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Isolation and Characterization of New Mono- and Polynuclear Complexes Formed in the Thermal Reaction of $Ru_3(CO)_{12}$ with 1-(4-Tolyl)-3-phenylaminoprop-2-en-1-one

Svetlana V. Osintseva, Fedor M. Dolgushin,* Nikolay A. Shtel'tser, Pavel V. Petrovskii, Alexander S. Peregudov, Arkadii Z. Kreindlin, and Mikhail Yu. Antipin

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, 119991 Moscow, Russian Federation

Received December 23, 2009

Thermal reaction of $Ru_3(CO)_{12}$ with 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one (**1**) proceeds in heptane with the formation of a number of new chelate mononuclear complexes, *cis*-$Ru(CO)_2[O{=}C(Tol)CH{=}CHNPh]_2$ (**2**), *cis*-$Ru(CO)_2[O{=}C(Tol)CH{=}CNHPh][O{=}C(Tol)CH{=}CH\text{-}NPh]$ (**3**), and *cis*-$Ru(CO)_2[O{=}C(Tol)CH{=}CNHPh][O{=}C(Tol)CH{=}CHNPh]$ (**4**), isolated as the main products, along with minor amounts of the polynuclear clusters $Ru_5(CO)_{14}(\mu_2\text{-}H)_2(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}CCHC(Tol){=}O)$ (**5**), $Ru_4(CO)_{11}(\mu_2\text{-}H)_2(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^2\text{-}NPhCCHC(Tol){=}O)$ (**6**), and $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}NPhCHCC(Tol){=}O)$ (**7**). Complexes of both series were characterized by a combination of spectroscopic IR and multinuclear NMR data and by single-crystal X-ray diffraction study, which revealed the existence of different types of metal-to-ligand bonding in these species. Chelated six-membered azaoxaruthenacycles are formed in **2**−**4** via N−H activation, while unexpected five-membered oxaruthenacycles are formed in **3**−**6** due to C_β−H activation. Among the products of the reaction, the butterfly cluster **7**, with open-chain coordination of the ligand formed as a result of N−H and C_α−H bond activation, is also isolated. Complex **5** proved to be the only reaction product in which the deamination of amino vinyl ketone **1** is observed. Possible pathways for the formation of the complexes obtained are discussed.

Introduction

The interest in the chemistry of β-amino vinyl ketones is caused by their extensive applications. Amino vinyl ketones and their metal complexes are frequently used as reagents, intermediates, or catalysts in chemical synthesis of drugs, polymers, and dyes.[1,2] The polar character of amino vinyl ketones, electronic interactions between substituents, and the olefin bond are responsible for their nonlinear optical properties.[3a] Complexes of amino vinyl ketone ligands with metals are used for the deposition of metal coatings,[3b,c] and they possess liquid-crystalline properties.[3d,e]

Amino vinyl ketones, the so-called "push−pull" olefins, are highly reactive organic compounds with an electron donor group on one side and a strong electron acceptor group on the other side of the ethylene double bond.[1,4] It is known from organic chemistry that β-amino vinyl ketones have three nucleophilic and two electrophilic centers capable of interacting with various reagents. Nucleophiles attack amino vinyl ketone at the carbonyl carbon or at the β-carbon. Electrophiles attack the carbonyl oxygen, nitrogen, and the α-carbon.[5a,b] Due to the rich and complex chemistry of β-amino vinyl ketones, they can be used to obtain substances often unobtainable by other synthetic routes.[1]

In organometallic reactions with the participation of the amino vinyl ketones, the oxygen atom serves as a site for strong coordination, whereas the nitrogen atom is likely to be less strongly bound and, hence, may lead to ligand hemilability and as a result to interesting catalytic behavior.[6] To gain a better understanding of the nature of the catalytic systems and to investigate the factors that affect the catalysis, it was desirable to isolate and characterize as many products of the reaction as possible.

Complexes with metals are obtained as a result of the reactions of neutral organic compounds or their salts. As the mechanisms of these reactions are various, the formed complexes can adopt different types of coordination.[7] The most

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*To whom correspondence should be addressed. Fax: +7(499)1355085. E-mail: fedya@xrlab.ineos.ac.ru.

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common organometallic compounds of *β*-amino vinyl ketones are the six-membered metallochelates (six-membered azaoxametallacycles, the so-called N−O coordination). Such complexes are obtained with both transition and non-transition metals. The ligand mainly forms delocalized chelate ring with some contribution of the imine-enol structure.[3c,8] Salts of metals and amino vinyl ketonates of alkaline metals are often used to prepare such complexes.

Upon an interaction of neutral organic molecules in addition to N−O coordination, the formation of complexes with monodentate coordination through the oxygen atom can also be observed.[6,8] The ligands in such complexes exist mainly in the keto-enamine form. An unusual mixed complex of zirconium $[(\eta^5\text{-Cp*})\{\mathrm{CH_3C(O)CHC(NHR)CH_3}\}\{\mathrm{CH_3C(O)CHC(NR)CH_3}\}\mathrm{ZrCl_2}]$, where R = *p*-$\mathrm{CF_3Ph}$, has been prepared by the reaction of 4-amino(R)-but-3-en-2-one and lithium 4-amino(R)-but-3-en-2-onate with $\mathrm{Cp^*ZrCl_3}$.[9] In this complex the first ligand is a monodentate one, coordinated through the oxygen atom, while the second ligand forms a six-membered metallochelate.

A number of metal complexes with an amino vinyl ketone fragment as a ligand have been obtained by indirect chemical reactions. For example, the complexes of rhenium with six-membered N−O cycles are obtained by the combination of enolates of rhenium and nitriles.[10a,b] Complexes obtained from nitrates of uranium with acetylacetone in the presence of primary and secondary amines result in keto-amine products, coordinated with an atom of uranium through the oxygen atom.[11a,b]

There are only two publications regarding the reactions of the transition metal carbonyls with *β*-amino vinyl ketones. It was shown that *β*-amino vinyl ketones do not react with iron carbonyls because of a substantial difference in energy of the lowest unoccupied π^*-orbital of the olefin and 3d,4s-orbitals of iron.[12] However, several salicylidenimines, which can also be viewed as amino vinyl ketones in the imine-enol tautomeric form, do react with metal carbonyls.[13] In particular, thermal reaction of $\mathrm{Ru_3(CO)_{12}}$ with *N*-phenylsalicylidenimine (Ph-SaEn) results in product with low yield, which was assumed to be *cis*-$\mathrm{Ru(Ph\text{-}SaEn)(CO)_2}$ on the basis of spectral data.

Recently, we have studied the reaction of amino vinyl ketone bearing a tertiary amino group, 1-phenyl-2-methyl-3-morpholinoprop-2-en-1-one, with $\mathrm{Ru_3(CO)_{12}}$.[14] This reaction was accompanied by ligand deamination, so that vinyl ketonic and morpholine fragments of the amino vinyl ketone are observed in different products of the reaction. This is in agreement with the behavior of tertiary amines substituted with alkyl and aryl groups in reactions with metal carbonyls.[15a−d] Similar processes were also described for acetylamines.[15e,f] Unlike tertiary amines, deamination of the secondary amines is not as common.[15b,16] Besides, there is an additional center of coordination (N−H bond), which provides a broader variety of types of coordination with transition metals. Therefore, it is interesting to study the behavior of amino vinyl ketones bearing a secondary amino group in reaction with metal carbonyls.

