

## The Reactivity of $\text{HRu}_3(\text{CO})_9\text{C}_2\text{Bu}^\dagger$ . Synthesis and Crystal Structure of $(\eta^5\text{-C}_5\text{H}_5)\text{NiRu}_3(\text{CO})_9\text{C}\cdot\text{C}(\text{H})\text{Bu}^\dagger$ , a New Mixed Ruthenium–Nickel Cluster

ENRICO SAPPA

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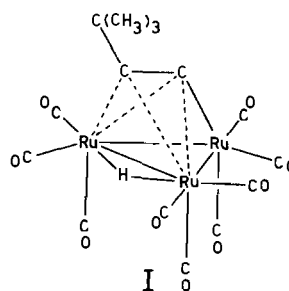
Received October 31, 1979

The title compound has been obtained by reacting the hydride  $\text{HRu}_3(\text{CO})_9\text{C}_2\text{Bu}^\dagger$  with  $(\eta^5\text{-C}_5\text{H}_5)_2\text{-Ni}_2(\text{CO})_2$  in hydrocarbon solvents, and has been characterized by elemental analysis, i.r. and mass spectroscopy. The crystal structure has been determined by X-ray methods. Crystals are monoclinic, space group  $\text{P2}_1/\text{n}$ , with  $Z = 4$  in a unit cell of dimensions  $a = 15.514(11)$ ,  $b = 17.003(13)$ ,  $c = 9.138(8)$  Å,  $\beta = 94.6(1)^\circ$ . The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to  $R = 0.036$  for 3806 independent observed reflections. The structure of the complex consists of a butterfly arrangement of three Ru and one Ni atoms, bonded to nine carbonyls through the Ru atoms, to a cyclopentadienyl group through the Ni atom and to a rearranged *t*-butylacetylene through all the metal atoms. The bonding of the alkyne to the cluster with the terminal carbon interacting with all the metals is quite uncommon. The formation of this complex can be interpreted as the reaction of a  $(\eta^5\text{-C}_5\text{H}_5)\text{-Ni}$  fragment on a Ru–Ru–C face of the tetrahedral  $\text{Ru}_3\text{C}$  core of the starting compound.

### Introduction

In the last years many tetranuclear clusters [1] have been reported; also, a considerable number of tri-, tetra- and polymetallic clusters containing two or three different metals have been synthesized [2–5]. Among the others, iron–nickel derivatives were obtained [6, 7]; instead, to our knowledge, no ruthenium–nickel derivatives were reported until now.

The major part of the above complexes was synthesized from mono- or bi-nuclear carbonyls as starting materials, and operating in polar conditions, or by means of photolysis or pyrolysis. We now report the synthesis of a mixed ruthenium–nickel cluster operating in relatively mild, apolar conditions, and starting from an alkyne substituted trinuclear ruthenium hydride,  $\text{HRu}_3(\text{CO})_9\text{C}_2\text{Bu}^\dagger$  (complex I) [8].



A preliminary account of this work has appeared [9]. The complex I is characterized by a  $\text{Ru}_3\text{C}$  core, which shows some similarities with the  $\text{Co}_3\text{C}$  one, found in the  $\text{Co}_3(\text{CO})_9\text{CR}$  derivatives [10]. In the new derivative  $(\eta^5\text{-C}_5\text{H}_5)\text{NiRu}_3(\text{CO})_9\text{C}\cdot\text{C}(\text{H})\text{Bu}^\dagger$  (complex II) a  $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}$  fragment is inserted into Ru–Ru and Ru–C bonds of the  $\text{Ru}_3\text{C}$  core or, with a better representation, bridges a Ru–Ru–C face of the tetrahedral  $\text{Ru}_3\text{C}$  core of the starting compound.

The addition of the nickel fragment has, as a consequence, the shift of the hydridic hydrogen to the 'alkyne' substituent; one of the carbons of the latter, the one interested in the  $\text{Ru}_3\text{C}$  core in complex I, is now co-ordinated to the four metals, whereas the substituted alkyne carbon interacts with one ruthenium atom.

