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Synthesis and Structural Characterization of the Isomeric Ruthenium–Nickel Derivatives $(\eta\text{-}C_5H_5)NiRu_3(CO)_8(C_6H_9)$ and Related Complexes

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The synthesis of two isomeric complexes $(\eta\text{-}C_5H_5)NiRu_3(CO)_8(C_6H_9)$ is reported, the structure of one of these derivatives has been determined by X-ray diffraction methods. The two isomers differ for the disposition of the asymmetrical organic ligand with respect to the cluster, this is shown by chemical as well as by ^1H n.m.r. evidence.

Crystals of $(\eta\text{-}C_5H_5)NiRu_3(CO)_8(C_6H_9)$ are monoclinic, space group $P2_1/n$, *with* $Z = 4$ *in a unit cell of dimensions* $a = 10.525(9)$, $b = 20.487(13)$, $c = 9.891(7)$ Å, $\beta = 92.11(7)^\circ$. *The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to* $R = 0.065$ *for 2810 independent observed reflections.*

The complex is characterized by a butterfly arrangement of three Ru and one Ni atoms with Ni atom occupying a hinge position, an allylic unit is bound to the four metal atoms, both via M–C(σ) and via Ru–C(π) bonds. The hydride of the starting product is lost during the reaction, some comments on the mechanism of formation of these derivatives are drawn, on the basis of the experimental evidence.

Introduction

Mixed metal clusters are an increasingly important subset representing a further development of the chemistry of transition metal clusters. Their syntheses and properties have been recently reviewed [1]. As part of our studies on the reaction between cluster carbonyls of the iron group with cyclopentadienylnickel derivatives [2–4], we have reacted the ruthenium hydrides $HRu_3(CO)_9RCCHCR'$ (I) [5] with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$. Tetranuclear ruthenium–nickel clusters are obtained, one species only is obtained for $R = R'$, whereas two isomers are formed for $R \neq R'$. These derivatives are the second example of mixed ruthenium–nickel clusters, the first being $(\eta\text{-}C_5H_5)NiRu_3(CO)_9CC(H)Bu^t$(II) [4] obtained from $HRu_3(CO)_9C_2Bu^t$(III) [6] and $[(\eta\text{-}C_5H_5)Ni(CO)]_2$. The structures of (I), (II), (III) are represented in Fig. 1.

An X-ray analysis has been performed for one of the isomers found from the reaction of $HRu_3(CO)_9\text{-}CH_3CCHCC_2H_5$, whereas the other derivatives have been characterized on the basis of the i.r., mass, and ^1H n.m.r. spectra. A preliminary account has already been published [7].

Experimental

Analysis of the Products

The complexes were 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 (KBr optics), the mass spectra on a Varian CH-5 single-focusing instrument, with direct inlet system, operating at 70 eV in electron-impact ionization. The ^1H n.m.r. spectra were obtained on a JEOL C 60 HL instrument.

Synthesis of $(\eta\text{-}C_5H_5)NiRu_3(CO)_8RCCHCR'$ (IV)

By refluxing complexes I with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ in a 1:4 molar ratio in n-heptane, under dry nitrogen, for 90 minutes, besides about 30% unreacted I, complexes IV are obtained in one species for $R = R'$ (25% yields) and in two isomeric species for $R \neq R'$ (total 20% yields, on ruthenium). Other products in trace amounts, and one, bright red, immediately decomposed, are also obtained which were not identified.

After filtration, the solvent was removed *in vacuo* and the residue, dissolved in $CHCl_3$, was chromatographed by t.l.c. preparative plates (thickness 1 mm, Kieselgel PF, Merck, eluant diethyl ether 10% and light petroleum mixture). Each compound was purified by crystallization from a saturated n-heptane–chloroform (1:1) solution kept under nitrogen atmosphere at −10 °C.

