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THE SYNTHESIS, REACTIVITY AND STRUCTURE OF FUNCTIONALLY SUBSTITUTED TRIMETALLIC CLUSTERS OF RUTHENIUM

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Summary

The reactions of $Ru_3(CO)_{12}$ with terminal acetylenes of the type HC≡CCRR'X (R = CH_3, R' = C_2H_5, C_6H_5, CH_3, X = OH, Cl, H) were studied. For R = CH_3, R' = C_6H_5, C_2H_5 and X = OH good yields of 1/1 trinuclear complexes of the type $HRu_3(CO)_9$(C≡CCRR'X) (II and III) are obtained, while only small yields of the analogous compounds are obtained with the other acetylenes. Both II and III can be dehydrated at room temperature in the presence of excess trifluoroacetic acid to yield the complexes $HRu_3(CO)_9[CH_3(H)C=C(CH_3)C_2]$ (VIII) and $HRu_3(CO)_9[CH_2=C(C_6H_5)C_2]$ (VII). The crystal structure of VII has been determined by X-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions a 9.675(8), b 14.096(12), c 8.985(8) Å, α 93.78(8), β 117.17(11), γ 92.15(8)°, V 1085(2) Å^3. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.054$ for 3715 observed reflections. The molecule is formed by a triruthenium cluster, in a nearly equilateral arrangement, bound to nine terminal CO groups; one hydridic hydrogen atom is bridge-bonding two ruthenium atoms on one side of the cluster. The substituted acetylene is bound to the three metals via a σ bond to one ruthenium and two η bonds to the other two ruthenium atoms, in a way quite similar to that found in the analogous t-butyl acetylide complex (I). The olefinic C—C bond distance is regular (1.337 Å) indicating that there is no conjugative interaction of the olefin with the cluster.

Introduction

The activation of carbon hydrogen bonds in small hydrocarbon molecules by triruthenium dodecacarbonyl leads to the formation of 1/1 hydrido/organo-

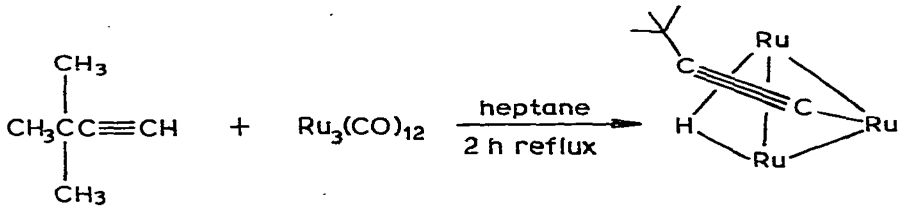
TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA

		Elemental analysis [a] (Found (calcd.) (%)) C	H	Mass spectrum [b] M^+ (Found (calcd.))	Infrared [c] ν(CO) (cm^{-1})	^{1}H NMR [d] (rel. int.) (δ, ppm) $\delta(C_6H_5)$	$\delta(CH_3)$	$\delta(CH_\eta)$	δ(OH)	$\delta(H_{olef})$	δ(H)
I	$HRu_3(CO)_9(C_6H_9)$	—	—	—	—	—	1.4s (9) 1.1t (3)	—	—	—	−21.0s (1)
II	$HRu(CO)_9(C_6H_9O)$	27.64 (27.57)	1.63 (1.54)	653 (653.29)	2085(w), 2065(s) 2040(s), 2000(s) 1985(s)	—	1.6s (3)	1.8m (2)	1.7s (1)	—	−21.0s (1)
III	$HRu_3(CO)_9(C_{10}H_9O)$	32.44 (32.52)	1.50 (1.44)	701 (701.45)	2085(w), 2050(s, br) 2000(s), 1990(s)	7.6m (5)	2.1s (3)		2.3s (1)	—	−21.0s (1)
IV	$HRu_3(CO)_9(C_5H_7O)$	—	—	—	2090(w), 2060(s) 2090(s), 1995(s) 1985(s)	—	1.6s (6)	—	2.2s (1)		−21.0s (1)
V	$HRu_3(CO)_9(C_5H_6Cl)$	—	—	—	2085(w), 2060(s) 2045(s), 1985(s) 1980(s)	—	1.8s (6)	—	—	.	−21.0s (1)
VI	$HRu_3(CO)_9(C_5H_7)$	—	—	—	2090(w), 2060(s) 2050(s), 1995(s) 1970(s)	—	1.4d (6) $^3J_{HH}$ = 6	2.9m (1)		—	−21.0s (1)
VII	$HRu_3(CO)_9(C_{10}H_7)$	33.77 (33.39)	1.45 (1.20)	683 (683.43)	2085(w), 2060(s) 2035(s), 1995(s) 1985(s)	7.5m (5)	—	—	—	5.63(1) 5.75s(1)	−21.0 (1)
VIII	$HRu_3(CO)_9(C_6H_7)$	28.54 (28.36)	1.34 (1.27)	635 (635.27)	2090(w), 2060(s) 2000(s), 1990(s) 1965(w)	—	2.0br (6)	—	—	5.50br (1)	−21.0

