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SYNTHESIS AND CRYSTAL STRUCTURE OF THE MIXED CLUSTER (η -C₅H₅)NiFe₂(CO)₆C₂-t-Bu

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Summary

The title complex has been obtained by treating Fe₃(CO)₁₂ with (η -C₅H₅)₂Ni₂-(HC₂t-Bu) in hydrocarbon solvents. The crystals are monoclinic, space group *P*2₁/*a*, with *Z* = 4 in a unit cell of dimensions: *a* = 13.716(9), *b* = 15.806(14), *c* = 8.979(8) Å, β = 104.0(1)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to *R* = 0.048 for 1926 independent observed reflections.

The structure of the complex consists of a triangular arrangement of two Fe and one Ni atoms, bonded to six terminal carbonyls (through Fe atoms only), to a cyclopentadienyl group (through the Ni atom) and to a rearranged t-butyl-acetylene (through all the metal atoms). The bonding of the alkyne to the metal atom cluster is similar to those reported for the homometallic derivatives Fe₃(CO)₉C₂Ph₂, (η -C₅H₅)Fe₃(CO)₇C₂Ph and HRu₃(CO)₉C₂t-Bu. In the cluster the Fe(2)–Ni distance is considerably shorter (2.378 Å) than Fe(1)–Ni (2.564 Å) and Fe(1)–Fe(2) (2.610 Å). Deviations from the E.A.N. formalism are also observed in the present complex.

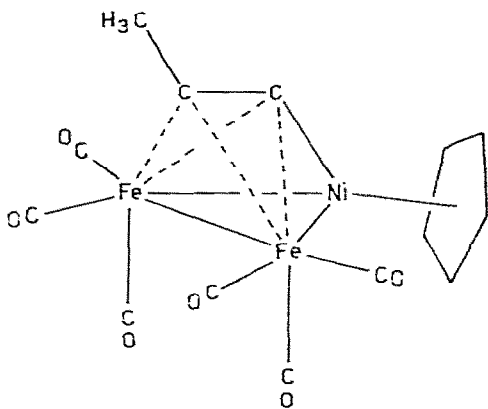
Introduction

Reactions between iron carbonyls and cyclopentadienylnickel derivatives, in presence of alkynes, were reported [1] to yield tri- and tetra-metallic mixed derivatives. By treating (η -C₅H₅)₂Ni₂(HC₂Me) with Fe₃(CO)₁₂ the complexes (η -C₅H₅)NiFe₂(CO)₆(C₂Me) (Ia) and (η -C₅H₅)NiFe₂(CO)₇(CEt) (IIa) were obtained [2], whose structures were proposed on the basis of spectroscopic evidence and the E.A.N. formalism.

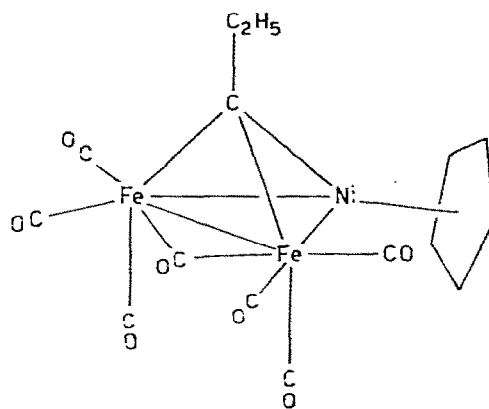
We now report the synthesis and the crystal structure of (η -C₅H₅)-

$\text{NiFe}_2(\text{CO})_6(\text{C}_2\text{t-Bu})$ (Ib). Treatment of 3,3-dimethyl-but-1-yne with $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ gave $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{HC}_2\text{t-Bu})$, and this latter complex reacted with $\text{Fe}_3(\text{CO})_{12}$ to yield Ib, which gives crystals more suitable for the X-ray studies than Ia.

