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Dimerization of Isopropenylacetylene on $Ru_3(CO)_{12}$. Synthesis and Crystal Structure of $Ru_3(CO)_8(C_{10}H_{12})$

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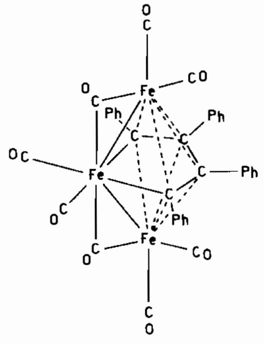
The new complex $Ru_3(CO)_8(C_{10}H_{12})$ has been synthesized by reacting $Ru_3(CO)_{12}$ and isopropenylacetylene in hydrocarbon solvents. It has been characterized by means of elemental analysis, i.r. and mass spectra; the crystal structure has been determined by X-ray methods. Crystals are triclinic, space group $P\bar{1}$ with Z = 2 in a unit cell of dimensions a = 8.877(8), b = 13.594(10), c = 8.849(7) Å, α = 92.01(8), β = 98.41(8), γ = 106.13(7)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.028 for 4462 observed reflections.

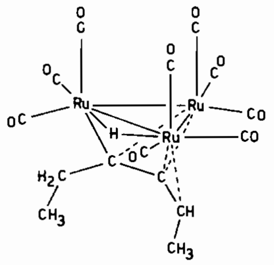
The complex is formed by a closed tri-metal atom cluster, bonded to eight carbonyls, two of which very asymmetrically bridging two metals, and to a six-carbon atom chain through σ- and η-bonds. This chain, derived from the dimerization of two molecules of isopropenylacetylene, presents an extensive bond delocalization, as two triple bonds and one double bond of an isopropenyl group are involved in its formation.

Introduction

The reactions of $Ru_3(CO)_{12}$ with alkynes have been recently studied; RC_2R alkynes [1] afford the non hydridic $Ru_3(CO)_9(RC_2R)$ and $Ru_3(CO)_8(RC_2R)_2$ (Ia) complexes; the latter present the same structure of $Fe_3(CO)_8(RC_2R)_2$ (I) with bridging carbonyls [2]. Dihydridic $H_2Ru_3(CO)_9(RC_2R)$ are obtained only in alkaline solution [3]. RC_2CH_2R' alkynes give the isomers $HRu_3(CO)_9(RC_2CHR')$ (II) and $HRu_3(CO)_9(RC_2HCR')$ (III) [4–6] and, with excess of alkyne, $Ru_3(CO)_8(RC_2CHR')(R''C_2R''')$ (Ib). The same hydrides are also obtained in the reactions of $Ru_3(CO)_{12}$ with acyclic dienes and olefins [7–8].



(I)



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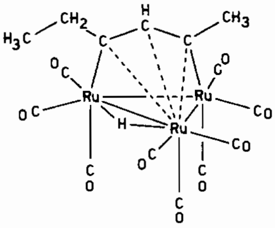
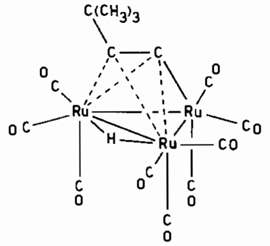


(III)

Finally the reaction of HC_2R alkynes with $Ru_3(CO)_{12}$ leads, as major products, to the monohydrides $HRu_3(CO)_9C_2R$ [9–10]. The reaction of $HRu_3(CO)_9C_2Bu^t$ (IV) with excess of alkyne leads to the two $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$ (V) isomers [11–12] and other polysubstituted complexes; the reac-



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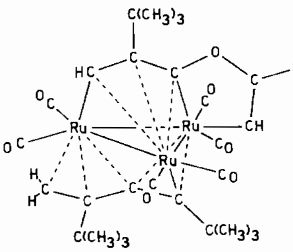
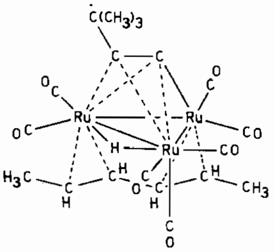


(V)

tions with some dienes lead to the $HRu_3(CO)_7(C_2\text{-}Bu^t)(C_6H_{10})$ (VI) derivative [13].



