Reactions of dodecacarbonyltriruthenium with oxadienes

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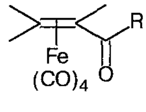
The results of the studies of thermal reactions of $Ru_3(CO)_{12}$ with oxadienes (4′-methylchalcone and benzylideneacetone) have been surveyed. The reactions yield a number of hitherto unknown bi- and polynuclear complexes, whose structures were determined by X-ray diffraction analysis, NMR, and IR spectroscopy. The complexes obtained contain η^3-coordinated structural moieties, *viz.*, five-membered chelate oxaruthena rings and/or dihydropyranyl rings. The fundamental differences in the chemical behavior of Ru and Fe carbonyls in the reactions with oxadienes and the differences between the reactions of Ru carbonyls with oxa- and azadienes have been discussed.

Key words: dodecacarbonyltriruthenium; iron carbonyls; bi- and polynuclear complexes; chelate five-membered oxaruthena rings; dihydropyranyl rings; X-ray structural study.

The reactions of iron carbonyls with functionally substituted olefins have been studied in detail.[1] In particular, it has been shown that the main products of the reactions with oxadienes are mononuclear complexes of η^2-tetracarbonyl- and η^4-tricarbonyliron of types



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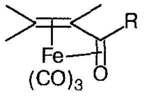

The interaction of these olefins with ruthenium and osmium carbonyls has been studied to a lesser degree. Carbonyls of these metals are known to react with olefins under conditions of photochemical and thermal processes. Photochemical reactions do not give new results compared with the reactions of Fe carbonyls, since in these cases mononuclear tetracarbonyl η^2-olefin complexes are produced.[2–4] On the other hand, during thermal reactions of Ru carbonyls, the cluster framework of the starting carbonyl is formally retained, but the olefinic ligand undergoes various transformations.[5] We have studied thermal reactions, most of all, in order to elucidate the principle distinctions between the behaviors of Ru and Fe carbonyls with respect to oxadienes.

Previously[6,7] cyclohexenone has been used as the oxadiene in thermal reactions of $Ru_3(CO)_{12}$. According to the data of systematic studies, thermal reactions of $Ru_3(CO)_{12}$ with mono- and diazadienes yield various bi- and polynuclear chelate complexes, rather than mononuclear olefin complexes.[8,9]

In the present work we survey the results obtained by us in a study of the thermal reactions of $Ru_3(CO)_{12}$ with oxadienes. We have attempted to show that, in contrast to the existing view that the ligand behavior of oxadienes is similar to that of their nitrogen-containing analogs, azadienes, the structures of complexes derived from these compounds are essentially different.

Results and Discussion

We used 4′-methylchalcone (**1a**) and benzylideneacetone (**1b**) as oxadienes. Thermal reactions of $Ru_3(CO)_{12}$ with compounds **1a** and **1b** in hydrocarbon solvents gave multi-component mixtures that were difficult to separate, from which complexes **2a**—**6a** (in the case of **1a**) and complexes **2b**, **3b**, and **7b** (in the case of **1b**) were isolated and identified (Scheme 1). The conditions of the reactions and the detailed results of X-ray structural studies have been reported previously.[10–12]

The courses of the reactions were monitored by the changes in the IR spectra of the reaction mixtures in the region of the stretching vibrations of metalcarbonyl groups. The products were separated by chromatography using columns with silica gel. The main difficulties lay in the fact that some complexes and compounds, $PhCH_2CH_2COR$, resulting from the reduction had similar R_f values. Therefore, in many cases, we had to chromatograph separate fractions repeatedly. All of the steps of the separation of mixtures and purification of complexes by crystallization were monitored by IR spectroscopy. Crystals for X-ray structural studies were prepared by recrystallization from hydrocarbon solvents or from their mixtures with dichloromethane.

No mononuclear complexes were isolated in the thermal reactions. The resulting bi- and polynuclear complexes (see Scheme 1), except for **6a**, incorporate a

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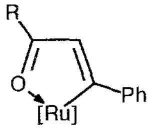
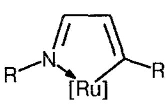
common structural fragment, which is a five-membered chelated oxaruthena ring (**A**).



