The Influence of Molecular Hydrogen on the Reaction between $[Ru_3(CO)_{12}]$ and $[Ni_2(\eta\text{-}C_5H_5)(C_2Ph_2)]$. Synthesis and Crystal Structure of the New Heteropentametallic Cluster $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_6(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}C_2Ph_2)]$ *

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The effect of the presence of H_2 on the reaction of $[Ru_3(CO)_{12}]$ with $[Ni_2(\eta\text{-}C_5H_5)_2(C_2Ph_2)]$ has been investigated; under these conditions the new square-pyramidal heteropentametallic cluster $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_6(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}C_2Ph_2)]$ is obtained in 6—10% yield, in conjunction with other heterometallic compounds. This complex has been characterized by spectroscopy and its crystal structure determined by *X*-ray methods. It crystallizes in the monoclinic space group $P2_1/n$, with $a = 16.459(8)$, $b = 20.280(9)$, $c = 9.423(6)$ Å, $\beta = 105.67(3)°$, and $Z = 4$. The structure has been solved by direct and Fourier methods and refined by full-matrix least squares to $R = 0.040$ for 3 114 observed reflections. The cluster adopts a square-pyramidal arrangement with alternating Ru and Ni atoms in the basal plane; the diphenylacetylene is co-ordinated to these basal metal atoms, through σ bonds to the Ni and π bonds to the Ru atoms. A comparison of this complex, which is the first example of a heteropentametallic alkyne-substituted cluster having a square-pyramidal arrangement, with other homo- and hetero-metallic clusters is made on the basis of isolobality.

We have previously reported the synthesis of several new heterometallic derivatives containing nickel and one of the iron triad metals.[1-6] The routes explored were based on the pyrolysis of the $[M_3(CO)_{12}]$ carbonyls (M = Fe, Ru, or Os) in the presence of $[Ni(\eta\text{-}C_5H_5)_2]$, $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$, or $[Ni_2(\eta\text{-}C_5H_5)_2(RC_2R')]$ (R = R' = Ph or Et; R = H, R' = Bu^t or isopropenyl), or on the thermal treatment of iron carbonylalkyne, ruthenium carbonylalkyne, and ruthenium hydridocarbonyl-alkyne clusters, or of osmium hydridocarbonyl-alkyne, -vinylidene, and -alkenyl derivatives in the presence of $[Ni(\eta\text{-}C_5H_5)_2]$ or $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$. We found that the structures of the heterometallic complexes were dependent on the nature of the starting compounds and in particular on the alkyne co-ordination either on the nickel or on the iron triad derivatives.[6] Some of the heterometallic clusters obtainable in the above reactions were found to be active in the homogeneous hydrogenation of small unsaturated molecules.[7]

All the above reactions were initially performed under dry nitrogen; however, the detection of a hydridic hydrogen in the complexes $[NiM_3(\eta\text{-}C_5H_5)(\mu\text{-}H)(CO)_9(\mu_4,\eta^2\text{-}C{=}CHR)]$ (M = Ru [4,8] or Os,[9] R = Bu^t or Pr^i), having an extra hydrogen with respect to the starting compounds ($[M_3H(CO)_9(C_2R)]$ acetylide clusters and $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$), induced us to employ a hydrogen atmosphere in order to increase the yields. The yields increased from about 20% to about 40% for M = Ru and R = Bu^t, and the presence of molecular hydrogen was found to be critical for the formation of the osmium derivative. Also, different yields were obtained under an (N_2 or H_2) atmosphere in the synthesis of the $[NiM_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_3(CO)_9]$ (M = Ru or Os) and $[Ni_3Os_3(\eta\text{-}C_5H_5)_3(CO)_9]$ derivatives.[7]

This prompted us to extend the use of molecular hydrogen to other reactions. The possibility of modifying, at least in part, the nature of the products, thus making more versatile simple pyrolytic reactions, is of considerable interest in rationalizing the methods for synthesizing heterometallic clusters. We have now found that for the reaction of $[Ru_3(CO)_{12}]$ and $[Ni_2(\eta\text{-}C_5H_5)_2(C_2Ph_2)]$ the presence of hydrogen leads to different yields of already known heterometallic species and to the synthesis of the new heteropentametallic complex $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_6(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}C_2Ph_2)]$ (1). The structure of the new cluster has been determined, and its isolobality with $[M_3(CO)_6(\mu\text{-}CO)_2(C_2R_2)_2]$ (2: M = Fe or Ru; black isomers, structure determined for the iron derivative only,[10] same structure attributed to the ruthenium derivative by spectroscopic methods [11,12]), $[Ru_3(CO)_6(\mu\text{-}CO)_2(RC_2R')_3]$ (3),[13,14] and $[NiRu_3(\eta\text{-}C_5H_5)(CO)_6(\mu\text{-}CO)_2(C_6H_9)]$ (4) [5] is discussed.