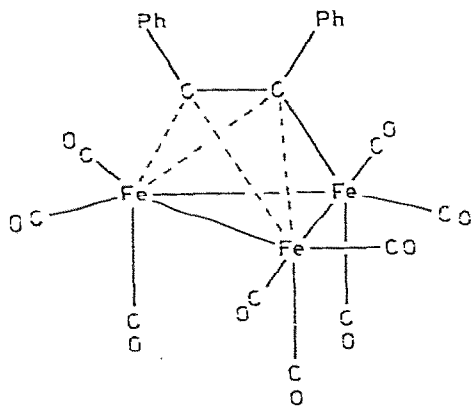
The structure of Ib was found to be different from that proposed for Ia [2]; considerable deviations from the E.A.N. rule are also observed for one iron and for the nickel atom. The structure, in particular the alkyne-carbons bonding to the metal atom cluster, can be compared with those found in $\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)$ (III) [3], $(\eta\text{-C}_5\text{H}_5)\text{Fe}_3(\text{CO})_7(\text{C}_2\text{Ph})$ (IV) [4] and $\text{HRu}_3(\text{CO})_9(\text{C}_2\text{t-Bu})$ (V) [5]. The structures postulated or found for complexes I-V are represented below.



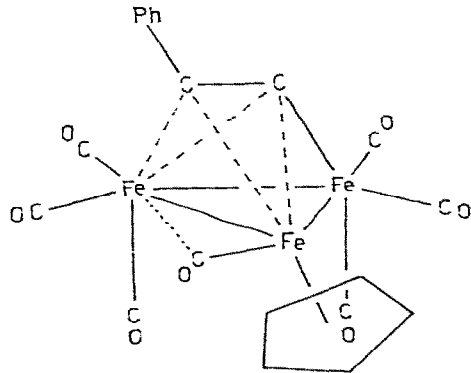
Ia



IIa



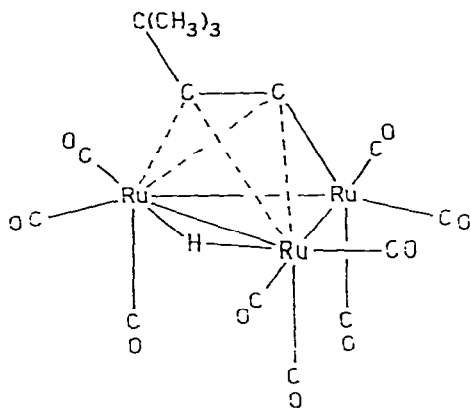
III



IV

Ib is the first example of this type of structure in a mixed complex.

The nature of the $(\eta\text{-C}_5\text{H}_5)\text{Ni}$ entity is noteworthy, as this metal-containing fragment behaves differently in the tetra-metallic $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_6(\text{RC}_2\text{R})$ (VI) [1,6], $(\eta\text{-C}_5\text{H}_5)\text{NiRu}_3(\text{CO})_9\text{C}(\text{H})\text{t-Bu}$ (VII) [7] and $(\eta\text{-C}_5\text{H}_5)\text{NiRu}_3(\text{CO})_8\text{-}(\text{C}_6\text{H}_9)$ (VIII) [8] complexes, occupying different positions in the clusters, and



V

interacting differently with the organic moieties. In particular, it can act as a tri- or tetra-dentate ligand, and sometimes shows deviations from the behaviour expected on the basis of the E.A.N. rule.

The above heterometallic complexes are also of interest because they provide evidence for the ability of the alkynes to promote "condensation" of metal fragments to give clusters.

Experimental

Synthesis and analysis of Ib

Refluxing equimolecular amounts of $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{HC}_2\text{t-Bu})$ and $\text{Fe}_3(\text{CO})_{12}$, under dry nitrogen for 35 min gave 19 products, from which Ib was isolated in 6% yield (on iron) and $(\eta\text{-C}_5\text{H}_5)\text{NiFe}_2(\text{CO})_7(\text{C.CH}_2\text{t-Bu})$ (Iib) in trace amount. For the separation of the products, after evaporation of the solvent under reduced pressure, the residue was dissolved in CHCl_3 and subjected to TLC (Kieselgel P.F. Merck, eluant mixtures of ethyl ether and petroleum ether). The dark-brown Ib was redissolved in n-heptane under nitrogen and the solution was kept -10°C for several days. Black crystals were obtained. These are air-stable for a considerable time.