A



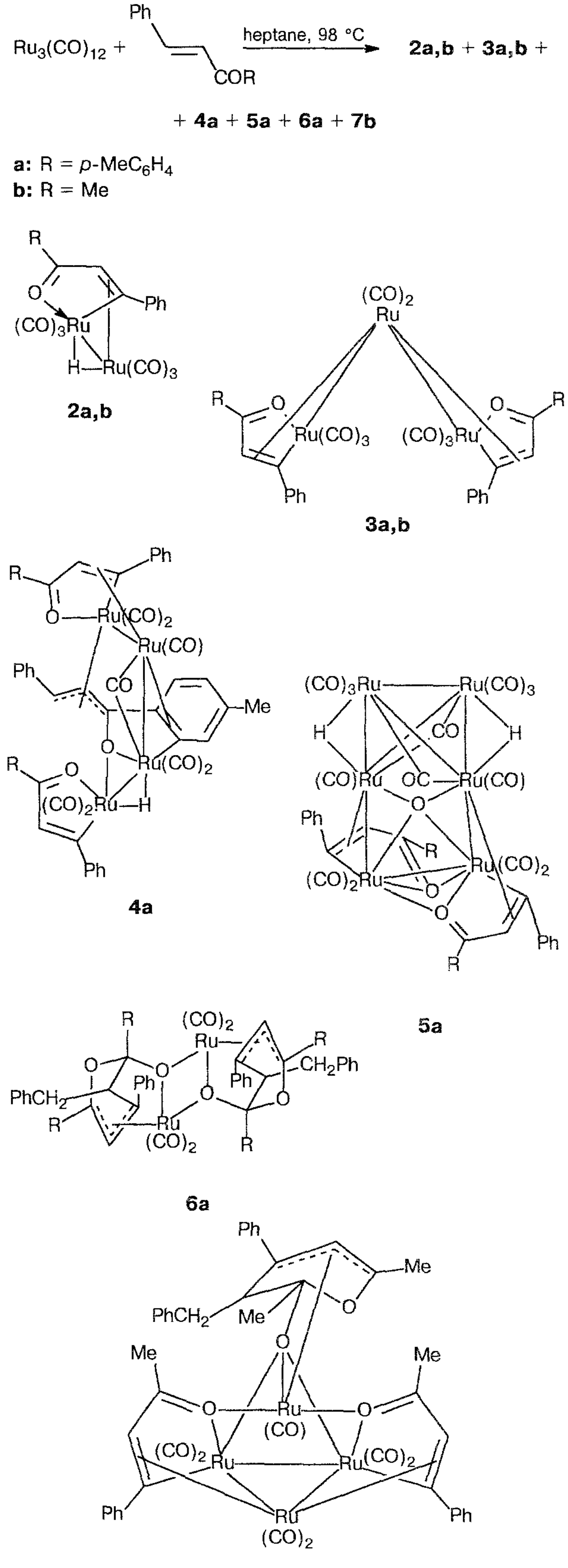
B

The reactions of azadienes with $Ru_3(CO)_{12}$ are known to yield complexes that incorporate analogous azaruthena rings[8] (**B**). Rings **A** and **B** are able to coordinate additional Ru atoms and to form bonds with other parts of the complex molecule. This ends the similarity between oxa- and azadienes in the reactions with $Ru_3(CO)_{12}$. The chelate ring **A** can act as a ligand and forms η^3-complexes that involve a C=C bond and a Ru atom (see Ref. 11), whereas chelate **B** reacts with $Ru_3(CO)_{12}$ to yield predominantly η^5-complexes in which ring **B** is analogous to the cyclopentadienyl ligand.[8]

All of the complexes isolated by us contain chelate ring **A** with η^3-type coordination of a Ru atom. Complexes **2a,b** and **3a,b** with this type of coordination are of particular interest. Compounds **2a,b** are stable and have been isolated in the individual state.[10] At the same time, the corresponding complexes cannot be isolated from the thermal reactions of azadienes due to their high reactivity.* One of the possible routes of their subsequent transformations in the presence of an excess of azadiene is the formation of azaruthena analogs of ruthenocene.[8] Under the same conditions, compounds **2** are probably converted into η^3-complexes **6**.

In order to elucidate the reasons for these distinctions, we compared the lengths of the normal C=O bond (1.222 Å) in unsaturated ketones[14] and of the C=O(−M) bond [1.30(2) Å] in the chelate ring of complex **4a** that is not coordinated by the second metal atom, and also the lengths of the normal C=N bond (1.279 Å)[14] and of the C=N(−M) bond [1.290(4) Å] in the azaruthena chelate ring.[15] The comparison showed that the C=O and C=N bonds are lengthened upon the formation of the chelate rings; the C=N bond is lengthened to a lesser degree. It is reasonable to suggest that the order of the C=O bond decreases more significantly than that of the C=N bond. This may be the reason for the inertness of the π-system of the C=O group with respect to interaction with the second metal atom. The steric restrictions caused by the R substituents (Me, p-MeC_6H_4), which are present in ring **A** and absent from ring **B**, are a possible, though a very doubtful, reason for the different behavior of rings **A** and **B**. On the other hand, it should be noted that the O atom in ring **A**, unlike the N atom in ring **B**, possesses a lone

Scheme 1



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* Nitrogen analogs of complexes **2** are prepared by an alternative method.[13]

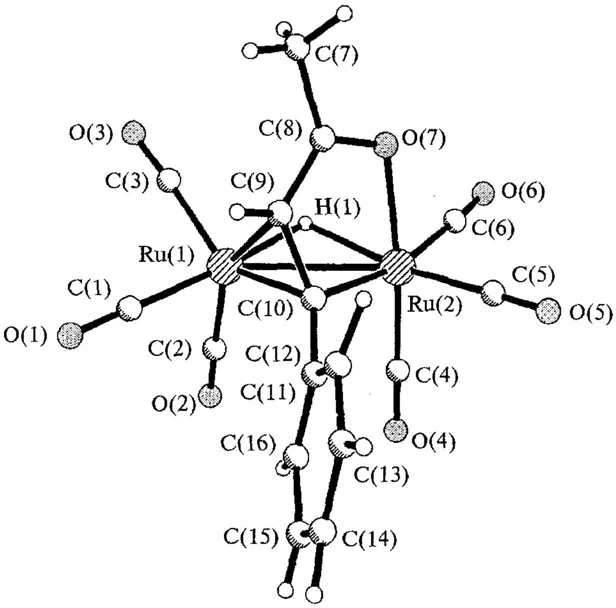


Fig. 1. The structure of molecule **2b**.

Table 1. The main bond lengths (*d*) in molecule **2b**

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Ru(2)	2.861(1)	O(7)—C(8)	1.265(5)
Ru(1)—C(9)	2.239(4)	C(8)—C(9)	1.411(6)
Ru(1)—C(10)	2.109(4)	C(9)—C(10)	1.468(5)
Ru(2)—O(7)	2.104(3)	Ru(1)—H(1)	1.82(7)
Ru(2)—C(10)	2.104(4)	Ru(2)—H(1)	1.98(7)

electron pair. Coordination of one more Ru atom by this electron pair is apparently preferred over its interaction with the π-electron system of the C=O bond.

