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Products of the Reaction of $Ru_3(CO)_{12}$ with 1,3-Cyclohexadiene. X-Ray Structure of (η-Benzene)nonacarbonyl-1-cyclohexen-1,2-ylenetetraruthenium, $Ru_4(CO)_9(C_6H_6)(C_6H_8)$

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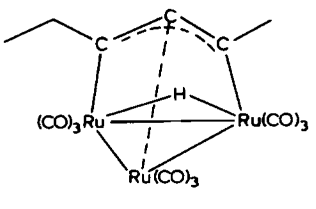
The reaction between $Ru_3(CO)_{12}$ and 1,3-cyclohexadiene has been carried on under different conditions: contrary to previous findings $Ru_3(CO)_{12}$ does not catalyze the cleavage and the hydrogenation of 1,3-cyclohexadiene. The products of the reaction have been characterized by i.r., n.m.r. and mass spectrometry. The crystal structure of the novel complex $Ru_4(CO)_9(C_6H_6)(C_6H_8)$ has been determined by X-ray methods. Crystals are monoclinic, space group $P2_1/c$ with Z = 4 in a unit cell of dimensions: a = 15.167(15), b = 10.114(9), c = 15.517(12) Å, β = 87.1(1)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.058 for 3828 observed reflections. A four metal atom cluster, in a "butterfly" arrangement, is coordinated by nine terminal CO groups, by a benzene molecule and a 1-cyclohexen-1,2-ylene unit obtained, respectively, by dehydrogenation and isomerization of two diene molecules.

Introduction

The potential of metal clusters in catalytic reactions and as models for chemisorption and heterogeneous catalysis has been recently discussed [1]. In particular, the activation of carbon–hydrogen bonds in a variety of molecules has been reported to occur in reactions with carbonyl clusters [2]. One notable example of the activation of both carbon–hydrogen and carbon–carbon bonds is the cleavage and the concomitant hydrogenation of 1,3-cyclohexadiene (CHD) by $Ru_3(CO)_{12}$ to produce the allyl ruthenium complex $HRu_3(CO)_9(C_6H_9)$ (I) [3]. However, the cleavage of a cyclic olefin has not been observed in the reactions of $H_4Ru_4(CO)_{12}$ and $Ru_3(CO)_{12}$ with cyclooctadienes [4], of $Ru_3(CO)_{12}$ with 1,5,9-cyclododecatriene [5] and of $H_2Os_3(CO)_{10}$ with CHD [6]. Additionally the formation of (I) has been reported to occur using n-heptane as a solvent, but not in benzene [3].



I

Thus we have reinvestigated the reaction of $Ru_3(CO)_{12}$ with CHD using different experimental conditions and various solvents. In this paper we report the results obtained and describe the crystal structure of the novel complex $Ru_4(CO)_9(C_6H_6)(C_6H_8)$, separated from the reaction products in n-octane.

Experimental

Reaction of $Ru_3(CO)_{12}$ and CHD in Cyclohexane

Dodecacarbonyltriruthenium (0.700 g, 1.09 mmol) and 1,3-cyclohexadiene (1.0 ml, 10.5 mmol) were dissolved in cyclohexane (500 ml) and refluxed for 16 hours. The cooled solution was filtered, concentrated under reduced pressure and separated by TLC (absorbent Kieselgel $PF_{254+366}$, eluent light petroleum and 20% diethyl ether) to give (II), (III) and (IV) with a large amount of unreacted $Ru_3(CO)_{12}$. (II), colourless oil, ν (cyclohexane): 2065 vs, 1995 s cm^{-1}; mass spectrum m/e 266 [M^+] followed by loss of three carbonyl groups. (III), pale yellow powder, ν(cyclohexane): 2014 m, 2075 s, 2053 vs, 2042 vs, 2027 m, 2012 s, 2003 m, 1986m, cm^{-1};

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mass spectrum m/e 638 [M^+] and fragments corresponding to loss of nine carbonyl groups concomitant with the loss of H_2. (IV), purple powder, ν(cyclohexane); 2091 m, 2063 vs, 2039 s, 2035 vs, 2013 s, 2003 m, cm^{-1}; mass spectrum, m/e 824 [M^+], followed by loss of twelve carbonyl groups.

Similar results were obtained when benzene or n-hexane were used as solvents.

