Synthesis and structural characterization
of (μ-H)$_2$Ru$_3$(CO)$_9$(μ_3-η^2-C$_8$H$_{12}$) and (μ-H)Ru$_3$(CO)$_9$(μ_3-η^3-C$_{12}$H$_{19}$)

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Abstract

The reaction between Ru$_3$(CO)$_{12}$ and a cyclic olefin (*cis*-cyclooctene or *trans*-cyclododecene) at 100 °C for several hours gives the title compounds (μ-H)$_2$Ru$_3$(CO)$_9$(μ_3-η^2-C$_8$H$_{12}$) (**1**), and (μ-H)Ru$_3$(CO)$_9$(μ_3-η^3-C$_{12}$H$_{19}$) (**2**), both of which have been characterized by X-ray diffraction studies, IR and NMR spectral measurements and elemental analysis. The prolonged reaction between Ru$_3$(CO)$_{12}$ and *cis*-cyclooctene gives compound HRu$_3$(CO)$_9$(C$_8$H$_{11}$) (**3**). Compound **3** has been characterized with IR and NMR spectral analyses. In **1** the cyclooctene ring is linked via a μ_3-η^2-alkyne type of bonding to the face of the Ru$_3$ cluster. It is formally σ-bonded to two of the three Ru atoms and π-bonded to the third Ru. The two hydrides in **1** are bridging Ru–Ru bonds. In **2** the cyclododecene ring is bonded to the Ru$_3$ face via the μ_3-η^3-CCHC linkage. There are two formal σ-bonds from the allyl part to the hydrido-bridged Ru atoms and the η^3-allyl linkage to the third Ru atom.

Keywords: Cluster; Ruthenium; Olefin; Cyclooctene; Cyclododecene; Bridging ligand

1. Introduction

Reactions of unsaturated hydrocarbons with Ru$_3$(CO)$_{12}$ at elevated temperatures have been of interest for several years [1,2]. Hydrocarbon fragments in these reactions tend to undergo extensive rearrangements, which may resemble those occurring on metal surfaces during catalytic processes. We have studied high-temperature reactions of Ru$_3$(CO)$_{12}$ with cyclic olefins and determined the crystal structures of the title compounds, in which the cyclic alkenes, cyclooctene and cyclododecene, rearrange in different ways.

Compound **1** has been synthesized previously by the direct reaction of Ru$_3$(CO)$_{12}$ with cyclooctene or by the reaction of α-H$_4$Ru$_4$(CO)$_{12}$ with either cycloocta-1,5-diene or the corresponding 1,3-isomer [3]. The structure of the cluster has been discussed in terms of spectroscopic data, and it has been proposed to contain two Ru–C σ-bonds, a π-bonded olefinic fragment and the two H ligands in the bridged position on a Ru–Ru edge.

Bruce et al. [4] have investigated the reaction of Ru$_3$(CO)$_{12}$ with cyclododeca-1,5,9-trienes and found the reaction happens slowly with all geometrical isomers of the triene in refluxing petroleum ether and gives

four complexes. These have been characterized spectroscopically, and the crystal structure of HRu$_3$(CO)$_9$(C$_{12}$H$_{15}$) has also been determined. The compound was found to contain a novel π-allyl system bonded to a triangular ruthenium cluster. Besides the μ_3-η^3-CCHC-linkage between C(1), C(2) and C(3), the double bonds were deduced to be between C(6)–C(7) and C(9)–C(10) and the hydride ligand to be terminal or bridging (the latter being favored by the geometry of the cluster). On the basis of spectral measurements proposals for structures of the three other complexes were not made. The μ_3-η^3 bonding mode, which is commonly found in homo- and heterometallic alkyne clusters similar to **1**, is one possible bonding mode at least for the *cis*-isomer of cyclic olefins although changes between different isomers may happen during reactions, as introduced by Sappa et al. [1]. With cycloalkenes the rearrangements are not as extensive; thus, it is easier to observe different bonding modes.

2. Experimental

2.1. General comments

Ru$_3$(CO)$_{12}$ (Johnson-Matthey) and *cis*-cyclooctene (95%; Aldrich) and *cis*/*trans*-cyclododecene (33.3%/

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67.7%; TCI) were from commercial sources and were used without further purification. Except for chromatographic separations all manipulations were carried out under nitrogen. IR spectra were recorded with a Nicolet 750 FT-IR spectrometer, and ^{1}H and ^{13}C NMR spectra on a Bruker AMX-400 or a Bruker AM-250 spectrometer at ambient temperature or at -55 °C to 0 °C with TMS as reference.

