The Reactivity of $HRu_3(CO)_9C_2Bu^t$. Synthesis and Crystal Structure of $Ru_3(CO)_7\{(C_2Bu^t)[PhC_2(H)Ph](C_2Ph_2)\}$

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The title complex was obtained by treating $HRu_3(CO)_9C_2Bu^t$ with C_2Ph_2 or $(\eta\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$, and its structure was determined by X-ray methods. Crystals of the complex are monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions: $a = 17.230(11)$, $b = 22.753(13)$, $c = 9.229(8)$ Å, $\beta = 93.57(7)°$. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.055$ for 3041 observed reflections.

The complex consists of an isosceles triangle of ruthenium atoms, bound to seven terminal carbonyls. One diphenylacetylene ligand, on one side of this triangle, forms two σ and one π bonds with the metal atoms. On the opposite side an organic ligand, formed by oligomerization of C_2Ph_2 and the C_2Bu^t group from the starting compound with shift of the hydridic hydrogen on C_2Ph_2, interacts through σ and η bonds with all the metal atoms.

Important features in the formation of the title complex are the attack of C_2Ph_2 to the α-carbon atom of the acetylide in the starting complex and the hydridic hydrogen shift on the new organic chain. The role of the title complex in the reaction sequence of $HRu_3(CO)_9C_2Bu^t$ with alkynes is discussed.

Introduction

The reaction of terminal alkynes, HC_2R, with $Ru_3(CO)_{12}$ leads to $HRu_3(CO)_9C_2R$ hydridic derivatives; the complex with $R = Bu^t$ (complex I) is obtained in very good yields [1] and has been extensively studied by X-ray and neutron diffraction [2, 3] and by NMR spectroscopy.

The reactivity of the hydride towards dienes [5], isopropenylacetylene [6] and $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ [7] has also been reported. Protonation experiments [8], as well as reactions with hydrogen [9] and excess t-butylacetylene [10], were also performed.

In particular, when excess t-butylacetylene was employed, isomeric complexes $Ru_3(CO)_6[(C_{12}H_{20})(C_{13}H_{20}O)]$ (complexes II) were obtained [10] by alkyne condensation, hydridic hydrogen shift and alkyne–CO–alkyne interaction on the Ru_3 core. We were able to show, by using the deuterated I hydride, that a hydridic hydrogen shift occurs and that the isomerism is due to different ways of coupling the alkynes.

However, we could not obtain evidence for the order in which alkyne–alkyne or alkyne–CO–alkyne condensation occurs. Moreover, reaction of $Os_3(CO)_{12}$ with HC_2Ph led to the $Os_3(CO)_{10}(HC_2Ph)_2$ cluster (complex III) [11], whereas, in contrast, reaction of isopropenylacetylene with $Ru_3(CO)_{12}$ afforded the $Ru_3(CO)_8(C_{10}H_{12})$ cluster (complex IV) [12], with a chain (obtained by alkyne condensation) comparable with those of the complexes II. Finally in the reaction of I with dienes, the core of I was maintained unaltered [5] with the dienic unit η interacting with two metals and no hydrogen shift was observed.

We now report the reaction of I with diphenylacetylene and diphenylacetylenic–nickel derivatives. The main product is the title complex (V), which has been characterized by IR, ^1H NMR and mass spectrometry; its structure has been determined by X-ray diffraction methods.

Complex V shows two different organic substituents: on one side of the triangular cluster a C_2Ph_2 ligand is bonded in a $(2\sigma + \pi)$ fashion, whereas on the opposite side a carbon-atom chain, formed by oligomerization of C_2Bu^t and C_2Ph_2 with hydridic hydrogen shift, interacts through σ and η bonds with all the metals. This organic chain is comparable with the ones found in complexes II.

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Experimental

Preparation, Analysis and Crystallization of V

$Ru_3(CO)_{12}$ and I were obtained by literature methods, as was $(\eta\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$. 3,3-dimethylbut-1-yne (t-butylacetylene) was purchased from K & K, diphenylacetylene from Fluka. The title complex V was obtained by reacting I with C_2Ph_2 in a 1:5 molar ratio in refluxing heptane for 10 hours under nitrogen atmosphere; yields of 5–10% based on ruthenium were obtained. The same stoichiometric amounts of reactants, treated in refluxing heptane under a hydrogen flow for 6 hours, gave comparable yields of V.

