

Alkyne Oligomerization and CO Activation on Ruthenium Clusters. Synthesis and Crystal Structure of $\text{Ru}_3(\text{CO})_5(\text{C}_{12}\text{H}_{20})(\text{C}_{19}\text{H}_{30}\text{O})$. The Stepwise Formation of a Heterocyclic Ring without Cluster Degradation

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The title complex was obtained in a reversible reaction by treating $\text{Ru}_3(\text{CO})_6(\text{C}_{12}\text{H}_{20})(\text{C}_{13}\text{H}_{20}\text{O})$ with excess *t*-butylacetylene in hydrocarbon solvents. From the two isomers of the starting product, the corresponding isomers of the new complex were obtained. The structure of one of the isomers has been determined by X-ray methods; crystals are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions $a = 11.830(8)$, $b = 17.096(7)$, $c = 10.368(9)$ Å, $\alpha = 102.31(4)$, $\beta = 113.61(5)$, $\gamma = 96.23(5)^\circ$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 5.0\%$ for 2299 observed reflections. The complex consists of a nearly equilateral triangle of ruthenium atoms bonded to five terminal carbonyls; two independent organic moieties interact with all the metals of the cluster. The former is formed by two oligomerized alkynes and is responsible for the isomerism of the complex, the latter is an heterocyclic organic ring obtained by the insertion of one carbonyl into three molecules of alkyne. The formation mechanism of the complex, starting from $\text{Ru}_3(\text{CO})_{12}$ and alkynes, is discussed on the basis of deuteration experiments and of the structures of intermediate derivatives.

Introduction

Treatment of $\text{Ru}_3(\text{CO})_{12}$ with HC_2Bu^t (3,3-dimethyl-but-1-yne, *t*-butylacetylene) in refluxing hydrocarbons leads to high yields of $\text{HRu}_3(\text{CO})_9\text{C}_2\text{Bu}^t$ (complex I) [1, 2]; longer reaction times lead to a variety of substituted alkyne-carbonyl clusters. We were able to characterize $\text{Ru}_3(\text{CO})_8(\text{HC}_2\text{Bu}^t)_3$ (complex II) [3] and the two isomers $\text{Ru}_3(\text{CO})_6(\text{C}_{12}\text{H}_{20})(\text{C}_{13}\text{H}_{20}\text{O})$ (complexes IIIa, IIIb) [4]. The isomerism of the complexes III is due to the different substitu-

tion of the $(\text{C}_{12}\text{H}_{20})$ 'dienic' ligand, obtained by alkyne dimerization, on these clusters.

The reactions of $\text{Ru}_3(\text{CO})_{12}$ or of I with other alkynes also lead to some complexes having structures related to those of the above complexes; thus, treatment of $\text{Ru}_3(\text{CO})_{12}$ with isopropenylacetylene gives $\text{Ru}_3(\text{CO})_8(\text{C}_{10}\text{H}_{12})$ (complex IV) [5] in which the 'dienic' chain is probably stabilized by the interaction of one of the double bonds with the metals. The corresponding complex of HC_2Bu^t was not isolated. Finally, complex I reacts with diphenylacetylene to give $\text{Ru}_3(\text{CO})_7\{(\text{C}_2\text{Bu}^t)[\text{PhC}_2(\text{H})\text{Ph}](\text{C}_2\text{Ph}_2)\}$ (complex V) [6] which also shows a 'dienic' ligand comparable with those of IIIa and IIIb.

The structures of the complexes I–V are schematically represented in Fig. 1.

Here we report the synthesis of the two isomeric complexes $\text{Ru}_3(\text{CO})_5(\text{C}_{12}\text{H}_{20})(\text{C}_{19}\text{H}_{30}\text{O})$ (VIa and VIb) and the crystal structure of the complex VIb. The structures of the complexes VIa and VIb are schematically represented in Fig. 2. Complexes VI are obtained either by reacting $\text{Ru}_3(\text{CO})_{12}$ or I with excess of *t*-butylacetylene; intermediates in their formation are the complexes III.

Complexes VI consist of ruthenium triangular clusters bonded to five terminal CO ligands and to two different organic moieties. One of these is a $(\text{C}_{12}\text{H}_{20})$ 'dienic' chain closely comparable with the ones found in IIIa and IIIb; as for the complexes III the isomerism in the complexes VI is due to the different substitution on this chain. The second ligand in VI is a heterocyclic ring formed by stepwise oligomerization of three alkyne molecules with insertion of one carbonyl group.

