New pentanuclear complex $Ru_5(CO)_{11}(\mu_4\text{-}O)(\mu_3\text{-}H)(p\text{-}MeC_6H_4C(O)C(H)=CPh)_3$. Transformations of the triruthenium cluster $Ru_3(CO)_{12}$ in thermal reactions with α,β-unsaturated carbonyl compounds

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The new pentanuclear complex $Ru_5(CO)_{11}(\mu_4\text{-}O)(\mu_3\text{-}H)(p\text{-}MeC_6H_4C(O)C(H)=CPh)_3$ was synthesized by the reaction of $Ru_3(CO)_{12}$ with 3-phenyl-1-*p*-tolylprop-2-en-1-one. The complex was characterized by elemental analysis and NMR and IR spectroscopy. The crystal structure of the complex was established by X-ray diffraction. Three of five ruthenium atoms form five-membered oxaruthenacycles with the organic ligands. The complex with an unusual structure has 84 valence electrons and is stabilized by one bridging μ_4-O ligand in a square-planar environment, one bridging μ_3-H ligand located in the plane passing through three ruthenium atoms, and a semibridging interaction with one of the carbonyl groups.

Key words: dodecacarbonyltriruthenium, oxadiene ligands, oxaruthenacyclopentadienyl rings, η^3-dihydropyran rings, polynuclear complexes, X-ray diffraction study, IR spectra, NMR spectra.

Thermal reactions of $Ru_3(CO)_{12}$ with unsaturated organic compounds afford a great variety of complexes. On the one hand, ligands undergo various transformations, *viz*., dehydrogenation, dimerization, isomerization, *etc.*[1] On the other hand, numerous transformations of the metal core are known.[2,3] In most studies, primary attention was focused on a search for the characteristic features of transformations of organic molecules in the coordination sphere of the metal atom, whereas transformations of the metal core were most often only mentioned.

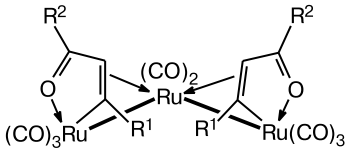
Thermal reactions of $Ru_3(CO)_{12}$ with functionalized olefins, in particular, with oxadienes, which we have studied earlier,[4—10] occur nonselectively to form a large number of products. Under drastic reaction conditions, the $Ru_3(CO)_{12}$ cluster is decomposed to give complexes with different nuclearities (from mononuclear to hexanuclear). The formation of five-membered oxaruthenacycles and dihydropyran rings from two molecules of the starting oxadiene is typical of this organic ligand. No regularities were revealed in the formation of clusters containing different numbers of metal atoms in different arrangements.

In the present study, the synthesis and structure of the new pentanuclear complex $Ru_5(CO)_{11}(\mu_4\text{-}O)(\mu_3\text{-}H)(p\text{-}MeC_6H_4C(O)C(H)=CPh)_3$ (**1**) are described. Complex **1** was prepared by the reaction of $Ru_3(CO)_{12}$ with 3-phenyl-1-*p*-tolylprop-2-en-1-one. We consider the structure of complex **1** in the light of structural analogies with other polynuclear complexes, which we have prepared earlier[4—6] by the reactions of $Ru_3(CO)_{12}$ with the oxadiene ligands. These data contribute to the overall picture of thermal transformations of the cluster.

Results and Discussion

Earlier, we have isolated the following five compounds from the products of the thermal reaction of $Ru_3(CO)_{12}$ with 3-phenyl-1-*p*-tolylprop-2-en-1-one: complexes **2—4**, $[Ru_4H(CO)_6(p\text{-}MeC_6H_4C(O)C(H)=CPh)_2[p\text{-}MeC_6H_3C(O)C(H)=C(H)Ph]$,[4] and $Ru_2O_2(CO)_4[\eta^3\text{-}OC(p\text{-}MeC_6H_4)C(H)(CH_2Ph)C(Ph)C(H)C(p\text{-}MeC_6H_4)]_2$.[8] The products were separated by silica-gel column chromatography. The main difficulties were that some complexes have similar R_f. Hence, further purification involved chromatography of individual fractions. All steps of separation of mixtures and purification of complexes by crystallization were monitored by IR spectroscopy. Less stable complexes or complexes obtained in minor amounts, while being identified in the initial steps of separation, were lost during the subsequent treatment. In the present study, we isolated, along with other compounds, new pentanuclear complex **1** in 3% yield from the reaction products of $Ru_3(CO)_{12}$ with 3-phenyl-1-*p*-tolylprop-2-en-1-one.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 403—408, March, 2006.