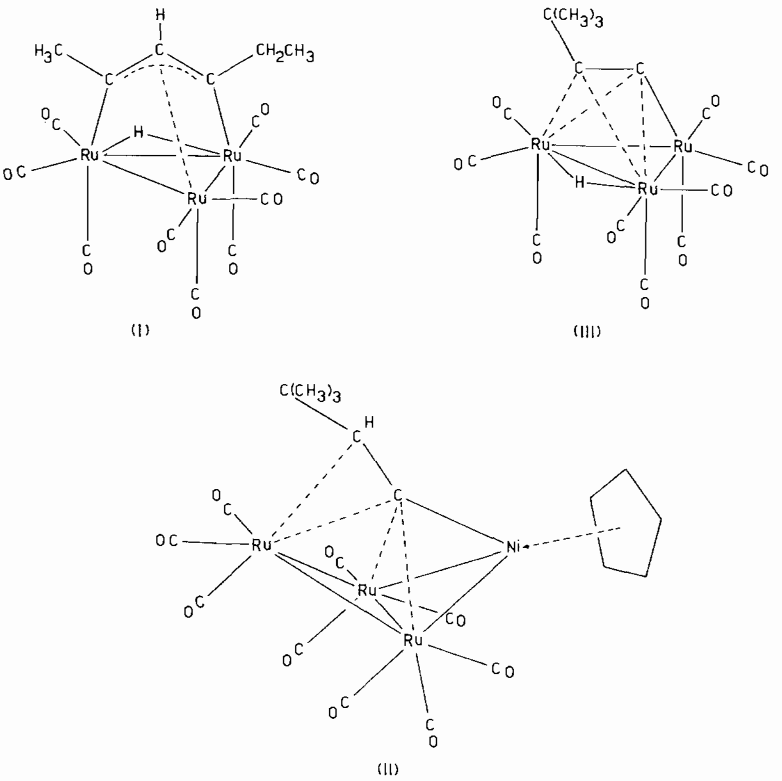


Fig. 1. Structure of I, II and III.

TABLE I. Analytical and Spectroscopic Data for the Complexes.

Complex	Analysis (%)[a]				M[a,b]	I.r. spectrum ν_{CO} (cm^{-1})[c]	^1H n.m.r. spectrum (τ/ppm)[d,e]
	C	H	Ru	Ni			
Ia $HRu_3(CO)_9MeCCHCMe$	(f)				(f)	(f)	C_2H 3.32(1, d), CH_3 7.16(6, s), hydride 30.1(1, d)[f]
Ib $HRu_3(CO)_9MeCCHCEt$	(f)				(f)	(f)	C_2H 3.36(1, d), C_1CH_3 7.16(3, s), CH_2 7.21(2, m), CH_2CH_3 8.58 (3,t), hydride 30.1(1, d)
IVa $(Cp)NiRu_3(CO)_8MeCCHCMe$	(30.1) 30.5	(1.7) 1.9	(42.2) 42.0	(8.2) 8.3	(718.2) 720	2044s, 2019vs, 1978s, 1964s, 1854m, 1835s.	C_2H 3.35(1, s), Cp 5.03(5, s), C_1CH_3 6.41 (3, s), C_3CH_3 8.14 (3, s).
IVb $(Cp)NiRu_3(CO)_8MeCCHCEt$	(31.2) 31.4	(1.9) 2.0	(41.4) 41.2	(8.0) 8.2	(732.2) 734	2049s, 2013vs, 1981s, 1964s. 1859m, 1837s.	C_2H 3.28(1, s), Cp 5.02(5, s), C_1CH_3 6.40(3, s), CH_2 7.95(2, q), CH_2CH_3 9.20(3, t).
IVc $(Cp)NiRu_3(CO)_8MeCCHCEt$	(as for IVb) 31.5	 2.1	 41.3	 8.2	(732.2) 734	2048s, 2011vs, 1978s, 1964s. 1854m, 1833s.	C_2H 3.42(1, s), Cp 5.05(5. s), CH_2 6.40(2, q), C_3CH_3 8.15 (3, s), CH_2CH_3 8.45(3, t)

[a] Calculated values are given in parentheses. [b] By mass spectrometry. [c] In n-heptane. [d] In $CDCl_3$. [e] Relative intensity and multiplicity in parentheses. [f] See references in the text.

The analytical and spectroscopic data for complexes IV are reported in Table I.

X-ray Data Collection

A roughly prismatic brown crystal of the compound IVc with dimensions of *ca.* 0.05 × 0.15 × 0.30 mm was used for the data collection. Preliminary cell parameters obtained by rotation and Weissenberg photographs were subsequently refined by least-squares fit to the θ angles of 17 reflections accurately measured on a Siemens AED single-crystal diffractometer. The crystal data are: triclinic, a =

10.525(9), b = 20.487(13), c = 9.891(7) Å, β = 92.11 (7)°, V = 2131(3) Å^3, M = 731.42, Z = 4, D_c = 2.279 g cm^{-3}, MoKα radiation (λ = 0.71069 Å), μ(MoKα) = 29.09 cm^{-1}, space group $P2_1/n$ from systematic absences.

A total of 4656 independent reflections with $3 < \theta < 27°$ were collected on the same Siemens diffractometer using the Nb-filtered MoKα radiation and the ω–2θ scan technique. 2810 of these were used in the structure analysis having $I > 2\sigma(I)$. The intensity data were corrected for Lorentz and polarization factors, 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 method.

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 program [8] with first isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms, excepting for H(16) (located in a difference map), were placed in their geometrically calculated positions. All the hydrogen atoms were included in the final structure factor calculations with uniform isotropic thermal parameters (U = 0.08 Å^2). Unit weights were chosen at each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to $|F_0|$. The final R was 0.065 (observed reflections only). The atomic scattering factors used (corrected for the anomalous dispersion of Ru) were taken from the International Tables [9]. The atomic fractional coordinates and thermal parameters for non hydrogen atoms are listed in Tables II and III, the calculated coordinates for the hydrogen atoms in Table IV. 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 Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with financial support from the University of Parma.

