Reaction of $Ru_3(CO)_{12}$ with 1,3-diferrocenylprop-2-ene-1-one. Crystal and molecular structures of the complexes $Ru_3(CO)_8(FcC{=}CHCOFc)_2$ and $[Ru(CO)_2Cl(FcC{=}CHCOFc)]_2$

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The reaction of $Ru_3(CO)_{12}$ with 1,3-diferrocenylprop-2-en-1-one, *trans*-FcCH=CHCOFc (where Fc is ferrocenyl), in boiling hexane afforded the complex $1,3,4\text{-}\eta^3\text{-}[\overline{O{=}C(Fc)CH{=}C(Fc)Ru}(CO)_3](\mu\text{-}H)Ru(CO)_3$ (**2c**), which was converted into $1,3,4\text{-}\eta^3\text{-}[\overline{O{=}C(Fc)CH{=}C(Fc)Ru}(CO)_3]_2Ru(CO)_2$ (**3c**) upon further heating. These complexes gave the complex $[\overline{O{=}C(Fc)CH{=}C(Fc)Ru}(CO)_2Cl_2]_2$ (**4**) containing two Cl-bridged oxaruthenacycles upon dissolution in $CHCl_3$ or CH_2Cl_2. The structures of complexes **3** and **4** were established by X-ray diffraction analysis. According to the data of ^1H NMR spectroscopy, the Cl-bridged complex exists in solutions as a mixture of isomers along with the monomeric form resulting from the cleavage of the halide bridges. All interconversions of the isomers occur with the participation of the monomeric form.

Key words: dodecacarbonyltriruthenium, 1,3-diferrocenylprop-2-en-1-one, oxaruthenapentadienyl rings, halogen-bridged complexes, dimeric and monomeric structures, X-ray diffraction analysis, IR spectra, NMR spectra.

Previously,[1] when studying the reactions of $Ru_3(CO)_{12}$ with functionally substituted olefins using unsaturated ketones RCOCH=CHR′ (**1a,b**: R = Me, R′ = Ph (**a**); or R = p-MeC_6H_4, R′ = Ph (**b**)) as examples, we have found that the reactions proceeded nonstereoselectively to form a wide variety of products. Bi- and polynuclear complexes containing η^3-coordinated five-membered oxaruthenacycles as well as η^3-coordinated dihydropyran rings formed from two molecules of the starting oxadiene were isolated from the reaction products and characterized. The resulting mixtures were difficult to separate, which hampered investigations.

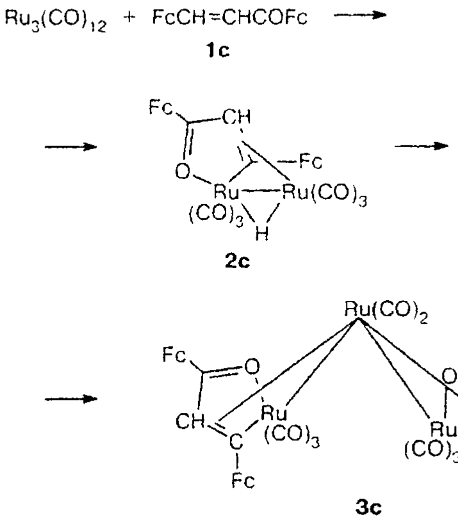
In the present work, we performed for the first time the reaction of $Ru_3(CO)_{12}$ with the use of 1,3-diferrocenylprop-2-en-1-one, FcCH=CHCOFc (**1c**, Fc = $C_5H_5FeC_5H_4$), containing bulky ferrocenyl substituents, which can substantially affect the course of the reaction and its selectivity.

Results and Discussion

The reaction of $Ru_3(CO)_{12}$ with ketone **1c** was carried out in boiling heptane. The course of the process was followed from the change in the region of stretching vibrations of the carbonylmetal groups in the IR spectra of the reaction mixture. After heating for 1 h, complex **2c** was predominantly formed (Scheme 1). Its yield reached 85% with respect to the consumed $Ru_3(CO)_{12}$. The reaction proceeded rather rapidly and selectively.

It is known that the maximum yields of complexes **2a** and **2b**, which are analogous to product **2c** and which were prepared from unsaturated ketones **1a,b**, were reached (50 and 20%, respectively) in 2.5 and 3.5 h,

Scheme 1



Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1616—1623, September, 2000.

1066-5285/00/4909-1605 $25.00

respectively.[2] In the case of ketone **1c**, minor products similar to those isolated in the reactions of ketones **1a** and **1b** with $Ru_3(CO)_{12}$ were not found. The high rate of formation of complex **2c** from ketone **1c** seems to be somewhat unexpected because the electron-releasing ferrocenyl substituents increase the electron density at the double bond and are unfavorable for the reaction at the C=C bond. However, the possibility of this reaction beginning with coordination of the metal atom through the lone electron pair of the oxygen atom of the starting ketone must not be ruled out.[3]

It should be noted that complex **2c** is unstable. An increase in the reaction time (>1 h) led to a gradual decrease in the amount of product **2c** and the appearance of complex **3c**. After the reaction mixture was refluxed for 1.5 h, complex **2c** completely disappeared and the solution contained only compound **3c**, whose formation was accompanied by the appearance of an unidentified precipitate. Complex **3c** was obtained in somewhat lower yield (45%) due to its instability. Analogous transformations of complexes **2a,b** prepared from ketones **1a,b** occurred more slowly (4—4.5 h).[2]

The structure of complex **2c** was proposed based on the data of IR and NMR spectroscopy (Table 1) and the similarity of its spectral characteristics to those of complex **2a**, whose structure has been established previously by X-ray diffraction analysis.[2] The IR spectrum of compound **2c** has six absorption bands in the carbonylmetal region, which are shifted to the low-frequency region by approximately 10 cm^{-1} with respect to the analogous bands in the spectrum of complex **2a**. These shifts are, apparently, associated with the electron-releasing effect of the ferrocenyl substituents. At the same time, it is noteworthy that the positions of the corresponding signals for the CH protons of the oxaruthenacycle and the hydride hydrogen in the ^1H NMR spectra of complexes **2a** and **2c** differ insignificantly.

