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THE REACTIONS OF RUTHENIUM CARBONYL AND ALKYNE-CARBONYL COMPLEXES WITH NICKELOCENE, $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ AND $(\eta\text{-}C_5H_5)_2Ni_2(RC_2R')$. CRYSTAL STRUCTURES OF TWO ISOSTRUCTURAL HETEROMETALLIC TRINUCLEAR CLUSTERS, $(\eta\text{-}C_5H_5)_2Ni_2Ru(CO)_3(C_2Ph_2)$ AND $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3(C_2Ph_2)$

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Summary

The reactions of nickelocene, $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ and $(\eta\text{-}C_5H_5)_2Ni_2(RC_2R')$ ($R = H$, $R' = Bu^t$; $R = R' = Et$, Ph) with $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $HRu_3(CO)_9C_2Bu^t$ and $HRu_3(CO)_9(C_6H_9)$ are reported and compared with those of the iron carbonyls and alkyne-carbonyls.

Some new products have been identified and characterized by spectroscpic analyses. The isostructural trimetallic $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (V) and $(\eta\text{-}C_5H_5)_2Ni_2Ru(CO)_3(C_2Ph_2)$ (Va) have been studied by X-ray methods. Crystals of V and Va are monoclinic, space group *Cc*. Unit cell parameters for V are: $a = 9.334(8)$, $b = 26.717(13)$, $c = 9.143(8)$ Å, $\beta = 95.15(7)°$, and for Va: $a = 9.201(9)$, $b = 27.076(15)$, $c = 9.303(8)$ Å, $\beta = 94.94(7)°$. Both structures have been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.049$ for V and 0.044 for Va.

The complexes consist of a triangular cluster formed by two Ni and one Fe atoms and two Ni and one Ru atoms, respectively. A cyclopentadienyl ligand is η-bonded to each Ni atom and three terminal carbonyls are attached to the unique metal atom. The diphenylacetylene, σ-bonded to the Ni atoms and π-bonded to Fe or Ru atom, lies almost parallel to the Ni—Ni side of the cluster.

The clusters are considerably smaller in size than other complexes of comparable structure. The elongation of the acetylenic C—C bond is different in the two complexes V and Va, although the alkyne—metal interactions are comparable.

Introduction

Heterometallic clusters are mainly studied because of their interest as potential catalysts [1]. Systematic synthetic procedures for these derivatives are being developed, and among these the pyrolysis of various derivatives has had considerable success because of the great variety of new products obtainable. We now report a further example of pyrolysis in inert solvents, and an attempt to study the processes occurring during the formation of mixed clusters (e.g. ligand transfer, cluster degradation) and the factors influencing the yield of the products.

We have already the reactions of nickelocene, $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ and $(\eta\text{-}C_5H_5)_2Ni_2(RC_2R')$ with iron carbonyl and alkynecarbonyl complexes [2], and we now report the results of the reactions of these compounds with $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $HRu_3(CO)_9C_2Bu^t$ and $HRu_3(CO)_9(C_6H_9)$. A comparison between the reactions of the iron and ruthenium complexes is made.

From the reactions with iron derivatives, the following complexes were obtained: $(\eta\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(\mu_3\text{-}CO)$ (complex I) [2,3], $(\eta\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6$-$(RC_2R')$ (complexes II) [2,3], $(\eta\text{-}C_5H_5)NiFe_2(CO)_6C_2R$ (complexes III) [2,4,5], $(\eta\text{-}C_5H_5NiFe_2(CO)_7CCH_2R$ (complexes IV) [2,4], and $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3$-$(C_2R_2)$ (complexes V) [2,11].

Some accounts of the reactions of $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ with $HRu_3(CO)_9C_2Bu^t$ [6] and $HRu_3(CO)_9(C_6H_9)$ [7] were given previously; the tetrametallic butterfly clusters $(\eta\text{-}C_5H_5)NiRu_3(CO)_9CC(H)Bu^t$ (complex VI) [8] and $(\eta\text{-}C_5H_5)NiRu_3$-$(CO)_8(C_6H_9)$ (two isomers, complexes VII) [9] were obtained. Finally, the reaction of $(\eta\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$ with $Ru_3(CO)_{12}$ leads to the chiral cluster $(\eta\text{-}C_5H_5)_2$-$NiRu_2(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)$ (complex VIII) [10], a detailed account of which is given elsewhere.

The structures of the complexes I, II ($R = R' = Et$) [2,3], III ($R = Bu^t$) [5], VI [8] and VII [9] were determined by X-ray diffraction; the proposed structures of IV [4] and V [11] were based on spectroscopic data.

Several new derivatives were obtained in the reactions of the ruthenium-nickel system and characterized by spectroscopic methods. The structures of the analogous complexes $(\eta\text{-}C_5H_5)_2Ni_2Ru(CO)_3(C_2Ph_2)$ (Va) and $(\eta\text{-}C_5H_5)_2Ni_2Fe$-$(CO)_3(C_2Ph_2)$ (V) have been determined by X-ray methods, and the complexes found to be isostructural. The triangular clusters, characterized by their small size, are $(2\sigma + \pi)$ bonded to the alkyne; their features are discussed and compared with other known examples of such an arrangement. In particular the C—C elongation is considered, and is shown to depend not only on the cluster size but also on electronic factors.

We also found several other features which require comment: (1) different metallic cores (Ni_2Fe_2 and $NiRu_3$) and structures are found for the tetrametallic derivatives; (2) alkyne isomerization is observed only in presence of ruthenium; (3) hydrogen and ligand transfer (CO, cyclopentadienyl and alkyne) are always observed, but are usually more evident for ruthenium; (4) the nature of the alkyne seems to play an important role in determining the nature of the mixed products, particularly in the case of ruthenium.

Experimental

Reactants

$Ru_3(CO)_{12}$ [12], the hydrido-carbonyl-alkyne ruthenium derivatives [6,7], $H_4Ru_4(CO)_{12}$ [14] and the $(\eta\text{-}C_5H_5)_2Ni_2(RC_2R')$ complexes [2,13] were made by published procedures. The other reactants were commercial products and used without further purification. Dried octane and heptane were used as solvents under dry nitrogen.

Reactions, recovery and analysis of the products

The reaction conditions and stoichiometries are summarized in Scheme 1. The product mixtures usually contained a large number of component and preparative TLC was the only reliable separation technique. When possible the products were crystallized from heptane or heptane/$CHCl_3$.

The physical characteristics, the elemental analyses and spectroscopic data for the new products (except for VIII) are listed in Table 1. The IR, ^1H and mass spectra were recorded on a Beckman IR-12, a JEOL C60 HL, an Hitachi-Perkin-Elmer RMU-6 H and a Varian CH-5 instrument, respectively.

Synthesis and crystallization of V and Va.

The deep-green complex V can be obtained in reasonable yields (10—20%) and its synthesis has already been reported [11]. Crystals suitable for X-ray analysis were obtained by cooling a solution in (1/1) heptane/$CHCl_3$ for several days at —10°C. Some decomposition was observed during crystallization, even under nitrogen.

