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Synthesis and Crystal Structure of Heptacarbonyl-Hydrido-(t-butylethynyl)-(2,4-hexadiene)-*triangulo*-triruthenium, $HRu_3(CO)_7(C_6H_9)(C_6H_{10})$

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*The reactions of $HRu_3(CO)_9C_2C(CH_3)_3$ with 2*cis*, 4*trans*-hexadiene and 1,5-hexadiene afford as main product the same complex $HRu_3(CO)_7(C_6H_9)(C_6H_{10})$ suggesting that isomerization of the non conjugated species occurs in the reaction. The crystal structure of this compound 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 = 10.230(8), b = 10.487(9), c = 19.084(13) Å, α = 49.3(1), β = 126.4(1), and γ = 127.9(1)°. 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 4303 observed reflections. The molecule is formed by a three-metal atom cluster with seven terminal CO groups; one hydridic hydrogen atom is bridge-bonding two ruthenium atoms on one side of the cluster. A t-butylethynyl group is bound to the three metals* via *a σ bond to one Ru and two η bonds to the other two Ru atoms; opposite to this group with respect to the cluster a 2*trans*, 4*trans*-hexadienic unit bridges two Ru atoms* via *two η bonds.*

Introduction

Recently it has been shown that cyclic and alicyclic dienes are capable of reaction with metal carbonyls of the iron triad yielding metal clusters in which several carbonyls are substituted and the diene retains its identity [1–4]. The diene is η bonded to one metal centre (*cis* form) or to two metal atoms (*trans* form) [2, 3] or σ and η bonded to three metal atoms forming a metallo-cyclopentadiene ring [1]. Alternatively the metal atoms may promote the activation of the carbon–hydrogen or carbon–carbon bonds of the diene causing a rearrangement of the diene and the hydrogen transfer from the ligand to the cluster [1, 2, 5–8].

By reacting $Ru_3(CO)_{12}$ with alkynes we have recently obtained complexes in which a dienic unit is formed: in the reactions of $Ru_3(CO)_{12}$ with non terminal alkynes the complexes $Ru_3(CO)_8L_2$ (L = alkyne) have been obtained in which a metallo-cyclopentadiene ring is present [9] whereas in the reactions of $Ru_3(CO)_{12}$ with terminal alkynes the complexes $Ru_3(CO)_6L_2[L(CO)L]$ (L = alkyne) (I) have been obtained, in which the unit L_2 is formed by dimerization of two molecules of alkyne [10] (Figure 1). Similarly it has been reported that t-butylacetylene dimerizes to *trans*-1,4-di-t-butylbutatriene in the presence of a catalytic amount of $H_2Ru(CO)(PPh_3)_3$ [11].

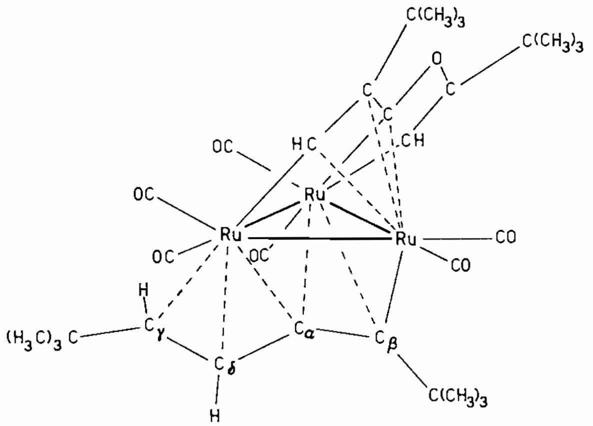

Figure 1. Molecular structure of I.

The complexes I are obtained either as minor products of the reaction of $Ru_3(CO)_{12}$ with 3,3-dimethyl-but-1-yne, or by reacting the main product of this reaction, $HRu_3(CO)_9C_2C(CH_3)_3$ [12] (II), whose structure is represented in Figure 2, with an excess of alkyne. By deuterium labelling experiments we have shown that the diene unit is formed by addition of one molecule of alkyne to the t-butylethynyl group coordinated to the metal atoms in II [13].

