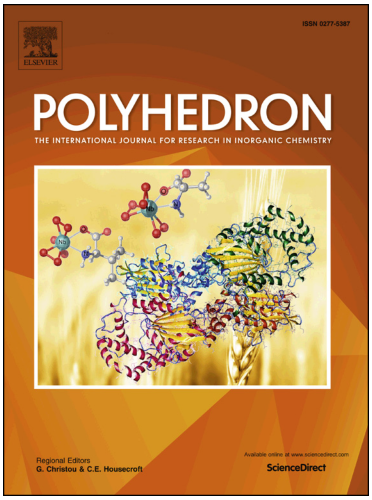

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Coordination preferences of 4-dimethylaminobut-3-en-2-one in thermally and photochemically activated reactions with $Ru_3(CO)_{12}$

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Abstract

The thermally and photochemically activated reactions of $Ru_3(CO)_{12}$ with 4-dimethylaminobut-3-en-2-one (**L**) were studied and several mononuclear and polynuclear products were isolated and fully characterized by a combination of spectroscopic IR and multinuclear NMR data as well by single-crystal X-ray diffraction studies. Chelate five-membered oxaruthenacycles found to be present in all the isolated organometallic products are formed via C_β-H activation reactions. These metallacycles can be bound to other ruthenium atoms in the different modes, namely, through π-coordination to the olefinic bond, through σ-coordination to the C_α atom of the starting ligand, and by coordination through the lone pair of the oxygen atom. The coordination of a metal atom to the C_α atom caused by an isomerization of the ligand to form partially imine C=N bond and migration of the olefinic bond has not been observed previously in reactions of $Ru_3(CO)_{12}$ with oxadienes. The formation of the six-membered chelate azaoxaruthenacycles in the reaction with **L** is accompanied by a migration and reduction of the olefinic bond. These chelates are significantly less stable than the five-membered chelates and involved coordination to other metal atoms to form polynuclear products. The structural and spectroscopic features and possible transformations pathways of the resulting complexes are discussed.

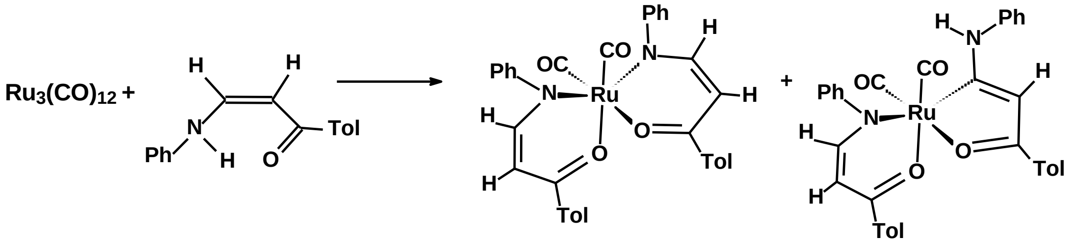
Keywords: Dodecacarbonyltriruthenium; Amino vinyl ketones; Five-membered metallacycles; C-H Activation; X-ray diffraction study.

1. Introduction

The chemistry of enamimones (or β-aminovinylketones) is attracting chemists' interest due to extensive applications of these compounds which have demonstrated a potential as multipurpose synthetic intermediates in organic synthesis [1, 2], in pharmaceutical developments [3], and in heterocyclic synthesis [4]. In coordination chemistry, enaminones, either as neutral or as anionic species, present valuable ligands for metal-ion chelation. These metal complexes are frequently used as reagents, intermediates, or catalysts in chemical synthesis of drugs, polymers and dyes [1, 2], for the deposition of metal coatings [5, 6], and they possess liquid-crystalline properties [7, 8]. Chelate enaminone complexes often demonstrate a good therapeutic activity and exhibit limited neurotoxicity in contrast to uncoordinated enaminones [3]. Most common organometallic compounds of enaminones are the six-membered N,O-metallochelates known for both transition and non-transition metals [9, 10, 11].

Earlier we studied the reaction between $Ru_3(CO)_{12}$ and 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one [12]. As expected the main reaction product~~s~~ were the six-membered N,O-metallochelate~~s~~. However, the unexpected complex containing the five-membered C,O-chelate ring was also found (Chart 1). The formation of the latter is occur via an activation of C_β-H rather than N-H bonds.

Chart 1



Amino vinyl ketones with secondary amino groups (for example, 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one) adopt *cis*-conformations [13] stabilized by an intramolecular N-H···O hydrogen bond. In order for coordination of the β-carbon atom to occur and a five-membered cycle to form, the breaking of the H-bond and spatial transformation of a molecule from *cis*- to *trans*-conformation is necessary.

One possible, more selective, way of obtaining these unusual five-membered chelates and to reduce the possibility of the formation of the six-membered chelates is to replace a secondary β-amino group by a tertiary one. Therefore, we studied the reaction of $Ru_3(CO)_{12}$ with 1-phenyl-2-metyl-3-morpholino-prop-2-en-1-one [14]. However, the reaction was accompanied by the deamination of the ligand and the expected chelate complexes were not found.

In order to ascertain whether deamination of tertiary amino vinyl ketones is a common process in their thermal reactions with $Ru_3(CO)_{12}$, we studied here the reaction with 4-dimethylaminobut-3-en-2-one (**L**). In this case, a completely different reaction pathway occurs including an activation of both $C_β$-H and $C_α$-H olefinic bonds and a formation of the target five-membered chelate complexes.

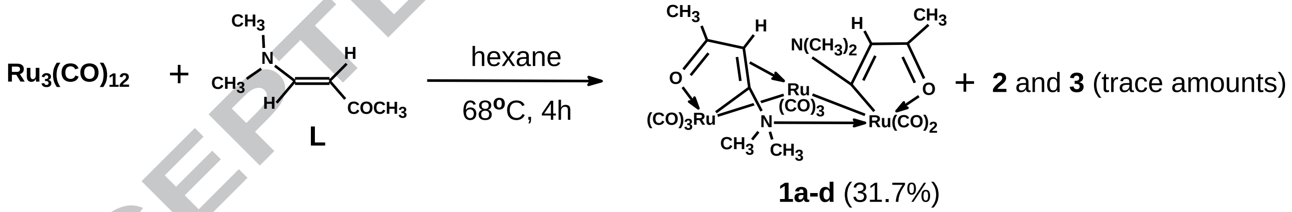
2. Results and discussion

2.1. Reaction course and transformation of the products

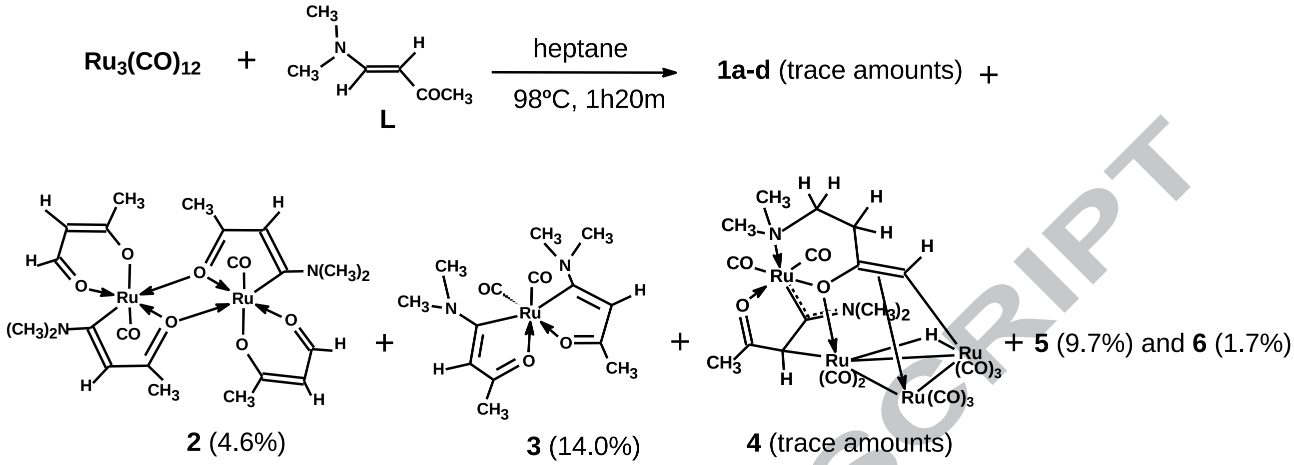
The thermally activated reaction of $Ru_3(CO)_{12}$ with compound **L** was carried out first in boiling hexane (68ºC) to afford the starting reactant and intermediate product and then in boiling heptane (98ºC) to isolate the end products. Both reactions lead to the same products. The difference is in the boiling point of the solvent and therefore in the temperature of the reaction. At a lower temperature (boiling hexane), the reaction proceeds at a slower rate, which makes it possible to optimize conditions for the formation of the intermediate products. At a higher reaction temperature (boiling heptane), the time of obtaining the end products significantly reduces. The course of the reaction at all stages of products separation and purification was monitored by IR spectroscopy paying a special attention to the spectral range corresponding to metalcarbonyl stretching vibrations. After slow cooling, the reaction mixture separated into a solution and a precipitate. The products of the reaction were characterized by IR, ^{1}H and ^{13}C NMR spectroscopy (Table 1) and their molecular structures were unambiguously determined by single-crystal X-ray diffraction studies.

After reflux in hexane for 4 h (the reaction time was defined by the maximum content of complexes **1** in the reaction solution) and silica gel column chromatography, isomeric complexes **1** (31.7% yield) and complexes **2** and **3** (trace amounts) were isolated (Scheme 1). A slight amount of unidentified precipitate was also isolated. The longer-term heating of the reaction mixture in hexane or heating in heptane for 1 h 20 min (the reaction time was defined by the maximum content of complexes **2** and **3** in the reaction solution) resulted in the disappearance of complexes **1** and slow accumulation of complexes **2** (4.6% yield), **3** (14.0% yield), and **4** (traces) in solution accompanied by abundant precipitation. The precipitate contained complex **5** (9.7% yield) and **6** (1.7% yield) as a red-brown oily substance (Scheme 2).

Scheme 1. Thermal reaction of $Ru_3(CO)_{12}$ with **L** in boiling hexane



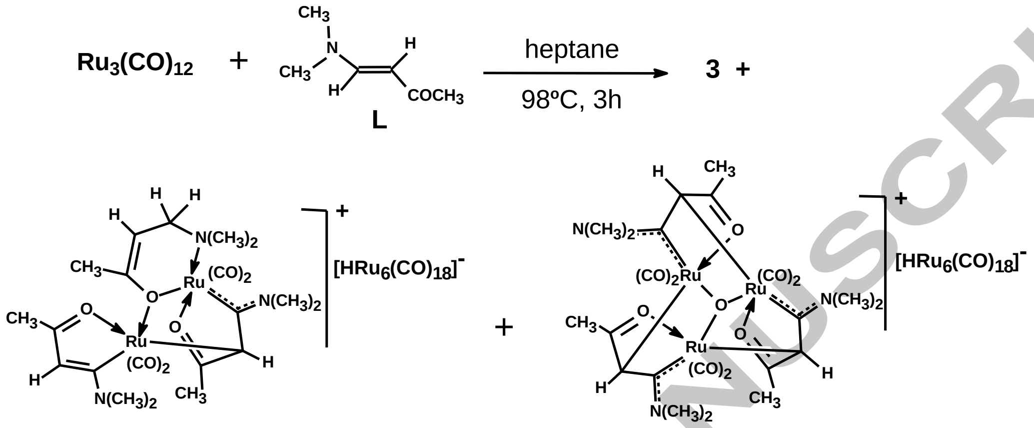
Scheme 2. Thermal reaction of $Ru_3(CO)_{12}$ with **L** in boiling heptane (1h20m)



Isomeric complexes **1** are the main products of the first stages of the thermal reaction of $Ru_3(CO)_{12}$ with **L**, and as $Ru_3(CO)_{12}$ are precursors of the complexes formed in the later stages of the reaction. In separate experiments, the reflux of complex **1** with excess **L** resulted in the formation of complexes **2**, **3**, and **4** according to the IR and ^{1}H NMR spectra (see Experimental part). Complex **3** is the end product of the reaction and the only complex remaining in the reaction solution. Complexes **2** and **4** are the minor products of the reaction and upon the long-term heating decompose.