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## Experimental

### Synthesis of the Complex II

Complex II was obtained, together with other products to be identified, by allowing I (640 mg, ~1 mM) to react with  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2$  (1 g, ~2.6 mM) in refluxing n-heptane, under dry nitrogen for 90 min; the reaction time is reduced to 30 min when operating in refluxing n-octane. In the latter reaction, yields of about 15% of II with respect to I were obtained. The reaction mixture was filtered, the solvent removed under vacuum, and the residual, dissolved in  $\text{CHCl}_3$ , was purified by means of preparative t.l.c. plates. The black solid II was crystallized by n-heptane at  $-10^\circ\text{C}$ . The crystals are air-stable for long periods, whereas the solutions of II decompose in some hours, at room temperature. The complex analyzes as follows: Found: C% 31.7, H% 1.9, Ni% 7.5, Ru% 39.6, O% 19.3. Calcd for  $\text{C}_{20}\text{H}_{15}\text{NiO}_9\text{Ru}_3$ : C% 31.5, H% 1.8, Ni% 7.7, Ru% 39.8, O% 18.9.

### Analysis of the Complex

Complex II was analyzed by means of an F & M 185 C, H, N Analyzer, and a Perkin Elmer 303 Atomic Absorption Spectrophotometer. The i.r. spectra were registered on a Beckman IR 12 instrument (KBr optics). The mass spectra were registered by means of an Hitachi Perkin Elmer RMU 6H and a Varian CH-5, single focusing instruments, operating at 70 eV and the  $^1\text{H}$  n.m.r. spectrum on a JEOL C 60 HL instrument in  $\text{CDCl}_3$  solutions.

### Crystal Data

$\text{C}_{20}\text{H}_{15}\text{NiO}_9\text{Ru}_3$ ,  $M = 761.25$ , monoclinic,  $a = 15.514(11)$ ,  $b = 17.003(13)$ ,  $c = 9.138(8)$  Å,  $\beta = 94.6(1)^\circ$ ,  $V = 2403(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.10$  g cm<sup>-3</sup>,  $F(000) = 1468$ ,  $\text{MoK}_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{MoK}_\alpha) = 26.37$  cm<sup>-1</sup>, space group  $P2_1/n$  from systematic absences.

A prismatic black crystal of the compound with dimensions of ca.  $0.12 \times 0.25 \times 0.40$  mm was used for the data collection. Preliminary cell parameters obtained from rotation and Weissenberg photographs were subsequently refined by a least-squares procedure applied to the  $\theta$  values of 18 reflections carefully measured on a Siemens AED single crystal diffractometer.

### Intensity Data

Intensity data were collected at room temperature on the same diffractometer using zirconium-filtered  $\text{MoK}_\alpha$  radiation and the  $\omega$ - $2\theta$  scan technique. The intensity of a 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.

TABLE I. Fractional Atomic Coordinates ( $\times 10^4$ ) for Non-hydrogen Atoms with e.s.d.'s in Parentheses.

	$x/a$	$y/b$	$z/c$
Ru(1)	1937(1)	4115(1)	1557(1)
Ru(2)	2907(1)	4706(1)	4067(1)
Ru(3)	3724(1)	3900(1)	1843(1)
Ni	1757(1)	3637(1)	4185(1)
O(1)	79(5)	4673(5)	1696(9)
O(2)	1538(6)	2581(5)	-41(9)
O(3)	2254(6)	4966(5)	-1274(7)
O(4)	1650(6)	5722(5)	5608(9)
O(5)	3963(5)	4389(4)	6928(8)
O(6)	4040(6)	6085(5)	3417(10)
O(7)	5613(5)	3795(5)	2958(9)
O(8)	3813(6)	2890(5)	-855(8)
O(9)	4099(5)	5422(4)	232(9)
C(1)	776(6)	4453(6)	1679(10)
C(2)	1668(6)	3159(6)	569(10)
C(3)	2146(6)	4645(6)	-189(9)
C(4)	2119(6)	5317(6)	5043(10)
C(5)	3574(6)	4487(6)	5827(10)
C(6)	3629(6)	5545(6)	3637(10)
C(7)	4901(6)	3825(6)	2551(10)
C(8)	3806(6)	3277(6)	157(10)
C(9)	3944(6)	4866(6)	871(10)
C(10)	2744(5)	3513(5)	3230(9)
C(11)	3228(6)	2826(6)	2889(10)
C(12)	3761(6)	2279(5)	3924(10)
C(13)	4480(7)	1904(6)	3097(11)
C(14)	4189(8)	2705(7)	5313(11)
C(15)	3180(8)	1650(6)	4463(15)
C(16)	1523(8)	2951(10)	6036(15)
C(17)	1085(9)	2629(8)	4835(16)
C(18)	512(7)	3186(10)	4230(14)
C(19)	558(8)	3855(8)	5066(15)
C(20)	1196(9)	3735(10)	6186(11)

A total of 5257 independent reflections was measured in the range  $2.5 < \theta < 27^\circ$ ; of these 3806, having  $I \geq 2\sigma(I)$ , were considered observed and used in the analysis. The structure amplitudes were obtained after the usual correction for Lorentz and polarization factors and the absolute scale was established by Wilson's method. No correction for absorption was applied because of the low value of  $\mu R$ .

