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Reaction of 2-methyl-3-morpholino-1-phenylprop-2-en-1-one with $Ru_3(CO)_{12}$

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The reaction of $Ru_3(CO)_{12}$ with 2-methyl-3-morpholino-1-phenylprop-2-en-1-one (**1**) produced the $Ru_6(CO)_{16}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}PhC(O){-}C(Me){=}C)_2$ (**2**), $Ru_2O_2(CO)_4(\eta^3\text{-}OC(Ph)C(Me)C(H)C(Me)_2C(Ph))_2$ (**3**), and $[Ru(CO)_2(PhCO_2)(O(CH_2{-}CH_2)_2NH]_2$ (**4**) complexes, which were characterized by IR and NMR spectroscopy. The structures of the complexes were established by X-ray diffraction. The formation of the complexes is accompanied by deamination of ligand **1**. Complexes **2** and **3** bearing the vinyl ketone groups contain five-membered oxaruthenacycles and dihydropyran rings. Morpholine is not removed from the reaction mixture and leads to the formation of complex **4**.

Key words: dodecacarbonyltriruthenium, oxaruthenacycles, η^3-dihydropyran rings, carboxylate rings, X-ray diffraction study, IR spectroscopy, NMR spectroscopy.

Earlier,[1] we have demonstrated that most of the complexes prepared by the reactions of $Ru_3(CO)_{12}$ with oxadienes (α,β-unsaturated ketones) contain the same structural fragments, *viz.*, five-membered oxaruthenacycles and dihydropyran rings, involved in π-coordination to metal atoms. The variation of substituents at the carbonyl group of oxadiene (aryls, alkyls, or amino groups) did not lead to new structural types. When a secondary amino group was attached to the C_β atom of the olefin fragment of oxadiene, the reaction with $Ru_3(CO)_{12}$ produced complexes with six-membered azaoxaruthenacycles[2] due to the appearance of an additional reaction center (active N—H bond of the secondary amino group). It was of interest to elucidate how the replacement of the secondary amino group in the β position of the olefin fragment of oxadiene by the tertiary amino group influences the structure of the resulting complexes. Earlier,[3] it has been demonstrated that β-aminovinyl ketones do not react with iron carbonyls. Other examples of the reactions of these ketones with iron-group metal carbonyls are lacking in the literature.[4,5] In the present study, we examined the reaction of $Ru_3(CO)_{12}$ with 2-methyl-3-morpholino-1-phenylprop-2-en-1-one (**1**).

Results and Discussion

The reaction of $Ru_3(CO)_{12}$ with compound **1** was carried out under reflux in heptane for 8 h. The course of the reaction was monitored by changes in the IR spectra in the metal carbonyl stretching region. The reaction afforded a mixture of products, from which three new ruthenium complexes **2**, **3**, and **4** (Scheme 1) were isolated by chromatography in 4, 18, and 25% yields, respectively.

The structures of complexes **2—4** were established by X-ray diffraction. In the crystals structure, hexanuclear complex **2** (Fig. 1, Table 1) occupies a special position on the twofold axis passing through the Ru(3) and Ru(4) atoms. The metal core looks like a twisted ladder consisting of two quadrangles fused at the Ru(3)—Ru(4) bond (Ru(1)—Ru(2)—Ru(3)—Ru(4) and Ru(1A)—Ru(2A)—Ru(3)—Ru(4)), each quadrangle being nonplanar. In complex **2**, there are seven Ru—Ru bonding distances in the range of 2.633(1)—2.9175(7) Å with the shortest distance between the Ru(3) and Ru(4) atoms. The formation of complex **2** is accompanied by elimination of the morpholine fragment from the starting ligand. The oxadiene fragments chelate the Ru atoms to form five-membered oxaruthenacycles, which are involved in π-coordination to the Ru(2) and Ru(2A) atoms. Earlier, we have observed the formation of structurally similar oxaruthenacycles in the reactions of $Ru_3(CO)_{12}$ with oxadiene ligands.[1,6] The oxaruthenacycles in complex **2** are distinguished mainly by the unusual μ_4 coordination of the C(11) atom (four Ru—C(11) distances are in the range 2.052(6)—2.234(6) Å). Apparently, this accounts for a slight nonplanarity of the oxadiene system (O(9)—C(9)—C(10)—C(11) torsion angle is 15.7°).