The heating of the reaction mixture in heptane for 3 h resulted in a significant increase in the amount of the precipitate, and the reaction solution contains only the complex **3** (Scheme 3). Upon long-term heating in heptane from 3 to 6 h, no changes occur in the reaction solution according to IR spectroscopy. Also, the total amount of the precipitate remains unchanged; however, the ratio of the complexes changes in favor of complex **6** (see Experimental part). This indirectly suggests the transformation of **5** into **6**. Unfortunately, we could not perform a separate experiment on the transformation **5** into **6**, since the complexes are insoluble in hydrocarbons. When performing the reactions in polar chlorine-containing solvents, the complexes being a source of the oxaruthenaycles required for the **5**-to-**6** transformation either decompose to unidentified precipitates or add chlorine atoms to form complexes with strong Ru-Cl bonds [15]. The relatively low yield of complexes **5** and **6** is due to the decomposition of the salt compounds during column chromatography on silica gel (see Experimental part).

Scheme 3. Thermal reaction of $Ru_3(CO)_{12}$ with **L** in boiling heptane (3h)



5 (17.1%)   **6** (6.6%)

Table 1. IR and NMR spectra for **1-7**

Comp.	IR (hexane, ν(CO)/cm^{-1}	^{1}H NMR (C_6D_6), δ	^{13}C NMR (C_6D_6), δ
L	1678m, 1628w, 1600s	7.43 (d, 1H, C*H*=C*H*, *J*=12.7 Hz); 5.04 (d, 1H, C*H*=CH, *J*=12.8 Hz); 2.46, (s, 6H, C*H*$_3$N); 2.09 (s, 3H, CH$_3$)	192.9 (*C*=O); 152.3 (C$_\beta$); 99.9 (C$_\alpha$); 43.7, 36.1 (N-(*C*H$_3$)$_2$); 28.4 (C(O)-*C*H$_3$)
L $^{*)}$		6.94 (d, 1H, C*H*=C*H*, *J*=12.8 Hz); 4.51 (d, 1H, C*H*=CH, *J*=12.7 Hz); 2.57, 2.33 (s, 3H, C*H*$_3$N); 1.55 (s, 3H, CH$_3$)	
1a	2072s, 2036v.s, 2008sh, 2000s, 1984s, 1968m, 1964m, 1946m	5.28 (s, 1H, C*H*=C); 3.40 (s, 1H, C*H*=C); 3.01, 2.89, 2.45, 2.13 (s, 3H, C*H*$_3$N); 1.81, 1.66 (c, 3H, CH$_3$)	
1b	2072s, 2016v.s, 2010s, 2004sh, 1984s, 1968m, 1960m, 1936m	5.42 (s, 1H, C*H*=C); 3.39 (s, 1H, C*H*=C); 3.34, 3.24, 2.72, 2.55 (s, 3H, C*H*$_3$N); 2.04, 1.58 (s, 3H, CH$_3$)	
1c	2072s, 2036v.s, 2008sh, 2000s, 1984s, 1968m, 1964m, 1936m	5.24 (s, 1H, C*H*=C); 3.01 (s, 1H, C*H*=C); 3.04, 2.50, 2.48, 2.46 (s, 3H, C*H*$_3$N); 2.11, 1.84 (s, 3H, CH$_3$)	
1d	2072s, 2016v.s, 2010s, 2004sh, 1984s, 1968m,	5.48 (s, 1H, C*H*=C); 3.92 (s, 1H, C*H*=C); 3.19, 3.05, 2.91, 2.55 (s, 3H, C*H*$_3$N); 2.01, 1.55 (s, 3H, CH$_3$)	

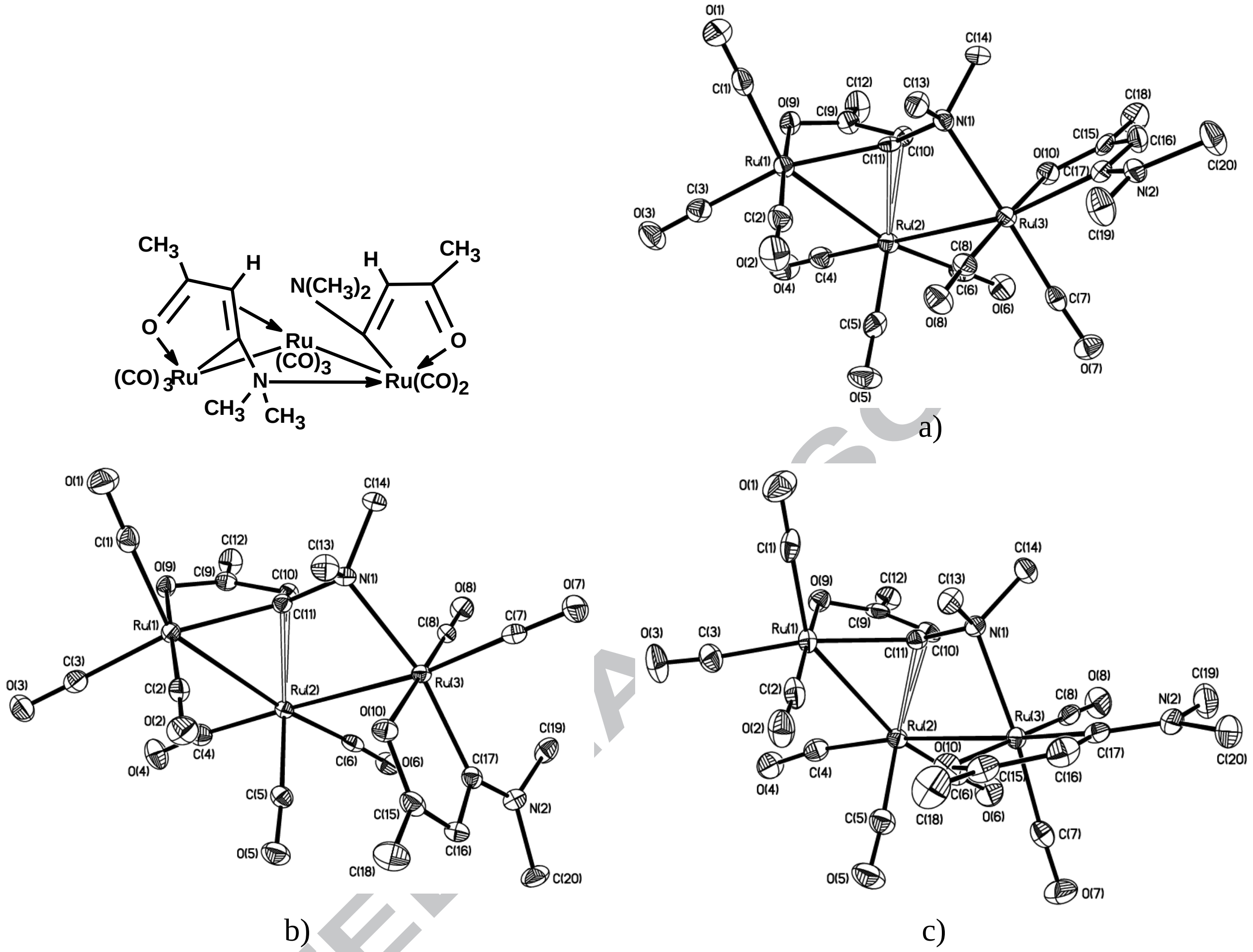
	1960m, 1926m		
2a	2030s, 1960s	7.77 (d, 1H, C*H*=C*H*, *J*=4.8 Hz); 5.13 (c, 1H, C*H*=C); 5.11 (d, 1H, C*H*=C*H*, *J*=4.8 Hz); 2.79, 2.24, (s, 3H, CH_3N); 1.96, 1.84 (s, 3H, CH_3)	216.0 (C_β); 200.9 (M-*C*=O); 198.4 (*C*=O); 196.4 (*C*=O); 190.8 (M-*C*=O); 175.9 (C_β); 105.5 (C_α); 100.7 (C_α); 49.1, 40.1 ($N\text{-}(CH_3)_2$); 27.8, 23.2 ($C(O)\text{-}CH_3$)
2b	2030s, 1960s	8.13 (d, 1H, C*H*=C*H*, J=4.4 Hz); 5.14 (s, 1H, C*H*=C); 5.10 (d, 1H, C*H*=C*H*, *J*=4.3 Hz); 2.78, 2.20, (s, 3H, CH_3N); 1.97, 1.73 (s, 3H, CH_3)	
3	2016s, 1946s	5.53 (s, 1H, C*H*=C); 3.25, 2.52 (s, 3H, CH_3N); 2.03 (s, 3H, CH_3)	
3$^{*)}$		5.48 (s, 1H, C*H*=C); 3.54, 3.15 (s, 3H, CH_3N); 2.04 (s, 3H, CH_3)	226.9 (C_β); 200.5 (M-*C*=O); 199.6 (*C*=O); 105.3 (C_α); 51.3, 40.5 ($N\text{-}(CH_3)_2$); 23.9 ($C(O)\text{-}CH_3$)
4$^{*)}$		5.56 (s, 1H, C*H*=C); 4.55 (s, 1H, C*H*=C); 4.38 (m, 1H, $CH_2\text{-}CH_2$); 3.78 (m, 1H, $CH_2\text{-}CH_2$); 3.65, 3.33, 3.17, 3.15, (s, 3H, CH_3N); 2.06 (s, 3H, CH_3); -14.02 (s, 1H, Ru-*H*)	
5$^{*)}$	2010vs, 1978w, 1962w, 1948w (CH_2Cl_2)	16.48 (s, 1H, Ru-*H*); 5.21 (s, 1H, C*H*=C); 4.69 (s, 1H, C*H*-C); 4.80 (t, 1H, C-*H*); 3.58, 3.52, 3.33, 3.17,	225.4 (C_β); 218.8, 215.8, 207.6; 201.3 ($[HRu_6(CO)_{18}]^-$); 200.7,

		2.96, 2.67 (s, 3H, CH_3N); 3.17 (m, 1H, C-H*H*); 2.11 (m, 1H, C-H*H*); 2.42, 1.93, 1.60 (s, 3H, CH_3)	199.5, 197.8, 194.6, 163.5, 105.3, 103.8, 72.0 (C_α-Ru); 57.3, 55.4, 52.0, 51.9, 50.5, 42.4, 42.3, 29.7, 27.3, 23.2
6$^{*)}$	2010vs, 1962w, 1948w (CH_2Cl_2)	16.44 (s, 1H, Ru-*H*); 4.41 (s, 1H, C*H*-C); 3.51, 3.15 (s, 3H, CH_3N); 2.25 (s, 3H, CH_3)	226.7 (C_β); 218.0, 201.6; 201.4 ($[HRu_6(CO)_{18}]^-$); 193.0, 71.4 (C_α-Ru); 51.5, 41.5, 27.9
7	2046 s, 1998 s, 1962 s (CH_2Cl_2)	5.52 (s, 1H, C*H*=C); 3.65, 3.24 (s, 3H, CH_3N); 1.08 (s, 3H, CH_3)	214.0 (C_β); 212.5 (M-*C*=O); 202.5 (*C*=O); 111.0 (Cα); 51.6, 41.5 (N-($CH_3)_2$); 21.3 (C(O)-CH_3)