In this paper we present the results of research on the thermal reaction between $\mathrm{Ru_3(CO)_{12}}$ and amino vinyl ketone 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one (**1**). Preliminary results of a part of this work have been published as a short communication.[17] This work is the continuation of our systematical studies on the reactivity of functionally substituted olefins in reactions with $\mathrm{Ru_3(CO)_{12}}$ (see ref 18 and references therein).

Results and Discussion

Reaction of $\mathrm{Ru_3(CO)_{12}}$ with **1** was carried out in boiling heptane for 5 h. The course of the reaction was monitored by the changes in IR spectra in the region of stretching vibrations of the metalcarbonyl groups. After slow cooling, the reaction mixture was separated into a solution and a precipitate.

From the solution, 10 mg of unreacted $\mathrm{Ru_3(CO)_{12}}$ (5.6% yield), hydride tetrahedral clusters $\mathrm{H_4Ru_4(CO)_{12}}$ (30 mg, 15.4% yield) and $\mathrm{H_2Ru_4(CO)_{13}}$ (14 mg, 6.9% yield), and complexes *cis*-$\mathrm{Ru(CO)_2[O{=}C(Tol)CH{=}CHNPh]_2}$ (**2**) (49.6 mg, 29.9% yield), *cis*-$\mathrm{Ru(CO)_2[O{=}C(Tol)CH{=}C\text{-}NHPh][O{=}C(Tol)CH{=}CHNPh]}$ (**3**) (16.5 mg, 10.0% yield), *cis*-$\mathrm{Ru(CO)_2[O{=}C(Tol)CH{=}CNHPh][O{=}C(Tol)CH{=}CHNPh]}$ (**4**) (6.6 mg, 4.0% yield), $\mathrm{Ru_5(CO)_{14}(\mu_2\text{-}H)_2(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}CCHC(Tol){=}O)}$ (**5**) (13.5 mg, 4.9% yield), $\mathrm{Ru_4(CO)_{11}(\mu_2\text{-}H)_2(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^2\text{-}NPhCCHC(Tol){=}O)}$ (**6**) (10.2 mg, 4.2% yield), and $\mathrm{Ru_4(CO)_{12}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}NPhCHCC(Tol){=}O)}$ (**7**) (10.0 mg, 3.8% yield) were isolated by column chromatography on silica gel (Scheme 1). All stages of separation and purification have been monitored by IR spectroscopy.

Formation of the hydride clusters was also observed in other reactions of $\mathrm{Ru_3(CO)_{12}}$ and was explained by the presence of traces of water at the reaction mixture.[19] However, in those reactions hydride clusters are formed at the first stage in a small amount, which is kept unchanged upon the continuation of the reaction. This testifies to the complete dehydration of the reaction mixture at the first stages of reaction.[20] At the same time, in the reaction of $\mathrm{Ru_3(CO)_{12}}$

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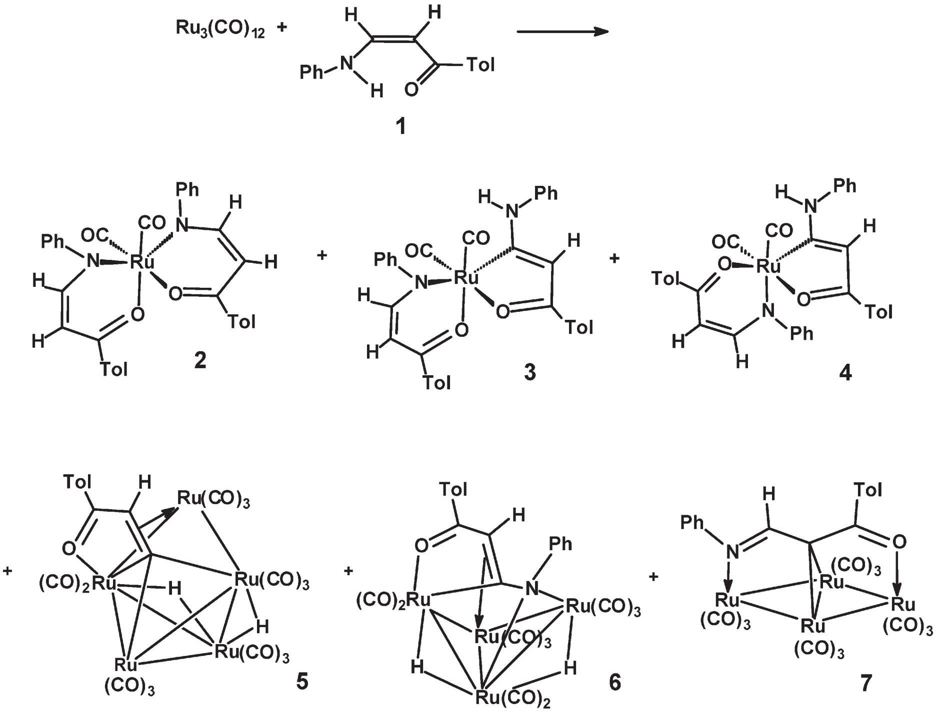
Scheme 1



with **1**, a considerable amount of hydride tetrahedral clusters $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ is formed, and their amounts continue to increases in the course of the reaction. In our opinion, the traces of water cannot serve as a source of protons because water is completely consumed at the first stage of the reaction; amino vinyl ketone **1**, which is deprotonated during the formation of complexes **2**–**7**, acts as a proton donor.

Upon formation of an oxaruthenacycle in reactions of $Ru_3(CO)_{12}$ with oxadienes, the ligand loses a hydrogen atom, while an excess amount of the ligand acts as a hydrogen acceptor and, thus, undergoes reduction to the corresponding saturated ketone.[20] However, in the reaction of $Ru_3(CO)_{12}$ with **1**, products of reduction of amino vinyl ketone are not observed. Thus, in this reaction, $Ru_3(CO)_{12}$ acts as the hydrogen acceptor and is reduced to the hydride clusters $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$.[21] This assumption is supported by the fact that in the absence of $Ru_3(CO)_{12}$ the hydride tetrahedral clusters do not react with **1** (vide infra), because of the lack of proton acceptors in the reaction mixture.

From 20 mg of the precipitate obtained in the reaction, we have separated an unidentified substance in trace amounts by chromatography. The IR spectrum of this substance shows signals in the region of stretching vibrations of metalcarbonyl groups: ν(CO), cm^{-1} (CH_2Cl_2) 2040w, 2010vs, 1982w, 1950w. In the ^{1}H NMR spectrum of its solution in $CDCl_3$ we have registered a single peak of low intensity at δ 16.46 ppm. Complexes with similar spectra have been separated from the reaction of $Ru_3(CO)_{12}$ with senecialdimine $(CH_3)_2C{=}CHCH{=}NR$ (R = *i*-Pr, *t*-Bu)[22] and have been characterized as salts of $[HRu_6(CO)_{18}]^-$ with an organic cation obtained as a result of ligand transformation. The data obtained allow us to assume that the precipitate consists of a salt-like substance with the $[HRu_6(CO)_{18}]^-$ anion. Identification of a cation by NMR spectroscopy appeared to be impossible, and our attempts to grow single crystals suitable for X-ray analysis were unsuccessful.

Complexes **2**–**7** have been characterized by IR and ^{1}H and ^{13}C NMR spectroscopy (Table 1), and their molecular structures have been unambiguously determined by single-crystal X-ray diffraction study.