Ib analyzes as: Found: C, 42.44; Fe, 23.00; H, 3.03; Ni, 12.15; O, 19.38, $\text{C}_{17}\text{Fe}_2\text{H}_{14}\text{NiO}_6$, calcd.: C, 42.13; Fe, 23.04; H, 2.91; Ni, 12.11; O, 19.81%.

IR spectrum (CO stretching, n-heptane solution): 2056vs, 2014vs, 1981vs, 1966s(sh) cm^{-1} . Mass spectrum: parent ion at m/e 484, loss of six CO groups, followed by fragmentation of the cluster (loss of iron) and of the organic moiety.

The complex was analysed by use of an F. & M. 185 model C,H,N, Analyzer, and a Perkin Elmer 303 Atomic Absorption spectrophotometer. The IR spectrum was recorded on a Beckman IR-12 Spectrometer and the mass spectra on a Varian CH-5 single-focusing mass spectrometer (direct inlet system, electron impact ion source, 70 eV).

X-Ray data collection

An irregular flat black crystal of the compound Ib with dimensions of ca.

0.06 × 0.21 × 0.34 mm. was used for the data collection. Preliminary cell parameters obtained by rotation and Weissenberg photographs were subsequently refined by least-squares from the θ values of 16 reflections accurately measured on a Siemens AED single-crystal diffractometer. The crystal data are: monoclinic, $a = 13.716(9)$, $b = 15.806(14)$, $c = 8.979(8)$ Å, $\beta = 104.0(1)^\circ$, $V = 1889(3)$ Å³, $M = 545.78$, $Z = 4$, $D_c = 1.919$ g cm⁻³, Mo- K_α radiation ($\bar{\lambda} = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 25.20$ cm⁻¹, space group $P2_1/a$ from systematic absences.

A total of 3323 independent reflections with $3 < \theta < 25^\circ$ were collected on the same Siemens diffractometer using the Nb-filtered Mo- K_α radiation and the θ - 2θ scan technique. 1926 of these, having $I > 2\sigma(I)$, were regarded observed and the remaining 1397 were excluded from the refinement procedure. One standard reflection was monitored every 20 measurements to ensure that the crystal was neither decomposing nor drifting. The intensity data were reduced to structure factors by standard methods, but no absorption correction was applied because of the low value of μR . The absolute scale and the mean temperature factor were determined by Wilson's methods.

Structure determination and refinement

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 [9] with the first isotropic and then aniso-

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR NON-HYDROGEN ATOMS WITH e.s.d.'s IN PARENTHESES

	x/a	y/b	z/c
Fe(1)	3003(1)	2697(1)	9536(2)
Fe(2)	2210(1)	4192(1)	8870(2)
Ni	1680(1)	3076(1)	7082(1)
O(1)	3754(7)	1091(6)	8675(11)
O(2)	1943(9)	1939(7)	11676(12)
O(3)	4762(7)	3225(7)	11863(11)
O(4)	1017(8)	3778(7)	11092(12)
O(5)	3701(8)	5283(6)	10815(13)
O(6)	780(9)	5493(7)	7473(13)
C(1)	3447(9)	1718(8)	8985(12)
C(2)	2333(10)	2234(8)	10832(18)
C(3)	4067(9)	3001(8)	10974(14)
C(4)	1498(10)	3920(8)	10204(16)
C(5)	3103(10)	4862(8)	10074(14)
C(6)	1357(10)	4986(8)	8009(12)
C(7)	3055(7)	3399(6)	7960(11)
C(8)	2726(7)	3964(6)	6935(12)
C(9)	2993(8)	4449(6)	5623(12)
C(10)	3945(9)	4964(8)	6322(16)
C(11)	2135(10)	5037(9)	4815(16)
C(12)	3202(10)	3790(9)	4460(14)
C(13)	592(10)	2977(9)	4966(17)
C(14)	1164(9)	2221(8)	5244(14)
C(15)	1051(9)	1877(8)	6575(14)
C(16)	411(10)	2419(10)	7243(17)
C(17)	132(9)	3099(10)	6174(18)