Va was obtained either by treating $(\eta\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$ with $Ru_3(CO)_{12}$ or by treating $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ with $Ru_4(CO)_{12}(C_2Ph_2)$ (see Scheme 1). The deep-green Va contained a brown impurity which was identified, after careful purification, as $(\eta\text{-}C_5H_5)NiRu_3(CO)_9(C_2Ph_2)$ by mass, IR and NMR spectra (complex IX). We were unable to obtain crystals of IX suitable for an X-ray study.

We were also unable to isolate Va free of traces of IX, and so satisfactory elemental analyses were not obtained. Keeping a 1/1 heptane/$CHCl_3$ solution of the impure Va at —10°C under nitrogen for some days gave crystals of Va suitable for the X-ray analysis.

X-ray data collection

Green-black, roughly prismatic crystals of V (with dimensions of ca. 0.12 × 0.19 × 0.27 mm) and of Va (with dimensions of ca. 0.10 × 0.14 × 0.20 mm) were used for the data collection. Preliminary cell parameters for both compounds, obtained by rotation and Weissenberg photographs, were subsequently refined by a least-squares procedure applied to the θ values of 16 (V) and 15 (Va) reflections carefully measured on a Siemens AED single crystal diffractometer. The crystal data are:

V, $C_{27}H_{20}FeNi_2O_3$. $M = 565.72$, monoclinic, $a = 9.334(8)$, $b = 26.717(13)$, $c = 9.143(8)$ Å; $\beta = 95.15(7)°$; $V = 2271(3)$ Å^3, $Z = 4$, $d_{calc} = 1.655$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 23.07$ cm^{-1}; space group *Cc* (from systematic absences and structure determination).

(Va) $C_{27}H_{20}Ni_2O_3Ru$. $M = 610.94$, monoclinic, $a = 9.201(9)$, $b = 27.076(15)$,

(Continued on p. 99)

SCHEME 1

Reactions of $(Cp)_2Ni$

with $Ru_3(CO)_{12}$	$\xrightarrow[25\ \text{min}]{3:1^a,\ \text{octane}}$	$[(Cp)Ru(CO)_2]_2$ (20%)^b, "$(Cp)NiRu_3(CO)_9$" (5%), unidentified products (5)^c (tr)^d	this work
with $HRu(CO)_9C_2Bu^t$	$\xrightarrow[180\ \text{min}]{1:3,\ \text{octane}}$	$HRu_3(CO)_9C_2Bu^t$ (40%), unidentified products (tr) (4), dec.	this work

Reactions of $[(Cp)Ni(CO)]_2$

with $Ru_3(CO)_{12}$	$\xrightarrow[90\ \text{min}]{2:1,\ \text{octane}}$	$H_2Ru_4(CO)_{13}$ (10%), $Ni(CO)_4$, $[(Cp)Ru(CO)_2]_2$ (25%), "$(Cp)NiRu_3(OO)_9$" (2%), unidentified products (tr) (7)	this work
with $H_4Ru_4(CO)_{12}$	$\xrightarrow[20\ \text{min}]{3:1,\ \text{octane}}$	$[(Cp)Ru(CO)_2]_2$ (10%), "$(Cp)NiRu_3(CO)_9$" (2%), unidentified products (1) (tr)	this work
with $HRu_3(CO)_9C_2Bu^t$	$\longrightarrow$	$(Cp)NiRu_3(CO)_9CC(H)Bu^t$ (15%), $(Cp)NiRu_2(CO)_6(C_2Bu^t)$ (1%) $(Cp)NiRu_2(CO)_7CCH_2Bu^t$ (0.5%), unidentified products (tr) (7)	[8]
with $HRu_3(CO)_9(C_nH_m)$	$\longrightarrow$	$(Cp)NiRu_3(CO)_8(C_nH_m)$ (10—10% $C_nH_m = C_6H_9$) (25% $C_nH_m = C_5H_7$)	[9]
with $Ru_4(CO)_{12}(C_2Ph_2)$	$\xrightarrow[60\ \text{min}]{1.5:1,\ \text{octane}}$	$Ni(CO)_4$, Ru (powder), $(Cp)NiRu_3(CO)_9(C_2Ph_2)$ (3%), $(Cp)_2Ni_2Ru(CO)_3(C_2Ph_2)$ (1%)^e, $Ru_3(CO)_8(C_2Ph_2)_2$ "orange" [29]	this work
with $Ru_3(CO)_{12} + HC_2Bu^t$	$\xrightarrow{f}$	$[(Cp)Ru(CO)_2]_2$ (15%), $H_2Ru_4(CO)_{13}$ (3%), $HRu_3(CO)_9C_2Bu^t$ (1%), $H_2Ru_3(CO)_9(HC_2Bu^t)$ (tr) [18b], $H_3Ru_3(CO)_9CCH_2Bu^t$ (1%), $Ru_3(CO)_6(C_{12}H_{26})(C_{13}H_{20}O)$ (1–1%) [18b], $(CpNiRu_3(CO)_9CCHBu^t$ (1%)	this work

with $Ru_3(CO)_{12}$ + C_2Et_2	$\xrightarrow{f}$	$HRu_3(CO)_9(C_6H_9)$ (15%) [7], $(Cp)NiRu_3(CO)_8(C_6H_9)$ (2—2%), unidentified products (11) (tr)	this work
with $Ru_3(CO)_{12}$ + C_2Ph_2	$\xrightarrow{f}$	$[(Cp)Ru(CO)_2]_2$ (5%), $Ru_4(CO)_{12}(C_2Ph_2)$ (5%) [17], $Ru_3(CO)_9(C_2Ph_2)$ (2%), $Ru_2(CO)_6(C_2Ph_2)$ [g], $Ni(CO)_4$, $Ru_3(CO)_8(C_2Ph_2)$ "violet" (2%), $Ru_3(CO)_8(C_2Ph_2)_2$ "orange" (10%) [29], $(Cp)NiRu_3(CO)_8(C_2Ph_2)$ (1%), $(Cp)_2NiRu_2(CO)_4(C_2Ph_2)$ [10]	this work
Reactions of $(Cp)_2Ni_2(RC_2R')$			
R = R' = Bu^t with $Ru_3(CO)_{12}$	$\xrightarrow[180 \text{ min}]{2:1, \text{ heptane}}$	$[(Cp)Ru(CO)_2]_2$ (10%), $H_2Ru_4(CO)_{13}$ (4%), $HRu_3(CO)_9C_2Bu^t$ (1%), $H_2Ru_3(CO)_9(HC_2Bu^t)$ (tr) [18b], $H_3Ru_3(CO)_9CCH_2Bu^t$ (1%), $Ru_3(CO)_6(C_{12}H_{20})(C_{13}H_{20}O)$ (1—1%) [18b], $Ru_3(CO)_8(HC_2Bu^t)$ (3%) [18a], $(Cp)NiRu_3(CO)_8CC(H)Bu^t$ (2%), unidentified products (tr) [4].	this work
R = R' = Et with $Ru_3(CO)_{12}$	$\xrightarrow[30 \text{ min}]{2:1, \text{ heptane}}$	$HRu_3(CO)_9(C_6H_9)$ (5%), $(Cp)NiRu_3(CO)_8(C_6H_9)$ (2—2%), unidentified products (tr) (8)	this work
R = R' = Ph with $Ru_3(CO)_{12}$	$\xrightarrow[20 \text{ min}]{1:1, \text{ octane}}$	$[(Cp)Ru(CO)_2]_2$ (10%), $Ni(CO)_4$, $Ru_4(CO)_{12}(C_2Ph_2)$ (3%) [17], $Ru_3(CO)_9(C_2Ph_2)$ (4%), $Ru_2(CO)_6(C_2Ph_2)$ (15%), $(Cp)NiRu_3(CO)_9(C_2Ph_2)$ (15%), $(Cp)_2Ni_2Ru(CO)_3(C_2Ph_2)$ (10%), unidentified products (8) (tr)	this work
R = R' = Ph with $HRu_3(CO)_9C_2Bu^t$	$\xrightarrow[75 \text{ min}]{1:1, \text{ heptane}}$	$(Cp)_2Ni_2(HC_2Bu^t)$ (tr), $[(Cp)Ru(CO)_2]_2$ (10%), $Ru_3(CO)_9(C_2Ph_2)$ (tr), $Ru_3(CO)_7[(C_2Bu^t)(PhC_2(H)Ph)](C_2Ph_2)$ (2%) [18c]	this work