Experimental

Synthesis and Purification of Complex (1).—The complex $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$ was refluxed with a 1.5 : 1 molar excess of diphenylacetylene in octane, under a nitrogen atmosphere, until the carbonyl-stretching bands of the nickel reactant disappeared (i.r. spectroscopy). The reaction mixture was allowed to cool, then $[Ru_3(CO)_{12}]$ was added (in a 1 : 1 mol ratio with respect to the initial nickel reactant) and the reaction was allowed to proceed for 20 min under reflux and with a slow current of hydrogen.

The reaction mixture was then cooled under hydrogen, rapidly filtered, and evaporated under reduced pressure. The residue was dissolved in chloroform and separated by preparative t.l.c. [Merck Kieselgel G. plates, with diethyl ether–light petroleum (1:9) as eluant]. The following products were isolated and identified (average yields in parentheses): $[NiRu_3(\eta\text{-}C_5H_5)(CO)_9(C_2Ph_2)]$ (10%);[6] $[Ru_4(CO)_{12}(C_2Ph_2)]$ (5%);[15] $[Ni_2Ru(\eta\text{-}C_5H_5)_2(CO)_3(C_2Ph_2)]$ (30%);[6] $[NiRu_2(\eta\text{-}C_5H_5)_2(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)]$ (5%);[16a] complex (1) (6—10%); considerable amounts of metal were also deposited on the walls of the reaction vessels {probably due to the formation

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* 2,5;4,5-Di-μ-carbonyl-2,2,4,4,5,5-hexacarbonyl-1,3-bis(η-cyclopentadienyl)-μ_4-[η-diphenylvinylene-C^1(Ni^1)C^2(Ni^3)C^{1-2}(Ru^{2,4})]-*cyclo*-dinickeltriruthenium(6*Ni*–*Ru*,2*Ru*–*Ru*).

Supplementary data available (No. SUP 23826, 23 pp.): H-atom co-ordinates, 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

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru(1)	3 180(1)	683(1)	9 581(1)	C(11)	1 097(5)	1 107(4)	8 576(11)
Ru(2)	3 710(1)	730(1)	7 083(1)	C(12)	375(6)	1 242(5)	7 475(11)
Ru(3)	2 391(1)	1 600(1)	6 437(1)	C(13)	−417(6)	1 211(6)	7 751(14)
Ni(1)	3 631(1)	1 802(1)	8 686(1)	C(14)	−468(7)	1 064(6)	9 161(13)
Ni(2)	2 146(1)	394(1)	7 122(1)	C(15)	244(7)	918(6)	10 242(14)
O(1)	2 492(5)	−377(4)	11 164(10)	C(16)	1 038(6)	954(5)	9 967(11)
O(2)	4 473(5)	940(4)	12 459(8)	C(17)	2 218(5)	2 180(4)	9 715(10)
O(3)	4 217(5)	−465(4)	9 087(9)	C(18)	2 573(7)	2 219(5)	11 220(11)
O(4)	3 569(6)	1 667(5)	4 491(9)	C(19)	2 337(8)	2 732(6)	12 008(13)
O(5)	5 576(5)	808(4)	7 667(9)	C(20)	1 721(8)	3 180(6)	11 300(14)
O(6)	3 820(6)	−229(5)	4 731(10)	C(21)	1 356(7)	3 141(6)	9 810(14)
O(7)	2 228(6)	3 048(4)	5 717(9)	C(22)	1 601(6)	2 632(5)	8 978(13)
O(8)	980(6)	1 407(5)	3 676(9)	C(23)	1 822(8)	−191(6)	5 169(14)
C(1)	2 747(6)	31(5)	10 542(13)	C(24)	1 086(7)	11(6)	5 548(14)
C(2)	3 986(6)	863(5)	11 392(11)	C(25)	1 081(7)	−249(5)	6 943(14)
C(3)	3 900(6)	43(4)	8 868(11)	C(26)	1 819(9)	−599(5)	7 407(14)
C(4)	3 310(7)	1 458(6)	5 412(11)	C(27)	2 298(8)	−580(5)	6 405(15)
C(5)	4 868(6)	803(5)	7 430(12)	C(28)	4 756(7)	2 204(5)	8 250(14)
C(6)	3 768(7)	132(6)	5 654(12)	C(29)	4 922(6)	1 960(5)	9 746(13)
C(7)	2 297(7)	2 500(5)	6 044(12)	C(30)	4 423(6)	2 332(5)	10 480(12)
C(8)	1 511(7)	1 461(5)	4 736(11)	C(31)	3 956(6)	2 788(5)	9 453(12)
C(9)	1 951(6)	1 123(5)	8 299(10)	C(32)	4 140(7)	2 712(5)	8 113(14)
C(10)	2 504(5)	1 655(4)	8 843(9)				

and thermal decomposition of [Ni(CO)$_4$] during the reaction}, and one product, in small amount, is as yet unidentified.