2.2. Preparation of compounds 1 and 3

Ru$_3$(CO)$_{12}$ (100 mg, 0, 156 mmol) was dissolved in 25 ml of cis-cyclooctene and heated at 100 °C. The mixture was stirred for 92 h under nitrogen, the unreacted cyclooctene was distilled under vacuum, and the light brown residue chromatographed on silica plates with hexane as eluent gave (i) a yellow band (1), 46 mg (44.3%) recrystallized from hexane; anal./calc. C (%) 30.87/30.55; H (%) 2.16/2.11; O (%) 21.27/21.64; IR (hexane, ν(CO), cm^{-1}): 2103.7 s, 2075.5 vs, 2053.5 vs, 2039.2 s, 2025.9 s, 2013.3 s, 2006.8 s, 1987.4 s; ^{1}H NMR (CDCl$_3$, 0 °C, ppm): 1.52 (s, 8H(CH$_2$)$_4$), 3.17 (dt, 2H(CH$_2$), J_{HH} = 4.1 Hz and J_{HH} = 12.2 Hz), 2.85 (td, 2H(CH$_2$), J_{HH} = 4.1 Hz and J_{HH} = 12.2 Hz), -15.92 (s, ^{1}H, RuHRu, -55 °C), -20.34 (s, ^{1}H, RuHRu, -55 °C); ^{13}C {^{1}H}NMR (CDCl$_3$, ppm): 14.8 (s, 2C, CH$_2$), 23.4 (s, 2C, CH$_2$), 32.3 (s, 2C, CH$_2$), 162.6 (s, 2C, C=C), 190.5–194.0 (9C, CO); (ii) a yellow-orange band, HRu$_3$(CO)$_9$(C$_8$H$_{11}$) (3), 36 mg (34.7%); IR (cyclohexane, ν(CO), cm^{-1}): 2092.3 m, 2064.2 vs, 2040.5 vs, 2023.9 s, 2017.5 m, 2004.3 m, 1995.6 m, 1987.5 w, 1981.3 w; ^{1}H NMR (CDCl$_3$, 0 °C, ppm): 3.71 (t, ^{1}H, J = 4.1 Hz), 3.06 (m, 2H), 2.78 (m, 2H), 2.40 (m, 2H), 1.90 (m, 4H) -20.46 (s, ^{1}H, RuHRu); (iii) a purple band (unidentified), 15 mg (14.5%).

2.3. Preparation of compound 2

Ru$_3$(CO)$_{12}$ (50 mg, 0.0782 mmol) was dissolved in 20 ml of (cis/trans-mixture) cyclododecene and heated at 100 °C. The mixture was stirred for 60 hours under nitrogen, the unreacted cyclododecene was distilled under vacuum, and the brown residue chromatographed on silica plates with hexane as eluent gave (i) a yellow band (2), 10 mg (17.8%), recrystallized from hexane; anal./calc: C(%) 35.28/34.91; H(%) 2.84/2.79; IR (hexane, ν(CO), cm^{-1}): 2094.3 m, 2067.6 s, 2043.1 vs, 2025.2 s, 2013.1 m, 2005.9s, 1994.1 w, 1972.0 w; ^{1}H NMR (CDCl$_3$, 20 °C, ppm): 1.56 (s, 14H, CH$_2$), 2.85 (td, 2H, CH$_2$, J_{HH} = 4.1 Hz and J_{HH} = 12.2 Hz), 3.17 (dt, 2H, CH$_2$, J_{HH} = 4.1 Hz and J_{HH} = 12.2 Hz) 6.66 (d, ^{1}H, CH, J_{HH} = 2.2Hz), -20.13 (d, ^{1}H, RuHRu, J_{HH} = 2.2Hz); ^{13}C ^{1}H NMR (CDCl$_3$, ppm): 14.8 (s, 3C, CH$_2$), 23.4 (s, 4C, CH$_2$), 30.4 (s, 2C, CH$_2$), 31.7 (s, 1C, CH), 32.3 (s, 2C, CCHC), 190–201 (9C, CO); (ii) a yellow band), 10 mg (17.8%); IR (CH$_2$Cl$_2$, ν(CO),

cm^{-1}): 2092.9 m, 2065.9 vs, 2039.7 vs, 2020.3 m, 2006.0 m br.; (iii) a yellow band, 3 mg (5.3%); IR (hexane, ν(CO), cm^{-1}): 2083.0 m, 2046.5 vs, 2013 s, 2000.6 s, 1989.5 m, 1982.3 w; ^{1}H NMR (CDCl$_3$, 0 °C, ppm): -21.22 (s, ^{1}H, RuHRu).

2.4. Crystallographic studies

Intensity measurements were done using a Nicolet R3m diffractometer at 20 °C with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å), ω-scan mode with a scan width of 1.2° for 1 and 1.6° for 2, and a variable scan speed of 2.49–29.30° min^{-1}. The data sets were corrected for Lorenz and polarization factors. An empirical absorption correction was made from ψ-scan data; the transmission factors were 0.137–0.213 and 0.380–0.500 for 1 and 2, respectively.