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[a] Reactant ratio. The first figure refers to the nickel complex.

[b] The yields of the products are based on ruthenium. Where two values are given these refer to the yields of two isomers.

[c] The number of unidentified products is given in parentheses.

[d] (tr) means trace amounts.

[e] The synthesis of this product is described in the text.

[f] These reactions were performed by refluxing equimolecular amounts of alkyne and $[(Cp)Ni(CO)]_2$ in heptane, for 3 hours until the solution turned dark green and contained almost exclusively $(Cp)_2Ni_2(RC_2R')$; an equimolecular amount of $Ru_3(CO)_{12}$ suspended in 25 ml of heptane was then added and the mixture refluxed for 3 hours. Alternatively for reactions with $(Cp)_2Ni_2(RC_2R')$ as reactant, pre-formed, crystalline nickel derivatives were used.

[g] This complex was obtained in better yields by reacting $HRu_3(CO)_9C_2Bu^t$ with free C_2Ph_2 under hydrogen (see ref. 18c).

TABLE 1

ANALYSES AND SPECTROSCOPIC DATA FOR THE Ru-Ni COMPLEXES

Complex		Elemental analysis (%) [a]					IR spectrum (cm^{-1}, heptane)	^{1}H NMR (ppm, CCl_4)	Mass spectrum (*m/e*)
		C	H	Ni	O	Ru			
(Cp)$NiRu_2(CO)_6C_2Bu^t$ (IIIa)	brown-black crystals	36.10 (35.50)	2.66 (2.45)	9.88 (10.21)	17.01 (16.69)	34.75 (35.15)	2068s, 2028vs, 1995s, 1964w	3.70m (5H) 8.50s (9H)	P^+ = 576 (Ru_2Ni) loss of 6 CO
(Cp)$NiRu_2(CO)_7CCH_2Bu^t$ (IVa)	black-green solid	35.88 (35.72)	2.60 (2.67)	9.81 (9.70)	18.15 (18.51)	32.26 (33.40)	2076s, 2038s, 2017s, 2000vs, 1959s, 1802m-s	3.80s (5H) 5.70s (2H) 8.40s (9H)	P^+ = 606 (Ru_2Ni) loss of 7 CO
$(Cp)_2Ni_2Ru(CO)_3(C_2Ph_2)$ (Va)	deep green crystals	see text					2070s, 2040s, 2024s, 2014s (sh), 1998vs, 1880w, 1850s	1.58s 3.85s 4.22s	*t* = 60—90°C $Ru_3(CO)_{12}$ *t* 100°C decomp.
(Cp)$NiRu_3(CO)_9(C_2Ph_2)$ (IX)	brown crystals	see text					2070s, 2040s, 2024vs, 2002vs, 1974vs, 1878m, 1858s	1.56s (10H) 3.84s (5H)	P^+ = 859 (Ru_3Ni) loss of 8 CO
(Cp)$NiRu_3(CO)_9$ (X)	black needle crystals	24.46 (24.76)	0.83 (0.74)	8.38 (8.65)	21.00 (21.20)	45.33 (44.65)	2060s, 2011vs	4.50s	P^+ = 648 (Ru_3Ni) loss of 9 CO

[a] Calculated values in parentheses.

$c = 9.303(8)$ Å; $\beta = 94.94(7)°$; $V = 2309(3)$ Å^3, $Z = 4$, $d_{calc} = 1.757$ g cm^{-3}, μ(Mo-K_α) = 22.83 cm^{-1}; space group *Cc* (from systematic absences and structure determination).

Intensity data were collected at room temperature on the same diffractometer using the Nb-filtered Mo-K_α radiation and the θ—2θ scan technique. The intensity of a standard reflection was measured after 20 reflections as a check on crystal and instrument stability. No significant change was observed in the measured intensities during the data collection. 2591 independent reflections were measured for V (with θ in the range 3—27°) and 2419 for Va (with θ in the range 3—26°); of these, 1524 for V and 1644 for Va were considered observed and used in the analysis (having $I \geqslant 2\sigma(I)$). The intensities were corrected for Lorentz and polarization factors, but no absorption corrections were applied in view of the low absorbance of both samples. The first absolute scale and the mean temperature factors were determined by Wilson's method.

TABLE 2

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

Atom	*x/a*	*y/b*	*z/c*
Ni(1)	1200	3609(1)	3123
Ni(2)	—1244(3)	3545(1)	2059(3)
Fe(1)	640(4)	3142(1)	919(4)
O(1)	3590(16)	2833(6)	530(16)
O(2)	—670(18)	2801(6)	—1884(17)
O(3)	—2(27)	2277(6)	2675(24)
C(1)	2415(23)	2949(8)	667(19)
C(2)	—141(21)	2930(7)	—758(21)
C(3)	225(26)	2640(9)	1958(27)
C(4)	1200(18)	3875(7)	1244(16)
C(5)	—172(18)	3834(6)	674(18)
C(6)	2399(18)	4138(6)	662(19)
C(7)	2867(19)	3994(7)	—742(19)
C(8)	3945(20)	4259(7)	—1296(19)
C(9)	4609(20)	4667(7)	—612(20)
C(10)	4172(19)	4815(7)	742(22)
C(11)	3077(18)	4562(6)	1382(19)
C(12)	—876(17)	4142(7)	—604(18)
C(13)	—2014(18)	3922(7)	—1539(17)
C(14)	—2598(19)	4214(9)	—2725(19)
C(15)	—2087(25)	4671(9)	—3024(21)
C(16)	—988(23)	4894(8)	—2085(23)
C(17)	—385(21)	4614(8)	—884(19)
C(18)	2643(34)	3223(12)	4668(22)
C(19)	3124(23)	3741(14)	4439(21)
C(20)	2112(29)	4042(10)	4916(21)
C(21)	1063(28)	3779(12)	5397(20)
C(22)	1376(31)	3283(11)	5283(22)
C(23)	—2636(26)	3847(11)	3510(27)
C(24)	—2427(19)	3347(10)	3891(24)
C(25)	—2842(29)	3054(10)	2730(30)
C(26)	—3443(19)	3396(15)	1632(34)
C(27)	—3282(28)	2897(12)	2127(34)

