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Alkyne Trimerization on Carbonyl Ruthenium Clusters. Synthesis and Crystal Structure of $Ru_3(CO)_8(HC_2Bu^t)_3$

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The title complex is a minor product of the reaction of $Ru_3(CO)_{12}$ or of $HRu_3(CO)_9(C_2Bu^t)$ with excess of 3,3-dimethyl-but-1-yne (t-butyl-acetylene); better yields of the product are obtained by reacting $(\eta\text{-}C_5H_5)_2Ni_2(HC_2Bu^t)$ with $Ru_3(CO)_{12}$, probably because of the known ability of nickel in promoting alkyne trimerization.

The crystal structure has been determined by X-ray methods. Crystals are triclinic, space group $P\bar{1}$ with Z = 2 in a unit cell of dimensions a = 11.665(8), b = 15.292(12), c = 8.877(7) Å, α = 109.45(8), β = 100.68(8), γ = 94.57(7)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to R = 0.046 for 2999 observed reflections.

The complex consists of a bent arrangement of three Ru atoms forming Ru–Ru bonds nearly perpendicular to each other. Eight (six terminal and two bridging) carbonyls coordinate to them and a ligand, deriving from trimerization of the alkyne, forms two σ-bonds with the central Ru atom, giving origin to a metalla-cyclopentadiene ring. The terminal Ru atoms lie on opposite sides with respect to this ring and are η-bonded to four carbon atoms of it.

Introduction

A considerable number of alkyne-substituted derivatives of the cluster carbonyls of the iron triad, as well as the other triads, has already been reported [1a–c, 2–6], together with the catalytic cyclotrimerization of alkynes in presence of nickel [1].

In the above clusters, up to four alkynes, dimerizated with or without CO insertion [7–8], can be found coordinated. Examples of clusters substituted by organic moieties formed by more than two alkynes are relatively rare, they include $Fe_3(CO)_8(HC_2Me)_4$ [4] and $Fe_3(CO)_7(HC_2Et)_4$ [5], where substituted cyclopentadienyls formed by alkyne oligomerization are present, and $Fe_3(CO)_8(HC_2Me)_3$ [6] and $Ru_3(CO)_8(C_{16}H_{22})$ [9] which is an 'open cluster' complex.

We now report a new example of alkyne trimerization on a ruthenium atom cluster: $Ru_3(CO)_8(HC_2Bu^t)_3$ which is indeed an 'open cluster' characterized by an alkyne trimer chelating to one ruthenium to form a metalla-cyclopentadiene ring. An 'open cluster' and a metalla-cyclopentadiene ring were already found in the 'black isomer', $Fe_3(CO)_8(C_2Ph_2)_2$ (I) [3], and hypothesized in a considerable number of $Fe_3(CO)_8(RC_2R')_2$ derivatives, as well as in the 'orange isomer' $Ru_3(CO)_8(C_2Ph_2)_2$ (Ia) [10], but two alkynes only were involved in forming these complexes.

Figure 1 represents the organic ligands, obtained by alkyne trimerization, found in $Fe_3(CO)_8(HC_2Me)_3$ [6], in $Ru_3(CO)_8(C_{16}H_{22})$ [9] and in the present complex $Ru_3(CO)_8(HC_2Bu^t)_3$ (II): the heterocycles are shown, but the interactions that the π electron clouds, delocalized along the ring, exert on the other metal atoms are omitted for clearness.

Experimental

Synthesis of the Complex II

This is obtained in about 1% yields (based on ruthenium) in the already reported reactions of $Ru_3(CO)_{12}$ or $HRu_3(CO)_9(C_2Bu^t)$ [11] with excess of 3,3-dimethyl-but-1-yne [9]. The reaction of a 2:1 molar excess of $Ru_3(CO)_{12}$ with $(\eta\text{-}C_5H_5)_2Ni_2(HC_2Bu^t)$ in refluxing heptane under dry nitrogen for 180 min yields 3% of II together with another fifteen products, among which $(\eta\text{-}C_5H_5)_2Ru_2(CO)_4$, $H_2Ru_4(CO)_{13}$, $H_2Ru_3(CO)_9(HC_2Bu^t)_2$, $H_3Ru_3(CO)_9(C\cdot CH_2Bu^t)$ [12], $HRu_3(CO)_9(C_2Bu^t)$, $Ru_3(CO)_6(C_{12}H_{20})(C_{13}H_{20}O)$ [8]; small amounts of $(\eta\text{-}C_5H_5)NiRu_3(CO)_9(C\cdot C(H)Bu^t)$ [13] are also obtained; the other products, mainly in trace amounts, were not identified.