We have further investigated the reactivity of II by reacting it with dienes (2*cis*-4*trans*-hexadiene and 1,5-hexadiene). These reactions give as main product

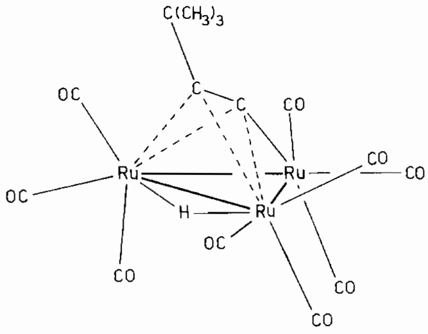

Figure 2. Molecular structure of II.

$HRu_3(CO)_7(C_6H_9)(C_6H_{10})$ (III), whose structure, determined by an X-ray analysis, shows that the diene (rearranged to *trans*,2,4-hexadiene) substitutes two carbonyl groups without significant modifications of the basic structure of II.

Experimental

*Reaction of $HRu_3(CO)_9C_2C(CH_3)_3$ with 2*cis, *4*trans-*hexadiene*

The ruthenium hydride (600 mg, 1 m*M ca.*) was refluxed with an excess of the diene (1 ml) in n-heptane for eight hours. After cooling the solution was filtered and the solvent removed under reduced pressure. The residue was extracted with $CHCl_3$ and separated by t.l.c. to give as main product (about 20% yield) a yellow solid which has been crystallized from n-heptane at 0 °C; crystals suitable for X-ray analysis were obtained by slowly evaporating n-heptane solutions. No other solvents were suitable for obtaining the compound in crystalline form.

On the basis of elemental analysis, i.r., mass and n.m.r. spectra, the compound has been identified as $HRu_3(CO)_7(C_{12}H_{19})$. It analyzes as follows: Calcd. for $C_{19}H_{20}O_7Ru_3$: C% 34.29, H% 3.03, 0% 16.83, Ru% 45.85. Found: C% 34.46, H% 3.12, 0% 17.26, Ru% 45.16. ν_{max} (CO stretching region, n-heptane): 2072 vs, 2032 vs, 2016 vs, 1992 s, 1977 s, 1962 s, cm^{-1}.

Mass spectrum: m/e 666 (M^+) followed by loss of seven carbonyl groups.

^1H n.m.r. spectrum (CCl_4, ppm downfield from T.M.S.): 4.36 (m, 2), 2.28 (d, 3), 2.14 (d, 3), 1.65 (s, 9), 1.47 (m, 2), −23.9 (s, 1).

Reaction of $HRu_3(CO)_9C_2C(CH_3)_3$ with 1,5-hexadiene

The reaction was carried out and the products separated as described above. The main product of the reaction has been identified as $HRu_3(CO)_7(C_{12}H_{19})$ and shown to have elemental composition and spectroscopic properties identical to those of the compound obtained using 2*cis*, 4*trans*-hexadiene.

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)	1792(1)	−243(1)	2449(1)
Ru(2)	−1823(1)	−1372(1)	1996(1)
Ru(3)	571(1)	−861(1)	3700(1)
O(1)	5580(13)	1280(16)	3537(9)
O(2)	2240(20)	1909(20)	480(10)
O(3)	−2934(21)	396(21)	−203(9)
O(4)	−5404(15)	−3059(20)	2137(11)
O(5)	−1476(19)	−2006(24)	4839(12)
O(6)	2194(15)	−3703(16)	5262(8)
O(7)	3723(16)	2099(18)	4289(10)
C(1)	4148(19)	695(19)	3130(12)
C(2)	2079(20)	1002(20)	1253(12)
C(3)	−2525(21)	−287(23)	655(12)
C(4)	−4064(19)	−2391(22)	2064(11)
C(5)	−723(20)	−1523(23)	4390(13)
C(6)	1591(18)	−2611(20)	4663(10)
C(7)	2558(19)	979(20)	4081(12)
C(8)	3743(21)	−3139(26)	3674(16)
C(9)	2294(17)	−2529(18)	2787(12)
C(10)	711(17)	−3188(19)	2885(10)
C(11)	−892(17)	−3056(16)	2071(11)
C(12)	−2567(16)	−4060(18)	2187(11)
C(13)	−4160(21)	−4619(25)	1422(14)
C(14)	521(16)	938(17)	2164(9)
C(15)	−631(16)	1050(17)	2204(10)
C(16)	−1296(20)	2404(21)	1837(13)
C(17)	−1927(39)	3295(35)	730(18)
C(18)	124(33)	3822(36)	2128(28)
C(19)	−2784(40)	1528(38)	2155(29)
H(1)	−80(14)	−170(14)	302(8)
H(81)	380(16)	−3460(16)	427(9)
H(82)	476(17)	−218(16)	345(9)
H(83)	352(15)	−448(17)	389(9)
H(9)	204(14)	−238(14)	206(8)
H(10)	48(14)	−405(14)	340(8)
H(11)	−104(14)	−290(14)	142(8)
H(12)	−264(14)	−486(15)	276(8)
H(131)	−431(15)	−581(16)	169(9)
H(132)	−418(15)	−377(16)	75(9)
H(133)	−535(15)	−494(15)	141(8)
H(171)	−235(14)	428(15)	44(8)
H(172)	−273(16)	245(17)	55(9)
H(173)	−88(17)	398(17)	47(9)
H(181)	−23(14)	475(15)	189(8)
H(182)	121(17)	462(17)	195(9)
H(183)	52(17)	340(17)	280(10)
H(191)	−253(17)	76(18)	294(9)
H(192)	−367(16)	70(18)	195(9)
H(193)	−304(15)	259(16)	191(9)