TABLE 2
FRACTIONAL COORDINATES ($\times 10^3$) FOR THE HYDROGEN ATOMS

	x/a	y/b	z/c
H(101)	385	538	700
H(102)	414	535	571
H(103)	439	471	670
H(111)	156	466	451
H(112)	212	560	563
H(113)	224	521	385
H(121)	327	410	334
H(122)	260	353	405
H(123)	365	344	492
H(13)	52	339	399
H(14)	156	197	457
H(15)	138	129	706
H(16)	13	233	825
H(17)	-36	354	617

tropic thermal parameters for all the non-hydrogen atoms. A difference Fourier map revealed clearly the positions of all the hydrogen atoms, which were not refined but were introduced into the final structure factor calculations with isotropic thermal parameters ($U = 0.06$ or 0.07 \AA^2). The final conventional R was

TABLE 3
THERMAL PARAMETERS ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS WITH e.s.d.'S IN PARENTHESES. THEY ARE IN THE FORM: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	428(8)	346(8)	352(8)	57(7)	93(7)	25(7)
Fe(2)	457(9)	344(8)	354(8)	-77(7)	56(7)	62(7)
Ni	363(7)	323(7)	346(7)	-32(6)	72(5)	-21(6)
O(1)	1020(74)	494(56)	726(65)	-67(48)	291(55)	114(53)
O(2)	1285(89)	954(80)	897(75)	277(64)	729(71)	-77(73)
O(3)	697(63)	1048(82)	673(64)	-27(59)	-195(52)	-54(61)
O(4)	1027(79)	1113(89)	796(74)	81(64)	583(65)	179(71)
O(5)	1025(85)	703(68)	1169(91)	-495(67)	-268(68)	-128(62)
O(6)	1206(92)	995(84)	983(84)	206(68)	177(69)	793(77)
C(1)	613(71)	469(74)	376(63)	38(52)	229(54)	-13(57)
C(2)	699(86)	384(68)	979(111)	104(73)	345(81)	56(63)
C(3)	564(72)	525(75)	498(70)	80(61)	39(59)	148(62)
C(4)	625(80)	590(84)	629(90)	-189(68)	84(70)	88(67)
C(5)	693(83)	403(70)	567(78)	-138(60)	2(66)	131(63)
C(6)	764(87)	688(82)	221(56)	-116(56)	21(56)	124(72)
C(7)	434(58)	300(51)	246(51)	-28(44)	108(44)	62(45)
C(8)	328(51)	301(55)	428(60)	-70(46)	63(45)	-13(40)
C(9)	531(63)	379(60)	385(62)	151(49)	99(50)	61(50)
C(10)	554(76)	506(76)	915(102)	193(73)	139(71)	-154(63)
C(11)	671(84)	684(87)	716(91)	422(76)	192(71)	188(70)
C(12)	845(94)	740(87)	392(71)	55(64)	334(67)	161(76)
C(13)	670(87)	552(88)	723(97)	37(76)	-253(75)	-159(74)
C(14)	740(83)	566(81)	428(71)	-140(62)	-14(61)	-179(66)
C(15)	568(74)	549(77)	559(80)	-43(66)	-76(62)	-197(65)
C(16)	543(79)	909(113)	853(98)	-207(88)	227(73)	-433(80)
C(17)	393(66)	742(95)	861(106)	-258(90)	-57(67)	-137(69)

0.048 for the observed reflections only. The atomic scattering factors used (corrected for the anomalous dispersion of Fe and Ni) were taken from ref. 10. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$. Unit weights were chosen at each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to $|F_0|$. Final atomic coordinates for non hydrogen atoms and for hydrogen atoms are given in Tables 1 and 2, respectively, the thermal parameters for the non-hydrogen atoms are given in Table 3. A list of observed and calculated structure factors is available from the authors on request.