Small yields of V (about 1% based on ruthenium) can also be obtained by treating equimolecular amounts of I and $(\eta\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$ in heptane, under nitrogen, for 75 min.

The reaction mixtures containing V were purified by t.l.c. preparative plates (Kieselgel P.F. Merck, eluants mixtures of light petroleum and ethyl ether). Complex V was analyzed by means of an F & M 185 C, H, N Analyzer and a Perkin Elmer 303 Atomic Absorption Spectrophotometer. The IR spectra were obtained on a Beckman IR-12 and the ^1H NMR spectra on a JEOL C-60 HL instrument. The mass spectra were registered on a Varian CH-5 signle-focusing instrument.

Complex V analyzes as: found C% 53.01, H% 3.27, O% 11.72, Ru% 32.00. Calcd. for $C_{41}H_{30}O_7Ru_3$: C% 52.50, H% 3.22, O% 11.94, Ru% 32.33.

Complex V is slightly soluble in heptane and very soluble in $CHCl_3$; thus 1:1 mixtures of these solvents were used. Upon prolonged storage at 0 °C a crystalline powder, unsuitable for X-ray analysis, was obtained. Crystals for the X-ray analysis were obtained by slowly evaporating (3 days at 0 °C) a $CHCl_3$-heptane-cyclohexane (50%, 30%, 20% in volume) solution of V; flat, brown platelets of V were collected.

X-Ray Data Collection

An irregularly shaped crystal of the complex V, having dimensions of approximately 0.12 X 0.15 X 0.22 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 19 θ values of accurately measured reflections on a Siemens AED single-crystal diffractometer. The crystal data are as follows: $C_{41}H_{30}O_7Ru_3$, $a = 17.230(11)$, $b = 22.753(13)$, $c = 9.229(8)$ Å, $\beta = 93.57(7)°$, $V = 3611(4)$ Å^3, $M = 937.89$, $Z = 4$, $D_c = 1.725$ g cm^{-3}, MoKα radiation ($\lambda = 0.710688$ Å), μ(MoKα) = 12.64 cm^{-1}, space group $P2_1/n$ from systematic absences.

A total of 5669 independent reflections with θ in the range 3–24° were measured on the same Siemens diffractometer using the Nb-filtered MoKα radiation and the $\theta/2\theta$ scan technique. Of these, 3041 having $I \geq 2\sigma(I)$ were considered observed, and were used in the analysis. The intensity data were corrected for Lorentz and polarization factors, while the absorption effects were disregarded in view of the low absorbance of the sample. Data were placed on an absolute scale first by the Wilson's method, and then as a least-squares parameter.

Structure Determination and Refinement

The structure was solved by a combination of direct methods and the heavy-atom technique. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [13] with first isotropic and then anisotropic thermal parameters for all non-hydrogen atoms. A difference Fourier map did not reveal clearly the positions of all the hydrogen atoms, so they were placed in their geometrically calculated positions (excepting for H(10), located in the difference Fourier map) and included in the final structure factor calculations. 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 value was 0.055 (observed reflections only). The atomic scattering factors used (corrected for the anomalous dispersion of Ru) were taken from International Tables [14]. The atomic fractional coordinates for the non-hydrogen and hydrogen atoms are listed in Tables I and II respectively, the thermal parameters and the list of observed and calculated structure factors are 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, Bologna, with financial support from the University of Parma.

Results and Discussion

Spectra

In heptane solution the IR spectrum of V shows the following absorption in the CO stretching region. 2069 vs, 2039 vs, 2016 s(sh), 2002 vs, 1994 vs(sh), 1984 m(sh), 1932 vs, cm^{-1}. The strong band at 1932 cm^{-1} is in the region reported for asymmetrical bridging CO ligands [15]. However, in the solid state structure no asymmetrical carbonyls were found.

In CCl_4 solution, the ^1H NMR spectrum shows signals at 2.85 m, 4.70 m (20 H), 5.70 s (1 H) and 8.40 s (9 H) τ.