### Structure Determination and Refinement

Initial coordinates for the metal atoms were obtained from a vector analysis of a three-dimensional Patterson function. Successive Fourier syntheses revealed the positions of all other non-hydrogen atoms. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [11], with initially isotropic and then anisotropic thermal parameters. The hydrogen atoms could not be precisely located in a difference map and then were placed in their geo-

TABLE II. Calculated Fractional Coordinates ( $\times 10^4$ ) for the Hydrogen Atoms.

	$x/a$	$y/b$	$z/c$
H(11)	2938	2425	1929
H(131)	4860	1515	3826
H(132)	4890	2360	2711
H(133)	4195	1573	2172
H(141)	4613	3163	4978
H(142)	4557	2286	5995
H(143)	3692	2961	5926
H(151)	2869	1338	3536
H(152)	2695	1918	5085
H(153)	3560	1243	5154
H(16)	2023	2671	6744
H(17)	1169	2041	4424
H(18)	90	3105	3243
H(19)	169	4378	4884
H(20)	1411	4155	7024

metrically calculated positions. These hydrogen atoms were included in the final structure factor calculations with uniform isotropic thermal parameters ( $U = 0.08 \text{ \AA}^2$ ). The final conventional  $R$  was 0.036 for the observed reflections only. The atomic scattering factors used (corrected for the anomalous dispersion of Ru and Ni) were taken from the ref. 12. The function minimized in the least-squares calculations was  $\sum w|\Delta F|^2$ . Unit weights were chosen at each stage of the refinement after analyzing the variation of  $|\Delta F|$  with respect to  $|F_o|$ . Final atomic coordinates for non-hydrogen atoms and for hydrogen atoms (in the calculated positions) are given in Tables I and II respectively. The thermal parameters are given in Table III. A list of observed and calculated structure factors is available from the authors on request.

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

TABLE III. Thermal Parameters  $\times 10^4$  with e.s.d. s in Parentheses. They are in the form  $\exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12})]$ .

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ru(1)	392(3)	397(4)	319(3)	-9(3)	-22(3)	10(3)
Ru(2)	354(3)	411(4)	320(3)	-28(3)	9(2)	-20(3)
Ru(3)	380(3)	413(4)	348(3)	56(3)	99(3)	31(3)
Ni	356(5)	479(6)	373(5)	6(5)	72(4)	-48(5)
O(1)	513(45)	1096(69)	906(60)	-9(52)	29(41)	178(46)
O(2)	990(63)	605(48)	792(55)	-195(42)	-254(47)	-134(44)
O(3)	1089(63)	814(54)	397(38)	98(37)	28(38)	46(47)
O(4)	861(59)	1008(67)	788(56)	-129(50)	147(46)	352(52)
O(5)	1056(62)	713(49)	526(42)	-113(37)	-352(41)	157(45)
O(6)	1005(64)	782(58)	905(60)	-114(48)	164(49)	-424(51)
O(7)	500(41)	805(53)	847(54)	136(47)	-89(37)	-44(38)
O(8)	1050(65)	955(62)	533(45)	-214(44)	85(42)	259(51)
O(9)	922(58)	622(48)	762(52)	246(41)	271(43)	-32(42)
C(1)	553(57)	659(60)	462(51)	-33(45)	17(42)	36(48)
C(2)	540(54)	491(54)	500(52)	26(43)	-109(42)	9(44)
C(3)	686(61)	502(54)	334(44)	-61(40)	-1(40)	-25(47)
C(4)	533(55)	697(65)	430(49)	-68(47)	16(41)	116(51)
C(5)	577(55)	508(54)	426(49)	-88(42)	-50(41)	20(44)
C(6)	576(58)	579(59)	503(52)	-31(44)	78(43)	-139(48)
C(7)	476(51)	512(54)	510(51)	62(43)	39(41)	-16(42)
C(8)	595(57)	560(59)	481(52)	60(46)	150(43)	161(47)
C(9)	495(51)	536(56)	464(49)	71(43)	112(40)	7(43)
C(10)	342(38)	419(45)	409(43)	39(35)	74(32)	25(33)
C(11)	508(51)	526(54)	437(48)	35(42)	63(39)	-19(43)
C(12)	583(55)	372(45)	447(47)	40(37)	25(40)	51(40)
C(13)	622(60)	561(58)	627(63)	8(48)	56(48)	237(49)
C(14)	953(85)	716(73)	470(58)	-35(52)	-72(56)	88(64)
C(15)	817(79)	517(63)	1123(100)	325(66)	183(71)	-6(57)
C(16)	564(69)	1360(126)	678(80)	451(84)	239(60)	-63(77)
C(17)	842(88)	715(82)	935(97)	-12(73)	419(77)	-270(71)
C(18)	520(60)	1215(114)	783(81)	105(81)	137(56)	-352(71)
C(19)	635(70)	901(91)	938(90)	92(75)	394(66)	-89(65)
C(20)	835(85)	1304(123)	488(55)	-143(67)	382(56)	-473(87)