The crystal structures were determined by direct methods and subsequent Fourier synthesis using the SHELXTL [5] program package. Non-hydrogen atoms were refined anisotropically except in 2, in which the disordered cyclododecene carbon atoms were refined isotropically. Hydrogen atoms were placed at calculated positions with fixed isotropic thermal parameters (C–H 0.96 Å and U 0.08 Å^2) except for the hydride ligands and the central allylic hydrogen atom in 2 which were located from difference Fourier maps and not refined (U 0.08 Å^2).

Details of crystal parameters, data collection parameters and refined data are summarized in Table 1. The atom coordinates are listed in Tables 2 and 3. Hydrogen atom coordinates, anisotropic displacement parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

The cyclic olefins, cis-cyclooctene and trans/cis-cyclododecene, react with Ru$_3$(CO)$_{12}$ at elevated temperature (100 °C) to give complexes 1, 3 and 2 respectively, involving different bonding modes. The title complexes, 1 and 2 (Scheme 1), were isolated with chromatographic separation and characterized with chemical analysis, IR, and NMR spectroscopy as well as X-ray diffraction.

For the prolonged reaction of Ru$_3$(CO)$_{12}$ with cis-cyclooctene the chromatographic separation of the reaction mixture gives the second band which consists of, in addition to the starting cluster, a compound which gives a different IR spectrum from that of 1 and has hydride resonance signals in the ^{1}H NMR spectrum at 3.71 ppm, t, 3.06 ppm, m, 2.2–2.9 ppm, m, and -20.46 ppm, s. According to Canty et al.[6] this complex is HRu$_3$(CO)$_9$(C$_8$H$_{11}$) (3), which they have characterized by mass spectroscopic and ^{1}H NMR data. The starting

Table 1

Crystallographic data for $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_{12})$ (1) and $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-C}_{12}\text{H}_{19})$ (2)

	1	2
FW	665.5	719.6
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9.173(2)	14.794(5)
b (Å)	16.646(5)	15.835(5)
c (Å)	28.609(7)	11.479(6)
β (°)	90.40(2)	109.23(3)
V (Å^3)	4368(2)	2539(2)
Z	8	4
D_{calc} (g cm^{-3})	1.771	1.882
Crystal dimensions (mm)	0.2×0.3×0.3	0.07×0.2×0.3
Centered reflections	25	25
Radiation	Mo K α	Mo K α
hkl range	0, 0, −37; 11, 21, 37	0, 0, −18; 14, 20, 18
2θ (°)	5-55	5-55
No. unique reflections	10075	5848
No. observed data, $I \geq 2\sigma(I)$	6326	2763
μ (mm^{-1})	1.796	1.773
No. parameters	523	295
R	0.0418	0.0659
wR [a]	0.0461	0.0652
Goof	1.21	1.49

[a] $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/(\sigma^2(F) + 0.0005F^2)$.

olefin contains 95% cis-isomer and thus the cis-complex 1 forms first, but longer warming causes the formation of trans-complex 3 also, which is observed in the reaction mixture after about 100 h. When refluxing in toluene solution (110 °C) for several hours, compound 1 forms an equilibrium mixture with compound 3. In the IR spectra ν(CO) frequencies for 3 are similar with those of 2. Thus, 3 has been identified as the trans-cyclooctene complex of $\text{Ru}_3(\text{CO})_{12}$ based on the IR and ^{1}H NMR spectroscopic measurements.

Accordingly the chromatographic separation of the reaction mixture of $\text{Ru}_3(\text{CO})_{12}$ with cis / trans-cyclododecene gave two yellow bands with CO-stretching frequencies resembling those of 1. It is possible that both cyclododecene complexes (cis- and trans) are present in solution, but the trans-complex, 2, is more stable, because the slow evaporation of solvent from the other yellow compound solution gives only crystals of the trans-complex, 2. In addition, when remaining a longer time in solution, the other yellow compounds form the complex 2 on the basis of IR and ^{1}H NMR measurements.

The cyclic olefins $\text{C}_n\text{H}_{2n-2}$ ($n = 6, 8, 12$) replace three axial carbonyl groups of the $\text{Ru}_3(\text{CO})_{12}$ cluster. All remaining carbonyl groups have IR signals in the typical terminal CO-group region. The IR spectra con-

sist of eight signals for 1 and 2 in hexane and nine signals for 3 in cyclohexane. The high number of IR signals indicates the lower symmetry of $\text{Ru}_3(\text{CO})_9$ moi-

Table 2

Atomic coordinates ($\times 10^4$) for $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_{12})$ (1)

