368(5) [g]			1.85(3) [f]		80(1)		
(6)	2.384(3) [h]	2.755(3) [i]	100.1(1)	1.905(8) [j]	2.266(8) [j]	76.3(3)	1.410(12) [e]	This work
	2.384(2) [h]		93.7(1)	1.868(8) [f]		77.3(3)		
	2.337(3) [g]			1.913(7) [f]		78.4(3)		
(8)	2.564(2) [k]	2.710(2)	110.8(1)	1.971(5) [k]	2.706(6)	78.6(2)	1.695(5) [l]	17
			109.4(1)			82.9(2)		
						81.9(2)		
(9)	2.709(1) [m]	2.574(1) [n]		2.281(3) [o]	2.404(3)		1.283(3) [p]	18
	2.404(1) [q]			1.869(2) [r]				

[a] Averaged values for two independent molecules. [b] Ru–Ni. [c] Ru–Ru. [d] Ru–C. [e] C^7–C. [f] Ni–C. [g] Ni–Ni. [h] Fe–Ni. [i] Fe–Fe. [j] Fe–C. [k] Fe–Fe or Fe–C, averaged values. [l] C^7–S. [m] Mo–Co. [n] Mo–Mo. [o] Mo–C. [p] C^7–O. [q] Co–Co. [r] Co–C.

C(1)–O(1) of 160.9(10)°. This situation is typical of a bent, semi-bridging CO ligand capping the metal triangle on the opposite side with respect to the C(7) carbon. The N(2)–C(2) distance being very long, this carbonyl can be considered either an an asymmetrically doubly bridging CO or as a very asymmetrically triply bridging CO. The value of ν(CO) in solution (1 785 cm^{-1}) is quite high for a triply bridging CO (values around 1 650 cm^{-1} are usual). However, the possibility of isomerism in solution for the CO (passing from triple- to double-bridging behaviour), as discussed for [NiRu$_2$-(η-C_5H_5)$_2$(CO)$_4$(C_2Ph_2)],[10] can be discarded on the basis of the quite low-field signal observed in the ^{13}C n.m.r. for this carbonyl.

In the similar complex (4) no bridging CO was observed, in particular the Ru(1)–C(1)–O(1) angle was found to be quite linear and both Ni–C(1) distances are very long.

The presence of the bridging CO in (6) makes it more comparable with (8), in which a sulphur atom bridges the metal triangle in a position similar to that of C(1)O(1).

Some Comments on the Formation of the Complexes (1b), (4), *and* (6), *and on the Isomerism within* (6) *and* (7).—*Complex* (1b). In the reactions described above, 2-methylbut-1-en-3-yne ligand displays different behaviour in its co-ordination to the metals, as well as in the hydrogenation-isomerization. Besides the Ni–Ni bond breaking, favouring the formation of (1b), the effect of H_2 is the hydrogenation of the isopropenyl group double bond. This is noteworthy, when considering that usually the C–C triple bonds are hydrogenated with greater facility. The possible explanation of this behaviour is that the co-ordination of the alkyne to the metal frame occurs first, and then oxidative addition of hydrogen occurs only on the 'exposed' double bond. Indeed, in comparable Fe_4 cluster frames, several reactions are observed which do not affect the α-carbon.[20]

Complexes (4) *and* (6). The influence of the hydrogen on the yields of these complexes is considerable; for (4) in particular, a sharp decrease is observed when H_2 is used. The negative effect of the hydrogen in the formation of spiked triangular clusters containing four metal–metal bonds is noteworthy; metal–metal bond hydrogenolysis would be expected. Instead, at least for iron, square-planar clusters are formed preferentially.

The majority of the reaction paths leading to heterometallic clusters are unexplored; however, at least for homometallic compounds, the reaction sequence shown in Figure 2 [21] is generally accepted.

This sequence has not been seen for the same cluster *family* (*i.e.* with the same substituents or the same metal core); however, much indirect evidence points to it. The electronic situation of the intermediate cluster frames ('flat butterflies', 'lozenge', and square-planar clusters) is far from being homogeneous and clearly understandable. * It is generally accepted that addition of ligands to 60-electron tetrahedral frames produces 62-electron butterflies, and then, by flattening, metal–metal bond cleavage, and rearrangement, to in-plane spiked triangular 64-electron clusters; on the other hand, edge-breaking in the presence of ligands would lead from butterfly clusters to 64 electron out-of-plane spiked-triangular clusters.