The analogous hexanuclear cluster $Ru_6(CO)_{16}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}CC(H)C(O)Me)_2$ was synthesized by the reaction of $Ru_3(CO)_{12}$ with but-3-yn-2-ol.[7] In spite of the difference in the nature of substituents at the C atoms of oxaruthenacycles, the structure of this cluster is com-

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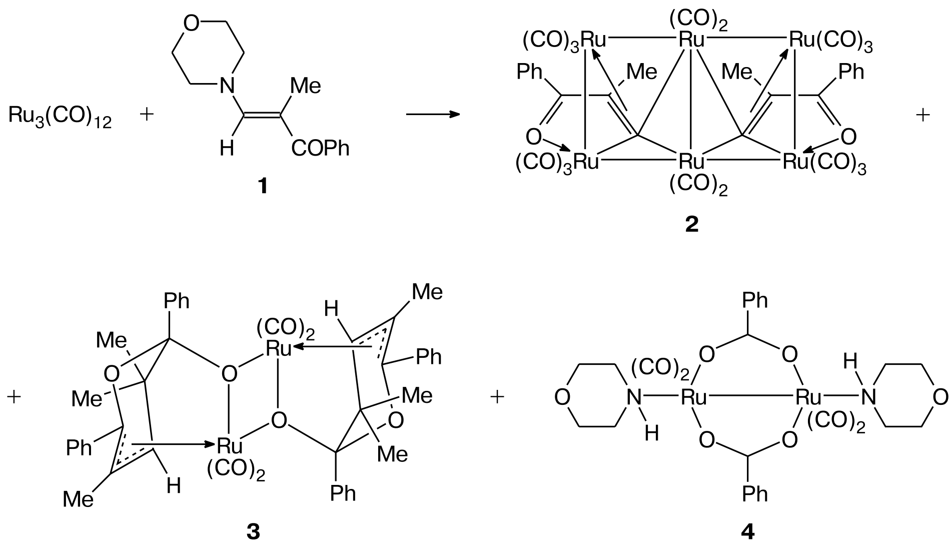
Scheme 1



pletely identical to that of complex **2**. It was hypothesized[7] that but-3-yn-2-ol is oxidized to the corresponding ketone in one of the reaction steps. Therefore, the mechanism of formation of complex **2** may be analogous to that for the complex described in the study.[7]

Centrosymmetric complex **3** (Fig. 2, Table 2) consists of two six-membered dihydropyran rings involved in η^3-coordination to the Ru atoms. The Ru atoms are linked to each other by the bridging O atoms to form the four-membered Ru_2O_2 ring. Earlier, we have synthesized structurally similar complexes by the reactions of $Ru_3(CO)_{12}$ with 4-phenylbut-3-en-2-one[6] and 1-*p*-tolyl-3-phenylprop-2-en-1-one.[1] In spite of the presence of different substituents in the starting ligands, all the compounds synthesized contain dihydropyran rings with similar structures.[1,6]

The formation of complex **3**, like the synthesis of complex **2**, is accompanied by elimination of the morpholine fragment from the starting ligand. The oxadiene system of ligand **1**, apparently, behaves analogously to oxadienes, which we have studied earlier.[1,6] It forms oxaruthenacycles, which are transformed into the dihydropyran rings in the presence of excess ligand (Scheme 2). Most probably, it is impossible to prepare complexes **2** and **3** from the corresponding oxadiene (2-methyl-1-phenylprop-2-en-1-one) by the direct reaction with $Ru_3(CO)_{12}$, be-