The synthesis of these complexes represents, to our knowledge, the first example of a stepwise formation of an organic heterocycle on a metal cluster, without degradation or opening of it. Hence this is a

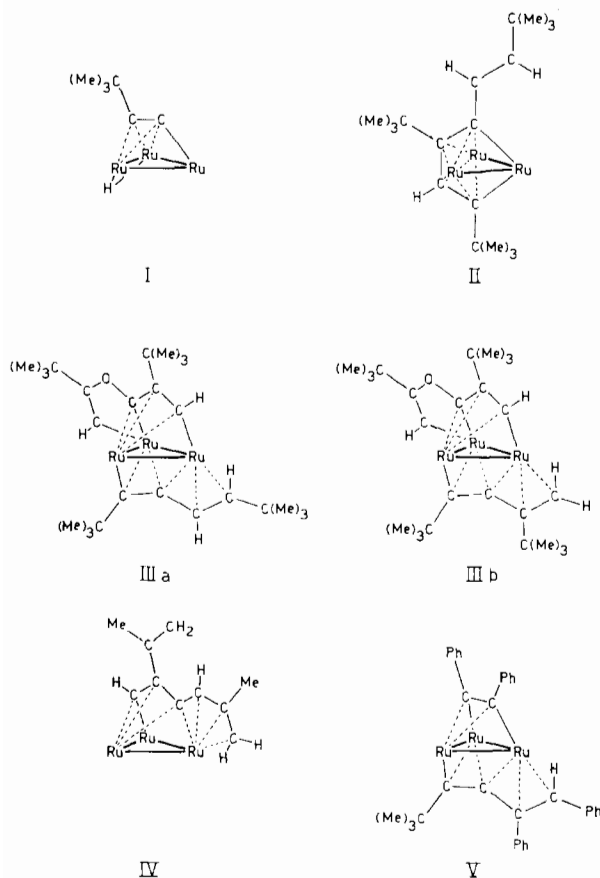


Fig. 1. Schematic structures of the complexes I–V. Carbonyls are omitted for clarity.

further example of the potentiality of the clusters in the building-up of organic molecules.

The stepwise formation of the complexes VI is discussed, as well as the possible reaction mechanism leading from III to VI.

Experimental

Synthesis, Purification and Crystallization of the Complexes VI

The complexes VI are found as by-products of the synthesis of I starting from $\text{Ru}_3(\text{CO})_{12}$ and HC_2Bu^t [1]. Better yields (5% on the ruthenium for each isomer) can be obtained by refluxing $\text{Ru}_3(\text{CO})_{12}$ with a 3:1 molar excess of HC_2Bu^t in heptane under nitrogen for 30–60 min, or by treating I with excess of alkyne in the same conditions.

Complexes VI can be also obtained by refluxing complexes III in light petroleum under nitrogen for 5–10 hours; from IIIa or IIIb yields of about 50% of VIa or VIb respectively are obtained together with some decomposition and unidentified products. The 'excess' alkyne required to form VI starting from III

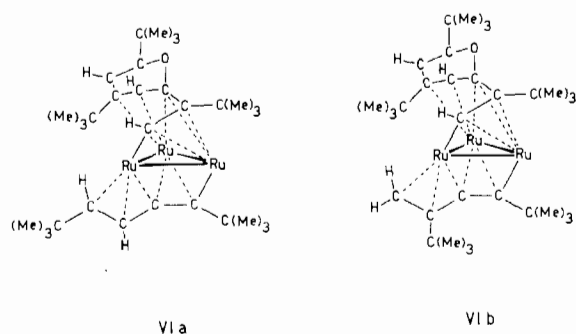


Fig. 2. Schematic structures of the two isomers VIa and VIb.

comes probably from the partial decomposition of III; treatment of complexes III, in the presence of HC_2Bu^t , leads to shorter reaction times (1 hour) in the same solvent and in slightly increased yields of VI. However, considerable amounts of binuclear ruthenium alkyne complexes are also obtained.

The reverse reaction also occurs; treatment of VIa or VIb in CCl_4 under nitrogen at 30 °C for 3–5 hours yields about 40% of IIIa or IIIb respectively and decomposition. The CO necessary for the partial interconversion is probably derived from the decomposition of VI (see also the mass spectra results); about 60% yields of complexes III can be obtained in 1 hour by operating under CO atmosphere, in the same solvent. Decomposition is still observed.

The reaction mixtures were purified by means of t.l.c. preparative plates (Kieselgel, P. F. Merck; as eluants, mixtures of light petroleum and ethyl ether). The isomers VI are easily recovered as pure fractions when using 20 × 40 cm plates disposed vertically; their elution order is the same of the complexes III. Indeed IIIa and VIa are closer to the solvent front with respect to IIIb and VIb.

Deep-red crystals of VIb were obtained after cooling for several days a heptane solution of the complex kept under nitrogen at –10 °C.

Reactants and Analyses of the Products

Dehydrated solvents and nitrogen were always used; t-butylacetylene was commercial grade (Fluka) and $\text{Ru}_3(\text{CO})_{12}$ and I were prepared with already reported procedures.

The elemental analyses of the complexes were performed on an F & M 185 C, H, N Analyzer and a Perkin Elmer 303 Atomic Absorption Spectrophotometer. The complexes analyze as follows: VIa and VIb: Calcd. for $\text{C}_{36}\text{H}_{50}\text{O}_6\text{Ru}_3$: C% 48.92, H% 5.70, O% 10.86, Ru% 34.52. VIa: Found: C% 49.05, H% 6.0, Ru% 33.9. VIb: Found: C% 48.7, H% 6.1, Ru% 34.8.