TABLE 3

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

Atom	*x/a*	*y/b*	*z/c*
Ru	640	3114(1)	919
Ni(1)	1182(3)	3625(1)	3152(3)
Ni(2)	−1284(3)	3569(1)	2097(3)
O(1)	3760(25)	2824(7)	338(23)
O(2)	−714(25)	2791(7)	−2027(22)
O(3)	142(33)	2160(10)	2538(29)
C(1)	2527(36)	2946(10)	549(29)
C(2)	−181(28)	2898(8)	−873(31)
C(3)	289(30)	2538(14)	1900(28)
C(4)	1248(24)	3897(8)	1231(22)
C(5)	−184(23)	3853(8)	645(22)
C(6)	2418(21)	4156(7)	655(22)
C(7)	2852(22)	4019(8)	−724(22)
C(8)	3992(26)	4270(8)	−1319(22)
C(9)	4613(20)	4674(8)	−610(21)
C(10)	4216(21)	4824(7)	745(23)
C(11)	3083(21)	4561(6)	1374(20)
C(12)	−820(22)	4150(8)	−604(20)
C(13)	−1984(21)	3948(7)	−1578(20)
C(14)	−2563(23)	4203(9)	−2719(22)
C(15)	−2089(24)	4672(9)	−3028(25)
C(16)	−961(26)	4878(7)	−2097(23)
C(17)	−367(23)	4638(7)	−902(23)
C(18)	2743(43)	3256(13)	4575(31)
C(19)	3099(30)	3784(14)	4438(32)
C(20)	2101(29)	4048(6)	4912(25)
C(21)	1132(35)	3747(12)	5400(23)
C(22)	1515(43)	3282(10)	5207(28)
C(23)	−2646(27)	3853(13)	3514(34)
C(24)	−2405(25)	3372(8)	3871(26)
C(25)	−2867(24)	3100(11)	2700(30)
C(26)	−3402(23)	3408(11)	1603(27)
C(27)	−3266(31)	3879(12)	2095(37)

TABLE 4

CALCULATED FRACTIONAL COORDINATES ($\times 10^4$) FOR THE HYDROGEN ATOMS OF COMPLEX V

Atom	*x/a*	*y/b*	*z/c*
H(7)	2372	3682	−1343
H(8)	4299	4141	−2335
H(9)	5445	4867	−1110
H(10)	4690	5131	1306
H(11)	2742	4687	2422
H(13)	−2406	3550	−1344
H(14)	−3492	4066	−3425
H(15)	−2525	4868	−3994
H(16)	−621	5268	−2283
H(17)	480	4773	−167
H(18)	3169	2878	4410
H(19)	4098	3855	3978
H(20)	2155	4446	4905
H(21)	108	3931	5815
H(22)	716	2981	5630
H(23)	−2323	4157	4225
H(24)	−1997	3214	4956
H(25)	−2744	2652	2646
H(26)	−3950	3287	572
H(27)	−3597	4237	1545

TABLE 5

CALCULATED FRACTIONAL COORDINATES ($\times 10^4$) FOR THE HYDROGEN ATOMS OF COMPLEX Va

Atom	*x/a*	*y/b*	*z/c*
H(7)	2307	3721	—1324
H(8)	4378	4145	—2331
H(9)	5429	4880	—1118
H(10)	4749	5132	1311
H(11)	2741	4677	2413
H(13)	—2389	3583	—1372
H(14)	—3424	4039	—3420
H(15)	—2568	4875	—3956
H(16)	—558	5240	—2347
H(17)	448	4817	—178
H(18)	3325	2935	4249
H(19)	4059	3926	4003
H(20)	2057	4447	4914
H(21)	170	3863	5884
H(22)	908	2965	5523
H(23)	—2395	4165	4223
H(24)	—1930	3233	4903
H(25)	—2823	2702	2635
H(26)	—3853	3295	534
H(27)	—3581	4210	1496

TABLE 6

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) FOR THE NONHYDROGEN ATOMS OF COMPLEX V IN THE FORM $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	392(14)	504(14)	252(11)	9(11)	—10(10)	—4(12)
Ni(2)	338(13)	550(14)	274(12)	18(12)	14(10)	—54(11)
Fe(1)	436(13)	359(13)	315(12)	—31(13)	39(10)	—34(13)
O(1)	513(89)	1050(118)	574(86)	—89(84)	13(71)	210(81)
O(2)	976(127)	1156(134)	698(104)	—455(100)	—268(90)	—32(98)
O(3)	1520(153)	845(108)	833(115)	134(127)	330(106)	—409(134)
C(1)	768(149)	573(120)	202(83)	—66(82)	—3(87)	—19(104)
C(2)	510(112)	451(101)	486(110)	—73(91)	170(90)	—85(85)
C(3)	873(167)	679(147)	689(150)	—223(128)	26(127)	—244(125)
C(4)	388(99)	421(99)	194(72)	—16(71)	—68(69)	20(79)
C(5)	350(93)	435(95)	274(81)	—61(75)	—18(73)	10(78)
C(6)	331(93)	358(90)	403(95)	65(76)	—25(75)	60(72)
C(7)	449(102)	561(110)	316(87)	44(84)	56(75)	79(85)
C(8)	513(112)	587(116)	340(96)	80(90)	79(83)	—28(92)
C(9)	461(111)	580(125)	343(97)	—27(89)	67(82)	—9(91)
C(10)	303(100)	623(128)	551(119)	101(104)	—31(87)	—29(84)
C(11)	397(93)	352(89)	359(100)	9(79)	—9(77)	—5(74)
C(12)	333(88)	611(118)	234(82)	8(82)	127(68)	—4(82)
C(13)	396(101)	817(131)	269(81)	—102(90)	—4(72)	74(90)
C(14)	368(104)	1002(148)	246(87)	61(98)	—9(74)	126(99)
C(15)	586(149)	1070(185)	386(101)	127(117)	90(99)	262(128)
C(16)	576(133)	863(155)	530(128)	165(114)	96(105)	148(112)
C(17)	614(126)	595(124)	324(94)	140(94)	120(86)	103(100)
C(18)	1243(212)	1355(229)	426(101)	—113(130)	—433(127)	749(190)
C(19)	411(119)	2641(343)	386(96)	240(147)	—256(88)	64(166)
C(20)	796(172)	1082(188)	380(96)	—94(111)	—394(107)	—80(144)
C(21)	774(179)	1405(215)	218(80)	—58(113)	—44(93)	—106(164)
C(22)	1057(192)	1063(217)	292(92)	153(122)	—185(108)	—199(168)
C(23)	756(153)	937(196)	701(162)	—22(148)	564(136)	57(138)
C(24)	383(94)	1032(176)	564(129)	175(129)	92(89)	—144(101)
C(25)	926(167)	1053(187)	722(162)	12(151)	224(135)	—643(148)
C(26)	162(79)	2705(367)	848(224)	63(248)	136(107)	—456(144)
C(27)	705(163)	1354(226)	881(200)	343(180)	414(147)	400(155)