All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with financial support from the University of Parma.

Results and discussion

The structure of Ib, represented in Figure 1, consists of a triangular heterometallic cluster of two iron and one nickel atoms. The cyclopentadienyl ring is η -coordinated to the nickel (the distance from Ni to the barycentre of the ring being 1.762 Å) and six carbonyls, three on each atom, are terminally bound to the iron atoms (the angles Fe—C—O are in the range 177.0–177.8°). The *t*-butylethynyl group interacts with all the three metal atoms: it is σ -bonded to the Fe(1) atom and π -bonded symmetrically to the Fe(2) and Ni

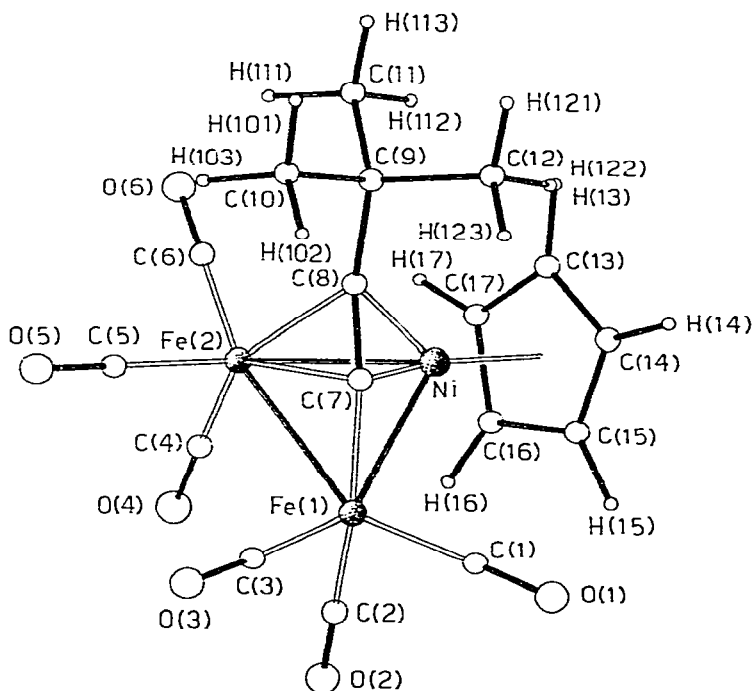


Fig. 1. Perspective view of the complex $(\eta\text{-C}_5\text{H}_5)\text{NiFe}_2(\text{CO})_6\text{C}_2\text{t-Bu}$ showing the atomic numbering scheme.