The optimal conditions for preparing complexes **2a,b** involve short-term boiling of the reaction mixture in heptane in the presence of a 3—4-fold excess of the ligand. Under these conditions, the yield of **2a** can be as high as 20 %, and that of **2b** can be up to 50 %. In boiling hexane, the reaction occurs too slowly and requires heating for many hours, and the yield of **2b** does not exceed 15 %. The structures of complexes **2** were determined based on the data of an X-ray structural study of complex **2b** and the similarity of spectral characteristics of **2a** and **2b**.

The Ru atoms in binuclear complex **2b** (Fig. 1, Table 1) are linked by a metal—metal bond and a μ-hydride bridge. The electron density in the chelate η^3-metallacycle is substantially redistributed with respect to that in the starting benzylideneacetone: the C=C and C=O double bonds are lengthened by 0.17 and 0.06 Å, respectively, and the C—C bond in the metallacycle is shortened by 0.09 Å compared to analogous values in the uncoordinated *p*-bromobenzylideneacetone[16] (there are no literature data on unsubstituted benzylideneacetone).

The IR spectra of complexes **2a,b** exhibit six bands corresponding to the stretching vibrations of the CO group, which coincide in their positions and relative intensities (Table 2). At the same time, due to the coordination with the metal, the absorption bands for keto groups are missing from their normal region. The ^{1}H NMR spectra (see Table 2) of both complexes exhibit the signals of the proton of the —COCH= group as doublets due to the spin-spin interaction with the hydride H atom. In the spectrum of **2b** this signal is located at a lower field. The doublets of the bridging hydride atoms in the spectra of both complexes have similar chemical shifts and identical spin coupling constants. In conformity with the structure determined for complexes **2a** and **2b**, the ^{13}C NMR signals of the olefinic α-C atoms located in the neighborhood of the keto group are shifted substantially upfield (with respect to those in the spectra of the starting oxadienes **1a** and **1b**), which is caused by the π coordination of the metal to the C=C bond; the signals of the β-C atoms, σ,π-bound to the metal atoms, and the signals of the C atoms of the coordinated keto groups are shifted downfield to lesser degrees.

The conclusion on the structure of complexes **3** was based on the results of an X-ray structural study of complex **3a**. Molecule **3a** contains two rings **A**, which are η^3-bound to the $Ru(CO)_2$ group (Fig. 2, Table 3) and has a second-order noncrystallographic symmetry axis, which is reflected in the fact that the IR and NMR spectra are simple. For example, the methyl groups of complex **3a** are responsible for a singlet at δ 2.35 in the ^{1}H NMR spectrum, and the protons of the oxaruthena rings exhibit a singlet at δ 3.45. The IR spectrum in hexane exhibits only five absorption bands associated with the carbonyl ligands (see Table 2). Its analogous spectral characteristics allow one to attribute a similar structure to complex **3b**.

In addition to compounds **2a** and **3a**, tetranuclear complex **4a** and hexanuclear complex **5a** (see Scheme 1) were isolated from the products of the reaction of $Ru_3(CO)_{12}$ with oxadiene **1a**. Molecule **4a** incorporates a metal chain consisting of four Ru atoms and three dehydrochalcone ligands, which are linked to the metal atoms in various ways (Fig. 3, Table 4). Two terminal ligands form oxaruthena rings **A**, one of which is linked to the rest of the molecule *via* a metal—metal bond and bridging H and O atoms. The other ring **A** is η^3-coordinated to the neighboring metal atom. Clearly the geometry of these metallacycles is somewhat different. In fact, in the case of the ring **A** that is η^3-coordinated to the neighboring metal atom, the length of the C=C bond [1.47(2) Å] involved in the coordination is 0.1 Å greater than the length of the corresponding C=C bond in the non-coordinated metallacycle [1.36(2) Å]. On the other hand, the lengths of the C=O bonds in both rings are identical to within the experimental error (1.26(2) and 1.30(2) Å for the coordinated and non-coordinated rings,

Table 2. The data of NMR and IR spectroscopy for compounds **1**—**7**

Compound	IR (hexane), $\nu(C{\equiv}O)/cm^{-1}$	^1H NMR ($CDCl_3$), δ ($J_{H,H}$/Hz)	
		δ ^1H	δ ^{13}C
1a		2.22 (s, 3 H); 6.59 (d, 1 H, *J* = 16.3); 7.39 (d, 1 H, *J* = 16.3); 7.2—7.4 (m, 5 H)	26.20, 126.03, 127.19, 127.82, 129.28, 133.40, 141.90, 196.53
1b		2.26 (s, 3 H); 7.44 (d, 1 H, *J* = 15.7); 7.72 (d, 1 H, *J* = 15.7); 7.1—7.9 (m, 9 H)	20.78, 121.11, 127.68, 127.89, 128.11, 128.55, 129.58, 134.20, 134.85, 142.68, 143.24, 188.49
2a	2098 m, 2062 v.s, 2038 s, 2014 v.s, 2004 s, 1982 m	−12.50 (d, 1 H, *J* = 1); 2.12 (s, 3 H); 3.55 (d, 1 H, *J* = 1); 7.0—7.5 (m, 5 H)	22.97, 55.11, 125.64, 127.09, 128.77, 144.32, 152.33, 189.38, 191.17, 193.44, 215.89
2b	2098 m, 2062 v.s, 2038 s, 2014 v.s, 2006 s, 1980 m	−12.21 (d, 1 H, *J* = 1); 2.36 (s, 3 H); 4.25 (d, 1 H, *J* = 1); 7.1—7.6 (m, 9 H)	21.57, 52.22, 125.65, 127.68, 127.99, 128.91, 129.22, 130.92, 143.12, 145.28, 189.61, 191.20, 193.50, 208.20
3a	2088 m, 2074 s, 2020 v.s, 1996 m, 1934 w	1.46 (s, 3 H); 2.61 (s, 1 H); 7.1—7.4 (m, 5 H)	
3b	2084 s, 2072 s, 2018 v.s, 1996 s, 1930 w	2.35 (s, 3 H); 3.45 (s, 1 H); 6.8—7.1 (m, 9 H)	21.75, 69.05, 126.25, 126.45, 127.57, 129.46, 131.78, 143.83, 151.81, 181.98, 192.93, 194.83, 198.85, 205.53, 207.37
4b	2054 m, 2040 s, 2030 m, 1988 s, 1980 v.s, 1960 w, 1860 w	−11.45 (s, 1 H); 2.28 (s, 3 H); 2.32 (s, 3 H); 2.42 (s, 3 H); 4.66 (s, 1 H); 4.86 (d, 1 H, *J* = 13.5); 5.46 (d, 1 H, *J* = 13.5); 6.21 (d, 1 H, *J* = 8.5); 6.08 (d, 1 H, *J* = 8.5); 6.8—7.9 (m, 24 H); 8.42 (s, 1 H)	
5a	2088 s, 2062 v.s, 2038 s, 2030 v.s, 2026 s, 1074 m, 1966 v.s, 1838 m	−12.56 (s, 1 H); 2.49 (s, 3 H); 4.79 (s, 1 H); 7.1—8.2 (m, 9 H)	
6a*	2076 m, 2064s, 2004 s		
7b	2040 m, 2036 m, 2006 s, 2002 s, 1998 v.s, 1964 s, 1948 s, 1936 v.s	0.89 (s, 3 H); 1.74 (s, 3 H); 1.91 (s, 6 H); 2.5—3.1 (m, 3 H); 3.82 (s, 1 H); 5.06 (s, 1 H); 5.17 (s, 1 H); 7.0—7.8 (m, 20 H)	