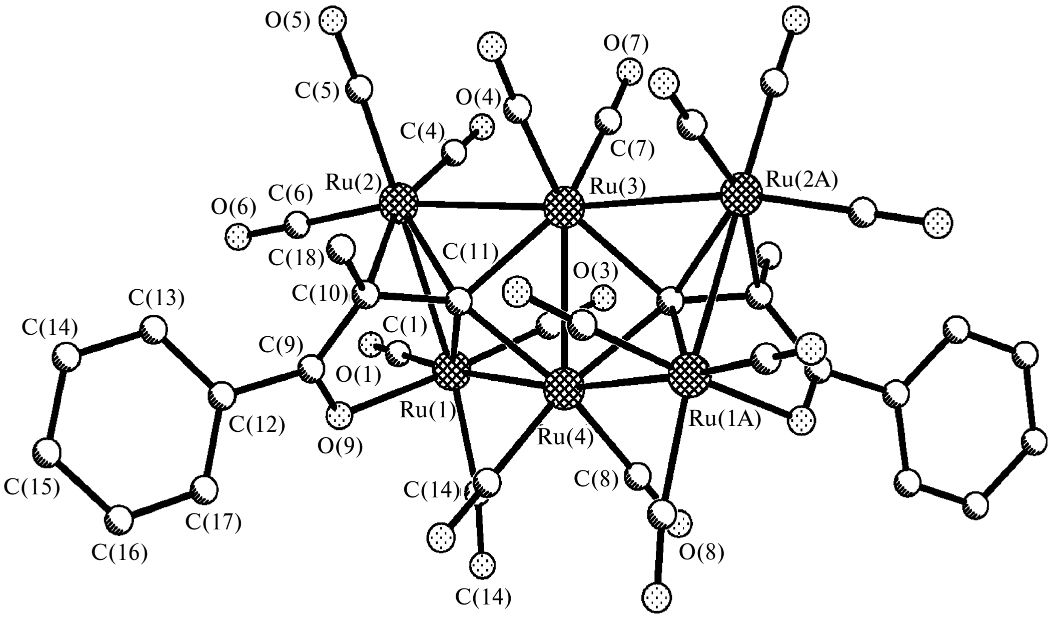


Fig. 1. Molecular structure of complex **2**.

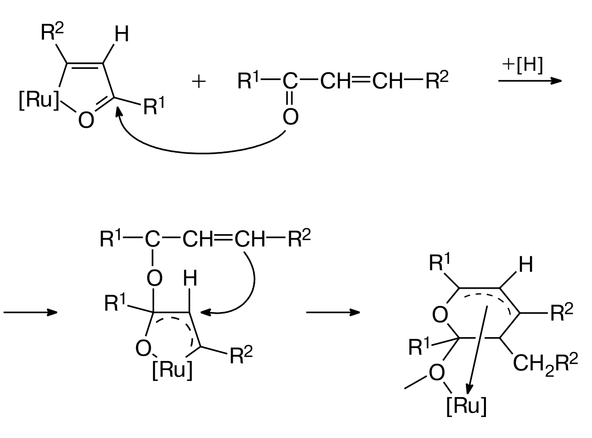
Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **2**

Parameter	Value
Bond	*d*/Å
Ru(1)—Ru(2)	2.7668(8)
Ru(1)—Ru(4)	2.8052(6)
Ru(1)—O(9)	2.106(4)
Ru(1)—C(11)	2.234(6)
Ru(2)—Ru(3)	2.9175(7)
Ru(2)—C(10)	2.220(6)
Ru(2)—C(11)	2.130(6)
Ru(3)—Ru(4)	2.6332(10)
Ru(3)—C(11)	2.111(6)
Ru(4)—C(11)	2.052(6)
O(9)—C(9)	1.256(7)
C(9)—C(10)	1.451(8)
C(10)—C(11)	1.466(9)
Angle	ω/deg
Ru(2)—Ru(1)—Ru(4)	92.09(2)
Ru(1)—Ru(2)—Ru(3)	80.80(2)
Ru(4)—Ru(3)—Ru(2)	92.41(2)
Ru(2)—Ru(3)—Ru(2A)*	175.18(3)
Ru(3)—Ru(4)—Ru(1)	85.28(2)
Ru(1)—Ru(4)—Ru(1A)*	170.56(3)
O(9)—Ru(1)—C(11)	76.6(2)
C(9)—O(9)—Ru(1)	115.8(4)
O(9)—C(9)—C(10)	120.0(6)
C(9)—C(10)—C(11)	113.3(5)
C(10)—C(11)—Ru(1)	105.3(4)

