Organometallic Chemistry

Selected properties of bi- and trinuclear complexes prepared by the reactions of $Ru_3(CO)_{12}$ with β-substituted oxadienes

S. V. Osintseva, F. M. Dolgushin, P. V. Petrovskii, N. A. Stelzer, A. Z. Kreindlin, L. V. Rybin, and M. I. Rybinskaya*†

A. N. Nesmeyanov Institute of Organoelement compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: cbeta@ineos.ac.ru

The reactions of $Ru_3(CO)_{12}$ with 4-phenylbut-3-en-2-one (**1a**), 3-phenyl-1-*p*-tolylprop-2-en-1-one (**1b**), and 1,3-diferrocenylprop-2-en-1-one (**1c**) afforded the $Ru_2(CO)_6(\mu\text{-}H)(O{=}C(R^1)C(H){=}C(R^2))$ (**2**) and $Ru_3(CO)_8(O{=}C(R^1)C(H){=}C(R^2))_2$ (**3**) complexes. Dissolution of these complexes in $CHCl_3$ or CH_2Cl_2 gave rise to the $Ru_2(CO)_4(\mu\text{-}Cl)_2(O{=}C(R^1)C(H){=}C(R^2))$ complexes (**4**). The thermal transformations of complexes **2** and **3** in the presence of an excess of the ligand yielded the $Ru_2O_2(CO)_4(\eta^3\text{-}OC(R^1)C(H)(CH_2R^2)C(R^2)C(H)C(R^1))_2$ (**5**) and $Ru(CO)_2(O{=}C(R^1)C(H){=}C(R^2))_2$ (**6**) complexes. Analogous complexes were obtained upon more prolonged heating of the starting reaction mixtures. The structures of complexes **4a**, **5a**, and **6c** were established by X-ray diffraction analysis and confirmed by spectroscopic data.

Key words: dodecacarbonyltriruthenium, 4-phenylbut-3-en-2-one, 3-phenyl-1-*p*-tolylprop-2-en-1-one, 1,3-diferrocenylprop-2-en-1-one, oxaruthenacyclopentadienyl rings, η^3-dihydropyran rings, halogen-bridged complexes, X-ray diffraction analysis, IR spectroscopy, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy.

We have carried out a series of studies on the reactivities of α,β-unsaturated ketones in thermal reactions with ruthenium carbonyls.[1—5] The reactions of $Ru_3(CO)_{12}$ with 4-phenylbut-3-en-2-one (**1a**), 3-phenyl-1-*p*-tolylprop-2-en-1-one (**1b**), and 1,3-diferrocenylprop-2-en-1-one (**1c**) afforded bi- and trinuclear complexes with the η^3-coordinated five-membered oxaruthenacycles $Ru_2(CO)_6(\mu\text{-}H)(O{=}C(R^1)C(H){=}C(R^2))$ (**2**) and $Ru_3(CO)_8(O{=}C(R^1)C(H){=}C(R^2))_2$ (**3**) as the major products (Scheme 1). In the present study, we describe selected properties of the complexes prepared earlier, pathways of their transformations, and a series of final reaction products.

Results and Discussion

When studying the reaction of $Ru_3(CO)_{12}$ with unsaturated ketone **1c**, we have demonstrated[2] that bi- and tri-

† Deceased.

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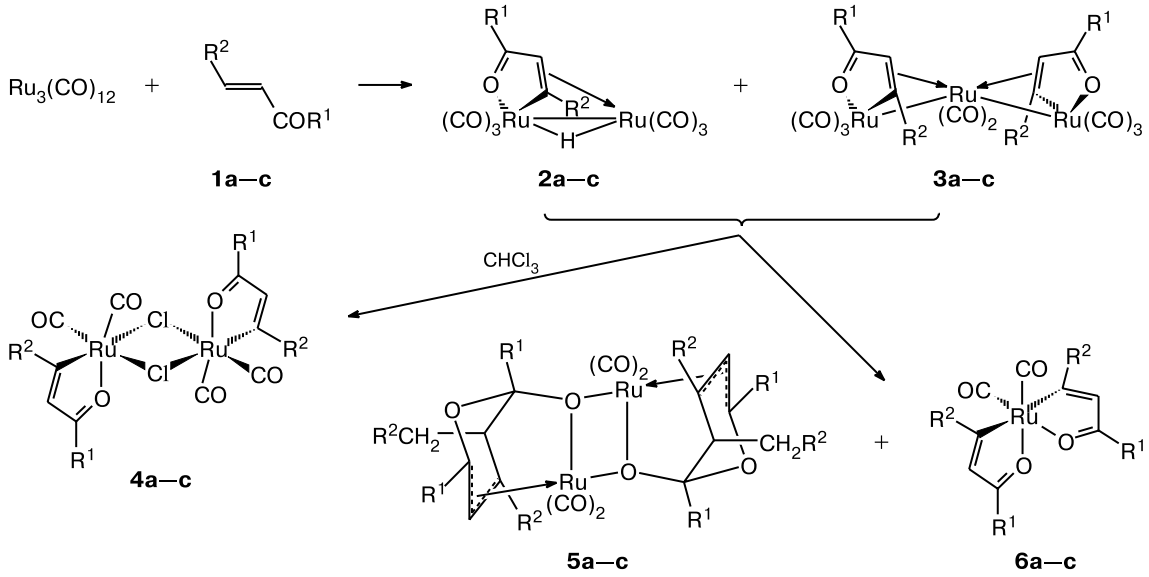
Scheme 1



a: R^1 = Me, R^2 = Ph
b: R^1 = *p*-MeC_6H_4, R^2 = Ph
c: R^1 = R^2 = Fc

nuclear complexes **2c** and **3c** were completely transformed into the $Ru_2(CO)_4(\mu\text{-}Cl)_2(O{=}C(Fc)C(H){=}C(Fc))_2$ complex (**4c**) upon storage in a solution in $CHCl_3$ for 2 days. The formation of the complex with the noncoordinated oxaruthenacycle was of particular interest because its use opens up the possibility of the synthesis of heterometallic compounds in which the oxaruthenacycle can serve as a ligand with respect to other transition metal atoms. Since such studies are conveniently performed with less sterically overcrowded molecules, we continued investigations of the reactions with the use of ketone **1a**.