* The IR spectrum was recorded in CH_2Cl_2.

respectively). It is of interest that both metallacycles exist in envelope conformations, however, the magnitudes of the deviation of the M atom from the plane in which the other four atoms lie are substantially different in these rings (0.20 and 0.54 Å, respectively). The central ligand in molecule **4a** is a μ_4-bridge, *i.e.*, it is linked to all four of the metal atoms. An important peculiarity of this bridge is the conversion of the oxadiene ligand into an oxyallyl ligand, which is probably due to the presence of the second aromatic substituent in the ligand. This substituent is *ortho*-metallated by one Ru atom and π-coordinated by another Ru atom through one of the double bonds. This disruption of the aromatic character of the substituents was not observed in the study of reactions of oxadienes with Fe carbonyls. The spectroscopic characteristics of cluster **4a** given in Table 2 are in agreement with the structure established.

Hexanuclear cluster **5a** has a second-order crystallographic symmetry axis (Fig. 4, Table 5). The Ru(1), Ru(1a), Ru(3), and Ru(3a) atoms form a "butterfly", the ends of whose "wings" are η^3-bonded to the oxaruthena rings. Each face of the wing has an asymmetrical bridging CO group on one side and a μ-hydride bridge on the other side. The presence of the latter has been confirmed by the ^1H NMR spectrum (δ −12.56). Because of the hydride bridges, the Ru—Ru bond length is 0.1 Å greater than the length of the Ru—Ru bonds that are drawn together only by carbonyl bridges, which is in agreement with the well known loosening effect of μ-hydride ligands.[17] The Ru(2) and Ru(2a) atoms incorporated in the oxaruthena rings are bonded to one another, which results in closure of the metallic framework of the cluster. In addition each of the Ru atoms of the chelate ring is linked to the O atom of the neighboring ring. Thus, both lone electron pairs of the O atoms are involved in the coordination with the metal atoms. It should be noted that the Ru—O bond in the chelate metallacycle [2.316(4) Å] is longer than analogous bonds in complexes **2b**, **3a**, and **4a** (2.09—2.12 Å) in which the O atom coordinates only one metal atom.

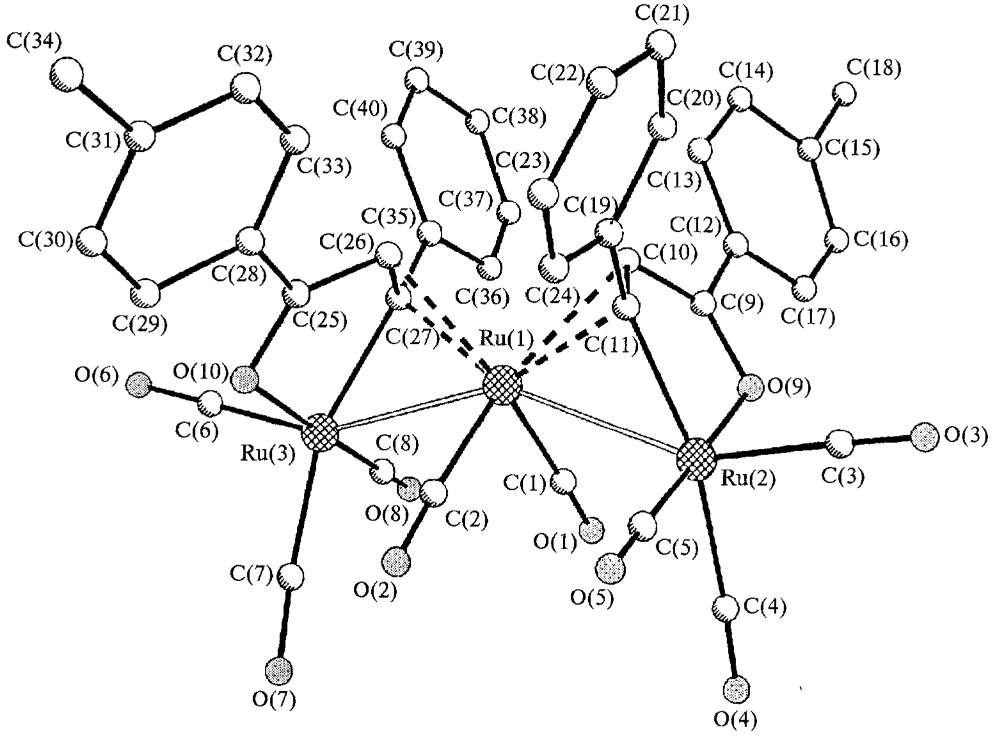


Fig. 2. The structure of molecule **3a**.