The i.r. spectra were obtained on a Perkin Elmer 580B instrument, the ^1H and ^{13}C n.m.r. on a JEOL C 60 HL and a JEOL PS 100 FT instrument, respectively (the latter in presence of $\text{Cr}(\text{acac})_3$ as shift

relaxation reagents). The mass spectra were obtained on a Varian CH-5 instrument equipped with direct inlet system, operating with a 70 eV ionization potential. Perfluoroalkanes were used as internal standards in some runs.

X-Ray Data Collection

A deep-red crystal of VIa, having approximate dimensions $0.12 \times 0.20 \times 0.20$ mm, was used for the X-ray data collection. Unit cell parameters, preliminarily determined from rotation and Weissenberg photographs, were refined by a least-squares procedure applied to the 29 θ values of accurately measured reflections on a Siemens AED single-crystal diffractometer, using the niobium-filtered MoK α radiation ($\lambda = 0.710688$ Å). Crystal data are as follows: $C_{36}H_{50}O_6Ru_3$, $M = 882.0$, triclinic, $a = 11.830(8)$, $b = 17.096(7)$, $c = 10.368(9)$ Å, $\alpha = 102.31(4)$, $\beta = 113.61(5)$, $\gamma = 96.23(5)^\circ$; $V = 1833(2)$ Å³, $Z = 2$, $D_c = 1.60$ g cm⁻³, $\mu(\text{MoK}\alpha) = 12.38$ cm⁻¹, space group: $P\bar{1}$ from structure determination.

A total of 5137 independent reflections with θ in the range $3\text{--}24^\circ$ were measured on the same diffractometer using the Nb-filtered MoK α radiation and the $\theta/2\theta$ scan technique. 2299 reflections, having $I \geq 2\sigma(I)$, were considered observed and used in the analysis. The structure amplitudes were obtained after the usual Lorentz and polarization corrections; no corrections were applied for the absorption effects, in view of the low value of μr . Data were placed on an approximate absolute scale by means of a Wilson plot which also provided the average overall temperature factor.

Structure Determination and Refinement

The structure was solved by Patterson and Fourier methods. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [7] with first isotropic and then anisotropic thermal parameters for all the atoms excepting the carbon atoms of the t-butyl groups. The H(7), H(13), H(19), H(311) and H(312) hydrogen atoms were clearly localized in a ΔF map, the other hydrogen atoms (belonging to the t-butyl groups) were placed in their geometrically calculated positions and included in the final structure factor calculation. The final R value was 0.050 for the observed reflections only. Atomic scattering factors, corrected for the anomalous dispersion of Ru, were taken from the International Tables [8]. The function minimized in the least-squares calculations was $\sum w_i |\Delta F_i|^2$; unit weights were used at each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to F_o . The final coordinates for the non-hydrogen and hydrogen atoms are given in Tables I and II respectively. The thermal parameters and a list of observed and calculated structure factors are available from the authors on request.

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	505(1)	2854(1)	3990(2)
Ru2	1195(2)	3773(1)	2406(2)
Ru3	1670(1)	2216(1)	2293(2)
O1	-243(17)	1833(11)	5663(20)
O2	-1598(13)	3675(10)	4106(19)
O3	134(17)	5260(10)	2856(22)
O4	3680(16)	4789(11)	2979(28)
O5	1518(15)	1603(10)	-716(19)
O6	2935(11)	2151(7)	5614(14)
C1	110(16)	2225(14)	5007(23)
C2	-785(19)	3363(13)	4111(25)
C3	506(21)	4683(13)	2648(33)
C4	2756(20)	4424(12)	2791(32)
C5	1604(17)	1860(12)	501(31)
C6	2728(16)	2780(11)	4830(20)
C7	3493(15)	2851(11)	4073(21)
C8	3657(17)	2132(12)	3386(22)
C13	1866(17)	3985(11)	4723(25)
C14	2482(16)	3510(11)	5594(20)
C19	3166(16)	1371(11)	3621(21)
C20	2992(18)	1445(13)	4816(25)
C25	-53(17)	2556(11)	1255(19)
C26	-266(17)	1994(11)	1985(25)
C31	630(21)	3416(14)	38(28)
C32	-360(19)	3030(12)	263(24)
C9	4667(20)	2084(12)	2722(24)
C10	5910(22)	2175(14)	4089(27)
C11	4390(21)	1272(14)	1588(26)
C12	4763(21)	2804(14)	2083(26)
C15	3106(19)	3807(12)	7303(23)
C16	2541(25)	3321(16)	8034(30)
C17	3083(25)	4716(16)	7860(30)
C18	4554(22)	3772(14)	7870(26)
C21	3007(20)	762(13)	5592(24)
C22	1997(24)	741(15)	6214(29)
C23	2773(26)	-88(17)	4553(31)
C24	4331(26)	981(17)	6870(32)
C27	-1144(19)	1118(12)	1285(23)
C28	-1367(24)	773(15)	-284(29)
C29	-2369(24)	1152(15)	1469(29)
C30	-459(21)	557(13)	2230(26)
C33	-1737(21)	3174(13)	-484(26)
C34	-2424(22)	3162(14)	465(27)
C35	-2425(28)	2479(18)	-1912(33)
C36	-1732(24)	3998(16)	-905(29)

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

Spectroscopic Data

The i.r. and n.m.r. data for the complexes VIa, VIb, IIIa and IIIb are reported in Table III. The i.r.