In the reaction of **1** with $Ru_3(CO)_{12}$, the main products are mononuclear complexes of identical composition (**2**–**4**), in which the ruthenium atom is chelated by two molecules of the ligand. In addition, in each complex there are two carbonyl ligands at *cis*-position in the octahedral environment of the ruthenium atom. The complex **2**, obtained with the maximum yield, consists of two six-membered azaoxaruthenacycles (N–O coordination). Azaoxaruthenacycles are formed via oxidative addition of the ruthenium atom to the N–H bond with simultaneous coordination with one electron lone pair of the oxygen atom.

In spite of the fact that numerous complexes of various metals with two azaoxaruthenacycles are reported in the literature, only a few complexes with carbonyl ligands have been described, namely, *cis*-$[Ru(hpNP)_2(CO)_2][BF_4]$, where hpNP = 2-(2-hydroxyphenyl)-1,8-naphthyridine,[23] *cis*-Ru(salalen)$(CO)_2$, where salalen = *N*,*N*′-ethylenbis(salicylidenimine),[2] and an osmium complex with one carbonyl ligand.[24] The ruthenium complexes with two phosphine ligands in axial positions, (acen)$Ru(PPh_3)_2$, where acen = *N*,*N*′-ethylenbis(trifluoroacetoneimine),[25] and with three ketoimine ligands in a coordination environment of the ruthenium atom,

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Table 1. IR and NMR Spectra for 1−7

compound	IR ν(CO), cm^{-1} (hexane)	NMR: δ ^{1}H, ppm *J*, Hz	NMR: δ ^{13}C, ppm
1^{a}	1638 w, 1603 w, 1592 w	2.40 (s, 3H, Me); 6.09 (d, 1H, C*H*=CH-NH, $^{3}J_{H-H}$ = 8.0); 7.05 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.8); 7.22−7.37 (m, 5H, Ph); 7.48 (dd, 1H, CH=C*H*-NH, $^{3}J_{H-H}$ = 8.0, 12.4); 7.84 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.8); 12.11 (br d, 1H, NH, $^{3}J_{H-H}$ = 12.4)	
1^{b}		2.13 (s, 3H, Me); 5.85 (d, 1H, C*H*=CH-NH, $^{3}J_{H-H}$ = 7.7); 6.60 (d, 2H, *o*-Ph, $^{3}J_{H-H}$ = 7.8); 6.80 (t, 1H, *p*-Ph, $^{3}J_{H-H}$ = 7.3); 6.95 (dd, 1H, CH=C*H*-NH, $^{3}J_{H-H}$ = 11.4, 7.7); 6.99 (dd, 2H, *m*-Ph, $^{3}J_{H-H}$ = 7.3, 7.8); 7.03 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.0); 8.01 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.0); 12.51 (br d, 1H, NH, $^{3}J_{H-H}$ = 11.4)	20.94 (Me); 93.46 (CH=*C*H−N); 115.82; 122.80; 127.88; 128.81; 129.31 (*C*H, Ar); 137.28 (*C*-N); 140.48, 141.39 (*C*, Ar), 143.59 (CH=*C*H-N), 190.02 (*C*=O)
2^{a}	2046 s, 1980 s	2.34 (s, 3H, 2Me); 5.76 (d, 1H, C*H*=CH-N, $^{3}J_{H-H}$ = 7.0); 7.15 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.0); 7.25−7.32 (m, 5H, Ph); 7.42 (d, 1H, CH=C*H*-N, $^{3}J_{H-H}$ = 7.0); 7.82 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.0)	
2^{b}		2.12 (s, 3H, Me); 5.87 (d, H, C*H*=CH-N, $^{3}J_{H-H}$ = 6.8); 7.37 (d, 1H, CH=C*H*-N, $^{3}J_{H-H}$ = 6.8); 6.99 (t, 1H, *p*-Ph, $^{3}J_{H-H}$ = 7.4); 7.03 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.1); 7.14 (dd, 1H, *m*-Ph, $^{3}J_{H-H}$ = 8.0, 7.4); 7,45 (d, 2H, *o*-Ph, $^{3}J_{H-H}$ = 8.0); 8.05 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.1)	21.30 (Me); 92,30 (*C*H=C); 124.21, 125.82, 127.62, 128.23, 129.32 (*C*H, Ar); 137.18, 140.15, 160.09 (*C*, Ar); 159.21 (CH=*C*-N); 174.58 (*C*=O); 198.33 (Ru-*C*O)
3^{a}	2034 vs, 1976 sh, 1960 vs	2.31 (s, 3H, Me); 2.33 (s, 3H, Me); 5.70 (d, 1H, C*H*=CH, $^{3}J_{H-H}$ = 6.5); 6.55 (s, 1H, HC=C*H*); 7.08−7.75 (m, 20H, 2Ph, 2Tol, CH=C*H*-N, N*H*)	
3^{b}		2.01 (s, 3H, Me); 2.09 (s, 3H, Me); 5.87 (d, 1H, C*H*=CH-N, $^{3}J_{H-H}$ = 6.7); 6.90 (m, 2H, C=C*H*, *p*-Ph); 6.99−7.66 (m, 17H, *o*-Ph, *m*-Ph, Tol, *p*-Ph, CH=C*H*-N, N*H*); 8.00 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.1)	22.79, 31.71 (Me); 92.87, 103.00 (*C*H=C); 123.53, 125.08, 127.28, 128.09, 128.11, 128.32, 128.73, 128.87, 129.06, 129.17 (*C*H, Ar); 134.54; 137.77, 139.52, 141.30, 159.11, 159.47, (*C*, Ar); 159.61 (CH=*C*-N); 174.81, 196.23 (*C*=O); 197.35, 201.06 (Ru−*C*O), 218.21 (*C*=Ru).
4^{a}	2042 vs, 1974 sh, 1960 vs	2.33 (s, 3H, Me); 2.40 (s, 3H, Me); 5.68 (d, 1H, C*H*=CH-N, $^{3}J_{H-H}$ = 7.5); 5.88 (s, 1H, C=C*H*); 6.69 (d, 2H, Tol, $^{3}J_{H-H}$ = 7.3); 6.90 (d, 2H, Tol, $^{3}J_{H-H}$ = 7.5); 7.23−7.30 (m, 10H, 2*Ph*); 7.34 (d, 1H, CH=C*H*-N, $^{3}J_{H-H}$ = 6.6); 7.48 (s, 1H, NH); 7.63 (d, 2H, Tol, $^{3}J_{H-H}$ = 7.3); 7.90 (d, 2H, Tol, $^{3}J_{H-H}$ = 7.5)	
4^{b}		2.19 (s, 3H, Me); 2.02 (s, 3H, Me); 5.94 (d, 1H, C*H*=CH-N, $^{3}J_{H-H}$ = 7.3); 6.25 (s, 1H, C*H*=C); 6.55 (d, 2H, *o*-Ph, $^{3}J_{H-H}$ = 6.4); 6.88 (d, 2H, Tol, $^{3}J_{H-H}$ = 7,3); 6.97−7.08 (m, 8H, Ph); 7.16 (d, 2H, Tol, $^{3}J_{H-H}$ = 7.8); 7.31 (br s, 1H, NH), 7.36 (d, 1H, CH=C*H*-N, $^{3}J_{H-H}$ = 7.3); 7.86 (d, 2H, Tol, $^{3}J_{H-H}$ = 7.3); 8.27 (d, 2H, Tol, $^{3}J_{H-H}$ = 7.8)	19.20, 30.66 (Me); 91.78, 102.68, (*C*H=C); 124.49, 124.90, 125.11, 128.23, 128.30, 128.87, 128.92, 130.54, 133.06, 134.37 (*C*H, Ar); 136.21, 137.78, 140.03, 141.30, 167.28, 171.97 (*C*, Ar); 159.84 (CH=*C*-N); 177.24, 195.50 (*C*=O); 194.49, 202.43 (Ru−*C*O); 217.70 (*C*=Ru)
5^{b}	2098 w, 2070 s, 2062 s, 2048 s, 2030 m, 2016 m, 2004 w, 1988 w	−27.86 (d, 1H, Ru-*H*, $^{2}J_{H-H}$ = 1.9); −21.08 (d, 1H, Ru-*H*, $^{2}J_{H-H}$ = 1.9); 1.88 (s, 3H, Me); 5.49 (s, 1H, C=C*H*); 6.69 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.3), 7.62 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.3)	21.17 (Me); 65.28 (*C*H=C−Ru); 128.86, 128.99 (*C*H, Ar); 129.76, 145.13 (*C*, Ar); 184.74 188.96, 191.83, 194.49, 195.62, 197.53, 199.18 (Ru-*C*O); 214.41 (*C*=O); 323.95 (CH=*C*-Ru)
6^{b}	2086 m, 2054 s, 2032 s, 2018 m, 2010 m, 2004 w, 1984 m, 1976 w	−14.44 (d, 1H, Ru-*H*, $^{2}J_{H-H}$ = 2.3); −14.02 (d, 1H, Ru-*H*, $^{2}J_{H-H}$ = 2.3); 1.86 (s, 3H, Me); 5.04 (s, 1H, C=C-*H*); 6.58 (t, 1H, *p*-Ph, $^{3}J_{H-H}$ = 7.2); 6.72 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.1); 6.82−7.11 (m, 4H, *o*-Ph, *m*-Ph); 7.60 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.1)	21.27 (Me); 57.23 (C=*C*H); 121.40, 125.27, 129.02, 129.40 130.05 (*C*H, Ar); 130.44, 130.53, 145.71 (*C*, Ar); 162.24 (CH=*C*-Ru); 181.74, 186.79, 189.83, 191.75, 194.44, 199.04, 199.85 (Ru-*C*O); 208.51 (*C*=O)
7^{b}	2090 m, 2060 s, 2030 s, 2012 m, 2002 w, 1968 w	1.93 (s, 3H, Me); 6.70 (d, 2H, *o*-Ph, $^{3}J_{H-H}$ = 7.7); 6.83 (t, 1H, *p*-Ph, $^{3}J_{H-H}$ = 7.0); 6.91−6.98 (m, 4H, *m*-Ph, Tol); 7.43 (d, 2H, Tol, $^{3}J_{H-H}$ = 8.1); 9.90 (s, 1H, C*H* = N)	20.98 (Me); 121.44, 126.88, 127.33, 129.40, 129.62(*C*H, Ar); 135.59, 141.74, 155.43 (*C*, Ar); 188.02, 188.61 (Ru-*C*O); 196.23 (C=*C*H-N); 199.20 (*C*=O); 202.89, 203.26, 204.68, 205.75 (Ru-*C*O); 223.92 (*C*=Ru)