The binuclear chloride-bridged $Ru_2(CO)_4(\mu\text{-}Cl)_2(O{=}C(CH_3)C(H){=}C(C_6H_5))_2$ complex (**4a**) was prepared upon storage of a solution of **2a** in $CHCl_3$ at room temperature. The course of the reaction was monitored by IR spectroscopy, the spectra being recorded at certain intervals in the region of stretching vibrations of the M—CO groups, and the gradual transformation of **2a** into **4a** was observed. After completion of the reaction (after two weeks), complex **4a** was isolated by column chromatography on silica gel. These reactions of the complexes with ketone **1a** proceeded more slowly as compared to those with **1c** due, apparently, to the fact that the π-coordination olefinic bond between the oxaruthenacycle and the second Ru atom in complexes **2** is strengthened on going from the ferrocenyl substituent to an aryl

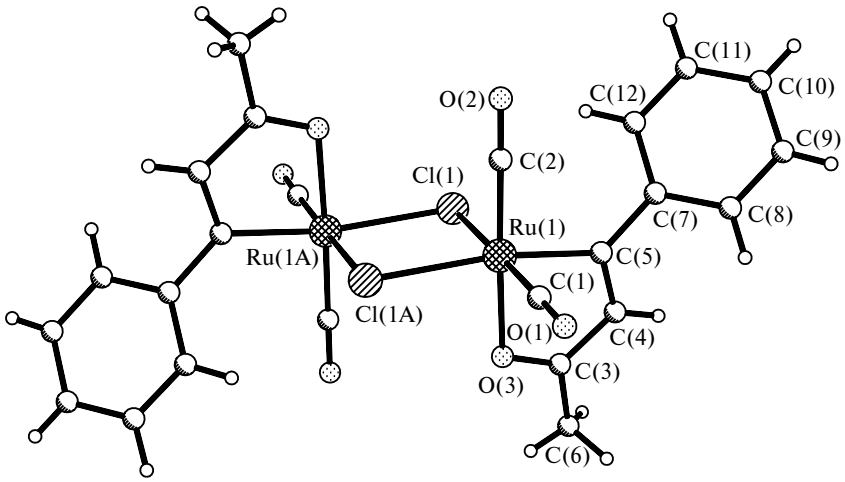


Fig. 1. Molecular structure of complex **4a**.

group.[2] Probably, it is this bond cleavage that is the limiting step of the reaction **2** → **4**.

It should be noted that we have previously detected the formation of complex **4a** (according to IR spectroscopy) by chromatography of a reaction solution containing complexes **2a** and **3a** on silica gel (with CH_2Cl_2 as the eluent).[3] The formation of complex **4a** on the adsorbent surface proceeded much more rapidly than in solution.

The structure of complex **4a** was established by IR and NMR spectroscopy (Table 1) and confirmed by single-crystal X-ray diffraction analysis (Fig. 1; selected bond lengths and bond angles are given in Table 2). In the crystal, centrosymmetrical molecule **4a** occupies a special position (an inversion center is located at the midpoint between the Ru atoms) and consists of two oxaruthenacycles linked through two unsymmetrical chloride bridges to form the planar four-membered ring Ru_2Cl_2. In addition, each Ru atom is coordinated by two carbonyl ligands. One of these ligands is in the *trans* position with respect to the O atom of the metallacycle and the second ligand is in the *trans* position with respect to the Cl atom. The oxaruthenacycles in molecule **4a** are planar (the maximum deviation from the mean plane is 0.01 Å) and form dihedral angles of 85.6° with the plane of the central Ru_2Cl_2 ring. The structural characteristics of complex **4a** are close to those of ferrocenyl-substituted analog **4c**,[2] which indicates that the substituents in the chain of the starting oxadiene has only an

Table 1. IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data for compounds **1a,c**, **4a**, **5a,b**, and **6a,c**

Compound	IR spectrum (heptane), ν(CO)/cm^{-1}	NMR spectra (δ, J/Hz)	
		^{1}H	^{13}C
1a[a]	—	2.22 (s, 3 H, Me); 6.59, 7.39 (both d, 1 H each, CH=CH, J = 16.3); 7.20—7.60 (m, 5 H, Ph)	26.20; 126.03; 127.19; 127.82; 129.28; 133.40; 141.90; 196.53
1c[a]	—	4.16, 4.19 (both s, 5 H each, Cp); 4.45, 4.54 (both t, 2 H each, Cp, J = 1.8); 4.58 (t, 2 H); 4.86 (t, 2 H, Cp, J = 1.8); 6.73, 7.69 (both d, 1 H each, CH=CH, J = 15.4)	—
4a[a]	2048 s, 1978 s	Dimeric form: 2.49 (s, 3 H, Me); 6.62 (s, 1 H, CH=C); 7.11—7.30 (m, 5 H, Ph)	Dimeric form: 26.58; 125.31; 128.19; 129.22; 133.90; 147.62; 189.62; 197.04; 214.11; 227.55
		Monomeric form: 2.46 (s, 3 H, Me); 6.60 (s, 1 H, CH=C); 7.11—7.30 (m, 5 H, Ph)	Monomeric form: 26.76; 125.50; 128.22; 129.29; 134.25; 147.37; 189.86; 197.50; 214.25; 227.52
5a[b]	2004 s, 1953 s	1.31 (s, 3 H, Me); 2.26 (s, 3 H, Me); 5.17 (s, 1 H); 6.80—7.33 (m, 5 H)	—
5b	2016 s, 1953 s	—	—
6a[a]	2018 s, 1954 s	2.17 (s, 3 H, Me); 6.46 (s, 1 H, CH=C); 7.00—7.80 (m, 5 H, Ph)	—
6c[b]	2008 s, 1938 s	4.05 (s, 5 H, Cp); 4.10, 4.12 (both m, 1 H each, Cp); 4.61 (m, 2 H, Cp); 4.66 (s, 5 H, Cp); 4.76, 5.00, 5.05, 5.37 (all m, 1 H each, Cp); 7.65 (s, 1 H, CH=C)	29.76; 30.13; 32.27; 64.46; 70.16; 70.73; 70.89; 71.12; 72.02; 72.98; 78.07; 78.29; 93.39; 203.11; 207.50; 235.28

[a] The NMR spectra were recorded in $CDCl_3$.
[b] The NMR spectra were recorded in C_6D_6.