$^{*)}$ NMR spectra were detected in $CDCl_3$

2.2. Spectral and structural characterization of isomeric complexes ***1***

Four isomeric complexes **1a-d** were obtained during the first stages of the thermal reaction of $Ru_3(CO)_{12}$ with **L** (Scheme 1). The structures of three complexes **1a-c** were established by X-ray diffraction study (Fig. 1, Table S1). Two molecules of the ligand in complexes **1** chelate two ruthenium atoms forming five-membered oxaruthenacycles. Each organic ligand donates three electrons with regard to the chelated ruthenium atoms and one of the ligands which links all three ruthenium atoms donates an additional four electrons through the π-coordination of the olefinic bond to the central Ru(2) atom and dative coordination of the nitrogen electron lone pair. Taking into account eight carbonyl ligands, the total number of cluster valence electrons is equal to 50, which implies two metal-metal bonds in the trimetallic core of the complexes **1** (the average values of Ru(1)-Ru(2) and Ru(2)-Ru(3) bond lengths from the three structures **1a-c** are 2.79 Å and 2.90 Å respectively, the Ru(1)…Ru(3) nonbonding distance is equal to 4.41 Å).



a)

b)

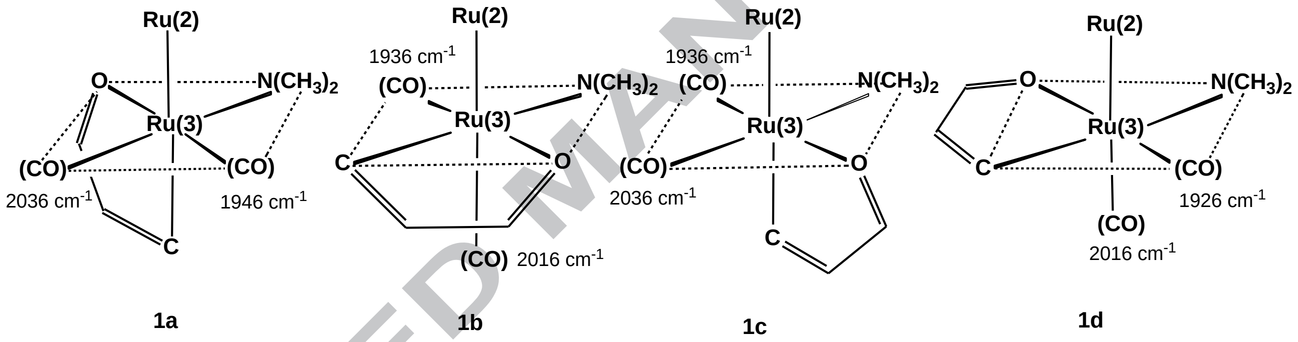
c)

Figure 1. Schematic presentation of complex **1** and molecular structures of the isomeric complexes **1a** (a), **1b** (b), and **1c** (c) with thermal ellipsoids drawn at the 50% probability level (the hydrogen atoms are omitted).

Complexes **1a-c** differ from each other by the spatial arrangement of the chelate ring and metalcarbonyl groups around the Ru(3) atom. These differences in complexes **1** can be seen clearly from the schematic representation of an octahedral ligand environment around the Ru(3) atom (Scheme 4) [16]. The number of possible stereoisomers is restricted by the positions of the N(1) and Ru(2) atoms which is specified by the structure of the unchangeable fragment of the complexes. The *cis* arrangement of two metalcarbonyl ligands is fixed taking into account the destabilizing effect of the *trans* arrangement of the “hardest” ligands in accordance with the theory of mutual *trans* influence of ligands [17, 18, 19, 20, 21]. One of the metalcarbonyl groups (C(8)O(8)) is always in the *trans* position with regard to the oxaruthenacycle O(10) atom (the “softest” ligand).

Thus, the difference between the complexes is defined by the arrangement of the second metalcarbonyl group (C(7)O(7)) on the Ru(3) atom. This group can be arranged in two ways: in the *trans* position to the N(1) atom (complex **1a**) or the Ru(2) atom (complex **1b**). The number of stereoisomers doubles taking into account the mirror replacement of the oxaruthenacycle O(10) atom and *trans*-positioned C(8)O(8) metalcarbonyl group at fixed positions of remaining ligands. As a result, complex **1a** has a stereoisomeric pair complex, **1c** and complex **1b** has a stereoisomeric pair complex, **1d** (whose proposed structure becomes clear from Scheme 4).

Scheme 4. Octahedral ligand environment around the Ru(3) atom in isomeric complexes **1**



The IR spectra of complexes **1** contain eight bands each in the region of metalcarbonyl stretching vibrations. Most of the bands coincide; however, there are characteristic bands corresponding to the metalcarbonyl groups at the Ru(3) atom, which allows spectral distinguishing of isomers or their mixtures (Scheme 4).

In the ^{1}H NMR spectra of the isomeric complexes **1a-d** (Table 1) the same sets of signals were obtained with insignificant differences due to the different ligand environment of the Ru(3) atom. The proton signals for the uncoordinated oxaruthenacycles in complexes **1a** and **1c** (δ 5.28 and 5.24, respectively) are upfield shifted by 0.2 ppm compared to the analogous signals in complexes **1b** and **1d** (δ 5.42 and 5.48, respectively). The proton signals for the π-coordinated oxaruthenacycles differ more strongly (from δ 3.01 to 3.92). Their positions are influenced by the ligand environment of the Ru(3) atom and this effect propagates through the Ru(2) and N(1) atoms.

The yield of the pair complexes **1b** and **1d** is significantly lower than that of the **1a** and **1c**, and isomer **1d** was obtained in trace amounts. The ratio of isomers formed in the reaction is described as **1a** : **1c** : **1b** + **1d** = 2 : 1 : 1. It follows from the ratio of the isomeric products that the *trans* position of the metalcarbonyl group with regard to the nitrogen atom (as in isomers **1a** and **1c**) is more preferred compared to the *trans* position with regard to the ruthenium atom (as in isomers **1b** and **1d**).

*2.3. Spectral and structural characterization of complex **3***

According to the X-ray diffraction data (Fig. 2), the ruthenium atom in the mononuclear complex **3** is chelated by two molecules of **L** and bound to two carbonyl ligands in the *cis* position. In the crystal, complex **3** occupies a special position on the twofold axis passing through the ruthenium atom. An octahedral ligand environment of the Ru atom is characterized by the transoid arrangement of the metallacycle C atoms, whereas the carbonyl ligands are in the *trans* positions with respect to the O atoms of the metallacycles. The analogous mononuclear complexes with two five-membered oxaruthenacycles were obtained in the reactions with oxadienes [22]. In the reaction with 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one, mononuclear complexes with chelate six-membered and five-membered metallacycles were also isolated (Chart 1) [12]. In all these reactions, the mononuclear complexes with two chelate ligands are the main end products.

The IR spectrum of complex **3** (Table 1) contains two equal-intensity bands in the region of metalcarbonyl stretching vibrations, which is typical for two CO ligands that are *cis* position to each other. The ^{1}H NMR spectrum of complex **3** displays one set of signals for the coordinated ligand (Table 1). The ^{13}C NMR spectrum of **3** displays three downfield signals. The signal at δ 226.9 ppm can be attributed to the β-carbon atom of the five-membered rings. This can be explained by a partial contribution of the carbene character of the Ru-C_β bond, which implies a partial furan structure of the five-membered oxaruthenacycle [22]. The low-intensity signal at δ 200.5 ppm can be attributed to the metalcarbonyl carbon. The slightly upfield shifted signal at δ 199.6 ppm corresponds to the keto carbon atom.

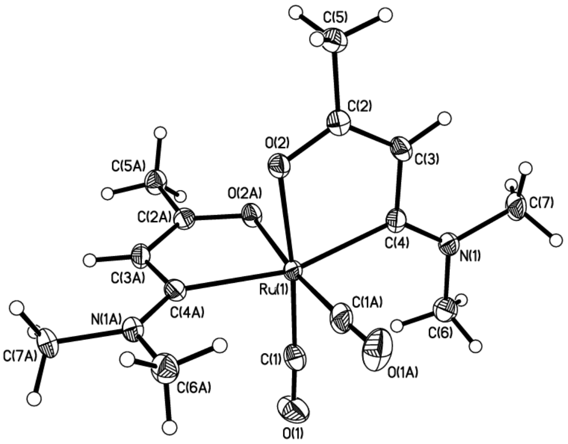


Figure 2. Molecular structure of the mononuclear complex **3** (thermal ellipsoids at the 50% probability level).

*2.4. Characterization of complexes **5** and **6** isolated from a precipitate*

The structures of two complexes isolated from a precipitate were unexpected. Complexes **5** and **6** are ionic compounds. Note that we observe for the first time the formation of salts in the reactions of $Ru_3(CO)_{12}$ with substituted oxadienes. According to the X-ray diffraction data (Fig. 3, Table S2), two ruthenium atoms in the cation of complex **5** coordinate to three ligand molecules and each ruthenium atom coordinates to two metalcarbonyl groups in the *cis* position. The distance Ru(1)…Ru(2) of 3.647(1) Å suggests the absence of the metal-metal interaction. The Ru(1) atom is chelated by two ligands to form the five-membered oxaruthenacycle and six-membered azaoxaruthenacycle, and the Ru(2) atom is chelated by the third ligand to form the five-membered oxaruthenacycle. The octahedral environment of the Ru(2) atom is supplemented by the coordination to the O(6) atom being involved in the chelation of the Ru(1) and by the C(6) atom forming a part of the five-membered metallacycle. The coordination to the C(6) atom (Ru(2)-C(6) bond length equals 2.370(9) Å) adopts an η^1-coordination mode; the Ru(2)-C(5) distance of

2.894(9) Å and the Ru(2)-C(7) distance of 3.045(9) Å suggest the absence of the interaction with the neighbouring atoms of the metallacycle. Note that Ru(2) adopts an 18 electron configuration with the bonding as described.

The η^1-coordinated five-membered oxaruthenacycle, in contrast to the uncoordinated one, has a nonplanar envelope conformation with the C(7) atom coming out of the Ru(1)O(5)C(5)C(6) plane by 0.49 Å in the direction opposite to the Ru(2) atom (the angle of bending along the Ru(1)…C(6) line is 29.3º). The Ru(2)-C(6) bond (2.370(9) Å) is significantly elongated compared to the *trans*-positioned Ru(2)-C(19) bond (2.087(9) Å). Nevertheless, additional coordination results in the sp^3-rehybridization of the C(6) atom, which is confirmed by an upfield shift of the proton singlet in ^1H NMR spectrum (see below). The interaction is weak and, therefore, the change in the neighbouring C-C bond lengths in the metallacycle (C(5)-C(6) is 1.423(13) Å and C(6)-C(7) is 1.442(13) Å) is not so significant as can be expected upon a change in the atom hybridization. However, they are noticeably elongated compared to the analogous bonds in uncoordinated five-membered oxaruthenacycle (C(17)-C(18) is 1.385(13) Å and C(18)-C(19) is 1.417(13) Å). The single character of the C(6)-C(7) bond, and a partially multiple N(1)-C(7) bond (1.339(12) Å), and a partial contribution of the carbene type to the Ru(1)-C(7) bond (2.042(9) Å) suggest delocalization of the positive charge on the Ru(1), C(7), and N(1) atoms. The C(5)-O(5) bond length of 1.255(11) Å suggests that the ketonic nature of the ligand is retained.