TABLE 4

BOND DISTANCES (Å) AND ANGLES (°) (NOT INVOLVING HYDROGEN ATOMS) WITH E.S.D.'s

i) in the coordination sphere of the metal cluster

Fe(1)—Fe(2)	2.610(3)	Fe(2)—C(7)	2.010(10)
Fe(1)—Ni	2.564(3)	Fe(2)—C(8)	2.060(10)
Fe(2)—Ni	2.378(3)	Ni—C(7)	1.929(10)
Fe(1)—C(1)	1.778(13)	Ni—C(8)	2.034(10)
Fe(1)—C(2)	1.803(15)	Ni—C(13)	2.119(15)
Fe(1)—C(3)	1.765(13)	Ni—C(14)	2.118(13)
Fe(1)—C(7)	1.813(10)	Ni—C(15)	2.086(13)
Fe(2)—C(4)	1.772(14)	Ni—C(16)	2.062(15)
Fe(2)—C(5)	1.775(13)	Ni—C(17)	2.082(14)
Fe(2)—C(6)	1.762(13)		
Fe(2)—Fe(1)—Ni	54.7(1)	C(8)—Fe(2)—Fe(1)	80.0(3)
Ni—Fe(2)—Fe(1)	61.7(1)	C(7)—Ni—C(8)	37.7(4)
Fe(1)—Ni—Fe(2)	63.6(1)	C(7)—Ni—C(13)	142.5(5)
Fe(2)—Fe(1)—C(1)	151.3(4)	C(7)—Ni—C(14)	126.6(5)
Fe(2)—Fe(1)—C(2)	105.4(4)	C(7)—Ni—C(15)	129.9(5)
Fe(2)—Fe(1)—C(3)	98.4(4)	C(7)—Ni—C(16)	149.7(5)
Fe(2)—Fe(1)—C(7)	50.2(3)	C(7)—Ni—C(17)	163.5(5)
Ni—Fe(1)—C(1)	100.6(4)	C(7)—Ni—Fe(1)	44.9(3)
Ni—Fe(1)—C(2)	106.5(5)	C(7)—Ni—Fe(2)	54.5(3)
Ni—Fe(1)—C(3)	148.6(4)	C(8)—Ni—C(13)	110.3(5)
Ni—Fe(1)—C(7)	48.7(3)	C(8)—Ni—C(14)	119.9(5)
C(1)—Fe(1)—C(2)	95.1(6)	C(8)—Ni—C(15)	150.9(5)
C(1)—Fe(1)—C(3)	99.3(6)	C(8)—Ni—C(16)	166.6(5)
C(1)—Fe(1)—C(7)	103.6(5)	C(8)—Ni—C(17)	129.1(5)
C(2)—Fe(1)—C(3)	95.7(6)	C(8)—Ni—Fe(1)	81.6(3)
C(3)—Fe(1)—C(7)	151.0(6)	C(8)—Ni—Fe(2)	55.0(3)
C(2)—Fe(1)—C(7)	102.9(5)	C(13)—Ni—C(14)	39.1(5)
Ni—Fe(2)—C(4)	98.5(4)	C(13)—Ni—C(15)	64.7(5)
Ni—Fe(2)—C(5)	155.1(5)	C(13)—Ni—C(16)	66.6(6)
Ni—Fe(2)—C(6)	99.8(4)	C(13)—Ni—C(17)	38.7(6)
Ni—Fe(2)—C(7)	51.3(3)	C(13)—Ni—Fe(1)	162.2(4)
Ni—Fe(2)—C(8)	54.0(3)	C(13)—Ni—Fe(2)	134.0(4)
C(4)—Fe(2)—C(5)	98.3(6)	C(14)—Ni—C(15)	37.6(5)
C(4)—Fe(2)—C(6)	93.1(6)	C(14)—Ni—C(16)	66.7(5)
C(4)—Fe(2)—C(7)	126.2(5)	C(14)—Ni—C(17)	65.8(6)
C(4)—Fe(2)—C(8)	152.3(5)	C(14)—Ni—Fe(1)	123.7(4)
C(4)—Fe(2)—Fe(1)	83.8(4)	C(14)—Ni—Fe(2)	171.7(4)
C(5)—Fe(2)—C(6)	97.4(6)	C(15)—Ni—C(16)	41.1(6)
C(5)—Fe(2)—C(7)	103.8(5)	C(15)—Ni—C(17)	66.5(6)
C(5)—Fe(2)—C(8)	106.9(5)	C(15)—Ni—Fe(1)	98.3(4)
C(5)—Fe(2)—Fe(1)	102.3(4)	C(15)—Ni—Fe(2)	150.0(3)
C(6)—Fe(2)—C(7)	130.8(5)	C(16)—Ni—C(17)	40.4(6)
C(6)—Fe(2)—C(8)	94.7(5)	C(16)—Ni—Fe(1)	104.8(4)
C(6)—Fe(2)—Fe(1)	160.3(4)	C(16)—Ni—Fe(2)	116.9(4)
C(7)—Fe(2)—C(8)	36.7(4)	C(17)—Ni—Fe(1)	141.6(4)
C(7)—Fe(2)—Fe(1)	43.9(3)	C(17)—Ni—Fe(2)	111.6(4)