The yields of II can be raised up to 10% by reacting $(\eta\text{-}C_5H_5)_2Ni_2(CO)_2$ with a stoichiometric

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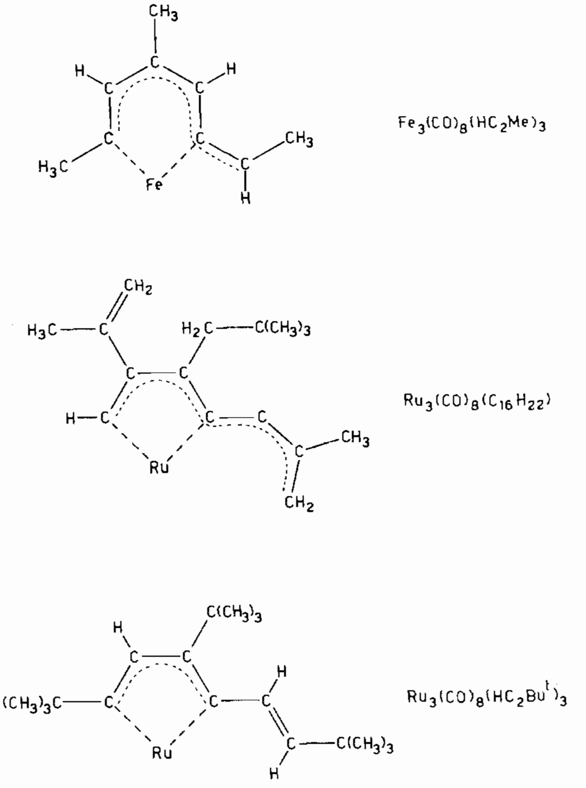

Fig. 1. Comparison of the organic ligands, obtained by alkyne trimerization in $Fe_3(CO)_8(HC_2Me)_3$, in $Ru_3(CO)_8(C_{16}H_{22})$ and in the present compound. The interactions of the electron clouds delocalized along the C–C bonds of the ring with the other metal atoms are omitted for clearness.

quantity of 3,3-dimethyl-but-1-yne for 180 min, in refluxing heptane, under nitrogen, until a dark-green solution containing $(\eta\text{-}C_5H_5)_2Ni_2(HC_2Bu^t)$ is formed (the yield of this complex is quantitative). A stoichiometric amount of $Ru_3(CO)_{12}$, suspended in 25 ml of heptane, is added to the above solution and the reaction is allowed to proceed for a further 180 min, under reflux.

Purification and analysis of II.

The reaction mixtures were purified by t.l.c. preparative plates (Kieselgel P.F. Merck, eluants mixtures of light petroleum and ethyl ether); some nickel derivatives and particularly $(\eta\text{-}C_5H_5)_2Ni_2(HC_2Bu^t)$ immediately decompose in the t.l.c. plates, as is shown by the quick change of the colour (deep green to brown) of the spots. The substance cannot be eluted from the support, after the change in colour. The orange-yellow solid II was then dissolved in heptane and allowed to cool to 0 °C. After some days well formed yellow crystals were recovered.

The complex was analyzed by means of an F & M 185 C, H, N Analyzer and a Perkin-Elmer 303 Atomic Absorption spectrophotometer; the mass spectra were registered on a Varian CH-5 single focusing instrument (direct inlet system, 70 eV) and the i.r. spectra were registered on a Beckman IR-12.

II analyzes as follows: Found, C% 40.51, H% 3.99, O% 16.39, Ru% 40.01. Calcd. for $C_{26}H_{30}O_8Ru_3$, C% 40.36, H% 3.91, O% 16.54, Ru% 39.19.

X-Ray Data Collection

A flatted yellow crystal of the complex II with dimensions of *ca.* 0.05 × 0.13 × 0.26 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 17 reflections accurately measured on a Siemens AED single-crystal diffractometer. The crystal data are: triclinic, $a = 11.665(8)$, $b = 15.292(12)$, $c = 8.877(7)$ Å, $\alpha = 109.45(8)$, $\beta = 100.68(8)$, $\gamma = 94.57(7)°$, $V = 1450(2)$ Å^3, $M = 879.99$, $Z = 2$, $D_c = 2.015$ g cm^{-3}, Mo K_α radiation ($\bar{\lambda} = 0.71069$ Å), μ(Mo K_α) = 15.14 cm^{-1}, space group $P\bar{1}$ from structure determination.