TABLE IV. Bond Distances (Å) and Angles (°) (not involving hydrogen atoms) with e.s.d. s.

i) In the coordination sphere of the metal cluster			
Ru(1)–Ru(2)	2.825(2)	Ru(2)–C(10)	2.176(9)
Ru(1)–Ru(3)	2.788(3)	Ru(3)–C(7)	1.892(10)
Ru(2)–Ru(3)	2.833(2)	Ru(3)–C(8)	1.882(10)
Ru(1)–Ni	2.572(3)	Ru(3)–C(9)	1.911(10)
Ru(2)–Ni	2.555(3)	Ru(3)–C(10)	2.159(8)
Ru(1)–C(1)	1.902(10)	Ru(3)–C(11)	2.227(10)
Ru(1)–C(2)	1.890(10)	Ni–C(10)	1.834(8)
Ru(1)–C(3)	1.883(9)	Ni–C(16)	2.110(15)
Ru(1)–C(10)	2.156(8)	Ni–C(17)	2.116(14)
Ru(2)–C(4)	1.883(10)	Ni–C(18)	2.082(12)
Ru(2)–C(5)	1.879(9)	Ni–C(19)	2.118(13)
Ru(2)–C(6)	1.875(10)	Ni–C(20)	2.094(11)
Ru(2)–Ru(1)–Ru(3)	60.6(1)	C(7)–Ru(3)–C(10)	119.0(4)
Ru(3)–Ru(2)–Ru(1)	59.0(1)	C(7)–Ru(3)–C(11)	98.9(4)
Ru(1)–Ru(3)–Ru(2)	60.3(1)	C(7)–Ru(3)–Ru(1)	165.1(3)
Ru(2)–Ru(1)–Ni	56.3(1)	C(7)–Ru(3)–Ru(2)	105.2(3)
Ru(3)–Ru(1)–Ni	93.0(1)	C(8)–Ru(3)–C(9)	94.4(4)
Ru(3)–Ru(2)–Ni	92.3(1)	C(8)–Ru(3)–C(10)	114.0(4)
Ru(1)–Ru(2)–Ni	56.8(1)	C(8)–Ru(3)–C(11)	86.5(4)
Ru(1)–Ni–Ru(2)	66.9(1)	C(8)–Ru(3)–Ru(1)	97.4(3)
Ru(2)–Ru(1)–C(1)	106.9(3)	C(8)–Ru(3)–Ru(2)	157.3(3)
Ru(2)–Ru(1)–C(2)	141.0(3)	C(9)–Ru(3)–C(10)	134.1(4)
Ru(2)–Ru(1)–C(3)	113.6(3)	C(9)–Ru(3)–C(11)	170.1(4)
Ru(2)–Ru(1)–C(10)	49.6(2)	C(9)–Ru(3)–Ru(1)	93.3(3)
Ru(3)–Ru(1)–C(1)	166.7(3)	C(9)–Ru(3)–Ru(2)	91.4(3)
Ru(3)–Ru(1)–C(2)	96.4(3)	C(10)–Ru(3)–C(11)	38.2(3)
Ru(3)–Ru(1)–C(3)	84.5(3)	C(10)–Ru(3)–Ru(1)	49.7(2)
Ru(3)–Ru(1)–C(10)	49.8(2)	C(10)–Ru(3)–Ru(2)	49.4(2)