Hence, the out-of-plane clusters (4) and (6) would derive from hypothetical Ni_2M_2 tetrahedral frames; however, we were not able to obtain a Ni_2Ru_2 tetrahedron, and, moreover, reacting [Ni_2Fe_2(η-C_5H_5)$_2$(CO)$_7$] with HC≡CC(=CH_2)CH_3, we obtained the planar complex (7) instead of (6) (see Experimental section).

An alternative hypothesis for the formation of complexes (4) and (6) could be the 'condensation' of fragments, as recently reported by Vahrenkamp and Wucherer.[22] Indirect evidence for this hypothesis also comes from the synthesis of complex (9) from dicobalt and dimolybdenum species.

The isomerism of complexes (6) and (7) could be accounted for either by the 'butterfly hypothesis' or by the 'fragment condensation hypothesis'; indeed, alternative cleavage of Ni–Ni or of Fe–Fe bonds in a Ni_2Fe_2 tetrahedron–butterfly sequence would account for either of the complexes, and for the observed effect of hydrogen (easier Ni–Ni bond breaking). On the other hand, different stereochemical interaction within Fe_2 and Ni_2 fragments would lead to the complexes (6) or (7);

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* A review on the syntheses and structures of the butterfly clusters is in preparation by A. J. Carty, E. Sappa, and A. Tiripicchio.

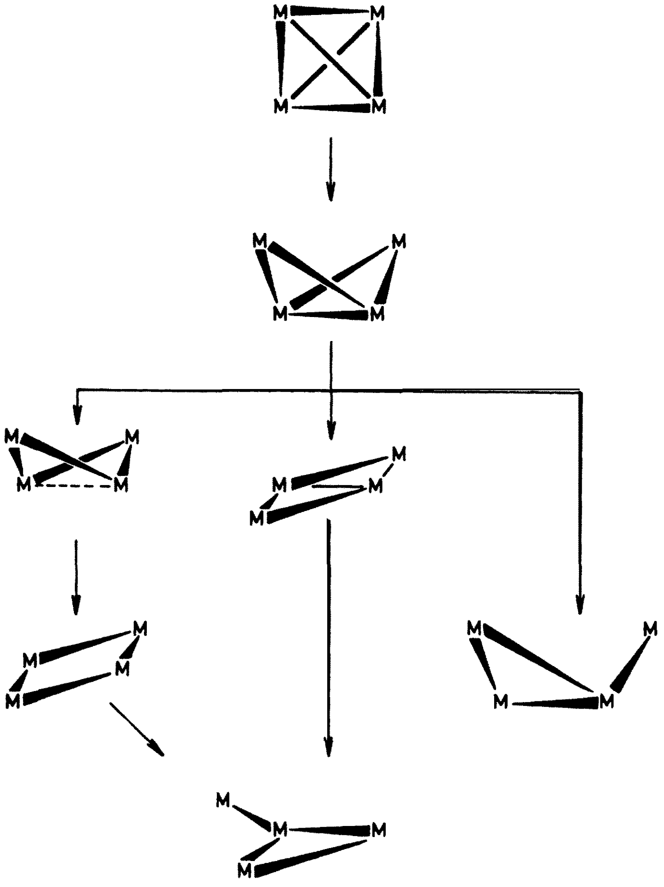

Figure 2. Hypothetical pathway leading from tetrahedral clusters to ' butterfly,' ' lozenge,' square-planar, and ' spiked-triangular ' clusters

the butterfly–lozenge isomerism for $[Mo_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_8S_2]$ complexes has been tentatively explained in this way.[23]

However, differently from the above iron–molybdenum derivatives, complexes (6) and (7) do not have the same electron counts; this can be ascribed to the differing electron-donor properties displayed by 2-methylbut-1-en-3-yne. However, it remains unclear why, during the formation of (7) under hydrogen, no hydrogenation of the C=C bond occurs, as observed in (1b).

Experiments on the formation mechanism of square-planar clusters showing ' unsaturated ' 62-electron counts, and on their expansion reactions, as well as on the possible isomerism, are being investigated at present in our laboratories.

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