Ru(1)	2480(1)	1386(1)	4718(1)
Ru(2)	286(1)	2580(1)	4367(1)
Ru(3)	56(1)	1957(1)	5250(1)
O(11)	5326(7)	1906(4)	4258(2)
O(12)	4179(8)	428(4)	5453(2)
O(13)	2020(9)	−42(4)	4036(2)
O(21)	1757(8)	3619(4)	3626(2)
O(22)	−2208(7)	3758(4)	4484(2)
O(23)	−1560(8)	1460(5)	3724(3)
O(31)	720(8)	1219(5)	6210(2)
O(32)	−1644(6)	3333(4)	5681(2)
O(33)	−2739(7)	1075(4)	4981(3)
C(1)	2319(7)	2422(4)	5152(2)
C(2)	1403(7)	3001(4)	4952(2)
C(3)	1409(8)	3868(4)	5128(3)
C(4)	2505(9)	4366(4)	4851(3)
C(5)	4026(9)	4003(5)	4822(3)
C(6)	4776(9)	3827(5)	5294(3)
C(7)	4805(8)	2959(5)	5449(3)
C(8)	3339(8)	2576(4)	5565(3)
C(11)	4282(9)	1714(5)	4429(3)
C(12)	3507(9)	777(4)	5188(3)
C(13)	2201(11)	461(5)	4291(3)
C(22)	−1271(9)	3322(5)	4448(3)
C(21)	1203(8)	3221(5)	3905(3)
C(23)	−890(9)	1869(5)	3964(3)
C(32)	−1013(8)	2804(5)	5526(3)
C(31)	494(9)	1476(5)	5856(3)
C(33)	−1705(9)	1405(5)	5081(3)
Ru(1B)	2495(1)	−681(1)	2645(1)
Ru(2B)	4743(1)	608(1)	2776(1)
Ru(3B)	4945(1)	−458(1)	2051(1)
O(11B)	−246(7)	176(5)	2985(3)
O(12B)	893(8)	−1963(4)	2072(2)
O(13B)	2896(9)	−1795(5)	3504(3)
O(21B)	3236(9)	1967(5)	3294(3)
O(22B)	7280(9)	1653(5)	2453(3)
O(23B)	6556(10)	−236(6)	3548(3)
O(31B)	4081(10)	−1793(5)	1370(3)
O(32B)	6640(7)	483(5)	1326(2)
O(33B)	7769(7)	−1118(4)	2483(2)
C(1B)	2719(8)	78(4)	2049(2)
C(2B)	3664(8)	707(4)	2137(2)
C(3B)	3761(9)	1434(4)	1807(3)
C(4B)	2768(10)	2105(5)	1953(3)
C(5B)	1200(13)	1859(7)	2059(5)
C(6B)	438(13)	1462(8)	1669(4)
C(7B)	268(9)	532(6)	1688(3)
C(8B)	1692(8)	56(5)	1631(3)
C(11B)	735(10)	−160(5)	2850(3)
C(12B)	1459(10)	−1486(5)	2280(3)
C(13B)	2718(10)	−1394(5)	3196(3)
C(21B)	3817(11)	1448(6)	3109(3)
C(22B)	6332(11)	1267(6)	2572(3)
C(23B)	5910(11)	100(6)	3282(3)
C(31B)	4427(10)	−1292(6)	1605(3)
C(32B)	6010(9)	131(6)	1594(3)
C(33B)	6703(10)	−878(5)	2316(3)

ety than that in the parent $Ru_3(CO)_{12}$ cluster, which has only three carbonyl signals in the IR.n

Complex **1** crystallizes in space group $P2_1/c$ with two molecules (A and B) in the asymmetric unit. The molecular structure of **1** (molecule A) is given with the atomic numbering scheme in Fig. 1. The selected bond lengths and angles are given in Tables 4 and 5, respectively. cis-Cyclooctene coordinates to the Ru_3 cluster via the two olefinic carbon atoms. On coordination the Ru_3 centre is activated by CO-dissociation, and the olefin undergoes an intramolecular oxidative addition to the Ru_3 centre; the hydride ligands bridge the Ru(1)–Ru(2) and Ru(1)–Ru(3) bonds. The Ru(1)–Ru(2) and Ru(1)–Ru(3) bonds are 26 and 12 pm longer, respectively, than the remaining Ru(2)–Ru(3) bond (274.1(1) pm for A and 273.8(1) pm for B) owing to the bridging hydrides (Table 4). The average metal–metal bond distance in the parent cluster $Ru_3(CO)_{12}$ is 285.4 pm [7]. The hydride ligands also induce the Ru(1)–Ru(2)–C(21), Ru(2)–Ru(1)–C(11) and Ru(1)–Ru(3)–C(33)

Table 3
Atomic coordinates ($\times 10^4$) for (μ-H)Ru$_3$(CO)$_9$(μ_3-η^3-C$_{12}$H$_{19}$) (2)