Results and Discussion

The main product of the reaction of I with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ is a tetranuclear species $(\eta\text{-}C_5H_5)$-$NiRu_3(CO)_8RCCHCR'$ (IV) which is present as one isomer for R = R′ and as two isomers for R ≠ R′. The mass spectra show, in each case, stepwise loss of 8 carbonyl groups from the molecular ion. Doubly charged ions corresponding to CO loss are present as intense peaks, indicating a great stability for these clusters. Weak peaks corresponding to $(\eta\text{-}C_5H_5)Ru^+$ are always detected, indicating migration of (C_5H_5) from nickel to ruthenium in the vapour phase.

TABLE II. Fractional Atomic Coordinates (× 10^4) for Non-hydrogen Atoms with e.s.d.'s.

	x/a	*y/b*	*z/c*
Ru(1)	2328(1)	2839(1)	3468(1)
Ru(2)	4096(1)	3683(1)	2593(1)
Ru(3)	837(1)	3905(1)	3555(2)
Ni	1906(2)	3594(1)	1324(2)
O(1)	2549(14)	2104(8)	6057(16)
O(2)	1692(17)	1544(7)	2112(17)
O(3)	−545(13)	2625(7)	3617(21)
O(4)	6612(14)	3849(9)	4176(16)
O(5)	5456(16)	3996(10)	38(17)
O(6)	4744(13)	2278(7)	2035(15)
O(7)	−358(18)	4247(9)	6148(18)
O(8)	−1489(16)	4470(9)	2090(19)
C(1)	2500(16)	2388(9)	5076(18)
C(2)	1945(16)	2030(8)	2620(20)
C(3)	289(19)	2974(10)	3605(28)
C(4)	5680(18)	3788(9)	3578(23)
C(5)	4956(18)	3872(11)	963(24)
C(6)	4191(18)	2719(10)	2398(19)
C(7)	129(20)	4118(10)	5196(18)
C(8)	−598(18)	4254(9)	2676(21)
C(9)	348(19)	3573(11)	−50(19)
C(10)	707(17)	2928(10)	299(19)
C(11)	1972(17)	2834(10)	−118(17)
C(12)	2392(19)	3411(11)	−707(18)
C(13)	1380(24)	3868(10)	−696(20)
C(14)	2336(21)	5030(9)	1466(23)
C(15)	2374(16)	4369(9)	2216(17)
C(16)	2807(17)	4393(8)	3759(21)
C(17)	2847(14)	3767(8)	4380(15)
C(18)	3306(21)	3769(10)	5835(19)
C(19)	3820(24)	4414(12)	6420(25)

The i.r. spectra, in the CO stretching region, show absorptions characteristic of terminal and bridging CO groups. In the ^{1}H n.m.r. spectra, constant features are two singlets, one of intensity 1 in the range 3.28–3.42 τ and one of intensity 5 in the range 5.02–5.05 τ; additionally the resonances of the R and R′ groups are observed. A comparison of these features with those of the corresponding complexes I shows: 1) one upfield resonance assigned to a hydride is present in I, but not in IV; 2) the resonance assigned in I to the hydrogen bound to C_2 is also observed in IV at almost identical chemical shift; 3) the signals of the R and R′ groups are comparable in I and IV for their intensity and multiplicity, but a sizeable difference of their chemical shifts is observed; 4) the resonance of intensity 5 in the spectra of IV, assigned to the cyclopentadienyl group, is absent in the spectra of I.

The above evidence suggests that, on reacting I with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$, the skeleton of the organic ligand is maintained but this framework, in IV, is

TABLE III. Anisotropic Thermal Parameters for Non-Hydrogen Atoms (× 10^3). They are in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + ...7 + 2hka^*b^*U_{12})]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	26(1)	27(1)	34(1)	5(1)	5(1)	–1(1)
Ru(2)	28(1)	39(1)	36(1)	6(1)	8(1)	–4(1)
Ru(3)	33(1)	32(1)	38(1)	3(1)	14(1)	3(1)
Ni	29(1)	34(1)	31(1)	3(1)	6(1)	1(1)
O(1)	53(9)	75(11)	58(9)	14(9)	–3(7)	–7(8)
O(2)	93(13)	36(8)	83(12)	–19(8)	–10(10)	–1(8)
O(3)	31(7)	46(9)	159(18)	15(10)	23(9)	–4(7)
O(4)	42(9)	107(14)	63(10)	11(10)	–11(7)	–13(9)
O(5)	73(11)	143(17)	56(10)	32(11)	34(9)	–18(11)
O(6)	45(8)	49(9)	71(10)	–8(7)	12(7)	11(7)
O(7)	104(14)	77(12)	76(12)	–13(10)	52(11)	5(10)
O(8)	54(10)	88(13)	93(13)	21(11)	7(9)	22(9)
C(1)	32(9)	46(10)	36(10)	9(8)	5(7)	1(8)
C(2)	37(9)	25(9)	55(11)	8(8)	7(8)	1(7)
C(3)	37(11)	35(11)	132(21)	1(12)	23(12)	1(9)
C(4)	37(11)	37(11)	76(14)	10(10)	15(10)	–1(8)
C(5)	29(10)	63(14)	77(16)	19(12)	–5(10)	–2(9)
C(6)	43(11)	51(12)	38(10)	–6(9)	8(8)	–6(9)
C(7)	64(13)	50(12)	26(9)	–7(8)	25(9)	–1(10)
C(8)	39(10)	38(10)	60(12)	14(9)	17(9)	9(8)
C(9)	53(12)	70(15)	33(10)	–4(10)	–15(9)	9(11)
C(10)	36(10)	55(12)	41(11)	–13(9)	–8(8)	3(9)
C(11)	42(10)	53(11)	29(9)	–13(9)	3(8)	–1(9)
C(12)	54(12)	68(14)	27(10)	6(9)	24(9)	2(10)
C(13)	90(17)	47(12)	36(11)	12(9)	–6(11)	11(12)
C(14)	69(14)	27(10)	70(15)	17(10)	3(11)	1(9)
C(15)	35(9)	39(10)	29(9)	5(7)	3(7)	1(7)
C(16)	34(9)	25(9)	67(13)	–5(8)	10(9)	–2(7)
C(17)	28(8)	44(10)	18(7)	1 (7)	6(6)	–8(8)
C(18)	69(14)	57(13)	27(10)	–2(9)	2(9)	–20(11)
C(19)	78(17)	66(15)	65(16)	–22(13)	–15(13)	–18(13)