[a] Analysis performed by Schwarzkopf Microanalytical Laboratories. [b] Mass spectral data obtained on an MS-9 instrument at the University of California at Los Angeles. Parent ions are quoted using Ru = 101. $M^+ - 28$ peaks observed for $<Ru_3(CO)_n$ (n = 4 to 9). [c] Infrared spectra recorded in the solid state as KBr discs on a Beckman-Aculab IR spectrometer. Values reported are ±10 cm^{-1}. [d] NMR spectra were recorded on a Varian EM-360 NMR spectrometer in $CDCl_3$ with TMS as internal reference, letters in parentheses indicate resonance multiplicities. δ values ± 0.05 ppm.

metal clusters which are excellent models for studying the properties of organic molecules bound to polymetallic sites [1]. The unusually high yield (80%) of the 1/1 complex (I) obtained with tertiary butyl acetylene [1] (eq. 1) led us to



(1)

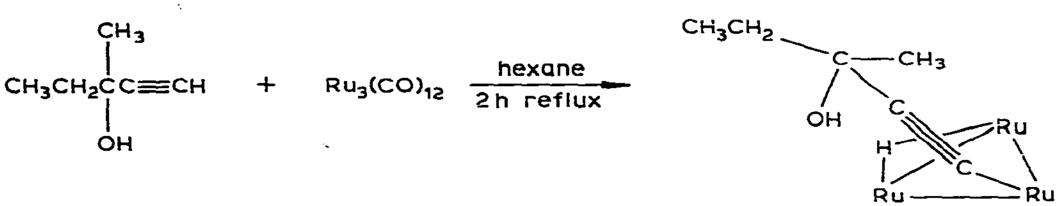
(I)

$(HRu_3(CO)_9(C_6H_9))$

investigate the reaction of $Ru_3(CO)_{12}$ with other functionally substituted bulky acetylenes, in the hope of studying the chemistry of organic functional groups α to carbon atoms bound to a trimetallic cluster. We report here the synthesis of α-hydroxy-substituted analogs of I and the structure of the products obtained from the reaction of these compounds with protic acids.

Results and discussion

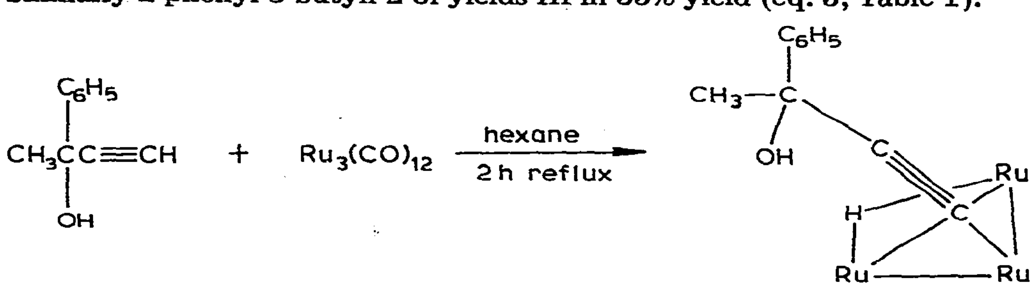
The reaction of 3-methyl-1-pentyn-3-ol with $Ru_3(CO)_{12}$ yields II in 58% yield (eq. 2).



(2)

(II)

The ^{1}H NMR of II shows the characteristic high field resonance for a μ_2-hydrido proton as well as the expected resonances for the ethyl, methyl and hydroxy groups (Table 1). The parent ion in the mass spectrum and the infrared data are all in excellent agreement with the proposed structure II (Table 1). Similarly 2-phenyl-3-butyn-2-ol yields III in 33% yield (eq. 3, Table 1).