* The atom labeled with the suffix A is related to the unlabeled atom by the symmetry operation $-x, y, -z + 1/2$.

cause vinyl ketones containing only H atoms in the β position are known[8,9] to be able to undergo polymerization.

Scheme 2



In complex **4** (Fig. 3, Table 3), two Ru atoms are linked by two benzoate bridges. Each Ru atom is additionally coordinated by two carbonyl groups and the lone

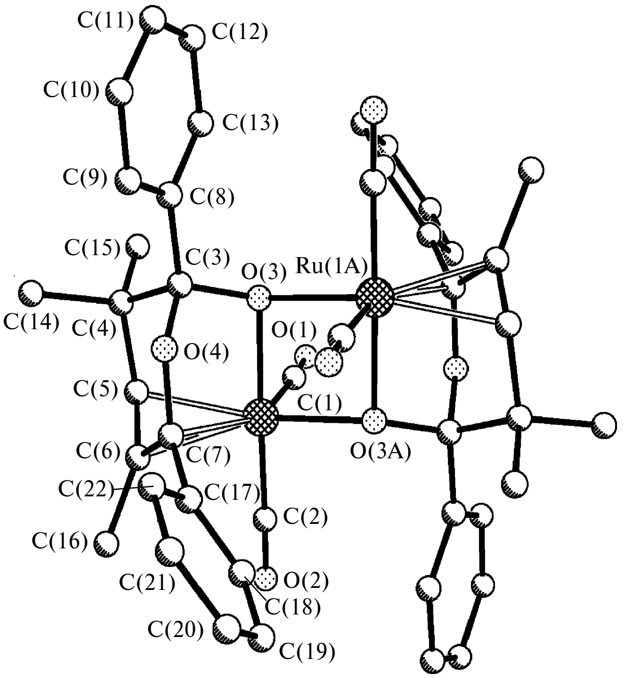


Fig. 2. Molecular structure of complex **3**.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **3**

Parameter	Value
Bond	*d*/Å
Ru(1)—O(3)	2.086(1)
Ru(1)—O(3)*	2.189(1)
Ru(1)—C(5)	2.148(2)
Ru(1)—C(6)	2.245(2)
Ru(1)—C(7)	2.449(2)
O(3)—C(3)	1.391(2)
O(4)—C(3)	1.456(2)
O(4)—C(7)	1.397(2)
C(3)—C(4)	1.559(3)
C(4)—C(5)	1.525(3)
C(5)—C(6)	1.430(3)
C(6)—C(7)	1.396(3)
Angle	ω/deg
O(3)—Ru(1)—O(3A)*	78.60(6)
Ru(1)—O(3)—Ru(1A)*	101.40(6)
C(3)—O(3)—Ru(1)	106.9(1)
C(3)—O(3)—Ru(1A)*	125.0(1)
C(7)—O(4)—C(3)	115.1(2)
O(3)—C(3)—O(4)	107.3(2)
O(3)—C(3)—C(4)	107.8(2)
O(4)—C(3)—C(4)	108.9(2)
C(5)—C(4)—C(3)	105.7(2)
C(6)—C(5)—C(4)	118.2(2)
C(7)—C(6)—C(5)	115.8(2)
C(6)—C(7)—O(4)	120.0(2)

* The atom labeled with the suffix A is related to the unlabeled atom by the symmetry operation $-x, -y + 1, -z$.