TABLE IV. Calculated Atomic Coordinates (× 10^4) for Hydrogen Atoms. The coordinates of H(16) are those found in a final difference Fourier synthesis.

	x/a	y/b	z/c
H(16)	3098	4821	3933
H(141)	2028	4954	424
H(142)	3274	5245	1504
H(143)	1679	5354	1945
H(181)	2518	3622	6435
H(182)	4058	3412	5941
H(191)	4114	4345	7468
H(192)	3084	4781	6350
H(193)	4624	4571	5855
H(9)	–553	3800	142
H(10)	126	2572	792
H(11)	2518	2390	1
H(12)	3322	3494	–1101
H(13)	1394	4356	–1109

bound to a different metal core than in I; additionally, one (C_5H_5) group is present in IV and any hydride is absent. These features have been confirmed by the results of the single-crystal X-ray analysis of IVc.

The two isomers, when reactant I has R ≠ R′, can be obtained either for the different position of the Ni atom in the cluster (on a wing or on the hinge) or for the different substituents on the carbon atoms σ-bound to the Ni and Ru atoms in the hinge of the butterfly metal core.

The first type of isomerism has been recently reported for the derivatives $FeRu_3(CO)_{12}RC_2R$ [10]; the isomers interconvert in refluxing hexane. Additionally, the second type of isomerism has been observed for $FeRu_3(CO)_{12}RC_2R'$ [10].

In our case the second type of isomerism is expected for the following reasons: i) one isomer only is observed for R = R′; ii) the chemical shift of the substituent α to C_1 in IVc is downfield of the corresponding resonance in Ib whereas the chemical shifts of the substituents α to C_3 in IVc are upfield of the corresponding resonance in Ib. This trend is observed in the other IV derivatives; the resonances of the substituents α to C_1 are shifted downfield of 0.75–0.81 τ whereas the resonances of the substituents α to C_3 are shifted upfield of 0.74–0.99 τ; iii) the same pattern of the i.r. spectra of all the IV derivatives suggests that they have the same symmetry; iv) refluxing of each isomer in hexane does not produce the other isomer.