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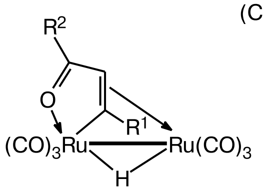

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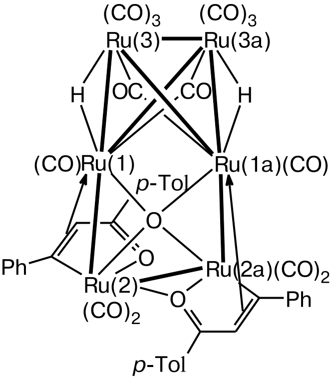


4

R^1, R^2 = Ph, Me; Ph, *p*-Tol; Fc, Fc; Ph, NMe_2; Ph, NEt_2; Ph, NHMe; Ph, $N(CH_2)_4$ (see Refs 4—6)

The structure of complex **1** was established by X-ray diffraction (Fig. 1, Table 1). The complex contains five ruthenium atoms, three of which, *viz.*, Ru(2), Ru(3), and Ru(4), form five-membered oxaruthenacycles with the organic ligand molecules. The five-membered oxaruthenacycles in complex **1** are analogous to those observed earlier[4—6] and are characterized by a flattened envelope conformation, in which the ruthenium atom deviates from the plane through the other four atoms of the ring toward the π-bonded ruthenium atom (average folding angle of the envelope is 10°).

The structure of complex **1** can be represented as a combination of the following two known fragments: the dinuclear fragment in which the oxaruthenacycle is π-coordinated to the Ru(5) atom (analogously to complex **2**) and the trinuclear fragment containing two oxaruthenacycles π-coordinated to the central Ru(1) atom (analogously to complex **3**).

The Ru(1), Ru(2), Ru(3), and Ru(4) atoms are located at the vertices of a tetragon, whose center is occupied by the μ_4-O(1M) atom. The coordination of the oxo atom is nearly square-planar (Ru(1)Ru(2)Ru(4)Ru(3) torsion angle is 13.5° and the dihedral angle between the Ru(1)O(1M)Ru(2) and Ru(3)O(1M)Ru(4) planes is 13.9°). Unlike the tetrahedral coordination of the μ_4-O atom, the square-planar coordination in metal complexes occurs rarely.[11]

Among the polynuclear reaction products of $Ru_3(CO)_{12}$ with 3-phenyl-1-*p*-tolylprop-2-en-1-one described earlier,[4] there is one complex with the μ_4-O atom (complex **4**). In complex **4**, the tetracoordinated oxygen atom is located in the center of a tetrahedron formed by the ruthenium atoms with equalized Ru—O distances of 2.097 Å.[4] In complex **1**, the Ru—O distances are nonequivalent (see Table 1).

The source of the μ_4-O atom in complexes **1** and **4** is unclear. Nevertheless, the atomic type was unambiguously established by X-ray diffraction. Attempts to refine this atom as another atomic type (for example, as a car-