The complex [Ru$_3$(CO)$_{12}$] was obtained by literature methods;[16b] the alkyne was purchased from Fluka. Nitrogen and hydrogen were commercial gases, dried prior to use, as were the solvents.

Physical Measurements.—The products were analyzed by means of an F & M 185 C,H,N Analyzer and a Perkin-Elmer atomic absorption spectrophotometer. The i.r. spectra were recorded on a Perkin-Elmer 580 B instrument, the ^{1}H n.m.r. on a JEOL C 60 HL. Mass spectra were obtained on a Hitachi-Perkin-Elmer RMU 6H single-focusing device operating with a direct-inlet system at 70 eV (*ca.* 1.1×10^{-17} J). Although the mass-spectrometric measurements were made at the lowest temperature compatible with the volatility of the samples, in some instances, *e.g.* with complex (1), decomposition was observed. Only fragments with Ru$_2$Ni$_2$ isotopic pattern could be observed at the highest *m/e* values.

X-*Ray Crystallography of Complex* (1).—The dark brown complex is moderately soluble in heptane; crystals suitable for the *X*-ray analysis were obtained from heptane–chloroform solutions kept at −10 °C for days, under a nitrogen atmosphere (Found: C, 41.0; H, 2.30; Ni, 12.3; Ru, 32.1. Calc. for $C_{32}H_{20}Ni_2O_8Ru_3$: C, 40.25; H, 2.10; Ni, 12.3; Ru, 31.95%). A plate-like crystal of dimensions *ca.* $0.10 \times 0.25 \times 0.30$ mm was used for data collection. The unit-cell parameters were refined by a least-squares procedure applied to the θ values of 28 reflections accurately measured on a Siemens AED single-crystal diffractometer.

Crystal data. $C_{32}H_{20}Ni_2O_8Ru_3$, $M = 953.13$, monoclinic, space group $P2_1/n$, $a = 16.459(8)$, $b = 20.280(9)$, $c = 9.423(6)$ Å, $\beta = 105.67(3)^\circ$, $U = 3\,028(3)$ Å^3, $Z = 4$, $D_c = 2.091$ g cm^{-3}, $F(000) = 1\,856$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 27.14 cm^{-1}.

Intensity data were collected on the same diffractometer using niobium-filtered Mo-K_α radiation and the θ–2θ scan technique. The intensity of one standard reflection was measured after 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A total of 5 322 independent reflections was measured (θ range 3—25°) of which 3 114, having $I \geqslant 2\sigma(I)$, were considered observed and employed in the analysis. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established first by Wilson's method and then by least-squares refinement. No correction for absorption was applied in view of the low absorbance of the sample.

Structure determination and refinement. The structure was solved by direct and Fourier methods and refined by full-matrix least squares using the SHELX system of computer programs,[17] with initially isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were placed at their geometrically calculated positions and included in the final structure-factor calculations with isotropic thermal parameters. The final *R* value was 0.040 (observed reflections only).

The atomic scattering factors used, corrected for the anomalous dispersion of Ru and Ni, were taken from ref. 18. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were chosen in the first stages of the refinement, then calculated as $w = K/[\sigma^2(F_o) + gF_o^2]$ with $K = 0.1950$ and $g = 0.012\,67$.

Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1. All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna.

Results and Discussion

Spectroscopic Properties of Complex (1).—This complex shows i.r. absorptions indicative of both terminal and bridging CO groups (Table 2). The values are comparable with those of complexes (2)—(4), but shifted to lower wavenumbers probably because of the presence of two 'electron-rich' nickel atoms.

In the ^{1}H n.m.r. (CDCl$_3$) complex (1) shows a multiplet at δ 6.90—7.10 and a singlet at 5.40, relative intensities 1 : 1, which are attributed to the phenyl groups and to the cyclo-

Table 2. Comparison of i.r. data (cm^{-1}, ν_{CO} region, hydrocarbon solvents)