ii) in the carbonyl groups

O(1)—C(1)	1.137(16)	O(4)—C(4)	1.173(18)
O(2)—C(2)	1.129(19)	O(5)—C(5)	1.138(17)
O(3)—C(3)	1.142(16)	O(6)—C(6)	1.147(17)
Fe(1)—C(1)—O(1)	177.8(1.0)	Fe(2)—C(4)—O(4)	177.0(1.2)
Fe(1)—C(2)—O(2)	177.7(1.4)	Fe(2)—C(5)—O(5)	177.4(1.3)
Fe(1)—C(3)—O(3)	177.0(1.2)	Fe(2)—C(6)—O(6)	177.8(1.2)

iii) in the organic ligands

C(7)—C(8)	1.284(14)	C(13)—C(14)	1.418(19)
C(8)—C(9)	1.523(15)	C(13)—C(17)	1.394(21)
C(9)—C(10)	1.538(17)	C(14)—C(15)	1.356(18)

TABLE 4 (continued)

iii) in the organic ligands			
C(9)—C(11)	1.537(18)	C(15)—C(16)	1.456(20)
C(9)—C(12)	1.550(17)	C(16)—C(17)	1.430(22)
Fe(1)—C(7)—Fe(2)	85.9(4)	C(10)—C(9)—C(12)	110.7(9)
Fe(1)—C(7)—Ni	86.4(4)	C(11)—C(9)—C(12)	109.5(9)
Fe(2)—C(7)—Ni	74.2(4)	C(11)—C(9)—C(8)	111.7(9)
C(8)—C(7)—Fe(1)	155.8(9)	C(12)—C(9)—C(8)	107.5(8)
C(8)—C(7)—Fe(2)	73.8(6)	C(14)—C(13)—C(17)	108.4(1.3)
C(8)—C(7)—Ni	75.6(6)	C(15)—C(14)—C(13)	108.5(1.2)
C(9)—C(8)—C(7)	142.8(9)	C(16)—C(15)—C(14)	109.6(1.2)
C(10)—C(9)—C(8)	106.9(9)	C(17)—C(16)—C(15)	104.8(1.2)
C(10)—C(9)—C(11)	110.5(9)	C(13)—C(17)—C(16)	108.7(1.3)

atoms through the C(7)—C(8) triple bond. Bond distances and angles in the complex are given in Table 4. The three metal atoms form an isosceles triangle, in which one side (Ni—Fe(2) = 2.378(3) Å) is shorter than the other two sides (Ni—Fe(1) = 2.564(3) and Fe(1)—Fe(2) = 2.610(3) Å).

The Fe(2)—Ni distance of 2.378(3) Å is markedly short, the only other Fe—Ni distance reported, for a binuclear alkyne derivative [11], being 2.420(1) Å. Ni—Ni bond distances are usually in the range 2.33–2.80 Å [12], the shortest being 2.329 Å in a cyclopentadienylalkyne binuclear complex [13]. For Fe—Fe bond distances values ranging from 2.37 to 2.88 and from 2.67 to 2.88 Å (with and without bridging groups respectively) have been reported [12], the shortest, 2.37 and 2.402 Å [14,15], in the presence of nitrogen donors. Fe—Fe bond distances of 2.316 and 2.215 Å [16,17] observed in the presence of *t*-butyl-substituted alkynes were considered to involve double bonds. Finally Co—Co bond distances of about 2.46 Å have usually been found [18], Co—Co being isoelectronic with Fe—Ni. Thus the short Fe—Ni bond in Ib is in the range of the shortest Fe—Ni bonds found or predictable, whereas the other Fe—Ni bond in this complex is in the expected range. Thus some multiple bond character can be envisaged for Fe(2)—Ni, this being favoured by the two strong electron donor ligands bound to these metals.