The structure of complex **3c** agrees with the data of ^1H and ^{13}C NMR and IR spectroscopy. In the IR spectrum of **3c**, the absorption bands corresponding to the carbonylmetal groups are shifted to the low-frequency region compared to the analogous bands in the spectra of complexes **3a,b**. The shapes of the NMR spectra and the positions of the signals differ only slightly from those for complexes **3a,b**, which is indicative of the similarity of these three compounds.

To establish the structure of complex **3c** and to elucidate the effect of the Fc substituents, we studied this complex by X-ray diffraction analysis. The structure of one of two crystallographically independent molecules of **3c** is shown in Fig. 1. The principal bond lengths and bond angles are given in Table 2. This molecule of **3c** contains a metal chain in which two terminal ruthenium atoms, *viz.*, Ru(2) and Ru(3), are incorporated into the chelate oxaruthenacycles formed by molecules **1c** and the $Ru(CO)_3$ fragments. Each oxaruthenacycle, in turn, is η^3-coordinated to the central Ru(1) atom through the ruthenaallyl fragment $-(CO)_3Ru-C(Fc)=CH-$. On the whole, the structure of complex **3c** is analogous to that of complex **3b** described previously.[4] However, a sophis-

Table 1. Parameters of the ^1H and ^{13}C NMR and IR spectra of complexes **1—4**

Compound	IR (heptane), $\nu(CO)/cm^{-1}$	NMR ($CDCl_3$)	
		δ_H (J_{H-H}/Hz)	δ_C
1c		4.164 (s, 5 H); 4.187 (s, 5 H); 4.451 (t, 2 H, J = 1.8); 4.543 (t, 2 H, J = 1.8); 4.582 (t, 2 H); 4.864 (t, 2 H, J = 1.8); 6.727 (d, 1 H, J = 15.4); 7.689 (d, 1 H, J = 15.4)	
2c	2094 m, 2054 v.s, 2030 s, 2012 v.s, 1996 s, 1974 m	−12.510 (d, 1 H, J = 1.1); 4.220 (s, 5 H); 4.190 (m, 1 H); 4.231 (s, 5 H); 4.301 (m, 1 H); 4.319 (d, 1 H, J = 1.1); 4.332 (m, 1 H); 4.395 (m, 1 H); 4.477 (m, 1 H); 4.499 (m, 1 H); 4.631 (m, 1 H); 4.648 (m, 1 H)	
3c	2078 v.s, 2064 s, 2008 v.s, 1980 s, 1946 m	3.643 (s, 1 H); 3.931 (m, 1 H); 4.125 (s, 5 H); 4.192 (s, 5 H); 4.290 (m, 1 H); 4.402 (m, 1 H); 4.459 (m, 1 H); 4.564 (m, 1 H); 4.625 (m, 1 H)	63.33, 67.57, 69.31,69.79, 69.85, 70.34, 70.61, 70.70, 70.87, 71.51, 75.19, 73.65, 75.54, 79.19, 99.23, 187.77, 191.21, 195.39, 200.18, 205.45, 206.95
4	2040 s, 1968 s	Dimeric form: 4.357 (s, 5 H); 4.375 (s, 5 H); 4.488—4.980 (m, 8 H); 7.033 (s, 1 H); Monomeric form: 4.144 (s, 5 H); 4.275 (s, 5 H); 4.488—4.980 (m, 8 H); 6.992 (s, 1 H)	Dimeric form: 69.97, 70.21, 71.04, 71.53, 71.81, 73.38, 90.54, 127.88, 191.24, 199.75, 204.84, 217.59; Monomeric form: 69.7, 70.15, 70.88, 71.69, 73.13, 73.23, 90.36, 128.28, 191.62, 199.38, 205.12, 217.97

Table 2. Principal bond lengths (*d*) and bond angles (ω) in complex **3c** (for two independent molecules **A** and **B**)