Reaction of $Ru_3(CO)_{12}$ and CHD in n-Octane

Dodecacarbonyltriruthenium (0.700 g, 1.09 mmol) and 1,3-cyclohexadiene (3.0 ml, 31.5 mmol) were dissolved in n-octane (500 ml) and refluxed for 5 hours. After filtration the solution was dried under reduced pressure. The residue was extracted with chloroform and separated by TLC, absorbent as above, eluent light petroleum and 40% diethyl ether to yield (II), (III) and (V) with a little amount of unreacted $Ru_3(CO)_{12}$. (V), violet needles, ν(cyclohexane): 2061 s, 2037 vs, 2051 s, 1987 vs (b), 1969 m cm^{-1}; ^1H n.m.r. (CCl_4): δ 5.60 (s), 3.37 (m), 1.85 (m) with integrated intensities 3:2:2; mass spectrum, m/e 818 [M^+] followed by loss of nine carbonyl groups.

I.r. spectra were recorded on a Beckman IR 4230 spectrophotometer. Proton n.m.r. spectra were determined on a Jeol 60 HL spectrometer and mass spectra on a Hitachi RMU 6H mass spectrometer using an ionizing energy of 70 eV. All solvents were pure grade commercial products and were dried on molecular sieves and distilled before use.

All reactions were carried on under nitrogen.

X-ray Analysis of the Compound (V)

A flatted crystal of the compound (V) with dimensions of *ca.* 0.10 × 0.25 × 0.30 mm was used for the collection of all the data. Preliminary cell parameters obtained by rotation and Weissenberg photographs were subsequently refined by least squares fit to θ values of 18 reflections carefully measured on a Siemens AED single crystal diffractometer. The crystal data are: $C_{21}H_{14}O_9Ru_4$: M = 814.62, monoclinic, a: 15.167(15), b = 10.114(9), c = 15.517(12) Å, β = 87.1(1)°, V = 2377(3) $Å^3$, Z = 4, D_c = 2.27 g cm^{-3}, MoKα radiation (λ = 0.71069 Å), μ(MoKα) = 24.95 cm^{-1}, space group $P2_1/c$ from systematic absences.

A total of 6089 independent reflections with $\theta \leqslant 29°$ were measured on the same Siemens diffractometer using the Zr-filtered MoKα radiation and the ω–2θ scan technique. 3828 of these were used in the structure analysis having $I \geqslant 2\sigma(I)$. The intensity data were corrected for Lorentz and polarization factors, but no absorption correction was applied because of the low value of μR. The absolute scale and the mean temperature factor were determined by Wilson's method.

TABLE I. Fractional Atomic Coordinates (×10^4) with e.s.d.'s.

	x/a (σ)	y/b (σ)	z/c (σ)
Ru(1)	1619(1)	−1319(1)	1278(1)
Ru(2)	3701(1)	194(1)	2294(1)
Ru(3)	1966(1)	−32(1)	2749(1)
Ru(4)	2576(1)	858(1)	1111(1)
O(1)	−53(10)	234(13)	1125(9)
O(2)	1709(11)	−1902(13)	−633(8)
O(3)	822(11)	−3992(14)	1788(11)
O(4)	3588(9)	3031(10)	2904(7)
O(5)	5404(10)	546(12)	1209(9)
O(6)	4631(10)	−1000(13)	3798(9)
O(7)	329(8)	−1490(12)	3365(9)
O(8)	1162(10)	2729(11)	2971(9)
O(9)	2636(11)	−252(12)	4542(7)
C(1)	552(11)	−367(14)	1205(11)
C(2)	1688(10)	−1713(14)	119(9)
C(3)	1094(15)	−2983(16)	1651(15)
C(4)	3611(11)	1954(15)	2706(9)
C(5)	4769(12)	399(13)	1628(12)
C(6)	4285(11)	−557(13)	3203(9)
C(7)	942(10)	−946(14)	3099(9)
C(8)	1437(12)	1683(15)	2917(10)
C(9)	2389(10)	−123(13)	3850(9)
C(10)	2765(9)	−1529(10)	2105(8)
C(11)	3074(8)	−1027(11)	1305(8)
C(12)	3686(10)	−1836(13)	649(9)
C(13)	4124(14)	−2976(16)	1148(12)
C(14)	3488(14)	−3727(14)	1691(11)
C(15)	3065(11)	−2916(12)	2436(2)
C(16)	3302(13)	2755(14)	733(11)
C(17)	2405(13)	3041(11)	1031(10)
C(18)	1677(13)	2454(16)	668(11)
C(19)	1804(14)	1578(15)	−9(10)
C(20)	2684(13)	1210(14)	−285(10)
C(21)	3428(12)	1802(14)	74(9)