In the mass spectrum, complex V shows the parent ion at 940 m/e, then the loss of a 110 m/e fragment (tentativcly considered to be t-butyl-alkyne plus CO), followed by loss of diphenylacetylene; finally, loss of six CO's is observed. Other intense fragments are found at 384 m/e (two diphenylacetylenes plus CO),

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) with e.s.d.'s in Parentheses for the Non-Hydrogen Atoms.

	x/a	y/b	z/c
Ru1	3159(1)	1692(1)	−1191(1)
Ru2	2430(1)	2188(1)	1198(1)
Ru3	3635(1)	1355(1)	1504(1)
O1	3891(9)	694(6)	−2896(15)
O2	3527(9)	2619(6)	−3396(14)
O3	1482(9)	1612(7)	−2429(16)
O4	717(8)	2432(6)	496(15)
O5	2246(7)	2413(6)	4343(13)
O6	4179(9)	1540(6)	4596(15)
O7	4811(8)	382(6)	1410(15)
C1	3608(11)	1055(8)	−2305(18)
C2	3400(10)	2265(8)	−2595(20)
C3	2116(13)	1657(9)	−1954(20)
C4	1347(11)	2314(7)	744(18)
C5	2295(9)	2337(6)	3118(18)
C6	3983(11)	1460(7)	3412(20)
C7	4355(10)	744(7)	1427(18)
C8	2354(9)	1291(7)	1531(17)
C9	2645(9)	1007(7)	370(17)
C10	2564(8)	3077(5)	16(16)
C11	3272(8)	2905(6)	754(14)
C12	3546(8)	2321(6)	416(14)
C13	4185(9)	1967(6)	324(15)
C14	5038(9)	2111(6)	68(19)
C15	5354(11)	1655(7)	−943(22)
C16	5503(10)	2113(10)	1559(20)
C17	5096(10)	2715(8)	−641(21)
C18	3721(8)	3305(6)	1848(17)
C19	3987(9)	3079(7)	3184(18)
C20	4405(9)	3456(7)	4128(19)
C21	4560(10)	4030(8)	3710(21)
C22	4303(11)	4223(7)	2374(20)
C23	3864(9)	3878(7)	1387(18)
C24	2080(8)	3587(7)	353(16)
C25	2005(10)	3821(7)	1739(16)
C26	1514(10)	4289(8)	1896(21)
C27	1092(12)	4533(8)	762(26)
C28	1150(12)	4300(8)	−595(23)
C29	1647(10)	3829(7)	−804(18)
C30	1867(10)	1004(6)	2657(18)
C31	1084(11)	1083(8)	2596(20)
C32	659(12)	846(9)	3731(26)
C33	1030(15)	538(9)	4824(23)
C34	1830(15)	409(10)	4834(23)
C35	2236(12)	670(8)	3738(22)
C36	2412(11)	419(7)	−254(16)
C37	1606(12)	332(8)	−685(21)
C38	1384(14)	−213(11)	−1262(22)
C39	1932(17)	−655(10)	−1419(26)
C40	2715(15)	−571(10)	−958(22)
C41	2967(12)	−35(7)	−394(20)

TABLE II. Calculated Fractional Coordinates ($\times 10^4$) for the Hydrogen Atoms. The Coordinates of the Hydrogen H(10) Have Been Found in a Difference Fourier Map.

	x/a	y/b	z/c
H10	2357	2806	−888
H151	5318	1225	−459
H152	5954	1754	−1121
H153	5015	1662	−1968
H161	6105	2213	1407
H162	5463	1686	2059
H163	5265	2441	2251
H171	4874	3046	63
H172	4759	2717	−1667
H173	5697	2809	−820
H19	3874	2629	3479
H20	4610	3303	5191
H21	4884	4321	4448
H22	4446	4666	2063
H23	3649	4041	339
H25	2328	3636	2671
H26	1462	4470	2967
H27	717	4904	926
H28	809	4482	−1508
H29	1694	3652	−1881
H31	792	1320	1707
H32	38	912	3723
H33	703	387	5713
H34	2113	125	5642
H35	2857	608	3738
H37	1185	678	−566
H38	781	−294	−1591
H39	1751	−1069	−1903
H40	3125	−927	−1043
H41	3573	36	−68

356 m/e (two diphenylacetylenes), 260 m/e (t-butylalkyne plus diphenylalkyne) and 178 m/e (diphenylacetylene). This indicates cluster and organic moiety demolition and rearrangement processes, involving CO in the gas phase.