Complex	Ref.	
(1) $[Ni_2Ru_3(\eta-C_5H_5)_2(CO)_8(C_2Ph_2)]$	This work	2 030s, 2 004vs, 1 974s, 1 962s, 1 945s, 1 865mw, 1 835m
(2a) $[Fe_3(CO)_8(C_2Ph_2)_2]$	10, 11	2 060m, 2 026vs, 2 023 (sh), 2 006 (sh), 1 975s, 1 869m, 1 858m
(2b) $[Ru_3(CO)_8(C_2Ph_2)_2]$	12	2 071m, 2 027vs, 2 023 (sh), 2 018 (sh), 1 977s, 1 882m, 1 861m
(3a) $[Ru_3(CO)_8(HC_2Bu^t)_3]$	13	2 065s, 2 024 (sh), 2 020vs, 2 003s, 1 971s, 1 878s, 1 859s
(3b) $[Ru_3(CO)_8(C_{12}H_{18})]$	14	2 068ms, 2 023vs, 2 008s, 1 977s, 1 880ms, 1 860ms
(4) $[NiRu_3(\eta-C_5H_5)(CO)_8(C_6H_9)]$	5	2 049s, 2 013vs, 1 981s, 1 964s, 1 859m, 1 837s

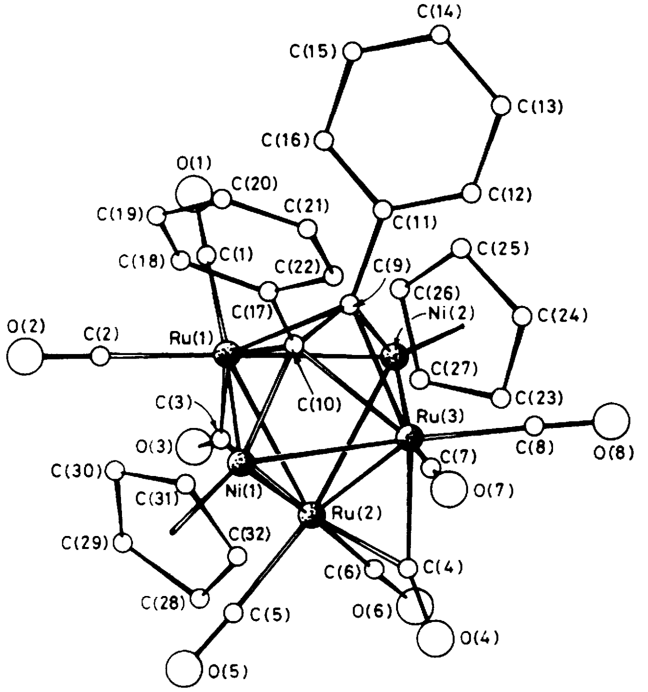


Figure 1. View of the molecular structure of the complex $[Ni_2Ru_3(\eta-C_5H_5)_2(CO)_8(C_2Ph_2)]$ with the atomic numbering scheme

pentadienyl ligands, respectively. No signals due to hydridic hydrogen could be detected in the range δ 0 to -25.

As already mentioned, complex (1) decomposes in the mass spectrometer giving fragments with Ru_2Ni_2 isotopic pattern, instead of the parent ion.

Crystal Structure of Complex (1).—The structure is represented in Figure 1 together with the atomic numbering scheme. The pentanuclear heterometallic framework adopts a square-pyramidal arrangement with Ru(2) at the apex and alternating Ni and Ru atoms, Ni(1), Ru(1), Ni(2), and Ru(3), in the basal plane. The diphenylacetylene ligand interacts with the four metals in this basal plane. Each Ni atom is η-co-ordinated by a cyclopentadienyl ligand and, of the eight carbonyls, six are terminal (two on each Ru atom) and two slightly unsymmetrically bridge two Ru–Ru edges of the cluster. Bond distances and angles are given in Table 3.

To our knowledge only one other example of a heterometallic pentanuclear ruthenium–nickel cluster has been reported, the nickel-bridged butterfly $[NiRu_4(CO)_9(\mu-PPh_2)_2(\mu_4,\eta^2-C{\equiv}CPr^i)_2]$.[19] Hence, complex (1) is the first heterometallic cluster with a 2 : 3 Ni : Ru ratio and with a square-pyramidal arrangement. Square-pyramidal clusters have been reported for the ruthenium homometallic derivatives $[Ru_5(CO)_{13}(PPh_2)(C_2Ph)]$ [20] and $[Ru_5(CO)_{13}(PPh_2)(C_2Ph)_2]$.[21] Heterometallic square-pyramidal clusters have been reported for carbido-clusters.[22] The Ni–Ru bond lengths are in the range 2.545—2.673 Å and hence are comparable with those found in other such clusters.[4–6,8,19]