The compounds were analyzed by means of an F. & M. 185 Model C, H, N. Analyzer, and a 303 Model Perkin Elmer Atomic Absorption Spectrophotometer. Infrared spectra were registered with a Beckman IR-12 instrument, with KBr optics and carbon monoxide as calibrant. ^1H n.m.r. spectra were

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

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	362(5)	440(5)	431(6)	−218(4)	109(4)	144(4)
Ru(2)	356(5)	427(5)	446(6)	−240(4)	46(4)	157(4)
Ru(3)	378(5)	523(6)	453(6)	−282(5)	106(4)	128(4)
O(1)	445(56)	897(82)	869(84)	−626(73)	6(54)	132(55)
O(2)	1167(114)	1115(112)	681(85)	−303(82)	415(81)	398(92)
O(3)	1399(132)	1155(113)	524(75)	−262(75)	−5(78)	770(104)
O(4)	496(67)	1149(111)	1361(127)	−662(100)	300(75)	199(70)
O(5)	902(103)	1840(150)	1194(123)	−904(119)	426(94)	382(103)
O(6)	719(72)	714(71)	539(63)	−209(56)	128(54)	304(60)
O(7)	605(71)	962(94)	1120(107)	−741(88)	84(69)	108(66)
C(1)	533(78)	484(75)	846(108)	−460(77)	249(75)	56(60)
C(2)	598(86)	532(80)	595(92)	−305(73)	174(72)	159(66)
C(3)	655(93)	731(103)	515(89)	−302(80)	30(71)	375(82)
C(4)	463(78)	683(95)	583(90)	−278(77)	123(67)	183(70)
C(5)	524(85)	807(108)	729(107)	−542(93)	161(77)	88(75)
C(6)	498(75)	552(80)	461(78)	−204(67)	191(62)	122(63)
C(7)	533(81)	573(85)	788(109)	−452(83)	151(75)	126(67)
C(8)	494(87)	803(120)	946(143)	−528(110)	86(86)	271(84)
C(9)	467(70)	533(72)	751(104)	−399(74)	95(68)	185(58)
C(10)	450(66)	577(78)	450(75)	−236(64)	86(56)	225(59)
C(11)	505(69)	393(59)	614(88)	−331(61)	73(62)	153(52)
C(12)	427(63)	419(68)	494(84)	−229(65)	65(58)	137(53)
C(13)	527(85)	534(100)	695(114)	−403(96)	57(77)	117(73)
C(14)	431(62)	467(67)	415(66)	−213(55)	77(51)	194(53)
C(15)	426(63)	435(65)	634(85)	−404(65)	81(58)	103(51)
C(16)	580(87)	621(90)	887(123)	−383(88)	155(83)	303(73)
C(17)	1338(228)	924(173)	1156(166)	−409(140)	52(157)	788(180)
C(18)	1080(178)	1096(172)	2587(352)	−1513(225)	−144(206)	434(149)
C(19)	1373(224)	1107(204)	2409(382)	−549(239)	1002(251)	601(182)
H(1)	24(28)					
H(81)	92(35)					
H(82)	78(33)					
H(83)	67(33)					
H(9)	66(28)					
H(10)	67(28)					
H(11)	65(28)					
H(12)	30(30)					
H(131)	60(31)					
H(132)	51(32)					
H(133)	59(29)					
H(171)	83(28)					
H(172)	87(34)					
H(173)	87(37)					
H(181)	65(28)					
H(182)	130(37)					
H(183)	103(37)					
H(191)	94(39)					
H(192)	117(36)					
H(193)	115(32)					

obtained on a JEOL C-60 HL instrument and the mass spectra were registered on a Varian CH-5 single-focusing instrument, operating at 70 eV, either in absence or in presence of perfluoroalkanes as internal standards.