Table 2. Principal bond lengths (d) and bond angles (ω) in complex **4a**

Bond	d/Å	Angle	ω/deg
Ru(1)—Cl(1)	2.4331(5)	C(1)—Ru(1)—Cl(1)	178.85(5)
Ru(1)—Cl(1A)*	2.5064(5)	C(2)—Ru(1)—Cl(1)	91.02(6)
Ru(1)—C(1)	1.859(2)	C(5)—Ru(1)—Cl(1)	89.78(5)
Ru(1)—C(2)	1.863(2)	O(3)—Ru(1)—Cl(1)	86.26(4)
Ru(1)—C(5)	2.032(2)	C(1)—Ru(1)—Cl(1A)*	94.21(6)
Ru(1)—O(3)	2.123(1)	C(2)—Ru(1)—Cl(1A)*	93.74(6)
O(1)—C(1)	1.142(2)	C(5)—Ru(1)—Cl(1A)*	167.97(5)
O(2)—C(2)	1.141(3)	O(3)—Ru(1)—Cl(1A)*	89.17(4)
O(3)—C(3)	1.257(2)	Cl(1)—Ru(1)—Cl(1A)*	85.56(2)
C(3)—C(4)	1.434(3)	C(1)—Ru(1)—C(2)	90.13(8)
C(3)—C(6)	1.496(3)	C(1)—Ru(1)—C(5)	90.23(7)
C(4)—C(5)	1.364(2)	C(2)—Ru(1)—C(5)	97.43(7)
C(5)—C(7)	1.474(2)	C(1)—Ru(1)—O(3)	92.61(6)
		C(2)—Ru(1)—O(3)	175.85(6)
		C(5)—Ru(1)—O(3)	79.45(6)
		Ru(1)—Cl(1)—Ru(1A)*	94.44(2)
		O(1)—C(1)—Ru(1)	178.9(2)
		O(2)—C(2)—Ru(1)	179.2(2)
		C(3)—O(3)—Ru(1)	112.1(1)
		O(3)—C(3)—C(4)	119.4(2)
		O(3)—C(3)—C(6)	119.7(2)
		C(4)—C(3)—C(6)	120.9(2)
		C(5)—C(4)—C(3)	116.2(2)
		C(4)—C(5)—C(7)	119.5(2)
		C(4)—C(5)—Ru(1)	112.8(1)
		C(7)—C(5)—Ru(1)	127.7(1)

* The atom is generated from the basis atom by the symmetry transformation $-x + 2, -y, -z + 1$.

insignificant effect both on the overall structure of the resulting complexes and the geometry of the oxaruthenacycles.

It should be noted that complexes **4** can exist in solution as several isomers depending on the orientations of the oxaruthenacycles with respect to the central Ru_2Cl_2 fragment.[2] However, X-ray diffraction study of complexes **4a** and **4c** demonstrated that crystallization afforded the centrosymmetrical isomers.

The IR and NMR spectra of complex **4a** are in complete agreement with the results of X-ray diffraction analysis. The IR spectrum has two intense bands in the stretching vibration region of CO ligands. This indicates that each Ru atom is coordinated by two CO ligands in *cis* positions with respect to each other. In the IR spectrum of complex **4a**, the stretching frequencies of the metal-carbonyl groups are shifted to high frequency by ~10 cm^{-1} relative to the corresponding frequencies of complex **4c** due, apparently, to the weaker electron-donating effect of the Me substituent as compared to that of Fc.

The ^1H and ^{13}C NMR spectra of complex **4a** each have two sets of signals because not only the initial molecule but also its monomeric form are present in solution. The latter is derived *via* dissociation of the bridging Ru—Cl bond and coordination by the solvent molecule (for example, $CHCl_3$). The less intense signals at higher field were assigned to the monomeric species whose formation has been observed previously[2] for complex **4c**. The degree of dissociation, which was determined from the integral intensities of singlets in the ^1H NMR spectrum measured in $CHCl_3$ at 20 °C, was at most 40%.

It is reasonable to assume that the formation of the monomeric species proceeds through the cleavage of the longer Ru—Cl bonds, which are in the *trans* positions with respect to the C_β atoms of the starting ligand (Ru(1)—Cl(1) bond; see Fig. 1 and Table 1). Coordination by the solvent molecule leads to an insignificant upfield shift of the ^{13}C signal for the C_β atom of the monomeric molecule (from δ_C 227.55 to δ_C 225.51). The remaining signals of the monomeric molecule assigned to the carbonyl groups are shifted downfield relative to the signals of the dimer. The assignment of the signals was made based on comparison of the ^{13}C NMR spectra of complexes **2a** [1] and **4a**. The coordination environment about the Ru atoms, which are involved in the oxaruthenacycles in complexes **2a** and **4a**, are octahedra. The carbonyl group of the oxaruthenacycle and one of the metal-carbonyl groups occupy the axial (*trans*) positions and the remaining ligands are in the equatorial planes. It can be assumed that the difference in the equatorial ligand environment about the Ru atoms in complexes **2a** and **4a** has, apparently, only a slight effect on the chemical shifts of the ligands located in the axial positions. Since the signals at δ_C 214.11 (214.25) and 189.62 (189.86) in the spectrum of complex **4a** are close to those observed in the spectrum of complex **2a** (at δ_C 215.89 and 189.39), they can be assigned respectively to the carbonyl group of the oxaruthenacycle and the metal-carbonyl group located in the *trans* position with respect to the former group (hereinafter, the signal of the dimeric complex is given for complex **4**, and the signal of its monomeric form is given in parentheses).

In the ^{13}C NMR spectrum of complex **4a**, the signal for C_β observed at δ_C 227.55 (227.51) is shifted downfield by >80 ppm as compared to that of the noncoordinated ligand (δ_C 141.9).[1] This is attributable to the partially carbene character of the Ru—C_β bond due to efficient back donation from the π^* orbital of the C_β atom to the d orbital of the Ru atom. In this case, the oxaruthenacyclopentadiene fragment can be represented as a resonance hybrid of two forms, **A** and **B**, with the contribution of the ruthenafuran system **B** (Scheme 2).

Scheme 2

A **B**

Similar low-field signals for the C_β atoms were observed in the spectra of the $Ru(CO)_2(MeC{=}C(H)C(H){=}NPr^i)_2$ complex (at δ_C 218.3 and 223.1)[6] containing two five-membered azaruthenacycles in the coordination sphere about the metal atom as well as in the spectra of the related $Ru(CO)_3Cl(MeC{=}C(H)C(H){=}NPr^i)$ complex (at δ_C 211.2).[7]

The investigation of the thermal reactions of complexes **2** and **3** with an excess of the ligand demonstrated that the resulting complexes are analogous to those obtained upon more prolonged heating of the starting reaction mixture. It is known that the thermal reactions of ruthenium carbonyls with organic molecules performed under severe conditions (refluxing in heptane) lead to further transformations of the initially formed polynuclear products accompanied by the cleavage of the metal—metal bonds to form mono- or binuclear complexes devoid of the metal—metal bond[6,8] or, more rarely, result in condensation of the clusters to give higher-nuclearity species.[1,8]

Among the final products of the thermal reactions of $Ru_3(CO)_{12}$ with ketones **1a—c**, we have previously[1,5] isolated and characterized the only complex **5b** containing the η^3-coordinated dihydropyran ring as the ligand. The structure of the complex was established by X-ray diffraction analysis of a single crystal, which was chosen from the precipitate obtained in the reaction of $Ru_3(CO)_{12}$ with **1b**.[5] The composition of the precipitate was con-

firmed by elemental analysis (see the Experimental section).

In the present study, we report the synthesis and structure of complex **5a** prepared by the reaction of $Ru_3(CO)_{12}$ with **1a** in boiling heptane. The course of the reaction was monitored by IR spectroscopy, the spectra being recorded in the region of stretching vibrations of the metal-carbonyl groups at regular intervals. The reaction mixture was heated for 4.5 h, cooled, and filtered. The precipitate recrystallized from heptane contained crystals of complex **5a**. The structure of the latter was established by spectroscopy and confirmed by X-ray diffraction analysis. According to the IR spectra, the solution contained also complex **5a**. However, we failed to find conditions for its chromatographic separation. Complex **5a** was also prepared by thermolysis of **2a** or **3a** in the presence of the ligand. The formation of **5a** was established by IR spectroscopy.

