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SYNTHESIS AND CRYSTAL STRUCTURE OF $(\eta\text{-}C_5H_5)_2Ru_2Ni(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)$. FACILE, ONE STEP SYNTHESIS OF A CHIRAL COMPLEX *

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Summary

The complex $(\eta\text{-}C_5H_5)_2Ru_2Ni(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)$ has been obtained by refluxing $(\eta\text{-}C_5H_5)_2Ni_2(C_2Rh_2)$ and $Ru_3(CO)_{12}$ in hydrocarbons. The structure of the complex has been determined by X-ray methods. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions a 12.737(7), b 12.228(10), c 15.975(9) Å, β 97.53(6)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 2.9\%$ for 3449 independent observed reflections. The complex consists of an isosceles triangle of two Ru and one Ni atoms (Ru(1)—Ru(2) 2.712(3), Ru(1)—Ni 2.550(3) and Ru(2)—Ni 2.553(2) Å) bonded to four carbonyls (three are terminal and attached to one Ru atom, while the other asymmetrically triply bridges all three metals), to two cyclopentadienyl ligands (through one Ru and one Ni atom) and to one diphenylacetylene molecule. The alkyne, σ-bonded to one Ru and one Ni atom and π-bonded to the other Ru atom, lies nearly parallel to one Ni—Ru side of the cluster. The presence of the cyclopentadienyl ligand bonded to the Ru atom demonstrates cyclopentadienyl exchange in the reaction. The carbon atom of the triply bridging carbonyl, which is surrounded by four different or differently-substituted atoms, makes the complex chiral.

An isomer with a doubly bridging carbonyl was detected in solution and subsequently isolated.

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* Dedicated to the memory of Professor Paolo Chini.

Introduction

Chiral clusters represent an increasingly important development of the chemistry of the heterometallic clusters [1,2] in view of their potential catalytic applications.

We have examined the reactions of nickelocene, bis(cyclopentadienylcarbonylnickel) and $(\eta\text{-}C_5H_5)_2Ni_2(RC_2R')$ with iron carbonyls and alkynecarbonyls [3] and with ruthenium carbonyls and alkynecarbonyls [4]. From the reactions with iron derivatives, several heterometallic clusters were obtained [3,5], and of these the trinuclear $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (complex I) was studied by X-ray diffraction [4]. Ligand exchange was observed in these reactions, involving either alkynes and cyclopentadienyls.

From the reactions with ruthenium derivatives, tetrametallic butterfly clusters [6,7] and some trimetallic mixed derivatives [4] were obtained. and of these $(\eta\text{-}C_5H_5)_2Ni_2Ru(CO)_3(C_2Ph_2)$ (complex Ia) was studied by X-ray methods [4]. Ligand exchange was also observed involving alkynes and cyclopentadienyls in these reactions.

We now report on one of the products of the reaction of $(\eta\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$ with $Ru_3(CO)_{12}$, namely $(\eta\text{-}C_5H_5)_2Ru_2Ni(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)$ (complex II); its structure, determined by X-ray diffraction, consists of an isosceles triangle of metal atoms bound to two cyclopentadienyl groups (through the Ni and one Ru atoms), to four carbonyls (three are terminally attached to one Ru atom and the fourth triply bridges all three metals) and to the diphenylacetylene molecule (through two σ-bonds with the Ni and one Ru atoms, and one π-bond with the other Ru atom).

The carbon of the triply bridging carbonyl is surrounded by four different or differently-substituted atoms, so the complex is chiral. The presence of the cyclopentadienyl group bonded to one Ru atom demonstrates cyclopentadienyl exchange between the metals in the reaction.

An isomer of II with a doubly bridging carbonyl was isolated (complex IIa).

Experimental

Synthesis and purification of II and IIa

$Ru_3(CO)_{12}$ [8] and $(\eta\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$ [9] were prepared by published methods. They were allowed to react in 1.0—1.2 molar ratio in refluxing octane for 20 min under dry nitrogen; II and IIa are obtained along with fifteen other products. The yields were about 10% based on the ruthenium. The mixture was filtered under nitrogen and the solvent removed under vacuum; $CHCl_3$ was added and the resulting solution was separated by TLC (Kieselgel P.F. Merck; eluation with mixtures of light petroleum and ethyl ether). A dark brown band containing both II and IIa was isolated; further treatment gave separate grey-green (II) and dark-violet bands (IIa).

