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Synthesis and Crystal Structure of $Ru_3(CO)_8(C_{16}H_{22})$. The Insertion of Isopropenylacetylene into Ru–C Bonds and the Opening of a Stable Closed Triruthenium Cluster

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The title complex is obtained by reaction of the very stable $HRu_3(CO)_9C_2Bu^t$ *hydride with excess of isopropenylacetylene in hydrocarbon solvents. It has been characterized by elemental analysis and i.r. spectra, although in the mass spectrometer decomposition occurs. 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* $a = 11.331(9)$, $b = 14.173(11)$, $c = 9.022(8)$ Å, $\alpha = 80.79(7)$, $\beta = 104.47(8)$, $\gamma = 105.48(8)°$. *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 5192 observed reflections. The complex consists of an open, bent tri-metal atom arrangement, coordinated by eight terminal carbonyls and, through* σ- *and* η-*bonds, by an organic moiety deriving from the condensation of two isopropenylacetylene molecules with one of t-butyl-acetylene. Hydrogen shift and transfer occurs in the reaction and the two isopropenylacetylenic molecules interact in a different way with the* $C(\sigma-\pi)$ *of the* C_2Bu^t *group of the parent hydride. The resulting substituted seven carbon chain interacts with the three metals in a different way. This cluster opening is noteworthy as, until now, only CO substitution was obtained in the reactions of* $HRu_3(CO)_9C_2Bu^t$.

Introduction

The hydride $HRu_3(CO)_9C_2Bu^t$ (I) is the main product of the reaction between $Ru_3(CO)_{12}$ and 3,3-dimethyl-but-1-yne (t-butylacetylene) [1]. Its structure has been studied both in the solid state [2, 3] and in solution [4]. Complex I, in presence of excess t-butyl-acetylene, gives two isomeric $Ru_3(CO)_6(C_{12}H_{20})(C_{12}H_{20}CO)$ derivatives(II) [5, 6] and other unidentified products; in presence of H_2 or strong acids neutral [7, 8] or positively charged [7] dihydrides are obtained; the reaction of I with 2-*cis*-4-*trans*-hexadiene yields the hydride $HRu_3(CO)_7(C_6H_9)(C_6H_{10})$ (III) [9]. All these reaction products still contain a closed triruthenium cluster; in particular complex III is formed by simple substitution of two CO's by the diene and the Ru_3C_2 core of the parent complex I is maintained nearly intact.

We have reported also the reaction of $Ru_3(CO)_{12}$ with isopropenylacetylene [10], from which a new complex $Ru_3(CO)_8(C_{10}H_{12})$ (IV) is obtained. We now report the reaction of $HRu_3(CO)_9C_2Bu^t$ with the same alkyne; in n-heptane a considerable number of derivatives is obtained. The title complex (V), in which the opening of the triruthenium cluster occurs, has been isolated as major product.

Complex V is formed by an open, bent tri-metal atom arrangement coordinated by eight terminal CO's and by an organic ligand, derived from the condensation of two isopropenylacetylene molecules with one of t-butylacetylene, and interacting with the metals through a chain of seven carbon atoms. It is noteworthy the tail-to-tail and head-to-tail disposition of the two isopropenylacetylene with respect to the t-butylacetylene and the interaction of both these alkynes with the former $C(\sigma-\pi)$ of I. Hydrogen shift occurs in this reaction both from the cluster and from isopropenylacetylene to the C_2Bu^t group, which becomes $C-CH_2-CMe_3$.