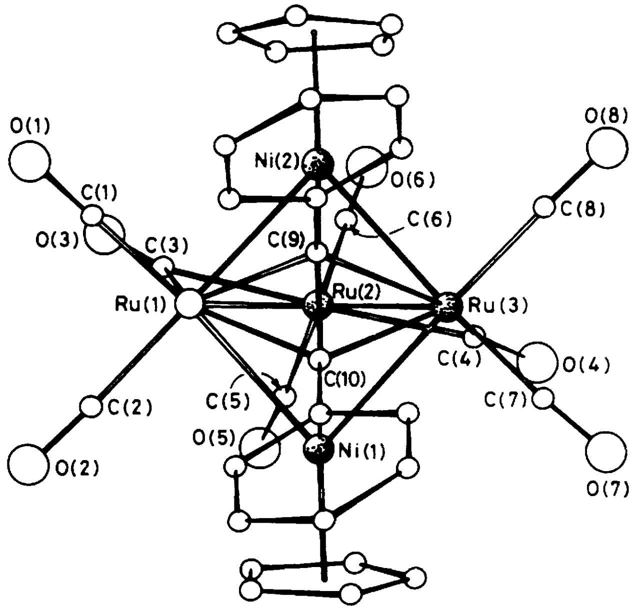


Figure 2. Molecular structure of the complex $[Ni_2Ru_3(\eta-C_5H_5)_2(CO)_8(C_2Ph_2)]$ showing the approximate C_2 symmetry

The pentametallic cluster can be also described as a trigonal bipyramid with the Ru atoms in the equatorial positions and the Ni atoms in the apical positions [Ni(1) and Ni(2) 1.897 Å and 1.891 Å respectively above and below the plane through the Ru atoms]. The Ru triangle is open [Ru(1)–Ru(2) 2.724(2), Ru(2)–Ru(3) 2.735(3), and Ru(1) $\cdots$ Ru(3) 3.441(2) Å; Ru(1)–Ru(2)–Ru(3) 78.2(1)°] and the two Ru(1)–Ru(2) and Ru(2)–Ru(3) sides are bridged by carbonyls.

Complex (1) has approximate C_2 symmetry as shown clearly by Figure 2. When considering the C(9) and C(10) carbon atoms of the alkyne together with the Ru and Ni metal atoms, the $Ni_2Ru_3C_2$ ' core ' of the complex can be described as a pentagonal bipyramid with Ru(1) and Ru(3) at the apices and

Table 3. Selected bond distances (Å) and angles (°) in complex (1)

(*a*) The metal co-ordination spheres

Ru(1)–Ru(2)	2.724(2)	Ru(3)–Ni(2)	2.589(3)	Ru(2)–C(4)	2.13(1)	Ru(3)–C(10)	2.23(1)
Ru(1)–Ni(1)	2.598(3)	Ru(1)–C(1)	1.85(1)	Ru(2)–C(5)	1.85(1)	Ni(1)–C(10)	1.92(1)
Ru(1)–Ni(2)	2.545(2)	Ru(1)–C(2)	1.89(1)	Ru(2)–C(6)	1.83(1)	Ni(1)–B(1) *	1.767(3)
Ru(2)–Ru(3)	2.735(3)	Ru(1)–C(3)	1.99(1)	Ru(3)–C(4)	2.02(1)	Ni(2)–C(9)	1.93(1)
Ru(2)–Ni(1)	2.670(3)	Ru(1)–C(9)	2.24(1)	Ru(3)–C(7)	1.86(1)	Ni(2)–B(2) *	1.767(3)
Ru(2)–Ni(2)	2.673(3)	Ru(1)–C(10)	2.28(1)	Ru(3)–C(8)	1.87(1)		
Ru(3)–Ni(1)	2.547(2)	Ru(2)–C(3)	2.14(1)	Ru(3)–C(9)	2.29(1)		