The complexes were analyzed by means of an F&M 185 C, H, N, analyzer and a Perkin—Elmer 303 atomic absorption spectrophotometer; the IR spectra were recorded on a Beckman IR-12 and a Perkin—Elmer 580 instruments. The mass spectra were obtained on a Varian CH-5 instrument.

The analyses of the complexes were as follows: II: Found: C, 49.51; H, 3.03;

Ni, 8.44; O, 9.72; Ru, 29.30%. $C_{28}H_{20}NiO_4Ru_2$ calcd.: C, 49.39; H, 2.96; Ni, 8.62; O, 9.39; Ru, 29.67%. IIa: Found: C, 49.67; H, 3.05; Ni, 8.38; O, 9.26; Ru, 29.64%.

II decomposes in the mass spectrometer. Its ^{1}H NMR shows three signals, at τ 1.60m (10 H), 3.90s (5 H), and 4.30s (5 H) ppm (in CCl_4).

The mass spectrum of IIa has intense peaks corresponding to $P^+ - 28$ m/e ($P^+ = 538$ weak, first intense peak 510 m/e) and $P^+ - 56$ m/e, then loss of ruthenium and complete fragmentation of the complex. The ^{1}H NMR spectrum is identical to the one of II; probably only IIa is present in solution.

Complex II was crystallized from heptane/CH_3Cl mixtures under nitrogen at −10°C. Grey-green crystals were obtained. No crystals of complex IIa suitable for the X-ray analysis could be obtained.

TABLE 1

FRACTIONAL ATOMIC COORDINATES (X10^4) (e.s.d. in parentheses) FOR NON-HYDROGEN ATOMS

	x/a	y/b	z/c
Ru(1)	−1167(1)	2476(1)	7421(1)
Ru(2)	208(1)	1918(1)	8797(1)
Ni	480(1)	3608(1)	7912(1)
O(1)	2490(4)	1137(5)	9186(3)
O(2)	−1058(4)	3(4)	9322(3)
O(3)	240(4)	2959(6)	10546(3)
O(4)	−1422(4)	3891(4)	8904(3)
C(1)	1629(5)	1425(5)	9046(4)
C(2)	−547(5)	705(5)	9130(4)
C(3)	228(5)	2602(6)	9889(4)
C(4)	−1031(5)	3277(6)	8455(4)
C(5)	200(4)	1431(4)	7552(3)
C(6)	389(4)	2392(4)	7140(3)
C(7)	232(4)	286(4)	7209(3)
C(8)	543(4)	−597(4)	7726(4)
C(9)	575(5)	−1648(5)	7416(4)
C(10)	283(5)	−1837(5)	6576(5)
C(11)	−30(5)	−985(5)	6050(4)
C(12)	−66(5)	64(5)	6353(4)
C(13)	878(4)	2573(4)	6359(3)
C(14)	1787(5)	2003(5)	6221(4)
C(15)	2300(6)	2220(6)	5534(4)
C(16)	1917(6)	3007(7)	4975(5)
C(17)	1020(6)	3567(6)	5082(4)
C(18)	499(6)	3352(5)	5755(4)
C(19)	−2306(6)	3254(8)	6447(6)
C(20)	−2042(6)	2263(7)	6164(5)
C(21)	−2394(6)	1466(8)	6688(6)
C(22)	−2856(6)	1991(10)	7315(6)
C(23)	−2802(6)	3108(9)	7165(7)
C(24)	1902(6)	4301(6)	8414(7)
C(25)	1744(7)	4536(7)	7575(6)
C(26)	869(8)	5157(6)	7406(5)
C(27)	443(7)	5334(6)	8137(5)
C(28)	1067(6)	4814(6)	8781(5)

X-Ray data collection

A prismatic grey-green crystal of complex II having dimensions of ca. 0.18 × 0.27 × 0.43 mm was used for the data collection. Preliminary cell parameters, obtained by rotation and Weissenberg photographs, were subsequently refined by least-squares from the θ values of 18 reflections accurately measured on a Siemens AED single crystal diffractometer. The crystal data are as follows: $C_{28}H_{20}NiO_4Ru_2$, $M = 681.31$, monoclinic, a 12.737(7), b 12.228(10), c 15.975(9) Å, β 97.53(6)°, V 2467(3) Å^3, $Z = 4$, $D_c = 1.834$ g cm^{-3}, Mo-K_α radiation ($\bar{\lambda}$ 0.71069 Å), μ(Mo-K_α) 19.77 cm^{-1}, space group $P2_1/n$ from systematic absences.