[a] ^{1}H NMR in $CDCl_3$. [b] ^{1}H and ^{13}C NMR in C_6D_6.

$[Ru(OC(CF_3)=CHC(CF_3)=NMe)_3]$,[3b] have been also described. The above-mentioned complexes were obtained from ruthenium chlorides and ketoiminates. Only one complex, namely, *cis*-Ru(Ph-SaEn)$(CO)_2$, was obtained in a thermal reaction of $Ru_3(CO)_{12}$ with *N*-phenylsalicylidenimine.[13]

In complexes **3** and **4**, one of the ligands chelates the ruthenium atom, forming a six-membered azaoxaruthenacycle, similar to that observed in **2**. The second ligand forms a five-membered oxaruthenacycle, which is unusual for amino vinyl ketones. These five-membered chelate oxaruthenacycles are formed via oxidative addition of the ruthenium atom to the C_β−H bond with simultaneous coordination of the keto-oxygen atom. Complexes **3** and **4** are isomers that are different in the spatial arrangement of the chelate cycles.

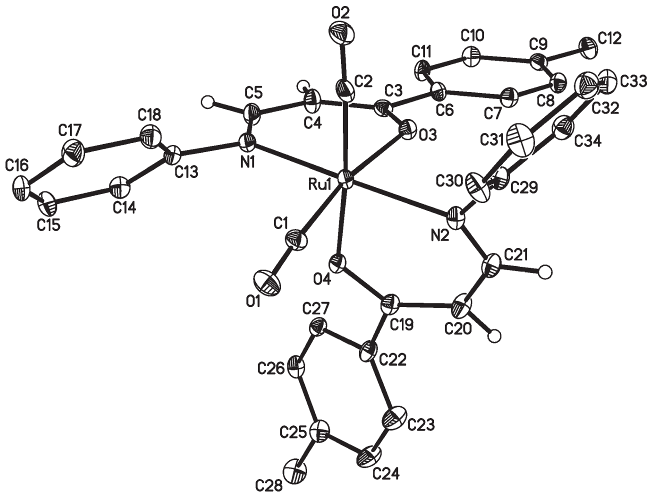

Figure 1. ORTEP drawing of the molecular structure of complex **2** with thermal ellipsoids at the 30% probability level (hydrogen atoms of the phenyl and tolyl substituents have been omitted for clarity).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 2

Ru(1)−C(1)	1.857(3)	C(4)−C(5)	1.403(4)
Ru(1)−C(2)	1.866(4)	N(1)−C(5)	1.299(4)
Ru(1)−O(3)	2.051(2)	N(1)−C(13)	1.428(3)
Ru(1)−O(4)	2.063(2)	O(4)−C(19)	1.280(3)
Ru(1)−N(1)	2.084(2)	C(19)−C(20)	1.382(4)
Ru(1)−N(2)	2.079(2)	C(20)−C(21)	1.397(5)
O(3)−C(3)	1.284(3)	N(2)−C(21)	1.286(4)
C(3)−C(4)	1.375(4)	N(2)−C(29)	1.426(4)
C(1)−Ru(1)−O(3)	171.9(1)	C(5)−N(1)−Ru(1)	121.1(2)
C(2)−Ru(1)−O(4)	174.3(1)	C(5)−N(1)−C(13)	117.0(2)
N(1)−Ru(1)−N(2)	170.71(9)	C(19)−O(4)−Ru(1)	125.6(2)
O(3)−Ru(1)−N(1)	90.60(8)	O(4)−C(19)−C(20)	125.5(3)
O(4)−Ru(1)−N(2)	90.54(9)	C(19)−C(20)−C(21)	126.4(3)
C(3)−O(3)−Ru(1)	126.8(2)	N(2)−C(21)−C(20)	128.7(3)
O(3)−C(3)−C(4)	124.3(3)	C(21)−N(2)−Ru(1)	121.6(2)
C(3)−C(4)−C(5)	126.7(3)	C(21)−N(2)−C(29)	118.1(3)
N(1)−C(5)−C(4)	129.2(3)		

In both complexes, one of the metalcarbonyl groups is positioned *trans* to the oxygen atom of the five-membered oxaruthenacycle. The second metalcarbonyl group is positioned either *trans* to the oxygen atom (complex **3**) or *trans* to the nitrogen atom (complex **4**) of the six-membered cycle. Thus, either the nitrogen atom (complex **3**) or the oxygen atom (complex **4**) of the six-membered metallacycle is positioned *trans* to the σ-bound carbon atom of the five-membered cycle.