In the complexes III, IV and V the arrangements of the alkyne carbons with respect to the trimetallic cluster is very similar to that in Ib. In Table 5 the more significant bond distances and angles in Ib are compared with those in the related complexes III, IV and V. One of the alkyne carbon atoms, namely C(7), in Ib, σ and π bonded to the metals, is nearly equidistant from the metals and gives a "close" arrangement comparable with the M_3C core of $Co_3(CO)_9CR$ [18], $Fe_3(CO)_8(HC_2Et)_4$ [19], and $H_3Ru_3(CO)_9CR$ (R = Me [20] and R = CH_2t -Bu [21]).

The C(7)—Fe(1) σ -bond (1.813 Å) in Ib is also very short in the light of the usual values reported for the Fe—C(σ) bonds [22]; it is comparable with the longest Fe—C (carbonyl) bonds, so that partial double-bond character can be ascribed to it.

The C(7)—C(8) (alkyne) distance (1.283 Å), comparable with that of IV (1.299 Å), shows a relatively small elongation compared with the original triple bond, and suggests low activation of the triple bond.

The *t*-butylethynyl ligand acts as a five electron donor towards the cluster;

TABLE 5
 COMPARISON OF SOME SIGNIFICANT BOND DISTANCES AND ANGLES IN COMPLEX Ib WITH THE CORRESPONDING ONES IN
 $\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)$ (III), $(\eta\text{-C}_5\text{H}_5)\text{Fe}_3(\text{CO})_7(\text{C}_2\text{Ph})$ (IV) AND $\text{HRu}_3(\text{CO})_9(\text{C}_2\text{-t-Bu})$ (V)

Complex	M-M ^a	M-M'	M-C(σ) ^b	M-C(π) ^c	C \equiv C	M-C(σ)-M ^d	ref.
Ib	2.610(3)	2.564(3) 2.378(3)	1.813(10)	2.010(10), 2.060(10) (M = Fe) 1.929(10), 2.034(10) (M = Ni)	1.284(14)	85.9(4), 86.4(4), 74.2(4)	this paper
III	2.480(10) 2.501(9) 2.579(11)	—	2.048(16)	2.098(15), 1.947(16) 2.043(15), 1.945(15)	1.409(22)	75.4(5), 73.5(5), 77.0(6)	3
IV	2.639(1) 2.632(1) 2.524(1)	—	1.829(6)	2.040(4), 2.081(5) 2.006(5), 2.031(5)	1.299(9)	85.8(12), 86.6(2), 77.2(2)	4
V	2.795(3) 2.799(3) 2.792(1)	—	1.947(3)	2.207(3), 2.268(3) 2.214(3), 2.271(3)	1.315(3)	84.3(1), 84.3(1), 78.3(1)	5

^a Fe-Fe, Ru-Ru. ^b Fe-C, Ru-C. ^c Fe-C, Ni-C, Ru-C. ^d Fe-C-Fe, Fe-C-Ni, Ru-C-Ru.

the bond distances M—C are consistent with this, since one Fe—C(σ) and two M—C(π) interactions are observed and no hydrides are present on the basis of ^1H NMR evidence. It is noteworthy that the ($\eta\text{-C}_5\text{H}_5$)Ni fragment is π -bonded to the alkyne, not σ -bonded as suggested [2]. According to the E.A.N. formalism the Ni atoms has 19 electrons in its coordination sphere, whereas Fe(1) has only 17. The alkyne, acting as a bridge between the metals having different electronic densities, balances these differences and so stabilizes the complex. This behaviour as an “electron sink” within metals having different electronic densities, can be compared with that of the “semi-bridging” CO’s [23]. In Ib, where the alkyne C—C distance is rather short, the “activation” of the triple bond of the alkyne [24] as a result of the bonding to the metals seems to be less important than the ability of the alkyne to stabilize the cluster.

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