A total of 5092 independent reflections with $3 < \theta < 25°$ were collected on the same Siemens diffractometer using the Nb-filtered Mo K_α radiation and the θ–2θ scan technique. 2999 of these, having $I > 2\sigma(I)$, were considered observed and used in the refinement procedure. The intensity data were reduced to structure factors by standard methods but no absorption correction was applied because of the low value of μR. The first 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 programs [14] with first isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms, in their geometrically calculated positions, were introduced in the final structure factor calculations with isotropic thermal parameters (these values were obtained from the average of the thermal parameters of the atoms to which the hydrogen were attached). The final conventional R was 0.046 for the observed reflections. The atomic scattering factors used (corrected for the anomalous dispersion of Ru) were taken from ref. 15. 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 $|F_0|$ Final atomic coordinates for non-hydrogen atoms and for hydrogen atoms are given in Tables I and II respectively; the thermal parameters for the non-hydrogen atoms are given in Table III. A list of observed and calculated structure factors is available from the authors on request.

TABLE I. Fractional Atomic Coordinates (× 10^4) for the Non-hydrogen Atoms with e.s.d.s in Parentheses.

	x/a	*y/b*	*z/c*
Ru1	2380(1)	6539(1)	6985(1)
Ru2	2896(1)	6716(1)	4284(1)
Ru3	2948(1)	8560(1)	5625(1)
O1	3584(12)	5822(10)	9527(16)
O2	2581(11)	4727(8)	4428(14)
O3	160(12)	5459(9)	7119(18)
O4	4800(10)	5718(9)	2825(15)
O5	1169(11)	5744(8)	1012(13)
O6	3623(12)	7913(8)	2357(15)
O7	4779(14)	10266(8)	6828(20)
O8	1428(15)	9673(9)	4155(19)
C1	3121(15)	6102(12)	8584(19)
C2	2586(13)	5533(10)	5015(17)
C3	1015(15)	5877(11)	7089(19)
C4	4120(14)	6106(10)	3380(18)
C5	1812(13)	6080(10)	2239(18)
C6	3320(14)	7832(10)	3477(17)
C7	4129(14)	9609(10)	6380(23)
C8	2032(20)	9247(11)	4777(21)
C9	3862(12)	7577(9)	6747(15)
C10	3212(13)	8106(9)	7849(18)
C11	1950(12)	8033(8)	7261(13)
C12	1582(11)	7410(9)	5609(15)
C13	295(12)	7185(9)	4655(18)
C14	−159(12)	7355(9)	3364(16)
C15	−1456(12)	7165(11)	2504(20)
C16	−1571(16)	6589(15)	667(19)
C17	−2194(13)	6599(17)	3223(28)
C18	−1873(19)	8094(13)	2651(29)
C19	1200(14)	8613(10)	8414(17)
C20	357(22)	8022(13)	8835(33)
C21	572(21)	9243(15)	7706(24)
C22	2051(18)	9290(14)	10023(21)
C23	5228(13)	7665(12)	7411(19)
C24	5546(14)	6675(13)	7416(22)
C25	5890(13)	8024(14)	6344(20)
C26	5656(15)	8349(14)	9241(19)

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

Results and Discussion

Mass Spectrum

II shows the parent ion at 776 m/e and loss of six CO's; the last two are released with greater difficulty, and competitively with complex fragmentation of the organic moiety. Intense doubly charged ions corresponding to the above fragmentation are found.

TABLE II. Calculated Fractional Coordinates (× 10^4) for the Hydrogen Atoms.

	x/a	*y/b*	*z/c*
H10	3647	8549	9087
H13	−315	6837	5129
H14	447	7666	2835
H161	−2488	6446	31
H162	−1240	5935	548
H163	−1065	6984	140
H171	−2122	6993	4506
H172	−1873	5941	3095
H173	−3107	6465	2575
H181	−2795	7973	2046
H182	−1362	8458	2082
H183	−1760	8515	3931
H201	818	7565	9349
H202	−298	7604	7744
H203	−71	8461	9722
H211	−44	8828	6572
H212	1204	9707	7469
H213	99	9652	8562
H221	2549	8887	10626
H222	1544	9699	10826
H223	2650	9754	9733
H241	5275	6164	6187
H242	5092	6455	8215
H243	6487	6733	7850
H251	5602	7558	5082
H252	6827	8047	6755
H253	5708	8720	6442
H261	5467	9043	9334
H262	6595	8376	9641
H263	5200	8099	10007

I.r. Spectrum

The following absorptions, in the CO stretching region (heptane solution) were observed for II: 2065 s, 2024 s (sh), 2020 vs, 2003 s, 1971 vs, 1878 s, 1859 s, cm^{-1}. This spectrum can be compared with the ones of I and Ia which, in heptane solution, show absorption at