(VI)

We now report the reactions of $HC_2C(=CH_2)CH_3$, isopropenylacetylene, with $Ru_3(CO)_{12}$ in hydrocarbon solvents; among the considerable number of products obtained $Ru_3(CO)_8(C_{10}H_{12})$ (VII), the major reaction product, has been characterized and studied by X-ray diffraction methods. This complex, although isoformular with the formerly reported $Fe_3(CO)_8(RC_2R)_2$ (I) [2] and $Ru_3(CO)_8(RC_2R)_2$ (Ia) [1] derivatives, shows a different structure as, instead of cluster opening and formation of an heterocyclic five-membered ring involving one metal atom, from the condensation of two molecules of alkyne a six-carbon chain, bonded to the cluster via σ- and η-bonds, is formed. The bonding of the organic moiety to the cluster presents some similarities with the ones observed in II, III and V ($C_{12}H_{20}$ ligand); thus VII can be hypothesized as intermediate in the formation of complexes like V.

It is noteworthy that one of the isopropenylacetylene molecules takes part in the formation of the organic ligand both through the triple and the double bond.

Experimental

Reaction of $Ru_3(CO)_{12}$ with Isopropenylacetylene

The dodecacarbonyltriruthenium has been prepared and purified by literature methods [14]; the alkyne, purchased from Fluka, was used without further purification.

Refluxing for 15–30 min, under dry nitrogen, a n-heptane solution of $Ru_3(CO)_{12}$ with a 2:1 molar excess of alkyne (dissolved in some benzene, in order to increase the very poor solubility shown by the isopropenylacetylene in cold n-heptane), leads to 7–11 products in small yields.

The reaction mixture is filtered, the solvent removed under reduced pressure; the residual is then dissolved in $CHCl_3$ and purified on t.l.c. preparative plates (Kieselgel P.F., eluant mixtures of ethyl ether and light petroleum). Yields of about 4% of VII are obtained, with respect to the dodecacarbonyltriruthenium.

The fraction containing VII must usually be further purified on t.l.c. plates; finally VII is dissolved in n-heptane (or in a n-heptane–$CHCl_3$ mixture) and allowed to crystallize at –20 °C for days. Usually very small, bright orange crystals are obtained, which are air stable for long periods. Complex VII analyzes as follows: Found, C% 32.9, H% 2.0, O% 19.1, Ru% 47.0. Calc. for $C_{18}H_{12}O_8Ru_3$, C% 32.7, H% 1.8, O% 19.4, Ru% 46.1.

Analysis of the Product

The analyses were accomplished by means of an F & M 185 C, H, N Analyzer, and a Perkin Elmer 303 Atomic Absorption Spectrophotometer. The mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6H instrument operating with direct inlet system and electron impact ion source, at 70 eV. The i.r. spectra were registered on a Beckman IR-12 (KBr optics) instrument.

X-Ray Data Collection

A roughly prismatic orange crystal of the compound VII with dimensions of *ca.* 0.17 × 0.25 × 0.40 mm was used for the collection of all the data. Preliminary cell parameters obtained by rotation and Weissenberg photographs were subsequently refined by least squares fit to the θ angles of 20 reflections accurately centered on a Siemens AED single-crystal diffractometer. The crystal data are: a = 8.877(8), b = 13.594(10), c = 8.849(7) Å, α = 92.01(8), β = 98.41(8), γ = 106.13(7)°, V = 1011(1) Å^3, M = 659.50, Z = 2, D_c = 2.17 g cm^{-3}, MoKα radiation ($\bar{\lambda}$ = 0.71069 Å), μ(MoKα) = 22.11 cm^{-1}, space group $P\bar{1}$ from structure determination.

A total of 5244 independent reflections with $3 \leqslant \theta \leqslant 29°$ were collected on the same Siemens diffractometer using the Zr-filtered MoKα radiation and the ω–2θ scan technique. 4462 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.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$ for Ru, O, C Atoms, $\times 10^3$ for H Atoms) with E.s.d.'s.