TABLE II. Calculated Atomic Coordinated ($\times 10^3$), Excepting for H(7), H(13), H(19), H(311) and H(312) which have been found, of the Hydrogen Atoms.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H7	406	340	427	H232	183	-23	367
H101	668	215	378	H233	286	-54	515
H102	582	168	456	H241	442	53	747
H103	611	276	488	H242	448	158	759
H111	352	121	64	H243	503	99	645
H112	430	77	205	H281	-184	116	-93
H113	515	125	127	H282	-195	16	-72
H121	496	337	291	H283	-47	75	-32
H122	388	275	115	H291	-289	153	84
H123	552	280	175	H292	-214	141	261
H13	170	454	529	H293	-294	54	108
H161	254	268	767	H301	41	51	215
H162	158	339	775	H302	-106	-5	183
H163	309	354	921	H303	-26	82	336
H171	348	508	735	H311	60	394	-44
H172	363	493	904	H312	121	319	2
H173	212	478	758	H341	-193	366	147
H181	464	315	751	H342	-246	258	72
H182	502	399	905	H343	-337	324	-12
H183	500	416	743	H351	-338	254	-248
H19	296	78	285	H352	-243	190	-167
H221	215	133	695	H353	-194	251	-260
H222	209	28	680	H361	-125	451	8
H223	106	59	532	H362	-269	405	-149
H231	346	-9	411	H363	-125	401	-159

spectra of VIa and VIb are similar. Some signals in the ^1H n.m.r. spectra of these complexes can be attributed to the hydrogen atoms of the 'dienic' chain by comparison with the ^1H spectra of the complexes IIIa and IIIb [4]; it is possible to see that the isomerism for VIa and VIb is the same of IIIa and IIIb in the 'dienic' ligand.

The ^{13}C n.m.r. spectra of the complexes IIIa and IIIb, previously not reported, show a characteristic signal lowfield to the ones of the carbonyls, which is attributed to the carbon atom sharing the two pentatomic rings. This carbon atom would show some 'carbenic' character, as for atoms of this type signals in the same region (or lowfield) have been found.

In the ^{13}C spectrum of VIa, the lowfield signal is not observed whereas, in the other regions of the spectrum, comparable chemical shift can be found. Owing to the low solubility of VIb we were unable to obtain a good registration of its ^{13}C spectrum.

The mass spectra of the complexes VIa and VIb show a marked temperature dependence; this has been found for other ruthenium-alkyne derivatives [9]. Indeed, when the introduction system is maintained under 25°C , both VIa and VIb show the parent ion at 884 m/e and gradual loss of CO's and organic fragments in a very complex pattern; when the temperature is raised up to 50°C the parent ions of IIIa and IIIb at 830 m/e are observed. Thus rearrangement and loss of one alkyne is observed in the ionized gas phase as well as in solution.

TABLE III. Spectroscopic Data for Complexes III and VI.

Complex	i.r. (ν_{CO} , heptane sol.)	^1H n.m.r. (δ , CCl_4)	^{13}C n.m.r. (δ , CDCl_3)
IIIa	2045 s(sh), 2043 vs, 2018 vs, 1983 s, 1872 vw, cm^{-1}	9.4 (s, 1) ^a , 6.5 (s, 1), <u>3.7 (s, 1)^b</u> , 2.1 (s, 18), 1.4 (s, 9), 1.2 (s, 9), <u>0.7 (s, 1)</u>	235.7 (1, C_3), 204.0-194.2 (6 signals, carbonyls), 182.5-123.1 (6 signals, $\text{C } \sigma-\pi$ bonded), 85.8-29.9 (8 signals, $\text{C}-\sigma$ bonded and Bu^t)
VIa	2038 m-s, 2010 vs, 1976 s, 1964 s(sh), cm^{-1}	9.30 (s, 1), 6.25 (s, 1), 6.40 (s, 1), <u>3.6 (s, 1)</u> , 2.0 (s, 9), 1.7 (s, 9), 1.40 (s, 18), 1.2 (s, 9), <u>0.9 (s, 1)</u>	206.0-195.3 (5 signals, carbonyls), 180.5-116.7 (5 signals, $\text{C } \sigma-\pi$), 84.0-27.5 (other carbons)
IIIb	2047 s, 2023 vs, 1992 s, 1865 w, cm^{-1}	9.6 (s, 1), 6.4 (s, 1), <u>4.6 (d, 1)</u> , <u>2.4 (d, 1)</u> , 2.1 (s, 18), 1.5 (s, 9), 1.3 (s, 9)	234.6 (1, C_3), 206.4-194.2 (6 signals, carbonyls), 182.1-118.4 (6 signals, $\text{C } \sigma-\pi$) 97.8-30.1 (other carbons)
VIb	2044 m-s, 2018 vs, 1984 s, 1973 m(sh), cm^{-1}	9.4 (s, 1), 6.30 (s, 1), 6.5 (s, 1), <u>4.4 (d, 1)</u> , <u>2.6 (d, 1)</u> , 2.1 (s, 9), 1.6 (s, 9), 1.35 (s, 18), 1.2 (s, 9)	

^aIn parentheses, multiplicity and integrated intensity.