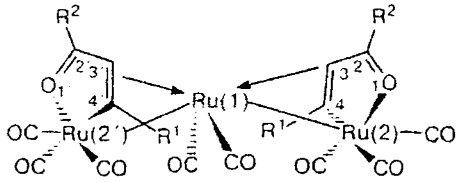
Bond	*d*/Å		Bond	*d*/Å		Bond	*d*/Å	
	A	**B**		**A**	**B**		**A**	**B**
Ru(1)—Ru(2)	2.782(1)	2.781(1)	Ru(2)—C(5)	1.864(6)	1.866(8)	O(10)—C(32)	1.282(7)	1.271(7)
Ru(1)—Ru(3)	2.774(1)	2.771(1)	Ru(2)—C(11)	2.056(6)	2.052(6)	C(9)—C(10)	1.440(8)	1.432(8)
Ru(1)—C(1)	1.884(7)	1.890(7)	Ru(2)—O(9)	2.106(4)	2.130(4)	C(9)—C(12)	1.436(8)	1.446(8)
Ru(1)—C(2)	1.900(6)	1.878(6)	Ru(3)—C(6)	1.896(6)	1.905(7)	C(10)—C(11)	1.449(8)	1.433(8)
Ru(1)—C(10)	2.298(5)	2.292(5)	Ru(3)—C(7)	1.986(7)	1.975(7)	C(11)—C(22)	1.466(8)	1.463(8)
Ru(1)—C(11)	2.269(5)	2.251(5)	Ru(3)—C(8)	1.856(6)	1.878(7)	C(32)—C(33)	1.417(8)	1.421(8)
Ru(1)—C(33)	2.318(5)	2.320(5)	Ru(3)—C(34)	2.049(6)	2.047(5)	C(32)—C(35)	1.455(8)	1.448(9)
Ru(1)—C(34)	2.303(6)	2.272(5)	Ru(3)—O(10)	2.119(4)	2.123(4)	C(33)—C(34)	1.449(8)	1.428(8)
Ru(2)—C(3)	1.891(7)	1.888(7)	O(9)—C(9)	1.272(7)	1.289(7)	C(34)—C(45)	1.456(8)	1.478(8)
Ru(2)—C(4)	1.976(7)	1.978(7)						

Angle	ω/deg		Angle	ω/deg	
	A	**B**		**A**	**B**
Ru(3)—Ru(1)—Ru(2)	158.20(2)	156.27(2)	O(10)—Ru(3)—Ru(1)	81.81(10)	81.64(11)
O(9)—Ru(2)—Ru(1)	82.51(11)	82.30(11)	C(34)—Ru(3)—Ru(1)	54.6(2)	53.8(2)
C(11)—Ru(2)—Ru(1)	53.4(2)	52.9(2)	C(34)—Ru(3)—O(10)	80.8(2)	79.9(2)
C(11)—Ru(2)—O(9)	80.8(2)	81.1(2)	C(32)—O(10)—Ru(3)	110.6(3)	111.5(3)
C(9)—O(9)—Ru(2)	112.0(3)	111.1(3)	O(10)—C(32)—C(33)	119.9(5)	119.1(5)
O(9)—C(9)—C(10)	118.6(5)	118.5(5)	O(10)—C(32)—C(35)	119.4(5)	117.8(5)
O(9)—C(9)—C(12)	119.2(5)	119.2(5)	C(33)—C(32)—C(35)	120.8(5)	123.1(5)
C(12)—C(9)—C(10)	122.2(5)	122.2(5)	C(32)—C(33)—C(34)	116.0(5)	116.2(5)
C(9)—C(10)—C(11)	116.1(5)	117.2(5)	C(33)—C(34)—C(45)	119.6(5)	118.7(5)
C(10)—C(11)—C(22)	118.4(5)	117.9(5)	C(33)—C(34)—Ru(3)	107.8(4)	108.8(4)
C(10)—C(11)—Ru(2)	107.4(4)	107.5(4)	C(45)—C(34)—Ru(3)	131.6(4)	131.4(4)
C(22)—C(11)—Ru(2)	133.5(4)	134.0(4)			

ticated comparison of the geometric parameters of complexes **3c** and **3b** made it possible to reveal a number of interesting differences in their structures. For convenience, the principal geometric parameters of these compounds are given in Table 3. Taking into account the overall symmetry of the complexes with respect to the central Ru atom, the average parameters for only one-half of the molecule are given. A comparison of the parameters of complex **3c** with the corresponding data of X-ray diffraction analysis for complex **3b** (see Table 3) demonstrated that the introduction of the ferrocenyl substituents results in straightening of the metal chain (the Ru(2)—Ru(1)—Ru(2′) angle increases by approximately 10°), the metallacycles being additionally rotated with respect to each other (the torsion angle ω was used for describing their mutual orientation). This change in the structure is accompanied by noticeable shortening of the Ru—Ru bonds (by more than 0.02 Å) and by a substantial change in the geometric parameters of π-coordination of the C(3)=C(4) double bond to the Ru(1) atom (see Table 3), the Ru(1)—C(4) distance changing most noticeably (by more than 0.1 Å).

The above-mentioned weakening of π-bonding in complex **3c** compared to that in complex **3b** agrees well with the known dependence of the strength of the π-bond between olefin and the transition metal atom on the donor-acceptor properties of the substituents at the double bond.[5,6] In particular, it was demonstrated that

Table 3. Geometric parameters of complexes **3b** and **3c**



Parameter	**3b**	**3c**
Distances/Å		
Ru(1)—Ru(2)	2.801	2.777
Ru(2)...Ru(2′)	5.390	5.445
Ru(1)—C(3)	2.25	2.31
Ru(1)—C(4)	2.16	2.27
Ru(2)—O(1)	2.12	2.12
Ru(2)—C(4)	2.07	2.05
C(2)—O(1)	1.28	1.28
C(2)—C(3)	1.43	1.43
C(3)—C(4)	1.45	1.44
Angles/deg*		
Ru(2)—Ru(1)—Ru(2′)	148.3	157.2
α	15.4	18.8
ω	67.1	91.6

* Here, α is the folding angle of the oxaruthenacycle along the O(1)...C(4) line and ω is the X(1)—Ru(2)—Ru(2′)—X(1′) torsion angle, where X(1) is the midpoint of the C(2)—C(3) bond and X(1′) is the midpoint of the C(2′)—C(3′) bond.