I 2060 m, 2023 s(sh), 2016 vs, 2006 s(sh), 1975 s, 1869 m, 1858 m, cm^{-1}

Ia 2071 m, 2032 s(sh), 2027 vs, 2018 s(sh), 1977 s, 1882 m, 1861 m, cm^{-1}

Structure of the Complex II

A view of the structure of the complex II is shown in Fig. 2; the bond distances and angles not involving the hydrogen atoms are given in Table IV. The complex consists of a bent arrangement of three ruthenium atoms coordinated to eight carbonyls (six are terminal and two are bridging two metal atoms) and through σ- and η-bonds to an organic ligand deriving from trimerization of the alkyne. The Ru–Ru bonds are equal [Ru(1)–Ru(2) = 2.669(1) and Ru(2)–Ru(3) = 2.661(2) Å, the non-bonded

TABLE III. Thermal parameters (× 10^4) for the Non-hydrogen Atoms with e.s.d.'s in Parentheses. They are in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru1	479(7)	417(7)	376(6)	159(5)	149(5)	112(5)
Ru2	379(7)	352(6)	330(6)	77(5)	125(5)	60(5)
Ru3	707(9)	330(7)	445(7)	81(5)	213(6)	8(6)
O1	1095(108)	1075(109)	782(86)	541(83)	251(78)	400(86)
O2	1100(97)	465(67)	634(73)	186(57)	370(69)	225(62)
O3	844(93)	794(89)	1303(118)	380(83)	506(86)	−66(73)
O4	644(76)	1043(95)	775(83)	158(70)	407(68)	411(70)
O5	695(82)	843(85)	439(67)	−13(60)	44(61)	34(67)
O6	1316(109)	534(69)	720(79)	156(59)	513(76)	−50(67)
O7	1862(134)	728(65)	1679(139)	−267(77)	761(112)	−984(84)
O8	1732(150)	628(81)	1111(118)	363(81)	507(108)	505(90)
C1	762(118)	727(112)	469(90)	372(85)	150(84)	197(92)
C2	682(103)	417(83)	373(80)	186(66)	148(73)	144(72)
C3	703(109)	473(88)	587(94)	174(73)	330(83)	116(81)
C4	592(96)	494(89)	503(91)	141(73)	212(78)	33(75)
C5	496(90)	429(81)	408(82)	135(66)	164(72)	129(68)
C6	708(103)	397(82)	375(79)	161(65)	117(74)	−12(72)
C7	986(108)	537(84)	1118(143)	−258(86)	446(99)	−499(81)
C8	1427(173)	378(91)	635(111)	236(83)	405(114)	251(101)
C9	436(78)	511(79)	388(71)	109(60)	82(60)	91(62)
C10	571(93)	410(75)	668(93)	187(68)	265(76)	85(66)
C11	620(87)	405(71)	255(60)	176(53)	113(58)	98(62)
C12	519(81)	401(71)	399(70)	150(57)	214(62)	108(60)
C13	516(87)	471(79)	698(99)	151(71)	270(76)	183(66)
C14	584(92)	459(80)	437(78)	181(64)	53(68)	125(67)
C15	444(82)	666(100)	813(109)	273(84)	74(75)	169(72)
C16	763(130)	1452(169)	479(89)	120(97)	−11(85)	132(116)
C17	462(86)	1975(228)	1530(189)	1158(180)	174(101)	−19(108)
C18	1323(173)	682(113)	1682(204)	269(124)	−520(149)	432(114)
C19	831(105)	516(83)	572(90)	177(70)	367(80)	401(77)
C20	2522(216)	787(124)	2965(265)	524(146)	2492(220)	452(131)
C21	2012(207)	1541(165)	944(136)	639(122)	940(145)	1419(158)
C22	1050(155)	1564(155)	926(117)	−734(112)	262(110)	349(124)
C23	395(85)	875(117)	566(94)	17(84)	7(72)	70(79)
C24	540(93)	1011(137)	888(126)	232(105)	−36(86)	340(90)
C25	438(89)	1562(170)	680(103)	410(109)	3(76)	−234(96)
C26	667(116)	1121(147)	573(94)	−90(93)	−102(82)	−5(103