The structure was solved by Patterson and Fourier methods and the refinement was carried out by least squares full-matrix cycles using the SHELX system of computer programs [7] with, initially, isotropic and then anisotropic thermal parameters. Attempts to localize the hydrogen atoms in a ΔF map were unsuccessful. The final conventional R was 0.058 for the observed reflections only. The atomic scattering factors used (corrected for the anomalous dispersion of ruthenium) were taken from the International Tables [8]. Unit weights were used in the first stages of the refinement, then a weighting factor $w^{-1} = \sigma^2(F_o) + 0.002F_o^2$ was introduced. The atomic fractional coordinates and thermal parameters are listed in Tables I and II. A list of observed and calculated structure factors is available from the authors on request.

All the calculations were performed on the CYBER 76 computer of Centro di Calcolo Elettro-

TABLE II. Thermal Parameters (×10^4) with e.s.d.'s. They are in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})]$.

	$U_{11}(\sigma)$	$U_{22}(\sigma)$	$U_{33}(\sigma)$	$U_{23}(\sigma)$	$U_{13}(\sigma)$	$U_{12}(\sigma)$
Ru(1)	296(6)	259(5)	444(6)	−33(4)	−71(5)	−27(4)
Ru(2)	277(6)	250(4)	338(5)	−10(4)	−37(4)	−19(3)
Ru(3)	311(6)	246(4)	320(5)	0(4)	13(4)	12(4)
Ru(4)	296(6)	224(4)	308(5)	28(4)	−14(4)	12(4)
O(1)	443(86)	643(87)	1017(95)	33(72)	−192(80)	158(63)
O(2)	1111(129)	691(86)	643(76)	−214(66)	−96(80)	214(75)
O(3)	871(128)	517(87)	1857(133)	70(86)	428(108)	−324(76)
O(4)	690(95)	364(52)	589(65)	−144(47)	−42(64)	−33(50)
O(5)	432(90)	699(85)	851(84)	−2(66)	114(75)	−119(60)
O(6)	656(103)	728(85)	740(83)	224(67)	−234(78)	11(66)
O(7)	287(74)	787(85)	1041(91)	209(70)	245(69)	−125(55)
O(8)	931(110)	445(63)	989(90)	−51(60)	276(81)	333(61)
O(9)	791(126)	670(80)	451(61)	−38(57)	−174(72)	−17(72)
C(1)	354(89)	380(76)	623(95)	−14(65)	13(77)	−1(56)
C(2)	221(74)	527(81)	466(72)	−112(61)	22(61)	71(54)
C(3)	651(150)	380(82)	1182(161)	−31(90)	229(127)	−125(80)
C(4)	508(102)	455(83)	401(67)	−48(60)	−151(68)	−37(65)
C(5)	441(107)	327(64)	660(103)	−54(64)	3(89)	−64(60)
C(6)	476(100)	414(73)	494(75)	53(59)	−22(71)	−53(59)
C(7)	361(89)	480(77)	473(74)	40(60)	35(67)	−2(56)
C(8)	643(115)	430(83)	682(89)	−22(68)	245(8)	149(69)
C(9)	459(91)	350(66)	414(66)	−29(55)	−6(63)	58(57)
C(10)	413(79)	205(46)	345(60)	60(41)	−29(56)	−18(43)
C(11)	231(67)	275(53)	388(57)	6(43)	−30(52)	74(41)
C(12)	412(87)	355(66)	549(76)	−66(57)	47(67)	127(55)
C(13)	818(144)	472(86)	671(102)	31(75)	−21(99)	298(81)
C(14)	946(138)	325(71)	660(94)	37(66)	262(92)	175(72)
C(15)	448(96)	255(56)	533(76)	70(51)	−36(71)	−2(52)
C(16)	704(125)	310(77)	631(96)	211(68)	0(91)	−62(69)
C(17)	786(125)	171(53)	785(95)	188(56)	255(89)	50(58)
C(18)	611(117)	440(94)	745(99)	268(78)	−171(89)	77(73)
C(19)	940(139)	461(84)	494(81)	246(67)	−86(85)	−8(76)
C(20)	795(128)	389(77)	466(84)	106(64)	−90(85)	26(70)
C(21)	581(113)	492(80)	400(69)	206(60)	61(71)	0(67)

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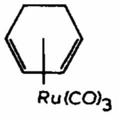
Results and Discussion