TABLE 7

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS OF COMPLEX Va IN THE FORM $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	404(8)	286(7)	348(7)	−20(9)	60(6)	−37(10)
Ni(1)	393(15)	386(14)	283(12)	14(11)	−6(10)	−10(12)
Ni(2)	323(15)	417(15)	336(13)	36(11)	56(11)	−30(12)
O(1)	651(143)	632(119)	693(164)	20(106)	240(125)	162(117)
O(2)	1066(185)	871(124)	557(138)	−279(109)	−155(129)	−47(122)
O(3)	1313(254)	323(238)	957(188)	165(195)	531(174)	124(222)
C(1)	664(231)	331(152)	590(159)	−83(122)	79(160)	−161(161)
C(2)	484(159)	397(125)	638(176)	58(123)	216(140)	−98(112)
C(3)	571(170)	1095(308)	348(141)	−95(177)	179(127)	−134(194)
C(4)	381(116)	185(110)	384(107)	−28(89)	−117(91)	31(93)
C(5)	251(100)	434(128)	360(107)	−73(98)	133(86)	84(97)
C(6)	278(108)	320(97)	352(113)	19(85)	−26(89)	−9(87)
C(7)	408(120)	279(126)	278(103)	77(97)	59(93)	−94(102)
C(8)	586(152)	529(116)	443(114)	156(97)	115(108)	−12(112)
C(9)	213(89)	479(142)	524(115)	145(102)	4(85)	−17(96)
C(10)	311(107)	486(107)	549(120)	−8(98)	24(93)	11(91)
C(11)	337(112)	246(81)	429(104)	79(74)	−22(88)	−44(81)
C(12)	470(116)	591(126)	220(93)	−81(89)	105(85)	156(104)
C(13)	368(118)	533(104)	379(102)	−99(85)	113(90)	86(91)
C(14)	390(119)	855(165)	416(114)	−30(114)	116(95)	170(120)
C(15)	430(130)	818(145)	542(133)	171(119)	93(109)	209(112)
C(16)	647(155)	506(93)	550(138)	119(91)	181(120)	244(101)
C(17)	415(117)	448(116)	499(111)	171(100)	187(93)	56(104)
C(18)	1284(298)	1201(253)	696(172)	−260(165)	−548(189)	1033(247)
C(19)	393(150)	1946(321)	575(190)	466(203)	−84(138)	−82(186)
C(20)	765(174)	376(74)	599(138)	−124(82)	−273(128)	22(92)
C(21)	1013(244)	1238(232)	204(108)	−2(122)	−157(127)	−211(196)
C(22)	1293(329)	705(147)	571(163)	197(124)	−386(189)	−377(188)
C(23)	496(147)	684(262)	874(214)	162(192)	371(146)	145(155)
C(24)	493(139)	644(119)	558(150)	133(107)	101(116)	57(105)
C(25)	512(136)	910(208)	968(179)	45(181)	464(132)	−462(155)
C(26)	345(121)	1497(211)	641(144)	375(154)	119(109)	−207(134)
C(27)	582(179)	1032(215)	1128(248)	491(196)	605(183)	507(167)

Structure determination and refinement

Initial coordinates of the metal atoms for both structures were obtained from Patterson maps. Successive Fourier syntheses revealed the positions of all other non-hydrogen atoms. The refinements were carried out by least-squares full-matrix cycles using the SHELX system of programs [15], with first isotropic and then anisotropic thermal parameters. The hydrogen atoms could not all be precisely localized in difference maps; so they were placed at the geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The final conventional R values were 0.049 for V and 0.044 for Va, observed reflections only. The atomic scattering factors used (corrected for the anomalous dispersion of the metal atoms) were taken from ref. 16. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$: unit weights were chosen at each stage of the refinements after analyzing the variation of $|\Delta F|$ with respect to $|F_0|$. Final atomic coordinates for non-hydrogen atoms are given in Table 2 for V and Table 3 for Va, those of the hydrogen atoms in Table 4 for V and Table 5 for Va; the thermal parameters of the non-hydrogen atoms are given in Table 6 for V and Table 7 for Va. Lists of observed and calculated structure factors for both compounds are available from the authors.

All the 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.

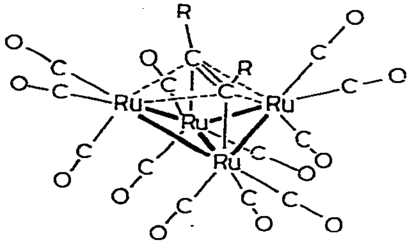
Results and discussion

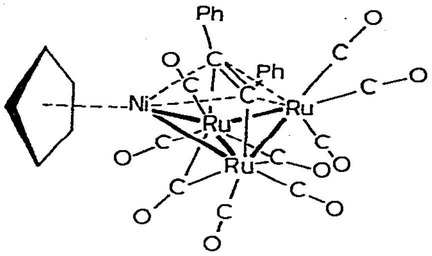
From the above reactions, the following new products were identified by spectroscopic methods: Va, VIII, IX, (η-C_5H_5)$NiRu_3(CO)_9$ (complex X), (η-C_5H_5)$NiRu_2(CO)_6C_2Bu^t$ (complex IIIa) and (η-C_5H_5)$NiRu_2(CO)_7CCH_2Bu^t$ (complex IVa). The structure of VIII is reported in ref. 10. For IIIa and IVa we propose structures similar to those of complexes III [5] and IV [4].

The proposed structures for IX and X are represented in Fig. 1. The structure of IX was proposed on the basis of the observed equivalence of the phenyl groups, the integration of the hydrogen atoms (^{1}H NMR) and the presence of bridging CO's (IR); it is wholly consistent with the spectroscopic data. The bonding of the alkyne is comparable with that in $Ru_4(CO)_{12}(C_2Ph_2)$ [17], which is one of the reaction products. As IX is also obtained by treating $Ru_4(CO)_{12}$-(C_2Ph_2) with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$, we believe that it might be formed by replacement of one $Ru(CO)_3$ group on the "wing" of the homo-tetrametallic cluster by the (η-C_5H_5)Ni group. The (η-C_5H_5)Ni group has already been shown to behave in some instances as a four-electron donor [2,5,8].