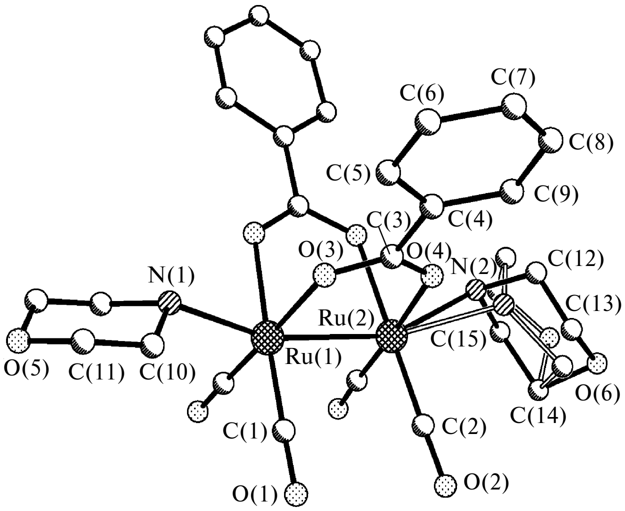


Fig. 3. Molecular structure of complex **4**.

Table 3. Selected bond lengths (*d*) and bond angles (ω) in complex **4**

Parameter	Value
Bond	*d*/Å
Ru(1)—Ru(2)	2.663(2)
Ru(1)—C(1)	1.827(14)
Ru(1)—O(3)	2.116(8)
Ru(1)—N(1)	2.158(17)
Ru(2)—C(2)	1.86(2)
Ru(2)—O(4)	2.108(8)
Ru(2)—N(2)	2.25(2)
Angle	ω/deg
N(1)—Ru(1)—Ru(2)	161.6(5)
N(2)—Ru(2)—Ru(1)	156.6(7)

electron pair of the N atom of the morpholine molecule. A large number of related ruthenium complexes with different nitrogen-containing ligands (pyridine, acetonitrile, pyrazole, *etc.*) and carboxylate bridges (acetate, pivalate, propionate, *etc.*) were described in the literature.* In all these complexes, the N atoms are sp^2-hybridized (pyridine and its derivatives) or sp-hybridized (acetonitrile). Complex **4** is the only complex containing the sp^3-hybridized N atoms. The Ru—Ru (2.663(2) Å) and Ru—N (2.16(2) and 2.25(2) Å) distances in complex **4** are similar to those observed in structurally related complexes (Ru—Ru and Ru—N, 2.672—2.712 and 2.16—2.27 Å, respectively). In the crystal structure, complex **4** occupies a special position on the mirror plane passing through the Ru(1), Ru(2), N(1), and O(5) atoms. One of the morpholine ligands is disordered over two positions. The possible route to the synthesis of complexes analogous to complex **4** has been described earlier in the study of the reaction of carboxylic acids with $Ru_3(CO)_{12}$ in the presence of amines.[10,11] Morpholine generated by deamination of the ligand is not removed from the reaction mixture, thus resulting in the formation of complex **4**.

The IR and NMR spectroscopic data for complexes **2**—**4** are in complete agreement with the X-ray diffraction data. The IR spectrum of complex **2** shows eight bands with different intensities in the metal carbonyl stretching region, which is consistent with the C_2 symmetry of the molecule in the crystal; ν(CO)/cm^{-1} (hexane): 2068 s, 2056 s, 2048 m, 2032 m, 2024 m, 2010 m, 1998 w, 1958 w. The ^{1}H NMR spectrum of complex **2** has one set of signals for the protons of two equivalent oxaruthenacycles; δ: 2.69 (s, 3 H, Me); 7.27—7.70 (m, 5 H, Ph).

The IR spectrum of complex **3** shows two well-resolved bands with equal intensities in the metal carbonyl stretching region, which is indicative of *cis* positions of two CO ligands and is consistent with the centrosymmetric structure of the complex; ν(CO)/cm^{-1} (hexane): 2026 s, 1958 s. The equivalence of two dihydropyran ligands in complex **3** is confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum has one set of signals for the protons of the dihydropyran ligands; δ: 0.68, 0.76, and 1.89 (all s, 3 H each, Me); 2.79 (s, H, CH); 7.30—7.89 (m, 10 H, 2 Ph).