Ru(2)–Ru(1)–Ni(1)	60.2(1)	C(1)–Ru(1)–C(2)	88.0(5)	Ni(1)–Ru(3)–C(7)	90.7(3)
Ru(2)–Ru(1)–Ni(2)	60.8(1)	C(1)–Ru(1)–C(3)	92.4(4)	Ni(1)–Ru(3)–C(8)	177.6(3)
Ni(1)–Ru(1)–Ni(2)	94.9(1)	C(1)–Ru(1)–C(9)	97.9(4)	Ni(1)–Ru(3)–C(9)	77.2(2)
Ru(3)–Ru(2)–Ni(1)	56.2(1)	C(1)–Ru(1)–C(10)	123.1(4)	Ni(1)–Ru(3)–C(10)	46.9(2)
Ru(3)–Ru(2)–Ni(2)	57.2(1)	C(2)–Ru(1)–C(3)	95.4(4)	Ni(2)–Ru(3)–C(4)	99.9(3)
Ru(3)–Ru(2)–Ru(1)	78.2(1)	C(2)–Ru(1)–C(9)	136.0(4)	Ni(2)–Ru(3)–C(7)	165.1(4)
Ni(1)–Ru(2)–Ni(2)	90.3(1)	C(2)–Ru(1)–C(10)	105.9(4)	Ni(2)–Ru(3)–C(8)	86.2(3)
Ni(1)–Ru(2)–Ru(1)	57.6(1)	C(3)–Ru(1)–C(9)	127.6(4)	Ni(2)–Ru(3)–C(9)	46.0(2)
Ni(2)–Ru(2)–Ru(1)	56.3(1)	C(3)–Ru(1)–C(10)	138.3(3)	Ni(2)–Ru(3)–C(10)	76.7(2)
Ni(1)–Ru(3)–Ni(2)	95.1(1)	C(9)–Ru(1)–C(10)	36.5(3)	C(4)–Ru(3)–C(7)	94.4(5)
Ni(1)–Ru(3)–Ru(2)	60.6(1)	Ru(3)–Ru(2)–C(3)	122.2(3)	C(4)–Ru(3)–C(8)	94.3(5)
Ni(2)–Ru(3)–Ru(2)	60.2(1)	Ru(3)–Ru(2)–C(4)	47.1(3)	C(4)–Ru(3)–C(9)	137.6(4)
Ru(1)–Ni(1)–Ru(2)	62.2(1)	Ru(3)–Ru(2)–C(5)	134.8(3)	C(4)–Ru(3)–C(10)	128.7(4)
Ru(1)–Ni(1)–Ru(3)	84.0(1)	Ru(3)–Ru(2)–C(6)	117.3(4)	C(4)–Ru(3)–Ru(2)	50.5(3)
Ru(2)–Ni(1)–Ru(3)	63.2(1)	Ni(1)–Ru(2)–C(3)	96.0(2)	C(7)–Ru(3)–C(8)	88.5(5)
Ru(1)–Ni(2)–Ru(2)	62.9(1)	Ni(1)–Ru(2)–C(4)	78.5(3)	C(7)–Ru(3)–C(9)	122.8(4)
Ru(1)–Ni(2)–Ru(3)	84.2(1)	Ni(1)–Ru(2)–C(5)	92.3(3)	C(7)–Ru(3)–C(10)	97.7(4)
Ru(2)–Ni(2)–Ru(3)	62.6(1)	Ni(1)–Ru(2)–C(6)	166.9(4)	C(7)–Ru(3)–Ru(2)	134.1(4)
Ru(2)–Ru(1)–C(1)	134.7(3)	Ni(2)–Ru(2)–C(3)	76.1(3)	C(8)–Ru(3)–C(9)	105.2(4)
Ru(2)–Ru(1)–C(2)	117.5(3)	Ni(2)–Ru(2)–C(4)	94.6(3)	C(8)–Ru(3)–C(10)	135.5(4)
Ru(2)–Ru(1)–C(3)	51.2(3)	Ni(2)–Ru(2)–C(5)	165.4(3)	C(8)–Ru(3)–Ru(2)	118.6(3)
Ru(2)–Ru(1)–C(9)	88.5(2)	Ni(2)–Ru(2)–C(6)	94.7(4)	C(9)–Ru(3)–C(10)	36.5(3)
Ru(2)–Ru(1)–C(10)	87.1(2)	C(3)–Ru(2)–C(4)	169.3(4)	C(9)–Ru(3)–Ru(2)	87.3(3)
Ni(1)–Ru(1)–C(1)	164.7(3)	C(3)–Ru(2)–C(5)	89.3(4)	C(10)–Ru(3)–Ru(2)	87.9(2)
Ni(1)–Ru(1)–C(2)	86.1(3)	C(3)–Ru(2)–C(6)	96.9(4)	C(10)–Ni(1)–Ru(1)	58.2(2)
Ni(1)–Ru(1)–C(3)	102.2(3)	C(3)–Ru(2)–Ru(1)	46.5(3)	C(10)–Ni(1)–Ru(2)	96.5(2)
Ni(1)–Ru(1)–C(9)	76.9(3)	C(4)–Ru(2)–C(5)	100.0(5)	C(10)–Ni(1)–Ru(3)	57.7(2)
Ni(1)–Ru(1)–C(10)	45.9(2)	C(4)–Ru(2)–C(6)	89.0(5)	C(9)–Ni(2)–C(10)	22.1(3)
Ni(2)–Ru(1)–C(1)	91.7(4)	C(4)–Ru(2)–Ru(1)	123.8(3)	C(9)–Ni(2)–Ru(1)	58.2(3)
Ni(2)–Ru(1)–C(2)	177.0(3)	C(5)–Ru(2)–C(6)	85.8(5)	C(9)–Ni(2)–Ru(2)	97.1(3)
Ni(2)–Ru(1)–C(3)	81.7(3)	C(5)–Ru(2)–Ru(1)	113.9(3)	C(9)–Ni(2)–Ru(3)	58.7(3)
Ni(2)–Ru(1)–C(9)	46.9(2)	C(6)–Ru(2)–Ru(1)	134.7(4)		
Ni(2)–Ru(1)–C(10)	76.7(2)	Ni(1)–Ru(3)–C(4)	83.4(3)		