Several complexes of transition metals containing oxametallacycles with amino substituents in β-position have been described in the literature. All these complexes have been synthesized as a result of coupling of organic fragments on transition metal centers rather than directly from amino vinyl ketones. For example, a cobalt five-membered cycle was obtained in the reaction of an isocyanidecobalt complex with an α-diazocarbonyl compound,[26a] and a palladium five-membered cycle was obtained in the reaction of an enolate palladium complex with isocyanide.[26b] Therefore it follows that the coordination of the transition metal atom to the C_β−H bond of amino vinyl ketones is unusual.

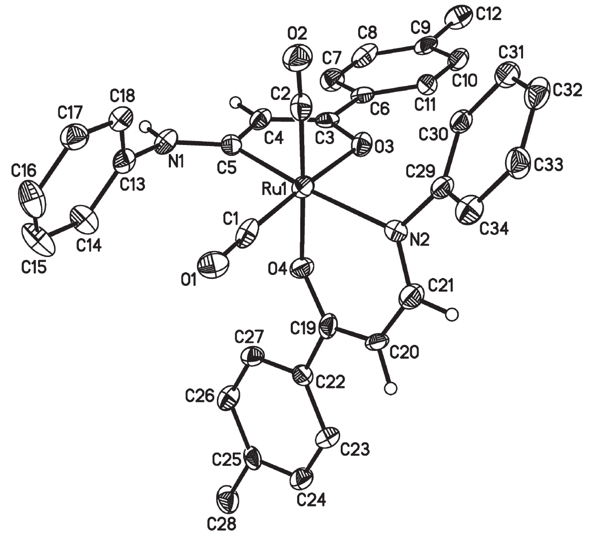

Figure 2. ORTEP drawing of one of two independent molecules of complex **3** with thermal ellipsoids at the 30% probability level (hydrogen atoms of the phenyl and tolyl substituents have been omitted for clarity).

1. Structure of Complexes 2−4. The structure of complex **2** has been previously determined at room temperature.[17] Since all other structures described in this work have been determined at 100 K, we repeated the structure determination of complex **2** (Figure 1, Table 2) at 100 K for a more proper comparison of the geometrical parameters of the isomeric complexes **2**−**4**. An asymmetric unit cell of crystal **3** contains two independent molecules that differ by the orientation of the phenyl fragments only (Figure 2, Table 3). Complex **4** forms a cocrystal with the molecule of the initial amino vinyl ketone **1** (Figure 3, Table 4). This fact allowed us to track the changes that occur in the molecule of amino vinyl ketone upon the formation of the chelate cycles of two types: five-membered oxaruthenacycle and six-membered azaoxaruthenacycle. In the crystal "**4** + **1**", the molecule of amino vinyl ketone **1** is in *cis*-form, which is stabilized by the intramolecular H-bond (N(3)···O(5) 2.635(10) Å, N(3)−H(3A)···O(5) 133°). The bond lengths in the central fragment of the molecule are localized to a considerable extent according to the type N−C=C−C=O (ketoenamine), except for the bond C(35)−O(5) of 1.283(10) Å, which is somewhat longer in comparison to the standard value of 1.22 Å for the C=O double bond in ketones.[27] This can be explained by the fact that the O(5) atom participates in formation of two N−H···O bonds simultaneously: the previously mentioned intramolecular bond as well as the intermolecular bond with complex **4** (N(1)···O(5) 2.801(10) Å, N(1)−H(1A)···O(5) 152°). Phenyl and tolyl substituents are slightly twisted relative to the central molecular plane (the dihedral angles between the planes of substituents and the O(5)C(35)C(36)C(37)N(3) plane are 13.7° and 10.1°, correspondingly).

As a result of N−O chelation of the ruthenium atom in the six-membered cycles of the complexes **2**−**4**, there is significant redistribution of the bond lengths with major contribution of the imine-enol form of the ligand. Thus, the C−C(O) bonds become systematically shorter than the C−C(N) bonds

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(26) (a) Strecker, B.; Zeier, B.; Schulz, M.; Wolf, J.; Werner, H. *Chem. Ber.* **1990**, *123*, 1787. (b) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D.; Jones, P. G. *Organometallics* **2005**, *24*, 2516.

(27) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Two Crystallographically Independent Molecules (A/B) of Complex 3

Ru(1)−C(1)	1.845(9)/1.856(8)	C(4)−C(5)	1.401(9)/1.391(9)
Ru(1)−C(2)	1.870(8)/1.844(9)	N(1)−C(5)	1.321(8)/1.323(8)
Ru(1)−O(3)	2.078(5)/2.088(5)	N(1)−C(13)	1.419(6)/1.413(6)
Ru(1)−O(4)	2.082(4)/2.080(5)	O(4)−C(19)	1.298(7)/1.292(7)
Ru(1)−C(5)	2.057(7)/2.077(7)	C(19)−C(20)	1.354(8)/1.360(9)
Ru(1)−N(2)	2.142(5)/2.140(6)	C(20)−C(21)	1.398(9)/1.399(10)
O(3)−C(3)	1.311(7)/1.299(7)	N(2)−C(21)	1.306(8)/1.292(8)
C(3)−C(4)	1.388(9)/1.383(9)	N(2)−C(29)	1.441(6)/1.433(7)
C(1)−Ru(1)−O(3)	175.9(3)/178.8(3)	C(4)−C(5)−Ru(1)	111.1(5)/110.6(5)
C(2)−Ru(1)−O(4)	177.2(2)/176.8(3)	C(5)−N(1)−C(13)	127.1(6)/127.7(6)
C(5)−Ru(1)−N(2)	166.9(3)/165.4(3)	C(19)−O(4)−Ru(1)	126.2(4)/127.6(5)
C(5)−Ru(1)−O(3)	79.7(2)/79.8(3)	O(4)−C(19)−C(20)	124.6(7)/123.9(7)
O(4)−Ru(1)−N(2)	86.9(2)/88.4(2)	C(19)−C(20)−C(21)	126.9(7)/128.3(7)
C(3)−O(3)−Ru(1)	113.3(4)/111.7(4)	N(2)−C(21)−C(20)	127.7(7)/128.3(7)
O(3)−C(3)−C(4)	118.3(7)/120.5(7)	C(21)−N(2)−Ru(1)	121.9(5)/121.9(6)
C(3)−C(4)−C(5)	117.2(6)/116.8(7)	C(21)−N(2)−C(29)	119.5(5)/118.7(6)