$Ru_3(CO)_{12}$ and CHD (molar ratio 1:9.6), when reacted in refluxing cyclohexane, benzene or n-hexane, yield a mixture of three products which are readily separated by TLC, in addition to a large amount of unreacted $Ru_3(CO)_{12}$. On the basis of the spectroscopic data the major product is identified as the mononuclear species $Ru(CO)_3(C_6H_8)$ (II) [3]. The two other species are obtained in low yields and identified as $H_2Ru_3(CO)_9(C_6H_6)$ (III) and $Ru_4(CO)_{12}(C_6H_8)$ (IV). I.r. and mass spectra reveal that (III) is homologue to $H_2Ru_3(CO)_9(C_8H_{10})$, obtained from $Ru_3(CO)_{12}$ and cyclooctadienes [4]. The structure proposed for (IV) is based on the X-ray



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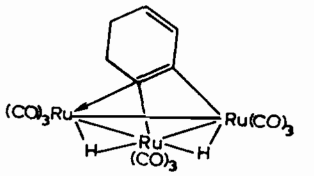
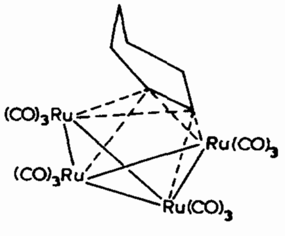


III



IV

TABLE III. Bond Distances (A) and Angles (°) with Their e.s.d.'s.