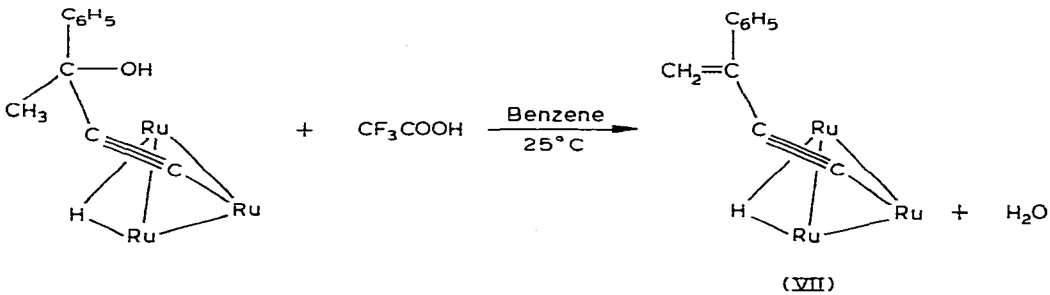


(3)

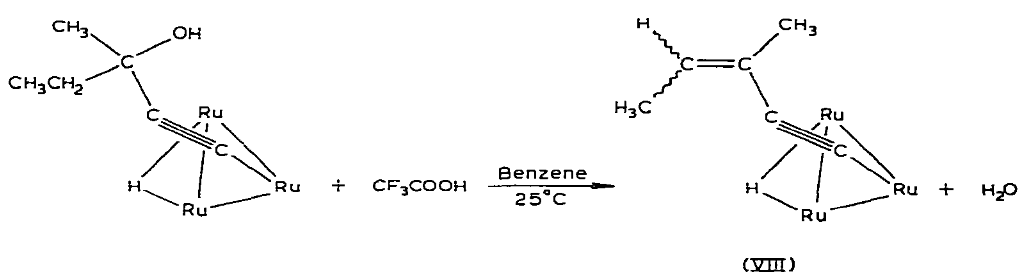
(III)

We have also attempted the reaction of $Ru_3(CO)_{12}$ with $(CH_3)_2C(OH)C{\equiv}CH$, $(CH_3)_2C(Cl)C{\equiv}CH$ and $(CH_3)_2C(H)C{\equiv}CH$. In all three cases a small amount (<5%) of the structural analog of I is obtained and was characterized by ^1H NMR and IR spectroscopy only (Table 1 compound IV—VI). The major product in these reactions is an insoluble ruthenium containing compound which shows no μ_2-hydride resonance in the NMR. We believe that these compounds have two cyclodimerized acetylenes bound to a binuclear ruthenium cluster in which no C—H bond cleavage has taken place [2], but we have not yet fully characterized these complexes.

The reactions of II or III with excess trifluoroacetic acid in benzene at room temperature gives the dehydration products VII or VIII in 20 and 55% yields, respectively (eqs. 4 and 5).



(4)



(5)

The structures of VII and VIII were determined from ^1H NMR, infrared, and mass spectroscopic data. We cannot determine the geometry of the double bond in VIII since small unresolved coupling(s) to the olefinic proton causes it to appear as a broadened singlet. The methyl groups appear as two overlapping broadened singlets (Table 1). ^1H-decoupling of the methyl groups causes the olefinic proton to collapse to a sharp singlet. This suggests that only one geometrical isomer is formed since the chemical shift of the olefinic proton would be expected to be different in the *cis*- and *trans*-isomers. VII and VIII represent a novel class of compounds, where an olefin is conjugated to a coordinated acetylene but is apparently not interacting with the metal cluster itself. In order to ascertain the effect, if any, of the olefin on the structural parameters of the bound acetylido ligand we undertook a single crystal X-ray diffraction study of VII.