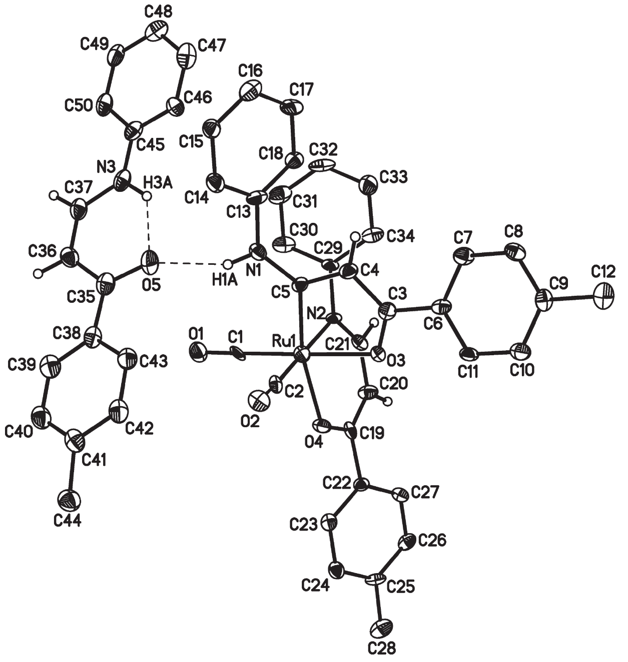

Figure 3. ORTEP drawing of the independent part of the unit cell for cocrystal "**4** + **1**" with thermal ellipsoids at the 30% probability level (hydrogen atoms of the phenyl and tolyl substituents have been omitted for clarity).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Ru(1)−C(1)	1.847(9)	O(4)−C(19)	1.295(9)
Ru(1)−C(2)	1.877(9)	C(19)−C(20)	1.383(10)
Ru(1)−O(3)	2.100(5)	C(20)−C(21)	1.389(10)
Ru(1)−O(4)	2.146(5)	N(2)−C(21)	1.326(9)
Ru(1)−C(5)	2.032(8)	N(2)−C(29)	1.449(7)
Ru(1)−N(2)	2.094(6)	O(5)−C(35)	1.283(10)
O(3)−C(3)	1.307(10)	C(35)−C(36)	1.422(12)
C(3)−C(4)	1.397(11)	C(36)−C(37)	1.378(12)
C(4)−C(5)	1.397(11)	N(3)−C(37)	1.382(10)
N(1)−C(5)	1.351(10)	N(3)−C(45)	1.402(8)
N(1)−C(13)	1.444(7)		
C(1)−Ru(1)−O(3)	178.5(3)	O(4)−C(19)−C(20)	126.0(8)
C(2)−Ru(1)−N(2)	174.4(3)	C(19)−C(20)−C(21)	126.5(8)
C(5)−Ru(1)−O(4)	166.3(3)	N(2)−C(21)−C(20)	129.5(8)
C(5)−Ru(1)−O(3)	80.0(3)	C(21)−N(2)−Ru(1)	122.5(5)
N(2)−Ru(1)−O(4)	89.2(2)	C(21)−N(2)−C(29)	114.9(6)
C(3)−O(3)−Ru(1)	111.1(5)	C(37)−N(3)−C(45)	129.7(8)
O(3)−C(3)−C(4)	120.8(8)	O(5)−C(35)−C(36)	119.9(9)
C(3)−C(4)−C(5)	114.6(8)	O(5)−C(35)−C(38)	119.0(8)
C(4)−C(5)−Ru(1)	113.2(6)	C(36)−C(35)−C(38)	121.1(9)
C(5)−N(1)−C(13)	127.0(7)	C(37)−C(36)−C(35)	123.1(9)
C(19)−O(4)−Ru(1)	125.2(5)	C(36)−C(37)−N(3)	124.2(9)

(average values are 1.373 and 1.398 Å, respectively), and the C−N bond is significantly shortened (average value is 1.307 Å). A similar distribution of the bond lengths with predominant imine-enol form of the ligand is observed in the majority of complexes with six-membered azaoxametallacycles.[28]

At the same time, in the five-membered cycles of complexes **3** and **4**, the C−C bonds are equalized (average distance is 1.393 Å), while the C−N bond is slightly elongated (average value is 1.332 Å). This means that the five-membered cycle is characterized by stronger delocalization than the six-membered cycle. It should be noted that the C═O bond is not sensitive to the changes in coordination, and in all complexes it is characterized by a nearly identical length that is insignificantly longer than that in **1**.

While discussing the bond lengths with participation of the ruthenium atom in octahedral complexes **2**−**4**, it is convenient to use the concept of mutual *trans*-influence of ligands.[29a,b] The considerable elongation of the Ru−O and Ru−N bonds *trans* to the carbon atom is in an agreement with known data on the strong *trans*-influence of σ-bound sp^2-hybridized carbon atoms.[29c] Taking the complexes with five-membered cycles as examples, we can make a conclusion about the stronger *trans*-influence of the nitrogen atom compared to the oxygen, taking into account the difference in Ru−C bond lengths *trans* to these atoms (2.057(7), 2.077(7) Å for that *trans* to N and 2.032(8) Å for that *trans* to O). The *trans*-influence of the metalcarbonyl ligand is comparable with the influence of the nitrogen atom (this can be concluded from the equality of the Ru−N bond lengths in complexes **2** and **4**). According to these data, for the ligand environment of the ruthenium atom in complexes **2**−**4** it is possible to suggest the following order of *trans*-influence: $C \gg CO \approx N > O$.

2. Spectral Data for 2−4. IR spectra of the complexes **2**−**4** (Table 1) contain two bands of equal intensity in the area of stretching vibrations of metalcarbonyl groups, which is normally observed for two CO ligands in *cis*-position to each other. The presence of additional bands of low intensity

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[28] Cambridge Structural Database (CSD), version 5.30 (November 2008).

[29] (a) Anderson, K. M.; Orpen, A. G. *Chem. Commun.* **2001**, 2682. (b) Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5. (c) Kapoor, P. N.; Kakkar, R. *J. Mol. Struct.* (*THEOCHEM*) **2004**, *679*, 149.

in complexes **3** and **4** is due to the distortion of the molecular symmetry because of the presence of two nonequivalent metallocycles (five- and six-membered cycles). The similarity of azaoxaruthenacycles in complex **2** is confirmed by ^{1}H and ^{13}C NMR spectra. In NMR spectra of complexes **3** and **4** a double set of signals is present, which is explained by the presence of cycles of different structure.

The spectral characteristics of the carbon atoms and the olefin protons of six-membered azaoxaruthenacycles in complexes **2**−**4** are similar. In ^{13}C NMR spectra the position of the signals of the carbon atoms in α-position is still nearly the same upon the cycle formation compared to **1**,[30] while the signals of the carbon atoms in *β*-position are shifted to low-field up to 160 ppm (143.6 ppm in **1**). The signals of the carbonyl carbon atoms are shifted relative to **1** (190.4 ppm) to high field up to 175 ppm in **2** and **3** and to 177.2 ppm in **4**. A similar shift of the signal of the carbonyl carbon atom is noticed in the analogous complexes, and it corresponds to the increase in the electron density at this atom.[6,31] The difference in the signal positions for complexes **2**, **3**, and **4** is probably caused by the fact that in complexes **2** and **3** the metalcarbonyl group is in *trans*-position to the oxygen atom of the azaoxaruthenacycle, while in **4** the carbon atom of the five-membered cycle appears to be oriented *trans* to this oxygen atom. The stronger *trans*-influence of the carbon atom leads to the low-field shift of the signal in **4**. Spatial differences have no influence on the proton doublets of the olefin groups of six-membered cycles. In the three complexes, the positions of the doublets of the olefin protons are nearly identical and are slightly different from the corresponding positions in **1** (Table 1). The spin−spin coupling constant of the olefin protons decreases from 8 to 7 Hz (on average) upon cycle formation. Thus, according to NMR spectra during the formation of the six-membered cycles in the organic ligand the order of carbonyl and olefin bonds decreases and a partial imine bond is formed, which corresponds to delocalization in the six-membered cycles with some apparent imine-enol structure.