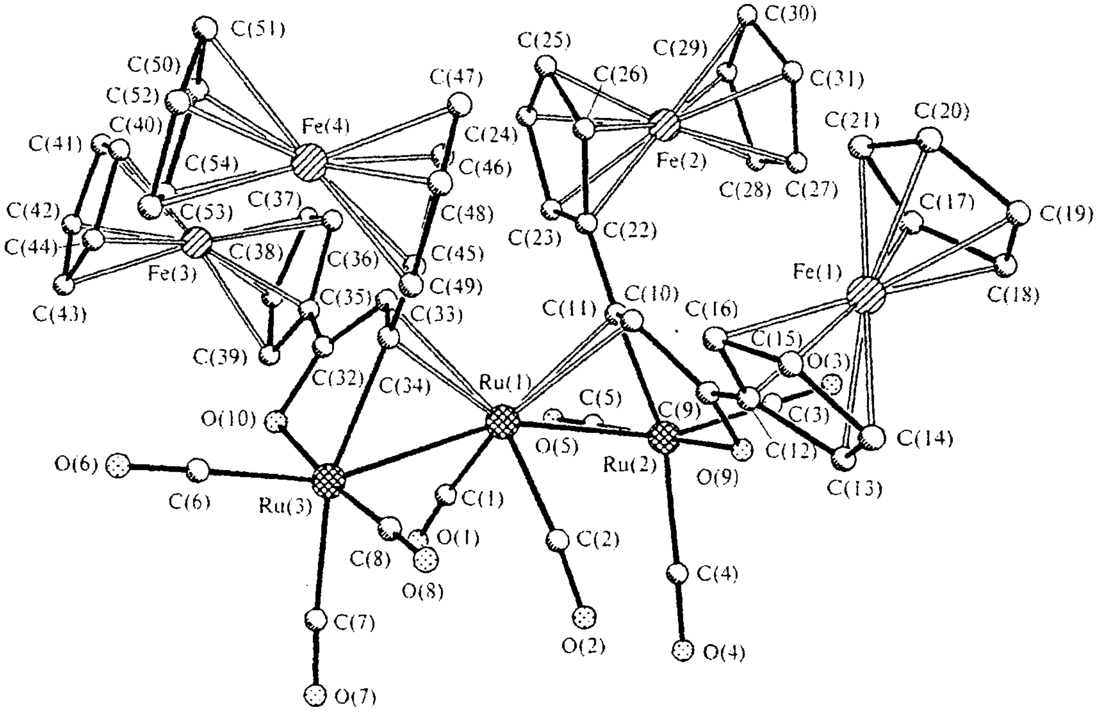


Fig. 1. Structure of molecule **3c** in the crystal.

an increase in the electron-donating ability of the substituent leads to a decrease in back donation of the electron density from the metal atom to the unoccupied π^*-orbitals of olefin and to weakening of π-bonding of olefin with the metal atom.

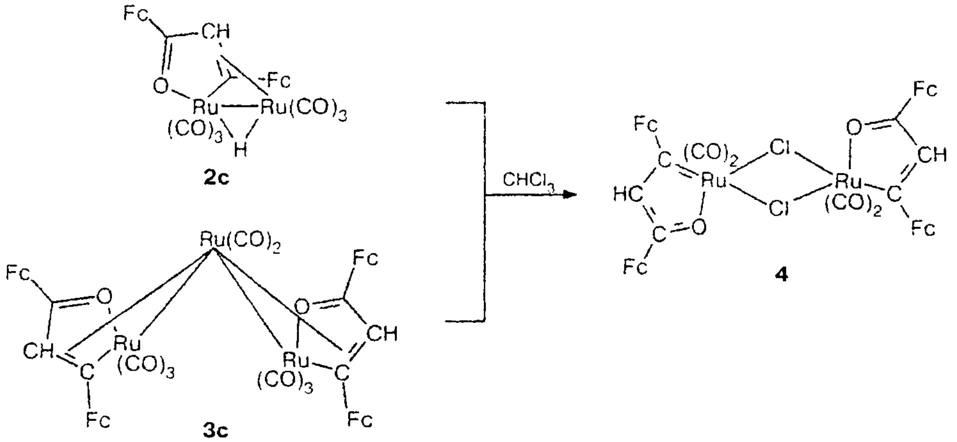
The five-membered π-coordinated metallacycles are characterized by equalization of the bond lengths in the C=C—C=O chain and adopt a flattened envelope conformation in which the Ru atom deviates from the plane passing through the remaining four atoms of the ring toward the π-bonded Ru atom. An analogous structure of the five-membered oxaruthenacycle has been also observed[2] in binuclear complex **2a**. Therefore, analysis of the geometric characteristics demonstrated that the oxaruthenacyclopentadiene fragment is structurally rigid and its geometry is independent of the nature of the substituents in the initial oxadiene. It can also be seen from Table 3 that the geometric parameters characterizing coordination of this fragment to the second metal atom (to put it differently, the ligand properties of the oxaruthenacycle) change substantially on going from aryl to ferrocenyl substituents.

The geometric parameters of eight ferrocenyl substituents in complex **3c** (two independent molecules have four substituents each) have standard values. The Fe—C_{Cp} distances are in the range of 1.98(1)—2.071(6) Å. The mutual orientation of the Cp rings in seven substituents is nearly eclipsed and this orientation in the eighth substituent is slightly skewed. The cyclopentadienyl ligands, which are σ-bound to the C(9) and C(32) atoms, lie virtually in the planes of the corresponding oxadiene fragments. The dihedral angles between these planes are, on the average, 15°. On the contrary, the Cp ligands, which are σ-bound to the C(11) and C(34) atoms, deviate substantially from the planes of the corresponding oxadiene fragments in a direction opposite to the central Ru atom; the corresponding dihedral angles are, on the average, 28°.