All reactions were carried out in an atmosphere of dry nitrogen; solvents were dried over molecular sieves. Dodecacarbonyl triruthenium was prepared according to the literature [14]. The dienes were purchased from Fluka and used directly. Separa-

TABLE III. Bond Distances (Å) and Angles (°) (Non-involving Hydrogen Atoms) with Estimated Standard Deviations in Parentheses.

i) In the Coordination Sphere of the Ruthenium Atoms

Ru(1)–Ru(2)	2.826(2)	Ru(2)–C(11)	2.371(24)
Ru(1)–Ru(3)	2.864(2)	Ru(2)–C(12)	2.239(21)
Ru(2)–Ru(3)	2.841(2)	Ru(2)–C(14)	2.165(13)
Ru(1)–C(1)	1.872(13)	Ru(2)–C(15)	2.243(20)
Ru(1)–C(2)	1.854(17)	Ru(3)–C(5)	1.928(22)
Ru(1)–C(9)	2.351(21)	Ru(3)–C(6)	1.873(18)
Ru(1)–C(10)	2.236(17)	Ru(3)–C(7)	1.909(17)
Ru(1)–C(14)	1.944(21)	Ru(3)–C(14)	2.209(13)
Ru(2)–C(3)	1.839(17)	Ru(3)–C(15)	2.252(14)
Ru(2)–C(4)	1.891(17)		

Ru(2)–Ru(1)–Ru(3)	59.9(1)	C(3)–Ru(2)–C(4)	95.2(7)
Ru(1)–Ru(2)–Ru(3)	60.7(1)	C(3)–Ru(2)–C(11)	89.2(10)
Ru(1)–Ru(3)–Ru(2)	59.4(1)	C(3)–Ru(2)–C(12)	94.6(10)
Ru(2)–Ru(1)–C(1)	152.3(7)	C(3)–Ru(2)–C(14)	96.1(8)
Ru(2)–Ru(1)–C(2)	104.5(5)	C(3)–Ru(2)–C(15)	99.2(10)
Ru(2)–Ru(1)–C(9)	108.9(4)	C(4)–Ru(2)–C(11)	120.4(10)
Ru(2)–Ru(1)–C(10)	75.6(4)	C(4)–Ru(2)–C(12)	84.6(10)
Ru(2)–Ru(1)–C(14)	49.9(5)	C(4)–Ru(2)–C(14)	133.7(10)
Ru(3)–Ru(1)–C(1)	93.2(7)	C(4)–Ru(2)–C(15)	99.5(10)
Ru(3)–Ru(1)–C(2)	151.2(8)	C(11)–Ru(2)–C(12)	35.8(6)
Ru(3)–Ru(1)–C(9)	120.7(4)	C(11)–Ru(2)–C(14)	104.6(7)
Ru(3)–Ru(1)–C(10)	93.7(5)	C(11)–Ru(2)–C(15)	138.4(6)
Ru(3)–Ru(1)–C(14)	50.4(4)	C(12)–Ru(2)–C(14)	138.7(7)
C(1)–Ru(1)–C(2)	96.7(8)	C(12)–Ru(2)–C(15)	165.2(5)
C(1)–Ru(1)–C(9)	89.8(9)	C(14)–Ru(2)–C(15)	34.3(7)
C(1)–Ru(1)–C(10)	115.6(9)	Ru(1)–Ru(3)–C(5)	168.0(6)
C(1)–Ru(1)–C(14)	109.1(10)	Ru(1)–Ru(3)–C(6)	84.9(6)
C(2)–Ru(1)–C(9)	86.4(10)	Ru(1)–Ru(3)–C(7)	96.2(7)
C(2)–Ru(1)–C(10)	106.1(10)	Ru(1)–Ru(3)–C(14)	42.7(6)
C(2)–Ru(1)–C(14)	100.8(9)	Ru(1)–Ru(3)–C(15)	75.9(5)
C(9)–Ru(1)–C(10)	35.4(6)	Ru(2)–Ru(3)–C(5)	108.9(6)
C(9)–Ru(1)–C(14)	158.6(6)	Ru(2)–Ru(3)–C(6)	112.4(7)
C(10)–Ru(1)–C(14)	123.7(7)	Ru(2)–Ru(3)–C(7)	140.3(5)
Ru(1)–Ru(2)–C(3)	100.3(6)	Ru(2)–Ru(3)–C(14)	48.8(5)
Ru(1)–Ru(2)–C(4)	164.4(5)	Ru(2)–Ru(3)–C(15)	50.7(6)
Ru(1)–Ru(2)–C(11)	61.6(4)	C(5)–Ru(3)–C(6)	98.2(9)
Ru(1)–Ru(2)–C(12)	95.5(4)	C(5)–Ru(3)–C(7)	95.1(10)
Ru(1)–Ru(2)–C(14)	43.4(6)	C(5)–Ru(3)–C(14)	133.0(8)
Ru(1)–Ru(2)–C(15)	76.8(4)	C(5)–Ru(3)–C(15)	99.1(8)
Ru(3)–Ru(2)–C(3)	145.8(8)	C(6)–Ru(3)–C(7)	94.1(9)
Ru(3)–Ru(2)–C(4)	105.0(6)	C(6)–Ru(3)–C(14)	127.6(8)
Ru(3)–Ru(2)–C(11)	103.3(4)	C(6)–Ru(3)–C(15)	159.3(9)
Ru(3)–Ru(2)–C(12)	114.3(4)	C(7)–Ru(3)–C(14)	91.7(7)
Ru(3)–Ru(2)–C(14)	50.2(3)	C(7)–Ru(3)–C(15)	95.6(8)
Ru(3)–Ru(2)–C(15)	51.0(4)	C(14)–Ru(3)–C(15)	33.9(7)