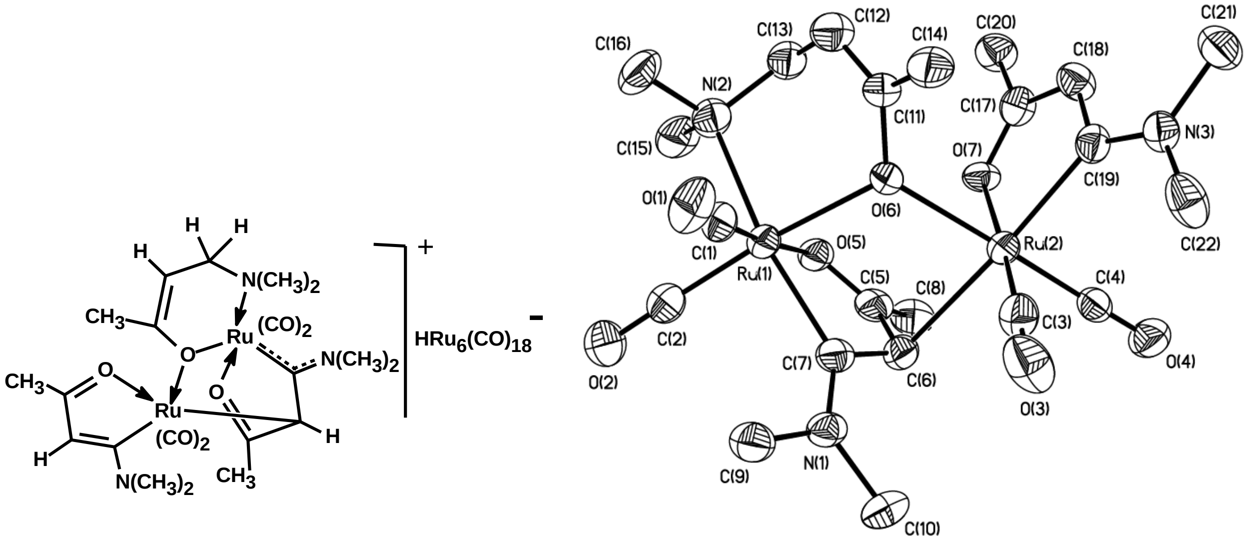


Figure 3. Schematic presentation of **5** and molecular structure of the binuclear cationic complex (thermal ellipsoids at the 50% probability level, hydrogen atoms are omitted). The cluster anion $[HRu_6(CO)_{18}]^-$ is not shown.

The Ru(1) atom is chelated by the second molecule of the ligand through the nitrogen and oxygen atoms to form a six-membered azaoxaruthenacycle. The ligand undergoes significant restructuring. The ketonic bond of the starting amino vinyl ketone becomes single-bond (O(6)-C(11) is 1.374(11) Å), the olefinic bond shifts to C(11)-C(12) (1.343(14) Å), the C(13) carbon atom forming a methylene group. The six-membered ring is nonplanar and has boat conformation (the angle of bending along the O(6)…C(13) is 51.1º). Thus, all three organic ligands in the cationic complex **5** have a different structure.

The formal description of the complex suggests that the organic ligand in the six-membered metallacycle is a 5e donor (coordination to the electron lone pair of the N(2) nitrogen atom and the O(6) oxygen atom donates three electrons to both ruthenium atoms), the organic ligand in the η^1-coordinated five-membered oxaruthenacycle is a 4e donor (coordination to the electron lone pair of the O(5) oxygen atom and two σ-bonds with the C_α and C_β atoms), and the organic ligand in uncoordinated five-membered oxaruthenacycle is a 3e donor. Taking into account four metalcarbonyl ligands and the overall positive charge, such consideration results in the completed 18e shell for both ruthenium atoms.

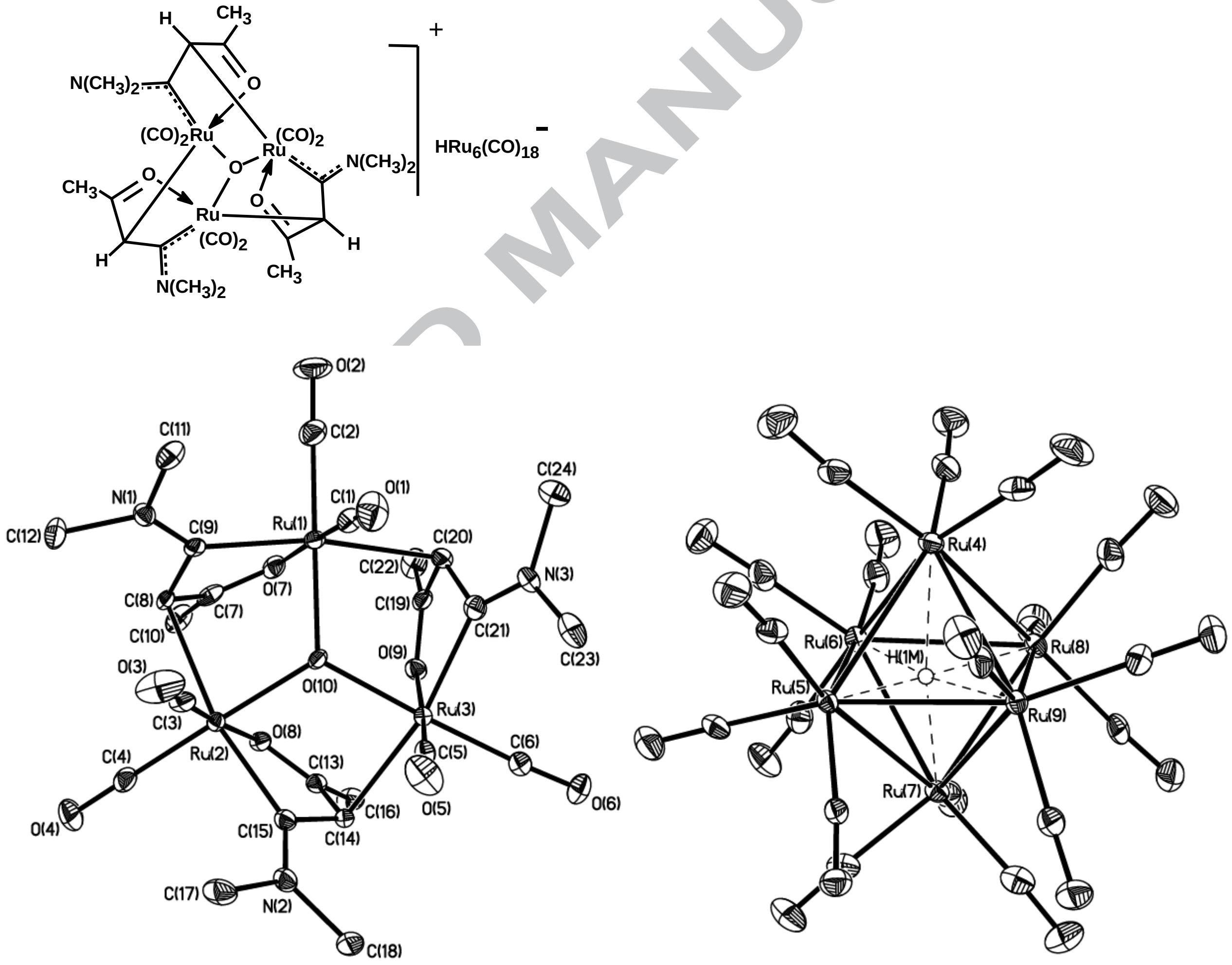
According to the X-ray diffraction data, the cation of complex **6** contains three ruthenium atoms (Fig. 4a, Table S3). Each ruthenium atom is chelated by the ligand to form the five-membered oxaruthenacycle and bound to two CO groups in the *cis* position. In addition, the ruthenium atoms are combined through the μ_3-oxo oxygen atom located in the plane of three ruthenium atoms (displacement from the plane is 0.15 Å). The complex has a non-crystallographic three-fold axis. Each ruthenium atom additionally bound to the C_α atom of one of the neighbouring oxaruthenacycles (three independent Ru-C_α bond lengths are 2.348(5), 2.380(5), and 2.347(4) Å). The cation of **6** has the same unusual η^1-coordination of the five-membered oxaruthenacycle as in the cation of **5**. The structure of these fragments in both complexes coincides. Taking into account that each fragment has a positive charge and the oxo ligand has a charge 2-, for the cation of **6** one obtains the total single positive charge.

The anion in complexes **5** and **6** is the well-known octahedral hydride cluster $[HRu_6(CO)_{18}]^-$ containing the interstitial hydride [23] (Fig. 4b). In the crystal structures of **5** and **6**, there are no specific anion-cation interactions and all intermolecular distances correspond to usual van-der-Waals contacts.

There are several examples of the formation of such anions in the reactions involving $Ru_3(CO)_{12}$ [24, 25]. In particular, the formation of salts with the $[HRu_6(CO)_{18}]^-$ anions was observed in the reactions between $Ru_3(CO)_{12}$ and functionalized indenes in refluxing heptane, whereas no anion formation was observed in the reactions performed in refluxing xylene [25].

Earlier, we have shown that the reaction of $Ru_3(CO)_{12}$ with 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one yields the hydride tetrahedral clusters $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ in considerable amounts [12]. Upon formation of the oxaruthenacycle, the ligand loses a hydrogen atom, while the $Ru_3(CO)_{12}$ acts as the hydrogen acceptor and is reduced to form the hydride clusters [26]. Similarly, in the reaction with **L**, the $Ru_3(CO)_{12}$ acts as a hydrogen acceptor giving rise to the hydride cluster $[HRu_6(CO)_{18}]^-$.

A different case was observed in the reactions between $Ru_3(CO)_{12}$ and oxadienes. In these reactions, an excess amount of the ligand acts as the hydrogen acceptor and undergoes reduction to the corresponding saturated ketone [22]. The formation of Ru_6 and Ru_4 hydrides in trace amounts, presumably, from trace water which inevitable enters the reaction medium was observed [27]. Such a difference between the behaviors of oxadienes and amino vinyl ketones is explained by the fact that the olefinic group in the latter is deactivated by the donor effect of amino group, which gives no way for the molecule to act as a hydrogen acceptor [28].



a) b)

Figure 4. Schematic presentation of **6** and molecular structures of the trinuclear cationic complex (a) and the cluster anion $[HRu_6(CO)_{18}]^-$ (b) forming a part of **6** (thermal ellipsoids at the 50% probability level, hydrogen atoms excluding hydride ligand are omitted).

The IR spectra of complexes **5** and **6** are characterized by the presence of one high-intensity band corresponding to the metalcarbonyl groups of the anion. In addition, these spectra display low-intensity bands corresponding to the metalcarbonyl groups in the cations of complexes **5** (three bands) and **6** (two bands) (Table 1).

The ^{1}H NMR spectra of complexes **5** and **6** display a single low-intensity peak at δ 16.46 ppm which corresponds to the interstitial hydride in the cluster anion [24, 29]. The η^1-coordination to the C_α atom of the five-membered oxaruthenacycle results in an upfield shift of the proton singlet up to δ 4.5 ppm (the average value for complexes **5** and **6**) compared to the proton singlet at δ 5.2 ppm in the uncoordinated cycle of complex **5** (Table 1).