Experimental

Reactions of $HRu_3(CO)_9C_2Bu^t$ *with Isopropenylacetylene*

$HRu_3(CO)_9C_2Bu^t$ (I) was obtained and purified as already described [1]; the alkyne was purchased from Fluka and used without further purification. Upon refluxing in n-heptane, under dry nitrogen, 650 mg (~1 m*M*) of I and 6 ml (~85 m*M*) of alkyne for 50 min, seven products, among which V in about 15% yield, were obtained. The reaction mixture was filtered, the solvent removed under vacuum, the residual dissolved in $CHCl_3$ and purified on t.l.c. preparative plates (Kieselgel P.F., eluant light petroleum containing 2% of ethyl ether). The yellow solid V was then dissolved in n-heptane containing 10% of $CHCl_3$ and allowed to crystallize at −20 °C for days. Complex V analyzes as follows: Found, C% 39.0, H% 2.9, O% 17.5, Ru% 40.5. Calc. for $C_{24}H_{22}O_8Ru_3$, C% 38.8, H% 2.8, O% 17.2, Ru% 41.2.

The elemental analysis was performed by means of an F & M 185 C,H,N Analyzer and a Perkin Elmer 303 Atomic Absorption Spectrophotometer. The i.r. spectra were obtained on a Beckman IR-12 instrument; the mass spectra were registered on a Hitachi-Perkin Elmer RMU 6H instrument operating at 70 eV and equipped with direct inlet system.

X-Ray Data Collection

A flattened yellow crystal of compound V with dimensions of *ca.* 0.18 × 0.32 × 0.38 mm was used for the X-ray data collection Unit cell parameters, preliminarly determined from rotation and Weissenberg photographs, were refined by a least-squares procedure applied to the 2θ θ values of accurately measured reflections on a Siemens AED single-crystal diffractometer. The crystal data are: a = 11.331(9), b = 14.173(11), c = 9.022(8) Å, α = 80.79(7), β = 104.47(8), γ = 105.48(8)°, V = 1345(2) $Å^3$, M = 741.64, Z = 2, D_c = 1.83 g cm^{-3}, MoKα radiation ($\bar{\lambda}$ = 0.71069 Å), μ(MoKα) = 16.74 cm^{-1}, space group $P\bar{1}$ from structure determination.

A total of 6487 independent reflections with $3 < \theta < 28°$ were measured on the same Siemens diffractometer using the Zr-filtered MoKα radiation and the ω–2θ scan technique. 5192 of these having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis. The intensity data were corrected for Lorentz and polarization factors, but no correction for absorption was applied because of the low value of μR. The absolute scale was obtained first by Wilson's method, then as a least-squares parameter.

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 with first isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms. An inspection of the bond distances in the molecule reveals that in the isopropenyl substituent the two C–C distances are equal and the values of 1.425 and 1.411 Å [for C(17)–C(18) and C(17)–C(19) respectively] are intermediate between those of the single and double bond. This result can be explained with the isopropenyl group being disordered and distributed in two positions of equivalent occupancy. A difference-Fourier map revealed clearly the positions of all the hydrogen atoms except, of

TABLE I. Fractional Atomic Coordinates (×10^4 for Ru, O, C Atoms, ×10^3 for H Atoms) with e.s.d.'s.