When describing the properties of complexes **2c** and **3c**, it should be noted that these complexes can be readily converted into complex **4** upon dissolution in chloroform[7] (Scheme 2). This process is accompanied by a change in the color, *viz.*, yellow complex **2c** and red complex **3c** were converted into violet complex **4**. Dark-violet crystals of **4** formed upon crystallization from chloroform were studied by X-ray diffraction analysis.

The centrosymmetrical molecule of complex **4** (Fig. 2, the crystallographic inversion center is located midway between two Ru atoms) consists of two oxaruthenacycles linked through two unsymmetrical Cl bridges (Ru(1)—Cl(1), 2.522(3) Å and Ru(1)—Cl(1A), 2.457(3) Å; Table 4). The Ru(1)....Ru(1A) distance is 3.675(1) Å. The five-membered oxaruthenacycles in molecule **4**, unlike those in the above-described complex **3c**, are not involved in additional coordination to another metal atom, which is clearly reflected in their geometric parameters. The oxaruthenacycles in complex **4** are virtually planar (the folding angle along the O(3)...C(5) line is only 6.4°) and the bond lengths in the oxadiene chain differ substantially from the analogous bonds in molecule **3c**. Apparently, the slight shortening of the endocyclic Ru—C and Ru—O bonds in molecule **4**

Scheme 2



(2.03(1) and 2.101(6) Å, respectively) compared to the corresponding bonds in the coordinated oxaruthenacycle of complex **3c** is indicative of a particular contribution of the ruthenafuran form O—Ru=C(Fc)CH=C(Fc) to the structure of the uncoordinated oxaruthenacycle.[2] In all ferrocenyl substituents in molecule **4**, the Cp rings are in eclipsed orientations. The angles between the plane of the oxadiene fragment and the planes of the Cp ligands bound to the C(3) and C(5) atoms are 11.7° and 21.8°, respectively.

The crystal of complex **4** contains a chloroform molecule of solvation whose hydrogen atom forms a shortened intermolecular contact with the oxygen atom of the oxaruthenacycle (C(1s)...O(3), 3.15(1) Å; H(1s A)...O(3), 2.26 Å; C(1s)—H(1sA)...O(3), 147°).

An analogous Cl-bridged complex containing the monoazadiene fragment has been prepared previously.[8]

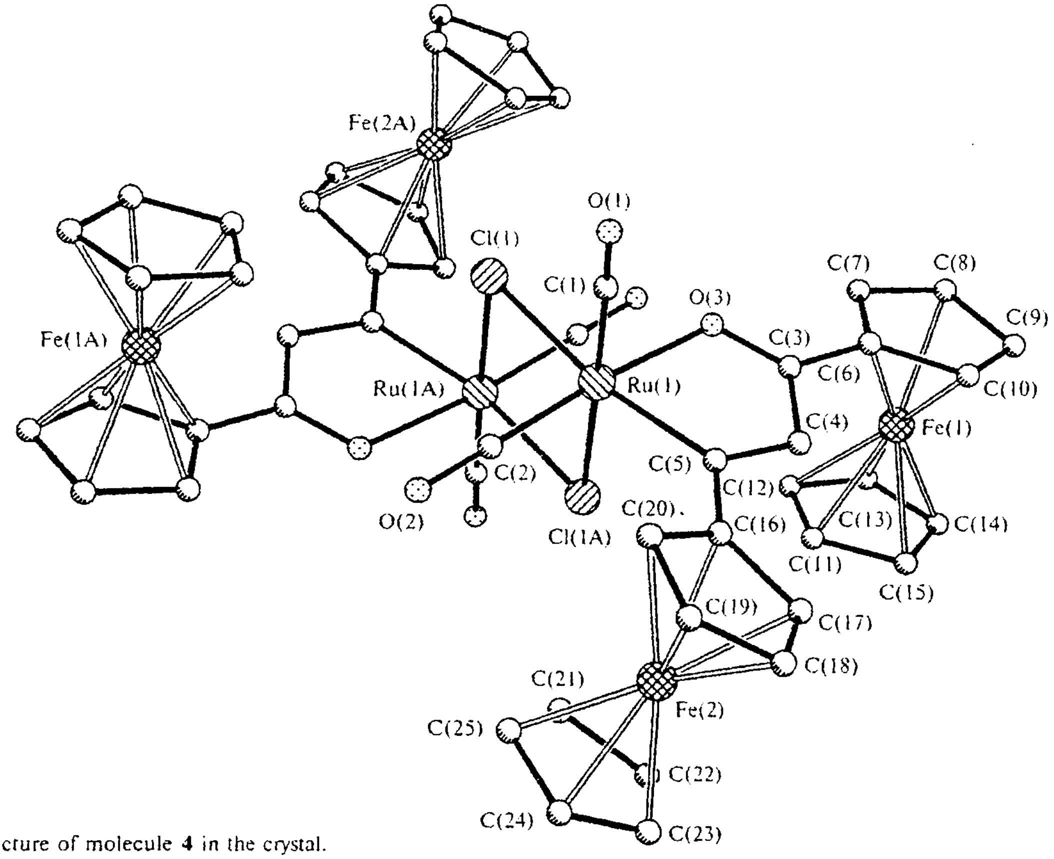
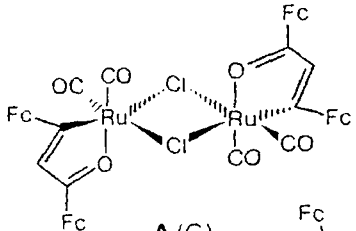
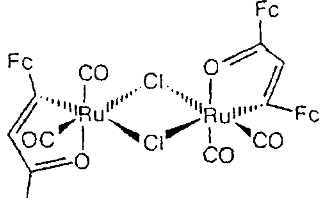