The ^{13}C NMR spectra of complexes **5** and **6** (Table 1) display very high-intensity peaks at δ 201.3 ppm corresponding to the metalcarbonyl groups of the $[HRu_6(CO)_{18}]^-$ anion. The signals at δ 225.4 ppm (**5**) and 226.7 ppm (**6**) can be attributed to carbon atoms in the β-position of the η^1-coordinated five-membered oxaruthenacycles. The signals at δ 72.0 ppm (**5**) and 71.4 ppm (**6**) can be attributed to carbon atoms in the α-position of the η^1-coordinated five-membered oxaruthenacycles (for comparison, the signal of the C_α atom of the uncoordinated five-membered oxaruthenacycle in complex **3** is located at δ 105.3 ppm).

Complexes **5** and **6** were isolated in the individual state by chromatography of the reaction precipitate (see Experimental). There have also been attempts to crystallize the precipitate without chromatographic separation. According to the X-ray diffraction data, one of the crystalline phases contained the cation of complex **6** and the disordered hydride cluster $[HRu_4(CO)_{13}]^-$ as the anion (complex **6_Ru4** in Supplementary data, Fig. S1). The ^{1}H NMR spectrum for the reaction precipitate displayed two singlet signals at δ 16.5 and -15.85 ppm. According to Ref. [30], the second signal corresponds to the hydride anion $[HRu_4(CO)_{13}]^-$. The integral intensities of singlets are approximately equal, but the interstitial hydrogen atom of the $[HRu_6(CO)_{18}]^-$ anion appears as a weaker signal in the ^{1}H NMR spectrum; therefore, the ratio of cluster anions contained in the reaction precipitate cannot be determined.

Thus, the reaction precipitate contains complexes with two different anions. However, only complexes with $[HRu_6(CO)_{18}]^-$ are present after chromatography (the individuality of sample volumes was confirmed by the elemental analysis). One can assume that the $[HRu_4(CO)_{13}]^-$-containing complexes decompose during chromatographic separation. Possibly, this explains a low total yield of the complexes obtained from the precipitate.

*2.5. Characterization of minor reaction products (complexes **2** and **4**)*

According to the X-ray diffraction data, complex **2** has centrosymmetrical structure and contains two ruthenium atoms each of which is chelated by two molecules of the ligand and coordinates to one metalcarbonyl group (Fig. 5, Table S4). One of the ligands forms the five-membered oxaruthenacycle. The second ligand forms the six-membered ruthenacycle. With each other, the ruthenium atoms are linked through the bridged oxygen atoms of the five-membered rings to form the Ru_2O_2 fragment.

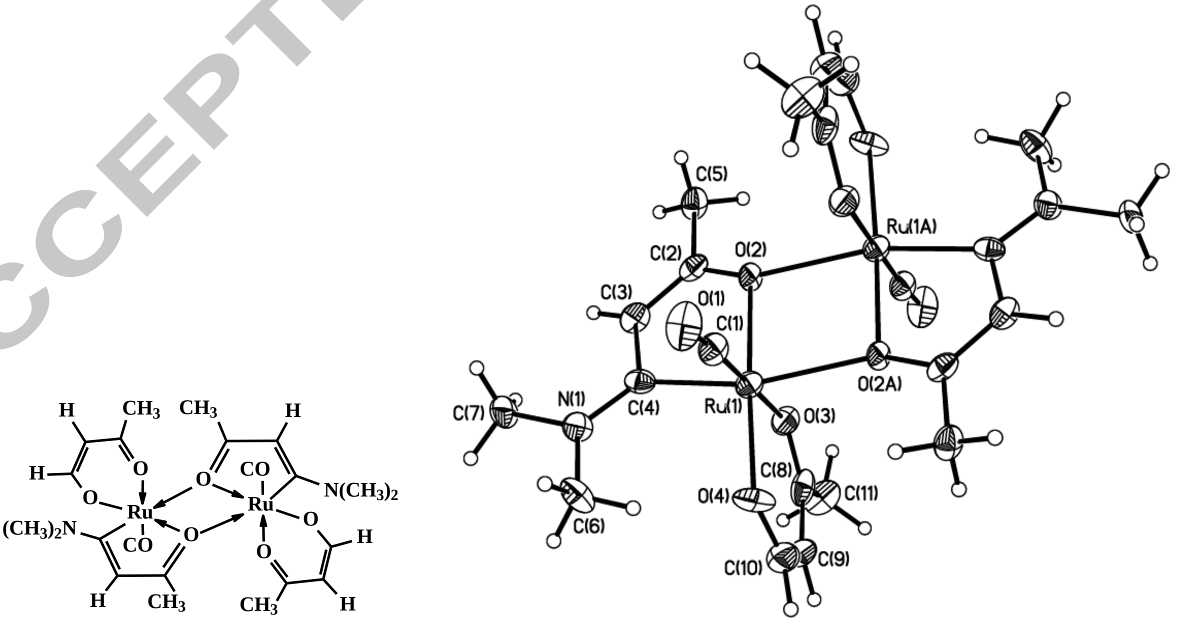


Figure 5. Schematic presentation and molecular structure of complex **2** (thermal ellipsoids at the 30% probability level).

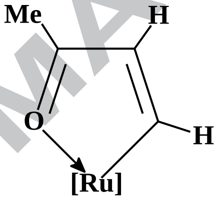
In the complex **2**, one of the ligands undergoes significant changes, namely, the deamination to form the 3-oxo-1-methyl-propenolato fragment occurs. Close transformations have been observed in the reaction between $Ru_3(CO)_{12}$ and 1-phenyl-2-metyl-3-morpholino-prop-2-en-1-one [14]. It should be noted that, due to a low quality of its crystals (small twin needles) and unsolved disorder (see below), the accuracy of structural data for complex **2** is low. Taking into account that the complex contains the ligand in an unusual deaminated form and the detailed discussion of its structural features is impossible, its spectral characteristics and behavior in solution should be considered in more detail.

To confirm complex **2** to be the reaction product rather than the chromatographic transformation product, the reaction solution was studied by ^{1}H NMR spectroscopy (see Fig. S2). This study shows the reaction solution to contain a mixture of complexes, including complexes **3** and **2** in a ratio of ~10 : 1. The IR spectrum for the reaction solution also contains signals corresponding to complex **2**. To confirm that complex **2** arises from the reaction between $Ru_3(CO)_{12}$ and **L** rather than from the transformation of complexes in the presence of trace water, a separate reaction between $Ru_3(CO)_{12}$ and **L** with addition of water was performed and the reaction solution was studied by ^{1}H NMR spectroscopy (see Fig. S3). According to this study, the addition of water does not result in an increase in the yield of complex **2** compared to the conventional reaction. The reaction solution contains a mixture of complexes, among which are complexes **3** and **2** in a ratio of ~15 : 1. In addition, the reaction mixture contains a great amount of ruthenium hydrides, which confirms the fact that the reaction solution undergoes dehydration due to the excess of $Ru_3(CO)_{12}$ [27].

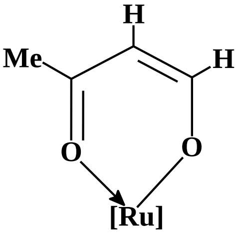
The ^{1}H NMR spectrum of complex **2**, including the spectrum of the reaction mixture, displays a double set of signals in a ratio of 1 : 2.5, which suggests that complex **2** exists as two isomers. The isomers can be distinguished only by the ^{1}H NMR spectra, since their IR spectra are identical.

Isomer **2a** obtained in high yield was isolated in the individual state by chromatography. Heating of the individual isomer **2a** affords a mixture of isomers with the same ratio as in the reaction mixture (Fig. S4). Heating of a mixture of isomers with **L** does not result in the formation of new complexes (see Experimental).

To assign the signals and to establish the structure, heteronuclear 2D NMR techniques, such as ^{1}H-^{13}C HSQC and HMBC, were used (the NMR spectra and their discussion are given in Supplementary data, Fig. S5 and S6). The spectral data suggest that complex **2a** contains two ligands. The singlet signal in the ^{1}H NMR spectrum at δ 5.13 ppm corresponds to the proton of an uncoordinated oxaruthenacycle. In the second ligand, the both protons of the olefinic bond are present (doublet of doublets at δ 7.77 and 5.11 ppm) and dimethylamino substituent does not detected. One can assume the formation of a five-membered oxaruthenacycle with two olefinic protons:

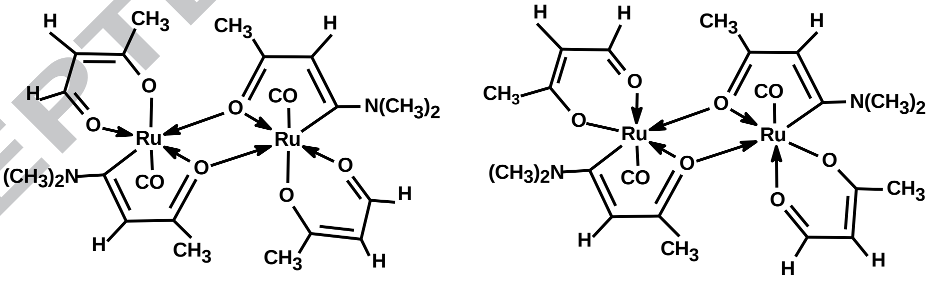


However, the proton signals for the complexes where the olefinic group is σ-bound to the metal atom (Ru-C_{β}(***H***)=C(H)) must be in the much more downfield region (δ ~11 ppm [31]) as compared to complex **2a**. In the ^{13}C NMR spectrum, the signal for the σ-bound C_{β} atom would be also in the more downfield region due to the contribution of the furan form of metallacycle (*vide supra*) as compared to **2a** (δ 175.9 ppm). Such a behavior is typical of the C_{β} atoms in the β-diketonate complexes [9, 32, 33]. Therefore, one of the ligands in complex **2** is present in the propenedionate form. The ^{13}C NMR spectrum for complex **2a** contains two signals for the carbonyl carbon atoms at δ 175.9 and 196.4 ppm, i.e. there is no delocalization in the metallacycle and the ligand is present in the 3-oxo-1-methyl-propenolato form:



In the ^{1}H NMR spectrum for a mixture of isomers **2a** and **2b**, the signals for the methyl protons and C_{β}-***H*** in the six-membered ring differ most strongly. The signal for the methyl group (C(O)-***C***H$_3$) in **2b** is more upfield shifted (δ 1.83 vs δ 1.94 ppm in **2a**). Conversely, the signal for the C_{β}-***H*** proton is more downfield shifted to be at δ 8.23 ppm (d, 1H, C*H*=C*H*, $^{3}J_{HH}$ =4.4 Hz) *versus* δ 7.86 ppm in **2a**. The positions of signals for the C_{α}-***H*** and five-membered ring protons change not so noticeably. Based on the structure of complex **2** (Fig. 5), one can assume that the isomers differ by the arrangement of the six-membered ring associated with relocation of the O(3) and O(4) atoms. Since the six-membered ring has nonsymmetric structure (due to the methyl substituent), relocation of the oxygen atoms results in a different isomer (Scheme 5). The superposition of these isomers is likely implemented in the crystal structure of **2**; however, we failed to solve the positions of disordered atoms (see Supplementary data for details of the crystal structure refinement).