Structure of the Complex V

The structure of the complex V 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 [Ru(1)–Ru(2) = 2.839(5), Ru(2)–Ru(3) = 2.812(3) and Ru(1)–Ru(3) = 2.682(7) Å], coordinated by seven terminal carbonyls [Ru(1) by three, Ru(2) and Ru(3) by two carbonyls] and σ- and η-bonded to a diphenylacetylene molecule and to an organic ligand, formed by oligomerization of one diphenylacetylene molecule and the C_2Bu^t group from the starting complex with shift of the hydridic hydrogen on C_2Ph_2. These two ligands are on opposite sides with respect to the metal triangle.

The diphenylacetylene ligand interacts with all the three metal atoms; it is, in an asymmetric way, σ-bonded to the Ru(1) and Ru(2) atoms [Ru(1)–C(9) = 2.33(2) and Ru(2)–C(8) = 2.07(2) Å] and

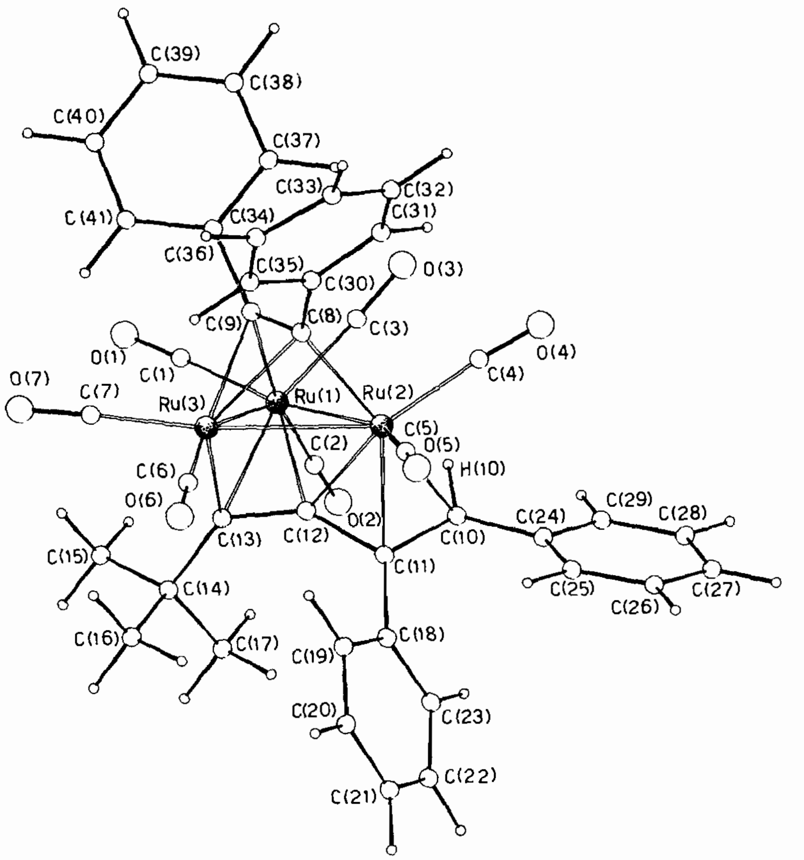


Fig. 1. View of the molecular shape of the complex $Ru_3(CO)_7\{(C_2Bu^t)[PhC_2(H)Ph](C_2Ph_2)\}$ with the atomic numbering system.