In the crystal of complex **5a** (Fig. 2, the principal geometric parameters are given in Table 3), there are two independent centrosymmetrical molecules. Each molecule occupies a special position (an inversion center is located at the midpoint between two Ru atoms) and consists of two identical fragments linked by the bridging O atoms to form the four-membered Ru_2O_2 ring. Each O atom is a three-electron donor and forms one short σ-bond (Ru(1)—O(4), 2.069 Å; hereinafter, the average bond lengths for two independent molecules are given) and one longer coordination bond (Ru(1)—O(4A), 2.215 Å) with the Ru atoms. The latter, in turn, are coordinated by the allylic fragments of the dihydropyran ligands. Due to the presence of two carbonyl ligands at each of two Ru atoms, both metal atoms have an 18-electron configuration. Complex **5a** is characterized by the essentially nonsymmetrical η^3-coordination of the dihydropyran rings to the Ru atoms (Ru(1)—C(3), 2.869 Å; Ru(1)—C(4), 2.309 Å; Ru(1)—C(5), 2.096 Å). Such a nonequivalence of the Ru—C_{All} bonds and a substantial difference in the bond lengths in the allylic fragment (see Table 2) suggest an alternative description of coordination to the Ru atom characterized by the presence of the Ru(1)—C(5) σ-bond

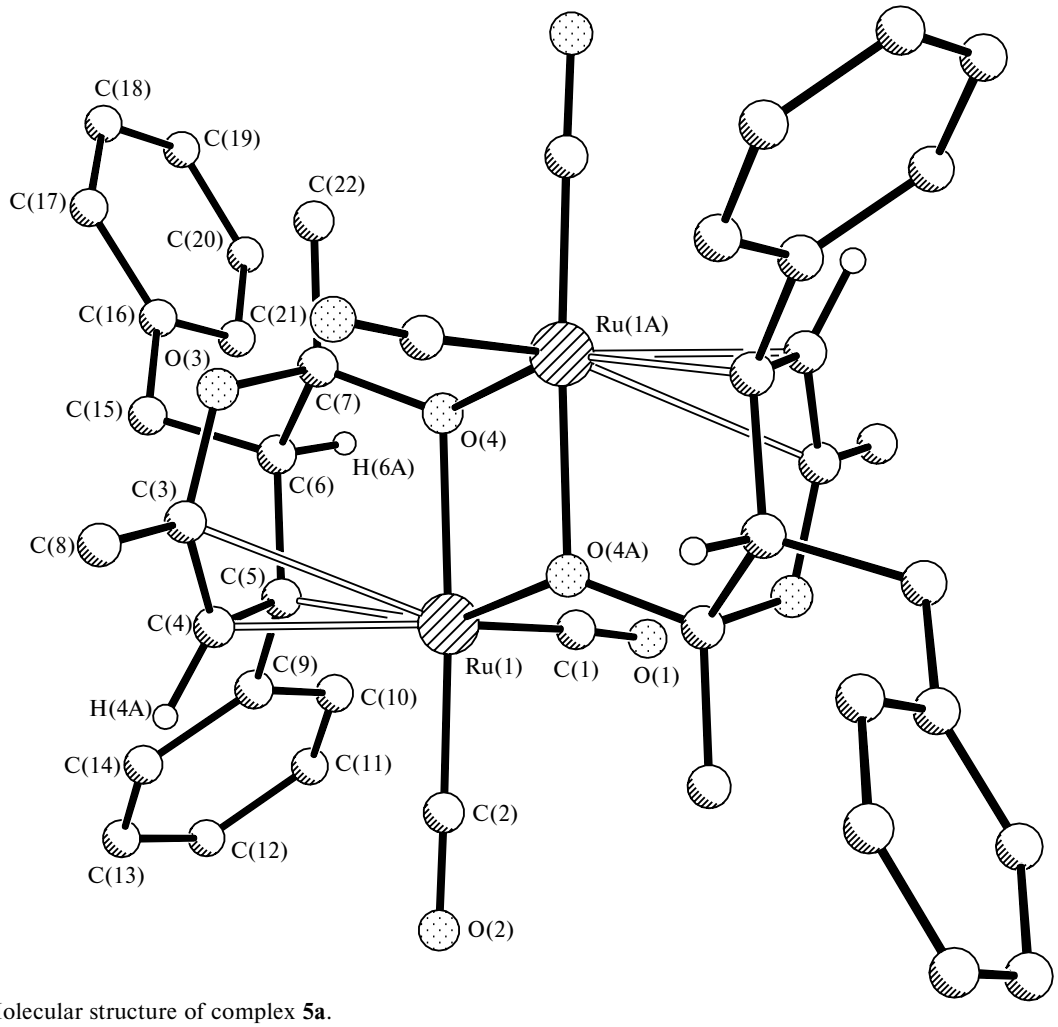


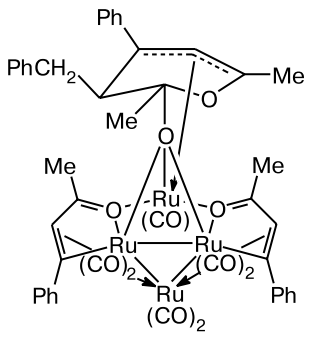
Fig. 2. Molecular structure of complex **5a**.

Table 3. Principal bond lengths (d) and bond angles (ω) in two independent molecules of complex **5a** (**A** and **B**)