(*b*) The carbonyl groups

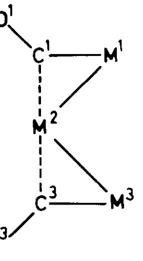
O(1)–C(1)	1.15(1)	Ru(1)–C(1)–O(1)	178.6(9)	Ru(3)–C(4)–O(4)	142.0(9)
O(2)–C(2)	1.11(1)	Ru(1)–C(2)–O(2)	176.8(9)	Ru(2)–C(4)–Ru(3)	82.4(4)
O(3)–C(3)	1.15(1)	Ru(1)–C(3)–O(3)	143.8(8)	Ru(2)–C(5)–O(5)	175.8(9)
O(4)–C(4)	1.15(1)	Ru(2)–C(3)–O(3)	133.5(8)	Ru(2)–C(6)–O(6)	177.6(9)
O(5)–C(5)	1.12(1)	Ru(1)–C(3)–Ru(2)	82.4(3)	Ru(3)–C(7)–O(7)	176.1(9)
O(6)–C(6)	1.16(1)	Ru(2)–C(4)–O(4)	135.4(9)	Ru(3)–C(8)–O(8)	176.6(9)
O(7)–C(7)	1.15(1)				
O(8)–C(8)	1.14(1)				

(*c*) The organic ligands

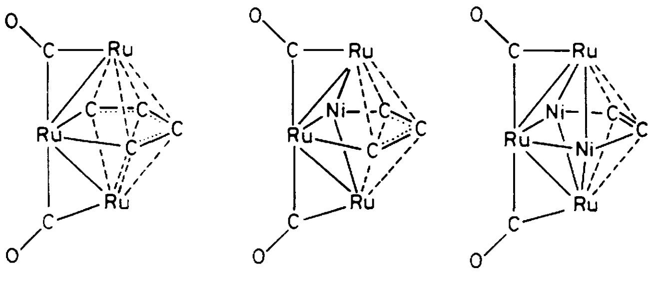
C(9)–C(10)	1.41(1)	C(19)–C(20)	1.39(2)	C(10)–C(9)–C(11)	119.7(8)
C(9)–C(11)	1.50(1)	C(20)–C(21)	1.37(2)	Ru(3)–C(9)–C(10)	69.5(5)
C(10)–C(17)	1.50(1)	C(21)–C(22)	1.42(2)	Ru(3)–C(9)–C(11)	130.5(7)
C(11)–C(12)	1.38(1)	C(23)–C(24)	1.41(2)	Ni(2)–C(9)–C(10)	127.1(7)
C(11)–C(16)	1.38(1)	C(23)–C(27)	1.45(2)	Ni(2)–C(9)–C(11)	113.2(7)
C(12)–C(13)	1.40(1)	C(24)–C(25)	1.42(2)	C(9)–C(10)–C(17)	118.3(8)
C(13)–C(14)	1.39(2)	C(25)–C(26)	1.37(2)	Ru(1)–C(10)–C(9)	70.4(5)
C(14)–C(15)	1.36(2)	C(26)–C(27)	1.38(2)	Ru(3)–C(10)–C(9)	74.0(5)
C(15)–C(16)	1.40(1)	C(28)–C(29)	1.45(2)	Ni(1)–C(10)–C(9)	129.0(7)
C(17)–C(18)	1.38(1)	C(29)–C(30)	1.42(1)	Ru(1)–C(10)–C(17)	130.4(6)
C(17)–C(22)	1.40(1)	C(30)–C(31)	1.41(1)	Ru(3)–C(10)–C(17)	130.0(6)
C(18)–C(19)	1.39(2)	C(31)–C(32)	1.38(2)	Ni(1)–C(10)–C(17)	112.6(6)

* B(1) and B(2) are the baricentres of the two cyclopentadienyl rings.

Table 4. Bond distances (Å) and angles (°) for the $M_3(\mu\text{-}CO)_2$ units in complexes (1)—(4)



Complex	M^1–M^2, M^2–M^3	M^1–M^2–M^3	M^1–C^1, M^2–C^1	M^1–C^1–O^1	M^3–C^3, M^2–C^3	M^3–C^3–O^3
(1) $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_8(C_2Ph_2)]$	2.724(2), 2.735(3)	78.2(1)	1.99(1), 2.14(1)	143.8(8)	2.02(1), 2.13(1)	142.0(9)
(2a) $[Fe_3(CO)_8(C_2Ph_2)_2]$	2.428(3), 2.435(3)	87.6(1)	1.842(19), 1.991(19)	143.8(1.5)	1.771(21), 1.998(21)	148.2(1.7)
(3a) $[Ru_3(CO)_8(HC_2Bu^t)_3]$	2.669(1), 2.661(2)	88.8(1)	1.98(1), 2.14(1)	144(1)	2.01(1), 2.12(2)	143(1)
(3b) $[Ru_3(CO)_8(C_{12}H_{18})]$	2.661(1), 2.645(2)	89.1(1)	1.990(7), 2.153(8)	144.3(6)	1.992(7), 2.148(8)	143.8(7)
(4) $[NiRu_3(\eta\text{-}C_5H_5)(CO)_8(C_6H_9)]$	2.693(3), 2.708(3)	84.3(1)	1.994(21), 2.173(21)	146.0(1.7)	1.987(21), 2.280(19)	147.8(1.6)