Ru(2)	3871(1)	5070(1)	2181(1)
Ru(3)	2239(1)	4388(1)	437(1)
Ru(1)	2884(1)	3575(1)	2729(1)
O(22)	4336(12)	6103(11)	199(13)
O(21)	4760(8)	6227(8)	4369(11)
O(23)	5797(10)	4102(11)	2718(16)
O(32)	1981(10)	5491(9)	−1851(11)
O(31)	657(8)	3129(8)	−841(12)
O(33)	3839(8)	3328(8)	34(11)
O(11)	3010(9)	3497(8)	5420(10)
O(12)	1718(10)	1968(8)	2020(11)
O(13)	4692(9)	2482(9)	2975(13)
C(22)	4217(13)	5754(12)	964(17)
C(21)	4428(9)	5816(11)	3531(15)
C(23)	5077(13)	4432(14)	2459(17)
C(32)	2061(12)	5080(11)	−1003(14)
C(31)	1224(12)	3614(11)	−384(13)
C(33)	3275(12)	3735(13)	283(14)
C(11)	3006(10)	3528(9)	4409(14)
C(12)	2157(12)	2570(11)	2284(16)
C(13)	4047(12)	2888(10)	2888(14)
C(41)	1650(9)	4304(10)	2076(11)
C(42)	1678(8)	5171(8)	1704(10)
C(43)	2506(10)	5589(9)	1612(11)
C(44)	2320(12)	6522(9)	1199(13)
C(45)	2610(12)	7136(9)	2294(16)
C(46)[a]	2461(19)	6842(17)	3561(25)
C(46')[a]	1851(29)	7104(25)	2951(34)
C(47)[a]	1352(25)	6928(22)	3346(32)
C(47')[a]	2027(29)	6628(25)	4052(36)
C(48)	1198(14)	6435(14)	4467(19)
C(49)[a]	1236(23)	5455(23)	4402(28)
C(49')[a]	572(26)	5675(25)	3833(32)
C(50)[a]	367(21)	5084(22)	3491(26)
C(50')[a]	1085(24)	4834(23)	4221(31)
C(51)	537(12)	4105(12)	3307(17)
C(52)	673(10)	4019(10)	2060(14)

[a] Occupancy factor of 0.5.

bond angles to open. The angles between equatorial CO ligands, C(12)–Ru(1)–C(11) and C(22)–Ru(2)–C(21), are significantly smaller (average 11.2°) than those in the parent cluster $(Ru_3(CO)_{12})$ (Table 5). It is obvious that metal hydrides cancel the repulsion between equatorial oxygens.

The cyclooctene ligand in **1** is formally σ-bonded to the Ru(1) and Ru(2) atoms and π-bonded to the Ru(3) atom. There is a slight difference in bond strength between the two formal σ-bonds because Ru(2)–C(2) and Ru(1)–C(1) have different bond lengths 207.7(7)/213.1(6) and 207.9(7)/213.3(7) pm in molecules A and B, respectively, indicating a stronger bond in the former case. In addition, the bonding type is reflected in Ru–C(olefin) bond lengths, the mean Ru(1)–C(olefin) and Ru(2)–C(olefin) interactions being approximately 13 pm shorter than the Ru(3)–C(olefin) interactions. Bonding also causes distortion in the ligand coordination at Ru_3: Ru–Ru–C(olefin) bond angles (mean of 60°) are clearly smaller (Table 5) than the Ru–Ru–C_{ax} angles (mean of 90°) in the parent cluster. In the C_8 ring the C(2)–C(1) bond length is 139.9(9) pm for molecule A and 138.2(10) pm for molecule B, indicating that the bond is slightly longer than a normal C–C double bond. Other C–C distances in the C_8 ring average 152.6 pm for A and 152.1 pm for B.

The complex **1** was also formed in a reaction of $H_4Ru_4(CO)_{12}$ with cis-cyclooctene. In cis-cyclooctene solution $H_4Ru_4(CO)_{12}$ gives a mixture that was chromatographed on silica plates with hexane as eluent (unreacted cis-cyclooctene was distilled first in vacuum). Separation gave (i) a yellow band of **1** and (ii) a yellow band of $Ru_3(CO)_{12}$.

Compound **1** shows a fluxional behavior, which is seen in the ^{1}H NMR spectra. Resonances at 2.48 and 3.05 ppm broaden above ambient temperature and coalesce to a single broad absorption at 2.82 ppm (ca. 40 °C) because of the rapid H-exhange at the C_8H_{12} ring. With the metal hydrides there is also rapid H-exhange between the Ru–Ru edges of the cluster. At ambient temperature the Ru–H–Ru signals are broadened to one very broad signal at −18.0 ppm because of the positional scrambling of the metal hydrides. On decreasing the temperature the broad signal is separated into two signals. At −55 °C the ^{1}H NMR spectrum in the high-field region consists of two sharp singlets at −15.92 and −20.34 ppm.