Ni–Ru(1)–C(1)	82.3(3)	C(11)–Ru(3)–Ru(1)	76.9(3)
Ni–Ru(1)–C(2)	97.9(3)	C(11)–Ru(3)–Ru(2)	84.2(3)
Ni–Ru(1)–C(3)	169.0(3)	C(10)–Ni–C(16)	121.4(5)
Ni–Ru(1)–C(10)	44.6(2)	C(10)–Ni–C(17)	119.3(5)
C(1)–Ru(1)–C(2)	96.5(4)	C(10)–Ni–C(18)	141.1(5)
C(1)–Ru(1)–C(3)	97.7(4)	C(10)–Ni–C(19)	173.2(5)
C(1)–Ru(1)–C(10)	126.9(4)	C(10)–Ni–C(20)	147.8(5)
C(2)–Ru(1)–C(3)	93.0(4)	C(10)–Ni–Ru(1)	55.6(3)
C(2)–Ru(1)–C(10)	91.4(4)	C(10)–Ni–Ru(2)	56.6(2)
C(3)–Ru(1)–C(10)	134.3(4)	C(16)–Ni–C(17)	37.5(6)
Ru(3)–Ru(2)–C(4)	162.1(3)	C(16)–Ni–C(18)	64.0(5)
Ru(3)–Ru(2)–C(5)	105.7(3)	C(16)–Ni–C(19)	65.1(5)
Ru(3)–Ru(2)–C(6)	84.8(3)	C(16)–Ni–C(20)	40.0(6)
Ru(3)–Ru(2)–C(10)	48.9(2)	C(16)–Ni–Ru(1)	164.1(4)
Ni–Ru(2)–C(4)	83.7(3)	C(16)–Ni–Ru(2)	126.3(4)
Ni–Ru(2)–C(5)	99.3(3)	C(17)–Ni–C(18)	38.5(6)
Ni–Ru(2)–C(6)	168.8(3)	C(17)–Ni–C(19)	64.4(5)
Ni–Ru(2)–C(10)	44.7(2)	C(17)–Ni–C(20)	64.6(6)
C(4)–Ru(2)–C(5)	92.2(4)	C(17)–Ni–Ru(1)	127.7(4)
C(4)–Ru(2)–C(6)	95.8(4)	C(17)–Ni–Ru(2)	161.7(4)
C(4)–Ru(2)–C(10)	128.3(4)	C(18)–Ni–C(19)	38.0(6)
C(4)–Ru(2)–Ru(1)	104.9(3)	C(18)–Ni–C(20)	64.0(5)
C(5)–Ru(2)–C(6)	91.9(4)	C(18)–Ni–Ru(1)	107.8(4)
C(5)–Ru(2)–C(10)	99.0(4)	C(18)–Ni–Ru(2)	156.2(5)
C(5)–Ru(2)–Ru(1)	147.7(3)	C(19)–Ni–C(20)	38.3(5)
C(6)–Ru(2)–C(10)	133.7(4)	C(19)–Ni–Ru(1)	117.7(4)
C(6)–Ru(2)–Ru(1)	112.9(3)	C(19)–Ni–Ru(2)	121.9(4)
C(10)–Ru(2)–Ru(1)	49.0(2)	C(20)–Ni–Ru(1)	151.0(4)
C(7)–Ru(3)–C(8)	96.6(4)	C(20)–Ni–Ru(2)	108.7(4)
C(7)–Ru(3)–C(9)	90.8(4)		

(continued on facing page)