	x/a	*y/b*	*z/c*
Ru(1)	3157(1)	4414(1)	2055(1)
Ru(2)	1326(1)	2754(1)	1350(1)
Ru(3)	−516(1)	2096(1)	3156(1)
O(1)	5866(4)	4954(4)	3613(6)
O(2)	3367(5)	5766(4)	−917(6)
O(3)	2276(4)	5859(3)	3527(6)
O(4)	58(4)	4167(3)	−909(5)
O(5)	−70(5)	1243(4)	−907(6)
O(6)	−15(4)	78(3)	3231(5)
O(7)	−2034(5)	1362(4)	5636(6)
O(8)	−2577(4)	1833(4)	256(6)
C(1)	4824(5)	4779(4)	3034(6)
C(2)	3307(5)	5274(4)	198(7)
C(3)	2583(5)	5334(3)	2956(6)
C(4)	566(5)	3649(4)	−18(6)
C(5)	458(5)	1799(4)	−55(6)
C(6)	−150(5)	846(4)	3244(6)
C(7)	−1481(5)	1635(4)	4697(7)
C(8)	−1827(5)	1905(4)	1366(8)
C(9)	3328(4)	3255(3)	1121(5)
C(10)	3255(4)	2327(3)	2014(5)
C(11)	2808(4)	2263(3)	3363(5)
C(12)	2486(4)	3184(3)	3511(5)
C(13)	1268(4)	3087(3)	3645(5)
C(14)	479(5)	3525(3)	4145(6)
C(15)	−630(5)	3647(4)	3083(7)
C(16)	721(7)	3702(5)	5810(7)
C(17)	3623(5)	1494(3)	1531(6)
C(18)	4878(6)	1694(5)	1334(8)
C(19)	2771(6)	574(4)	1302(8)
C(20)	2774(5)	1439(3)	4650(6)
C(21)	3902(5)	1614(4)	6020(6)
C(22)	3919(11)	2466(6)	6838(9)
C(23)	5109(7)	1791(9)	5537(11)
C(24)	3782(9)	695(6)	7153(9)
H(9)	357(5)	329(4)	26(6)
H(151)	−131(5)	378(4)	345(6)
H(152)	−58(5)	387(4)	210(6)
H(161)	−5(5)	366(4)	611(6)
H(162)	117(5)	330(4)	653(6)
H(163)	114(5)	424(4)	596(6)
H(201)	201(5)	136(4)	503(6)
H(202)	280(5)	86(4)	430(6)
H(221)	310(5)	218(4)	723(6)
H(222)	393(5)	302(4)	624(6)
H(223)	466(5)	254(4)	771(6)
H(231)	583(5)	192(4)	633(6)
H(232)	524(5)	223(4)	494(7)
H(233)	512(5)	112(4)	498(6)
H(241)	451(5)	77(4)	797(6)
H(242)	388(5)	28(4)	670(6)
H(243)	297(5)	67(4)	745(6)

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: $\exp[-2\pi^2(h^2a^{*2}U_{11} + 2hka^*b^*U_{12})]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	396(2)	257(2)	433(2)	−36(1)	80(2)	18(1)
Ru(2)	347(2)	267(2)	325(2)	−41(1)	77(1)	45(1)
Ru(3)	377(2)	328(2)	513(2)	1(2)	178(2)	77(1)
O(1)	508(24)	897(33)	984(35)	−350(27)	−22(23)	81(22)
O(2)	1076(37)	797(31)	828(33)	378(26)	364(29)	161(27)