Table 3. The main bond lengths (*d*) in molecule **3a**

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Ru(2)	2.796(2)	C(10)—C(11)	1.45(3)
Ru(1)—Ru(3)	2.807(2)	C(9)—C(12)	1.47(3)
Ru(1)—C(10)	2.25(2)	C(11)—C(19)	1.47(3)
Ru(1)—C(11)	2.17(2)	Ru(3)—O(10)	2.12(1)
Ru(1)—C(26)	2.25(2)	Ru(3)—C(27)	2.06(2)
Ru(1)—C(27)	2.14(2)	C(10)—C(25)	1.32(3)
Ru(2)—O(9)	2.12(1)	C(25)—C(26)	1.39(3)
Ru(2)—C(11)	2.08(2)	C(26)—C(27)	1.46(3)
O(9)—C(9)	1.24(3)	C(25)—C(28)	1.48(3)
C(9)—C(10)	1.46(3)	C(27)—C(35)	1.46(3)

The presence of the tetracoordinated O(9) atom located in the middle of the tetrahedron formed by Ru(1), Ru(1a), Ru(2), and Ru(2a) in molecule **5a** is quite unexpected. It may be formally considered that this O atom is linked to two Ru atoms by σ bonds and is linked to the other two Ru atoms by n-donor bonds. Actually all four of these bonds are equalized (two crystallographically independent values are 2.097(4) and 2.098(4) Å). The origin of this O atom is unclear. Complex **5a** as a whole has a system of fused rings containing Ru atoms.

To complete the consideration of complexes **2—5**, it should be once again emphasized that they are prone to form η^3-ruthenaallyl (rather than η^5-ruthenaoxacyclopentadienyl) chelate rings and that the O atoms of the chelate rings of these complexes participate in additional coordination due to their second lone electron pairs.

Of the products of thermal reactions of oxadienes **1a,b**, we also managed to isolate and characterize two complexes **6a** and **7b**, which differ from those considered above by the fact that they contain a new ligand, a η^3-dihydropyranyl ring formed from two oxadiene molecules.[12] It should be noted that the nitrogen analog of this ligand was not detected in the products of thermal reactions of $Ru_3(CO)_{12}$ with azadienes.

Binuclear complex **6a** was isolated from the mixture of crystals that directly precipitated from the reaction mixture. Unfortunately, we could not choose the conditions for the chromatographic isolation of this compound, and separated characteristic crystals of **6a** from the main bulk of the precipitate mechanically. The molecule of complex **6a** is centrosymmetrical and consists of two identical fragments connected by two bridging O atoms that form a Ru_2O_2 four-membered ring (Fig. 5, Table 6). Each of the Ru atoms is η^3-coordinated by the dihydropyranyl ligand.

Tetranuclear complex **7b** is of interest, since it incorporates both of the above-mentioned fragments, namely, two oxaruthena rings and a dihydropyranyl ring (Fig. 6, Table 7). In this complex, three Ru atoms are combined into a three-membered ring; two of them are constituents of the oxaruthena rings, and the third atom is η^3-coordinated by these rings. The Ru(4) atom is not directly linked to the ruthenium triangle, but is bonded to the O atoms of the oxaruthena rings. In addition