A complete set of intensity data was collected within the angular range $3 \leqslant \theta \leqslant 25°$. The $\theta/2\theta$ scan technique was used with a variable scan rate ranging from 2.5 to 10°/min. The scan range was ±0.5° from the peak centre. A standard reflection was remeasured after every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensities of these reflections was observed during data collection. A total of 4261 independent reflections were measured, of which 3449 were employed in the analysis, having $I \geqslant 2\sigma(I)$; the remaining 812 were considered unobserved. The structure amplitudes were obtained after the usual Lorentz and polarization corrections. The absolute scale and the mean temperature factor were established by Wilson' method. No correction for absorption was applied.

Solution and refinement

Initial coordinates of the three heavy atoms were determined by a Patterson map. A Fourier synthesis, calculated with phases of the three metal atoms,

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times10^4$) AND ISOTROPIC THERMAL PARAMETERS ($\times10^3$) FOR THE HYDROGEN ATOMS (e.s.d. in parentheses)

	x/a	y/b	z/c	U
H(8)	721(43)	−465(46)	8355(35)	41(16)
H(9)	831(42)	−2326(46)	7846(35)	58(17)
H(10)	278(42)	−2531(47)	6380(34)	70(16)
H(11)	−186(43)	−1090(47)	5445(34)	47(17)
H(12)	−261(43)	656(46)	5928(35)	71(17)
H(14)	2015(44)	1447(49)	6586(36)	65(17)
H(15)	2915(47)	1837(50)	5428(36)	64(17)
H(16)	2231(45)	3114(50)	4563(38)	65(17)
H(17)	778(45)	4096(50)	4730(38)	74(17)
H(18)	−244(47)	3794(50)	5832(36)	59(17)
H(19)	−2136(45)	4050(52)	6166(36)	85(17)
H(20)	−1696(45)	2101(50)	5665(39)	85(18)
H(21)	−2299(46)	568(52)	6615(37)	85(18)
H(22)	−3097(48)	1706(51)	7755(39)	69(19)
H(23)	−3104(45)	3761(48)	7537(36)	105(17)
H(24)	2555(46)	3804(48)	8744(37)	85(17)
H(25)	2265(49)	4263(49)	7104(37)	80(18)
H(26)	520(45)	5445(49)	6850(38)	92(17)
H(27)	−278(47)	5812(51)	8206(36)	82(17)
H(28)	960(45)	4743(49)	9273(39)	79(17)

revealed the positions of all other non-hydrogen atoms. Refinement was carried out by full-matrix least-squares, using the SHELX system of computer programs [10], isotropically to R = 7.2% and anisotropically to R = 3.3%. At this stage a ΔF synthesis revealed the positions of all the hydrogen atoms, which were refined with isotropic thermal parameters; the improvement of R index was to 2.9%. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were chosen at each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to F_0. The atomic scattering factors (corrected for anomalous dispersion of Ru and Ni) were taken from International Tables [11]. The final coordinates for the non-hydrogen and hydrogen atoms are given in Tables 1 and 2, respectively. Anisotropic thermal parameters are listed in Table 3. A list of observed and calculated structure factors is available from the authors on request.