O(3)	814(30)	599(25)	1014(36)	−336(24)	73(26)	279(22)
O(4)	939(31)	625(25)	537(24)	59(20)	−12(22)	343(23)
O(5)	1031(36)	831(32)	968(36)	−601(28)	−14(28)	−32(27)
O(6)	800(28)	361(19)	879(30)	−56(19)	282(23)	140(18)
O(7)	977(36)	937(36)	1011(36)	193(28)	675(31)	247(29)
O(8)	588(28)	1280(45)	879(35)	−246(32)	−21(26)	198(28)
C(1)	487(29)	433(27)	609(33)	−128(24)	84(25)	42(22)
C(2)	556(30)	393(26)	678(36)	35(25)	161(27)	42(22)
C(3)	511(30)	351(23)	617(33)	−79(22)	48(25)	77(21)
C(4)	544(29)	412(25)	404(26)	−51(20)	55(22)	119(22)
C(5)	587(31)	451(28)	573(32)	−173(24)	98(25)	35(23)
C(6)	449(26)	404(25)	573(31)	−23(22)	208(23)	44(20)
C(7)	570(33)	483(29)	783(40)	22(27)	324(31)	138(25)
C(8)	381(27)	616(34)	785(41)	−61(29)	144(28)	63(24)
C(9)	422(23)	360(21)	384(24)	−44(18)	129(19)	53(18)
C(10)	382(22)	319(20)	393(23)	−58(17)	112(18)	50(17)
C(11)	356(21)	289(19)	400(23)	−47(17)	84(18)	59(16)
C(12)	401(22)	307(19)	296(20)	−41(15)	55(17)	90(16)
C(13)	447(24)	298(20)	360(22)	−19(16)	112(18)	95(17)
C(14)	567(29)	308(21)	489(28)	−48(19)	215(23)	119(20)
C(15)	552(29)	418(25)	696(38)	−9(25)	233(27)	217(22)
C(16)	783(45)	641(40)	574(34)	−163(30)	243(32)	233(36)
C(17)	545(29)	386(24)	517(28)	−47(20)	197(23)	164(21)
C(18)	666(37)	649(36)	825(43)	−35(31)	340(33)	273(30)
C(19)	837(43)	435(30)	905(47)	−178(30)	324(37)	109(28)
C(20)	484(27)	316(22)	431(25)	27(19)	93(21)	129(19)
C(21)	589(32)	482(28)	433(27)	20(22)	14(23)	168(24)
C(22)	1558(89)	679(48)	625(44)	−191(37)	−313(51)	405(54)
C(23)	576(42)	1643(96)	919(64)	102(65)	−105(42)	201(51)
C(24)	1116(70)	662(43)	626(44)	110(35)	−82(45)	309(44)
H(9)	49(14)					
H(151)	56(14)					
H(152)	63(15)					
H(161)	76(15)					
H(162)	81(16)					
H(163)	87(17)					
H(201)	40(15)					
H(202)	50(15)					
H(221)	85(17)					
H(222)	87(15)					
H(223)	108(14)					
H(231)	98(14)					
H(232)	86(17)					
H(233)	112(15)					
H(241)	75(15)					
H(242)	80(18)					
H(243)	84(16)					