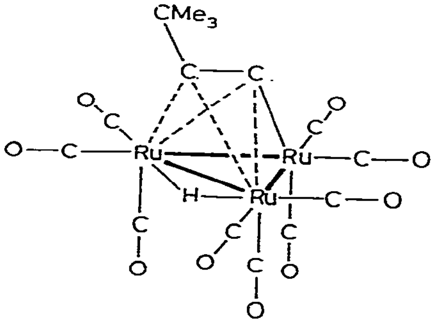
Complex IX is of interest for a comparison of the behaviour of the ruthenium-nickel systems in the presence of different alkynes. Thus, terminal HC_2Bu^t reacts with $Ru_3(CO)_{12}$ to give $HRu_3(CO)_9C_2Bu^t$, which, in the presence of $[(\eta\text{-}C_5H_5)Ni(CO)]_2$, gives VI with hydrogen transfer; this latter process is common in the chemistry of $HRu_3(CO)_9C_2Bu^t$ [18]. $Ru_3(CO)_{12}$ reacts with internal alkynes (e.g. C_2Et_2) having hydrogens α to the triple bond to give "allylic" hydrides, such as $HRu_3(CO)_9(C_6H_9)$, by alkyne isomerization; these react with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ to give complex VII, which has the same organic ligand. Alkyne isomerization also occurs when $(\eta\text{-}C_5H_5)_2Ni_2(C_2Et_2)$ is treated with ruthenium carbonyls. With C_2Ph_2 neither hydrogen transfer nor isomerization would be expected and a new structure, IX, is obtained. Indeed, VI, VII and IX show different metal arrangements and bridging CO positions compared with those of the basic "butterfly" structure. The interaction of the alkynes with the metals seems to depend strongly on the nature of the alkyne in the homometallic or the heterometallic clusters. In Fig. 1 the structures of IX, VI and VII are compared to those of the starting compounds.

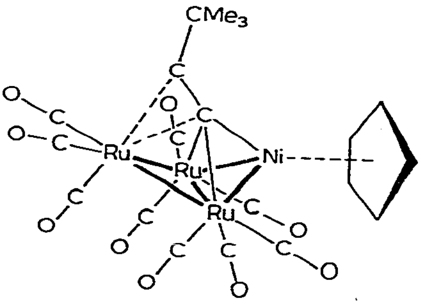
Complex X is tentatively formulated as (η-C_5H_5)$NiRu_3(CO)_9$ on the basis of analytical and spectroscopic data. In particular, the mass spectrum shows the loss of 9 CO's, and isotopic pattern calculations on the ion resulting after CO loss agree with a Ru_3Ni formulation. The high local symmetry shown by the IR spectra and the synthesis of X from $H_4Ru_4(CO)_{12}$ (via "substitution" as previously discussed), point to a tetrahedral structure; indeed, too few metal—metal bonds are available for a butterfly, lozenge or square-planar structure. X lacks three electrons; a triply bridging hydrogen [19] would provide a more "satur-



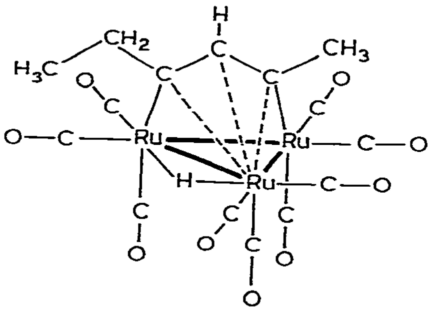


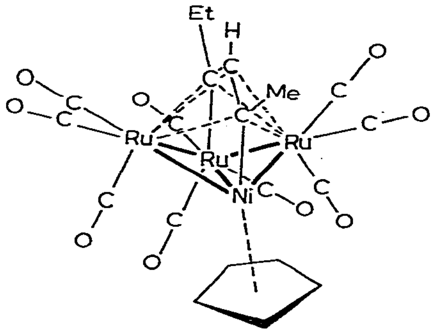
IX



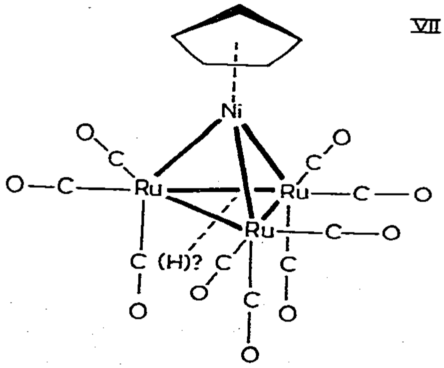


VI





VII



X

Fig. 1. On the right: proposed structures for IX and X and determined structures for VI and VII; on the left: structures of the starting complexes used to obtain IX, VI and VII.

ated" electronic situation. In the ^{1}H NMR spectrum, however, only signals due to (C_5H_5) were detectable; no hydrogen signals were found in the ^{1}H NMR spectrum of $HCo_3(CO)_9$ [20]. This behaviour, for the cobalt as distinct from the nickel or ruthenium, can be explained on the basis of the quadrupole moment of the cobalt. An alternative possibility of explaining the presence of X in the reaction products would be the degradation of a more complex cluster (e.g. $(\eta\text{-}C_5H_5)_2Ni_2Ru_3(CO)_9$). An X-ray structural study of X was not possible because suitable crystals could not be obtained.

Structure of the complexes V and Va

The complexes V and Va are isostructural; the structure of V is represented in Fig. 2. Selected bond distances and angles in both V and Va are compared in Table 8. The complexes involve a triangular cluster formed by two Ni and one Fe atoms and two Ni and one Ru atoms, respectively. A cyclopentadienyl group is η-coordinated to each Ni atom (the distance from the barycentre of the rings being 1.779 for Ni(1) and 1.758 Å for Ni(2) in V, 1.767 for Ni(1) and 1.688 Å for Ni(2) in Va) and three carbonyls are terminally bonded to the unique metal atom. The diphenylacetylene interacts with all the three metal atoms, and is σ-bonded to the Ni atoms [Ni(1)—C(4) and Ni(2)—C(5) are 1.86(2) and 1.85(2) Å in V, 1.92(2) and 1.91(2) Å in Va] and π-bonded to the unique metal through the C(4)—C(5) triple bond [Fe—C(4) and Fe—C(5) are 2.04(2) and 2.00(2) Å in V, Ru—C(4) and Ru—C(5), 2.21(2) and 2.15(2) Å in Va]; the alkyne lies with the C(4)—C(5) bond nearly parallel to the Ni—Ni side of the triangular cluster in an ideal orientation to coordinate to the cluster. Such bonding of the alkyne means that each metal atom obeys the E.A.N. rule. Neglecting the phenyl substituents the complexes have a close C_s-m symmetry, as an approximate mirror plane passes through Fe or Ru and the midpoint of the Ni—Ni bond..The structure of V is in agreement with that deduced from the spectroscopic data [11].

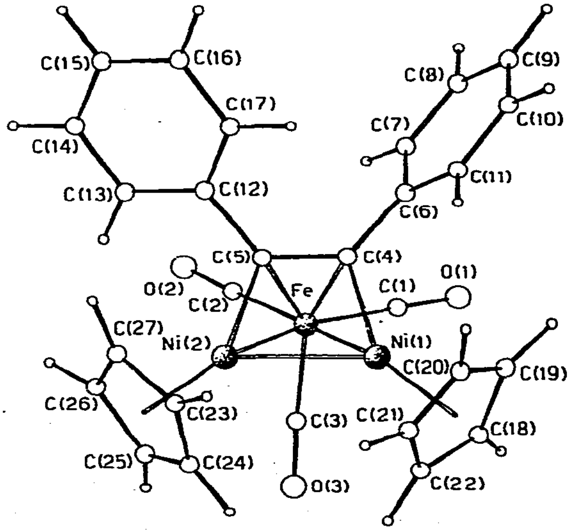


Fig. 2. View of the molecular shape of the iron complex V with the atomic numbering scheme.