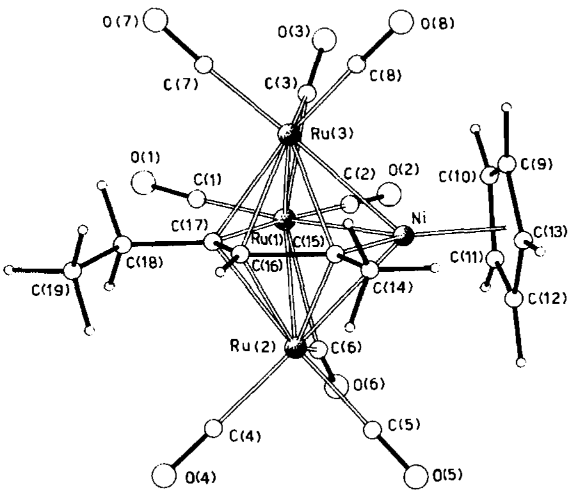


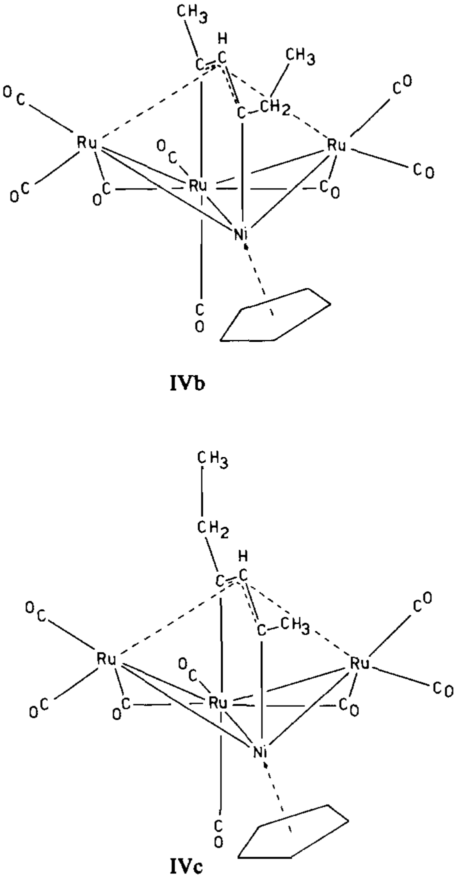
Fig. 2. View of the shape of the complex $(\eta\text{-}C_5H_5)NiRu_3(CO)_8(C_6H_9)$ with the atomic numbering scheme.

The Structure of IVc

The structure of IVc is represented in Fig. 2. Bond distances and angles not involving the hydrogen atoms are given in Table V. The isomerism of IVb and IVc is represented in Fig. 3.

The tetranuclear metal cluster of IVc is in a butterfly arrangement and is formed by three Ru atoms, deriving from the opening of the cluster of I, and one Ni atom. The cluster is bonded to eight carbonyls (through the Ru atoms only) to a cyclopentadienyl group (through the Ni atom) and to a 1-methyl-3-ethylallyl unit (through all the metals). The Ni atom occupies a corner of the hinge-side of the cluster and is bound to all the Ru atoms. The dihedral angle between the two 'wings' is 104.5° and the non-bonded distance Ru(2)–Ru(3) is 3.614 Å. The only other example of a mixed-metal hinge in a butterfly metal arrangement was reported for $FeRu_3(CO)_{12}C_2Ph_2$ [10]. The butterfly metal arrangement is rather common in the homo- and heterometallic tetranuclear clusters, either containing alkynes or other organic ligands. The following are the more significant for this discussion: $(\eta\text{-}C_5H_5)NiRu_3(CO)_9C.C(H)Bu^t$ [4], $Co_4(CO)_{10}C_2Et_2$ [11], $Ru_4(CO)_{10}(C_{12}H_{16})$ [12], $Ru_4(CO)_{11}(C_8H_{10})$ [13], $Ru_4(CO)_{12}C_2Ph_2$ [14], $Ru_4(CO)_9(C_6H_6)(C_6H_8)$ [15] and $Ir_4(CO)_5(C_8H_{12})(C_8H_{10})$ [16].

The structures of all these derivatives have been determined by X-ray methods; homo- and heterometallic phosphine derivatives of Pt and Pt–Mo have also been reported [17] showing butterfly clusters, and butterfly arrangements have been proposed for Ni–Fe clusters [18]. Different dihedral angles were found, sometimes depending on the number and nature of the substituents.



IVb

IVc

Fig. 3. Isomerism of IV.

The heterometallic hinge in IVc has no negative effects on the stability of the cluster, at least when considering the mass spectral behaviour. The allyl group in this cluster, as well as the alkyne in II, acts as a stabilizing factor, in the same way as the bridging COs [19], probably reducing electron density differences within different metals.

The Ru–Ru bond distances [2.708(3) and 2.693 (3) Å] do not differ from those found in the Ru clusters; the Ru(2)–Ni and Ru(3)–Ni bond distances [2.595(5) and 2.611(3) Å] agree well with those reported in the only other Ni–Ru mixed cluster $(\eta\text{-}C_5H_5)NiRu_3(CO)_9C.C(H)Bu^t$ [4] [2.555 and 2.572 Å], whereas the Ni–Ru(1) is longer [2.664(3) Å] than the other ones, according with the lengthening of the hinge side observed in almost all the butterfly clusters.

The cyclopentadienyl group is η-coordinated to the Ni atom (the distance from Ni to the barycentre of the ring being 1.747 Å), this indicating that, after the Ni–Ni bond breaking, one $(\eta\text{-}C_5H_5)Ni$ group acts as a tetradentate ligand.

TABLE V. Bond Distances (Å) and Angles (°) (non involving hydrogen atoms) with e.s.d.s.