	x/a	y/b	z/c
Ru(1)	1632(1)	2051(1)	2570(1)
Ru(2)	−20(1)	2588(1)	4760(1)
Ru(3)	−1611(1)	1994(1)	1770(1)
O(1)	3145(7)	1348(5)	8(6)
O(2)	4357(6)	1725(5)	4828(6)
O(3)	−471(5)	−59(3)	3000(6)
O(4)	−700(9)	4326(4)	6480(7)
O(5)	2432(7)	2497(5)	7441(6)
O(6)	−2568(6)	727(4)	5632(5)
O(7)	−4507(6)	256(4)	2117(6)
O(8)	−3170(7)	3441(5)	3119(7)
C(1)	2557(7)	1627(5)	926(7)
C(2)	3321(7)	1825(5)	3991(7)
C(3)	122(7)	779(4)	2802(7)
C(4)	−507(9)	3662(5)	5812(7)
C(5)	1496(8)	2514(5)	6433(7)
C(6)	−1648(7)	1417(4)	5308(6)
C(7)	−3399(7)	918(5)	2004(7)
C(8)	−2408(8)	2900(5)	2830(8)
C(9)	1826(6)	3538(4)	3811(6)
C(10)	1793(5)	3743(3)	2255(5)
C(11)	516(5)	3022(3)	1277(5)
C(12)	−637(6)	3130(4)	46(5)
C(13)	−1853(6)	2260(4)	−699(5)
C(14)	−1653(7)	1280(4)	−529(6)
C(15)	−3321(7)	2410(5)	−1619(7)
C(16)	3011(6)	4566(4)	1679(6)
C(17)	2878(8)	4762(5)	220(7)
C(18)	4398(8)	5186(5)	2797(8)
H(9)	283(7)	385(5)	459(7)
H(12)	−81(7)	384(5)	−16(7)
H(141)	−268(8)	66(5)	−97(7)
H(142)	−97(8)	109(5)	−12(7)
H(151)	−425(8)	179(5)	−177(7)
H(152)	−320(7)	264(5)	−270(8)
H(153)	−359(8)	298(5)	−136(8)
H(171)	218(8)	446(5)	−58(7)
H(172)	375(8)	532(5)	−3(7)
H(181)	498(7)	478(5)	327(7)
H(182)	401(7)	554(5)	339(8)
H(183)	499(8)	569(5)	218(8)

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 [15] with initially isotropic and then anisotropic thermal parameters. A final ΔF map gave the positions of all the hydrogen atoms. Further least-squares cycles were then computed including these hydrogen atoms with isotropic thermal parameters. 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 0.028 (observed reflections only). The atomic scattering factors used (corrected for the anomalous dispersion of ruthenium) were taken from the International Tables [16]. The atomic fractional coordinates and thermal parameters are listed in Tables I and II. 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 Elettro-

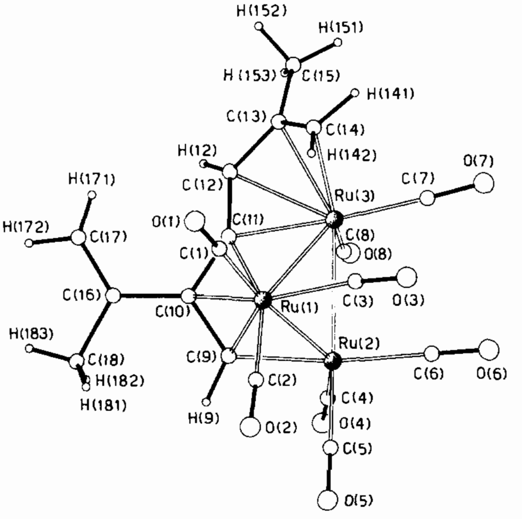


Fig. 1. View of the molecular shape with the atomic labelling scheme.

TABLE II. Thermal Parameters ($\times 10^4$ for non Hydrogen Atoms, $\times 10^3$ for H Atoms) with Their Estimated Standard Deviations in Parentheses. They are in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots 2hka^*b^*U_{12})]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	252(2)	274(2)	275(2)	23(1)	−4(1)	88(1)
Ru(2)	369(2)	298(2)	253(2)	42(1)	64(1)	80(2)
Ru(3)	256(2)	299(2)	290(2)	60(1)	3(1)	39(1)
O(1)	900(39)	982(42)	546(29)	177(28)	344(28)	578(34)
O(2)	600(32)	1027(46)	629(33)	54(31)	−206(26)	335(31)
O(3)	535(26)	323(21)	708(30)	125(20)	61(22)	109(18)
O(4)	1444(59)	541(32)	843(41)	30(29)	545(40)	374(35)

(continued overleaf)