a) *In the Cluster*

Ru(1)–Ru(3)	2.702(3)	Ru(2)–C(10)	2.276(12)
Ru(1)–Ru(4)	2.643(3)	Ru(2)–C(11)	2.221(12)
Ru(2)–Ru(3)	2.700(4)	Ru(3)–C(7)	1.865(15)
Ru(2)–Ru(4)	2.655(3)	Ru(3)–C(8)	1.923(16)
Ru(3)–Ru(4)	2.809(3)	Ru(3)–C(9)	1.857(14)
Ru(1)–C(1)	1.891(16)	Ru(3)–C(10)	2.153(12)
Ru(1)–C(2)	1.840(14)	Ru(4)–C(11)	2.078(12)
Ru(1)–C(3)	1.938(18)	Ru(4)–C(16)	2.274(16)
Ru(1)–C(10)	2.222(14)	Ru(4)–C(17)	2.227(12)
Ru(1)–C(11)	2.229(13)	Ru(4)–C(18)	2.243(18)
Ru(2)–C(4)	1.894(15)	Ru(4)–C(19)	2.264(18)
Ru(2)–C(5)	1.888(18)	Ru(4)–C(20)	2.193(16)
Ru(2)–C(6)	1.865(15)	Ru(4)–C(21)	2.227(16)
Ru(3)–Ru(1)–Ru(4)	63.4(1)	Ru(1)–Ru(3)–C(9)	147.6(4)
Ru(3)–Ru(2)–Ru(4)	63.3(1)	Ru(1)–Ru(3)–C(10)	53.0(4)
Ru(1)–Ru(3)–Ru(4)	57.3(1)	Ru(2)–Ru(3)–C(7)	154.8(5)
Ru(2)–Ru(3)–Ru(4)	57.6(1)	Ru(2)–Ru(3)–C(8)	110.7(5)
Ru(1)–Ru(3)–Ru(2)	92.8(1)	Ru(2)–Ru(3)–C(9)	82.4(5)
Ru(1)–Ru(4)–Ru(2)	95.2(1)	Ru(2)–Ru(3)–C(10)	54.5(3)
Ru(1)–Ru(4)–Ru(3)	59.3(1)	C(7)–Ru(3)–C(8)	94.1(7)
Ru(2)–Ru(4)–Ru(3)	59.1(1)	C(7)–Ru(3)–C(9)	91.7(6)
Ru(3)–Ru(1)–C(1)	90.5(5)	C(7)–Ru(3)–C(10)	103.2(6)
Ru(3)–Ru(1)–C(2)	157.8(5)	C(8)–Ru(3)–C(9)	94.7(6)
Ru(3)–Ru(1)–C(3)	105.1(7)	C(8)–Ru(3)–C(10)	156.6(6)
Ru(3)–Ru(1)–C(10)	50.7(3)	C(9)–Ru(3)–C(10)	100.3(6)
Ru(3)–Ru(1)–C(11)	71.6(3)	Ru(1)–Ru(4)–C(11)	54.8(13)
Ru(4)–Ru(1)–C(1)	92.1(5)	Ru(1)–Ru(4)–C(16)	169.9(4)
Ru(4)–Ru(1)–C(2)	94.6(5)	Ru(1)–Ru(4)–C(17)	140.0(5)
Ru(4)–Ru(1)–C(3)	165.5(7)	Ru(1)–Ru(4)–C(18)	106.9(5)
Ru(4)–Ru(1)–C(10)	72.2(3)	Ru(1)–Ru(4)–C(19)	92.3(4)
Ru(4)–Ru(1)–C(11)	49.6(3)	Ru(1)–Ru(4)–C(20)	104.2(4)
C(1)–Ru(1)–C(2)	93.3(7)	Ru(1)–Ru(4)–C(21)	136.4(4)
C(1)–Ru(1)–C(3)	96.9(8)	Ru(2)–Ru(4)–C(11)	54.3(3)
C(1)–Ru(1)–C(10)	141.2(6)	Ru(2)–Ru(4)–C(16)	94.1(5)
C(1)–Ru(1)–C(11)	141.7(5)	Ru(2)–Ru(4)–C(17)	111.7(5)
C(2)–Ru(1)–C(3)	96.1(8)	Ru(2)–Ru(4)–C(18)	144.7(4)
C(2)–Ru(1)–C(10)	122.4(6)	Ru(2)–Ru(4)–C(19)	170.9(5)
C(2)–Ru(1)–C(11)	92.3(6)	Ru(2)–Ru(4)–C(20)	134.9(5)
C(3)–Ru(1)–C(10)	93.8(7)	Ru(2)–Ru(4)–C(21)	103.8(4)
C(3)–Ru(1)–C(11)	120.1(7)	Ru(3)–Ru(4)–C(11)	71.4(3)
C(10)–Ru(1)–C(11)	36.7(5)	Ru(3)–Ru(4)–C(16)	129.5(4)
Ru(3)–Ru(2)–C(4)	86.5(5)	Ru(3)–Ru(4)–C(17)	109.5(4)
Ru(3)–Ru(2)–C(5)	161.9(6)	Ru(3)–Ru(4)–C(18)	109.3(5)
Ru(3)–Ru(2)–C(6)	105.2(5)	Ru(3)–Ru(4)–C(19)	129.7(5)
Ru(3)–Ru(2)–C(10)	50.4(3)	Ru(3)–Ru(4)–C(20)	161.9(5)
Ru(3)–Ru(2)–C(11)	71.8(3)	Ru(3)–Ru(4)–C(21)	160.7(4)
Ru(4)–Ru(2)–C(4)	87.6(5)	C(11)–Ru(4)–C(16)	129.5(6)
Ru(4)–Ru(2)–C(5)	99.1(6)	C(11)–Ru(4)–C(17)	164.1(6)
Ru(4)–Ru(2)–C(6)	166.5(5)	C(11)–Ru(4)–C(18)	159.3(6)
Ru(4)–Ru(2)–C(10)	71.2(3)	C(11)–Ru(4)–C(19)	127.7(5)
Ru(4)–Ru(2)–C(11)	49.5(3)	C(11)–Ru(4)–C(20)	106.4(5)
C(4)–Ru(2)–C(5)	97.3(6)	C(11)–Ru(4)–C(21)	107.2(5)
C(4)–Ru(2)–C(6)	99.0(6)	C(16)–Ru(4)–C(17)	37.4(7)
C(4)–Ru(2)–C(10)	136.8(6)	C(16)–Ru(4)–C(18)	66.9(7)
C(4)–Ru(2)–C(11)	136.9(6)	C(16)–Ru(4)–C(19)	78.1(6)
C(5)–Ru(2)–C(6)	91.8(7)	C(16)–Ru(4)–C(20)	66.3(6)

(continued on facing page)

TABLE III. *(continued)*

C(5)–Ru(2)–C(10)	122.5(6)	C(16)–Ru(4)–C(21)	36.5(6)
C(5)–Ru(2)–C(11)	93.9(6)	C(17)–Ru(4)–C(18)	36.4(7)
C(6)–Ru(2)–C(10)	96.3(5)	C(17)–Ru(4)–C(19)	64.7(6)
C(6)–Ru(2)–C(11)	122.2(5)	C(17)–Ru(4)–C(20)	77.7(5)
C(10)–Ru(2)–C(11)	36.3(4)	C(17)–Ru(4)–C(21)	66.4(6)
Ru(4)–Ru(3)–C(7)	130.8(4)	C(18)–Ru(4)–C(19)	35.7(6)
Ru(4)–Ru(3)–C(8)	87.1(5)	C(18)–Ru(4)–C(20)	66.2(6)
Ru(4)–Ru(3)–C(9)	137.3(5)	C(18)–Ru(4)–C(21)	79.0(6)
Ru(4)–Ru(3)–C(10)	69.7(3)	C(19)–Ru(4)–C(20)	37.4(7)
Ru(1)–Ru(3)–C(7)	79.2(4)	C(19)–Ru(4)–C(21)	67.1(7)
Ru(1)–Ru(3)–C(8)	116.8(5)	C(120)–Ru(4)–C(21)	37.4(6)