In ^{13}C NMR spectra of **3** and **4** three low-field signals are observed. The signals located at 218.4 (**3**) and 217.7 (**4**) ppm can possibly be attributed to carbon atoms in *β*-position of the five-membered cycles. This can be explained by a partial contribution of carbene character of the Ru−C$_\beta$ bond, which implies a partial furan structure of the five-membered cycle.[20] In the ^{13}C NMR spectrum of complex $Ru(CO)_2(O{=}C(Fc)\text{-}CH{=}C(Fc))_2$ a similar signal was observed at even lower field, at 235.3 ppm.[20] The signals located at 197.4 and 201.1 ppm in **3** and at 194.0 and 202.4 ppm in **4** can be attributed to metalcarbonyl groups. We assume that the signal at 197.4 ppm in **3** corresponds to the metalcarbonyl group located *trans* to the oxygen atom of the six-membered cycle. The fact that the metalcarbonyl groups of complex **2** with similar spatial environment appear as a singlet at 198.3 ppm supports this assumption. The slightly high-field-shifted signal at 194.0 ppm in **4** corresponds to the metalcarbonyl group located *trans* to the nitrogen atom of the six-membered cycle, which is a weaker base than the oxygen atom. Two close signals at 201.1 in **3** and 202.4 ppm in **4** can be attributed to the metalcarbonyl groups being in *trans*-position to the oxygen atoms of the five-membered cycles in both complexes. This allows us to assume that the oxygen atom in the five-membered cycle is a stronger base than oxygen in the six-membered cycle.

The signals of the carbon atoms in the α-position in the five-membered cycles in **3** (103.0 ppm) and **4** (102.7 ppm) are shifted toward low field in comparison with those in **1** (93.5 ppm), unlike similar signals in six-membered cycles (91.8−92.9 ppm). The position of the carbonyl carbon atom remains unchanged. The singlets of amine protons in the ^{1}H NMR spectra are observed in the field of aromatic protons, which means that the exocyclic nitrogen atom forms a partial imine bond with the carbon atom in *β*-position. So, according to the spectral data, the delocalized system of bonds is formed in the five-membered cycles with some contribution of the keto-imine structure.

3. Formation of Chelate Metallacycles. There is a traditional point of view that the tautomeric equilibrium in *β*-amino vinyl ketones is shifted to the keto-enamine form.[1,7] However, in several publications the authors proved that *β*-amino vinyl ketones exist in imine-enol form as well. Depending on substituents and solvents, one of the two forms prevails.[3c,32]

According to the ^{1}H,^{1}H COSY and ^{1}H,^{13}C HMQC spectral data, amino vinyl ketone **1** exists in the keto-enamine tautomeric form (Table 1), which agrees with the X-ray structural data. We assume that formation of complexes **2**−**4** with relatively high yield is explained by this fact. This is confirmed by the fact that a very low yield of the product is obtained in the reaction of $Ru_3(CO)_{12}$ with *N*-phenylsalicylidenimine,[20] which exists predominantly in the imine-enol form.

Most of amino vinyl ketones with secondary amino groups adopt a *cis*-conformation,[33] which is stabilized by intramolecular hydrogen bond. However, in a number of publications it was noticed that the conformation of the molecule is influenced by both substituents and solvent.[34a,b] A phenyl substituent at the nitrogen atom stabilizes the intramolecular hydrogen bond; therefore amino vinyl ketones with aromatic substituents are observed only in a *cis*-conformation, whereas amino vinyl ketones with methyl substituents (for example, 4-methylamino-3-butene-2-one) are present in solution in both *cis*- and *trans*-conformations.[34b] The methyl substituent at the carbon atom in α-position stabilizes the *trans*-conformation independently of other substituents. For a number of amino vinyl ketones a mixture of *cis*- and *trans*-conformers was observed in $(CD_3)_2SO$, a solvent that strongly binds the protons, while in $CDCl_3$ only *cis*-conformers were observed.[34a]

According to the ^{1}H NMR spectrum recorded at room temperature in $CDCl_3$, the protons of the olefin group in **1** are in *cis*-conformation ($^3J_{H-H}$ = 8.0 Hz, Table 1). The proton of the amino group and the proton of the carbon atom in *β*-position are in *s-trans*-conformation since the last one appears as a doublet of doublets with two spin−spin coupling constants $^3J_{H-H}$ = 8.0 and 12.4 Hz.

Replacement of a labile proton by an ion of a transition metal leads to the formation of a six-membered chelate cycle. In order for coordination of an amino vinyl ketone on a carbon atom at *β*-position to occur and a five-membered

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[31] Kwiatkowski, M.; Kwiatkowski, E.; Olechnowicz, A.; Ho, D. M.; Deutsch, E. *J. Chem. Soc., Dalton Trans.* **1990**, 2497.

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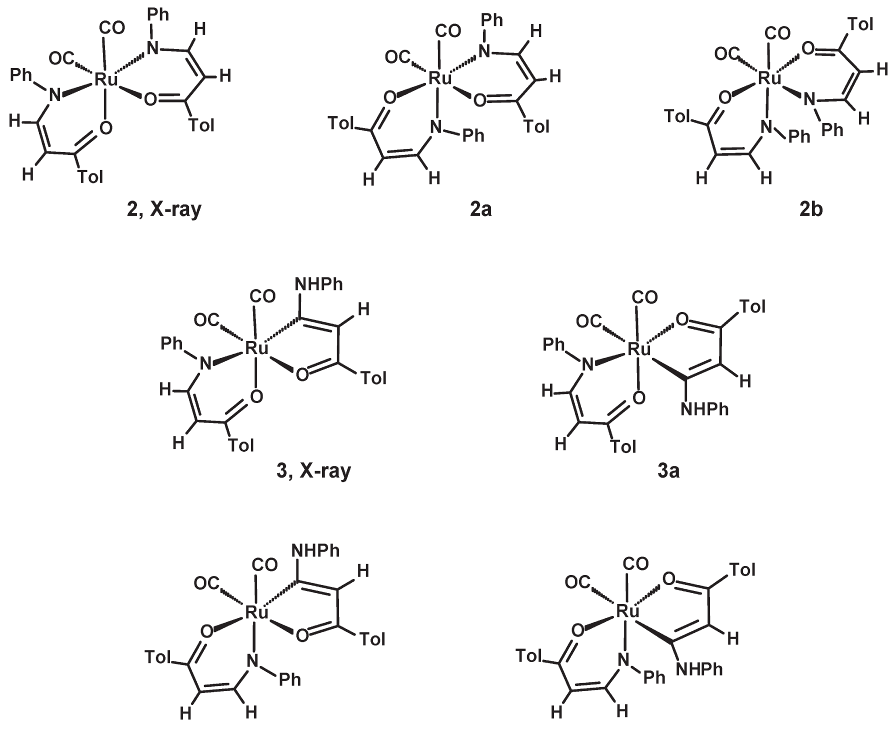
Scheme 2. Possible Stereoisomers for Complexes 2−4



2, X-ray **2a** **2b**

3, X-ray **3a**

4, X-ray **4a**

cycle to form, the spatial transformation of a molecule from *cis*- to *trans*-conformation is necessary.

Transformation of molecule **1** and C_β−H bond activation can occur as a result of ruthenium coordination to an oxygen atom or on heating of the reaction mixture.[35] To test the last assumption, we have recorded ^{1}H NMR spectra of **1** on heating from room temperature to 363 K. No changes indicating the presence of the *trans*-conformer were observed (see Experimental Section). Therefore, we believe that the transformation of molecule **1** with further C_β−H bond activation most likely results from coordination of ruthenium to an oxygen atom.