The IR spectrum of complex **4** shows two strong and one weak bands in the metal carbonyl stretching region (ν(CO)/cm^{-1} (hexane): 2030 v.s, 1980 w, 1950 s). Similar IR spectroscopic data for related complexes were published in the studies.[10—12] The presence of three bands in the IR spectrum of complex **4** can be a consequence of a lowering of the molecular symmetry due to disorder of the amine ligands at the Ru atoms. The ^{1}H NMR spectrum of complex **4** has one set of signals for the protons of two morpholine and two carboxylate ligands; δ: 2.91 (br.s, 1 H, NH); 3.40 (q, 4 H, CH_2O); 3.81 and 4.10 (both dt, 2 H each, CH_2N); 7.30—7.83 (m, 5 H, Ph). The ^{1}H NMR spectrum provides evidence for the nonequivalence of the protons of each CH_2 group bound to the N atoms. The presence of the amine proton observed in the ^{1}H NMR spectrum of complex **4** confirms that deamination of ligand **1** leads to the formation of morpholine.

It is known that tertiary amines in reactions with iron-group metal carbonyls undergo a series of transformations: the C—N bond cleavage, activation of α- and β-aliphatic and aromatic C—H bonds, and decarbonylation of one of the metal carbonyl CO groups.[4,13] The C—N bond cleavage was observed also in the reactions of $Ru_3(CO)_{12}$ with alkyneamines.[14,15] In the present study, we demonstrated that similar processes occur with tertiary β-aminovinyl ketone.

In the reaction with $Ru_3(CO)_{12}$, 2-methyl-3-morpholino-1-phenylprop-2-en-1-one undergoes the following transformations: 1) coordination of the metal atom at the oxadiene fragment is accompanied by deamination with

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* Cambridge Structural Database, May 2005.

the result that complexes **2** and **3** do not contain morpholine; 2) coordination of the metal atom at the amine fragment leads to activation of the C—H bonds resulting in the appearance of additional H atoms necessary for the formation of complex **3**; 3) coordination of amine at one of the metal carbonyl groups leads to decarbonylation of the complex. In our opinion, the CO group serves as a source of oxygen for the formation of the benzoate fragment in complex **4**.

Therefore, the replacement of the secondary amino group at the C_β atom of oxadiene[2] with the tertiary amino group results in the fragmentation of aminovinyl ketone in the reaction with $Ru_3(CO)_{12}$. The amine and vinyl ketone groups of the ligand are present in different reaction products.

Experimental

The ^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 MHz) in $CDCl_3$ with the use of residual signals of chloroform (δ 7.25) as the internal standard. The IR spectra were measured on a Specord IR-75 spectrophotometer. The reactions were carried out under argon. The chromatographic separation was performed in air. The preparative separation was performed with the use of silica gel L (100—160 μm) (Chemapol). The organic solvents were distilled under argon over the corresponding drying agents.