i) in the coordination sphere of the metal cluster

Ru(1)-Ru(2)	2.708(3)	Ru(1)-C(17)	2.169(16)	Ru(3)-C(15)	2.338(17)
Ru(1)-Ru(3)	2.693(3)	Ru(2)-C(4)	1.916(20)	Ru(3)-C(16)	2.304(18)
Ru(1)-Ni	2.664(3)	Ru(2)-C(5)	1.930(23)	Ru(3)-C(17)	2.260(15)
Ru(2)-Ni	2.595(5)	Ru(2)-C(6)	1.987(21)	Ni-C(9)	2.099(20)
Ru(3)-Ni	2.611(3)	Ru(2)-C(15)	2.313(18)	Ni-C(10)	2.099(19)
Ru(1)-C(1)	1.855(18)	Ru(2)-C(16)	2.330(18)	Ni-C(11)	2.123(19)
Ru(1)-C(2)	1.898(17)	Ru(2)-C(17)	2.261(15)	Ni-C(12)	2.142(18)
Ru(1)-C(3)	2.173(21)	Ru(3)-C(3)	1.994(21)	Ni-C(13)	2.146(20)
Ru(1)-C(6)	2.280(19)	Ru(3)-C(7)	1.876(19)	Ni-C(15)	1.877(18)
		Ru(3)-C(8)	1.861(20)		
Ru(2)-Ru(1)-Ru(3)	84.3(1)	C(4)-Ru(2)-C(6)	96.7(8)	C(8)-Ru(3)-Ru(1)	139.5(6)
Ru(2)-Ru(1)-Ni	57.8(1)	C(4)-Ru(2)-C(15)	132.6(7)	C(15)-Ru(3)-C(16)	40.1(7)
Ru(3)-Ru(1)-Ni	58.3(1)	C(4)-Ru(2)-C(16)	100.7(8)	C(15)-Ru(3)-C(17)	66.5(6)
Ni(-Ru(2)-Ru(1)	60.3(1)	C(4)-Ru(2)-C(17)	96.1(8)	C(15)-Ru(3)-Ru(1)	84.0(4)
Ni-Ru(3)-Ru(1)	60.3(1)	C(4)-Ru(2)-Ru(1)	120.1(6)	C(16)-Ru(3)-C(17)	36.4(6)
Ru(1)-Ni-Ru(2)	62.0(1)	C(5)-Ru(2)-C(6)	95.2(9)	C(16)-Ru(3)-Ru(1)	80.3(4)
Ru(1)-Ni-Ru(3)	61.4(1)	C(5)-Ru(2)-C(15)	97.5(8)	C(17)-Ru(3)-Ru(1)	51.0(4)
Ru(2)-Ni-Ru(3)	88.3(1)	C(5)-Ru(2)-C(16)	126.6(8)	C(9)-Ni-C(10)	39.4(8)
Ru(2)-Ru(1)-C(1)	123.4(5)	C(5)-Ru(2)-C(17)	162.6(8)	C(9)-Ni-C(11)	65.6(8)
Ru(2)-Ru(1)-C(2)	123.4(6)	C(5)-Ru(2)-Ru(1)	138.5(7)	C(9)-Ni-C(12)	65.6(8)
Ru(2)-Ru(1)-C(3)	129.1(6)	C(6)-Ru(2)-C(15)	129.0(7)	C(9)-Ni-C(13)	39.0(9)
Ru(2)-Ru(1)-C(6)	46.0(5)	C(6)-Ru(2)-C(16)	134.6(7)	C(9)-Ni-C(15)	120.8(8)
Ru(2)-Ru(1)-C(17)	53.9(4)	C(6)-Ru(2)-C(17)	100.7(7)	C(9)-Ni-Ru(1)	128.0(6)
Ru(3)-Ru(1)-C(1)	114.5(6)	C(6)-Ru(2)-Ru(1)	55.6(6)	C(9)-Ni-Ru(2)	168.2(5)
Ru(3)-Ru(1)-C(2)	127.5(5)	C(15)-Ru(2)-C(16)	40.1(7)	C(9)-Ni-Ru(3)	102.2(5)
Ru(3)-Ru(1)-C(3)	46.9(5)	C(15)-Ru(2)-C(17)	66.9(6)	C(10)-Ni-C(11)	39.4(7)
Ru(3)-Ru(1)-C(6)	127.9(5)	C(15)-Ru(2)-Ru(1)	84.1(4)	C(10)-Ni-C(12)	65.5(8)
Ru(3)-Ru(1)-C(17)	54.1(4)	C(16)-Ru(2)-C(17)	36.1(6)	C(10)-Ni-C(13)	65.3(8)
Ni-Ru(1)-C(1)	172.8(6)	C(16)-Ru(2)-Ru(1)	79.5(4)	C(10)-Ni-C(15)	157.5(7)
Ni-Ru(1)-C(2)	97.0(6)	C(17)-Ru(2)-Ru(1)	50.8(4)	C(10)-Ni-Ru(1)	95.4(5)
Ni-Ru(1)-C(3)	80.8(7)	Ni-Ru(3)-C(3)	85.5(8)	C(10)-Ni-Ru(2)	142.3(5)
Ni-Ru(1)-C(6)	78.9(5)	Ni-Ru(3)-C(7)	177.7(6)	C(10)-Ni-Ru(3)	107.7(5)
Ni-Ru(1)-C(17)	82.0(4)	Ni-Ru(3)-C(8)	93.4(6)	C(11)-Ni-C(12)	38.3(8)
C(1)-Ru(1)-C(2)	87.9(8)	Ni-Ru(3)-C(15)	44.2(4)	C(11)-Ni-C(13)	64.5(8)
C(1)-Ru(1)-C(3)	94.3(9)	Ni-Ru(3)-C(16)	76.5(5)	C(11)-Ni-C(15)	158.0(7)
C(1)-Ru(1)-C(6)	107.1(7)	Ni-Ru(3)-C(17)	81.6(4)	C(11)-Ni-Ru(1)	96.3(5)
C(1)-Ru(1)-C(17)	93.4(7)	C(3)-Ru(3)-C(7)	94.4(1.0)	C(11)-Ni-Ru(2)	109.4(5)
C(2)-Ru(1)-C(3)	86.9(8)	C(3)-Ru(3)-C(8)	98.6(9)	C(12)-Ni-C(13)	141.5(5)
C(2)-Ru(1)-C(6)	82.5(7)	C(3)-Ru(3)-C(15)	127.6(8)	C(12)-Ni-Ru(3)	38.6(8)
C(2)-Ru(1)-C(17)	177.2(7)	C(3)-Ru(3)-C(16)	132.3(7)	C(12)-Ni-C(13)	122.0(8)
C(3)-Ru(1)-C(6)	155.7(9)	C(3)-Ru(3)-C(17)	98.0(7)	C(12)-Ni-Ru(1)	128.3(6)
C(3)-Ru(1)-C(17)	95.5(7)	C(3)-Ru(3)-Ru(1)	52.7(6)	C(12)-Ni-Ru(2)	103.6(5)
C(6)-Ru(1)-C(17)	94.8(6)	C(7)-Ru(3)-C(8)	88.9(9)	C(12)-Ni-Ru(3)	167.3(6)
Ni-Ru(2)-C(4)	177.0(6)	C(7)-Ru(3)-C(15)	135.2(8)	C(13)-Ni-C(15)	106.2(8)
Ni-Ru(2)-C(5)	92.2(6)	C(7)-Ru(3)-C(16)	102.0(8)	C(13)-Ni-Ru(1)	159.4(6)
Ni-Ru(2)-C(6)	86.0(6)	C(7)-Ru(3)-C(17)	96.2(7)	C(13)-Ni-Ru(2)	129.3(7)
Ni-Ru(2)-C(15)	44.5(4)	C(7)-Ru(3)-Ru(1)	117.9(6)	C(13)-Ni-Ru(3)	129.3(6)
Ni-Ru(2)-C(16)	76.4(5)	C(8)-Ru(3)-C(15)	98.1(7)	C(15)-Ni-Ru(1)	94.4(5)
Ni-Ru(2)-C(17)	81.9(4)	C(8)-Ru(3)-C(16)	125.9(7)	C(15)-Ni-Ru(2)	59.8(5)
C(4)-Ru(2)-C(5)	89.1(9)	C(8)-Ru(3)-C(17)	162.3(7)	C(15)-Ni-Ru(3)	60.2(5)