distance Ru(1)···Ru(3) = 3.73 Å] and nearly perpendicular to each other [Ru(1)–Ru(2)–Ru(3) = 88.8(1)°]. The bending angle in II is very close to the one [87.6(1)°] found in $Fe_3(CO)_8(C_2Ph_2)_2$ [3], but much narrower than the one [118.1(1)°] found in $Ru_3(CO)_8(C_{16}H_{22})$ [9]. The Ru–Ru bonds are shorter than the ones commonly found in triangular clusters (close to 2.80 Å). Similarly also in $Fe_3(CO)_8(C_2Ph_2)_2$ short Fe–Fe bonds were found [2.428(3) and 2.435(3) Å] against the values in the range 2.50–2.60 Å observed in triangular clusters; whereas in $Ru_3(CO)_8(C_{16}H_{22})$ the Ru–Ru bonds are different [2.731(2) and 2.838(2) Å] and longer than in II. The shortening of the metal–metal bonds both in I and II can be due to the presence of bridging CO s.

Of eight carbonyls six, two on each metal atom, are terminal, as shown by the Ru–C–O angles in the range 175.8–178.6°). Two carbonyls are bridging the terminal and the central metal atoms; these bridges are slightly asymmetrical [Ru(1)–C(2) = 1.976, Ru(2)–C(2) = 2.142; Ru(3)–C(6) = 2.008 and Ru(2)–C(6) = 2.117 Å] with the carbon atoms closer to the terminal metals.

The central Ru(2) atom forms two rather long σ-bonds with the organic ligand [Ru(2)–C(9) = 2.172 and Ru(2)–C(12) = 2.226 Å] giving rise to a metallacyclopentadiene ring. The terminal Ru(1) and Ru(3) atoms are η-bonded to the carbon atoms of this ring (Ru–C bonds in the range 2.234–2.340 Å) and lie on opposite sides with respect to it. The double bonds are delocalized over the three C–C bonds of the ring

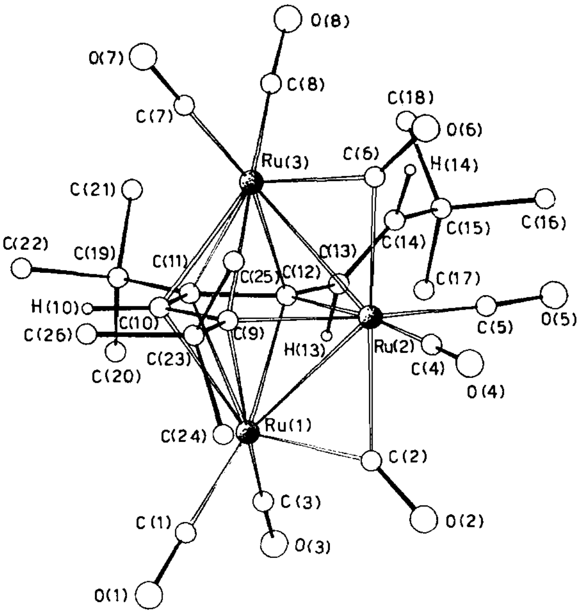

Fig. 2. View of the molecular shape of the complex $Ru_3(CO)_8(HC_2Bu^t)_3$ with the atomic numbering scheme. The hydrogen atoms of the methyl groups are omitted for clearness.

as shown by the distances C(9)–C(10), C(10)–C(11) and C(11)–C(12) [1.426, 1.450 and 1.419 Å respectively]. The heterocyclic ring is strictly planar, Ru(2), C(9), C(10), C(11) and C(12) being unsignificantly displaced from the mean plane passing through them. Also the C(13), C(19) atoms of the organic ligand and the C(4) and C(5) atoms of the carbonyls bound to Ru(2) are nearly coplanar with the heterocycle, their displacements being only –0.02, 0.04, –0.13 and 0.06 Å respectively. A view of the metallacyclopentadiene ring is shown in Fig. 3.

In $Ru_3(CO)_8(C_{16}H_{22})$ a terminal metal atom, through two σ-bonds, chelates to the organic ligand giving origin to a heterocycle. The Ru–Ru–Ru bending angle in this compound is larger than that present in II, and this can be explained by the fact that now chelation involves the central atom instead of the terminal one.

In the organic ligand the C(13)–C(14) bond is very short [1.29 Å]; these carbon atoms do not interact with the metals, so a double bond can be considered localized between them.