Parameter	A	B	Parameter	A	B
Bond	d/Å		Angle	ω/deg	
Ru(1)—O(4)	2.074(4)	2.064(4)	C(1)—Ru(1)—C(2)	88.6(3)	89.3(3)
Ru(1)—O(4A)*	2.218(4)	2.212(4)	C(1)—Ru(1)—O(4)	94.2(3)	93.7(3)
Ru(1)—C(1)	1.819(7)	1.781(9)	C(2)—Ru(1)—O(4)	176.9(2)	176.6(3)
Ru(1)—C(2)	1.855(8)	1.840(7)	C(1)—Ru(1)—O(4A)*	103.5(2)	103.8(2)
Ru(1)—C(3)	2.890(7)	2.848(7)	C(2)—Ru(1)—O(4A)*	103.3(2)	103.0(2)
Ru(1)—C(4)	2.301(7)	2.317(7)	O(4)—Ru(1)—O(4A)*	77.5(2)	77.8(2)
Ru(1)—C(5)	2.078(7)	2.114(6)	C(3)—O(3)—C(7)	116.9(5)	115.9(5)
O(3)—C(3)	1.338(8)	1.351(8)	C(7)—O(4)—Ru(1)	111.4(4)	111.1(4)
O(3)—C(7)	1.486(8)	1.484(7)	C(7)—O(4)—Ru(1A)*	127.7(4)	128.5(4)
O(4)—C(7)	1.390(7)	1.406(7)	Ru(1)—O(4)—Ru(1A)*	102.5(2)	102.2(2)
C(3)—C(4)	1.375(9)	1.366(9)	O(1)—C(1)—Ru(1)	174.9(5)	174.1(6)
C(3)—C(8)	1.505(9)	1.509(9)	O(2)—C(2)—Ru(1)	178.9(6)	178.5(7)
C(4)—C(5)	1.454(9)	1.449(9)	O(3)—C(3)—C(4)	124.0(6)	122.9(6)
C(5)—C(9)	1.521(9)	1.512(9)	O(3)—C(3)—C(8)	113.9(6)	111.6(6)
C(5)—C(6)	1.527(9)	1.531(9)	C(4)—C(3)—C(8)	122.0(7)	124.9(6)
C(6)—C(7)	1.556(9)	1.521(9)	C(3)—C(4)—C(5)	120.5(6)	122.3(6)
C(6)—C(15)	1.537(9)	1.537(10)	C(4)—C(5)—C(9)	116.7(6)	119.4(6)
C(7)—C(22)	1.473(9)	1.497(8)	C(4)—C(5)—C(6)	113.6(5)	112.3(6)
C(15)—C(16)	1.510(10)	1.524(10)	C(9)—C(5)—C(6)	113.6(6)	115.9(5)
			C(5)—C(6)—C(7)	107.1(5)	108.5(5)
			C(5)—C(6)—C(15)	113.7(6)	111.9(6)
			C(15)—C(6)—C(7)	113.7(5)	114.1(6)
			O(4)—C(7)—O(3)	106.2(5)	106.1(5)
			O(4)—C(7)—C(22)	113.6(5)	112.3(5)
			C(22)—C(7)—O(3)	104.1(5)	103.8(5)
			O(4)—C(7)—C(6)	107.5(5)	106.7(5)
			O(3)—C(7)—C(6)	108.3(5)	110.2(5)
			C(22)—C(7)—C(6)	116.5(6)	117.2(5)
			C(16)—C(15)—C(6)	115.8(6)	115.7(6)

* The atom is generated from the basis atom by the symmetry transformation $-x + 2, -y + 1, -z + 1$ or $-x, -y + 2, -z + 2$ for two independent molecules, respectively.

and the substantially weakened η^2-coordination with the olefinic C(3)=C(4) bond. It should be noted that complex **5b** is also characterized by the asymmetrical η^3-coordination of the dihydropyran ligand to the Ru atom. However, the nonequivalence of the Ru—C_{All} bond lengths in the latter complex is less pronounced (the corresponding values are 2.531(4), 2.229(4), and 2.158(4) Å) in the case of the stronger π-bond. Weakening of the π-coordination in complex **5a** is, apparently, caused by the stronger electron-donating properties of the Me substituent in this complex as compared to those of the *para*-tolyl substituent in complex **5b**.



7

A radically different situation is observed in tetranuclear complex **7**, which we have obtained previously[1,5] as one of the minor products in the reaction of $Ru_3(CO)_{12}$ with **1a** and which contains simultaneously the five-membered oxaruthenacycles and the dihydropyran ligand. This complex is characterized by the symmetrical η^3-coordination of the dihydropyran ligand to the Ru atom (Ru—C_{All}, 2.18(1), 2.11(1), and 2.17(1) Å), which is attributable to the equivalent ligand environment about the Ru atom involved in coordination. By contrast, complexes **5** contain the C(1)O(1) carbonyl group and the coordinated O(4A) atom possessing substantially different electron-donating properties in the pseudo-*trans* positions with respect to the allylic fragment. Apparently, it is the C(1)O(1) group that influences the position of the

signal for the allylic proton in the ^{1}H NMR spectrum of complex **5a** (see Table 1). The spectrum of complex **5a** has this signal at δ_H 5.16, whereas this signal in the spectrum of complex **7** is shifted upfield and is observed at δ_H 3.82.[1,5]

Upon heating, the reaction of $Ru_3(CO)_{12}$ with ketone **1a** afforded new complex **6a**, which was isolated from the solution by chromatography on silica gel. Complex **6a** was also prepared by thermolysis of **2a** or **3a** in the presence of the ligand, which was proved by IR spectroscopy. Analogously, thermolysis of complex **3c** gave rise to the $Ru(CO)_2(O{=}C(Fc)C(H){=}C(Fc))_2$ complex (**6c**) (see Scheme 1).

The structure of complex **6c** was established by X-ray diffraction analysis and is shown in Fig. 3. The principal geometric parameters are given in Table 4. In the crystal, complex **6c** occupies a special position on a twofold axis. The Ru atom is chelated by two oxadiene ligands to form two oxaruthenacycles and is coordinated by two carbonyl ligands located in *cis* positions. The distorted ligand environment about the Ru atom is characterized by the transoid arrangement of the σ-bound C atoms of the metallacycles, whereas the carbonyl ligands are in the *trans* positions with respect to the O atoms of the metallacycles. It should be noted that the *trans* effect is observed in all complexes prepared by us. The metal-carbonyl CO group is always located in the *trans* position with respect to the O atom of the oxaruthenacycle, which donates the lone pair to the Ru atom.[1,2] The oxaruthenacycles in complex **6c** are slightly nonplanar (the folding angle along the O(2)...C(4) line is 5.1°), all bond lengths in these fragments being virtually equal to those observed in chloride complexes **4a** and **4c**. We will point out only a slight elongation of the endocyclic Ru—C σ-bonds in complex **6c** (Ru(1)—C(4), 2.117(6) Å) as compared to the analogous bonds in complexes **4a** and **4c**