ii) in the carbonyl groups

O(1)-C(1)	1.139(24)	Ru(1)-C(1)-O(1)	176.9(1.6)	Ru(2)-C(5)-O(5)	178.2(2.1)
O(2)-C(2)	1.144(23)	Ru(1)-C(2)-O(2)	178.8(1.6)	Ru(1)-C(6)-Ru(2)	78.5(7)
O(3)-C(3)	1.133(25)	Ru(1)-C(3)-Ru(3)	80.4(7)	Ru(1)-C(6)-O(6)	133.8(1.6)
O(4)-C(4)	1.136(25)	Ru(1)-C(3)-O(3)	133.5(1.6)	Ru(2)-C(6)-O(6)	147.8(1.6)
O(5)-C(5)	1.109(28)	Ru(3)-C(3)-O(3)	146.0(1.7)	Ru(3)-C(7)-O(7)	176.3(1.9)
O(6)-C(6)	1.141(25)	Ru(2)-C(4)-O(4)	179.2(1.9)	Ru(3)-C(8)-O(8)	178.2(1.9)
O(7)-C(7)	1.128(26)				
O(8)-C(8)	1.173(26)				

iii) in the organic ligands

C(9)-C(10)	1.414(30)	C(12)-C(13)	1.419(32)	C(16)-C(17)	1.424(24)
C(10)-C(11)	1.423(26)	C(9)-C(13)	1.419(31)	C(17)-C(18)	1.514(24)
C(11)-C(12)	1.399(29)	C(14)-C(15)	1.547(27)	C(18)-C(19)	1.535(32)
		C(15)-C(16)	1.591(27)		

(Continued on facing page)