All calculations were performed on the Cyber 7600 computer of the Centro

TABLE 3

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$)(e.s.d. in parentheses) FOR THE NON-HYDROGEN ATOMS (in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})]$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	264(2)	372(2)	450(3)	31(2)	7(2)	11(2)
Ru(2)	334(2)	342(2)	336(2)	—7(2)	36(2)	—6(2)
Ni	316(4)	268(3)	485(4)	—30(3)	62(3)	—7(3)
O(1)	508(29)	965(42)	867(38)	—128(32)	—13(26)	204(28)
O(2)	728(33)	754(36)	746(34)	226(29)	—9(27)	—332(30)
O(3)	820(37)	1397(56)	615(33)	—479(36)	—29(27)	335(37)
O(4)	585(29)	616(30)	683(30)	—47(24)	203(23)	205(24)
C(1)	485(39)	452(34)	435(32)	—42(28)	72(27)	18(30)
C(2)	516(36)	534(38)	370(32)	76(29)	21(26)	—59(31)
C(3)	425(35)	677(44)	505(37)	—114(35)	6(27)	122(32)
C(4)	417(34)	583(42)	537(37)	—1(32)	86(28)	96(31)
C(5)	291(26)	299(26)	321(27)	36(22)	—8(21)	7(22)
C(6)	286(26)	301(27)	397(28)	—9(24)	—1(21)	24(22)
C(7)	330(28)	322(29)	410(31)	33(24)	75(23)	—24(23)
C(8)	377(31)	321(29)	528(36)	33(26)	29(26)	—28(24)
C(9)	465(35)	307(32)	697(44)	—2(29)	10(30)	8(26)
C(10)	654(41)	329(36)	772(48)	—158(36)	87(35)	—56(32)
C(11)	629(41)	474(37)	570(41)	—128(32)	26(32)	—87(31)
C(12)	550(36)	370(33)	473(36)	—59(28)	62(28)	—40(28)
C(13)	368(29)	300(27)	420(29)	34(24)	44(23)	—27(24)
C(14)	448(32)	428(35)	487(35)	25(30)	96(26)	18(28)
C(15)	512(41)	707(50)	590(41)	—12(35)	219(33)	7(36)
C(16)	742(48)	752(49)	511(42)	54(39)	287(36)	—149(41)
C(17)	883(53)	490(40)	400(35)	130(32)	77(33)	—63(38)
C(18)	572(42)	381(33)	494(34)	84(26)	71(30)	30(30)
C(19)	479(43)	827(72)	1002(63)	127(54)	—241(42)	90(43)
C(20)	471(40)	950(64)	618(51)	32(46)	—159(36)	30(40)
C(21)	458(41)	709(58)	888(59)	—4(50)	—271(39)	—121(41)
C(22)	335(38)	1302(84)	767(60)	—3(60)	24(37)	—199(46)
C(23)	314(38)	1033(73)	1180(78)	—293(65)	—119(42)	232(44)
C(24)	442(43)	530(44)	1176(76)	—126(48)	—169(45)	—117(35)
C(25)	655(52)	693(50)	1100(70)	—314(49)	458(51)	—356(43)
C(26)	1027(67)	393(39)	721(57)	29(38)	79(50)	—218(43)
C(27)	727(51)	347(36)	938(57)	—172(37)	115(44)	28(36)
C(28)	773(50)	608(44)	581(51)	—142(40)	113(41)	—248(39)

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Results and discussion

IR spectra in solution and in KBr discs

The IR spectrum of II in heptane solution shows υ(CO) bands at 2058vs, 2002s, 1984s, 1780m, 1670s cm^{-1}. More bands appear than can be predicted on the basis of the solid state structure. In a KBr disc, II shows sharp bands at 2040vs, 1990s, 1975s and 1610s cm^{-1}; the last is superimposed on a broad band of medium intensity (ranging from 1600 to 1700 cm^{-1} with maximum around 1650) probably due to the C=C or C—H vibrations of the organic ligands.

In heptane solution, IIa shows bands at 2058vs, 2000s, 1980s, 1780 cm^{-1}, and in a KBr disc at 2036vs, 1986s, 1968s, 1750 cm^{-1}.

From these data we suggest that in solution II is in equilibrium with IIa, but under the conditions used for the crystallization only the complex with the triply-bridging carbonyl is obtained in the solid state. From the IR spectrum of IIa a structure with a doubly-bridging carbonyl is likely.