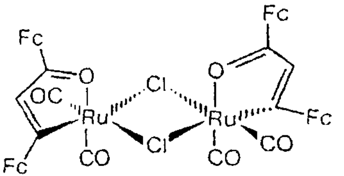
Fig. 2. Structure of molecule **4** in the crystal.



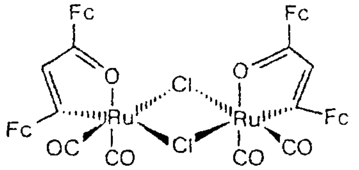
A (C_i)



B (C_2)



C (C_2)



D (C_s)

In the cited work, it was mentioned that such complexes can exist as mixtures of four isomers. The number of isomers and their structures are determined primarily by the rules of the mutual effect of the ligands.[9] In our case, complex **4** can also be represented as four analogous isomers **A**—**D** possessing particular symmetry elements.* According to the X-ray diffraction data, the crystals of **4** obtained by us contain centrosymmetrical molecules **A**.

The ^{1}H NMR spectra of complex **4** testify that solutions of **4** contain a mixture of isomers and the composition of the mixture depends on the mode of treatment of the reaction product with chloroform.

The ^{1}H NMR spectrum of a solution of a sample of complex **4**, which was prepared for X-ray diffraction study, in $CDCl_3$ has two pairs of singlet signals with equal integral intensities in pairs (their values are given in parentheses) in the region characteristic of resonance of unsubstituted Cp rings at δ 4.375 and 4.357 (2.5) and at δ 4.275 and 4.144 (1.0). These signals correspond to two nonequivalent Cp ligands in two complexes, which are present in 70 and 30% amounts, respectively. After the sample was kept for one week, the ^{1}H NMR spectrum showed a new signal at δ 4.367 instead of the signal at δ 4.375, the intensity of the former being equal to that of the latter. Two low-intensity peaks at δ 4.275 and 4.144 were retained, the ratio between the integral intensities of the signals for the protons of the unsubstituted Cp rings remaining unchanged. The ^{1}H NMR spectrum measured after rapid concentration of the mixture followed by dissolution of the solid sample also did not reproduce the initial spectral pattern corresponding to pure isomer **A**. The ^{1}H NMR spectrum of complex **4** dissolved in C_6D_6 has two pairs of singlet signals at δ 4.397 (4.0) and 4.330 (4.0) and at δ 4.210 (1.0) and 4.160 (1.0). The ^{1}H NMR spectrum of complex **4** dissolved in CD_3CN has two pairs of signals at δ 4.395 (17.0) and 4.325 (17.0) and at δ 4.370 (1.0) and 4.359 (1.0). Therefore, the ^{1}H NMR spectrum of complex **4** changes with time and depends on the nature of the solvent. Based on the change in the ratio between the intensities observed on going from one solvent to another, it can be concluded that the low-intensity peaks in chloroform and benzene and, on the contrary, the intense peaks in the coordinating solvent, CD_3CN belong to the monomeric form formed upon dissociation of the bridging Ru—Cl bond as a result of coordination with the solvent molecule.[10] Clearly, the complex in the coordinating solvent (CD_3CN) dissociates to a greater extent. Changes in the NMR spectra observed in the region of 4.380—4.330 ppm upon storage of the solution of the sample are indicative of the conversion of one isomer into another, which apparently occurs with the participation of the monomeric form. Unfortunately, we failed to assign the observed signals to particular isomers, except for isomer **A**.

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

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Cl(1)	2.522(3)	O(2)—C(2)	1.152(12)
Ru(1)—Cl(1A)	2.457(3)	O(3)—C(3)	1.259(12)
Ru(1)—O(3)	2.101(6)	C(3)—C(4)	1.464(14)
Ru(1)—C(1)	1.884(13)	C(3)—C(6)	1.446(12)
Ru(1)—C(2)	1.862(10)	C(4)—C(5)	1.376(12)
Ru(1)—C(5)	2.031(10)	C(5)—C(16)	1.488(14)
O(1)—C(1)	1.104(14)		
Angle	**ω/deg**	**Angle**	**ω/deg**
Ru(1A)—Cl(1)—Ru(1)	95.14(11)	C(5)—C(4)—C(3)	114.0(9)
Cl(1A)—Ru(1)—Cl(1)	84.86(11)	C(4)—C(5)—C(16)	117.2(9)
C(5)—Ru(1)—O(3)	79.7(3)	C(4)—C(5)—Ru(1)	113.5(7)
C(3)—O(3)—Ru(1)	112.8(6)	C(16)—C(5)—Ru(1)	129.3(7)
O(3)—C(3)—C(6)	119.4(9)	O(1)—C(1)—Ru(1)	177.8(9)
O(3)—C(3)—C(4)	119.5(8)	O(2)—C(2)—Ru(1)	177.5(9)
C(6)—C(3)—C(4)	121.0(9)		

In $CDCl_3$, the protons at the C=C double bond of the oxaruthenacycle give two signals at δ 7.033 and 6.992 with the integral intensity ratio of 2 : 1, whereas in CD_3CN these protons give two signals at δ 7.280 and 7.160 with the integral intensity ratio of 1 : 17. Therefore, the low-field signals belong, apparently, to the dimeric form of the complex, whereas the higher-field signals belong to the monomeric form regardless of the nature of the solvent.