course, those belonging to the disordered isopropenyl group. Further least-squares cycles were then computed including the found hydrogen atoms. Unit weights were used in each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to $|F_o|$. The final R was 0.028 (observed

TABLE III. Bond Distances (A) and Angles (°) (not Involving Hydrogen Atoms) with e.s.d.'s.

i) *In the Coordination Sphere of the Ruthenium Atoms*

Ru(1)–Ru(2)	2.731(2)	Ru(2)–C(10)	2.332(5)
Ru(1)–C(1)	1.846(6)	Ru(2)–C(11)	2.302(5)
Ru(1)–C(2)	1.923(6)	Ru(2)–C(12)	2.138(5)
Ru(1)–C(3)	1.960(5)	Ru(2)–C(13)	2.216(5)
Ru(1)–C(9)	2.035(5)	Ru(3)–C(6)	1.910(6)
Ru(1)–C(12)	2.098(5)	Ru(3)–C(7)	1.909(6)
Ru(2)–Ru(3)	2.838(2)	Ru(3)–C(8)	1.901(7)
Ru(2)–C(4)	1.851(6)	Ru(3)–C(13)	2.119(5)
Ru(2)–C(5)	1.903(6)	Ru(3)–C(14)	2.242(5)
Ru(2)–C(9)	2.241(5)	Ru(3)–C(15)	2.226(6)
Ru(2)–Ru(1)–C(1)	139.8(2)	C(9)–Ru(2)–C(10)	36.2(2)
Ru(2)–Ru(1)–C(2)	109.0(2)	C(9)–Ru(2)–C(11)	63.1(2)
Ru(2)–Ru(1)–C(3)	112.4(2)	C(9)–Ru(2)–C(12)	71.0(2)
Ru(2)–Ru(1)–C(9)	53.7(1)	C(9)–Ru(2)–C(13)	107.3(2)
Ru(2)–Ru(1)–C(12)	50.5(1)	C(9)–Ru(2)–Ru(1)	47.1(1)
C(1)–Ru(1)–C(2)	96.1(3)	C(10)–Ru(2)–C(11)	35.5(2)
C(1)–Ru(1)–C(3)	96.2(3)	C(10)–Ru(2)–C(12)	64.6(2)
C(1)–Ru(1)–C(9)	95.7(2)	C(10)–Ru(2)–C(13)	98.4(2)
C(1)–Ru(1)–C(12)	101.7(2)	C(10)–Ru(2)–Ru(1)	72.1(1)
C(2)–Ru(1)–C(3)	93.5(2)	C(11)–Ru(2)–C(12)	38.7(2)
C(2)–Ru(1)–C(9)	92.2(2)	C(11)–Ru(2)–C(13)	64.9(2)
C(2)–Ru(1)–C(12)	159.5(2)	C(11)–Ru(2)–Ru(1)	74.0(1)
C(3)–Ru(1)–C(9)	166.1(2)	C(12)–Ru(2)–C(13)	37.0(2)
C(3)–Ru(1)–C(12)	94.7(2)	C(12)–Ru(2)–Ru(1)	49.2(1)
C(9)–Ru(1)–C(12)	76.0(2)	C(13)–Ru(2)–Ru(1)	72.3(1)
Ru(3)–Ru(2)–C(4)	97.5(2)	C(6)–Ru(3)–C(7)	92.4(3)
Ru(3)–Ru(2)–C(5)	91.8(2)	C(6)–Ru(3)–C(8)	94.5(3)
Ru(3)–Ru(2)–C(9)	151.5(1)	C(6)–Ru(3)–C(13)	104.4(2)
Ru(3)–Ru(2)–C(10)	123.4(1)	C(6)–Ru(3)–C(14)	136.1(2)
Ru(3)–Ru(2)–C(11)	90.5(1)	C(6)–Ru(3)–C(15)	171.3(2)
Ru(3)–Ru(2)–C(12)	81.7(1)	C(6)–Ru(3)–Ru(2)	84.0(2)
Ru(3)–Ru(2)–C(13)	47.6(1)	C(7)–Ru(3)–C(8)	99.5(3)
Ru(3)–Ru(2)–Ru(1)	118.1(1)	C(7)–Ru(3)–C(13)	120.7(2)
C(4)–Ru(2)–C(5)	87.6(3)	C(7)–Ru(3)–C(14)	94.3(2)
C(4)–Ru(2)–C(9)	103.0(2)	C(7)–Ru(3)–C(15)	93.3(2)
C(4)–Ru(2)–C(10)	138.3(2)	C(7)–Ru(3)–Ru(2)	168.8(2)
C(4)–Ru(2)–C(11)	155.8(2)	C(8)–Ru(3)–C(13)	134.0(2)
C(4)–Ru(2)–C(12)	119.9(2)	C(8)–Ru(3)–C(14)	126.8(2)
C(4)–Ru(2)–C(13)	104.4(2)	C(8)–Ru(3)–C(15)	91.0(2)
C(4)–Ru(2)–Ru(1)	82.1(2)	C(8)–Ru(3)–Ru(2)	91.4(2)
C(5)–Ru(2)–C(9)	108.5(2)	C(13)–Ru(3)–C(14)	37.5(2)
C(5)–Ru(2)–C(10)	98.1(2)	C(13)–Ru(3)–C(15)	66.9(2)
C(5)–Ru(2)–C(11)	115.2(2)	C(13)–Ru(3)–Ru(2)	50.6(1)
C(5)–Ru(2)–C(12)	152.4(2)	C(14)–Ru(3)–C(15)	36.8(2)
C(5)–Ru(2)–C(13)	138.4(2)	C(14)–Ru(3)–Ru(2)	81.2(2)
C(5)–Ru(2)–Ru(1)	149.2(2)	C(15)–Ru(3)–Ru(2)	89.2(2)

ii) *In the Carbonyl Groups*

O(1)–C(1)	1.143(7)	O(5)–C(5)	1.132(8)
O(2)–C(2)	1.135(8)	O(6)–C(6)	1.141(7)
O(3)–C(3)	1.136(7)	O(7)–C(7)	1.136(8)
O(4)–C(4)	1.150(7)	O(8)–C(8)	1.139(8)
Ru(1)–C(1)–O(1)	175.8(6)	Ru(2)–C(5)–O(5)	178.7(5)
Ru(1)–C(2)–O(2)	178.2(6)	Ru(3)–C(6)–O(6)	175.1(5)