Canty et al. [3] have previously identified compound **1** (made from $H_4Ru_4(CO)_{12}$) by mass spectroscopic analysis and ^{1}H NMR spectroscopy. They have observed similar conformational changes as we, when measuring the ^{1}H NMR spectra at different temperatures. They claimed that the fluxional behavior of the C_8H_{12} was a consequence of conformational changes about carbon atoms C_3 and C_8, thereby interconverting $H_{ax} \leftrightarrow H_{eq}$. They supposed that the formation of Ru_3

Table 4
Selected bond lengths (pm) in (μ-H)$_2$Ru$_3$(CO)$_9$(μ_3-η^2-C$_8$H$_{12}$) (1A and 1B), (μ-H)Ru$_3$(CO)$_9$(μ_3-η^3-C$_{12}$H$_{19}$) (2), HRu$_3$(CO)$_9$(C$_{12}$H$_{15}$) [8] (5) and Ru$_3$(CO)$_{12}$ [7] (6)

|	1A	1B	2	5	6
Ru(1)–Ru(2)	299.7(1)	299.8(1)	295.6(2)	292.9(4)	285.95(4)
Ru(1)–Ru(3)	286.6(1)	285.2(1)	280.0(2)	277.9(4)	285.12(4)
Ru(2)–Ru(3)	274.1(1)	273.8(1)	279.7(2)	277.5(4)	285.18(4)
Ru(1)–C(1)/C(41)	213.1(6)	213.3(7)	208.0(13)	202(3)	194.7(4)
Ru(2)–C(2)/C(43)	207.7(7)	207.9(7)	207.7(13)	201(2)	195.3(5)
Ru(3)–C(1)/C(41)	223.5(6)	222.8(7)	232.3(15)	223(3)	
Ru(3)–C(2)/C(43)	230.0(6)	228.2(7)	229.0(13)	218(3)	
Ru(3)–C(42)			226.6(14)	219(2)	195.0(4)
Ru(1)–C(11)	193.1(8)	192.7(9)	188(2)	179(4)	192.5(5)
Ru(1)–C(12)	192.6(8)	194.3(9)	189(2)	189(4)	191.8(5)
Ru(1)–C(13)	198.1(8)	198.3(9)	199(2)	200(5)	192.9(4)
Ru(2)–C(21)	189.9(8)	189.7(9)	191(2)	179(4)	193.4(5)
Ru(2)–C(22)	190.3(9)	191.9(10)	196(2)	184(6)	190.9(5)
Ru(2)–C(23)	196.9(9)	198.2(9)	198(2)	199(5)	193.2(5)
Ru(3)–C(31)	194.9(9)	194.3(9)	193(2)	183(4)	193.0(4)
Ru(3)–C(32)	189.4(8)	190.8(8)	193(2)	184(4)	190.8(5)
Ru(3)–C(33)	191.7(8)	191.0(9)	191(2)	186(4)	194.3(4)
Ru(1)–H(12)	164	167	169		
Ru(2)–H(12)	182	169	169		
Ru(1)–H(13)	160	160			
Ru(1)–H(13)	168	162			

cluster compounds was possibly due to the formation of Ru$_3$(CO)$_{12}$ during the reaction, so they have also made complex 1 directly from Ru$_3$(CO)$_{12}$ and cis-cyclooctene.

The molecular structure of 2 is given with the atomic numbering scheme in Fig. 2. The bond lengths and relevant bond angles are presented in Tables 4 and 5. trans-Cyclododecene coordinates in the Ru$_3$ cluster via
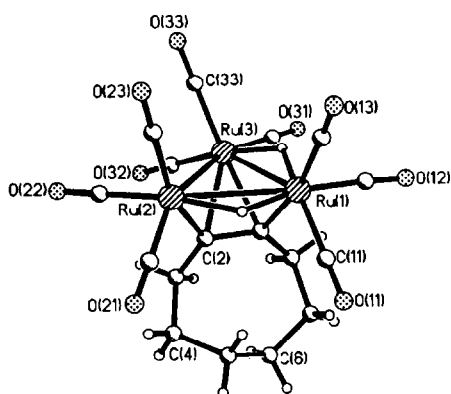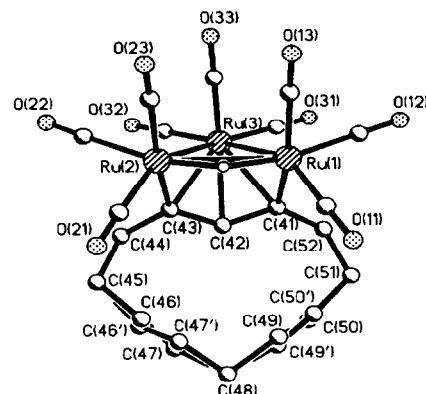
Table 5
Selected bond angles (°) in (μ-H)$_2$Ru$_3$(CO)$_9$(μ_3-η^2-C$_8$H$_{12}$) (1A and 1B), (μ-H)Ru$_3$(CO)$_9$(μ_3-η^3-C$_{12}$H$_{19}$) (2) and Ru$_3$(CO)$_{12}$ (6)