Table 1. Selected geometric parameters of complex **1**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Ru(1)—Ru(2)	3.063(2)	Ru(2)—O(12)	2.090(8)	Ru(2)—O(1M)—Ru(3)	163.7(5)
Ru(1)—Ru(3)	3.216(2)	Ru(3)—O(13)	2.081(8)	Ru(2)—O(1M)—Ru(4)	79.9(3)
Ru(2)—Ru(4)	2.758(2)	Ru(4)—O(14)	2.092(8)	Ru(2)—O(1M)—Ru(1)	92.2(3)
Ru(3)—Ru(4)	3.068(2)	Ru(2)—C(14)	2.053(13)	Ru(3)—O(1M)—Ru(1)	98.1(3)
Ru(4)—Ru(5)	2.917(2)	Ru(3)—C(30)	2.066(12)	Ru(3)—O(1M)—Ru(4)	91.0(3)
Ru(1)—O(1M)	2.179(8)	Ru(4)—C(46)	2.053(13)	Ru(1)—O(1M)—Ru(4)	170.0(4)
Ru(2)—O(1M)	2.070(9)	Ru(1)—C(13)	2.247(12)	C(12)—O(12)—Ru(2)	113.4(8)
Ru(3)—O(1M)	2.079(8)	Ru(1)—C(14)	2.123(14)	C(28)—O(13)—Ru(3)	113.1(7)
Ru(4)—O(1M)	2.220(9)	Ru(1)—C(29)	2.306(14)	C(44)—O(14)—Ru(4)	112.2(7)
Ru(1)—C(1)	1.837(15)	Ru(1)—C(30)	2.284(13)	O(7)—C(7)—Ru(4)	163.4(11)
Ru(1)—C(2)	1.921(14)	Ru(5)—C(45)	2.187(14)	O(7)—C(7)—Ru(2)	119.6(10)
Ru(2)—C(3)	1.831(17)	Ru(5)—C(46)	2.089(14)	Ru(4)—C(7)—Ru(2)	77.0(5)
Ru(2)—C(4)	1.828(15)	O(12)—C(12)	1.299(15)	O(12)—C(12)—C(13)	116.4(12)
Ru(2)—C(7)	2.508(13)	O(13)—C(28)	1.276(15)	C(12)—C(13)—C(14)	119.7(12)
Ru(3)—C(5)	1.836(15)	O(14)—C(44)	1.267(15)	C(13)—C(14)—Ru(2)	107.5(9)
Ru(3)—C(6)	1.851(14)	C(12)—C(13)	1.423(17)	O(13)—C(28)—C(29)	118.4(11)
Ru(4)—C(7)	1.845(16)	C(13)—C(14)	1.442(17)	C(30)—C(29)—C(28)	116.5(12)
Ru(4)—C(8)	1.832(15)	C(28)—C(29)	1.457(17)	C(29)—C(30)—Ru(3)	108.9(9)
Ru(5)—C(9)	1.868(16)	C(29)—C(30)	1.417(17)	O(14)—C(44)—C(45)	117.6(11)
Ru(5)—C(10)	1.880(14)	C(44)—C(45)	1.459(17)	C(46)—C(45)—C(44)	118.7(12)
Ru(5)—C(11)	1.924(16)	C(45)—C(46)	1.411(18)	C(45)—C(46)—Ru(4)	107.4(9)