Crystal Structure of $HRu_3(CO)_9(C_{10}H_7)$ (VII)

The structure of $HRu_3(CO)_9(C_{10}H_7)$ (VII) is represented in Fig. 1. Bond distances and angles not involving hydrogen atoms are given in Table 2. The complex contains a triruthenium cluster in a nearly equilateral triangular arrangement, with three terminal carbonyl groups bonded to each Ru atom. The three Ru—Ru bonds are very similar to those found in the analogous t-butyl acetylide complex (I) (2.795(3), 2.799(3) and 2.792(3) Å) [3]. The hydridic atom H(1) bridges the edge Ru(2)—Ru(3) of the cluster, forming a symmetrical bent Ru—H—Ru tricentric bond (Ru(2)—H(1) 1.66 and Ru(3)—H(1) 1.70 Å) in a way quite similar to that present in I, accurately determined by neutron diffraction [3]. The substituted acetylenic ligand interacts, through its triple bond and the carbon atom C(11) without substituent, with the three metal atoms forming one σ bond with Ru(1) (Ru(1)—C(10) 1.904 Å) and two η bonds with Ru(2) and Ru(3) (Ru(2)—C(10) 2.178; Ru(2)—C(11) 2.188, Ru(3)—C(10) 2.190 and Ru(3)—C(11) 2.276 Å). This bonding of the acetylenic ligand towards the metal cluster is very similar to that found in complex I, even if the C(10)—C(11) bond distance (1.272 Å) and the C(12)—C(11)—C(10) angle (145.9°) in the present compound are shorter and larger than in I (1.315 Å and 141.0°, respectively).

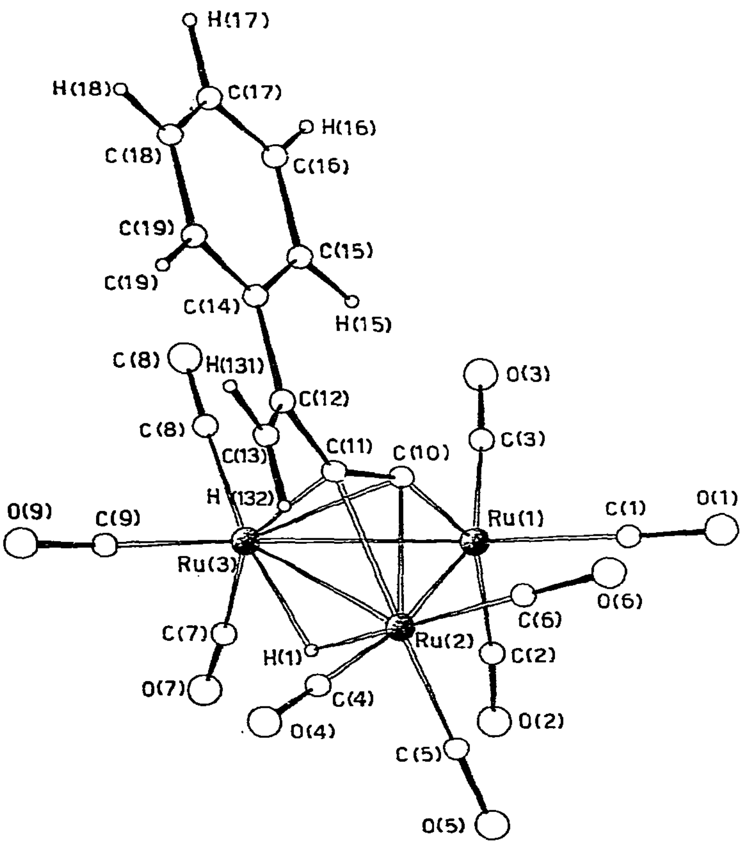


Fig. 1. View of the complex showing the atomic numbering scheme.

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) (not involving hydrogen atoms) WITH ESDs IN PARENTHESES

(i) in the coordination sphere of the metal cluster

Ru(1)—Ru(2)	2.812(2)	Ru(2)—C(6)	1.841(17)
Ru(1)—Ru(3)	2.810(2)	Ru(2)—C(10)	2.178(15)
Ru(2)—Ru(3)	2.791(2)	Ru(2)—C(11)	2.188(14)
Ru(1)—C(1)	1.876(17)	Ru(3)—C(7)	1.897(17)
Ru(1)—C(2)	1.894(17)	Ru(3)—C(8)	1.902(16)
Ru(1)—C(3)	1.915(19)	Ru(3)—C(9)	1.892(21)
Ru(1)—C(10)	1.904(14)	Ru(3)—C(10)	2.190(15)
Ru(2)—C(4)	1.937(20)	Ru(3)—C(11)	2.276(14)
Ru(2)—C(5)	1.853(15)		