TABLE III. 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)	2.839(5)	Ru(2)–C(5)	1.83(2)
Ru(1)–Ru(3)	2.682(7)	Ru(2)–C(8)	2.07(2)
Ru(2)–Ru(3)	2.812(3)	Ru(2)–C(10)	2.32(1)
Ru(1)–C(1)	1.96(2)	Ru(2)–C(11)	2.24(1)
Ru(1)–C(2)	1.90(2)	Ru(2)–C(12)	2.12(1)
Ru(1)–C(3)	1.89(2)	Ru(3)–C(6)	1.84(2)
Ru(1)–C(9)	2.33(2)	Ru(3)–C(7)	1.87(2)
Ru(1)–C(12)	2.14(1)	Ru(3)–C(8)	2.21(2)
Ru(1)–C(13)	2.27(2)	Ru(3)–C(9)	2.10(2)
Ru(2)–C(4)	1.91(2)	Ru(3)–C(13)	2.04(1)
Ru(2)–Ru(1)–Ru(3)	61.2(1)	Ru(3)–Ru(2)–C(10)	122.8(4)
Ru(3)–Ru(2)–Ru(1)	56.7(1)	Ru(3)–Ru(2)–C(11)	91.5(4)
Ru(1)–Ru(3)–Ru(2)	62.2(1)	Ru(3)–Ru(2)–C(12)	56.6(4)
Ru(2)–Ru(1)–C(1)	155.2(5)	C(4)–Ru(2)–C(5)	90.2(7)
Ru(2)–Ru(1)–C(2)	112.5(6)	C(4)–Ru(2)–C(8)	96.4(7)
Ru(2)–Ru(1)–C(3)	81.4(6)	C(4)–Ru(2)–C(10)	83.7(6)
Ru(2)–Ru(1)–C(9)	65.3(4)	C(4)–Ru(2)–C(11)	119.1(6)
Ru(2)–Ru(1)–C(12)	47.9(4)	C(4)–Ru(2)–C(12)	143.1(6)
Ru(2)–Ru(1)–C(13)	77.2(4)	C(5)–Ru(2)–C(8)	91.5(6)
Ru(3)–Ru(1)–C(1)	99.6(5)	C(5)–Ru(2)–C(10)	108.4(6)
Ru(3)–Ru(1)–C(2)	139.5(6)	C(5)–Ru(2)–C(11)	99.5(6)
Ru(3)–Ru(1)–C(3)	124.2(6)	C(5)–Ru(2)–C(12)	118.4(6)
Ru(3)–Ru(1)–C(9)	48.9(4)	C(8)–Ru(2)–C(10)	160.1(6)

(continued on facing page)

TABLE III. *(continued)*

Ru(3)–Ru(1)–C(12)	58.9(4)	C(8)–Ru(2)–C(11)	142.6(6)
Ru(3)–Ru(1)–C(13)	47.7(4)	C(8)–Ru(2)–C(12)	105.0(6)
C(1)–Ru(1)–C(2)	92.3(8)	C(10)–Ru(2)–C(11)	36.1(5)
C(1)–Ru(1)–C(3)	99.8(8)	C(10)–Ru(2)–C(12)	66.1(5)
C(1)–Ru(1)–C(9)	90.4(7)	C(11)–Ru(2)–C(12)	38.8(5)
C(1)–Ru(1)–C(12)	137.9(7)	Ru(1)–Ru(3)–C(6)	155.9(5)
C(1)–Ru(1)–C(13)	102.0(7)	Ru(1)–Ru(3)–C(7)	110.1(5)
C(2)–Ru(1)–C(3)	91.0(8)	Ru(1)–Ru(3)–C(8)	77.4(4)
C(2)–Ru(1)–C(9)	170.2(7)	Ru(1)–Ru(3)–C(9)	56.9(4)
C(2)–Ru(1)–C(12)	86.7(7)	Ru(1)–Ru(3)–C(13)	55.6(4)
C(2)–Ru(1)–C(13)	92.1(6)	Ru(2)–Ru(3)–C(6)	101.7(6)
C(3)–Ru(1)–C(9)	79.2(7)	Ru(2)–Ru(3)–C(7)	170.3(5)
C(3)–Ru(1)–C(12)	122.3(7)	Ru(2)–Ru(3)–C(8)	46.8(4)
C(3)–Ru(1)–C(13)	157.8(7)	Ru(2)–Ru(3)–C(9)	68.4(4)
C(9)–Ru(1)–C(12)	97.6(5)	Ru(2)–Ru(3)–C(13)	81.4(4)
C(9)–Ru(1)–C(13)	96.6(5)	C(6)–Ru(3)–C(7)	87.4(8)
C(12)–Ru(1)–C(13)	36.1(5)	C(6)–Ru(3)–C(8)	105.3(7)
Ru(1)–Ru(2)–C(4)	111.3(5)	C(6)–Ru(3)–C(9)	137.1(7)
Ru(1)–Ru(2)–C(5)	156.0(5)	C(6)–Ru(3)–C(13)	106.7(7)
Ru(1)–Ru(2)–C(8)	76.0(4)	C(7)–Ru(3)–C(8)	128.1(7)
Ru(1)–Ru(2)–C(10)	85.4(4)	C(7)–Ru(3)–C(9)	102.8(7)
Ru(1)–Ru(2)–C(11)	79.9(3)	C(7)–Ru(3)–C(13)	99.0(7)
Ru(1)–Ru(2)–C(12)	48.5(4)	C(8)–Ru(3)–C(9)	37.0(6)
Ru(3)–Ru(2)–C(4)	146.0(5)	C(8)–Ru(3)–C(13)	123.2(6)
Ru(3)–Ru(2)–C(5)	99.5(5)	C(9)–Ru(3)–C(13)	112.4(6)