Scheme 5



2a **2b**

The second minor product isolated from a solution is a polynuclear complex **4**. According to the X-ray diffraction data, the metal core in complex **4** contains a triangle of ruthenium atoms and the fourth ruthenium atom bound thereto through organic fragments (Fig. 6, Table S5). The metal-metal bonds in the triangular cluster are inequivalent: there are two shorter bonds, *viz*., Ru(1)-Ru(3) 2.7383(3) Å and Ru(2)-Ru(3) 2.7267(3) Å, and one longer bond, *viz*., Ru(1)-Ru(2) 2.9963(3) Å. The bridged hydride ligand is located on the longer bond. These three ruthenium atoms coordinate to eight terminal metalcarbonyl groups.

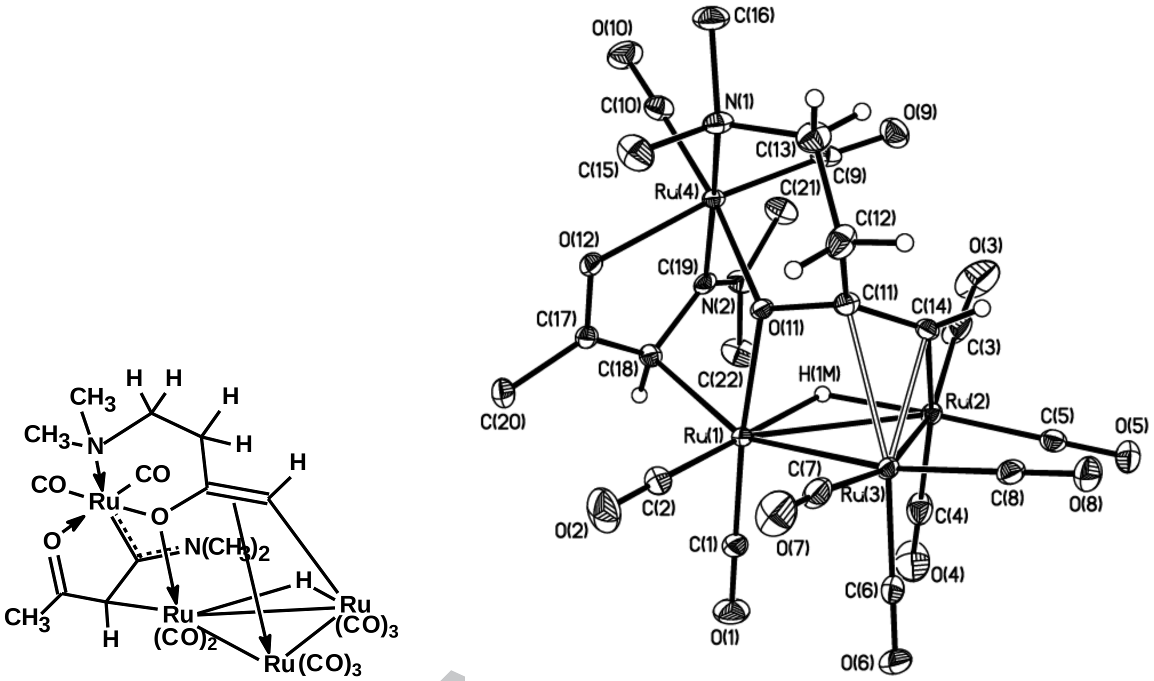


Figure 6. Schematic presentation and molecular structure of complex **4** (thermal ellipsoids at the 50% probability level; the methyl hydrogen atoms are omitted).

The Ru(4) atom is bonded with two metalcarbonyl groups in the *cis* position and chelated by two organic ligands to form five- and six-membered metallacycles. The structure of the five-membered ring, including the η^1-coordination of the C_α atom (Ru(1)-C(18) is 2.388(2) Å) and, correspondingly, the sp^3-hybridization of this carbon atom, coincides completely with the same fragment in complexes **5** and **6**. Upon formation of the six-membered azaoxaruthenacycle on the Ru(4) atom, the ligand undergoes transformations close to those observed upon formation of **5**, except for one important difference. The migration of the olefinic bond (formal *1,3-H* shift and metal-induced allyl rearrangement) results in a new exocyclic olefinic group (C(11)-C(14) 1.386(3) Å), which is involved in the π-coordination to the Ru(3) atom of the ruthenium triangle (the Ru(3)-C(11) distance is 2.411(2) Å and the Ru(3)-C(14) distance is 2.235(2) Å). The C(14) atom of the former methyl group forms the σ-bond with the Ru(2) atom of the ruthenium triangle (Ru(2)-C(14) 2.095(2) Å) and remains only one proton. The displaced protons of the methyl group reduce the olefinic bond of the chelate six-membered metallacycle (C(12)-C(13) is 1.518(4) Å), while complex **5** has endocyclic olefinic bond. As a consequence, the conformation of the cycle changes from boat in **5** to chair in **4**. In the six-membered metallacycle of complex **4**, the Ru(4), N(1), C(11), and C(12) atoms are in one plane (the maximum deviation is less than 0.001 Å) and the O(11) and C(13) atoms deviate from this plane to different sides by 0.748 and 0.638 Å, respectively. As in complex **5**, the ketonic bond of the starting amino vinyl ketone upon formation of the six-membered metallacycle becomes single-bond (O(6)-C(11) 1.374(3) Å) and the O(11) oxygen atom is involved in the coordination to Ru(1) atom of the ruthenium triangle (the distances Ru(4)-O(11) (2.087(2) Å) and Ru(1)-O(11) (2.088(2) Å) coincide). Thus, the organic ligand being involved in chelation of the Ru(4) atom to form the six-membered azaoxaruthenacycle combines all four atoms of the metal cluster.

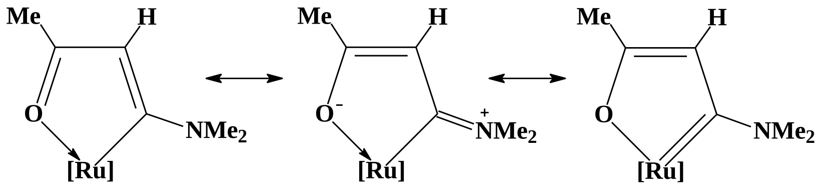
By analogy with compounds **5** and **6**, the five-membered metallacycle in complex **4** has a positive charge. Since complex **4** is neutral, it should be considered as a zwitter-ionic compound with a negative charge being localized, presumably, on the triangular cluster. Indeed, taking into account eight carbonyl groups, H ligand, two σ-bonds (C(8)-Ru(1) and C(14)-Ru(2)), *n*-donor O(11)-Ru(1) bond, and the π-coordination of the C(11)-C(14) olefinic bond to the Ru(3) atom, for the triangular cluster one get 47 valence electrons, which can correspond to three M-M bonds only provided that this fragment has a negative charge. The Ru(4) atom has completed 18e shell.

2.6. Five-membered oxaruthenacycles

All isolated organometallic products of the thermal reaction of $Ru_3(CO)_{12}$ with **L** comprise chelate five-membered oxaruthenacycles forming via C_β-H bond activation. The structure of the five-membered oxaruthenacycles in complexes varies according to the type of coordination with other metal atoms and these features are discussed below.

The uncoordinated five-membered oxaruthenacycle (in complexes **1**, **3** and **5**, Table 2) is planar and the sp^2-hybridized nitrogen atom (the sum of bond angles at the N atom is equal to 360º) is involved in conjugation with the oxadiene fragment (the dihedral angle between the mean plane of metallacycle and the plane of amino group in complexes does not exceed 15º). The C_β-N bond length of 1.33 Å (average) coincides with the value of 1.329(2)Å for the C-N bond in 3-dimethylamino-1-(4-methylphenyl)prop-2-en-1-one (**L'**) [34]. However, the distribution of the C-C bond lengths in metallacycle differs from the bond sequence in **L'** where the lengths of olefinic and single C-C bonds are 1.362(2) and 1.434(2) Å, respectively. Upon formation of the matallacycle, the former olefinic C_α=C_β bond elongates to 1.43 Å and the single C_α-C(O) bond shortens to 1.38 Å. The elongation in the C=O bond upon coordination to the ruthenium atom (on the average by 1.29 Å compared to 1.239(2) Å in **L'**) is also observed. Thus, upon formation of the five-membered oxaruthenacycle the contribution of the imine-enol form of **L** becomes more significant, although several resonance forms of the metallacycle can be suggested (Chart 2). The imine form of the fragment agrees with the ^{1}H NMR spectra of complexes **1** and **3** which display two signals corresponding to the methyl groups at the nitrogen atom (rotation around the C-N bond is hindered) in contrast to **L** (Table 1). The downfield shifted signal of the β-carbon atom in the ^{13}C NMR spectrum of complex **3** indicates a partial contribution of the carbene character of the Ru-C_β bond.

Chart 2



The displacement of the olefinic bond in the five-membered oxaruthenacycles derived from **L** distinguishes them from the analogous rings in the oxadiene complexes $Ru(CO)_2(O{=}C(Fc)C(H){=}C(Fc))_2$ [22] and $Ru_2(CO)_4(\mu\text{-}Cl)_2(O{=}C(R^1)C(H){=}C(R^2))_2$ [15] where the C-C bond lengths distribution coincides with that in the starting ligands. In the mononuclear complex *cis*-Ru(CO)$_2$[O=C(Tol)C(H)=C(NHPh)][O=C(Tol)C(H)=C(H)-N(Ph)] (Chart 1), the C-C bonds in the five-membered metallacycle are more equalized [12].

Table 2. Bond lengths (Å) in the uncoordinated five-membered oxaruthenacycles Ru-O=C(R^1)-C(H)=C(R^2).

Compound	Ru-C$_\beta$	C$_\alpha$=C$_\beta$	C$_\alpha$-C(O)	C=O	Ru-O	N-C$_\beta$	Ref.
1a	2.094(4)	1.425(6)	1.379(6)	1.281(5)	2.101(3)	1.324(5)	
1b	2.068(2)	1.427(3)	1.380(4)	1.292(3)	2.101(2)	1.339(3)	
1c	2.113(4)	1.421(6)	1.377(6)	1.298(5)	2.092(3)	1.324(6)	
3	2.135(2)	1.418(4)	1.388(3)	1.287(3)	2.085(2)	1.329(3)	
5	2.087(9)	1.417(13)	1.385(13)	1.280(11)	2.079(6)	1.325(12)	
R^1 = R^2 = Fc $^{a)}$	2.117(6)	1.364(8)	1.437(8)	1.260(7)	2.100(4)		[22]
R^1 = R^2 = Fc $^{b)}$	2.031(10)	1.376(12)	1.464(14)	1.259(12)	2.101(6)		[15]
R^1 = Me, R^2 = Ph	2.032(2)	1.364(2)	1.434(3)	1.257(2)	2.123(1)		[22]
R^1 = Tol, R^2 = NHPh	2.067(7)	1.401(9)	1.388(9)	1.311(7)	2.078(5)	1.321(8)	[12]

$^{a)}$ in the mononuclear complex Ru(CO)$_2$(O=C(Fc)-C(H)=C(Fc))$_2$

$^{b)}$ in the binuclear complex Ru$_2$(CO)$_4$(μ-Cl)$_2$(O=C(Fc)-C(H)=C(Fc))$_2$

Thus, the structure of the five-membered oxaruthenacycles derived from **L** significantly differs from the structure of previously described oxarutenacycles, and as a result, their coordination with other metal atoms is different.