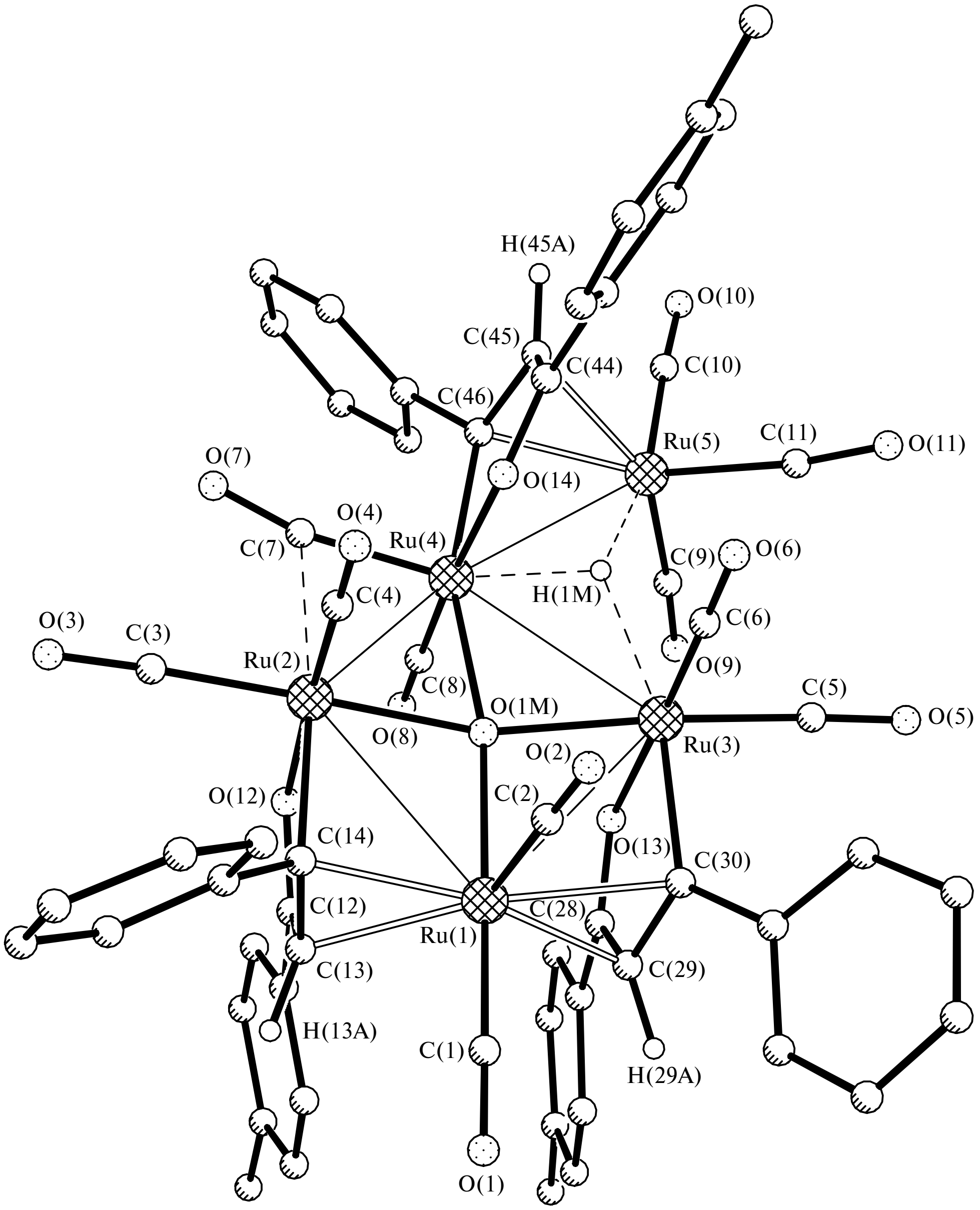
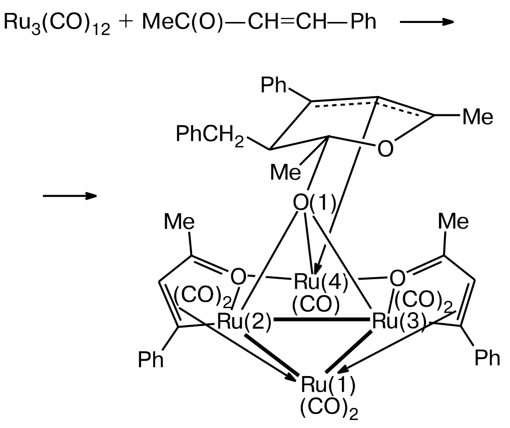


Fig. 1. Molecular structure of complex **1**. The hydrogen atoms of the phenyl and *p*-tolyl substituents are omitted.

bon atom) led to a very low thermal parameter and a noticeable increase in the *R* factors. We did not perform special experiments aimed at revealing the source of the oxygen atom. However, some conclusions can be drawn from the results of monitoring of the course of the reaction. The possible presence of traces of water in the reaction mixture cannot serve as a source of the oxo oxygen atom in complexes **1** and **4**. In the first steps, water reacts with $Ru_3(CO)_{12}$ to form ruthenium hydrides, as was demonstrated in the study[12] and is consistent with our chromatographic data. The fact that the amount of hydrides did not increase with increasing reaction time indicates that complete dehydration of the reaction mixture occurs in the first steps of the reaction. At the same time, the reactions of $Ru_3(CO)_{12}$ with oxadienes are characterized by the formation of unstable complexes with the η^3-dihydropyran rings.[7] In particular, we isolated[4] complex **5** as a product of the reaction with 4-phenylbut-3-en-2-one (Scheme 1). In this complex, the O(1) atom of the dihydropyran ligand is coordinated to three ruthenium atoms. Decomposition of complex **5** accompanied by elimination of the η^3-dihydropyran ring and the subsequent addition of species present in the reaction mixture (dinuclear hydride complex **2** or a Ru_4 butterfly) can afford both complexes **1** and **4**.