ii) In the carbonyl groups

O(1)–C(1)	1.11(2)	O(5)–C(5)	1.15(2)
O(2)–C(2)	1.12(2)	O(6)–C(6)	1.14(2)
O(3)–C(3)	1.16(3)	O(7)–C(7)	1.14(2)
O(4)–C(4)	1.13(2)		
Ru(1)–C(1)–O(1)	177(2)	Ru(2)–C(5)–O(5)	176(1)
Ru(1)–C(2)–O(2)	177(2)	Ru(3)–C(6)–O(6)	178(2)
Ru(1)–C(3)–O(3)	177(2)	Ru(3)–C(7)–O(7)	178(2)
Ru(2)–C(4)–O(4)	175(1)		

iii) In the organic ligands

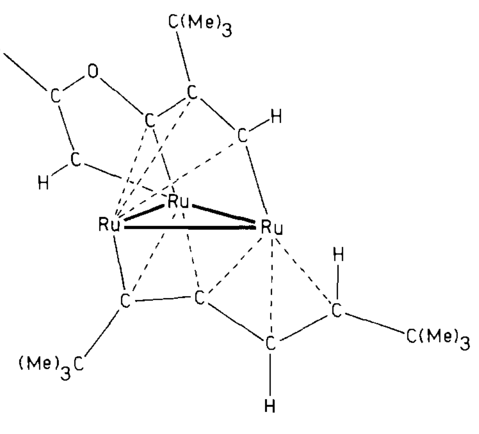
C(8)–C(9)	1.37(2)	C(11)–C(18)	1.33(2)
C(8)–C(30)	1.52(2)	C(12)–C(13)	1.37(2)
C(9)–C(36)	1.50(2)	C(13)–C(14)	1.54(2)
C(10)–C(11)	1.41(2)	C(14)–C(15)	1.52(2)
C(10)–C(24)	1.47(2)	C(14)–C(16)	1.55(3)
C(11)–C(12)	1.45(2)	C(14)–C(17)	1.53(2)
C(9)–C(8)–C(30)	125(1)	C(18)–C(11)–Ru(2)	128.2(9)
C(9)–C(8)–Ru(2)	108.6(9)	C(11)–C(12)–C(13)	146(1)
C(9)–C(8)–Ru(3)	67.0(9)	C(11)–C(12)–Ru(1)	132.1(9)
C(30)–C(8)–Ru(2)	124.5(9)	C(11)–C(12)–Ru(2)	75.1(8)
C(30)–C(8)–Ru(3)	123.9(9)	C(13)–C(12)–Ru(1)	77.3(8)
Ru(2)–C(8)–Ru(3)	82.0(6)	C(13)–C(12)–Ru(2)	133.4(9)
C(8)–C(9)–C(36)	128(1)	Ru(1)–C(12)–Ru(2)	83.7(5)
C(8)–C(9)–Ru(1)	109.8(9)	C(12)–C(13)–C(14)	132(1)
C(8)–C(9)–Ru(3)	76.0(9)	C(12)–C(13)–Ru(1)	66.6(8)
C(36)–C(9)–Ru(1)	117.5(9)	C(12)–C(13)–Ru(3)	88.1(9)
C(36)–C(9)–Ru(3)	135.8(9)	C(14)–C(13)–Ru(1)	132.7(9)
Ru(1)–C(9)–Ru(3)	74.2(5)	C(14)–C(13)–Ru(3)	135.1(9)
C(11)–C(10)–C(24)	127(1)	Ru(1)–C(13)–Ru(3)	76.8(5)
C(11)–C(10)–Ru(2)	68.9(7)	C(13)–C(14)–C(15)	109(1)
C(24)–C(10)–Ru(2)	120.9(9)	C(13)–C(14)–C(16)	108(1)
C(10)–C(11)–C(12)	116(1)	C(13)–C(14)–C(17)	110(1)
C(10)–C(11)–C(18)	123(1)	C(15)–C(14)–C(16)	111(1)
C(10)–C(11)–Ru(2)	75.0(8)	C(15)–C(14)–C(17)	108(1)
C(12)–C(11)–C(18)	122(1)	C(16)–C(14)–C(17)	110(1)
C(12)–C(11)–Ru(2)	66.1(8)		