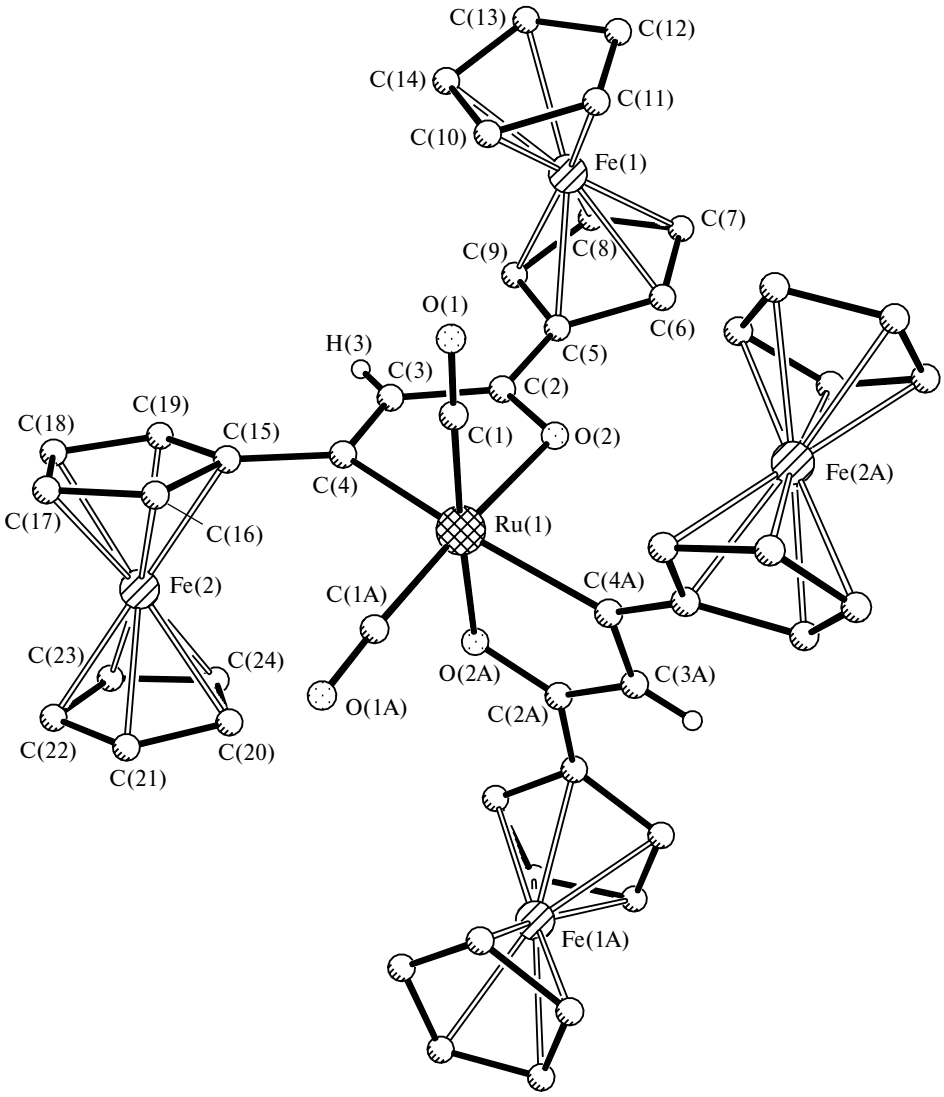


Fig. 3. Molecular structure of complex **6c**.

Table 4. Principal bond lengths (d) and bond angles (ω) in complex **6c**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Ru(1)—C(1)	1.869(6)	C(1)—Ru(1)—C(1A)*	93.5(4)	O(1)—C(1)—Ru(1)	176.7(5)
Ru(1)—O(2)	2.100(4)	C(1)—Ru(1)—O(2A)*	175.0(2)	C(2)—O(2)—Ru(1)	114.1(4)
Ru(1)—C(4)	2.117(6)	C(1)—Ru(1)—O(2)	91.4(2)	O(2)—C(2)—C(3)	119.2(5)
Fe(1)—C_{Cp}	2.018(5)—2.067(6)	O(2)—Ru(1)—O(2A)*	83.6(2)	O(2)—C(2)—C(5)	118.3(5)
Fe(2)—C_{Cp}	2.038(7)—2.063(5)	C(1)—Ru(1)—C(4A)*	101.8(2)	C(3)—C(2)—C(5)	122.4(5)
O(1)—C(1)	1.130(7)	O(2)—Ru(1)—C(4A)*	87.16(18)	C(4)—C(3)—C(2)	116.9(5)
O(2)—C(2)	1.260(7)	C(1)—Ru(1)—C(4)	91.3(2)	C(3)—C(4)—C(15)	118.5(5)
C(2)—C(3)	1.437(8)	O(2)—Ru(1)—C(4)	78.62(19)	C(3)—C(4)—Ru(1)	110.8(4)
C(2)—C(5)	1.462(8)	C(4)—Ru(1)—C(4A)*	160.9(3)	C(15)—C(4)—Ru(1)	130.7(4)
C(3)—C(4)	1.364(8)				
C(4)—C(15)	1.454(8)				

* The atom is generated from the basis atom by the symmetry transformation $-x + 1$, y, $-z + 0.5$.

(2.032 and 2.031 Å, respectively), which is, apparently, caused by the mutual *trans* effect of the different ligands in complexes **6** and **4**. The structure of complex **6c** is characterized by a substantial deviation of the ferrocenyl substituent at the C(2) atom from the standard geometry. Thus, the C(5)—C(2) bond forms an angles of 7.5° with the plane of the cyclopentadienyl C(5)—C(9) ligand and the C(2) atom deviates from the plane by 0.182 Å toward the Fe(1) atom. The Fe(1)...C(2) distance is 2.992 Å. Conceivably, this change in the geometry of the ferrocenyl substituent is indicative of the presence of a positive charge on the C(2) atom, which is confirmed by the data[9] on the structure of the starting ferrocenyl carbocationic complex $[C_5Me_5FeC_5Me_4CH_2]^+$ in which the angle between the C_{Cp}—C_α bond and the plane of the Cp ring is 23.6° and the Fe—C_α distance is 2.57(1) Å. It should be noted that the second ferrocenyl substituent at the C(4) atom in complex **6c** has a standard structure and the C(4) atom deviates from the plane of the corresponding Cp ring by only 0.030 Å. The above-described difference in the structure of two ferrocenyl substituents in the oxadiene chain, though less pronounced, is observed in chloride complex **4c**.

The data from IR and NMR spectroscopy are in complete agreement with the results of X-ray diffraction analysis (see Table 1). The IR spectrum of complex **6c** has two bands with equal intensities in the region of stretching vibrations of metal-carbonyl groups, which is indicative of the presence of two CO ligands in *cis* positions with respect to each other. In the IR spectra of complex **6c**, the absorption bands are observed in the lower-frequency region as compared to the corresponding bands in the IR spectra of complexes **4a** and **4c**, which is, apparently, associated with the presence of the strong acceptors, *viz.*, Cl atoms, in the latter complexes.

The equivalence of the oxaruthenacycles is confirmed by the NMR spectra. The ^1H and ^{13}C NMR spectra each have one set of signals of the 1-oxa-2-ruthenacyclopentadienyl ligand. This is the difference between complex **6c** and $Ru(CO)_2(MeC{=}C(H)C(H){=}NPr)_2$.[6] The NMR spectra of the latter complex have double sets of signals resulting from the nonequivalence of the azaruthenacycles. The authors of the cited study believed that these data correspond to a complex (X-ray diffraction data are lacking) in which the N atom of the azaruthenacycle is located in the *trans* position with respect to one metal-carbonyl CO group and the C_β atom is in the *trans* position relative to another metal-carbonyl group.