The ^{1}H NMR spectroscopic data for complex **1** provide evidence for the hydride ligand. We failed to unambiguously locate the position of the hydride ligand based

Scheme 1



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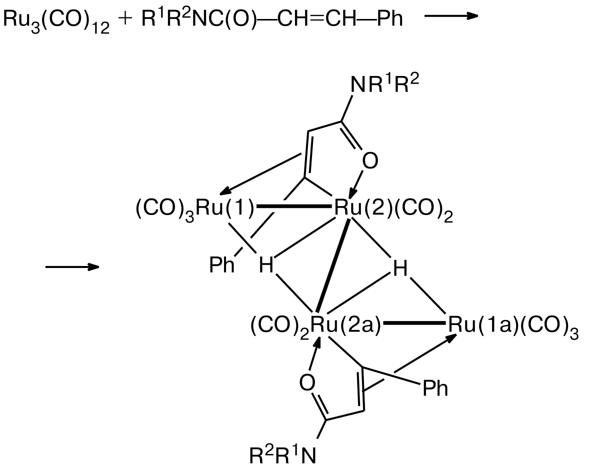
Scheme 2



6a—d

$R^1 + R^2 = (CH_2)_4$ (**a**); $R^1 = R^2 = Me$ (**b**); $R^1 = R^2 = Et$ (**c**); $R^1 = H$, $R^2 = Me$ (**d**)

on X-ray diffraction data (small needle-like and twin crystals give a very weak X-ray diffraction pattern). The signal for the hydride hydrogen in the ^{1}H NMR spectrum is observed at high field (δ –16.04) characteristic of the bridging ligands, through which three ruthenium atoms are linked to each other.[13] The structure of complex **1** indicates that the μ_3-H atom is, more probably, located between the Ru(3), Ru(4), and Ru(5) atoms. An analysis of difference electron density maps revealed an electron density peak between these atoms. This peak was assigned to the H(1M) atom. The Ru(3)—H(1M), Ru(4)—H(1M), and Ru(5)—H(1M) distances are 2.19, 1.79, and 1.60 Å, respectively, and the nonbonded Ru(3)...Ru(5) distance is 3.586(2) Å. This arrangement of the hydride ligand in complex **1** is evidenced by a close analogy to dinuclear hydride complexes **2**.[4] In addition, due to the arrangement of μ_3-H in the plane between the Ru(3), Ru(4), and Ru(5) atoms, the coordination of the Ru(3) and Ru(4) atoms becomes octahedral (without considering the metal—metal bonds) and the coordination of the Ru(5) atom becomes trigonal-bipyramidal. The pyramidal arrangement of μ_3-H above the plane of the triangular face is more characteristic of polynuclear ruthenium complexes.* The arrangement of the μ_3-hydride ligand in the plane of three metal atoms has been observed earlier in tetranuclear complex **6** (Scheme 2)[6] and the hexanuclear complex $Ru_6(CO)_{12}(\mu\text{-}H)_4(\mu_3\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2\text{-}NH_2\text{-}6\text{-}MeC_5H_4N)_2[P(4\text{-}MePh)_3]_2$.[14] In the spectrum of the latter complex, the singlet for the hydride hydrogen is observed at δ –16.21, which is consistent with our data for complex **1**.

Yet another characteristic feature of complex **1** is that one of the metal carbonyl groups is essentially nonlinear (Ru(4)—C(7)—O(7), 163(1)°). This distortion is indicative of a semibridging interaction between this group and the Ru(2) atom (Ru(2)...C(7), 2.51(1) Å) with the result that the coordination of the Ru(2) atom becomes octahedral.

Five ruthenium atoms in complex **1** are nearly coplanar (maximum deviation from the mean plane is 0.193 Å). Taking into account the additional coordination by the semibridging carbonyl group C(7)O(7) and the μ_3-hydride ligand, the coordination of the Ru(2), Ru(3), and Ru(4) atoms can be described as distorted octahedral. The other ruthenium atoms, Ru(1) and Ru(5), have a coordination number 5 (if the π-coordination to the olefinic bond of the oxaruthenacycle is considered as one coordination site), and their configuration corresponds to a distorted trigonal bipyramid. The number of cluster electrons (e) in complex **1** was estimated as 84 (each organic ligand donates 5e, and the oxo atom donates 6e). According to the effective atomic number rule, this implies the presence of only three metal—metal bonds in the pentanuclear complex.

All the Ru—Ru distances (see Table 1), except for the longest distance between the Ru(1) and Ru(3) atoms (3.216(2) Å), fall in a range typical of the Ru—Ru bonding distances in polynuclear ruthenium complexes (2.75—3.15 Å).[2] It is impossible to unambiguously determine which of the Ru—Ru distances given in Table 1 are bonding and which distances are forced due to the tightening effect of the bridging ligands.