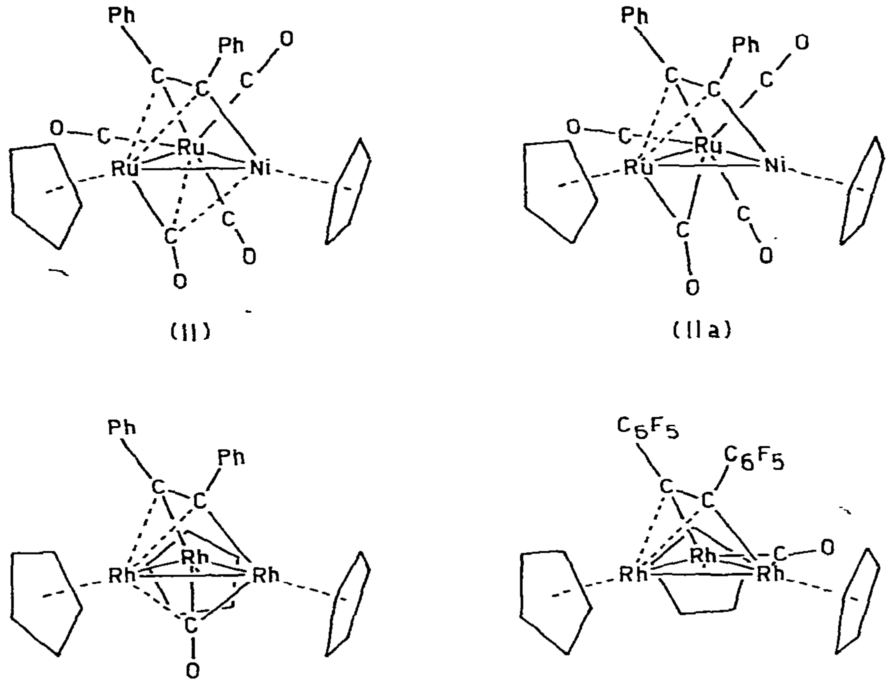
Behaviour comparable with that observed for II and IIa has been observed for the complexes $(\eta\text{-}C_5H_5)_3Rh_3(\mu_3\text{-}CO)(C_2Ph_2)$ (complex III) (υ(CO) 1675 cm^{-1} in solution) and $(\eta\text{-}C_5H_5)_3Rh_3(\mu_2\text{-}CO)[C_2(C_6F_5)_2]$ (complex IIIa) (ν(CO) 1810 cm^{-1}, in solution) [12]; in the solid state the former complex contains a triply-bridging carbonyl and the latter a doubly bridging carbonyl. Apparently whether a triply- or a doubly-bridging carbonyl is present in III and IIIa depends upon the electron-donor power of the alkyne substituent. The structures of II, III, IIIa and that proposed for IIa are depicted in Fig. 1. A triply-bridging carbonyl has also recently been found in the solid state of $Fe_3(CO)_{10}S$ [13], whereas a doubly bridging carbonyl is present in solution.

Crystal structure of complex II

The structure of complex II, with the atomic numbering scheme, is presented in Fig. 2 and selected bond distances and angles are given in Table 4. The complex is characterized by an isosceles triangle of two Ru and one Ni atoms, bonded to two cyclopentadienyl groups (through one Ni and one Ru atoms), to four carbonyls (three are terminal and attached to one Ru atom and one is triply bridging the three metals) and to the diphenylacetylene (through all the metal atoms).

The metal—metal bond distances (Ru(1)—Ru(2) 2.712(2), Ru(1)—Ni 2.550(3) and Ru(2)—Ni 2.553(2) Å) are rather short, values close to 2.80 Å for Ru—Ru bonds and 2.65 Å for those Ru—Ni generally being reported. Short metal—metal bonds have also been found in I and Ia [4] as well as in other iron—nickel derivatives [3,5].

The cyclopentadienyl ligands are η-coordinated to the metals, the distance from Ni and Ru(1) to the barycentre of the ring being 1.753 and 1.861 Å, respectively. The presence of the cyclopentadienyl group bonded to the Ru(1) atom demonstrates cyclopentadienyl transfer from the starting Ni compound to the Ru atom; this is the first example of a heterometallic cluster showing



(II) (IIa)

(III) (III a)

Fig. 1. Schematic structures found for II, III and IIIa and proposed for IIa.