ii) In the Carbonyl Groups

O(1)–C(1)	1.137(16)	O(5)–C(5)	1.150(21)
O(2)–C(2)	1.172(22)	O(6)–C(6)	1.149(22)
O(3)–C(3)	1.181(21)	O(7)–C(7)	1.134(22)
O(4)–C(4)	1.144(22)		

Ru(1)–C(1)–O(1)	179.4(19)	Ru(3)–C(5)–O(5)	176.1(22)
Ru(1)–C(2)–O(2)	174.1(22)	Ru(3)–C(6)–O(6)	178.7(16)

(continued on facing page)

TABLE III. *(continued)*

Ru(2)–C(3)–O(3)	177.6(23)	Ru(3)–C(7)–O(7)	178.5(19)
Ru(2)–C(4)–O(4)	177.5(8)		
iii) In the Organic Ligands			
C(8)–C(9)	1.498(29)	C(14)–C(15)	1.303(27)
C(9)–C(10)	1.397(23)	C(15)–C(16)	1.514(30)
C(10)–C(11)	1.448(16)	C(16)–C(17)	1.516(31)
C(11)–C(12)	1.423(20)	C(16)–C(18)	1.487(40)
C(12)–C(13)	1.500(27)	C(16)–C(19)	1.516(37)
C(10)–C(19)–C(8)	119.4(15)	C(17)–C(16)–C(18)	108.1(25)
C(11)–C(10)–C(9)	123.5(14)	C(15)–C(16)–C(17)	107.6(25)
C(10)–C(11)–C(12)	123.2(13)	C(15)–C(16)–C(18)	109.7(22)
C(11)–C(12)–C(13)	119.9(16)	C(15)–C(16)–C(19)	111.6(26)
Ru(1)–C(14)–C(15)	156.6(14)	C(17)–C(16)–C(19)	107.8(23)
C(14)–C(15)–C(16)	141.8(16)	C(18)–C(16)–C(19)	111.9(30)

tions were performed by t.l.c., absorbent Kieselgel PF, Merck, eluent petroleum ether.

Crystal Data

$C_{19}H_{20}O_7Ru_3$, M = 663.57, Triclinic, a = 10.230(8), b = 10.487(9), c = 19.084(13) Å, α = 49.3(1), β = 126.4(1), γ = 127.9(1)°, V = 1159(2) Å^3, Z = 2, D_c = 1.90 g cm^{-3}, $F(000)$ = 644, Mo-K$_\alpha$ radiation, $\bar{\lambda}$ = 0.71069 Å, μ(Mo-Kα) = 19.27 cm^{-1}, space group $P\bar{1}$ from structure determination.