The Ru(1)—Ru(2) and Ru(1)—Ru(3) distances (3.063(2) and 3.216(2) Å, respectively) are noticeably longer than the Ru—Ru distances (2.771—2.807 Å) in trinuclear complexes **3**.[4,5] Apparently, a saturation of the electronic configuration of the Ru(1) atom through coordination to the O(1M) atom results in a substantial weak-

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* The Cambridge Structural Database, May 2005 release.

ening of the bonding interactions between the ruthenium atoms in the trinuclear fragment of complex **1**.

The Ru(4)—Ru(5) distance (2.917(2) Å) is similar to the Ru—Ru bond lengths (2.861 Å (see Ref. 4) and 2.871 Å (see Ref. 6)) in dinuclear hydride complexes **2** and the dinuclear fragments of tetranuclear complex **6** with μ_3-H-ligands (2.926 Å).[6]

The nonequivalence of the two other Ru—Ru distances (Ru(2)—Ru(4), 2.758(2) Å; Ru(3)—Ru(4), 3.068(2) Å) characterizes the general asymmetry of complex **1** and is, apparently, due to the tightening effect of the semibridging carbonyl group C(7)O(7) and the antibonding effect of the μ-hydride ligand, respectively.

Therefore, the type of the metal core (cyclic, chain, *etc.*, see Refs 2 and 3) cannot be unambiguously described based on analysis of the geometric structure of complex **1**.

The same ambiguity in the description of the metal-core type was observed in other polynuclear complexes, which we have prepared by thermal reactions of $Ru_3(CO)_{12}$ with oxadienes. Hexanuclear complex **4** contains 98 cluster valence electrons, which implies the presence of five metal—metal bonds, although there are eight distances, which formally fall in a range typical of bonding distances in ruthenium clusters (Table 2).[4] Tetranuclear complex **5** has 68 cluster valence electrons, and, hence, the presence of two rather than three metal—metal bonds can be assumed based on the distances given in Table 2.[4] Tetranuclear complex **6** contains 64 cluster valence electrons, which implies the presence of four metal—metal bonds, whereas only three bonds were found.[6] Presumably, the electron-unsaturated ruthenium atoms are stabilized by the μ_3-hydride ligand.

Of all pentanuclear ruthenium complexes described in the literature, the $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CCPh_2)(\mu\text{-}PPh_2)(\mu_4\text{-}Ph_2CNC(O)N)$,[15] $Ru_5(CO)_{11}(\mu_5\text{-}C_2H)(\mu_3\text{-}SPh)(\mu\text{-}PPh_2)_2$,[16] and $Ru_5(CO)_{11}(\mu_5\text{-}C_2C(O)CH_2CH{=}CH_2)(\mu\text{-}PPh_2)_2)(\mu\text{-}Br)$ complexes[17] contain the metal cores most structurally similar to complex **1**. The complexes involve the Ru_4 fragment terminally linked to the fifth ruthenium atom. Each complex has 80 electrons and five Ru—Ru bonds. Other metal cores most commonly observed in pentanuclear complexes exhibit a tetragonal-pyramidal geometry (74e, eight Ru—Ru bonds), consist of three fused triangles (76e, seven Ru—Ru bonds), or adopt an envelope (78e, six Ru—Ru bonds), scorpion-like (80e, five Ru—Ru bonds), pentagon (80e, five Ru—Ru bonds), or an open pentagon (82e, four Ru—Ru bonds)* conformation. Complex **1** is a rare example of a pentanuclear ruthenium complex having 84 valence electrons.

Table 2. Selected bond lengths in complexes **4**—**6**

Bond	*d*/Å	Bond	*d*/Å
Complex **4**		Complex **5**	
Ru(1)—Ru(2)	3.114	Ru(1)—Ru(2)	2.916
Ru(1)—Ru(3)	3.016	Ru(1)—Ru(3)	2.908
Ru(1)—Ru(3a)	2.901	Ru(2)—Ru(3)	2.864
Ru(2)—Ru(2a)	3.081	Ru(2)—Ru(4)	3.431
Ru(3)—Ru(3a)	2.934	Ru(3)—Ru(4)	3.366
Ru(1)—Ru(1a)	3.435		
Complex **6**			
Ru(1)—Ru(2)	2.926	Ru(2)—Ru(2a)	3.011

The NMR and IR spectroscopic data are consistent with the structure of complex **1**. The IR spectrum shows nine absorption bands of CO ligands with different intensities, which indicates that molecule **1** is unsymmetrical. The spectrum in hexane shows no absorption of the semibridging metal carbonyl group in a region typical of this group due, apparently, to the fact that the bridging interaction is weak.