^bUnderlined are the hydrogens of the 'dienic' moiety.

TABLE IV. Selected 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)	2.780(3)	Ru(2)–C(13)	2.14(2)
Ru(1)–Ru(3)	2.763(3)	Ru(2)–C(25)	2.19(2)
Ru(2)–Ru(3)	2.768(4)	Ru(2)–C(31)	2.19(3)
Ru(1)–C(1)	1.80(2)	Ru(2)–C(32)	2.22(2)
Ru(1)–C(2)	1.87(2)	Ru(3)–C(5)	1.79(3)
Ru(1)–C(6)	2.44(2)	Ru(3)–C(6)	2.33(2)
Ru(1)–C(13)	2.15(2)	Ru(3)–C(7)	2.16(2)
Ru(1)–C(14)	2.24(2)	Ru(3)–C(8)	2.20(2)
Ru(1)–C(26)	2.05(2)	Ru(3)–C(25)	2.10(2)
Ru(2)–C(3)	1.85(3)	Ru(3)–C(26)	2.16(2)
Ru(2)–C(4)	1.89(3)		
Ru(2)–Ru(1)–Ru(3)	59.9(1)	C(13)–Ru(2)–C(31)	172.4(9)
Ru(1)–Ru(2)–Ru(3)	59.8(1)	C(13)–Ru(2)–C(32)	142.6(8)
Ru(1)–Ru(3)–Ru(2)	60.3(1)	C(25)–Ru(2)–C(31)	66.4(8)
Ru(2)–Ru(1)–C(6)	79.9(5)	C(25)–Ru(2)–C(32)	37.0(7)
Ru(2)–Ru(1)–C(13)	49.4(6)	C(31)–Ru(2)–C(32)	37.1(9)
Ru(2)–Ru(1)–C(14)	78.2(5)	Ru(1)–Ru(3)–C(6)	56.6(5)
Ru(2)–Ru(1)–C(26)	80.8(6)	Ru(1)–Ru(3)–C(7)	89.7(5)
Ru(3)–Ru(1)–C(6)	52.8(4)	Ru(1)–Ru(3)–C(8)	118.9(5)
Ru(3)–Ru(1)–C(13)	87.2(6)	Ru(1)–Ru(3)–C(25)	61.7(5)
Ru(3)–Ru(1)–C(14)	83.3(5)	Ru(1)–Ru(3)–C(26)	47.3(6)
Ru(3)–Ru(1)–C(26)	50.7(6)	Ru(2)–Ru(3)–C(6)	82.1(5)
C(6)–Ru(1)–C(13)	62.6(7)	Ru(2)–Ru(3)–C(7)	84.5(5)
C(6)–Ru(1)–C(14)	35.8(7)	Ru(2)–Ru(3)–C(8)	116.9(6)
C(6)–Ru(1)–C(26)	100.3(8)	Ru(2)–Ru(3)–C(25)	51.3(5)
C(13)–Ru(1)–C(14)	36.7(8)	Ru(2)–Ru(3)–C(26)	79.4(5)
C(13)–Ru(1)–C(26)	128.3(9)	C(6)–Ru(3)–C(7)	36.8(7)
C(14)–Ru(1)–C(26)	133.9(8)	C(6)–Ru(3)–C(8)	62.6(7)
Ru(1)–Ru(2)–C(13)	49.8(6)	C(6)–Ru(3)–C(25)	115.4(7)
Ru(1)–Ru(2)–C(25)	60.6(5)	C(6)–Ru(3)–C(26)	100.6(8)
Ru(1)–Ru(2)–C(31)	127.0(7)	C(7)–Ru(3)–C(8)	36.3(8)
Ru(1)–Ru(2)–C(32)	93.7(6)	C(7)–Ru(3)–C(25)	134.5(7)
Ru(3)–Ru(2)–C(13)	87.3(5)	C(7)–Ru(3)–C(26)	136.5(8)
Ru(3)–Ru(2)–C(25)	48.5(5)	C(8)–Ru(3)–C(25)	167.3(8)
Ru(3)–Ru(2)–C(31)	85.3(7)	C(8)–Ru(3)–C(26)	152.3(8)
Ru(3)–Ru(2)–C(32)	78.0(6)	C(25)–Ru(3)–C(26)	38.4(8)
C(13)–Ru(2)–C(25)	110.0(7)		
ii) in the carbonyl groups			
O(1)–C(1)	1.20(3)	O(4)–C(4)	1.12(3)
O(2)–C(2)	1.15(3)	O(5)–C(5)	1.20(3)
O(3)–C(3)	1.14(3)		
Ru(1)–C(1)–O(1)	174(2)	Ru(2)–C(4)–O(4)	178(3)
Ru(1)–C(2)–O(2)	176(2)	Ru(3)–C(5)–O(5)	178(2)
Ru(2)–C(3)–O(3)	177(3)		
iii) in the organic ligands			
C(6)–O(6)	1.47(2)	C(20)–C(21)	1.55(3)
C(6)–C(7)	1.43(3)	C(21)–C(22)	1.57(4)
C(6)–C(14)	1.45(3)	C(21)–C(23)	1.53(4)
C(7)–C(8)	1.36(3)	C(21)–C(24)	1.53(4)
C(8)–C(9)	1.60(3)	C(25)–C(26)	1.40(3)
C(8)–C(19)	1.47(3)	C(25)–C(32)	1.40(3)
C(9)–C(10)	1.54(3)	C(26)–C(27)	1.56(3)