TABLE II. *(continued)*

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(5)	824(38)	822(40)	473(28)	173(27)	−226(26)	−7(30)
O(6)	581(28)	503(26)	550(27)	148(21)	164(22)	51(21)
O(7)	537(29)	675(34)	771(37)	86(28)	126(26)	−217(25)
O(8)	909(42)	865(42)	896(41)	91(33)	293(34)	578(36)
C(1)	444(31)	494(33)	397(29)	90(25)	90(24)	233(26)
C(2)	392(30)	514(34)	438(31)	43(26)	−18(24)	180(26)
C(3)	387(28)	358(27)	420(29)	41(23)	18(22)	116(22)
C(4)	813(48)	387(31)	483(35)	107(27)	314(33)	204(31)
C(5)	534(35)	457(33)	343(28)	66(24)	28(25)	29(26)
C(6)	432(29)	388(28)	333(26)	63(22)	55(22)	116(23)
C(7)	354(28)	437(31)	451(31)	70(25)	8(23)	28(23)
C(8)	604(39)	453(33)	563(38)	110(29)	259(31)	186(29)
C(9)	366(26)	281(23)	292(23)	14(18)	30(19)	62(19)
C(10)	266(21)	257(21)	299(22)	32(17)	17(17)	78(17)
C(11)	278(22)	264(21)	275(21)	35(17)	40(17)	76(17)
C(12)	316(23)	330(25)	276(22)	72(19)	24(18)	86(19)
C(13)	334(24)	384(26)	245(22)	69(19)	−5(18)	77(20)
C(14)	401(30)	376(27)	328(25)	−39(21)	−67(21)	111(23)
C(15)	355(28)	521(36)	428(31)	99(27)	−82(23)	138(26)
C(16)	278(22)	301(23)	364(25)	40(19)	58(19)	75(18)
C(17)	446(33)	500(34)	378(30)	67(26)	112(25)	−11(26)
C(18)	378(29)	423(33)	507(36)	48(28)	6(26)	−62(25)
H(9)	30(18)					
H(12)	14(18)					
H(141)	38(18)					
H(142)	73(19)					
H(151)	69(18)					
H(152)	60(18)					
H(153)	81(19)					
H(171)	57(18)					
H(172)	64(18)					
H(181)	38(18)					
H(182)	66(19)					
H(183)	86(19)					

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Results and Discussion

I.r. and Mass Spectra

In the i.r. spectrum the following absorptions are observed in the CO stretching region (n-heptane solution): 2076 m, 2037 vs, 2013 s, 2001 m, 1989 m cm^{-1}. No signals were detected in the region typical of the bridging CO groups.

In the mass spectrum the complex VII shows the parent ion at 662 m/e and gradual loss of eight CO groups, then a complex fragmentation of the organic moiety, with loss of H_2, CH_2 and C_2H_4 fragments. Intense are the doubly charged ions corresponding to the loss of the CO's.

X-Ray Structure of the Complex VIII

The structure of the complex is represented in Fig. 1. Bond distances and angles are given in Table III. The complex consists of a cluster of three ruthenium atoms, at the corners of an isosceles triangle, coordinated by eight carbonyls and σ- and η-bonded to an organic ligand, derived from two dimerized alkyne molecules.

The Ru–Ru bond distances [2.787, 2.788 and 2.841 Å] are of the same order of magnitude with respect to other substituted ruthenium clusters [6–8, 17] and very close to those found for IV [10], V [12] and VI [13]. Two metals, Ru(1) and Ru(2), are bonded to three carbonyl groups, and the third one, Ru(3), to two CO's only. Of the eight carbonyls, six are terminal, as shown by the angles (in the range 175.7–178.7°) and two are very unsymmetrically bridging the Ru(1)–Ru(3) and Ru(2)–Ru(3) sides of the cluster [Ru(1)–C(3) 1.910, Ru(3)–C(3) 2.652, Ru(3)–C(8) 1.869 and Ru(2)–C(8) 2.661 Å]. The

TABLE III. Bond Distances (A) and Angles (°) (not involving hydrogen atoms) with E.s.d.'s.