The π-coordination of the olefinic bond is usual for polynuclear complexes derived from oxadienes [35], but it is not typical for amino vinyl ketones where the olefinic group is deactivated due to the donor effect of the amino group. This type of coordination becomes possible in complexes **1** since the nitrogen atom is out of conjugation with the oxadiene fragment due to coordination of the electron lone pair of the nitrogen atom to the ruthenium atom (Figure 1, the N(1)-C(11) bond is elongated to 1.45 Å). In contrast to the uncoordinated five-membered oxaruthenacycle, the π-coordinated cycle is non-planar and has flattened envelope conformation: the bend angle along the O(9)…C(11) line is on the average 19º. The olefinic bond being involved in the π-coordination significantly elongates to 1.45 Å (average value, Table S1) and the formally single C(9)-C(10) bond length of 1.42 Å coincides with that in **L'** (1.434(2) Å). The geometry of the π-coordinated metallacycles in complexes **1** is almost the same as the geometry of the analogous fragments in the products of reactions between $Ru_3(CO)_{12}$ and oxadienes [35].

The above mentioned redistribution of the C-C bond lengths in the five-membered oxaruthenacycle, resulting from a conjugation with the dimethylamino group, leads to η^1-coordination of the metallacycle through the new Ru-C_α σ-bond formation. This type of coordination is observed in several products of the thermal reaction of $Ru_3(CO)_{12}$ with **L** including the cationic complexes **5** and **6** isolated from a precipitate and occurs for the first time in the transition metal complexes with amino vinyl ketones and oxadienes [36].

*2.6. Concurrent transformation of amino vinyl ketone **L***

Besides organometallic complexes, the thermal reaction of $Ru_3(CO)_{12}$ with **L** affords an organic molecule, 1,3,5-triacetylbenzene. The presence of 1,3,5-triacetylbenzene among the reaction products is confirmed by ^{1}H NMR spectroscopy of the reaction mixture (δ 8.62 ppm) (see Fig. S2). The formation of 1,3,5-triacylbenzenes from amino vinyl ketones as a result of deamination accompanying acid catalyzed condensation is well documented [37, 38]. It appears that 1,3,5-triacetylbenzene can results from a concurrent transformation of amino vinyl ketone **L** in conditions of the thermal reaction with $Ru_3(CO)_{12}$.

The yields of complex **2** and 1,3,5-triacetylbenzen arising from the deaminated form of the organic ligand are low and comparable. Nevertheless, one can expect the presence of the amine resulting from deamination either in the reaction products or in a free state. However, no dimethylamine complexes were observed among the reaction products of $Ru_3(CO)_{12}$ and **L**. We also failed to detect gaseous dimethylamine evolving from the reaction medium by passing the gas fraction through the Nessler reagent.

2.7. Photochemical reactions of $Ru_3(CO)_{12}$ with ***L***

The photochemical activation of the organometallic reagents differs from thermal conditions by much higher selectivity. The photochemical reactions of $Ru_3(CO)_{12}$ at $\lambda \geq 210$ nm and $\lambda \geq 350$ nm are known to be effective in the cleavage of Ru–CO and Ru–Ru bonds, respectively [39, 40, 41, 42, 43]. Irradiation at different wavelength allows one to obtain additional data on processes occurring in the reaction between $Ru_3(CO)_{12}$ and an organic molecule. The emphasis was on the question which reaction center of the amino vinyl ketone is guiding in the chemical transformation.

The photochemical reactions of $Ru_3(CO)_{12}$ with **L** in two wavelength ranges with $\lambda \geq 210$ nm and $\lambda \geq 350$ nm were performed. Upon excitation at $\lambda \geq 210$ nm, the final solution contained **L**, and complex **7** (45 mg, 25% yield) was isolated from the precipitate. Upon excitation at $\lambda \geq 350$ nm, no products of the reaction between $Ru_3(CO)_{12}$ and **L** were produced and only the photodecomposition products of $Ru_3(CO)_{12}$ were observed.

According to the X-ray diffraction data, two molecules of **L** in complex **7** are coordinated to the Ru_3 cluster moiety (Fig. 7, Table S6). In the crystal, complex **7** occupies a special position on two-fold axis passing through the Ru(2) atom and the center of the Ru(1)-Ru(1A) bond. Each ligand chelates one ruthenium atom to form the five-membered oxaruthenacycle. The oxygen atom of the oxaruthenacycle additionally coordinates to the second chelated ruthenium atom. The oxaruthenacycle is planar (the maximum deviation from the mean plane is 0.046 Å for the C(5) atom). The structure of the metallacycle is similar to that described for the uncoordinated cycle in **1**, **3**, and **5** (Table 2). The O(5)-C(5) ketonic bond elongates to be 1.335(5) Å, which is explained by additional coordination to the second ruthenium atom (Ru(1)-O(5A) is 2.167(2) Å). This is accompanied by elongation in the Ru(1)-O(5) endocyclic bond (2.125(3) Å) compared to the analogous distances in Table 2.

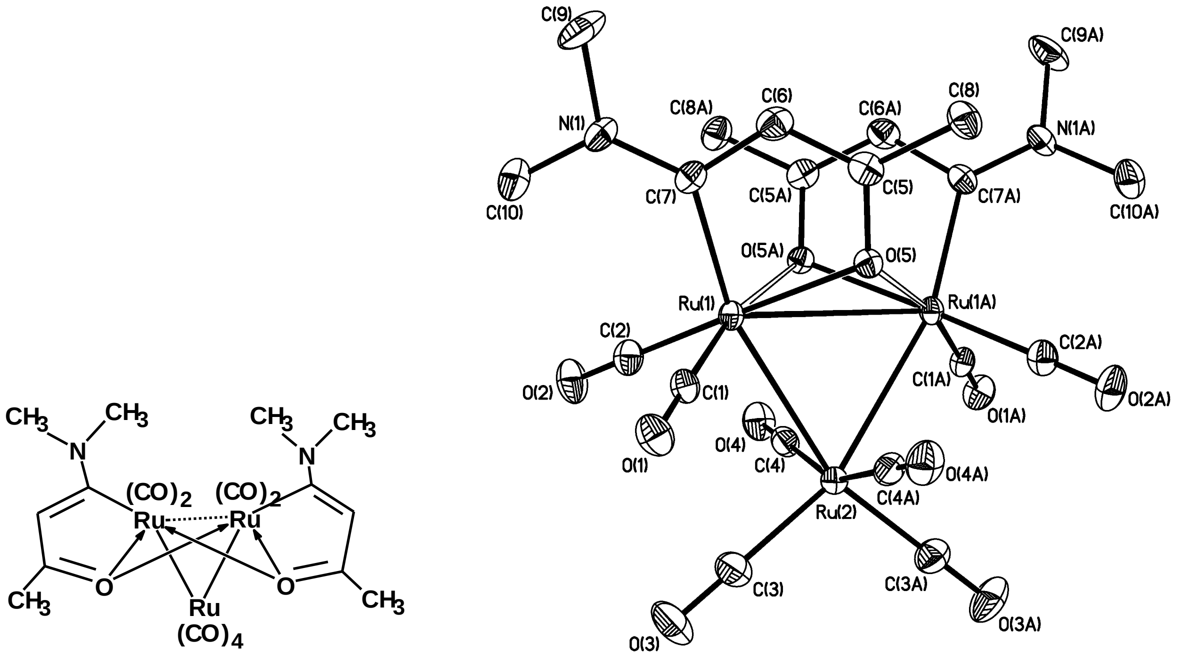


Figure 7. Schematic presentation and molecular structure of complex **7** (thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted).

Considering each organic ligand as a 5e donor and taking into account eight metalcarbonyl groups, one obtain 50 cluster electrons, which, for the trinuclear cluster implies only two metal-metal bonds. This is confirmed by the increased Ru(1)-Ru(1A) distance 3.0866(6) Å compared to two other bonds, Ru(1)-Ru(2) and Ru(2)-Ru(1A) with a length of 2.8437(5) Å each. In addition, for the Ru(1) and Ru(1A) atoms, without considering the bond between them we obtain an octahedral six-coordinated environment.

The ^{1}H NMR spectrum of complex **7** displays one set of signals for the coordinated ligand. The positions of signals differ slightly from those for complex **3**, besides the signal for the methyl substituent at the keto group which is upfield shifted due to additional coordination to the oxygen atom (Table 1). The ^{13}C NMR spectrum of **7** displays three downfield signals. The signals at δ 214.0 ppm can be attributed to the β-carbon atoms of five-membered cycles. The signal at δ 212.5 ppm can be attributed to the metalcarbonyl group in the *trans* position with regard to the oxygen atom of the five-membered ring. The slightly upfield signal at δ 202.5 ppm corresponds to the carbonyl carbon atom. The signals for the α-carbon atoms of the five-membered cycles in **7** (111.0

ppm) are downshifted compared to those for complex **3** (δ 105.3 ppm). In the N-$(CH_3)_2$ group, the signals for the methyl groups are different due to the existence of a partially imine C=N bond.

It should be noted that, the secondary amino vinyl ketone 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one does not react with $Ru_3(CO)_{12}$ under the photochemical activation conditions (UV irradiation at $\lambda \geq 210$ nm). The reaction mixture contained only photodecomposition products of $Ru_3(CO)_{12}$. Probably, the lone pairs of the oxygen atom possess insufficient activity without additional heating due to its involvement in strong intramolecular N-H…O hydrogen bonding. The tertiary amino vinyl ketone **L** has no intramolecular N-H…O hydrogen bond and the photochemical reaction with $Ru_3(CO)_{12}$ occurs. Therefore, one can conclude that the oxygen atom is a guiding reaction center in an interaction of amino vinyl ketones with ruthenium carbonyls.

3. Conclusions

The common feature of thermally and photochemically activated reactions between $Ru_3(CO)_{12}$ and amino vinyl ketone **L** is the formation of five-membered oxaruthenacycles, which are present in all isolated organometallic products. Deamination of the ligand is not a characteristic feature of the reactions and observed only in one of the minor reaction products. Upon formation of the five-membered oxaruthenacycles, the main coordination centers are the electron lone pair of the keto oxygen atom and the C_β-H bond. Comparison of the data for the photochemical reactions of $Ru_3(CO)_{12}$ with secondary and tertiary amino vinyl ketones showed the oxygen atom to be the guiding reaction center in these processes. This agrees with the fact that, in contrast to $Ru_3(CO)_{12}$, iron carbonyl undergoes no reactions with amino vinyl ketones [28]. Iron is more prone to the π-coordination to an olefinic bond which is significantly deactivated in amino vinyl ketones by the donor effect of the amino group.

The five-membered oxaruthenacycles in the reaction products can be either uncoordinated or bound to other ruthenium atoms in the different modes, namely, through π-coordination to the olefinic bond (as in complexes **1**), through σ-coordination to the C_α atom (as in complexes **4-6**), and by coordination with lone pair of the oxygen atom (as in complexes **2** and **7**). The conjugation in the ligand chain results in an isomerization of the ligand to form partially imine C=N bond and migration of the olefinic bond. This results in the coordination of the ruthenium atom to the C_α atom, which was not previously observed in reactions of $Ru_3(CO)_{12}$ with oxadienes.

It is established that the thermally activated reactions proceed differently for secondary and tertiary amino vinyl ketones. The reaction with tertiary amino vinyl ketone **L** yields the mononuclear complex **3** containing five-membered oxaruthenacycles as the main product. Meanwhile, the reaction with secondary amino vinyl ketone 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one affords mononuclear metallochelates with six-membered azaoxaruthenacycles. The difference in reactivity is primarily governed by the *trans*- and *cis*-arrangements of olefinic protons in the initial amino vinyl ketones.

Thus, substituents at the nitrogen atom in β-amino vinyl ketones have significant effect on the reaction pathway and the structures of resulting products.