(continued overleaf)

TABLE IV. (continued)

C(9)–C(11)	1.52(3)	C(27)–C(28)	1.51(3)
C(9)–C(12)	1.53(3)	C(27)–C(29)	1.54(4)
C(13)–C(14)	1.39(3)	C(27)–C(30)	1.57(3)
C(14)–C(15)	1.56(3)	C(31)–C(32)	1.41(4)
C(15)–C(16)	1.51(4)	C(32)–C(33)	1.57(4)
C(15)–C(17)	1.55(4)	C(33)–C(34)	1.51(4)
C(15)–C(18)	1.58(4)	C(33)–C(35)	1.53(4)
C(19)–C(20)	1.32(3)	C(33)–C(36)	1.56(4)
C(20)–O(6)	1.34(3)		
Ru(1)–C(6)–Ru(3)	70.7(5)	C(6)–C(14)–C(13)	115(2)
Ru(1)–C(6)–O(6)	108(1)	C(6)–C(14)–C(15)	121(2)
Ru(1)–C(6)–C(7)	128(1)	C(13)–C(14)–C(15)	123(2)
Ru(1)–C(6)–C(14)	64(1)	O(6)–C(20)–C(19)	124(2)
Ru(3)–C(6)–O(6)	112(1)	O(6)–C(20)–C(21)	111(2)
Ru(3)–C(6)–C(7)	65(1)	C(19)–C(20)–C(21)	125(2)
Ru(3)–C(6)–C(14)	123(1)	Ru(2)–C(25)–Ru(3)	80.3(7)
O(6)–C(6)–C(7)	114(2)	Ru(2)–C(25)–C(26)	123(1)
O(6)–C(6)–C(14)	114(2)	Ru(2)–C(25)–C(32)	73(1)
C(7)–C(6)–C(14)	120(2)	Ru(3)–C(25)–C(26)	73(1)
C(6)–O(6)–C(20)	113(2)	Ru(3)–C(25)–C(32)	129(2)
Ru(3)–C(7)–C(6)	78(1)	C(26)–C(25)–C(32)	157(2)
Ru(3)–C(7)–C(8)	73(1)	Ru(1)–C(26)–Ru(3)	82.0(8)
C(6)–C(7)–C(8)	116(2)	Ru(1)–C(26)–C(25)	94(1)
Ru(3)–C(8)–C(7)	70(1)	Ru(1)–C(26)–C(27)	136(2)
Ru(3)–C(8)–C(9)	128(1)	Ru(3)–C(26)–C(25)	69(1)
Ru(3)–C(8)–C(19)	86(1)	Ru(3)–C(26)–C(27)	122(1)
C(7)–C(8)–C(9)	123(2)	C(25)–C(26)–C(27)	128(2)
C(7)–C(8)–C(19)	118(2)	Ru(2)–C(31)–C(32)	73(1)
C(9)–C(8)–C(19)	117(2)	Ru(2)–C(32)–C(25)	70(1)
Ru(1)–C(13)–Ru(2)	80.8(8)	Ru(2)–C(32)–C(31)	70(1)
Ru(1)–C(13)–C(14)	75(1)	Ru(2)–C(32)–C(33)	127(2)
Ru(2)–C(13)–C(14)	129(2)	C(25)–C(32)–C(31)	117(2)
Ru(1)–C(14)–C(6)	80(1)	C(25)–C(32)–C(33)	121(2)
Ru(1)–C(14)–C(13)	68(1)	C(31)–C(32)–C(33)	121(2)
Ru(1)–C(14)–C(15)	131(1)	C(8)–C(19)–C(20)	117(2)

Crystal Structure of VIb

The structure of the complex VIb is represented in Fig. 2; bond distances and angles in it are given in Table IV.

The complex consists of a nearly equilateral triangle of ruthenium atoms [Ru(1)–Ru(2) = 2.780(3), Ru(1)–Ru(3) = 2.763(3) and Ru(2)–Ru(3) = 2.768(4) Å] bonded to five terminal carbonyls (two carbonyls are bound to the Ru(1) and Ru(2) atoms, one carbonyl to the Ru(3) atom); two different organic ligands interact with all the metals. In the comparable complexes IIIa and V the metal triangles are isosceles, the Ru–Ru bonds being 2.828(1), 2.820(1), 2.686(1) in IIIa and 2.812(3), 2.839(5), 2.682(7) Å in V.