b) *In the Carbonyl Groups*

O(1)–C(1)	1.113(22)	O(6)–C(6)	1.174(20)
O(2)–C(2)	1.181(19)	O(7)–C(7)	1.140(19)
O(3)–C(3)	1.117(23)	O(8)–C(8)	1.139(20)
O(4)–C(4)	1.132(18)	O(9)–C(9)	1.162(18)
O(5)–C(5)	1.144(23)		
Ru(1)–C(1)–O(1)	176.0(5)	Ru(2)–C(6)–O(6)	177.3(13)
Ru(1)–C(2)–O(2)	176.4(13)	Ru(3)–C(7)–O(7)	175.7(13)
Ru(1)–C(3)–O(3)	173.0(20)	Ru(3)–C(8)–O(8)	175.3(15)
Ru(2)–C(4)–O(4)	175.5(13)	Ru(3)–C(9)–O(9)	176.2(12)
Ru(2)–C(5)–O(5)	178.1(15)		

c) *In the Organic Ligands*

C(10)–C(11)	1.400(17)	C(16)–C(17)	1.444(27)
C(10)–C(15)	1.569(17)	C(16)–C(21)	1.411(21)
C(11)–C(12)	1.572(19)	C(17)–C(18)	1.397(26)
C(12)–C(13)	1.556(22)	C(18)–C(19)	1.380(23)
C(13)–C(14)	1.461(26)	C(19)–C(20)	1.430(28)
C(14)–C(15)	1.532(22)	C(20)–C(21)	1.416(25)
C(11)–C(10)–C(15)	121.7(11)	C(12)–C(13)–C(14)	112.7(16)
C(11)–C(10)–Ru(1)	71.9(7)	C(13)–C(14)–C(15)	113.3(13)
C(11)–C(10)–Ru(2)	69.7(7)	C(10)–C(15)–C(14)	110.4(11)
C(11)–C(10)–Ru(3)	108.2(7)	C(17)–C(16)–C(21)	117.4(16)
C(15)–C(10)–Ru(1)	121.5(8)	C(17)–C(16)–Ru(4)	69.5(8)
C(15)–C(10)–Ru(2)	116.7(9)	C(21)–C(16)–Ru(4)	69.9(9)
C(15)–C(10)–Ru(3)	130.0(9)	C(16)–C(17)–C(18)	122.5(14)
Ru(1)–C(10)–Ru(2)	120.8(5)	C(16)–C(17)–Ru(4)	73.1(8)
Ru(1)–C(10)–Ru(3)	76.3(4)	C(18)–C(17)–Ru(4)	72.4(8)
Ru(2)–C(10)–Ru(3)	75.0(3)	C(17)–C(18)–C(19)	119.8(18)
C(10)–C(11)–C(12)	123.1(9)	C(17)–C(18)–Ru(4)	71.2(9)
C(10)–C(11)–Ru(1)	71.4(7)	C(19)–C(18)–Ru(4)	73.0(10)
C(10)–C(11)–Ru(2)	74.0(7)	C(18)–C(19)–C(20)	119.2(17)
C(10)–C(11)–Ru(4)	110.7(8)	C(18)–C(19)–Ru(4)	71.3(10)
C(12)–C(11)–Ru(1)	118.1(8)	C(20)–C(19)–Ru(4)	68.6(10)
C(12)–C(11)–Ru(2)	118.5(8)	C(19)–C(20)–C(21)	121.5(14)
C(12)–C(11)–Ru(4)	126.2(8)	C(19)–C(20)–Ru(4)	74.0(9)
Ru(1)–C(11)–Ru(2)	123.1(5)	C(21)–C(20)–Ru(4)	72.6(9)
Ru(1)–C(11)–Ru(4)	75.6(4)	C(16)–C(21)–C(20)	119.5(16)
Ru(2)–C(11)–Ru(4)	76.2(4)	C(16)–C(21)–Ru(4)	73.6(9)
C(11)–C(12)–C(13)	108.4(12)	C(20)–C(21)–Ru(4)	70.0(9)

structure determination of $Ru_4(CO)_9(C_6H_6)(C_6H_8)$ (V), described below. Moreover the i.r. spectrum of (IV) is strictly related to those of tetraruthenium complexes obtained from $Ru_3(CO)_{12}$ and alkynes [9]. The complex (I) is not observed in the products of these reactions. If the reaction of $Ru_3(CO)_{12}$ and