Unit cell dimensions, preliminarly determined from rotation and Weissenberg photographs, were refined by a least-squares procedure minimizing the differences between the observed and calculated 2θ values for 18 reflections measured on a single-crystal diffractometer.

Reduced cell parameters (a = 10.230, b = 14.596, c = 9.103 Å, α = 102.8, β = 114.6, γ = 70.4°) are obtained by applying the matrix // $\bar{1}$ 0 0 / 0 $\bar{1}$ 1 / 1 1 0 //.

Intensity Data

Intensity data were collected on a Siemens AED diffractometer by use of Zirconium-filtered Mo-K$_\alpha$ radiation and the ω–2θ scan technique. A prismatic crystal of dimensions *ca.* 0.20 × 0.25 × 0.40 mm was aligned with its c axis parallel to ϕ axis of the diffractometer and all reflections with $\theta < 29°$ were measured. Of 4990 independent reflections 4303 were considered observed, having $I \geqslant 2\sigma(I)$, and used in the analysis. The intensity data were corrected for Lorentz and polarization factors, but the absorption effect was neglected because of the low value of μR. The absolute scale and the mean temperature factor were determined by Wilson's method.

Structure Determination and Refinement

The structure was solved by Patterson and Fourier methods and the refinement was performed by means of SHELX system of computer programs [15]. Four cycles of full-matrix least squares using anisotropic thermal parameters for all the non hydrogen atoms were carried out. At this stage a ΔF map revealed clearly the positions of the hydrogen atoms of the two organic ligands. Great care was taken to localize the hydridic hydrogen atom; a peak only could be attributed to hydridic atom in the expected position bridging two Ru atoms so forming a symmetrical Ru–H–Ru bond, although the low accuracy of the determination of this type of hydrogen by X-ray was confirmed by the too short Ru–H distances (1.50 Å). Further least squares cycles were then computed including all the hydrogen atoms with isotropic thermal parameters. Unit weights were used at each stage of the refinement by analyzing the variation of $|\Delta F|$ as a function of $|F^o|$. Atomic scattering factors (corrected for anomalous dispersion effect of Ru) were taken from ref. [16]. The final R was 0.054 (observed reflections only). Final atomic co-ordinates and thermal parameters are given in Tables I and II. A list of calculated and observed structure factors is available from the authors on request.

All the calculations were carried out on a Cyber 76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna).

Results and Discussion

Structure of the Compound

The structure of $HRu_3(CO)_7(C_6H_9)(C_6H_{10})$ (III) is represented in Figure 3. Bond distances and angles not involving hydrogen atoms are given in Table III.

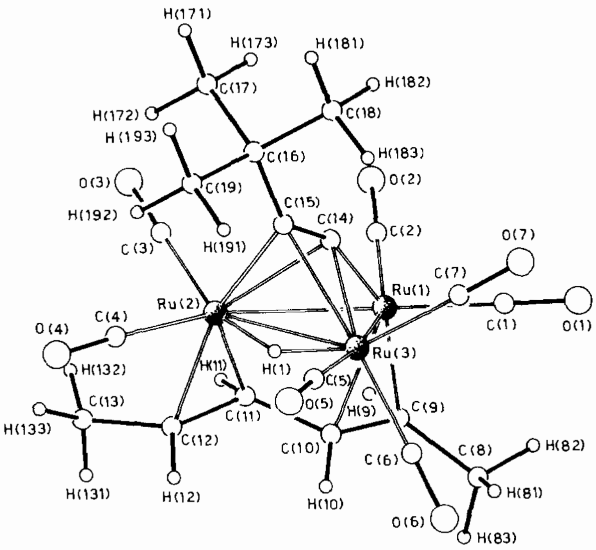

Figure 3. Molecular structure of $HRu_3(CO)_7(C_6H_9)(C_6H_{10})$ (III).

The molecule III can be considered as derived from II by substituting two carbonyls with the diene. The triruthenium cluster is in nearly equilateral triangular arrangement, the three Ru–Ru bonds [2.826, 2.841, 2.864 Å] being slightly longer than those in II [2.792, 2.795, 2.799 Å]. Two metals, Ru(1) and Ru(2), are bonded to two CO groups, and the third one, Ru(3), to three CO's. Of these seven terminal CO's, three, one for each metal atom, are equatorial and the other four, one for Ru(1) and Ru(2) and two for Ru(3), are axial; thus the substitution of two carbonyls with a diene in II has influenced the spatial disposition of the remaining carboxyls in the sense that they have been repelled towards the t-butylethynyl ligand.