One of the two organic ligands is derived from two head-to-tail joined alkynes with shift of an hydrogen atom on C(31). The four adjacent carbon atoms C(26), C(25), C(32) and C(31) are involved in a complex bonding with all the metals: the C(26) through one σ -bond with Ru(1) [Ru(1)–C(26) =

2.05(2) Å], C(26) and C(25) with Ru(3), C(25), C(32) and C(31) with Ru(2) through an extensive η -bonding [Ru–C distances range from 2.10 to 2.22 Å]. The substituted tetraatomic chain is characterized by an extensive bond delocalization [as shown by the C–C bond distances of 1.40–1.41 Å] and by a large angle [C(26)–C(25)–C(32) = 157(2) $^\circ$] at the carbon atom C(25) η -interacting with two metal atoms, Ru(2) and Ru(3). The torsion angle C(31)–C(32)–C(25)–C(26) in this chain is $-168.5(4)^\circ$; C(31), C(32), C(25) and C(26) deviate from the mean plane passing through them by 0.018, 0.010, -0.038 and 0.031 Å respectively and the dihedral angle between this plane and the cluster plane 55.6 $^\circ$. This substituted chain is the same present in the complex IIIb [4] and is very similar to that present in the complex V [6]. The different substitution on this chain is responsible for the isomerism in the complexes VIa and VIb and in the complexes IIIa and IIIb. So in the formation of VIa and VIb from IIIa and IIIb this ligand remains practically unchanged.

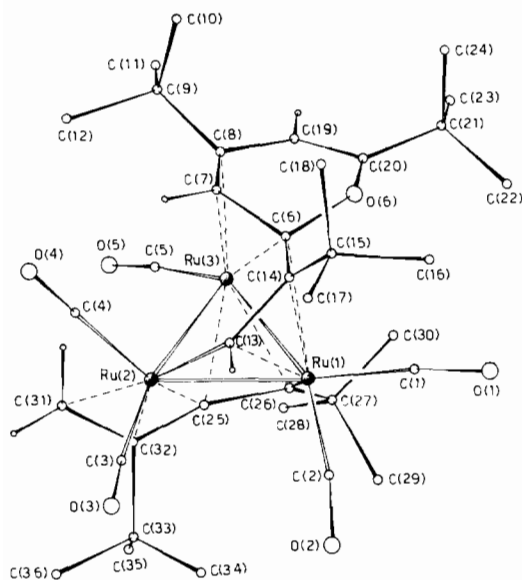


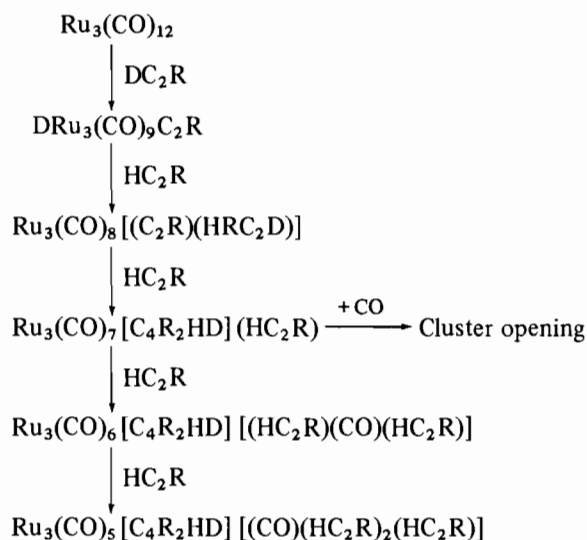
Fig. 3. View of the molecular shape of the complex $\text{Ru}_3(\text{CO})_5(\text{C}_{12}\text{H}_{20})(\text{C}_{19}\text{H}_{30}\text{O})$ with the atomic numbering scheme.

The second organic ligand, consisting of a substituted heterocyclic ring with a 'side chain' bonded through σ - and η -bonds to the metal atoms, is derived by the cyclo-oligomerization of three alkyne molecules with insertion of one carbonyl group. The terminal carbon atom C(13) of the 'side chain' is σ -bonded to the Ru(2) atom [$\text{Ru}(2)\text{--C}(13) = 2.14(2)$ Å], while C(8), C(7) and C(6), belonging to the heterocycle, and C(6), C(14) and C(13), the last two belonging to the 'side chain', are involved in a complex η -bonding with Ru(3) and Ru(2) respectively. The C–C bonds corresponding to the carbon atoms involved in the η -interactions with two metal atoms range from 1.36 to 1.45 Å. The heterocycle is puckered, the deviations of the atoms C(6), C(7), C(8), C(19), C(20) and O(6) from the mean plane passing through the ring are 0.324, -0.133 , -0.132 , 0.184, 0.005 and -0.124 Å respectively; the dihedral angle between this plane and the metal cluster plane is 13.3° . The torsion angles within this ring and in the 'side chain' are: $\text{C}(8)\text{--C}(19)\text{--C}(20)\text{--O}(6) = 16.8$, $\text{C}(19)\text{--C}(20)\text{--O}(6)\text{--C}(6) = 16.2$, $\text{C}(20)\text{--O}(6)\text{--C}(6)\text{--C}(7) = -45.1$, $\text{O}(6)\text{--C}(6)\text{--C}(7)\text{--C}(8) = 39.8$, $\text{C}(6)\text{--C}(7)\text{--C}(8)\text{--C}(19) = -6.8$, $\text{C}(7)\text{--C}(8)\text{--C}(19)\text{--C}(20) = -22.3$, $\text{C}(7)\text{--C}(6)\text{--C}(14)\text{--C}(13) = 60.4$ and $\text{O}(6)\text{--C}(6)\text{--C}(14)\text{--C}(13) = -158.7^\circ$.