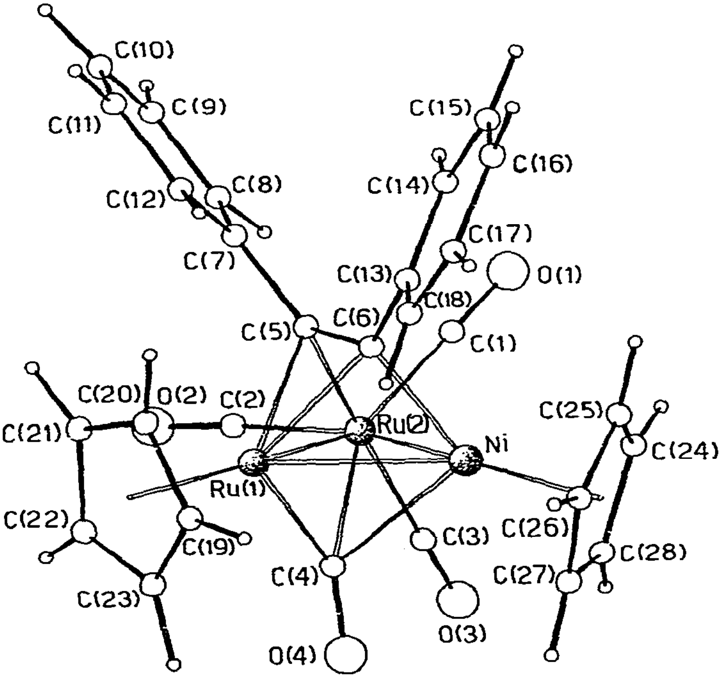


Fig. 2. View of the molecular shape of complex II with the atomic numbering scheme.

TABLE 4

BOND DISTANCES (Å) AND ANGLES (Å) OF THE NON-HYDROGEN ATOMS (e.s.d. in parentheses)