(continued on facing page)

TABLE III. *(continued)*

Ru(1)–C(3)–O(3)	177.6(5)	Ru(3)–C(7)–O(7)	178.6(6)
Ru(2)–C(4)–O(4)	176.6(5)	Ru(3)–C(8)–O(8)	176.4(6)
iii) *In the Organic Ligands*			
C(9)–C(10)	1.422(6)	C(21)–C(22)	1.506(11)
C(10)–C(11)	1.412(6)	C(21)–C(23)	1.484(10)
C(10)–C(17)	1.509(7)	C(21)–C(24)	1.519(10)
C(17)–C(18)	1.425(9)	C(12)–C(13)	1.384(6)
C(17)–C(19)	1.411(8)	C(13)–C(14)	1.406(7)
C(11)–C(12)	1.480(6)	C(14)–C(15)	1.410(8)
C(11)–C(20)	1.509(7)	C(14)–C(16)	1.508(8)
C(20)–C(21)	1.537(8)		
C(10)–C(9)–Ru(1)	119.1(3)	C(14)–C(13)–Ru(3)	76.0(3)
C(10)–C(9)–Ru(2)	75.4(3)	C(14)–C(13)–C(12)	144.5(5)
C(11)–C(10)–C(17)	123.9(4)	Ru(2)–C(13)–Ru(3)	81.8(2)
C(11)–C(10)–Ru(1)	78.5(3)	Ru(2)–C(13)–C(12)	68.4(3)
C(11)–C(10)–Ru(2)	71.1(3)	Ru(3)–C(13)–C(12)	139.5(3)
C(11)–C(10)–C(9)	114.1(4)	C(15)–C(14)–C(16)	122.1(5)
C(17)–C(10)–C(9)	121.9(4)	C(15)–C(14)–Ru(3)	71.0(3)
Ru(2)–C(10)–C(9)	68.4(3)	C(15)–C(14)–C(13)	116.8(5)
C(12)–C(11)–C(20)	120.4(4)	C(16)–C(14)–C(13)	120.5(5)
C(12)–C(11)–Ru(2)	64.7(2)	Ru(3)–C(14)–C(13)	66.5(3)
C(12)–C(11)–C(10)	111.8(4)	C(18)–C(17)–C(19)	122.5(5)
C(20)–C(11)–C(10)	127.4(4)	C(18)–C(17)–C(10)	115.9(5)
Ru(2)–C(11)–C(10)	73.4(3)	C(19)–C(17)–C(10)	121.6(5)
C(13)–C(12)–Ru(1)	114.2(3)	C(21)–C(20)–C(11)	114.3(4)
C(13)–C(12)–Ru(2)	74.6(3)	C(22)–C(21)–C(23)	109.3(8)
C(13)–C(12)–C(11)	115.7(4)	C(22)–C(21)–C(24)	108.0(6)
Ru(1)–C(12)–Ru(2)	80.3(2)	C(22)–C(21)–C(20)	111.5(6)
Ru(1)–C(12)–C(11)	115.7(3)	C(23)–C(21)–C(24)	108.2(7)
Ru(2)–C(12)–C(11)	76.6(3)	C(23)–C(21)–C(20)	111.7(5)
C(14)–C(13)–Ru(2)	132.9(4)	C(24)–C(21)–C(20)	107.9(5)

reflections only). The atomic scattering factors used (corrected for the anomalous dispersion of ruthenium) were taken from the International Tables [12]. 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 Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with financial support from the University of Parma.