In the synthesis of the complexes VI alkyne cyclo-oligomerization and CO 'functionalization' is observed to give a substituted heterocycle; to our knowledge this is the first example of an heterocycle (not including metal atoms) on a metal cluster, obtained without opening or degradation of the cluster itself.

Evidence for a Stepwise Formation of the Heterocycle and Proposed Formation Mechanism of the Complexes VI

The preparative, spectroscopic and structural data, as well as the known structures of the complexes I–V [1–6], support the reaction sequence shown in the Scheme, which leads from $\text{Ru}_3(\text{CO})_{12}$ to the complexes VI via the stepwise substitution of CO ligands by alkynes on the metal cluster.

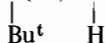


Scheme

Thus HC_2Bu^t first splits into an acetylide and a hydride bridge, forming I; then I reacts with another alkyne to give the 'dienic' chain upon insertion (or by nucleophilic attack) of the alkyne on the Ru–C(σ) bond. Evidence for these steps has been obtained by the use of DC_2Bu^t and deuterated I in the synthesis of complexes III [4]. Further treatment of the deuterated isomer IIIb with alkyne results in deuterated VIb; the intensity of the signal at 2.6 ppm from TMS in the ^1H n.m.r. spectrum of this latter (see Table I) indicates that deuterium is mainly on C(31) and hence in a similar position as found in IIIb. No deuteration experiments for complexes IV and V are available; these have been reported as deuterated in the scheme only for comparison reasons.

Also the synthesis of IV from isopropenylacetylene supports the hypothesis that the 'dienic' chain is formed first. The next step is probably the coordination of a third alkyne to the dienic complex; this is indirectly supported by the synthesis and structure of the complex V. The solid state structure of V shows only terminal carbonyls, whereas in the solution i.r. spectrum a sharp band at 1930 cm^{-1} is observed, which could indicate the presence of a 'semibridging' CO. The nucleophilic attack of the alkyne on this CO could lead to the complexes III whereas attack of CO on the cluster would result in

cluster opening to give the complex II. Reactions of coordinated CO's with nucleophiles, to give carbenes, are well known at present [10]; the synthesis, in comparable conditions, of $\text{Os}_3(\text{CO})_9(\text{HC}_2\text{Ph})(\text{CO})(\text{HC}_2\text{Ph})$ [11] shows that this process could be general in the ruthenium and osmium cluster chemistry. Finally in the last reaction step the complexes VI are obtained from the complexes III. The comparison of the structure of VIb with the one of IIIb shows that the side chain C(13)–C(14)–C(6) remains practically unmodified in structural parameters and in bonding with the cluster. The atomic group C(6)–O(6)–C(20)–C(19), which in VIb is part



of the heterocycle with the C(7)H–C(8)Bu^t alkyne, in IIIb is bound to the Ru(3) atom through two σ -bonds involving the terminal C(6) and C(19) atoms. It is reasonable that in the formation of VI from III the fifth alkyne molecule substitutes one of the CO ligands and then a nucleophilic attack of the alkyne on the organic moiety could occur either on C(6) or on C(19) with insertion in it through these carbon atoms and formation of the heterocycle; in this case two Ru–C(σ) bonds should be broken. This reactivity is known for carbenes [10]; we also reported several insertions and nucleophilic attacks on Ru–C(σ) bonds in the complex I [1–6].

Some indirect evidence points to the attack on the carbenic carbon of III (C(6) in VIb), which is expected to be more nucleophilic because of the nearby oxygen atom; indeed in the ^{13}C n.m.r. spectra of IIIa and IIIb signals at about 235 ppm downfield with respect to TMS are observed and were assigned to this carbenic carbon atom, whereas the chemical shifts of the other carbon atoms σ - η bonded to the cluster fall over 190 ppm.

Noteworthy is the partial reversibility of the formation reaction of the complexes VI, as shown either by the reactions in solution (in which probably

an excess of CO is present because of some decomposition and hence the complexes III can be reformed) and by the results in the ionized gas phase.

Further studies on the reactivity of the complexes IIIa and IIIb towards nucleophiles and electrophiles are in progress.

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