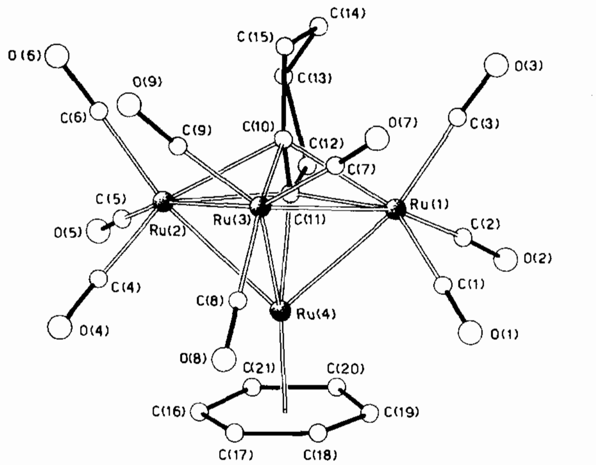


Fig. 1. View of the shape of the complex $Ru_4(CO)_9(C_6H_6)(C_6H_8)$ (V).

CHD is carried on in refluxing n-heptane, (I) is indeed obtained (20%), but its yield decreases when the reaction is repeated in the n-heptane distilled from the previous first reaction. After some of such runs the yield of (I) is almost negligible. The next step has been to reflux in n-heptane only the ruthenium carbonyl without any addition of CHD. (I) is obtained in the same yield as when CHD is in the reaction mixture and its yield becomes negligible on repeating the above procedure.

Thus, we feel that (I) is formed by the reaction of $Ru_3(CO)_{12}$ with acyclic C_6 unsaturated hydrocarbons present as impurities in the n-heptane. Actually complexes homologous to (I) are the main products in the reactions of $Ru_3(CO)_{12}$ with olefins [10], non-terminal alkynes [11] and dienes [12].

When the reaction between $Ru_3(CO)_{12}$ and CHD is carried out in refluxing n-octane with a large excess of CHD (molar ratio 1:28.9), in addition to (II) and (III) the complex (V) is obtained. Treatment of (IV) with an excess of CHD in n-octane at reflux for 5 hours also leads to (V). The low field singlet, observed in its ^1H n.m.r. spectrum, suggests the presence of a coordinated benzene unit, since similar values of chemical shifts have been found for aromatic hydrocarbons η-bonded to a ruthenium cluster [13].

Description of the Crystal Structure of (V)

The structure of the complex $Ru_4(CO)_9(C_6H_6)(C_6H_8)$ (V) is represented in Figure 1. Bond distances and angles are given in Table III. The structure is characterized by a tetranuclear cluster of Ru atoms coordinated by nine carbonyls and by two organic ligands, a benzene molecule and a 1-cyclohexen-1,2-ylene unit. The cluster consists of a 'butterfly' arrangement of metal atoms, in which the hinge side Ru(3)–Ru(4) has a bond length (2.809 Å) significantly longer than the others (in the range 2.643–2.702 Å). The dihedral angle between the two planes containing Ru(1)–Ru(3)–Ru(4) and Ru(2)–Ru(3)–Ru(4) is 118.5° and the non-bonded distance Ru(1)–Ru(2) is 3.912 Å.

This 'butterfly' configuration of the tetranuclear cluster has been previously reported only for $Co_4(CO)_{10}(Et_2C_2)$ [14], $Ru_4(CO)_{11}(C_8H_{10})$ [15], $Ru_4(CO)_{10}(C_{12}H_{16})$ [16], $(Me_3NCH_2Ph)[Fe_4(CO)_{13}H]$ [17], $Ru_4(CO)_{12}(Ph_2C_2)$ [18], $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ [19], and $FeRu_3(CO)_{12}(Ph_2C_2)$, two isomers [20]. In the Fe cluster only were all the five metal–metal bond distances found to be equivalent, whereas the hinge bond was found longer than the other bonds in all the remaining 'butterfly' clusters.

The nine carbonyl groups are terminal (the angles Ru–C–O are in the range 173.0–178.1°) and attached to three Ru atoms only (three per each metal), Ru(1), Ru(2) and Ru(3); Ru(4) does not carry any carbonyl but is η-bonded to a benzene molecule (the distance from Ru(4) to the barycentre of the ring being 1.736 Å), derived from a 1,3-cyclohexene (CHD) molecule by dehydrogenation.