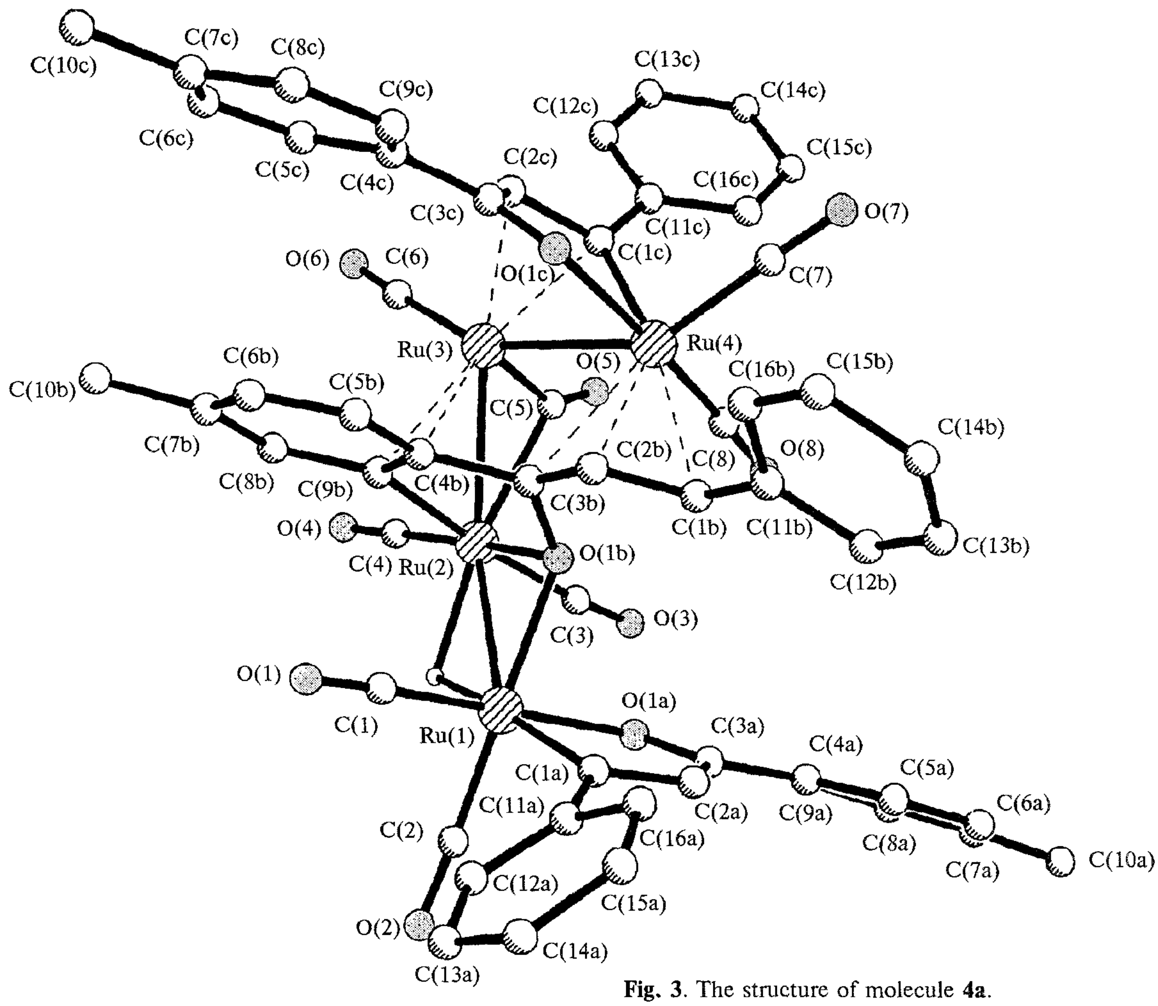


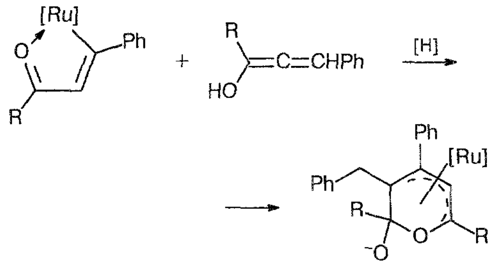
Fig. 3. The structure of molecule **4a**.

Table 4. The main bond lengths (*d*) in molecule **4a**

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Ru(2)	2.867(2)	Ru(3)—Ru(4)	2.854(2)
Ru(1)—O(1a)	2.12(1)	Ru(3)—C(5)	1.96(2)
Ru(1)—O(1b)	2.12(1)	Ru(3)—C(4b)	2.47(1)
Ru(1)—C(1a)	2.06(2)	Ru(3)—C(9b)	2.26(2)
O(1a)—C(3a)	1.30(2)	Ru(3)—C(1c)	2.12(2)
C(1a)—C(2a)	1.36(2)	Ru(3)—C(2c)	2.22(2)
C(2a)—C(3a)	1.43(2)	Ru(4)—O(1c)	2.09(1)
Ru(2)—Ru(3)	2.735(2)	Ru(4)—C(1c)	2.12(2)
Ru(2)—O(1b)	2.10(1)	Ru(4)—C(1b)	2.42(1)
Ru(2)—C(5)	2.28(2)	Ru(4)—C(2b)	2.21(2)
Ru(2)—C(9b)	2.11(1)	Ru(4)—C(3b)	2.39(2)
O(1b)—C(3b)	1.39(2)	O(1c)—C(3c)	1.26(2)
C(1b)—C(2b)	1.35(2)	C(1c)—C(2c)	1.47(2)
C(2b)—C(3b)	1.43(2)	C(2c)—C(3c)	1.41(2)
C(3b)—C(4b)	1.47(2)	Ru(1)—H(0)	2.0(1)
C(4b)—C(9b)	1.41(2)	Ru(2)—H(0)	1.9(1)

Ru(4) is η^3-coordinated to the dihydropyranyl ring. The O atom of the hydroxy group of the dihydropyranyl ligand, along with the bond with Ru(4), participates in the n-donor interaction with two Ru atoms of the oxaruthena rings. The latter two Ru—O bonds are equalized; their length (aver.) is 2.22 Å, whereas the Ru(4)—O(10) bond is substantially shorter [2.114(6) Å].

Due to the complex structure of complexes **6a** and **7b**, it is difficult to discuss the pathways for their formation. However, one may suggest that the η^3-dihydropyranyl ring in these complexes is formed from the five-membered oxaruthena rings **A** *via* insertion of the second oxadiene molecule in the dienol allene form with the addition of an H atom (reaction (1)).



(1)

This assumption is in agreement with the literature data[18] on a similar transformation of oxametallacycles into η^3-pyranyl complexes by the reaction with alkynes (reaction (2)).