Discussion of the Results

I.r. and Mass Spectra

In the i.r. spectrum the following absorptions in the CO stretching region were observed (n-heptane solution): 2055 vs, 2005 vs, 2001 vs(sh), 1984 s, 1956 m–w, cm^{-1}. In the mass spectrum instead of the parent ion at 744 m/e expected for V, a peak at 634 m/e is observed, corresponding to $Ru_3(CO)_7(C_5H_6)_2$; thus in the mass spectrometer decomposition of V occurs with loss of t-butylacetylene and one CO group. The complex with m/e 634 undergoes loss of nine fragments having 28 m/e, probably the seven remaining CO's and two ethylene units.

X-Ray Structure of Complex V

The structure of complex V is represented in Fig. 1. Bond distances and angles not involving hydrogen atoms are given in Table III.

The complex consists of an open, bent arrangement of three ruthenium atoms, coordinated by eight carbonyls and, through σ- and η-bonds, to an organic ligand derived from the condensation of two isopropenylacetylene molecules with one of t-butylacetylene.

The three metal atoms are non-linearly disposed, the angle Ru(1)–Ru(2)–Ru(3) being of 118.1°. The two metal–metal bonds are considerably different in length, as Ru(1)–Ru(2) is 2.731 and Ru(2)–Ru(3) 2.838 Å; these values are among those currently

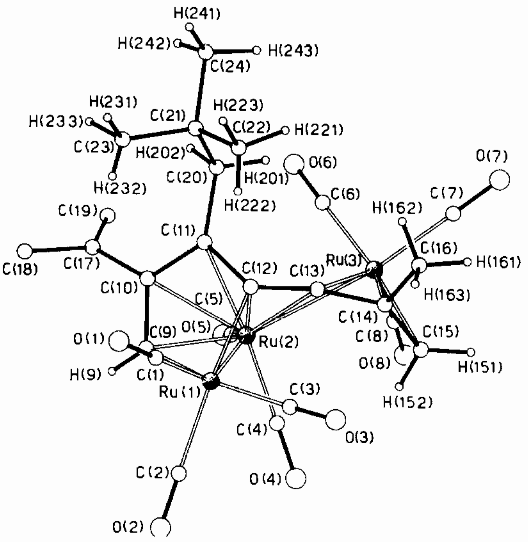

Fig. 1. View of the molecular shape with the atomic numbering system.

found in the closed triruthenium clusters, which range from 2.686 [6] to 2.994 Å [13]. The Ru–Ru bond distances in dinuclear complexes are generally longer (the following values were reported: 2.937[14], 2.862[15], 2.865[16], 2.891[17], 2.889[18], 3.05 Å [19]) even when the dinuclear derivatives are highly substituted.

To our knowledge complex V is the first example of a ruthenium open trinuclear complex, substituted with alkynes. In fact for $Ru_3(CO)_8(C_2Ph_2)_2$ [20] a structure similar to the one of $Fe_3(CO)_8(C_2Ph_2)_2$ [21] was proposed only. In this last complex two alkynes are dimerized to form a metallacyclopentadienic ring with opening of the trinuclear cluster, as is currently obtained from $Fe_3(CO)_{12}$. The Fe–Fe–Fe angle (87.6°) is narrower than in the present ruthenium compound. Also when treating $Os_3(CO)_{12}$ with halogens [22] the linear $Os_3(CO)_{12}L_2$ (L = halogen) is obtained. Some other iron derivatives containing a non close arrangement of atoms were described [23]. Other "open" arrangements of metal atoms can be usually obtained from species of lesser nuclearity [24–26].

The eight carbonyl groups of the complex are disposed two on the central metal Ru(2) and three on the external ones Ru(1) and Ru(3). All these carbonyls are terminal as shown by the angles Ru–C–O (in the range 175.1–178.7°).