TABLE 8

SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN THE IRON AND RUTHENIUM COMPLEXES [a]

(i) In the coordination sphere of the metals					
Ni(1)—Ni(2)	2.404(4)	2.418(4)	M—C(1)	1.77(2)	1.87(3)
Ni(1)—M	2.388(4)	2.493(3)	M—C(2)	1.73(2)	1.85(3)
Ni(2)—M	2.381(5)	2.496(3)	M—C(3)	1.71(2)	1.85(4)
Ni(1)—C(4)	1.86(2)	1.92(2)	M—C(4)	2.04(2)	2.21(2)
Ni(2)—C(5)	1.85(2)	1.91(2)	M—C(5)	2.00(2)	2.15(2)
Ni(2)—Ni(1)—M	59.6(1)	61.1(1)	C(2)—M—C(4)	121.6(8)	120.1(9)
M—Ni(2)—Ni(1)	59.9(1)	60.9(1)	C(2)—M—C(5)	94.5(8)	94.2(9)
Ni(1)—M—Ni(2)	60.6(1)	58.0(1)	C(2)—M—Ni(1)	163.8(7)	161.5(7)
Ni(2)—Ni(1)—C(4)	74.5(5)	76.0(7)	C(2)—M—Ni(2)	105.5(7)	106.6(8)
M—Ni(1)—C(4)	55.8(6)	58.3(7)	C(3)—M—C(4)	137.7(9)	143.4(9)
M—Ni(2)—C(5)	54.8(5)	56.5(7)	C(3)—M—C(5)	133.2(9)	140.2(9)
C(5)—Ni(2)—Ni(1)	72.3(5)	73.1(6)	C(3)—M—Ni(1)	89.1(8)	95.6(9)
C(1)—M—C(2)	96.5(9)	94.8(9)	C(3)—M—Ni(2)	84.2(8)	92.4(9)
C(1)—M—C(3)	96.1(9)	95.3(9)	C(4)—M—C(5)	38.8(7)	37.4(8)
C(1)—M—C(4)	93.9(9)	91.3(9)	C(4)—M—Ni(1)	48.9(4)	47.8(5)
C(1)—M—C(5)	127.1(9)	122.4(9)	C(4)—M—Ni(2)	72.1(5)	69.8(6)
C(1)—M—Ni(1)	97.2(6)	99.1(9)	C(5)—M—Ni(1)	70.4(5)	68.0(6)
C(1)—M—Ni(2)	157.8(6)	156.5(9)	C(5)—M—Ni(2)	49.1(5)	47.9(6)
C(2)—M—C(3)	97.9(9)	95.3(9)			
(ii) In the carbonyl groups					
O(1)—C(1)	1.16(3)	1.23(4)	O(3)—C(3)	1.20(3)	1.19(4)
O(2)—C(2)	1.15(3)	1.17(3)			
M—C(1)—O(1)	178(2)	178(2)	M—C(3)—O(3)	177(2)	176(3)
M—C(2)—O(2)	178(2)	176(2)			
(iii) In the organic ligands					
C(4)—C(5)	1.34(2)	1.40(3)	C(10)—C(11)	1.40(3)	1.43(3)
C(4)—C(6)	1.46(2)	1.43(3)	C(12)—C(13)	1.43(2)	1.45(3)
C(5)—C(12)	1.53(2)	1.48(3)	C(12)—C(17)	1.37(3)	1.42(3)
C(6)—C(7)	1.44(2)	1.41(3)	C(13)—C(14)	1.41(3)	1.33(3)
C(6)—C(11)	1.43(2)	1.40(3)	C(14)—C(15)	1.35(3)	1.38(3)
C(7)—C(8)	1.36(3)	1.41(3)	C(15)—C(16)	1.41(3)	1.41(3)
C(8)—C(9)	1.38(3)	1.38(3)	C(16)—C(17)	1.40(3)	1.35(3)
C(9)—C(10)	1.40(3)	1.39(3)			
Ni(1)—C(4)—M	75.3(7)	73.9(7)	C(8)—C(7)—C(6)	119(2)	120(2)
C(5)—C(4)—C(6)	129(2)	129(2)	C(9)—C(8)—C(7)	124(2)	120(2)
C(5)—C(4)—M	69(1)	69(1)	C(10)—C(9)—C(8)	118(2)	122(2)
C(6)—C(4)—Ni(1)	126(1)	128(2)	C(11)—C(10)—C(9)	121(2)	119(2)
C(6)—C(4)—M	127(1)	128(1)	C(6)—C(11)—C(10)	120(2)	121(2)
Ni(2)—C(5)—M	76.2(6)	75.6(8)	C(13)—C(12)—C(17)	121(2)	117(2)
C(12)—C(5)—Ni(2)	122(1)	124(2)	C(13)—C(12)—C(5)	119(2)	120(2)
C(12)—C(5)—M	136(1)	135(1)	C(17)—C(12)—C(5)	121(2)	123(2)
C(12)—C(5)—C(4)	126(2)	124(2)	C(14)—C(13)—C(12)	117(2)	121(2)
Ni(2)—C(5)—C(4)	109(1)	108(1)	C(15)—C(14)—C(13)	123(2)	122(2)
M—C(5)—C(4)	72(1)	73(1)	C(16)—C(15)—C(14)	121(2)	118(2)
C(7)—C(6)—C(11)	118(2)	119(2)	C(17)—C(16)—C(15)	118(2)	122(2)
C(7)—C(6)—C(4)	120(2)	119(2)	C(12)—C(17)—C(16)	121(2)	120(2)
C(11)—C(6)—C(4)	122(2)	122(2)			

[a] The data in the first column refer to the iron complex V (M = Fe), those in the second column to the ruthenium complex Va (M = Ru).

The $(2\sigma + \pi)$ bonding mode between the acetylene and a metal triangular cluster (often indicated as μ_3 (η^2-||) type [21]) such as that found in V and Va, has already been found in several homo-metallic clusters, $Ir_7(CO)_{12}(C_8H_{12})$-

$(C_8H_{11})(C_8H_{10})$ (XI) [22], $Fe_3(CO)_8(C_2Ph_2)_2$ "violet isomer" (XII) [23], $Ni_3(CO)_3[C_2(CF_3)_2](C_8H_8)$ (XIII) [24], $Os_3(CO)_{10}(C_2Ph_2)$ (XIV) [25], $(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_2Ph_2)$ (XV) [26], $(\eta\text{-}C_5H_5)_3Rh_3(CO)[C_2(C_6F_5)_2]$ (XVI) [26], $Os_3(CO)_7(C_2Ph_2)_3$ (XVII) [27], but in the case of heterometallic clusters the only samples are $FeCo_2(CO)_9(C_2Et_2)$ (XVIII) [28], and $(\eta\text{-}C_5H_5)_2NiRu_2(CO)_4(C_2Ph_2)$ (VIII) [10]. In Table 9 the more relevant structural features of V, Va, VIII and XI—XVIII are compared.