Ru(2)—Ru(1)—Ru(3)	59.5(1)	C(5)—Ru(2)—C(11)	160.8(6)
Ru(3)—Ru(2)—Ru(1)	60.2(1)	C(5)—Ru(2)—Ru(1)	86.4(5)
Ru(1)—Ru(3)—Ru(2)	60.3(1)	C(6)—Ru(2)—C(10)	92.9(6)
Ru(2)—Ru(1)—C(1)	98.9(5)	C(6)—Ru(2)—C(11)	94.6(6)
Ru(2)—Ru(1)—C(2)	106.6(5)	C(6)—Ru(2)—Ru(1)	98.5(6)
Ru(2)—Ru(1)—C(3)	154.2(6)	C(10)—Ru(2)—C(11)	33.9(6)
Ru(2)—Ru(1)—C(10)	50.7(4)	C(10)—Ru(2)—Ru(1)	42.5(4)
Ru(4)—Ru(1)—C(1)	155.2(5)	C(11)—Ru(2)—Ru(1)	75.8(4)
Ru(3)—Ru(1)—C(2)	105.0(6)	C(7)—Ru(3)—C(8)	93.4(7)
Ru(3)—Ru(1)—C(3)	101.7(6)	C(7)—Ru(3)—C(9)	101.9(9)
Ru(3)—Ru(1)—C(10)	51.1(5)	C(7)—Ru(3)—C(10)	129.8(8)
C(1)—Ru(1)—C(2)	92.5(7)	C(7)—Ru(3)—C(11)	157.2(7)
C(1)—Ru(1)—C(3)	94.1(8)	C(7)—Ru(3)—Ru(1)	87.4(7)
C(1)—Ru(1)—C(10)	106.6(7)	C(7)—Ru(3)—Cu(2)	109.0(5)
C(2)—Ru(1)—C(3)	94.9(7)	C(8)—Ru(3)—C(9)	92.5(8)
C(2)—Ru(1)—C(10)	151.6(8)	C(8)—Ru(3)—C(10)	96.0(7)
C(3)—Ru(1)—C(10)	104.2(7)	C(8)—Ru(3)—C(11)	102.4(6)
Ru(3)—Ru(2)—C(4)	107.9(5)	C(8)—Ru(3)—Ru(1)	97.0(6)
Ru(3)—Ru(2)—C(5)	111.9(4)	C(8)—Ru(3)—Ru(2)	146.1(5)
Ru(3)—Ru(2)—C(5)	142.9(5)	C(9)—Ru(3)—C(10)	126.6(7)
Ru(3)—Ru(2)—C(10)	50.5(4)	C(9)—Ru(3)—C(11)	93.7(7)
Ru(3)—Ru(2)—C(11)	52.7(4)	C(9)—Ru(3)—Ru(1)	166.3(5)
C(4)—Ru(2)—C(5)	95.6(7)	C(9)—Ru(3)—Ru(2)	106.8(6)
C(4)—Ru(2)—C(6)	93.6(8)	C(10)—Ru(3)—C(11)	33.0(6)
C(4)—Ru(2)—C(10)	134.1(6)	C(10)—Ru(3)—Ru(1)	42.6(4)
C(4)—Ru(1)—C(11)	100.3(6)	C(10)—Ru(3)—Ru(2)	50.1(4)
C(4)—Ru(2)—Ru(1)	167.5(6)	C(11)—Ru(3)—Ru(1)	74.6(4)
C(5)—Ru(2)—C(6)	95.1(7)	C(11)—Ru(3)—Ru(2)	49.9(4)
C(5)—Ru(2)—C(10) 1	128.9(6)		

(ii) in the carbonyl groups

O(1)—C(1)	1.146(22)	O(6)—C(6)	1.199(23)
O(2)—C(2)	1.153(21)	O(7)—C(7)	1.147(20)
O(3)—C(3)	1.140(24)	O(8)—C(8)	1.139(20)
O(4)—C(4)	1.155(26)	O(9)—C(9)	1.148(29)
O(5)—C(5)	1.155(20)		

Ru(1)—C(1)—O(1)	175.9(1.4)	Ru(2)—C(6)—O(6)	173.0(1.7)
Ru(1)—C(2)—O(2)	174.6(1.7)	Ru(3)—C(7)—O(7)	175.9(2.0)
Ru(1)—C(3)—O(3)	175.6(1.8)	Ri(3)—C(8)—O(8)	176.7(1.7)
Ru(2)—C(4)—O(4)	176.4(1.5)	Ru(3)—C(9)—O(9)	176.5(1.7)
Ru(2)—C(5)—O(5)	179.2(1.6)		