The organic ligand, formed by three molecules of alkyne (two isopropenylacetylene and one t-butylacetylene) with hydrogen shift, is a 2-methyl-5-neopentyl-6-isopropenyl substituted heptaatomic chain. The seven adjacent carbon atoms C(9), ...C(14) are involved in a very complex bonding with all the metal atoms. The C–C bond distances in the chain show that the multiple bonds are delocalized on all the bonds excepting C(11)–C(12) which presents mainly character of single bond (1.480 against 1.384, 1.406, 1.410, 1.412 and 1.422 Å of the other ones). To fulfil the E.A.N. rule, this organic ligand must be considered a ten electron donor towards the metal atoms.

The bonding of the organic ligand with the metals can be described as follows: two σ-bonds involve C(9) and C(12) with Ru(I) and correspond to the shortest distances [Ru(1)–C(9) = 2.035 and Ru(1)–C(12) = 2.098 Å]; the π-electron cloud over C(9)–C(11) interacts with Ru(2), the one over C(12)–C(13) with Ru(2) and the one over C(13)–C(15) with Ru(3), so two extensive η-bondings are realized between the organic moiety and the metals. C(12), C(13) and C(14) constitute a bent allenic group comparable with those found in II [6], in IV [10] and in $HRu_3(CO)_9(C_6H_9)$ [13]. In all these allenic groups the central carbon is η-coordinated to two different metals through two bonds shorter than the other involved in η-coordination and the bent angles range from 133.0 in IV to 151.8° in II.

The conformation of the organic ligand is indicated by the torsion angles:

C(9)C(10)C(11)C(12)	−1.4°
C(10)C(11)C(12)C(13)	−123.3
C(11)C(12)C(13)C(14)	−158.6
C(12)C(13)C(14)C(15)	−128.4
C(9)C(10)C(17)C(18)	−58.3
C(9)C(10)C(17)C(19)	122.1
C(10)C(11)C(17)C(18)	122.0
C(10)C(11)C(17)C(19)	−57.6

In the organic ligand of the present complex the two "former" isopropenylacetylene molecules are disposed the one with respect to the other and are bonded to the metals in a very similar way as found for IV [10]; however in the present complex a further carbon atom, belonging to the C_2Bu^t group, participates in the formation of the chain and the C–C bond distances show greater irregularities. Thus this organic moiety could be considered as derived from a double insertion of isopropenylacetylene molecules into the C(σ–π)–Ru bonds of the complex I with hydrogen shift from the cluster and from C(13) to C(20). One of the isopropenylacetylenes is disposed head-to-tail and the second tail-to-tail with respect to the former C_2Bu^t, probably in order to balance the electronic effects of the substituents. Also the cluster opening, probably required by the sterical bulk of the substituent, instead of the breaking of two Ru–Ru bonds to leave a dinuclear complex, could be due to the considerable stabilization of the cluster of complex I because of the presence of the C_2Bu^t substituent.

Hydrogen shift in the formation of the organic ligands as observed in IV [10] and in the present compound V is rather common in the chemistry of alkyne carbonyls of the iron triad; examples were observed in the formation of $Fe_3(CO)_8(HC_2Me)_4$ [28], $Fe_2Ni(C_5H_5)(CO)_7(CEt)$ [29], $(C_5H_5)Ru_3(CO)_8CCH_2Bu^t$ [29] and $Fe_3(CO)_8(HC_2Me)_3$ [30]; in this latter a trimerization of alkynes in which two molecules are disposed head-to-tail and the third tail-to-tail was found.

Trimerization of alkynes is not very common in these reactions; more commonly dimerization (with or without further reaction) is observed also in heavily substituted derivatives as II, $Fe(CO)_7(HC_2Et)_4$ [31] and $Os_3(CO)_7(C_2Ph_2)_3$ [32]. When trimerization occurs, generally cyclopentadienyl units are obtained as in $Fe_3(CO)_8(HC_2Me)_4$ [28]; only in $Fe_3(CO)_8(HC_2Me)_3$ [30] and in V is trimerization with formation of 'linear' substituent observed.

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