In II, as well as in $Fe_3(CO)_8(HC_2Me)_3$ [6] and in $Ru_3(CO)_8(C_{16}H_{22})$ [9], the alkyne trimerization is obtained through two head-to-tail and one tail-to-

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

i) In the coordination sphere of the ruthenium atoms

Ru(1)–Ru(2)	2.669(1)	Ru(1)–C(11)	2.32(1)	Ru(3)–C(6)	2.01(1)
Ru(2)–Ru(3)	2.661(2)	Ru(1)–C(12)	2.23(1)	Ru(3)–C(7)	1.87(2)
Ru(1)–C(1)	1.86(2)	Ru(2)–C(2)	2.14(2)	Ru(3)–C(8)	1.79(2)
Ru(1)–C(2)	1.98(1)	Ru(2)–C(4)	1.92(2)	Ru(3)–C(9)	2.29(1)
Ru(1)–C(3)	1.85(2)	Ru(2)–C(5)	1.90(1)	Ru(3)–C(10)	2.28(1)
Ru(1)–C(9)	2.34(1)	Ru(2)–C(6)	2.12(2)	Ru(3)–C(11)	2.32(1)
Ru(1)–C(10)	2.32(1)	Ru(2)–C(9)	2.17(1)	Ru(3)–C(12)	2.27(1)
		Ru(2)–C(12)	2.23(1)		
Ru(1)–Ru(2)–Ru(3)	88.8(1)	C(3)–Ru(1)–C(11)	105.5(7)	C(2)–Ru(2)–C(5)	90.4(6)
Ru(2)–Ru(1)–C(1)	134.5(5)	C(3)–Ru(1)–C(12)	99.5(6)	C(2)–Ru(2)–C(6)	175.1(6)
Ru(2)–Ru(1)–C(2)	52.4(5)	C(9)–Ru(1)–C(10)	35.6(5)	C(2)–Ru(2)–C(9)	91.6(5)
Ru(2)–Ru(1)–C(3)	126.0(5)	C(9)–Ru(1)–C(11)	63.9(5)	C(2)–Ru(2)–C(12)	90.6(6)
Ru(2)–Ru(1)–C(9)	50.9(3)	C(9)–Ru(1)–C(12)	70.0(5)	C(4)–Ru(2)–C(5)	89.3(7)
Ru(2)–Ru(1)–C(10)	76.5(4)	C(10)–Ru(1)–C(11)	36.4(5)	C(4)–Ru(2)–C(6)	89.6(7)
Ru(2)–Ru(1)–C(11)	79.0(3)	C(10)–Ru(1)–C(12)	62.3(5)	C(4)–Ru(2)–C(9)	101.3(6)
Ru(2)–Ru(1)–C(12)	53.1(3)	C(11)–Ru(1)–C(12)	36.2(4)	C(4)–Ru(2)–C(12)	173.3(6)
C(1)–Ru(1)–C(2)	98.9(7)	Ru(1)–Ru(2)–C(2)	46.9(4)	C(5)–Ru(2)–C(6)	89.7(6)
C(1)–Ru(1)–C(3)	84.7(8)	Ru(1)–Ru(2)–C(4)	120.4(5)	C(5)–Ru(2)–C(9)	169.3(6)
C(1)–Ru(1)–C(9)	104.6(7)	Ru(1)–Ru(2)–C(5)	118.6(5)	C(5)–Ru(2)–C(12)	96.2(6)
C(1)–Ru(1)–C(10)	105.1(7)	Ru(1)–Ru(2)–C(6)	136.7(4)	C(6)–Ru(2)–C(9)	89.3(5)
C(1)–Ru(1)–C(11)	129.1(6)	Ru(1)–Ru(2)–C(9)	56.7(4)	C(6)–Ru(2)–C(12)	94.3(6)
C(1)–Ru(1)–C(12)	165.3(6)	Ru(1)–Ru(2)–C(12)	53.4(4)	C(9)–Ru(2)–C(12)	73.2(5)
C(2)–Ru(1)–C(3)	93.5(7)	Ru(3)–Ru(2)–C(2)	135.7(4)	Ru(2)–Ru(3)–C(6)	51.6(5)
C(2)–Ru(1)–C(9)	91.1(6)	Ru(3)–Ru(2)–C(4)	125.9(5)	Ru(2)–Ru(3)–C(7)	134.8(5)
C(2)–Ru(1)–C(10)	125.3(6)	Ru(3)–Ru(2)–C(5)	117.1(5)	Ru(2)–Ru(3)–C(8)	125.5(6)
C(2)–Ru(1)–C(11)	129.0(5)	Ru(3)–Ru(2)–C(6)	48.1(4)	Ru(2)–Ru(3)–C(9)	51.4(3)
C(2)–Ru(1)–C(12)	94.9(6)	Ru(3)–Ru(2)–C(9)	55.5(4)	Ru(2)–Ru(3)–C(10)	77.4(4)
C(3)–Ru(1)–C(9)	168.8(7)	Ru(3)–Ru(2)–C(12)	54.5(4)	Ru(2)–Ru(3)–C(11)	79.2(3)
C(3)–Ru(1)–C(10)	136.5(7)	C(2)–Ru(2)–C(4)	85.5(6)	Ru(2)–Ru(3)–C(12)	52.9(3)