TABLE IV. (continued)

ii) In the carbonyl groups			
O(1)–C(1)	1.146(12)	O(6)–C(6)	1.145(13)
O(2)–C(2)	1.140(13)	O(7)–C(7)	1.138(12)
O(3)–C(3)	1.156(11)	O(8)–C(8)	1.136(12)
O(4)–C(4)	1.153(13)	O(9)–C(9)	1.147(12)
O(5)–C(5)	1.143(12)		
Ru(1)–C(1)–O(1)	177.1(9)	Ru(2)–C(6)–O(6)	176.1(9)
Ru(1)–C(2)–O(2)	177.4(9)	Ru(3)–C(7)–O(7)	178.4(9)
Ru(1)–C(3)–O(3)	178.3(9)	Ru(3)–C(8)–O(8)	176.5(9)
Ru(2)–C(4)–O(4)	176.8(9)	Ru(3)–C(9)–O(9)	176.2(9)
Ru(2)–C(5)–O(5)	176.4(9)		
iii) In the organic ligands			
C(10)–C(11)	1.436(13)	C(16)–C(17)	1.359(20)
C(11)–C(12)	1.523(13)	C(16)–C(20)	1.437(23)
C(12)–C(13)	1.535(14)	C(17)–C(18)	1.384(20)
C(12)–C(14)	1.563(14)	C(18)–C(19)	1.369(21)
C(12)–C(15)	1.507(15)	C(19)–C(20)	1.381(18)
C(11)–C(10)–Ru(1)	121.1(6)	C(14)–C(12)–C(11)	113.3(8)
C(11)–C(10)–Ru(2)	141.9(6)	C(15)–C(12)–C(11)	109.1(8)
C(11)–C(10)–Ru(3)	73.5(5)	C(17)–C(16)–C(20)	107.1(1.2)
C(11)–C(10)–Ni	131.9(7)	C(17)–C(16)–Ni	71.5(8)
Ru(1)–C(10)–Ru(2)	81.4(3)	C(20)–C(16)–Ni	69.4(8)
Ru(1)–C(10)–Ru(3)	80.5(3)	C(18)–C(17)–Ni	69.4(8)
Ru(1)–C(10)–Ni	79.8(3)	C(18)–C(17)–C(16)	108.1(1.3)
Ru(2)–C(10)–Ru(3)	81.6(3)	Ni–C(17)–C(16)	71.0(9)
Ru(2)–C(10)–Ni	78.7(3)	C(19)–C(18)–Ni	72.4(8)
Ru(3)–C(10)–Ni	153.9(5)	C(19)–C(18)–C(17)	110.0(1.2)
C(12)–C(11)–Ru(3)	125.3(6)	Ni–C(18)–C(17)	72.1(7)
C(12)–C(11)–C(10)	129.0(8)	C(20)–C(19)–Ni	69.9(7)
Ru(3)–C(11)–C(10)	68.3(5)	C(20)–C(19)–C(18)	107.0(1.2)
C(13)–C(12)–C(14)	108.3(8)	Ni–C(19)–C(18)	69.6(7)
C(13)–C(12)–C(15)	110.1(8)	Ni–C(20)–C(16)	70.6(8)
C(13)–C(12)–C(11)	109.1(8)	Ni–C(20)–C(19)	71.8(7)
C(14)–C(12)–C(15)	106.9(9)	C(16)–C(20)–C(19)	107.7(1.2)

## Results and Discussion

### *I.r. and Mass Spectra*

The i.r. spectrum of the complex II in n-heptane solution shows the following absorptions in the CO stretching region: 2079 s, 2054 vs, 2040 vs, 2008 vs, 2002 vs(sh), 1979 m,  $\text{cm}^{-1}$ .

Several mass spectra of II were recorded operating at the lowest possible temperatures; however, in all the runs, the mass spectrum of I was obtained. No secondary fragmentation, indicative of the nature of II, was observed.

The complex II has proven diamagnetic (Evans' method); thus the alkynic moiety must behave as five electron formal donor in order to obtain the expected number of 62 electrons for a butterfly shape. The  $^1\text{H}$  n.m.r. spectrum shows the following resonances ( $\tau$ ): 8.00 s (6H), 7.85 s (3H), 5.50 m and 4.60 m (6H).

This spectrum reveals stereochemical rigidity of both organic ligands; the chemical shift of the proton on C(11) unexpectedly falls in the same range as the cyclopentadienylic protons. No hydridic signal was detected.