(i) In the coordination sphere of the metal			
Ru(1)—Ru(2)	2.712(3)	Ru(2)—C(2)	1.882(7)
Ru(1)—Ni	2.550(3)	Ru(2)—C(3)	1.932(7)
Ru(2)—Ni	2.553(2)	Ru(2)—C(4)	2.307(7)
Ru(1)—C(4)	1.909(7)	Ru(2)—C(5)	2.075(5)
Ru(1)—C(5)	2.148(6)	Ni—C(4)	2.249(7)
Ru(1)—C(6)	2.091(7)	Ni—C(6)	1.926(5)
Ru(2)—C(1)	1.900(7)		
Ru(2)—Ru(1)—Ni	57.9(1)	C(1)—Ru(2)—C(4)	151.8(3)
Ni—Ru(2)—Ru(1)	57.8(1)	C(1)—Ru(2)—C(5)	89.7(2)
Ru(1)—Ni—Ru(2)	64.2(1)	C(1)—Ru(2)—Ru(1)	138.2(2)
Ru(2)—Ru(1)—C(4)	56.8(2)	C(2)—Ru(2)—C(3)	91.9(3)
Ru(2)—Ru(1)—C(5)	48.9(1)	C(2)—Ru(2)—C(4)	106.0(3)
Ru(2)—Ru(1)—C(6)	68.4(1)	C(2)—Ru(2)—C(5)	96.1(2)
Ni—Ru(1)—C(4)	58.5(2)	C(2)—Ru(2)—Ru(1)	97.3(2)
Ni—Ru(1)—C(5)	70.7(1)	C(3)—Ru(2)—C(4)	80.2(3)
Ni—Ru(1)—C(6)	47.8(1)	C(3)—Ru(2)—C(5)	171.0(3)
C(4)—Ru(1)—C(5)	103.9(3)	C(3)—Ru(2)—Ru(1)	123.6(2)
C(4)—Ru(1)—C(6)	103.3(2)	C(4)—Ru(2)—C(5)	93.6(2)
C(5)—Ru(1)—C(6)	38.1(2)	C(4)—Ru(2)—Ru(1)	43.8(2)
Ni—Ru(2)—C(1)	100.3(2)	C(5)—Ru(2)—Ru(1)	51.2(2)
Ni—Ru(2)—C(2)	154.9(2)	C(4)—Ni—C(6)	97.2(2)
Ni—Ru(2)—C(3)	99.4(2)	C(4)—Ni—Ru(1)	46.3(2)
Ni—Ru(2)—C(4)	54.8(2)	C(4)—Ni—Ru(2)	57.0(2)
Ni—Ru(2)—C(5)	71.7(2)	C(6)—Ni—Ru(1)	53.5(2)
C(1)—Ru(2)—C(2)	101.5(3)	C(6)—Ni—Ru(2)	74.2(1)
C(1)—Ru(2)—C(3)	92.8(3)		
(ii) In the carbonyl groups			
O(1)—C(1)	1.146(3)	O(3)—C(3)	1.135(8)
O(2)—C(2)	1.143(8)	O(4)—C(4)	1.192(8)
Ru(2)—C(1)—O(1)	178.9(6)	Ru(1)—C(4)—O(4)	147.8(5)
Ru(2)—C(2)—O(2)	176.0(6)	Ru(2)—C(4)—O(4)	129.6(5)
Ru(2)—C(3)—O(3)	177.0(7)	Ni—C(4)—O(4)	124.4(5)
(iii) In the organic ligands			
C(5)—C(6)	1.383(7)	C(16)—C(17)	1.362(11)
C(5)—C(7)	1.506(7)	C(17)—C(18)	1.361(10)
C(6)—C(13)	1.482(7)	C(19)—C(20)	1.351(13)
C(7)—C(8)	1.385(7)	C(19)—C(23)	1.392(14)
C(7)—C(12)	1.397(8)	C(20)—C(21)	1.396(12)
C(8)—C(9)	1.380(8)	C(21)—C(22)	1.384(13)
C(9)—C(10)	1.363(10)	C(22)—C(23)	1.390(16)
C(10)—C(11)	1.366(9)	C(24)—C(25)	1.360(14)
C(11)—C(12)	1.374(9)	C(24)—C(28)	1.425(11)
C(13)—C(14)	1.393(8)	C(25)—C(26)	1.346(13)
C(13)—C(18)	1.396(8)	C(26)—C(27)	1.368(12)
C(14)—C(15)	1.375(9)	C(27)—C(28)	1.371(11)
C(15)—C(16)	1.359(11)		
C(6)—C(5)—C(7)	127.0(4)	C(7)—C(12)—C(11)	120.6(6)
C(6)—C(5)—Ru(1)	68.7(3)	C(14)—C(13)—C(18)	116.8(5)
C(6)—C(5)—Ru(2)	103.5(3)	C(14)—C(13)—C(6)	120.5(5)
C(7)—C(5)—Ru(1)	125.3(3)	C(18)—C(13)—C(6)	122.6(5)
C(7)—C(5)—Ru(2)	128.2(3)	C(15)—C(14)—C(13)	121.4(6)
Ru(1)—C(5)—Ru(2)	79.9(2)	C(16)—C(15)—C(14)	119.6(7)
C(13)—C(6)—Ru(1)	133.5(4)	C(17)—C(16)—C(15)	120.6(7)
C(13)—C(6)—Ni	115.3(3)	C(18)—C(17)—C(16)	120.4(7)
C(13)—C(6)—C(5)	130.2(4)	C(13)—C(18)—C(17)	121.2(6)
Ru(1)—C(6)—Ni	78.7(2)	C(20)—C(19)—C(23)	108.7(9)
Ru(1)—C(6)—C(5)	73.2(3)	C(21)—C(20)—C(19)	108.2(8)

TABLE 4 (continued)

Ni—C(6)—C(5)	110.5(3)	C(22)—C(21)—C(20)	108.1(9)
C(8)—C(7)—C(12)	116.9(5)	C(23)—C(22)—C(21)	107.2(9)
C(8)—C(7)—C(5)	121.8(4)	C(25)—C(24)—C(28)	106.9(7)
C(12)—C(7)—C(5)	121.3(5)	C(26)—C(25)—C(24)	109.2(8)
C(9)—C(8)—C(7)	122.1(6)	C(27)—C(26)—C(25)	109.2(8)
C(10)—C(9)—C(8)	119.6(6)	C(28)—C(27)—C(26)	108.1(8)
C(11)—C(10)—C(9)	119.7(6)	C(24)—C(28)—C(27)	106.6(8)
C(12)—C(11)—C(10)	121.1(6)		

cyclopentadienyl transfer to ruthenium.

The diphenylacetylene molecule interacts with all three metal atoms: it is σ-bonded unsymmetrically to Ru(2) and Ni atoms (Ru(2)—C(5) 2.075(5) and Ni—C(6) 1.926(5) Å) and π-bonded to the Ru(1) atom through the multiple C(5)—C(6) bond (Ru(1)—C(5) 2.148(6) and Ru(1)—C(6) 2.091(7) Å).