The ^{13}C NMR spectrum of complex **3c**, which was measured with suppression of spin-spin ^{13}C—^{1}H coupling,

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* The data of elemental analysis of the mixture correspond to complex **4**.

has six signals in the region characteristic of the carbon atoms of the carbonyl groups. In the spectrum measured without suppression of spin-spin ^{13}C—^{1}H coupling, only one of these signals is observed, at δ 206.95 as a doublet with the spin-spin coupling constant $^{2}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ = 7.0 Hz. This fact allows us to assign the lowest-field signal to the C(9) and C(32) atoms adjacent to the C(10) and C(33) atoms, respectively, which are directly bound to the hydrogen atoms. Most probably, an analogous signal at δ 217.59 in the spectrum of complex **4** should be assigned to the C(3) atom adjacent to the C(4)H group. Of the remaining five signals observed at low field, which correspond to the carbonylmetal groups, two signals at δ 205.5 and 191.2 in the spectrum of compound **3c**, which are similar in position to signals in the spectrum of complex **4**, belong, apparently, to the carbonyl groups coordinated to the Ru atom involved in the oxaruthenacycle. The third CO group coordinated to the same Ru atom in molecule **3c** is replaced by the Cl atom on going to complex **4**. Clearly, the remaining singlet at δ 199.75 in the spectrum of complex **4** should be assigned to the C(5) atom. This assignment is also supported by the fact that the only singlet at δ 199.75 corresponds to the dimeric form of **4** and the singlet corresponding to the monomeric form is observed at higher field (δ 199.38). Actually, the ^{13}C NMR spectrum of complex **4** has two sets of signals at low field at δ 217.97, 205.12, 199.38, and 191.63 and at δ 217.59, 204.84, 199.75, and 191.24 with equal integral intensities in each set. We assigned the signals of the first (less intense) and second (more intense) groups to the monomeric and dimeric forms of complex **4**, respectively, because (as was mentioned above) dissociation in $CDCl_3$ is not higher than 30%. It is known[11,12] that in the NMR spectra of Fe complexes with analogous ligands, the signal for the carbon atom bound to the Fe atom through a single bond is observed at δ 168.7. In the case of formation of the furan structure with the partially double Fe=C bond, the carbon atom acquires the carbene character and the signal is shifted downfield to δ 247.0.

In studies of the isomers of complex **4** and their mutual conversions, the carbonylmetal regions of the IR spectra are less informative. All IR spectra of complex **4** in $CHCl_3$ have two intense bands in the region of CO stretching vibrations. This indicates that the Ru atoms have two CO ligands each in *cis* positions with respect to one another.

Treatment of the precipitate, which formed from the reaction mixture in the synthesis of complex **3c**, with chloroform afforded a number of products. According to the data of IR and NMR spectroscopy, isomers of **4** are the major products. Therefore, the precipitate also contained complexes with five-membered oxaruthenacycles. Previously, only complexes with η^3-dihydropyran rings have been found in analogous precipitates which formed in the reactions of $Ru_3(CO)_{12}$ with ketones **1a,b** and which were not treated with chloroform.[1]

Chloride-bridged complexes were also obtained in the reactions of ketones **1a,b** (which was confirmed by IR spectroscopy), but the rates of the reactions were lower than that in the case of formation of complex **4** from **3c**. This fact is consistent with the data of X-ray diffraction study, which indicate that the π-bond in molecule **3c** is substantially elongated compared to the π-bond in molecule **3b**.

The synthesis of complexes with uncoordinated oxaruthenacycles opens up possibilities of using these compounds for the preparation of heteronuclear complexes in which the uncoordinated oxaruthenacycle can act as a ligand.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 MHz) in solutions in $CDCl_3$, CD_2Cl_2, C_6D_6, and CD_3CN with trace signals of $CHCl_3$ (δ 7.25) and partially deuterated $CHDCl_2$ (δ 5.32), C_6HD_5 (δ 7.25), and CHD_2CN (δ 4.32) as the internal standards, respectively. The ^{13}C NMR spectra were measured on a Bruker AMX-400 instrument (100.61 MHz) with $CDCl_3$ as the internal standard (δ 76.91). The IR spectra were recorded on a Specord 75-IR spectrophotometer. Ketone **1c** was prepared according to a known procedure.[13]

2,3,4-η^3-(3,5-Diferrocenyl-1-oxa-2-tricarbonylruthenacyclopenta-3,5-diene)-μ-hydridotricarbonylruthenium (2c). A mixture of $Ru_3(CO)_{12}$ (64 mg, 0.1 mmol) and ketone **1c** (84 mg, 0.2 mmol) in heptane (50 mL) was refluxed for 1 h. After cooling to −20 °C, the reaction mixture was filtered and the filtrate was chromatographed on a column with silica gel. Elution with heptane afforded $Ru_3(CO)_{12}$ (9 mg) and a mixture of $Ru_3(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ (2 mg). Elution with a 3 : 1 heptane—CH_2Cl_2 mixture gave red-orange complex **2c** (78 mg, 85%) and traces of dark-violet complex **4**, which were identified by IR and NMR spectroscopy (see Table 1). $Ru_3(CO)_{12}$ was isolated from the precipitate by elution in a yield of 5 mg.