The three metal atoms form an equilateral triangle in V [Ni(1)—Ni(2) = 2.404(4), Ni(1)—Fe = 2.388(4) and Ni(2)—Fe = 2.381(4) Å] and an isosceles triangle in Va [Ni(1)—Ni(2) = 2.418(4), Ni(1)—Ru = 2.493(3) and Ni(2)—Ru = 2.496(3) Å]. These metal clusters are characterized by their small size, the Ni—Fe or Ni—Ru and Ni—Ni distances being close to the shortest ever found in heterometallic clusters. In the trimetallic III the values for the Ni—Fe bond lengths are 2.378 and 2.564 Å [5]; in the tetrametallic I the values for the Ni—Fe bond distances range from 2.408 to 2.432 Å and the value for the unique Ni—Ni bond length is 2.441 Å [2,3]; in the tetrametallic II, values ranging from 2.414 to 2.426 Å [2,3] were found for the Ni—Fe bond distances, and in the only two known mixed Ni—Ru clusters the Ni—Ru bond lengths are 2.555 and 2.572 in VI [8], 2.595, 2.611 and 2.644 Å in VII [9]. The very short metal—metal bonds in V and Va could be explained either by the bridging by the organic ligand or by the good electron-donor properties of the $(\eta\text{-}C_5H_5)Ni$ ligand, as already pointed out for III [5], VI [8], and VII [9]. The alkyne C(4)—C(5) bond lengths are 1.34(2) in V and 1.40(3) Å in Va; this difference is noteworthy, considering that the two clusters differ only in the unique metal atom, which makes V an equilateral and Va an isosceles triangle of metals. The C—C alkyne bond lengths for V, Va and clusters VII—XVIII are compared in Table 9. Rationalization of the C—C bond lengthening upon coordination to the metals is difficult, even when the comparison is restricted to diphenylacetylene monosubstituted complexes. For complexes V, XII, Va and XIV an increase of the C—C length is observed, in general agreement with the size of the $FeNi_2$, Fe_3, $RuNi_2$ and Os_3 clusters, and with the M—C(σ) bond lengths. When the whole series of complexes is considered, this trend is not confirmed; thus, complex XV has a larger cluster than Va and a similar C—C bond length; complexes XIV and XVII show very different C—C bond lengths and clusters of comparable size.

Our opinion is that in the complexes considered above, which probably represent the largest series of derivatives having the same alkyne—metal interactions ever studied by X-ray methods, factors other than the cluster size probably influence the C—C distances. For example, the side of the cluster parallel to the alkyne is generally the longest. However, exceptions are observed when more rigid polymetallic clusters are considered; and furthermore, when cyclopentadienyls replace CO's on the metals, smaller elongations are observed. This is probably due to electronic or steric effects of the substituents.

A comparison between the iron-nickel and the ruthenium-nickel systems

Considerable differences are found in the two systems; see for example the reactions in Scheme 1 and ref. 3. Intramolecular hydrogen transfer occurs either for iron or ruthenium; alkyne isomerization occurs only for the latter.

TABLE 9

METAL—METAL, METAL—CARBON AND CARBON—CARBON DISTANCES IN V, Va, XI—XIX AND RELATED COMPLEXES (Å)

Complex	M—M[a]	M—C(σ)	M—C(π)	C—C	Reference
$Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$	$\underline{2.690}$, 2.738, 2.678	2.04, 2.08	2.20, 2.20	1.32[b]	22
$Os_3(CO)_7(C_2Ph_2)_3$	$\underline{2.680}$, 2.814, 2.744	2.08, 2.16	2.22, 2.28	1.33	27
$(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3(C_2Ph_2)$	$\underline{2.404}$, 2.388[c], 2.381[c]	1.85, 1.86	2.00, 2.04	1.34	This work
$FeCo_2(CO)_9(C_2Et_2)$	$\underline{2.576}$, 2.479[c], 2.489[c]	1.961[d], 1.957[d]	2.047[e], 2.045[e]	1.37	28
$Ni_3(CO)_3\{C_2(CF_3)_2\}(C_8H_8)$	$\underline{2.7017}$, 2.4560, 2.4583	1.889, 1.898	1.989, 2.013	1.381	24
$Fe_3(CO)_8(C_2Ph_2)_2$ "violet"	$\underline{2.592}$, 2.469, 2.457	1.995, 2.036	1.980, 1.980	1.375, 1.395	23
$(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_2Ph_2)$	$\underline{2.674}$, 2.655, 2.638	2.022, 2.040	2.110, 2.154	1.385	26
$(\eta\text{-}C_5H_5)_2NiRu_2(CO)_4(C_2Ph_2)$	$\underline{2.553}$[c], 2.550[c], 2.712	1.926, 2.075[f]	2.091, 2.148[f]	1.383	10
$(\eta\text{-}C_5H_5)_2Ni_2Ru(CO)_3(C_2Ph_2)$	$\underline{2.418}$, 2.493[c], 2.496[c]	1.91, 1.92	2.15[f], 2.21[f]	1.40	This work
$(\eta\text{-}C_5H_5)_3Rh_3(CO)\{C_2(C_6F_5)_2\}$	$\underline{2.672}$, 2.599, 2.588	2.02, 2.03	2.09, 2.09	1.41	26
$Os_3(CO)_{10}(C_2Ph_2)$	$\underline{2.883}$, 2.844, 2.711	2.182, 2.070	2.188, 2.293	1.439	29

[a] The M—M distances parallel to the C—C alkyne bond are underlined. [b] The complexes are disposed in order of increasing C—C distances, e.g. of alkyne "activation". [c] Heterometallic M—M′ distances. [d] Co—C distances. [e] Fe—C distances. [f] Ru—C distances.

Exchange of alkyne from nickel to the other metal is more important for ruthenium; this process is sometimes competitive with the formation of mixed clusters, and is particularly evident when $HRu_3(CO)_9C_2Bu^t$ is reacted with $(\eta\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$.

In the presence of alkynes, iron and nickel give a square-planar structure, whereas ruthenium and nickel always give butterfly clusters; Fe_2Ni_2 and $NiRu_3$ cores respectively, are present. Apparently the synthesis of the $NiRu_3$ butterfly clusters is more selective, and depends on the alkyne-substituted parent ruthenium reactants; three different mechanisms of formation have been noted for VI ("addition") [8], VII ("insertion") [9], and IX ("substitution" of $(\eta\text{-}C_5H_5)Ni$ on the preformed alkyne-ruthenium complexes).

In the ruthenium-nickel system the formation of mixed-metal clusters is observed when the alkyne is bound to the ruthenium reactant; usually alkyne transfer occurs when this is coordinated to the nickel parent product. In the iron-nickel system, on the other hand, cluster degradation and "metal fragment condensation" is probably the main reaction pattern; indirect support for this is provided by the low selectivity of the reactions and the higher yields of trimetallic mixed products.

The synthesis of V in good yields from $(\eta\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$ and iron carbonyls and in lower yields from $Fe_3(CO)_9(C_2Ph_2)$ and cyclopentadienyl, carbonyl nickel derivatives and the synthesis of Va via $Ru_4(CO)_{12}(C_2Ph_2)$ support the above hypotheses.

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