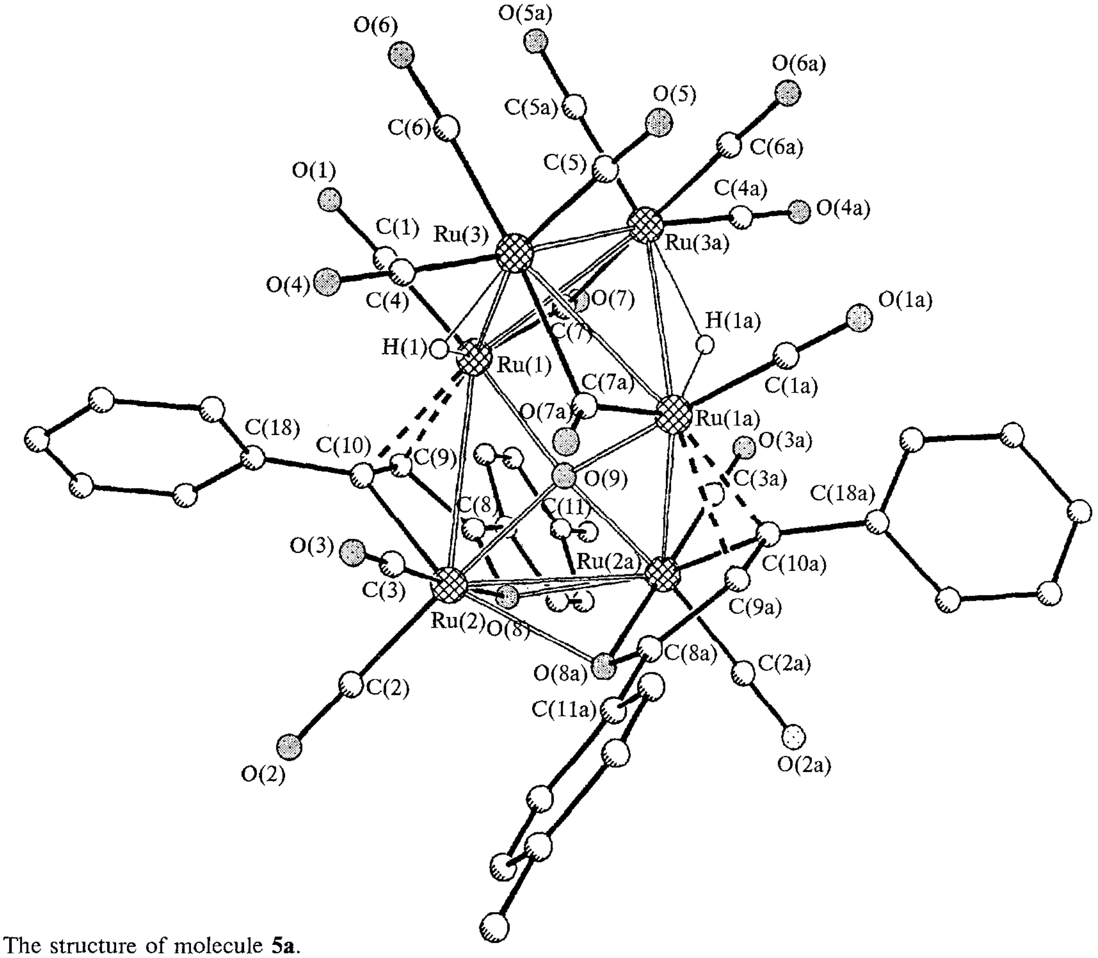
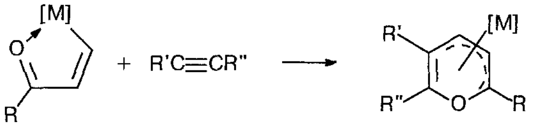


Fig. 4. The structure of molecule **5a**.



(2)

This scheme is supported to some extent by some peculiarities of the reactions under study. According to IR spectroscopy data, the accumulation of complex **7b** containing a η^3-dihydropyranyl ring is accompanied by a decrease in the relative amounts of complexes **2b** and **3b** incorporating oxaruthena rings. Similarly, in the reaction mixture ($Ru_3(CO)_n$ + **1a**) in the presence of excess ligand, compounds **2a** and **3a** are converted into a mixture of products, one of which is complex **6a**, which precipitates as a crystalline solid. At the same time, no complex **6a** was detected in the product mixture formed from **2a** and **3a** in the absence of the ligand.

* * *

Table 5. The main bond lengths (*d*) in molecule **5a**

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Ru(2)	3.114(1)	Ru(1)—C(10)	2.151(6)
Ru(1)—Ru(3)	3.016(1)	Ru(2)—O(8)	2.316(4)
Ru(1)—Ru(3a)	2.901(1)	Ru(2)—O(8a)	2.127(5)
Ru(2)—Ru(2a)	3.081(1)	Ru(2)—C(10)	2.058(6)
Ru(3)—Ru(3a)	2.934(1)	O(8)—C(8)	1.304(7)
Ru(1)—C(7)	1.966(9)	C(9)—C(8a)	1.422(9)
Ru(3)—C(7)	2.287(7)	C(9)—C(10)	1.46(1)
Ru(1)—O(9)	2.097(4)	C(8)—C(11)	1.47(1)
Ru(2)—O(9)	2.098(4)	C(10)—C(18)	1.480(9)
Ru(1)—C(9)	2.234(6)		

The results presented above indicate that thermal reactions of $Ru_3(CO)_{12}$ with oxadienes give bi- and polynuclear complexes whose structures differ fundamentally from that of the carbonylruthenium complexes prepared from azadienes. The distinctions observed are to a large extent associated with the fact that the π electrons of the C=O group in the oxaruthena ring have a substantially lower tendency to participate in coordination with a Ru atom than those of the C=N group in a similar azametallacycle. In addition, the lone electron pair of the O atom of the oxaruthena ring participates in the formation of the bond with another Ru atom, which results in the appearance of more complex fused struc-

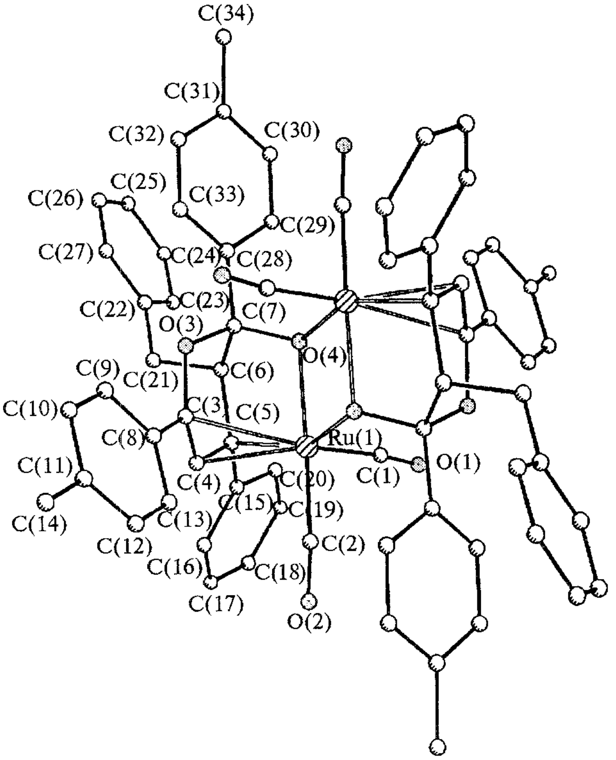


Fig. 5. The structure of molecule **6a**.