(2b), (3) (4) (1)

Figure 3. Comparison of the pentagonal-bipyramidal arrangements of the ' cores ' and of the ' open ' triangular arrangements of the Ru atoms with two CO groups bridging the two Ru–Ru sides in complexes (1)—(4)

Ru(2), Ni(1), C(10), C(9), and Ni(2) in the equatorial positions. This description is consistent with Wade's approach to cluster structures,[23] the two C–Ph units, forming the alkyne, each contributing three electrons to the total. Hence the 74-electron cluster (1) (if the alkyne is considered as a formal donor of four electrons) would have a *closo* structure (seven skeletal atoms and eight skeletal bond pairs) which is strictly comparable with those of the 48-electron clusters (2) and (3) and of the 62-electron cluster (4); all these clusters show skeletons having a pentagonal-bipyramidal structure (Figure 3).

Indeed, all complexes (1)—(4) contain an ' open ' metal triangle with two CO groups bridging the two short sides; the spectroscopic similarities within these complexes, already mentioned, support this comparison. The dimensions of these triangular arrangements together with the two bridging CO groups are compared in Table 4.

The structures of complexes (4) and (1) can be derived from those of (2) or (3) by gradual substitution of one and two carbons with nickel atoms (see Figure 3); hence the $Ni(\eta\text{-}C_5H_5)$ group would be isolobal[24] with the ≡C–R groups co-ordinated to the clusters. Indeed, both these units contribute three electrons to the cluster bonding in Wade's approach.

The co-ordination of the alkyne to the four basal metals of the pyramid in (1) is unique for pentanuclear clusters. The alkyne is σ-bonded to the Ni atoms [Ni(1)–C(10) 1.92(1) and Ni(2)–C(9) 1.93(1) Å] and π-bonded to the Ru(1) and Ru(3) atoms [Ru–C distances ranging from 2.23 to 2.29 Å], lying at the opposite vertices of a slightly tetrahedrally distorted square [Ru(1), Ni(1), Ru(3), and Ni(2) deviate by −0.12, 0.12, −0.12, and 0.12 Å from the mean plane passing through them, with Ru(2) out of plane by 2.00 Å]. The C(9)–C(10) bond is nearly perpendicular to the line passing through the Ru(1) and Ru(3) atoms [angle between the C(9)–C(10) and Ru(1)–Ru(3) vectors 87.5°] and is nearly parallel to the line passing through the Ni(1) and Ni(2) atoms [angle between the C(9)–C(10) and Ni(1)–Ni(2) vectors 1.6°]. A similar co-ordination of an alkyne to four metals in a slightly tetrahedrally distorted square-planar cluster has been found in $[Ni_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_6(C_2Et_2)]$[3] and in $[Fe_4(CO)_{11}(HC_2Et)_2]$.[25]

With respect to the ' alkyne activation ' upon co-ordination to the four metals, the C(9)–C(10) bond length in complex (1) [1.41(1) Å] is comparable with those found in $[Fe_4(CO)_{11}(HC_2Et)_2]$ [1.397(16) Å] and in $[Ni_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_6(C_2Et_2)]$ [1.374(15) Å]. This elongation (with respect to the free alkyne) is considerable, although slightly shorter than in homometallic butterfly clusters with the alkynic bond disposed parallel to the hinge side as in $[Ru_4(CO)_{12}(C_2Ph_2)]$[15] [1.46(2) Å] or in the heterometallic isomers $[FeRu_3(CO)_{12}(C_2Ph_2)]$[26] [1.460(3) and 1.458(4) Å respectively].

In the above reaction between $[Ru_3(CO)_{12}]$ and $[Ni_2(\eta\text{-}C_5H_5)_2(C_2Ph_2)]$ under an H_2 atmosphere an increase in yield of the species containing one nickel atom only is observed with respect to that obtained under N_2. Also in complex (1), which is obtained only under H_2, no Ni–Ni bond is observed. Therefore our previous hypotheses about the role of hydrogen are presumably correct; in contrast to nitrogen which only acts as an inert atmosphere, the hydrogen probably behaves as a reactant which favours Ni–Ni bond breaking.

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