(iii) in the organic ligand

C(19)—C(11)	1.272(22)	C(14)—C(19)	1.366(23)
C(11)—C(12)	1.529(21)	C(15)—C(16)	1.381(21)
C(12)—C(13)	1.337(27)	C(16)—C(17)	1.406(26)

TABLE (continued)

(iii) in the organic ligand

C(12)—C(14)	1.492(20)	C(17)—C(18)	1.358(29)
C(14)—C(15)	1.421(22)	C(18)—C(19)	1.388(24)
Ru(1)—C(10)—Ru(2)	86.8(6)	Ru(3)—C(11)—C(10)	69.7(9)
Ru(1)—C(10)—Ru(3)	86.4(5)	C(13)—C(12)—C(14)	122.5(1.4)
Ru(2)—C(10)—Ru(3)	79.4(5)	C(13)—C(12)—C(11)	120.2(1.4)
C(11)—C(10)—Ru(1)	156.3(1.3)	C(14)—C(12)—C(11)	117.3(1.3)
C(11)—C(10)—Ru(2)	73.5(9)	C(15)—C(14)—C(19)	118.9(1.4)
C(11)—C(10)—Ru(3)	77.2(9)	C(15)—C(14)—C(12)	120.6(1.3)
C(12)—C(11)—Ru(2)	135.6(1.0)	C(19)—C(14)—C(12)	120.4(1.4)
C(12)—C(11)—Ru(3)	126.8(1.0)	C(16)—C(15)—C(14)	119.2(1.5)
C(12)—C(11)—C(10)	145.9(1.4)	C(17)—C(16)—C(15)	119.9(1.7)
Ru(2)—C(11)—Ru(3)	77.4(4)	C(19)—C(18)—C(17)	119.5(1.8)
Ru(2)—C(11)—C(10)	72.6(9)	C(14)—C(19)—C(18)	121.8(1.8)

TABLE 3

CRYSTAL DATA FOR $HRu_3(CO)_9(C_{10}H_7)$

a 9.675(8) Å	Triclinic
b 14.096(12) Å	Space group: $P\bar{1}$
c 8.985(8) Å	Mo-K_α radiation
α 93.78(8)°	μ(Mo-K_α) 20.70 cm^{-1}
β 117.17(11)°	$Z = 2$
γ 92.15(8)°	$d_{calc.}$ 2.09 g cm^{-3}
V 1085(2) $Å^3$	

TABLE 4

FRACTIONAL ATOMIC COORDINATES (X 10^4)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Ru(1)	3943(1)	7171(1)	5598(1)	C(9)	—897(20)	7808(13)	5235(22)
Ru(1)	2525(1)	6297(1)	7332(1)	C(10)	3329(16)	7732(10)	7169(16)
Ru(3)	963(1)	7624(1)	5083(1)	C(11)	2491(14)	7825(10)	7916(17)
O(1)	7216(14)	6619(9)	7702(15)	C(12)	2130(17)	8438(10)	8191(17)
O(2)	3243(16)	5779(10)	2560(16)	C(13)	1799(27)	8026(13)	10258(23)
O(3)	4909(81)	8907(9)	4334(19)	C(14)	2410(15)	9494(10)	9224(16)
O(4)	245(16)	5484(10)	8549(18)	C(15)	3201(17)	9900(10)	8391(17)
O(5)	2671(18)	4449(9)	5553(17)	C(16)	3405(20)	10880(11)	8465(19)
O(6)	5532(18)	6094(9)	10483(16)	C(17)	2867(19)	11463(12)	8392(22)
O(7)	—364(17)	6693(9)	1505(14)	C(18)	2153(22)	11070(12)	10226(25)
O(8)	1151(17)	9607(8)	4015(15)	C(19)	1936(19)	10085(12)	10140(21)
O(9)	—1982(19)	7948(11)	5402(21)	H(1)	1244	6451	5378
C(1)	5978(17)	6816(11)	6852(19)	H(131)	1591	8449	11137
C(2)	3585(18)	6305(11)	3733(21)	H(132)	1648	7298	10235
C(3)	4580(20)	8237(13)	4781(22)	H(15)	3637	9447	7708
C(4)	1137(21)	5788(10)	8148(19)	H(16)	3977	11199	7811
C(5)	2604(16)	5157(10)	6233(18)	H(17)	3023	12229	9441
C(6)	4293(19)	6156(11)	9293(20)	H(18)	1757	11521	10951
C(7)	190(22)	7046(11)	2856(21)	H(19)	1377	9778	10816
C(8)	1061(20)	8875(11)	4444(18)				