i) *In the coordination sphere of the rutenium atoms*

Ru(1)–Ru(2)	2.787(1)	Ru(2)–C(5)	1.875(7)
Ru(1)–Ru(3)	2.841(1)	Ru(2)–C(6)	1.959(6)
Ru(2)–Ru(3)	2.788(1)	Ru(2)–C(9)	2.088(5)
Ru(1)–C(1)	1.917(6)	Ru(3)–C(7)	1.879(6)
Ru(1)–C(2)	1.912(6)	Ru(3)–C(8)	1.869(7)
Ru(1)–C(3)	1.910(6)	Ru(3)–C(11)	2.127(4)
Ru(1)–C(9)	2.218(6)	Ru(3)–C(12)	2.295(5)
Ru(1)–C(10)	2.294(5)	Ru(3)–C(13)	2.216(5)
Ru(1)–C(11)	2.129(5)	Ru(3)–C(14)	2.214(5)
Ru(2)–C(4)	1.886(7)		

Ru(2)–Ru(1)–Ru(3)	59.4(1)	Ru(3)–Ru(2)–C(6)	84.7(2)
Ru(3)–Ru(2)–Ru(1)	61.3(1)	Ru(3)–Ru(2)–C(9)	87.1(2)
Ru(1)–Ru(3)–Ru(2)	59.4(1)	C(4)–Ru(2)–C(5)	91.1(3)
Ru(2)–Ru(1)–C(1)	174.0(2)	C(4)–Ru(2)–C(6)	99.3(3)
Ru(2)–Ru(1)–C(2)	96.3(2)	C(4)–Ru(2)–C(9)	95.7(3)
Ru(2)–Ru(1)–C(3)	76.9(2)	C(5)–Ru(2)–C(6)	93.3(3)
Ru(2)–Ru(1)–C(9)	47.7(1)	C(5)–Ru(2)–C(9)	88.0(3)
Ru(2)–Ru(1)–C(10)	75.6(1)	C(6)–Ru(2)–C(9)	164.9(2)
Ru(2)–Ru(1)–C(11)	81.2(1)	Ru(1)–Ru(3)–C(7)	127.1(2)
Ru(3)–Ru(1)–C(1)	114.7(2)	Ru(1)–Ru(3)–C(8)	119.3(2)
Ru(3)–Ru(1)–C(2)	150.3(2)	Ru(1)–Ru(3)–C(11)	48.2(1)
Ru(3)–Ru(1)–C(3)	64.4(2)	Ru(1)–Ru(3)–C(12)	83.0(1)
Ru(3)–Ru(1)–C(9)	83.4(1)	Ru(1)–Ru(3)–C(13)	103.6(1)
Ru(3)–Ru(1)–C(10)	77.6(1)	Ru(1)–Ru(3)–C(14)	89.6(1)
Ru(3)–Ru(1)–C(11)	48.1(1)	Ru(2)–Ru(3)–C(7)	103.7(2)
C(1)–Ru(1)–C(2)	89.0(3)	Ru(2)–Ru(3)–C(8)	66.3(2)
C(1)–Ru(1)–C(3)	99.7(3)	Ru(2)–Ru(3)–C(11)	81.2(1)
C(1)–Ru(1)–C(9)	135.4(3)	Ru(2)–Ru(3)–C(12)	112.9(1)
C(1)–Ru(1)–C(10)	104.9(2)	Ru(2)–Ru(3)–C(13)	149.5(2)
C(1)–Ru(1)–C(11)	95.6(2)	Ru(2)–Ru(3)–C(14)	148.2(2)
C(2)–Ru(1)–C(3)	95.3(3)	C(7)–Ru(3)–C(8)	89.2(3)
C(2)–Ru(1)–C(9)	92.2(3)	C(7)–Ru(3)–C(11)	170.3(2)
C(2)–Ru(1)–C(10)	115.1(2)	C(7)–Ru(3)–C(12)	141.7(2)
C(2)–Ru(1)–C(11)	152.2(2)	C(7)–Ru(3)–C(13)	106.5(2)
C(3)–Ru(1)–C(9)	124.6(2)	C(7)–Ru(3)–C(14)	89.4(3)
C(3)–Ru(1)–C(10)	140.8(2)	C(8)–Ru(3)–C(11)	100.5(3)
C(3)–Ru(1)–C(11)	110.9(2)	C(8)–Ru(3)–C(12)	95.3(3)
C(9)–Ru(1)–C(10)	36.4(2)	C(8)–Ru(3)–C(13)	110.1(3)
C(9)–Ru(1)–C(11)	65.6(2)	C(8)–Ru(3)–C(14)	143.8(3)
C(10)–Ru(1)–C(11)	37.4(2)	C(11)–Ru(3)–C(12)	37.3(2)
Ru(1)–Ru(2)–C(4)	146.5(2)	C(11)–Ru(3)–C(13)	69.5(2)
Ru(1)–Ru(2)–C(5)	94.5(2)	C(11)–Ru(3)–C(14)	82.3(2)
Ru(1)–Ru(2)–C(6)	113.2(2)	C(12)–Ru(3)–C(13)	36.7(2)
Ru(1)–Ru(2)–C(9)	51.7(2)	C(12)–Ru(3)–C(14)	65.2(2)
Ru(3)–Ru(2)–C(4)	116.8(2)	C(13)–Ru(3)–C(14)	36.9(2)
Ru(3)–Ru(2)–C(5)	152.0(2)		