In the ^{1}H NMR spectrum, the protons of the σ,π-coordinated C=C bonds in the oxaruthenacycles appear as individual signals due to the nonequivalence of the ligand environment of the ruthenium atoms in the oxaruthenacycles. We assigned two closely-spaced singlets at δ 5.213 and 5.209 to the protons at the C(13) and C(29) atoms, respectively, because the difference in their spatial environment are very small. In the spectrum of complex **4**, the chemical shifts of the signals for the protons differ more substantially (δ 5.17 and 5.06).[4] In this complex, the Ru atoms in the oxaruthenacycles have the same ligand environment, but the η^3-dihydropyran fragment, which is not directly bound to the oxaruthenacycles, is unsymmetrical. In the spectrum of complex **5** having a twofold symmetry axis, the signals for the protons of both oxaruthenacycles are identical.[4] The signal for the proton of the σ,π-coordinated C=C bond of the third oxaruthenacycle in complex **1** appears as a doublet at δ 4.39 due to spin-spin coupling with the hydride hydrogen, whose signal appears as a doublet at δ −16.04. The spin-spin coupling constant is 1.0 Hz. The hydride hydrogen is involved in spin-spin coupling with the proton of only one oxaruthenacycle because it is far remote from the other oxaruthenacycles. An analogous spin-spin coupling (J = 1.0 Hz) was observed[4,6] in binuclear complexes **2**.

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The reactions of $Ru_3(CO)_{12}$ with α,β-unsaturated carbonyl compounds afford complexes containing different numbers of ruthenium atoms. These are mononuclear complexes and di-, tri-, and tetranuclear complexes containing no metal—metal bonds, in which the ruthenium atoms are linked to each other by bridging organic ligands.[7—9] Polynuclear clusters are generated in minor amounts upon decomposition of molecular fragments.

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* The Cambridge Structural Database, May 2005 release.

In addition to the hydride clusters $H_2Ru_4(CO)_{13}$, $H_4Ru_4(CO)_{12}$, and $H_2Ru_6(CO)_{18}$, the following clusters containing organic ligands were obtained: chain Ru_3 (for example, **3**)[4,7] and Ru_4 (for example, **6**) clusters,[4,6] a butterfly-like cluster Ru_4,[18] a Ru_4 cluster consisting of the Ru_3 triangle and the quaternary ruthenium atom, which is not directly bound to this triangle (**5**),[4] a Ru_5 cluster containing a dipper-type metal core (**1**), a Ru_6 cluster having a butterfly structure with two Ru atoms occupying wing-tip positions (**4**),[4] and a Ru_6 cluster consisting of two fused quadrangles.* We observed the retention of the triangular metal core only in the reaction with cinnamaldehyde.[10]

The transformation of $Ru_3(CO)_{12}$ follows two pathways. 1. The reaction affords polyhedral clusters (tetrahedron, a trigonal bipyramid, and an octahedron) containing a rigid metal core consisting of the metal triangles fused in different fashions.[19] Among these complexes are hydride complexes with carbonyl ligands and complexes containing a minimum number of organic ligands. 2. The presence of an organic ligand results in the formation of mono- or dinuclear species containing an organic ligand (generally, the five-membered oxaruthenacycle) in the first steps of the process, and then these species are assembled to form polynuclear complexes. Strong interactions between the metal atoms can be absent from the resulting complexes, and the charge redistribution occurs through the bridging organic ligands. The metal cores of the complexes can be flexible and adjust themselves to the steric and electronic features of the organic ligand.

Experimental

The ^1H NMR spectra were recorded on a Bruker Avance-300 spectrometer (300.13 MHz) in C_6D_6 with the use of the residual signal of incompletely deuterated C_6D_6 (δ_H 7.25) as the internal standard. The IR spectra were measured on a Specord-75 IR spectrophotometer.