The nonequivalence of two ferrocenyl substituents in complex **6c** revealed from the X-ray diffraction data is also manifested in the ^1H NMR spectrum, *viz.*, in the difference in singlets of the protons of the unsubstituted Cp rings (the spectra were recorded in $CDCl_3$; the singlets were observed at δ_H 4.07 and 4.49; $\Delta\delta_H = 0.42$). It should be noted that the signals of the Cp rings in the spectrum of free ligand **1c** are observed at δ_H 4.16 and 4.19 ($\Delta\delta_H = 0.03$). By contrast, the spectrum of complex **4c** has a double set of singlets of the unsubstituted Cp rings,[2] the singlets at δ_H 4.36 and 4.38 ($\Delta\delta_H = 0.02$) belonging to the dimeric molecule and the singlets at δ_H 4.14 and 4.28 ($\Delta\delta_H = 0.14$) being assigned to the monomeric molecule. The singlet of the proton at the C_α atom in the spectrum of complex **6c** is observed at δ_H 7.32 and is shifted downfield as compared to the signal at δ_H 7.03 (6.99) in the spectrum of molecule **4c**.

The ^{13}C NMR spectrum of complex **6c** has three signals in the low-field region. The signal at the lowest field (δ_C 235.28) can be assigned to the C_β atom, which is attributable to the contribution of the metallacumulene system (see above).

Therefore, we prepared new mononuclear complex **6c** by the thermal reaction of $Ru_3(CO)_{12}$ with **1c** and demonstrated that it contains two five-membered oxaruthenacycles in the coordination sphere about the metal atom. Mononuclear complexes containing one oxaruthenacycle have been described previously, for example, $CpRu(PPh_3)[MeOC(O)C{=}C(H)(MeO)C{=}O]$[10]

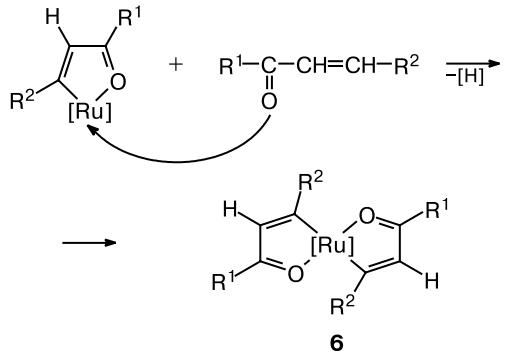
and $HRu(PPh_3)_3[C(H)=C(Me)C(O)OR]$.[11] It should be noted that complexes containing two oxaruthenacycles are few in number. The $[Ru(CO)_2(PhC(O)CH=CC(O)Ph)]_2(PhC(O)CHCHC(O)Ph)$ complex, which we have prepared by the thermal reaction of $Ru_3(CO)_{12}$ with dibenzoylethylene,[12] is the closest analog of complex **6c**.

When studying the thermal reactions of $Ru_3(CO)_{12}$ with α,β-unsaturated ketones, we found that the resulting complexes contain the five-membered chelate oxaruthenacycles generated *via* the oxidative addition of the Ru atom at the C_β—H bond and coordination at the lone pair of the O atom of the keto group. Further, acting as ligands, the oxaruthenacycles can form η^3-complexes through the C=C bond and the Ru atom. The rate of complex formation, all other conditions being equal (temperature, reagent ratio), depends on the nature of the substituents in the starting ketone.

The simplest binuclear complexes **2** containing the η^3-coordinated oxaruthenacycle are the primary and major reaction products (for example, after refluxing of the reaction mixture for 2 h, the yield of **2a** was 50%[1]). Further heating of the reaction mixture afforded trinuclear complexes **3** with two η^3-coordinated oxaruthenacycles, which were also obtained as the major reaction products. For example, complex **3c** was obtained in 45% yield when heating of the reaction mixture containing complex **1c** was terminated as soon as the content of **3c** reached the maximum (according to the IR spectroscopic data).[2] To elucidate the pathways of formation of complexes **3**, we refluxed complex **2a** in heptane in the presence of the ligand. The formation of complex **3a** was confirmed by IR spectroscopy.[2] It is not inconceivable that complex **3** is generated not only from complex **2** but also directly from $Ru_3(CO)_{12}$ and the ligand (see the Experimental section). Upon the formation of the oxaruthenacycle, the ligand molecule loses hydride hydrogen, while an excess of the ligand acts as a hydrogen acceptor and is reduced to the corresponding saturated ketones. These ketones were isolated from the reaction mixture and their structures were confirmed by IR and NMR spectroscopy.[1,2]

Upon further heating, complexes **2** and **3** were transformed into complexes **5** and **6**, respectively. Both complexes were derived from the oxaruthenacycles by the insertion of the second molecule of the starting ketone. Their formation is attributable to the fact that the oxaruthenacycle has two electron-deficient atoms, *viz.*, the Ru atom and the C atom of the keto group, which are attacked by the nucleophilic group of the ligand, *viz.*, the O atom of the keto group. In the former case (Scheme 3), the addition occurs at the Ru atom followed by chelation of this Ru atom by the ligand and the formation of the second oxaruthenacycle giving rise to complex **6** (1,4-addition of α,β-unsaturated ketone).

Scheme 3



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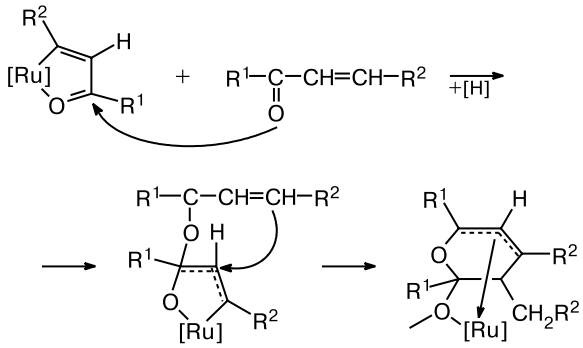
In the latter case (Scheme 4), the addition occurs at the C atom of the carbonyl group of the oxaruthenacycle to form the η^3-dihydropyran rings yielding complexes **5**.

Scheme 4



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To summarize, we described several major products, *viz.*, complexes **2**, **3**, **5**, and **6**, obtained in the thermal reactions of $Ru_3(CO)_{12}$ with α,β-unsaturated ketones **1a—c**. In addition, these reactions afforded polynuclear complexes as minor products. The difference in the ligand behavior of oxadienes is manifested in the structures of the latter products.[1]

Experimental

The ^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 MHz) in solutions in $CDCl_3$ and C_6D_6 with the use of the residual signals of $CHCl_3$ (δ_H 7.25) and C_6HD_5 (δ_H 7.25) as the internal standards. The ^{13}C NMR spectra were measured on a Bruker AMX-400 spectrometer (100.61 MHz) with $CHCl_3$ (δ_C 76.91) and C_6D_6 (δ_C 127.96) as the internal standards. The IR spectra were recorded on a Specord IR-75 spectrophotometer.