### *Structure of the Complex*

The structure of the complex II,  $(\eta^5\text{-C}_5\text{H}_5)\text{NiRu}_3(\text{CO})_9\text{C}\cdot\text{C}(\text{H})\text{Bu}^t$ , is represented in Fig. 1. Bond distances and angles not involving the hydrogen atoms are given in Table IV. The structure is characterized by a tetranuclear metal cluster of three Ru and one Ni atoms, in a 'butterfly' arrangement, rather common in the tetranuclear alkyne or alkene substituted metal carbonyls [5, 13–16]. The  $\text{Ru}_3\text{Ni}$  cluster is bonded to nine carbonyls (three for each Ru atom), to a cyclopentadienyl group (through the Ni atom) and to a rearranged t-butylacetylene (through all the

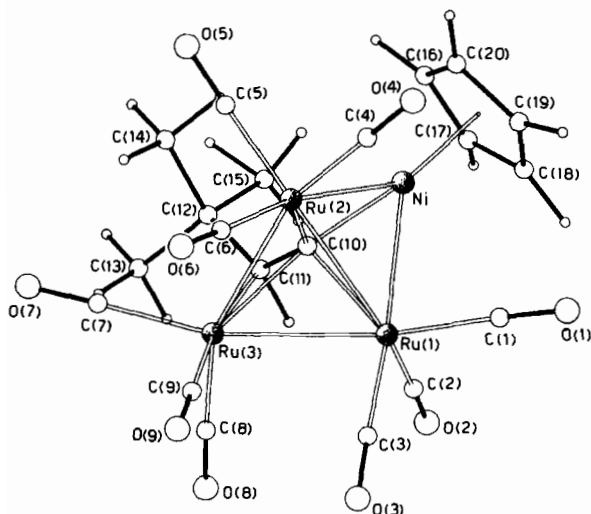


Fig. 1. View of the shape of the complex  $(\eta^5\text{-C}_5\text{H}_5)\text{NiRu}_3\text{-(CO)}_9\text{C}\cdot\text{C}(\text{H})\text{Bu}^t$  (II) with the atomic numbering scheme.

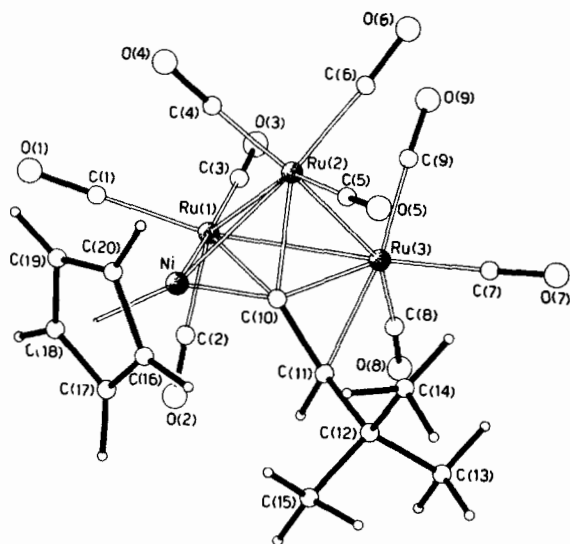


Fig. 2. View of the bonding of the alkyne with the tetranuclear metal cluster.

metal atoms). The two triangular 'wings' NiRu(1)-Ru(2) and Ru(3)Ru(1)Ru(2) share the 'hinge' side Ru(1)-Ru(2), the dihedral angle between the two planes containing the 'wings' being of  $116.6^\circ$  and the non-bonded distance Ru(3)-Ni of 3.892 Å.

The Ru-Ru bond distances [Ru(1)-Ru(2) 2.825(2), Ru(1)-Ru(3) 2.788(3), Ru(2)-Ru(3) 2.833(2) Å] are only slightly different from those found in I [2.795, 2.799 and 2.792 Å] [8b]. Unlike the other Ru 'butterfly' clusters, the hinge side is not longer than the other ones. No comparison can be found for the two Ru-Ni bond distances [Ru(1)-Ni 2.572(3) and Ru(2)-Ni 2.555(3) Å], as this is the first case in which these distances are reported; however, when considering that in other binuclear [17] and tetrahedral tetranuclear [18] nickel derivatives substituted with alkynes, the Ni-Ni distances range within 2.4 and 2.6 Å, and that the Ru-Ru distances are commonly of about 2.8 Å, these Ru-Ni distances are regular.

The nine carbonyl groups are all terminal (the angles Ru-C-O are in the range  $176.1\text{--}178.4^\circ$ ) and attached to the three Ru atoms only (three to each metal). The Ni atom does not carry any carbonyl but is  $\eta$  bonded to a cyclopentadienyl unit (the distance from Ni to barycentre of the ring being 1.743 Å). Thus, apparently no CO substitution has occurred in complex I to give II, as nine carbonyls are still present; instead an 'addition' can be considered the fundamental process for the formation of II. After Ni-Ni bond breaking, a  $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}$  fragment bridges the Ru(1)-Ru(2)-C(10) face of the tetrahedral core Ru<sub>3</sub>C of I; this process requires the hydric hydrogen transfer to the alkyne.