(Continued overleaf)

TABLE IV *(Continued from previous page)*

C(6)–Ru(3)–C(7)	100.7(7)	C(7)–Ru(3)–C(9)	101.1(6)	C(8)–Ru(3)–C(12)	101.5(8)
C(6)–Ru(3)–C(8)	94.1(7)	C(7)–Ru(3)–C(10)	100.4(7)	C(9)–Ru(3)–C(10)	36.4(5)
C(6)–Ru(3)–C(9)	88.8(6)	C(7)–Ru(3)–C(11)	125.3(6)	C(9)–Ru(3)–C(11)	64.7(5)
C(6)–Ru(3)–C(10)	124.1(6)	C(7)–Ru(3)–C(12)	161.1(7)	C(9)–Ru(3)–C(12)	70.2(5)
C(6)–Ru(3)–C(11)	129.4(6)	C(8)–Ru(3)–C(9)	171.5(8)	C(10)–Ru(3)–C(11)	36.8(5)
C(6)–Ru(3)–C(12)	95.9(6)	C(8)–Ru(3)–C(10)	138.4(8)	C(10)–Ru(3)–C(12)	62.5(5)
C(7)–Ru(3)–C(8)	86.2(9)	C(8)–Ru(3)–C(11)	107.5(8)	C(11)–Ru(3)–C(12)	36.0(4)
ii) In the carbonyl groups					
O(1)–C(1)	1.13(2)	O(4)–C(4)	1.12(2)	O(7)–C(7)	1.11(2)
O(2)–C(2)	1.17(2)	O(5)–C(5)	1.13(2)	O(8)–C(8)	1.18(2)
O(3)–C(3)	1.15(2)	O(6)–C(6)	1.16(2)		
Ru(1)–C(1)–O(1)	178(2)	Ru(1)–C(3)–O(3)	179(1)	Ru(2)–C(6)–O(6)	137(1)
Ru(1)–C(2)–Ru(2)	80(1)	Ru(2)–C(4)–O(4)	177(1)	Ru(3)–C(6)–O(6)	143(1)
Ru(1)–C(2)–O(2)	144(1)	Ru(2)–C(5)–O(5)	176(1)	Ru(3)–C(7)–O(7)	176(2)
Ru(2)–C(2)–O(2)	135(1)	Ru(2)–C(6)–Ru(3)	80(1)	Ru(3)–C(8)–O(8)	177(2)
iii) In the organic ligand					
C(9)–C(10)	1.43(2)	C(15)–C(16)	1.55(2)	C(19)–C(22)	1.56(2)
C(10)–C(11)	1.45(2)	C(15)–C(17)	1.53(3)	C(23)–C(9)	1.57(2)
C(11)–C(12)	1.42(2)	C(15)–C(18)	1.51(3)	C(23)–C(24)	1.59(3)
C(12)–C(13)	153(2)	C(19)–C(11)	1.57(2)	C(23)–C(25)	1.53(2)
C(13)–C(14)	1.29(2)	C(19)–C(20)	1.46(3)	C(23)–C(26)	1.57(2)
C(14)–C(15)	1.52(2)	C(19)–C(21)	1.48(3)		
Ru(1)–C(9)–Ru(2)	72(1)	Ru(1)–C(11)–C(19)	127(1)	C(13)–C(14)–C(15)	127(1)
Ru(1)–C(9)–Ru(3)	107(1)	Ru(3)–C(11)–C(10)	70(1)	C(14)–C(15)–C(16)	108(1)
Ru(1)–C(9)–C(10)	72(1)	Ru(3)–C(11)–C(12)	70(1)	C(14)–C(15)–C(17)	111(1)
Ru(1)–C(9)–C(23)	127(1)	Ru(3)–C(11)–C(19)	126(1)	C(14)–C(15)–C(18)	108(1)
Ru(2)–C(9)–Ru(3)	73(1)	C(10)–C(11)–C(19)	120(1)	C(16)–C(15)–C(17)	109(2)
Ru(2)–C(9)–C(10)	118(1)	C(10)–C(11)–C(12)	111(1)	C(16)–C(15)–C(18)	109(2)
Ru(2)–C(9)–C(23)	125(1)	C(12)–C(11)–C(19)	129(1)	C(17)–C(15)–C(18)	111(1)
Ru(3)–C(9)–C(10)	71(1)	Ru(1)–C(12)–Ru(2)	73(1)	C(11)–C(19)–C(20)	113(1)
Ru(3)–C(9)–C(23)	126(1)	Ru(1)–C(12)–Ru(3)	112(1)	C(11)–C(19)–C(21)	112(1)
C(10)–C(9)–C(23)	117(1)	Ru(1)–C(12)–C(11)	75(1)	C(11)–C(19)–C(22)	109(1)
Ru(1)–C(10)–Ru(3)	108(1)	Ru(1)–C(12)–C(13)	123(1)	C(20)–C(19)–C(21)	110(2)
Ru(1)–C(10)–C(9)	73(1)	Ru(2)–C(12)–Ru(3)	73(1)	C(20)–C(19)–C(22)	109(2)
Ru(1)–C(10)–C(11)	72(1)	Ru(2)–C(12)–C(11)	120(1)	C(21)–C(19)–C(22)	104(1)
Ru(3)–C(10)–C(9)	72(1)	Ru(2)–C(12)–C(13)	117(1)	C(9)–C(23)–C(24)	109(1)
Ru(3)–C(10)–C(11)	73(1)	Ru(3)–C(12)–C(11)	74(1)	C(9)–C(23)–C(25)	109(1)
C(9)–C(10)–C(11)	118(1)	Ru(3)–C(12)–C(13)	125(1)	C(9)–C(23)–C(26)	112(1)
Ru(1)–C(11)–Ru(3)	107(1)	C(11)–C(12)–C(13)	123(1)	C(24)–C(23)–C(25)	111(1)
Ru(1)–C(11)–C(10)	72(1)	C(12)–C(13)–C(14)	129(1)	C(24)–C(23)–C(26)	105(1)
Ru(1)–C(11)–C(12)	69(1)			C(25)–C(23)–C(26)	109(1)