TABLE V. *(Continued)*

C(10)–C(9)–C(13)	107.9(1.8)	Ni–C(13)–C(9)	68.7(1.1)	Ni–C(15)–C(14)	120.6(1.3)
C(10)–C(9)–Ni	70.3(1.1)	Ni–C(13)–C(12)	70.5(1.1)	C(17)–C(16)–Ru(2)	69.3(9)
C(13)–C(9)–Ni	72.3(1.2)	C(9)–C(13)–C(12)	108.1(1.8)	C(17)–C(16)–Ru(3)	70.1(9)
C(11)–C(10)–Ni	71.2(1.1)	C(16)–C(15)–Ru(2)	70.5(9)	Ru(2)–C(16)–Ru(3)	102.9(7)
C(11)–C(10)–C(9)	107.4(1.7)	C(16)–C(15)–Ru(3)	68.8(9)	Ru(2)–C(16)–C(15)	69.4(9)
Ni–C(10)–C(9)	70.3(1.2)	C(16)–C(15)–Ni	123.1(1.2)	Ru(3)–C(16)–C(15)	71.1(9)
C(12)–C(11)–Ni	71.6(1.1)	C(16)–C(15)–C(14)	116.3(1.5)	C(18)–C(17)–C(16)	114.7(1.5)
C(12)–C(11)–C(10)	108.8(1.8)	Ru(2)–C(15)–Ru(3)	102.4(7)	C(19)–C(17)–C(16)	83.5(1.2)
Ni–C(11)–C(10)	69.4(1.1)	Ru(2)–C(15)–Ni	75.7(6)	Ru(1)–C(17)–C(16)	127.1(1.2)
C(13)–C(12)–Ni	70.8(1.1)	Ru(2)–C(15)–C(14)	128.1(1.3)	Ru(2)–C(17)–C(16)	74.6(1.0)
C(13)–C(12)–C(11)	107.8(1.8)	Ru(3)–C(15)–Ni	75.7(6)	Ru(3)–C(17)–C(16)	73.5(1.0)
Ni–C(12)–C(11)	70.1(1.1)	Ru(3)–C(15)–C(14)	128.8(1.3)	C(19)–C(18)–C(17)	117.6(1.7)

Two CO's on each Ru atom are terminal as shown by the Ru–C–O angles (in the range 176.3–179.2°); the remaining two are asymmetrically bridging the Ru(1)–Ru(2) and Ru(1)–Ru(3) adjacent sides. This behaviour is probably due to electronic requirements and differs from the disposition observed in $Co_4(CO)_{10}C_2Et_2$ [11] and in $Ir_4(CO)_5(C_8H_{12})(C_8H_{10})$ [16], where the bridging CO's are found on not adjacent sides of the cluster.

The substituted allylic ligand is bound to all the metals; the atoms C(15) and C(17) are σ-bonded to the hinge atoms of the cluster: Ni–C(15) = 1.877 and Ru(1)–C(17) = 2.169 Å. These two carbon atoms, together with C(16), form a C_3 system equidistant from both Ru(2) and Ru(3) [C(15–Ru(2) = 2.313, C(15)–Ru(3) = 2.338, C(16)–Ru(2) = 2.330, C(16)–Ru(3) = 2.304, C(17)–Ru(2) = 2.261 and C(17)–Ru(3) = 2.260 Å], so acting as a symmetrical η-allyl bridge between Ru(2) and Ru(3). The C(15), C(16), C(17) atoms form with Ru(1) and Ni a strictly planar pentaatomic heterocycle. C(15), C(16), C(17), Ru(1), Ni, C(14), C(18), Ru(2) and Ru(3) are displaced from the mean plane passing through this pentaatomic ring by 0.005, –0.015, 0.010, 0.001, 0.001, 0.010, 0.047, 1.813, –1.811 Å.

The bonding of the allylic ligand in the present complex is closely similar to that reported for $Ru_4(CO)_{10}(C_{12}H_{16})$ [12]. By considering the allylic groups as a five-electron donor, as suggested for I [5], $HRu_3(CO)_9(C_{12}H_{15})$ [20], $HRu_3(CO)_9(PhC.C_6H_4)$ [21] and $Ru_4(CO)_{10}(C_{12}H_{16})$ [12], the electronic requirement of the Ru_3Ni core is not satisfied, though the complex is diamagnetic. This feature has been pointed out also for $Ru_4(CO)_{10}(C_{12}H_{16})$ [12].

Isomerism in IV

The isomerism found in complexes IV when R ≠ R′ leads to some comments on the formation of these derivatives. The processes which occur in the formation of IV, not necessarily in order, include hydrogen loss of the hydride in I, breaking of one Ru–Ru bond and of one Ru–C(σ) bond of I (for instance Ru(1)–Ru(3) and Ru(1)–C(1)) and linkage of the $(\eta\text{-}C_5H_5)$Ni group to the open cluster. The formation of two isomers – as previously discussed – is easily accounted by such process, since the only requirement is the breaking of other equivalent Ru–Ru and Ru–C(σ) bonds (according to the above example, Ru(2)–Ru(3) and Ru(2)–C(3)).

It is interesting to compare the structures of IVc and II; in the first case, the starting Ru_3 cluster of I is altered and the Ni atom is bonded to all three Ru atoms, whereas in II the starting Ru_3 cluster of III is maintained with the Ni atom bonding two Ru atoms. Additionally, in the formation of IV, the organic group of I is maintained nearly unaltered, though the coordination to the metal core is changed, whereas in the formation of II, the organic group adds the hydridic proton and changes its coordination to the metal core.

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