Two substituent moieties are above and below the plane of the cluster; one of them is a t-butylethynyl ligand forming two η bonds with Ru(2) and Ru(3) and one σ bond with Ru(1), through its acetylenic triple bond and the carbon atom C(14) without substituent. This situation is quite similar, both in the bonding towards the metals in the C–C distance to the one found in II: Ru(1)–C(14) 1.944 in III, 1.947 in II, Ru(2)–C(14) and Ru(2)–C(15) 2.165 and 2.243 in III, 2.207 and 2.268 in II, Ru(3)–C(14) and Ru(3)–C(15) 2.209 and 2.252 in III, 2.214 and 2.271 in II, C(14)–C(15) 1.303 in III and 1.315 Å in II, C(14)–C(15)–C(16) 141.8 in III, 141.0° in II. The other organic ligand is a 2*trans*, 4*trans*-hexadienic unic η bonded to Ru(1) and Ru(2). The C–C bond distances show that the double bonds and the conjugated character of the diene are maintained, even if an isomerization from 2*cis*, 4*trans*-hexadiene or from 1,5-hexadiene has occurred. No hydrogen transfer from this ligand to the cluster is observed. This bonding situation of the diene is likely to be similar to the one in $Os_3(CO)_{10}$(s-*trans*-1,3-butadiene) [3], but unfortunately no comparison of structural data can be made. The carbon atoms C(9), C(10), C(11) and C(12) are roughly coplanar, the equation of the mean plane passing through them being: $0.2198X + 0.9666Y - 0.1317Z = -0.9179$*. C(9), C(10), C(11), C(12), C(8), C(13), Ru(1), Ru(2) and Ru(3) are displaced from this plane by −0.07, 0.04, 0.11, −0.08, −0.50, −0.67, 2.16, 2.15 and 3.20 Å respectively. The dihedral angle between this plane and the plane of the cluster is 64.8°.

The hydride atom H(1), poorly localized, bridges the edge Ru(2)–Ru(3) of the cluster, forming a symmetrical bent Ru–H–Ru tricentric bond in a way quite similar to that present in II, accurately determined by neutron diffraction [12].

^{1}H *N.m.r. Spectrum*

The ^{1}H n.m.r. spectrum of III shows resonances which are assigned, from low to high field, to the internal hydrogens and to the methyls of the dienic system, to the methyls of the Bu^t group, to the external hydrogens of the diene and to the hydride atom, respectively. The larger size of the upfield shift upon complexation of the protons bonded to C(9) and C(12) is in accord with what is normally found in coordinated dienes [17]. Close to each of the above resonances, other signals are present in the n.m.r. spectrum: they are less intense, and well defined only close to the two singlets at 1.65 and −23.9 ppm (at 1.68 and −24.1 ppm respectively). The integrated intensity of the peak at −24.1 ppm is one fourth of that at −23.9 ppm.

On this basis we interpret the additional resonances as indication of the presence, in solution, of a second species, which could not be separated from the main one either by t.l.c. or by column chromatography. Since the main difference is in the chemical shift of the hydride, we cannot exclude that the less abundant species is an isomer of the title compound in which the hydride is bridging one of the other two edges of the metallic triangle.

The identity of the main products obtained in the reaction of $HRu_3(CO)_9C_2C(CH_3)_3$ with a conjugated and a non-conjugated diene suggests that the isomerization occurs during the reaction with the substrate. Similar observations have been reported in the studies of the isomerization of dienes promoted by various metallic substrates [1, 6, 18].

The comparison of the products of the reaction of II with nucleophilic reagents such as alkynes and dienes shows that in the former case the entering alkyne is capable of insertion into the metal–carbon bond promoting as well hydrogen transfer from the

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*X, Y, Z are orthogonal coordinates in Å obtained from the fractional one applying the matrix: $//a\sin\gamma, 0, -c\sin\alpha\cos\beta^*/a\cos\gamma, b, c\cos\alpha/0, 0, c\sin\alpha\sin\beta^*//$.

metals to the ligand, whereas in the second case only substitution of carbonyls occurs.

So II, which is obtained from $Ru_3(CO)_{12}$ in very high yields and with a quite simple procedure, proves to be a suitable intermediate for the synthesis of a variety of substituted compounds.

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