Synthesis of tris[2,3,4-η^3-4-phenyl-2-(*p*-tolyl)-1-oxabuta-1,3-diene]-(μ_4-oxo)-tri(μ-hydrido)undecacarbonylpentaruthenium (1). A solution of 3-phenyl-1-*p*-tolylprop2-en-1-one (444 mg, 2 mmol) in heptane (150 mL) was added to $Ru_3(CO)_{12}$ (320 mg, 0.5 mmol) and the reaction mixture was refluxed for 4 h. After cooling to room temperature, the reaction mixture was filtered. The filtrate was chromatographed on a silica gel column. Elution with heptane afforded 9 mg of $Ru_3(CO)_{12}$ and 2 mg of a mixture of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$. Elution with a 10 : 1 mixture of heptane and CH_2Cl_2 gave small amounts of the $H_2Ru_4(CO)_{13}$ and $H_2Ru_6(CO)_{18}$ complexes, 11 mg (3%) of the $Ru_2(CO)_6(\mu\text{-}H)(p\text{-}MeC_6H_4C(O)C(H){=}CPh)$ complex (**2**), 80 mg (18%) of the $Ru_3(CO)_8(p\text{-}MeC_6H_4C(O)C(H){=}CPh)_2$ complex (**3**), 5 mg (2%) of the $Ru_6(CO)_{12}(\mu_2\text{-}CO)_2(\mu_4\text{-}O)(\mu_2\text{-}H)_2(p\text{-}MeC_6H_4C(O)C(H){=}CPh)_2$ complex (**4**), 9 mg (2%) of the $[Ru_4H(CO)_6(p\text{-}MeC_6H_4C(O)C(H){=}CPh]_2[p\text{-}MeC_6H_3C(O)C(H){=}C(H)Ph]$ complex, and 13.5 mg (3%) of the $Ru_5(CO)_{11}(\mu_4\text{-}O)(\mu_3\text{-}H)(p\text{-}MeC_6H_4C(O)C(H){=}CPh)_3$ complex (**1**). Complex **1**. IR, n(CO)/cm^{-1} (hexane): 2070 s, 2046 s, 2032 v.s, 2018 m, 2012 m, 1990 w, 1976 m, 1966 s, 1958 w. ^1H NMR of complex **1** (C_6D_6), d: −16.09 (d, 1 H, RuH, *J* = 1 Hz); 2.36, 2.38, and 2.43 (all s, 3 H each, CH_3); 4.39 (d, 1 H, C=CH, *J* = 1 Hz); 5.20 and 5.21 (both s, 1 H each, C=CH); 6.84—7.97 (m, 28 H, Ph). Found (%): C, 44.32; H, 2.65. $C_{59}H_{40}O_{15}Ru_5 \cdot CHCl_3$. Calculated (%): C, 44.66; H, 2.56. Small dark-red needle-like crystals were grown from a 1 : 2 chloroform—hexane mixture.

X-ray diffraction study. Crystals of $\mathbf{1} \cdot 2.5CHCl_3$ are triclinic, $C_{61.5}H_{42.5}Cl_{7.5}O_{15}Ru_5$, M = 1792.68, crystal dimensions 0.18×0.05×0.03 mm, space group $P\bar{1}$, at 120 K a = 12.650(3) Å, b = 13.517(3) Å, c = 22.098(5) Å, α = 97.432(6), β = 100.507(5), γ = 117.156(4)°, V = 3207(1) Å^3, Z = 2, d_{calc} = 1.857 g cm^{-3}, μ(Mo-Kα) = 15.28 cm^{-1}. The intensities of 26093 reflections (11273 independent reflections, R_{int} = 0.097) were measured on an automated Bruker SMART 1000 diffractometer equipped with an area detector (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, the ω scan step was 0.3°, the exposure time per frame was 40 s, $2\theta_{max}$ = 50°). The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The crystal structure contains chloroform solvate molecules, two of which are disordered. The hydride ligand (H(1M) atom) was located from a difference electron density map and included in the final refinement with fixed atomic coordinates and the isotropic displacement parameter. Other hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. The final R factors were R_1 = 0.0771 (refinement against F_{hkl} for 5321 reflections with $I > 2\sigma(I)$), wR_2 = 0.1806, and S = 0.966 (refinement against F^2_{hkl} for all independent reflections). All calculations were carried out on a PC using the known program packages.[20,21] The tables of atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters were deposited with the Cambridge Structural Database.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 04-03-32371 and 03-03-32499).

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* The complex was synthesized by the reaction of $Ru_3(CO)_{12}$ with 2-methyl-3-morpholino-1-phenylprop-2-en-1-one. The results will be published elsewhere.

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Received November 30, 2005;
in revised form January 19, 2006