Noteworthy is the bonding of the alkyne to the cluster (Fig. 2), as the terminal C(10) carbon is at a bonding distance from all the four metals [Ru(1)-C(10) 2.156(8), Ru(2)-C(10) 2.176(9), Ru(3)-C(10) 2.159(8) and Ni-C(10) 1.834(8) Å] and the substituted alkynic C(11) carbon is tilted toward Ru(3) to give a short bonding interaction [Ru(3)-C(11) 2.227(10) Å]. This is the first example of a similar coordination of an alkyne on a tetranuclear metal cluster.

Although some carbido-carbonyls, in which a carbon coordinates to five or six metals and is lying at the centre of a regular polyhedron of metal atoms, were reported [19], the only other coordination example of a carbon atom, comparable with C(10), is  $[\text{HFe}_4(\text{CO})_{13}]^-$  [16] in which an unusually bridging CO is found. This also indicates comparable activation of CO and HC<sub>2</sub>R alkynes on metal clusters.

The Ru-C(10) bonding distances are comparable with the ones of the carbide Ru<sub>6</sub>C(CO)<sub>14</sub>(C<sub>6</sub>H<sub>3</sub>-Me<sub>3</sub>) [19], whereas they differ from those in I [1.947, 2.207 and 2.214 Å] where one distance corresponds to a  $\sigma$ -bond. Ni-C  $\sigma$ -bond distances (1.90–1.95 Å [20]) were reported for mononuclear complexes, but no data are available for mixed metal clusters; thus the value for Ni-C(10) cannot be compared with others. However some indication of its probable nature as a  $\sigma$ -bond can be obtained when considering that this bond is shorter than all the Ni-C  $\pi$ -bonds so far reported [17, 18, 21].

The bonding situation of C(10) in the present complex is comparable with that in  $[\text{HFe}_4(\text{CO})_{13}]^-$  where a carbon interacts with three iron atoms with distances of 2.101, 2.103, 2.174 Å and with the

fourth iron with a shorter distance of 1.805 Å, this latter corresponding to the present Ni-C(10).

The alkynic C(10)-C(11) distance [1.436(13) Å] is much longer than in I (1.315 Å) indicating a lower multiple bond character, determined both by the more numerous interactions of the terminal carbon with the metals and by the presence on C(11) of a hydrogen atom, shifted from the cluster in the reaction carrying I to II. The different bonding of the alkynic carbons in II with respect to I influences also the C(10)-C(11)-C(12) angle [129.0(8)°] which is narrower than in I (141.0°).

The Ru<sub>3</sub>NiC core in II can be seen as formed by a carbon triply bridging both the faces Ru(1)Ru(2)-Ru(3) and Ru(1)Ru(2)Ni of the cluster. So each of the two Ru<sub>3</sub>C and Ru<sub>2</sub>NiC pyramidal groups is comparable with the Ru<sub>3</sub>C core of I, with the Co<sub>3</sub>C core of the Co<sub>3</sub>(CO)<sub>9</sub>CR complexes [10], with the Fe<sub>3</sub>C core of Fe<sub>3</sub>(CO)<sub>8</sub>(HC<sub>2</sub>Me)<sub>4</sub> [22] and with the Ru<sub>3</sub>C core of H<sub>3</sub>Ru<sub>3</sub>(CO)<sub>9</sub>CMe [23]. The M-C-M angles in these CM<sub>3</sub> cores can be of interest; in the cobalt derivatives a mean value of 81° is reported, in H<sub>3</sub>Ru<sub>3</sub>(CO)<sub>9</sub>CMe and Fe<sub>3</sub>(CO)<sub>8</sub>(HC<sub>2</sub>Me)<sub>4</sub> values of 86° and 80.7-82.6° were found, in I values from 78.3-84.3 were reported. In II these angles are in the range 78.7-81.6°, and in the comparable tetranuclear [HFe<sub>4</sub>(CO)<sub>13</sub>]<sup>-</sup> in the range 75.8-84.6° [24].

Further studies on mixed Ru-Ni carbonyl complexes are in progress in our laboratories.

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