π-bonded to the Ru(3) atom through the C(8)–C(9) triple bond [Ru(3)–C(8) = 2.21(2) and Ru(3)–C(9) = 2.10(2) Å], which is disposed nearly parallel to the Ru(1)–Ru(2) side of the cluster in an ideal orientation to coordinate to all the metals. This bonding mode between an alkyne and a metal triangle, indicated as $(2\sigma + \pi)$ or $\mu_3 - \eta^2$ type, has already been found in several homometallic and a few heterometallic complexes whose structural parameters have been recently summarized and compared [16].

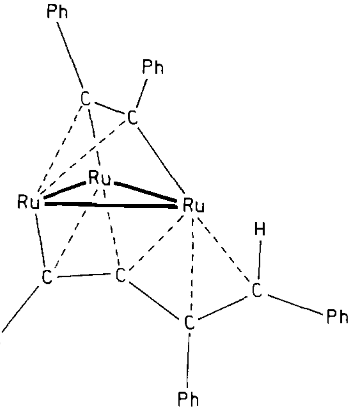
The latter ligand is formed by oligomerization of the C_2Bu^t group of the starting complex I and one diphenylacetylene molecule, inserted into the former Ru–C(σ) bond of I, with shift of the hydridic hydrogen on the diphenylacetylene molecule. Insertion of neutral molecules in this bond has already been found as t-butylacetylene and isopropenylacetylene undergo this reaction [6, 10]; on the contrary, dienes do not insert. The four adjacent carbon atoms C(10), C(11), C(12) and C(13) are involved in a complex bonding with all the metal atoms: the terminal C(13) through one σ-bond with Ru(3) [Ru(3)–C(13) = 2.04(1) Å], C(10), C(11) and C(12) with Ru(2), C(12) and C(13) with Ru(1) through an extensive η-bonding [Ru–C distances range from 2.12 to 2.32 Å]. The C(10)–C(13) chain is characterized by an extensive bond delocalization, as shown by the C–C bond distances in the range 1.37–1.45 Å. The large C(11)–C(12)–C(13) angle [146°] is noteworthy. The bonding of C(10), C(11) and C(12) with Ru(2) could be considered as an allylic linkage and C(11), C(12) and C(13) constitute a bent allenic group where the central C(12) is η-coordinated to two different metals.

This organic chain is comparable with the ones found in complexes II: the same allylic interaction and the allenic group with the large angle at the central carbon have been found. Indeed, the formation of allylic groups either by isomerization or oligomerization of alkynes is a common feature of the chemistry of this alkyne–ruthenium carbonyl cluster. Large angles (in the range 133–152°) at the central carbon of bent allenic systems have been observed in $HRu_3(RC_2HCR')$ [17], $Ru_3(CO)_8(C_{10}H_{12})$ [12], $Ru_3(CO)_8(C_{16}H_{22})$ [6], in complexes II and in the related complexes $Fe_2(CO)_6(C_7H_{10}CO)$ and $Fe_2(CO)_6(C_9H_{14}CO)$ [18].