ii) *In the carbonyl groups*

O(1)–C(1)	1.135(9)	O(5)–C(5)	1.132(9)
O(2)–C(2)	1.136(8)	O(6)–C(6)	1.136(8)
O(3)–C(3)	1.146(7)	O(7)–C(7)	1.154(8)
O(4)–C(4)	1.128(9)	O(8)–C(8)	1.174(10)

Ru(1)–C(1)–O(1)	176.3(6)	Ru(2)–C(5)–O(5)	178.1(7)
Ru(1)–C(2)–O(2)	177.5(6)	Ru(2)–C(6)–O(6)	178.5(5)

(continued overleaf)

TABLE III. *(continued)*

Ru(1)–C(3)–O(3)	164.0(5)	Ru(3)–C(7)–O(7)	178.7(6)
Ru(2)–C(4)–O(4)	175.7(7)	Ru(3)–C(8)–O(8)	161.8(6)
iii) *In the organic ligands*			
C(9)–C(10)	1.412(7)	C(11)–C(12)	1.423(7)
C(10)–C(16)	1.487(7)	C(12)–C(13)	1.423(7)
C(16)–C(17)	1.322(8)	C(13)–C(14)	1.402(8)
C(16)–C(18)	1.488(9)	C(13)–C(15)	1.500(8)
C(10)–C(11)	1.425(6)		
C(10)–C(9)–Ru(1)	74.7(3)	Ru(3)–C(11)–C(10)	130.9(3)
C(10)–C(9)–Ru(2)	126.4(4)	C(3)–C(12)–Ru(3)	68.6(3)
Ru(1)–C(9)–Ru(2)	80.6(2)	C(13)–C(12)–C(11)	121.1(5)
C(11)–C(10)–C(16)	123.4(4)	Ru(3)–C(12)–C(11)	64.9(3)
C(11)–C(10)–Ru(1)	65.0(2)	C(14)–C(13)–C(15)	121.8(5)
C(11)–C(10)–C(9)	112.2(4)	C(14)–C(13)–Ru(3)	71.5(3)
C(16)–C(10)–C(9)	124.3(4)	C(14)–C(13)–C(12)	118.7(5)
Ru(1)–C(10)–C(9)	68.8(3)	C(15)–C(13)–C(12)	119.5(5)
C(12)–C(11)–Ru(1)	149.0(4)	Ru(3)–C(13)–C(12)	74.7(3)
C(12)–C(11)–Ru(3)	77.8(3)	Ru(3)–C(14)–C(13)	71.6(3)
C(12)–C(11)–C(10)	133.0(4)	C(17)–C(16)–C(18)	120.0(6)
Ru(1)–C(11)–Ru(3)	83.7(2)	C(17)–C(16)–C(10)	121.8(5)
Ru(1)–C(11)–C(10)	77.6(3)	C(18)–C(16)–C(10)	118.2(5)

bridging character of these CO groups is confirmed by the angles Ru(1)–C(3)–O(3) [164.0°] and Ru(3)–C(8)–O(8) [161.8°] which are narrower than those formed by the terminal carbonyls and typical of semi-bridging CO's [18–19]. Unsymmetrical bridging carbonyls have been, until now, found only in two ruthenium clusters: $Ru_3(CO)_6(C_7H_7)(C_7H_9)$ [20] and $Ru_3(CO)_{10}(C_4H_4N_2)$ [21]. Instead several examples of very asymmetrically bridging CO's have been reported for alkyne iron clusters as $Fe_3(CO)_8(HC_2Me)_3$ [22], $Fe_3(CO)_7(HC_2Et)_4$ [23], $Fe_4(CO)_{11}(HC_2Et)_2$ [24] and $(C_5H_5)Fe_3(CO)_7C_2C_6H_5$ [25].