TABLE 5

ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS. THEY ARE IN THE FORM: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots U_{12}hka^*b^*]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	437(6)	415(6)	385(6)	65(4)	230(5)	65(5)
Ru(2)	487(5)	335(5)	361(5)	104(4)	197(5)	59(4)
Ru(3)	412(6)	395(6)	342(5)	120(4)	187(5)	73(4)
O(1)	513(71)	976(92)	683(78)	62(66)	205(62)	221(64)
O(2)	952(100)	809(86)	686(81)	−105(68)	448(76)	113(73)
O(3)	1213(118)	698(82)	1197(116)	354(79)	790(101)	−13(77)
O(4)	940(100)	863(94)	985(1010	257(78)	662(88)	−51(75)
O(5)	1224(116)	501(70)	780(86)	−14(62)	474(84)	65(71)
O(6)	1242(115)	636(79)	631(81)	277(65)	−68(79)	−44(75)
O(7)	1124(107)	782(84)	403(65)	−30(60)	185(68)	102(75)
O(8)	1171(107)	497(67)	632(74)	266(58)	268(73)	4(66)
O(9)	983(112)	1116(114)	1406(134)	570(98)	775(106)	287(89)
C(1)	482(82)	561(87)	535(82)	56(67)	317(71)	98(66)
C(2)	499(85)	622(89)	626(96)	149(76)	397(79)	161(69)
C(4)	570(102)	746(118)	618(102)	16(88)	377(88)	23(87)
C(4)	842(116)	387(68)	486(86)	139(61)	334(86)	84(70)
C(5)	435(77)	452(78)	515(80)	76(84)	206(66)	30(61)
C(6)	663(99)	429(82)	542(93)	179(70)	259(83)	92(71)
C(7)	858(122)	402(76)	563(96)	90(68)	350(92)	33(76)
C(8)	763(113)	520(89)	311(72)	75(64)	107(74)	74(78)
C(9)	543(96)	708(110)	725(111)	351(89)	369(89)	221(81)
C(10)	477(77)	373(72)	346(67)	77(56)	145(61)	10(58)
C(11)	310(61)	458(78)	427(75)	105(61)	201(59)	42(54)
C(12)	584(85)	425(75)	416(70)	72(58)	299(67)	79(63)
C(13)	1375(182)	667(115)	675(116)	104(92)	781(131)	118(115)
C(14)	396(71)	456(72)	354(67)	20(55)	152(58)	67(56)
C(15)	556(86)	438(76)	407(73)	99(59)	169(67)	−6(64)
C(16)	743(110)	441(85)	469(77)	114(65)	109(76)	−23(76)
C(17)	532(95)	481(90)	678(105)	−12(78)	104(83)	28(73)
C(18)	707(118)	557(96)	817(128)	−34(88)	370(104)	47(84)
C(19)	634(96)	536(95)	627(96)	−13(75)	358(83)	123(76)

The olefinic bond distance C(12)—C(13) (1.337 Å) agrees with a localized double bond and indicates that there is no conjugative interaction of the olefin with the cluster. The C(11)—C(12)—C(13)—C(14) moiety is perfectly planar, the plane passing through these atoms is nearly parallel to that passing through the phenyl ring C(14)···C(19) (the dihedral angle between the two planes is 13.0°) and forms a dihedral angle of 61.1° with the plane through the metal atoms of the cluster. Final atomic coordinates and thermal parameters are given in Tables 4 and 5. A list of observed and calculated structure factors is available from the authors on request.

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

Experimental

I. Synthetic Procedure

Materials. $Ru_3(CO)_{12}$ was made by established procedures from $RuCl_3 \cdot 1$—3

H_2O purchased from Mathey—Bishop. All reactions were carried out under an atmosphere of pre-purified nitrogen. All solvents used were dried over molecular sieves. Thin layer chromatography was performed using silica gel 60PF-254 (EM Reagents) (plates prepared as per directions). Column chromatography was performed using grade III activity silica gel also prepared from the above silica (200 mesh).