tail linkages, the latter requiring a hydrogen shift. This behaviour agrees with that observed in cyclo-oligomerization of the alkynes induced by nickel-carbonyl phosphines, when the 1,2,4-substituted benzenes are obtained in greater yields than the 1,3,5-derivatives [1]. Thus, the mechanism of formation of II could be compared with those proposed for the nickel reactions, especially when considering that in the reactions reported in the experimental section, only II, among the products obtainable from $Ru_3(CO)_{12}$ or $HRu_3(CO)_9(C_2Bu^t)$, show a marked increase of yields when nickel is present.

Evidently, 'ligand exchange' is a fundamental process in the above discussed reactions as, starting from an alkyne nickel derivative, all the products, typical for the reaction of $Ru_3(CO)_{12}$ with free alkyne, are obtained. On the contrary low yields of heterometallic derivatives are observed.

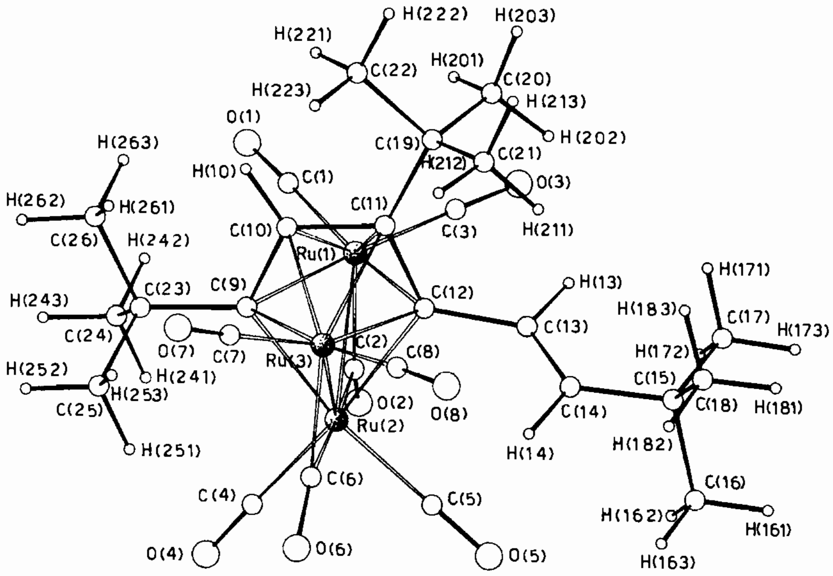

Fig. 3. Conformation of the organic ligand, obtained by trimerization of the alkynes, which forms with Ru(2) atom a metallacyclopentadiene ring.

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