	1A	1B	2	6
Ru(2)–Ru(1)–C(11)	104.1(2)	102.5(3)	111.3(4)	98.9(1)
C(13)–Ru(1)–C(11)	93.6(3)	96.3(4)	95.5(6)	90.5(2)
C(12)–Ru(1)–C(11)	91.8(3)	93.8(4)	95.6(7)	104.0(2)
Ru(2)–Ru(1)–C(13)	103.0(3)	105.2(3)	89.1(5)	89.6(1)
Ru(3)–Ru(1)–C(13)	119.2(3)	118.3(3)	110.8(5)	89.2(1)
C(12)–Ru(1)–C(13)	94.8(3)	93.6(4)	87.8(7)	90.2(2)
Ru(3)–Ru(1)–C(12)	100.4(2)	98.8(3)	98.3(5)	97.1(1)
Ru(1)–Ru(2)–C(21)	107.8(2)	106.3(3)	115.8(6)	98.8(1)
C(23)–Ru(2)–C(21)	100.0(3)	100.9(4)	93.4(7)	90.2(2)
C(22)–Ru(2)–C(21)	93.3(3)	94.3(4)	95.3(8)	105.0(2)
Ru(1)–Ru(2)–C(23)	99.3(3)	98.8(3)	92.2(6)	89.1(1)
Ru(3)–Ru(2)–C(23)	105.5(3)	103.7(3)	115.9(6)	90.6(1)
C(22)–Ru(2)–C(23)	93.0(4)	93.4(4)	88.0(9)	90.2(2)
Ru(3)–Ru(2)–C(31)	94.1(2)	94.8(3)	94.0(5)	96.4(1)
Ru(1)–Ru(3)–C(31)	100.4(2)	96.2(3)	97.9(5)	96.4(1)
C(33)–Ru(3)–C(31)	101.3(3)	101.6(4)	97.5(8)	92.0(2)
C(32)–Ru(3)–C(31)	92.3(3)	92.4(4)	94.5(7)	103.3(2)
Ru(1)–Ru(3)–C(33)	111.2(2)	112.5(3)	78.6(5)	90.5(1)
Ru(2)–Ru(3)–C(33)	91.1(2)	89.9(2)	75.2(5)	87.0(1)
C(32)–Ru(3)–C(33)	91.4(3)	91.5(4)	96.6(8)	89.0(2)
Ru(2)–Ru(3)–C(32)	98.4(2)	102.9(3)	103.6(5)	100.2(1)
Ru(3)–Ru(1)–C(1)/C(41)	50.5(2)	50.6(2)	54.5(4)	89.6(1)
Ru(3)–Ru(2)–C(2)/C(43)	55.0(2)	54.5(2)	53.6(3)	88.9(1)
Ru(2)–Ru(1)–C(1)/C(41)	67.0(2)	66.8(2)	85.1(4)	89.1(1)
Ru(1)–Ru(2)–C(2)/C(43)	68.1(2)	67.9(2)	83.5(4)	90.2(1)
Ru(2)–Ru(3)–C(2)/C(43)	71.1(2)	71.0(2)	75.0(3)	90.1(1)
Ru(1)–Ru(3)–C(1)/C(41)	47.4(2)	47.7(2)	74.5(3)	89.9(1)

Scheme 1.