Preparation of $HRu_3(CO)_9(C_{10}H_9O)$ (II). A mixture of 0.5 g $Ru_3(CO)_{12}$ 0.78 mmol), 1.0 g 2-phenyl-3-butyn-2-ol (6.8 mmol) and 600 ml hexane was refluxed for 3 h after which the $Ru_3(CO)_{12}$ was consumed. The solution was filtered, and evaporated to dryness. TLC was used to isolate the product, with 1/1 hexane benzene as eluant. A single yellow band was extracted with CH_2Cl_2 and recrystallized from heptane. (Yield: 180 mg, 33%).

Preparation of $HRu_3(CO)_9(C_6H_9O)$ (III). A mixture of 0.5 g $Ru_3(CO)_{12}$ (0.78 mmol), 0.5 ml 3-methyl-1-pentyn-3-ol (4.4 mmol) and 500 ml hexane was refluxed for 2 h. The solution was filtered and evaporated. Column chromatography with benzene as eluant was used to isolate the product. Upon evaporation of the product fraction, the compound crystallized as a bright yellow solid which was recrystallized from heptane (yield: 290 mg, 58%).

Preparation of IV—VI. The reaction of $Ru_3(CO)_{12}$ with $(CH_3)_2C(X)C{\equiv}CH$ (X = Cl, OH, H) was carried out in a variety of solvents (30—60 petroleum ether, hexane, cyclohexane) and with various ratios of acetylene: $Ru_3(CO)_{12}$ (2/1—6/1). In all three cases small amounts of the expected complex (HRu_3-$(CO)_9((CH_3)_2C(X)(C{\equiv}C))$) was isolated by TLC (hexane/benzene 1/1). An insoluble Ru containing precipitate were isolated in all three cases in amounts which accounted for most of the reactant mass.

Preparation of $HRu_3(CO)_9(C_{10}H_7)$ (VII). A mixture of 100 mg $HRu_3(CO)_9$-$(C_{10}H_9O)$ (0.14 mmol) in 15 ml C_6H_6 and 50 μl CF_3COOH (0.67 mmol) in 10 ml C_6H_6 was stirred for 3.5 h at room temperature. 75 μl triethylamine was then added to neutralize the excess acid. Upon column chromatography (elution with 1/1 hexane/benzene) a bright yellow band was obtained, and the fraction which included this was evaporated to dryness and the product recrystallized from warm heptane (yield: 20 mg, 20%).

Preparation of $HRu_3(CO)_9(C_6H_7)$ (VIII). A mixture of 100 mg $HRu_3(CO)_9$-(C_6H_9O) (0.15 mmol), 15 ml C_6H_6 and 1 ml CF_3COOH in 10 ml C_6H_6 was stirred for 45 min at room temperature. The solution was washed with two 30 ml portions of 10% Na_2CO_3, then dried over $MgSO_4$, filtered, and column chromatographed with 1/1 hexane/benzene as eluent. The product was recrystallized from heptane (yield: 50 mg, 55%).

II. Crystallographic Data

A yellow crystal of $HRu_3(CO)_9(C_{10}H_7)$ (VII) with dimensions of ca. 0.35 × 0.42 × 0.50 mm was used for data collection. Preliminary unit-cell parameters were determined from rotation and Weissenberg photographs and refined by a least-squares procedure applied to the θ values of 19 reflections carefully measured on a Siemens AED single-crystal diffractometer. Cell dimensions and crystal data are summarized in Table 3.

Intensity data were collected at room temperature on the same diffractometer, by use of Nb-filtered Mo-K_α radiation and the θ—2θ scan technique. 4502 independent reflections with θ in the range 3—27° were measured, 3715 of them, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was made. The first absolute scaling and the overall isotropic temperature factor were obtained by the Wilson's method.

The structure was solved by Patterson and Fourier methods and refined by least-squares full-matrix cycles using the SHELX system of computer programs [4], with initially isotropic and then anisotropic thermal parameters for the non-hydrogen atoms. The hydridic hydrogen was localized clearly in a difference map, whereas the other hydrogen atoms could not be precisely localized, and were placed in their geometrically calculated positions. All the hydrogen atoms were included in the final structure factors calculations with isotropic thermal parameters, but not refined. Unit weights were chosen at every stage of the refinement by analyzing the variation of $|\Delta F|$ with $|F_0|$. The final R was 0.054 (observed reflections only). The atomic scattering factors used (corrected for the anomalous dispersion of Ru) were taken from the International Table [5].

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