The organic ligand is formed upon dimerization of two molecules of isopropenylacetylene, with hydrogen shift from C(11) to the adjacent C(12), and through σ- and η-bonds interacts with all the metal atoms. The resulting unit is a 2-methyl-5-isopropenyl substituted hexaatomic chain characterized by extensive bonding delocalization, as shown by the C–C bond distances in the range 1.402–1.425 Å. It is noteworthy that two triple bonds of the former alkynes and one double bond of an isopropenyl substituent are involved in the formation of the chain. To fulfil the E.A.N. rule, this organic ligand must be considered as an eight electron donor towards the whole cluster. The six adjacent carbon atoms C(9), C(10), C(11), C(12), C(13) and C(14) are involved in a complex interaction with the metal cluster: C(9) through a σ-bond with Ru(2), C(9), C(10) and C(11) with Ru(1), C(11), C(12), C(13) and C(14) with Ru(3) through an extensive η-bonding. The Ru(2)–C(9) σ-bond corresponds to the shortest distance (2.088 Å); the Ru(1)–C(11) and Ru(3)–C(11) distances involving the carbon coordinated to two metal atoms are shorter than those involving the other η-coordinated carbons (2.129 and 2.127 Å against the other in the range 2.214–2.295 Å) in agreement with the results obtained in similar situations [12, 26]. The organic ligand and its interaction with the metals are comparable to the ones found in $Fe_2(CO)_6(C_9H_{14}CO)$ and $Fe_2(CO)_6$-$C_7H_{10}CO)$ [27], in III [6] and in V ($C_{12}H_{20}$ ligand) [12]. In particular C(11) in the present complex is comparable with C(13) in III and C(26) in V [C(10)–C(11)–C(12) = 133.0, C(12)–C(13)–C(14) = 142.3, C(21)–C(26)–C(27) = 151.8°]. In both V and the present complexes the organic moiety is obtained by dimerization of two alkynes.

The isopropenyl substituent in the chain is quite regular: the atoms C(10), C(16), C(17) and C(18) are perfectly coplanar, and the double bond is localized on C(16)–C(17) (bond distance 1.322 Å). The conformation of the organic ligand is shown by the following torsion angles:

Ru(2)C(9)C(10)C(11)	16.0°
C(9)C(10)C(11)C(12)	–133.7
C(10)C(11)C(12)C(13)	176.8
C(11)C(12)C(13)C(14)	18.3
C(9)C(10)C(16)C(18)	–3.0
C(9)C(10)C(16)C(17)	176.3

C(10)C(11)C(16)C(17)	−8.4
C(10)C(11)C(16)C(18)	172.4

The $C_{12}H_{20}$ ligand in V was shown to be originated by interaction of the C_2Bu^t ligand of $HRu_3(CO)_9$-C_2Bu^t with excess of alkyne [11]; by analogy we consider that a complex $HRu_3(CO)_9C_2(C_3H_5)$ is intermediate in the formation of VII. Indeed, very small yields of a complex which, on the basis of elemental analyses and mass spectra, has been characterized as $Ru_3(CO)_9(C_5H_6)$ have been obtained in the same reaction; however the very poor yields prevented the measurement of suitable ^1H n.m.r. spectra, in order to detect the possible hydridic hydrogen.

Despite a considerable number of attempts, we were unable to isolate a ruthenium complex containing only one of the two ligands present in V, to be considered as the intermediate in the formation of V from IV; we only had indirect evidence for the formation of isopropenyl-homologues of V has been synthesis of VII (in which a double bond of the alkyne participates in the bonding) can be considered as a further evidence of the formation of the "dienic" ligand prior to the "carbenic" one. The presence of semibridging CO's, in which the hybridization of the carbon atom is considerably different than in terminal ones, could account for a subsequent formation of a "carbenic" moiety. Some evidence for the formation of isopropenyl-homologues of V has been indeed obtained [28] when operating in considerable excess of isopropenylacetylene.

Thus, not only VII is an example of a new structure within the $M_3(CO)_8L_n$ derivatives (M = Fe, Ru, Os and L = alkyne), but it represents the determination of a new step in the reaction sequence from $Ru_3(CO)_{12}$ to complexes V.

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