The H(10) hydrogen atom has apparently migrated from a bridging position in I onto the diphenylacetylene molecule attached to C(12). There are several reasons to believe that H(10) is derived from the hydridic hydrogen of I: the C(10)–C(13) chain of V is closely comparable to those present in complexes II, where deuteration experiments [10] showed convincingly that the hydridic hydrogen was shifted to a position corresponding to that of H(10) in V. The following scheme shows the identical position of this hydrogen in V and in one of the two isomer complexes II.



(II)



(V)

The results of the present structure determination tend to confirm our previous hypotheses concerning the mode of formation of II. Thus we considered that the 'dienic' chain of II was formed first by initial attack of the incoming acetylene at the α-carbon of the acetylide, followed by a hydrogen migration.

However we were unable to obtain either an intermediate showing a dienic chain only, as found for osmium [19], or a complex showing an alkyne–CO–alkyne chain, like in III [11]. Only by reacting isopropenylacetylene with $Ru_3(CO)_{12}$ and isolating IV have we found indirect evidence for our hypothesis.

It is tempting to suggest that complex V could be a model intermediate in the formation of complexes with structures comparable with those of II, since further reaction of the unique diphenylacetylene ligand with CO (probably one of the cluster bound CO's) and alkyne would lead ultimately to homologues of II. It is also probable that when diphenylacetylene instead of t-butylacetylene is reacted with I, the reaction stops with the formation of V; indeed, alkyne–CO–alkyne chains were found, until now, only when unsymmetrical HC_2R alkynes were reacted.

Further experiments are in progress to confirm the proposed mechanism.

References

1 E. Sappa, O. Gambino, L. Milone and G. Cetini, *J. Organometal. Chem., 39,* 169 (1972).
2 G. Gervasio and G. Ferraris, *Cryst. Struct. Comm., 2,* 447 (1973).
3 M. Catti, G. Gervasio and S. A. Mason, *J. Chem. Soc. Dalton,* 2260 (1977).
4 S. Aime, L. Milone, O. Gambino, E. Sappa and E. Rosenberg, *Inorg. Chim. Acta, 15,* 53 (1975).
5 S. Aime, L. Milone, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *Inorg. Chim. Acta, 32,* 163 (1979).
6 E. Sappa, A. M. Manotti Lanfredi and A. Tiripicchio, *Inorg. Chim. Acta, 36,* 197 (1979).
7 E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *Inorg. Chim. Acta, 41,* 11 (1980).
8 S. Aime, G. Gervasio, L. Milone, E. Sappa and M. Franchini Angela, *Inorg. Chim. Acta, 26,* 223 (1978).
9 M. Castiglioni, G. Gervasio and E. Sappa, *Inorg. Chim. Acta, 49,* 217 (1981).
10 S. Aime, G. Gervasio, L. Milone, E. Sappa and M. Franchini Angela, *Inorg. Chim. Acta, 27,* 145 (1978).
11 G. Gervasio, *J. Chem. Soc. Chem. Comm.,* 25 (1976).
12 O. Gambino, E. Sappa, A. M. Manotti Lanfredi and A. Tiripicchio, *36,* 189 (1979).
13 G. M. Sheldrick, System of Computing Programs, University of Cambridge (1976).
14 International Tables of X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974).
15 F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc., 96,* 1233 (1974); idem, ibidem, *96,* 1233 (1974).
16 E. Sappa, A. M. Manotti Lanfredi and A. Tiripicchio, *J. Organometal. Chem.,* in press.
17 S. Aime, L. Milone, D. Osella and M. Valle, *J. Chem. Res.* (S), 77 (1978), (M) 0785-0797 (1978) and references therein.
18 F. A. Cotton, J. D. Jamerson and B. R. Stults, *Inorg. Chim. Acta, 17,* 235 (1976).
19 M. Tachikawa, J. R. Shapley, R. C. Haltiwanger and C. G. Pierpoint, *J. Am. Chem. Soc., 98,* 4651 (1976).