Bis(2,3,4-η^3-3,5-diferrocenyl-1-oxa-2-tricarbonylruthenacyclopenta-3,5-diene)dicarbonylruthenium (3c). *A.* A mixture of $Ru_3(CO)_{12}$ (64 mg, 0.1 mmol) and complex **2c** (84 mg, 0.2 mmol) in heptane (100 mL) was refluxed for 1 h 45 min. After cooling to −20 °C, the reaction mixture was filtered and the precipitate was extracted three times with boiling heptane. The heptane solution and the extract were combined and chromatographed on a column with silica gel. Elution with heptane afforded $H_4Ru_4(CO)_{12}$ (4 mg) and $Ru_3(CO)_{12}$ (1 mg). Elution with a 3 : 1 heptane—CH_2Cl_2 mixture gave dark-cherry complex **3c** (55 mg, 46%) and complex **4** (13 mg). The precipitate formed from the reaction mixture was extracted with boiling hexane and its IR spectrum was recorded (Nujol mulls): ν(CO)/cm^{-1}: 2043 s, 2018 s, 1970 s. Found (%): C, 31.09; H, 2.92.

B. A mixture of complex **2c** (8 mg, 0.01 mmol) and ketone **1c** (4 mg, 0.01 mmol) was heated in heptane (15 mL). The course of the reaction was followed from changes in the IR spectra. After the reaction mixture was heated for 30 min, complex **2c** completely disappeared, the solution contained complex **3c**, and a small amount of precipitate formed. The solution was filtered and chromatographed on a column with silica gel (a 3 : 1 heptane—CH_2Cl_2 mixture as the eluent). Compound **3c** was isolated in a yield of 4 mg (43.5%) (see Table 1).

Bis(dicarbonyl-μ-chloro-3,5-diferrocenyl-1-oxa-2-ruthenacyclopentadiene) (4). *A.* Complex **3c** (14 mg, 0.01 mmol) was dissolved in $CHCl_3$. The reaction mixture was kept at −20 °C for 48 h, after which the color of the solution changed from cherry-red (**3c**) to violet (**4**).

Table 5. Crystallographic data and the parameters of the refinement of the structures of complexes **3c** and **4**

Parameter	**3c**	**4**
Molecular formula	$C_{54}H_{46}O_{10}Fe_4Ru_3 \cdot$ $\cdot 0.5C_7H_{16}$	$C_{50}H_{38}O_6Cl_2Fe_4Ru_2 \cdot$ $\cdot 2CHCl_3$
Molecular weight	1423.55	1469.98
Space group	$P\bar{1}$	$P\bar{1}$
Temperature/K	193(2)	153(2)
a/Å	14.040(4)	10.934(5)
b/Å	19.588(5)	11.532(5)
c/Å	20.610(5)	11.842(5)
α/deg	81.00(2)	65.61(3)
β/deg	80.29(2)	79.41(3)
γ/deg	74.99(2)	76.50(3)
V/Å^3	5358(3)	1316(1)
Z	4	1
d_{calc}/g cm^{-3}	1.765	1.855
Diffractometer	Syntex $P2_1$	Siemens P3/PC
Radiation	Mo-Kα (λ = 0.71073 Å)	
μ/cm^{-1}	19.33	20.89
Scanning mode	θ—2θ	θ—2θ
2θ$_{max}$/deg	46	50
Number of independent reflections	14920	3816
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0466 (12339 reflections)	0.0792 (2815 reflections)
wR_2 (based on F^2 for all reflections)	0.1453	0.2626
Number of refinable parameters	1327	325
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = 1/3(F_o^2 + 2F_c^2)$	
a	0.0902	0.1864
b	6.2197	0.0

Recrystallization from $CHCl_3$ afforded dark-violet crystals of **4** (see Table 1) in a yield of 11 mg (60%). Found (%): C, 48.09; H, 3.16; Cl, 5.66. $C_{50}H_{38}Cl_2Fe_4O_6Ru_2$. Calculated (%): C, 48.77; H, 3.11; Cl, 5.75.

B. The precipitate (20 mg) that formed from the reaction mixture in the synthesis of complex **3c** was extracted three times with boiling heptane. The residue was dried and the product, which was obtained in a yield of 18 mg, was dissolved in $CHCl_3$. The color of the solution gradually changed from dark-cherry to violet. Recrystallization from $CHCl_3$ afforded dark-violet crystals of **4** in a yield of 14 mg (see Table 1).

X-ray diffraction study. Single-crystalline samples of complexes **3c** and **4** suitable for X-ray diffraction study were prepared by crystallization from heptane and chloroform, respectively. Information on the instruments, the crystallographic characteristics, and the principal details of the refinement of compounds **3c** and **4** are given in Table 5. Both structures were solved by direct methods. The coordinates and the thermal parameters of the nonhydrogen atoms were refined isotropically and then anisotropically by the block-diagonal least-squares method and by the full-matrix least-squares method for the crystal structures of **3c** and **4**, respectively. The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. All calculations were carried out on a PC with the use of the SHELXTL PLUS 5 program package.[14]

The complete tables of the bond lengths, bond angles, atomic coordinates, and thermal parameters were deposited with the Cambridge Structural Database.

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Received December 7, 1999;
in revised form March 17, 2000