Bis(dicarbonyl-μ-chloro-5-methyl-3-phenyl-1-oxa-2-ruthenacyclopentadiene) (4a). A solution of complex **2a** (164 mg, 0.32 mmol) in $CHCl_3$ was kept at ~20 °C for 14 days, the IR spectra of the solution being changed and the gradual transfor-

mation **2a** → **4a** being observed (see Table 1). Complex **4a** was isolated by column chromatography on silica gel (light petroleum—CH_2Cl_2, 2 : 1). Recrystallization from heptane afforded yellow crystals of complex **4a** in a yield of 92 mg (42.6%).

Di{μ-[4,5,6-η³-3-benzyl-4-phenyl-2,6-di(*p*-tolyl)-3,4-dihydropyran-2-yl]oxo}bis(dicarbonylruthenium) (5b). A mixture of $Ru_3(CO)_{12}$ (260 mg, 0.4 mmol) and ketone **1b** (444 mg, 2 mmol) in heptane (150 mL) was refluxed for 7 h. After cooling to ~20 °C, the reaction mixture was filtered. The precipitate that formed was washed with boiling hexane (3×10 mL). Complex **5b** was isolated in a yield of 94 mg (21%). Found (%): C, 65.3; H, 4.4. $Ru_2C_{68}H_{56}O_8$. Calculated (%): C, 67.0; H, 4.6.

Di[μ-(4,5,6-η³-3-benzyl-2,6-dimethyl-4-phenyl-3,4-dihydropyran-2-yl)oxo]bis(dicarbonylruthenium) (5a) and bis(2-methyl-4-phenyl-1-oxabutadien-4-yl)dicarbonylruthenium (6a). ***A.*** A mixture of $Ru_3(CO)_{12}$ (320 mg, 0.5 mmol) and ketone **1a** (292 mg, 2 mmol) in heptane (150 mL) was refluxed for 4.5 h. After cooling to ~20 °C, the reaction mixture was filtered. The precipitate that formed was washed with benzene. Recrystallization from heptane afforded yellow crystals of complex **5a** in a yield of 114 mg (25.4%). The heptane solution was chromatographed on a column with silica gel. Insignificant amounts of complexes **2a** and **3a** were isolated by elution with a light petroleum—CH_2Cl_2 mixture (2 : 1). Elution with CH_2Cl_2 afforded complex **6a** in a yield of 15 mg and complex **4a** in an insignificant amount.

B. The reaction solution analogous to that described above was cooled with dry ice. The crystals that precipitated were washed with hexane and complex **5a** was isolated in a yield of 45 mg. The remaining solution was cooled with dry ice and a crystalline precipitate containing a mixture of complexes **5a** and **6a** (~1 : 1, according to the IR spectroscopic data) was isolated in a yield of 20 mg.

Bis(2,4-diferrocenyl-1-oxabutadien-4-yl)dicarbonylruthenium (6c). ***A.*** A mixture of $Ru_3(CO)_{12}$ (64 mg, 0.1 mmol) and complex **1c** (84 mg, 0.2 mmol) in heptane (50 mL) was refluxed for 2.5 h. After cooling to ~20 °C, the reaction mixture was filtered. The precipitate that formed was chromatographed on Silufol plates in CH_2Cl_2. Cherry complex **6c** was isolated in a yield of 32 mg (16%). In addition, an unidentified crimson complex (IR spectrum (hexane), ν(CO)/cm^{-1}: 2018 s, 1956 s) and traces of dark-violet complex **4c** [2] were obtained. Recrystallization from benzene afforded cherry crystals of complex **6c** suitable for X-ray diffraction analysis.

B. A solution of complex **3c** (55 mg) and complex **1c** (20 mg) in heptane was kept at ~20 °C for 7 days, the IR spectra of the solution being changed. Chromatogaphy on Silufol plates (CH_2Cl_2 as the eluent) afforded complex **6c** in a yield of 24.16 mg (20%) and the above-described (see method ***A***) unidentified complex.

Bis(2,3,4-η³-5-methyl-3-phenyl-1-oxa-2-tricarbonylruthenacyclopenta-3,5-dien-2-yl)dicarbonylruthenium (3a). A mixture of complex **2a** (36 mg, 0.07 mmol) and ketone **1a** (10 mg, 0.07 mmol) in heptane (50 mL) was refluxed for 2 h. According to the data from IR spectroscopy, an amount of complex **3a** was not increased after heating for 1 h. After cooling to ~20 °C, the reaction mixture was filtered. The precipitate was chromatographed on silica gel using a light petroleum—C_6H_6 mixture (3 : 1) to obtain complex **3a** in a yield of 7 mg (15.4%).

X-ray diffraction study of complexes 4a, 5a, and 6c. The X-ray diffraction data sets were collected on an automated Bruker SMART 1000 CCD diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, the ω scan step was 0.3°, frames were exposed for 20 s, T = 110 K). The crystallographic data and details of the refinement of compounds **4a**, **5a**, and **6c**

Table 5. Crystallographic data and details of the refinement of compounds **4a**, **5a**, and **6c**

Parameter	**4a**	**5a**	**6c**
Molecular formula	$C_{24}H_{18}O_6Cl_2Ru_2$	$C_{47.5}H_{48}O_8Ru_2$	$C_{66}H_{56}O_4Fe_4Ru$
Molecular weight	675.42	949.00	1237.58
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$
a/Å	8.9855(8)	11.917(2)	23.237(6)
b/Å	15.963(2)	12.863(2)	12.822(4)
c/Å	9.7088(9)	13.956(3)	18.508(5)
α/deg	—	88.076(5)	—
β/deg	113.372(2)	83.607(5)	108.639(5)
γ/deg	—	89.074(5)	—
V/Å^3	1278.3(2)	2124.8(7)	5225(3)
Z 2	2	4	
d_{calc}/g cm^{-3}	1.755	1.483	1.573
μ/cm^{-1}	14.27	7.64	14.18
$2\theta_{max}$/deg	60	54	55
Number of independent reflections (R_{int})	3707 (0.0183)	9174 (0.0786)	6037 (0.0647)
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0260 (3365)	0.0659 (4481)	0.0680 (4022)
wR_2 (based on F^2 for all reflections)	0.0738	0.1521	0.2108
Number of parameters in the refinement	190	550	340
GOF	1.090	0.824	1.062

are given in Table 5. The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2_{hkl} with anisotropic thermal parameters for all nonhydrogen atoms. Since the transmission coefficients μ were small, absorption was ignored. The crystal structure of **5a** contains a heptane molecule of solvation disordered around an inversion center. The structure of **6c** contains two independent benzene molecules of solvation one of which occupies a general position and the second molecule is located in a special position on a crystallographic twofold axis. The positions of the H atoms in the structure of **4a** were revealed from the difference synthesis and refined isotropically. The H atoms in the structures of **5a** and **6c** were placed in geometrically calculated positions and refined using the riding model. All calculations were carried out on a personal computer with the use of conventional program packages.[13,14]

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