4. Experimental

4.1. General considerations

All reactions were carried out under a dry argon atmosphere using standard Schlenk techniques. All solvents were dried according to standard procedures. Chromatography was performed on a column with silica gel (Aldrich, 70-230 mesh). Amino vinyl ketone **L** was prepared by the published method [44]. Elemental analysis was performed at the Laboratory of Microanalysis of the Institute of Organoelement Compounds of the Russian Academy of Sciences. IR spectra were recorded in solution on a Specord 75 IR spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance 400 spectrometer, Avance 600 spectrometer, and Avance 500 spectrometer using residual signals for deuterated solvents as the internal standard (δ 7.25 for $CDCl_3$; δ 7.26 for C_6D_6; all signals vs Me_4Si). ^1H and $^{13}C\{^1H\}$ NMR and 2D experiments (HSQC and HMBC for **2**) were performed at 298 K using standard pulse sequences from the Bruker library.

*4.2. Preparation of complexes **1a-d** from $Ru_3(CO)_{12}$ and **L***

A mixture of $Ru_3(CO)_{12}$ (160 mg, 0.25 mmol) and **L** (150 mg, 1.33 mmol) purged with argon was added to hexane (150 mL) and the resulting suspension was refluxed for 4 h. After cooling to 20°C, the reaction mixture was filtered, concentrated, and chromatographed on a silica gel column. $Ru_3(CO)_{12}$ (10 mg) was eluted first with pure hexane. Next, a mixture of complexes **1b** (14 mg, 7.9%), **1a** (27.0 mg, 15.3%), and **1c** (15.0 mg, 8.5%) and complex **1d** (traces) was eluted with hexane/benzene (1 : 1) mixture.

The resulting compounds were recrystallized from hexane to yield analytically pure samples of **1a-d** which were characterized by elemental analysis and IR, ^1H and ^{13}C NMR spectroscopy (see Table 1). A mixture of complexes **1a-d**: Anal. Calcd for $Ru_3C_{20}H_{10}N_2O_{10}$: C, 31.96; H, 2.66. Found: C, 31.59; H, 2.76.

*4.3. Preparation of complexes **2**, **3**, and **4** from $Ru_3(CO)_{12}$ and **L***

A mixture of $Ru_3(CO)_{12}$ (160 mg, 0.25 mmol) and **L** (150 mg, 1.33 mmol) in heptane (150 mL) was refluxed for 1 h 20 min. After cooling to 20°C, the reaction mixture was filtered, concentrated, and chromatographed on a silica gel column under the stream of argon using benzene as the eluent to yield a mixture of complexes **1 a-d** (slight amount), **2** (10.5 mg, 4.59%), **3** (36 mg, 14.03%), **4** (4 mg, 2.50%).

The crystals of **2** (yellow needles), **3** (colourless prisms) and **4** (orange prisms) suitable for X-ray diffraction study were grown by slow evaporation of a hexane/benzene mixture and a hexane solution. Anal. Calcd for **3** $RuC_{14}H_{20}N_2O_3$: C, 46.02; H, 5.51. Found: C, 45.72; H, 5.65.

IR and ^1H NMR spectra for 1,3,5-triacetylbenzene: IR (hexane, $\nu(CO)/cm^{-1}$): 1688s, 1590w; ^1H NMR ($CDCl_3$), δ: 8.69 (s, 1H, C*H*=C), 2.70 (s, 3H, CH_3).

*4.4. Preparation of complexes **2**, **3**, and **4** from compounds **L** and **1***

A mixture of compounds **L** (30 mg, 0.27 mmol) **and 1** (30 mg, 0.04 mmol) in hexane (50 mL) was refluxed for 4 h. The resulting solution was chromatographed on a silica gel column under the stream of argon. Unreacted residues of complexes **1** were eluted first with benzene. The remaining complexes were eluted with a benzene/chloroform (3 : 1) mixture. Complexes **2**, **3**, and **4** (according to the IR spectra) were isolated in negligible amounts.

*4.5. Preparation of complexes **5** and **6** from $Ru_3(CO)_{12}$ and **L***

a) A mixture of $Ru_3(CO)_{12}$ (160 mg, 0.25 mmol) and **L** (150 mg, 1.33 mmol) was refluxed in heptane (150 mL) for 1 h 20 min. After cooling to 20°C, the reaction mixture was filtered, the precipitate was dissolved in CH_2Cl_2 and chromatographed on a silica gel column. The first fraction was eluted with hexane/CH_2Cl_2 (3 : 1) mixture to give after evaporation complex **5** (15.0 mg, 9.68%). Subsequent elution with hexane/CH_2Cl_2 (1 : 1) afforded complex **6** (2.5 mg, 1.66%).

b) A mixture of $Ru_3(CO)_{12}$ (160 mg, 0.25 mmol) and **L** (150 mg, 1.33 mmol) in heptane (150 mL) was refluxed for 3 h. According to the IR spectra, the only complex **3** remains in the reaction solution. After cooling to 20°C, the reaction mixture was filtered, the precipitate (140 mg) was dissolved in CH_2Cl_2 and chromatographed on a silica gel column to yield complexes **5** (26.5 mg, 17.11%) and **6** (10 mg, 6.62%).

c) A mixture of $Ru_3(CO)_{12}$ (160 mg, 0.25 mmol) and **L** (150 mg, 1.33 mmol) in heptane (150 mL) was refluxed for 6 h. According to the IR spectra, the total intensity of the spectrum for the reaction solution slightly decreased after heating for additional 3 h. After cooling to 20°C, the reaction mixture was filtered, the precipitate (151 mg) was dissolved in CH_2Cl_2 and chromatographed on a silica gel column to yield complexes **5** (17 mg, 10.97%) and **6** (28 mg, 17.22%). The total amount of the precipitate remained unchanged and the ratio of complexes changed in favor complex **6**.

Single crystals suitable for X-ray diffraction study were obtained by slow crystallization of **5** and **6** from a hexane/CH_2Cl_2 mixture. Complex **5**: Anal. Calcd for $Ru_8C_{40}H_{33}N_3O_{25}$: C, 27.23; H, 1.89. Found: C, 26.87; H, 1.95. Complex **6**: Anal. Calcd for $Ru_9C_{42}H_{30}N_3O_{28}$: C, 26.08; H, 1.56. Found: C, 25.89; H, 1.66.

*4.6. Heating of complex **2a** in hexane*

A solution of **2a** in C_6D_6 in an NMR tube was heated on a boiling hexane bath. The NMR spectrum was recorded every 5 h. After first 5 h, the solution contained complexes **2a** and **2b**. After heating for 30 h, the ratio of complexes **2a** and **2b** corresponded to that in the reaction mixture (**2a** : **2b** ~ 1 : 2.5). Information-bearing spectral fragments are shown in Supplementary data (Fig. S4).

*4.7. Heating of complex **2** and **L***

A solution of complexes **2a** and **2b** with compound **L** in C_6D_6 was heated in an NMR tube on a boiling hexane bath for 10 h. No complex **3** was detected in the NMR spectrum for the resulting solution.

*4.8. Reaction of $Ru_3(CO)_{12}$ and **L** with addition of water*

A mixture of $Ru_3(CO)_{12}$ (80 mg, 0.125 mmol), **L** (75 mg, 0.67 mmol), and water (two drops) in heptane (150 mL) was refluxed for 1 h 20 min. After cooling to 20°C, the reaction mixture was filtered and evaporated. The residue was dissolved in C_6D_6 and the ^1H NMR spectrum was recorded. Information-bearing spectral fragments are shown in Supplementary data (Fig. S3).

*4.9. Preparation of complex **7** from $Ru_3(CO)_{12}$ and **L** (irradiation)*

a) A mixture of $Ru_3(CO)_{12}$ (160 mg, 0.25 mmol) and **L** (150 mg, 1.33 mmol) in hexane (150 mL) was irradiated in a water-jacketed immersion-type quartz photoreactor for 5 h at room temperature. The reaction mixture was filtered. According to the IR spectrum, the reaction solution contains compound **L**. The precipitate formed was filtered off and dissolved in CH_2Cl_2. The resulting solution was evaporated slowly to yield complexes **7** (45 mg, 25.04%). Single crystals of **7** (red prisms) suitable for X-ray diffraction study was obtained by recrystallization from CH_2Cl_2. Compound **7**: Anal. Calcd for $Ru_3C_{20}H_{20}N_2O_{10}$: C, 31.30; H, 2.63. Found: C, 31.05; H, 2.68.

b) A mixture of $Ru_3(CO)_{12}$ (160 mg, 0.25 mmol) and **L** (150 mg, 1.33 mmol) in hexane (150 mL) was irradiated in a water-jacketed glass flask for 10 h at room temperature. After 2 h of irradiation, suspended substance appeared in a solution. Its amount increased insignificantly with further irradiation. On completion of the reaction (the absence of $Ru_3(CO)_{12}$ in solution), the resulting suspension was filtered and the filter residue was dissolved in CH_2Cl_2. The solution contained a mixture of unidentified complexes among which no complex **7** was detected.

4.10. Irradiation of a mixture of $Ru_3(CO)_{12}$ and 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one.

A mixture of $Ru_3(CO)_{12}$ (160 mg, 0.25 mmol) and 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one (200 mg, 0.84 mmol) in hexane (150 mL) was irradiated in a water-jacketed immersion-type quartz photoreactor for 20 h at room temperature. IR spectroscopy shows the reaction solution to contain only 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one. The reaction mixture was filtered and the filter residue was dissolved in CH_2Cl_2. The resulting solution contained a mixture of unidentified complexes the IR spectrum of which is identical with mixture of unidentified complexes obtained in the photochemical reaction of $Ru_3(CO)_{12}$ with **L** in the procedure (b).

4.11. X-ray diffraction study

Single-crystal X-ray diffraction experiments were carried out on a Bruker SMART APEX II diffractometer (graphite monochromated MoK$_\alpha$ radiation, λ = 0.71073 Å, ω-scan technique, and CuK$_\alpha$ radiation, λ = 1.54178 Å for complex **2**). The APEX II software [45] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, and the SHELXTL program package [46] was used for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of hydride ligands in the structures of **4** and **5** were located in difference Fourier synthesis. The rest hydrogen atoms in the structures of **1-7** were placed geometrically and included in the structure factors calculation in the riding motion approximation. The principal experimental and crystallographic parameters are given in Table S7.

Appendix A. Supplementary data

Selected bond lengths and angles of compounds **1-7** in Tables S1-S6. Main experimental and crystallographic parameters in Table S7. Molecular structure of complex **6_Ru4** (Figure S1). ^{1}H NMR spectrum for the reaction mixture (Figures S2 and S3) and isomers of complex **2** (Figure S4). Discussion of the HSQC and HMBC NMR spectra for complex **2a** (Figures S5 and S6). CCDC 1552760-1552769 contains the supplementary crystallographic data for **1-7** in CIF file format. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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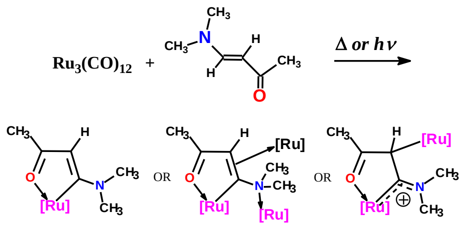
Graphical Abstract - Pictogram



Graphical Abstract - Synopsis

The common feature of thermally and photochemically activated reactions between $Ru_3(CO)_{12}$ and 4-dimethylaminobut-3-en-2-one is the formation of five-membered oxaruthenacycles. The structural and spectroscopic features, possible transformations pathways of the resulting complexes, and the differences in reactivity of tertiary and secondary amino vinyl ketones are discussed.