Reaction of $Ru_3(CO)_{12}$ with compound 1. Synthesis of bis(μ_4-η^2-2-benzoyl-2-methylethynylidene)hexadecacarbonylhexaruthenium $Ru_6(CO)_{16}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}PhC(O){-}C(Me){=}C)_2$ (2), di{μ-[4,5,6-η^3-5-methyl-3-dimethyl-2,6-diphenyl-3,4-dihydropyran-2-yl]oxo}bis(dicarbonylruthenium) $Ru_2O_2(CO)_4(\eta^3\text{-}OC(Ph)C(Me)C(H)C(Me)_2C(Ph))_2$ (3), and di(μ-benzoato)tetracarbonyl-bis(morpholine)diruthenium $[Ru(CO)_2(PhCO_2)(O(CH_2{-}CH_2)_2NH]_2$ (4). A mixture of $Ru_3(CO)_{12}$ (320 mg, 0.5 mmol) and compound **1** (231 mg, 1 mmol) in heptane (150 mL) was refluxed for 8 h and then concentrated. The residue was chromatographed on a silica gel column (CH_2Cl_2 as the eluent); two fractions were collected. The first fraction contained a mixture of complexes **2** and **3**; the second fraction, complex **4**. After recrystallization of the first fraction from hexane, complex **3** was isolated as pale-yellow crystals (161.6 mg, 18%); complex **2** (53.7 mg, 4%), as dark-red crystals. Complex 2. Found (%): C, 32.39; H, 1.24. $C_{36}H_{16}O_8Ru_6$. Calculated (%): C, 32.19; H, 1.19. Complex 3. Found (%): C, 58.91; H, 4.61. $C_{44}H_{40}O_8Ru_2$. Calculated (%): C, 58.79; H, 4.45. After recrystallization of the second fraction from a hexane—CH_2Cl_2 mixture, complex **4** was isolated (182 mg, 25%) as pale-yellow crystals. Complex 4. Found (%): C, 42.39; H, 3.79; N, 3.65. $C_{26}H_{28}N_2O_{10}Ru_2$. Calculated (%): C, 42.74; H, 3.83; N, 3.83. ^1H NMR of ligand **1** (δ): 1.91 (s, 3 H, Me); 3.26 (t, 4 H, CH_2N); 3.51 (t, 4 H, CH_2O); 6.68 (s, H, C=CH); 7.18—7.24 (m, 5 H, Ph).

X-ray diffraction study of complexes 2—4. Crystallographic data and the refinement statistics for compounds **2—4** are given in Table 4. The structures were solved by direct methods and refined by the full-matrix least-squares method against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms, except for the atoms of the disordered morpholine fragment in the structure of **4**. For compounds **2** and **4**, multiscan

Table 4. Crystallographic data and the refinement statistics for compounds **2—4**

Parameter	2	3	4
Molecular formula	$C_{36}H_{16}O_{18}Ru_6$	$C_{44}H_{40}O_8Ru_2$	$C_{26}H_{28}N_2O_{10}Ru_2 \cdot CH_2Cl_2$
Molecular weight	1342.91	898.90	815.57
Space group	$C2/c$	$P\bar{1}$	$Pbcm$
Temperature/K	120	293	120
a/Å	15.897(3)	8.760(2)	8.582(1)
b/Å	9.778(2)	10.672(2)	19.406(3)
c/Å	24.653(4)	11.684(2)	18.544(3)
α/deg	—	99.29(2)	—
β/deg	92.819(4)	110.36(2)	—
γ/deg	—	102.02(2)	—
V/Å^3	3828(1)	968.5(4)	3088.4(8)
Z	4	1	4
d_{calc}/g cm^{-3}	2.330	1.541	1.754
μ/cm^{-1}	23.88	8.33	12.08
Diffractometer (λ(Mo-Kα) = 0.71073 Å)	«SMART 1000»	«Siemens P3/PC»	«SMART 1000»
Scanning mode	ω	θ/2θ	ω
Absorption correction, T_{min}/T_{max}	0.796/0.954	—	0.698/0.927
$2\theta_{max}$/deg	56	58	46
Number of independent reflections (R_{int})	4632 (0.0816)	5099 (0.0213)	2173 (0.1187)
Number of observed reflections with $I > \sigma(I)$	2737	4104	1512
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0445	0.0280	0.0846
wR_2 (based on F^2 for all reflections)	0.0897	0.0580	0.1912
Number of parameters in refinement	272	247	207
GOOF	0.870	0.902	1.101

absorption corrections were applied based on equivalent reflections with the use of the SADABS program.[16] For complex **3**, absorption was ignored. The structure of **4** contains a dichloromethane solvate molecule. The H atoms were placed in geometrically calculated positions and refined using a riding model. All calculations were carried out on a PC with the use of the program packages.[17,18]

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