Fig. 2. Structure of (μ-H)Ru$_3$(CO)$_9$(μ_3-η^3-C$_{12}$H$_{19}$) (2).
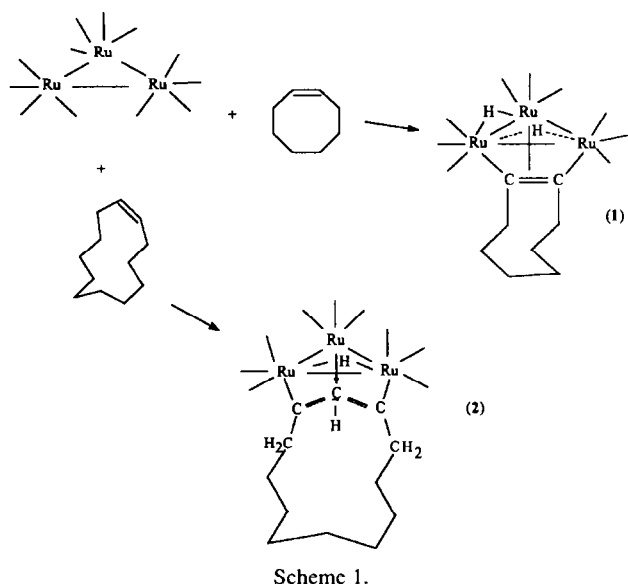
the μ_3-η^3-CCHC linkage. As in cluster **1** the coordination of olefin is activated by CO-dissociation. The olefin undergoes an intramolecular oxidative addition to a Ru centre with the hydride bridging the Ru(1)–Ru(2) bond, which is clearly longer (295.6 pm) than the remaining two Ru(2)–Ru(3) and Ru(1)–Ru(3) bond lengths (279.7 pm and 280.0 pm, respectively) (Table 5). The hydride ligand also induces the Ru(2)–Ru(1)–C(11) and Ru(1)–Ru(2)–C(21) bond angles to open. As in **1**, angles between equatorial CO ligands, C(12)–Ru(1)–C(11) and C(21)–Ru(2)–C(22), are smaller than those in the Ru$_3$(CO)$_{12}$ cluster because the effect of the repulsion caused by the hydride ligand is stronger than that of the equatorial oxygen. The organic ring is bonded with two formal σ-bonds, Ru(1)–C(41); Ru(2)–C(43), to the hydride-bridged Ru atoms and π-bonded to the Ru(3) atom. This is reflected, as in **1**, in Ru–C(olefin) bond lengths: the effect is approximately the same as in

1. The Ru–Ru–C(olefin) bond angles are also clearly smaller (Table 5) than the mean Ru–Ru–C$_{ax}$ angles of 90° in the parent cluster. The four ring carbon atoms (C46, C47, C49, C50) are disordered. The C atoms in the ring have high thermal motion resulting from the free movement of the nine carbon atoms that are not bonded to the metal cluster. The allylic bonds, C(41)–C(42) and C(42)–C(43), are 144.2(20) pm and 142.6(20) pm, respectively, which are shorter than normally observed for the single C–C bonds, indicating a delocalised double bond of the allylic unit.

In **2** the central allylic hydrogen of the μ_3-η^3-CCHC part of the C$_{12}$ ring and the hydride ligand show an intramolecular interaction; the coupling of the two protons is detected in ^{1}H NMR measurements: the metal hydride resonance is observed at -20.13 ppm and the allylic hydrogen at 6.66 ppm ($J_{HH} = 2.2$ Hz). These signals are found to broaden on decreasing the temperature below -30 °C. At -50 °C both signals, -20.13 and 6.66 ppm, appear as broad singlets ($\delta v = 7.5$ Hz). The coupling between the central allylic hydrogen and the metal hydride is obviously present at these low temperatures. In addition, a coupling of these two protons with other hydrogens of the dodecene ring (namely, those bonded to C(44) and C(52)) starts to appear at lower temperatures when the motion of the dodecene ring is slowed down. This additional coupling broadens the signals at -20.13 and 6.66 ppm and obscures the coupling observed at higher temperatures. In addition, other signals of the hydrogens in the cyclododecene ring broaden when decreasing the temperature because of the same kind of additional coupling.

A coupling similar to that in compound HRu$_3$(CO)$_9$-(C$_{12}$H$_{19}$) (2) has also been detected in the HRu$_3$(CO)$_9$-(C$_{12}$H$_{15}$) complex [4,8], which is isostructural with **2**. Its ^{1}H NMR spectrum consists of two doublets at 6.19 ppm and -20.24 ppm because of the allylic hydrogen and metal hydride, respectively. The protons are coupled together; $J_{HH} = 2.7$ Hz [8] or 2.5 Hz [4]. At least one example of the opposite also exists: in the HRu$_3$-

Fig. 1. Structure of (μ-H)$_2$Ru$_3$(CO)$_9$(μ_3-η^2-C$_8$H$_{12}$) (1).

$(CO)_9(\eta\text{-}C_5H_9)$ complex the high-field signal is not coupled detectably to the central allylic proton of the hydrocarbon [9].

4. Conclusion

The reactions of $Ru_3(CO)_{12}$ with some cyclic olefins resulted in two different coordination modes depending on the ligand. The coordination of cis-cyclic olefins seems to involve the $\mu_3\text{-}\eta^2$-bonding mode and coordination of trans-cyclic olefins tends to involve the μ_3-η^3-CCHC linkage to the metal core. Both cis-cyclooctene and trans-cyclododecene replace three axial carbonyls from the parent cluster. The coordination of cis-cyclooctene involves the $\mu_3\text{-}\eta^2$-bonding mode and that of trans-cyclododecene, the $\mu_3\text{-}\eta^3$-CCHC linkage to the Ru_3 triangle. The geometry of the parent $Ru_3(CO)_{12}$ cluster is changed during the ligand coordination, which is clearly seen in X-ray and spectroscopic characterization.

Acknowledgements

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