A second CHD molecule, by isomerization to a 1-cyclohexen-1,2-ylene unit, interacts with all the metal atoms of the cluster: the two carbon atoms C(10) and C(11) form two metal–carbon σ-bonds of average length 2.115 Å with the hinge atoms of the cluster and two π-bonds of average length 2.237 Å with the other two metal atoms so that these carbons are equidistant from both Ru(1) and Ru(2).

This isomerized CHD molecule is trapped between the two "butterfly" wings in a way very similar to the acetylenic or cyclooctadienic derivatives in $Co_4(CO)_{10}(Et_2C_2)$, $Ru_4(CO)_{12}(Ph_2C_2)$ and $Ru_4(CO)_{11}(C_8H_{10})$.

A charge transfer from the acetylenic bond C(10)–C(11) to the Ru atoms is indicated also by the lengthening of the bond to 1.400 Å.

The conformation of the cyclic ligand, determined by the bonding and steric requirements of the cluster, is "half-chair". The atoms C(10), C(11), C(12) and C(15) are nearly coplanar; the equation of the mean plane passing through them is $-0.8185X - 0.4065Y - 0.4058Z = -4.2819$ where X, Y and Z are orthogonal coordinates (Å) obtained from fractional ones by applying the matrix $\|a, 0, c\cos\beta\,|\,0, b, 0\,|\,0, 0, c\sin\beta\|$. C(10), C(11), C(12), C(15), C(13) and C(14) are displaced from this plane by 0.019, −0.017, 0.011, −0.013, 0.410 and 0.312 Å. The torsion angles in the ring are

C(11)C(10)C(15)C(14)	−15.9
C(15)C(10)C(11)C(12)	4.4
C(10)C(11)C(12)C(13)	−19.3
C(11)C(12)C(13)C(14)	48.9
C(12)C(13)C(14)C(15)	−65.8
C(13)C(14)C(15)C(10)	46.0

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References

1 E. L. Muetterties and S. T. Olin, *Bull. Soc. Chim. Belg., 84,* 959 (1975).
2 J. Lewis and B. F. G. Johnson, *Pure and Appl. Chem.,* 43 (1975).
3 T. H. Whitesides and R. A. Budnik, *Chem. Comm.,* 87 (1973).
4 A. J. Canty, A. P. J. Domingos, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. Dalton,* 2056 (1973).
5 M. I. Bruce, M. A. Cairns and M. Green, *J. Chem. Soc. Dalton,* 1293 (1972).
6 E. G. Bryan, B. F. G. Johnson, J. W. Kelland, J. Lewis and M. McParthin, *Chem. Comm.,* 254 (1976).
7 G. Sheldrick, System of Computing Programs, University of Cambridge (1976).
8 International Tables of X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974).
9 B. F. G. Johnson, J. Lewis and K. T. Schorpp, *J. Organometal. Chem., 91,* C13 (1975).
10 M. Castiglioni, L. Milone, D. Osella, G. A. Vaglio and M. Valle, *Inorg. Chem., 15,* 396 (1976).
11 S. Aime, L. Milone, D. Osella and M. Valle, *J. Chem. Research,* (S) 77 (1978); (M) 0785–0797 (1978).
12 O. Gambino, M. Valle, S. Aime and G. A. Vaglio, *Inorg. Chim. Acta, 8,* 71 (1974).
13 B. F. G. Johnson, R. D. Johnston and J. Lewis, *J. Chem. Soc. A,* 2865 (1968).
14 L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc., 84,* 2450 (1962).
15 R. Mason and K. M. Thomas, *J. Organometal. Chem., 43,* C39 (1972).
16 R. Belford, M. I. Bruce, M. A. Cairns, M. Green, H. P. Taylor and P. Woodward, *Chem. Comm.,* 1159 (1970).
17 M. Manassero, M. Sansoni and G. Longoni, *Chem. Comm.,* 919 (1976).
18 B. F. G. Johnson, J. Lewis, B. E. Reichert, K. T. Schorpp and G. M. Sheldrick, *J. Chem. Soc. Dalton,* 1417 (1977).
19 C. G. Pierpont, *175th A.C.S. National Meeting, Anaheim,* March 12–17 (1978).
20 G. L. Geoffroy, J. R. Fox. V. W. Day, S. Abdel-Meguid and I. Tavanaiepour, *175th A.C.S. National Meeting, Anaheim,* March 12–17 (1978).