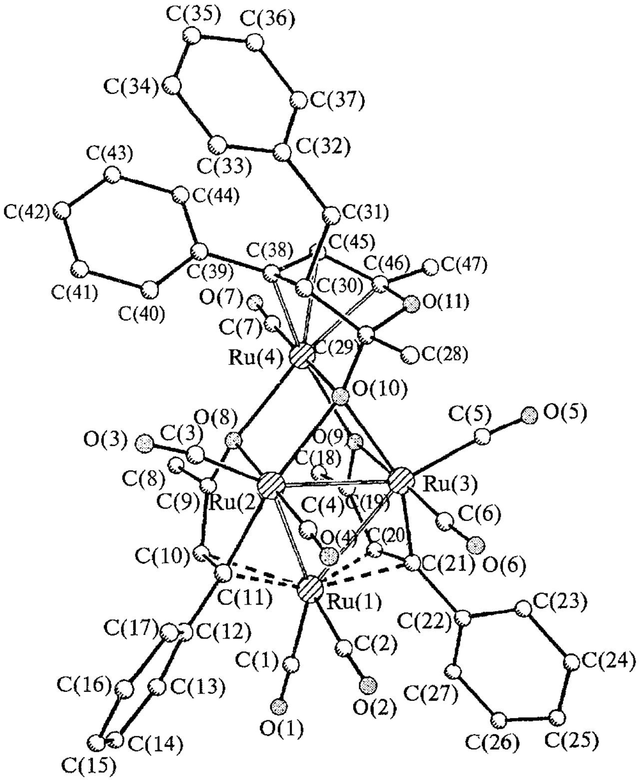


Fig. 6. The structure of molecule **7b**.

Table 6. The main bond lengths (*d*) in molecule **6a**

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Ru(2)	2.916(2)	C(20)—C(21)	1.43(1)
Ru(1)—Ru(3)	2.908(2)	Ru(2)—O(10)	2.224(8)
Ru(2)—Ru(3)	2.864(1)	Ru(3)—O(10)	2.215(8)
Ru(1)—C(10)	2.31(1)	Ru(4)—O(8)	2.234(8)
Ru(1)—C(11)	2.15(1)	Ru(4)—O(9)	2.221(9)
Ru(1)—C(20)	2.27(1)	Ru(4)—O(10)	2.114(6)
Ru(1)—C(21)	2.22(1)	Ru(4)—C(38)	2.18(1)
Ru(2)—O(8)	2.131(6)	Ru(4)—C(45)	2.11(1)
Ru(2)—C(11)	2.07(1)	Ru(4)—C(46)	2.17(1)
O(8)—C(9)	1.30(2)	O(10)—C(29)	1.44(2)
C(9)—C(10)	1.40(2)	O(11)—C(29)	1.44(1)
C(10)—C(11)	1.46(1)	O(11)—C(46)	1.42(1)
Ru(3)—O(9)	2.137(6)	C(29)—C(30)	1.51(2)
Ru(3)—C(21)	2.05(1)	C(30)—C(38)	1.55(1)
O(9)—C(19)	1.31(2)	C(38)—C(45)	1.41(2)
C(19)—C(20)	1.40(2)	C(45)—C(46)	1.43(2)

Table 7. The main bond lengths (*d*) in molecule **7b**

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—O(4)	2.069(2)	C(5)—C(6)	1.536(3)
Ru(1)—O(4a)	2.199(3)	C(6)—C(7)	1.550(6)
Ru(1)—C(3)	2.531(4)	C(7)—O(3)	1.460(5)
Ru(1)—C(4)	2.229(4)	C(7)—O(4)	1.393(4)
Ru(1)—C(5)	2.158(4)	C(3)—C(8)	1.479(6)
O(3)—C(3)	1.374(3)	C(5)—C(15)	1.492(5)
C(3)—C(4)	1.395(5)	C(6)—C(21)	1.546(6)
C(4)—C(5)	1.437(6)	C(7)—C(28)	1.510(3)

tures. It is clear that the latter is impossible in the case of azadienes, since an N atom has only one lone electron pair, which is involved in the formation of the chelate metallacycle. In addition, it was shown for the first time that the reaction of $Ru_3(CO)_{12}$ with oxadienes affords a new cyclic ligand, a η^3-coordinated dihydropyranyl ring, no nitrogen analog of which was detected in the case of azadienes.

The study also revealed substantial distinctions between the behavior of Ru and Fe carbonyls in their reactions with oxadienes. In fact, Fe carbonyls react with oxadienes to give mononuclear complexes, whereas dodecacarbonyltriruthenium yields bi- and polynuclear complexes. The ability of Ru to give the products of oxidative addition at the C(β)—H bond, which was not observed for Fe compounds, is also important. In addition, the differences in the behavior of these metals are manifested in the fact that Fe forms a π-complex bond with the C=O group (η^2-coordination), while Ru coordinates predominantly to the O atom of the keto group *via* its lone electron pair (η^1-coordination).

Using ruthenium complexes with oxadienes as an example one can see that unsaturated ligands in polynuclear Ru complexes make, as a rule, the most use of their coordination potentialities.

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