The C(5)C(6)NiRu(2) group is nearly planar; the C(7), C(13) and Ru(1) atoms are displaced from the mean plane passing through them by —0.175, —0.544 and 1.901 Å, respectively. Owing to the complicated bonding involved, the C(7)C(5)C(6)C(13) skeleton is only roughly planar, the displacements of these atoms from the mean plane through them being 0.022, —0.051, 0.053 and —0.023 Å. This plane (leaving Ru(2), Ni, Ru(1) out of —0.746, —0.401 and 1.628 Å) is inclined at ca. 73° to the cluster triangle, placing the C(5)—C(6) fragment parallel to the Ru(2)—Ni side of the cluster, in an ideal orientation to coordinate to Ru(1) atom.

From the C(5)—C(6) length of 1.383(7) Å it is clear that the acetylenic bond has been reduced below an olefinic bond order in accord with its behaviour as a four-electron donor to the metal cluster. A similar ($2\sigma + \pi$) bonding of the alkyne has been already reported for I and Ia [4], III and IIIa [12] and for the following complexes, $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ [14], $Ni_3(CO)_3[C_2(CF_3)_2](C_8H_8)$ [15], $Fe_3(CO)_8(C_2Ph_2)_2$ "violet isomer" [16], $Os_3(CO)_{10}(C_2Ph_2)$ [17], $Os_3(CO)_7(C_2Ph_2)_3$ [18] and $FeCo_2(CO)_9(C_2Et_2)$ [19]; such bonding is therefore rather common for homo- and hetero-metallic clusters. The bonding in these complexes has been discussed in ref. 4.

Complex II differs from the other heterometallic complexes with ($2\sigma + \pi$) alkyne bonding in that the alkyne is σ-bonded to two different metals; in the other complexes, two identical metal atoms are always involved in such bonding.

Thus, whereas all the previously reported complexes are characterized by considerable symmetry (RC_2R alkynes are usually the ligands), II is very unsymmetrical owing to this σ-bonding and to the transfer of the cyclopentadienyl ligand to a Ru atom.

Three carbonyls are terminally bonded to the Ru(2) atom, as shown by the Ru(2)—C—O angles which range from 176.0 to 178.9°; the fourth one is unsymmetrically triply-bridging the three metals as shown by the M—C distances and the M—C—O angles: Ru(1)—C(4) = 1.909(7), Ru(2)—C(4) 2.307(7) and Ni—C(4) 2.249(7) Å; Ru(1)C(4)O(4) 147.8(5)°, Ru(2)C(4)O(4) 129.6(5)° and NiC(4)O(4) 124.4(5)°. The C(4) carbon atom is surrounded by four different or differently substituted atoms, so the complex is chiral. It is surprising that the Ru(1)—C(4) bond distance is of the same order of magnitude as the Ru—C distances for terminal carbonyls since a considerable elongation was excepted in the light of the bridging of the carbonyl with the C(4) atom.

The $(\eta\text{-}C_5H_5)$Ni ligand is bound to four atoms, so complex II does not obey the E.A.N. rule. The behaviour of this ligand is not exceptional, since similar behaviour was observed for other nickel—iron and nickel—ruthenium complexes [3,5].

The presence of a carbonyl doubly-bridging the Ru atoms can be suggested for complex IIa, as the E.A.N. rule would be obeyed in this case.

The mechanism of formation of complexes II and IIa could not be investigated in detail mainly because of the simultaneous formation of several other derivatives. It is noteworthy that, whereas for I and Ia only Ru—Ru bond breaking is required (although for Ia a complex reaction occurs, as discussed in ref. 4), for II and IIa both Ru—Ru and Ni—Ni breaking is necessary. Thus, in these reactions a low selectivity is found, as expected for pyrolytic processes; however the synthesis of II is, to our knowledge, one of the easiest one step processes leading to chiral clusters even reported.

It is noteworthy that by use of HC_2R and RC_2R' alkynes, homologues of II and IIa can be obtained, and should show geometrical isomerism. Preliminary results with HC_2Bu^t and C_2Et_2 indicate that complexes isostructural with II are obtained from these alkynes. Further studies are in progress.

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