4. Isomerism of the Mononuclear Complexes. For the mononuclear complexes containing two azaoxaruthenacycles, there is a possibility of the formation of stereoisomers differing in the mutual orientation of ligands in the coordination sphere of the metal. It was noticed in a number of works that steric hindrance at nitrogen atoms makes the formation of stereoisomers with *cis*-arrangement of nitrogen less probable for both square-planar[3c] and octahedral ligand environments.[8] In structurally characterized octahedral ruthenium complexes with two azaoxaruthenacycles various mutual arrangements of ligands are observed: in complex (F_6-acen)Ru(PPh_3)$_2$ the cyclic ligand is located in an equatorial plane with the *trans*-orientation of oxygen and nitrogen atoms (*trans* O−N) and two thriphenylphosphine ligands in axial positions;[25] two complexes *cis*-Ru(salalen)-(CO)$_2$ are characterized by the *trans*-orientation of O−N, O−CO, and N−CO atoms;[2] cationic complex (hpNP)$_2$-Ru(CO)$_2$ is characterized by the *trans*-orientation of N−N and O−CO atoms.[23] In the complex [Ru(HOC(CF_3)=CHCH=NMe)$_3$] the relative arrangement of three chelate cycles is such that there is a *trans*-orientation of O−O, O−N, and N−N atoms.[3b] It is necessary to point out that all these complexes are obtained from salts and, hence, the mechanisms of their formation can differ significantly from the processes occurring in the thermal reaction of $Ru_3(CO)_{12}$ with **1**.

Among the reaction products of $Ru_3(CO)_{12}$ with **1**, only one complex with two azaoxaruthenacycles (**2**) in which the oxygen atoms are located in *trans*-positions to metalcarbonyl groups and the nitrogen atoms are in *trans*-position to each other has been isolated. For complex **2** it is possible to suggest the existence of two more stereoisomers (Scheme 2). The number of possible stereoisomers is limited to the *cis*-arrangement of metalcarbonyl ligands (taking into account the destabilizing effect of the *trans*-arrangement of the two metalcarbonyl groups). For example, in the complex (salalen)Ru(CO)$_2$ the necessity of *cis*-arrangement of the two metalcarbonyl groups leads to the distortion of the rigid organic molecule.[2]

In order to study which isomer (**2**, **2a**, and **2b**) would be energetically preferable, we have carried out the quantum chemical calculations of these three isomers at the PBE0/DGDZVP level of theory, using the Gaussian03 program.[36]

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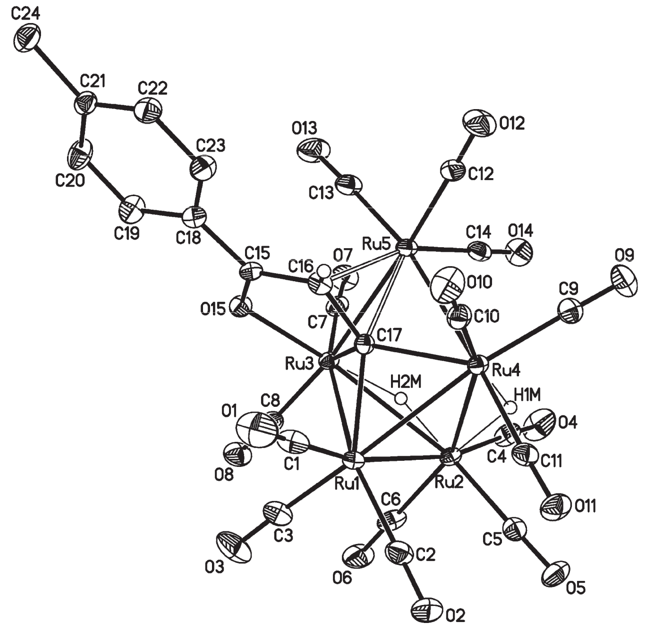

Figure 4. ORTEP drawing of the molecular structure of complex **5** with thermal ellipsoids at the 50% probability level (hydrogen atoms of the phenyl and tolyl substituents have been omitted for clarity).

The obtained results show that all isomers correspond to the stable conformations, which is also proved by frequency analysis. It was found that the experimentally observed isomer (complex **2**) corresponds to a global minimum, while isomers **2a** and **2b** appear to be sufficiently higher in energy by 3.3 and 5.4 kcal/mol (including ZPVE correction).

The calculations coincide with the *trans*-choice of ligands theory, according to which in the coordination sphere of a metal the "hardest" and "softest" ligands are located in *trans*-position.[37a−d]

According to the obtained data it is possible to suggest the following scheme of formation of complex **2**. After the formation of the first azaoxaruthenacycle, the conditions for addition of the second molecule of amino vinyl ketone **1** are created. Thus, the consecutive replacement of two metalcarbonyl groups occurs according to the *trans*-choice theory. The "hardest" oxygen atom attacks one of axial metalcarbonyl groups, as their mutual *trans*-influence is at a maximum. Chelation is completed with the coordination of a nitrogen atom in *trans*-position to the nitrogen atom of the first cycle, as a *trans*-arrangement of the oxygen atom and metalcarbonyl group from the point of view of the *trans*-choice is most favorable. The *trans*-arrangement of nitrogen atoms is probably also caused by steric repulsions, as mentioned earlier.[8]

For complexes with two different chelate metallacycles in the coordination sphere of the metal there is a possibility of the existence of four stereoisomers, two of which (complexes **3** and **4**) are isolated from the reaction. The absence of the isomers **3a** and **4a** (Scheme 2) among the reaction products is apparently caused by the destabilizing effect of the mutual *trans*-arrangement of CO and the carbon atom (the two "softest" ligands). This qualitative conclusion is also confirmed by quantum chemical calculations, showing that stereoisomer **3a** lies higher in energy, by 6.9 kcal/mol, than isomer **3**. At the same time, the difference in energy between **3** and **4** is only 0.6 kcal/mol, and both complexes are found among the reaction products. In spite of the fact that in **4** the less favorable arrangement of a nitrogen atom in *trans*-position to CO is observed, the total energy decreases, apparently, due to the energetically more favorable *trans*-arrangement of the O−C atoms, in comparison with the *trans*-arrangement of the N−C atoms in complex **3**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex 5

Ru(1)−Ru(2)	2.7759(4)	Ru(2)−C(6)	1.908(3)
Ru(1)−Ru(3)	2.8738(4)	Ru(3)−C(7)	1.880(3)
Ru(1)−Ru(4)	2.8337(4)	Ru(3)−C(8)	1.928(3)
Ru(2)−Ru(3)	2.9619(4)	Ru(3)−O(15)	2.107(2)
Ru(2)−Ru(4)	3.0337(4)	Ru(3)−C(17)	2.095(3)
Ru(3)−Ru(5)	2.8297(4)	Ru(4)−C(9)	1.930(3)
Ru(4)−Ru(5)	2.8455(4)	Ru(4)−C(10)	1.911(3)
Ru(2)−H(1M)	1.77	Ru(4)−C(11)	1.931(3)
Ru(2)−H(2M)	1.65	Ru(4)−C(17)	2.146(3)
Ru(4)−H(1M)	1.75	Ru(5)−C(12)	1.931(3)
Ru(3)−H(2M)	1.72	Ru(5)−C(13)	1.917(3)
Ru(1)−C(1)	1.925(4)	Ru(5)−C(14)	1.931(3)
Ru(1)−C(2)	1.918(3)	Ru(5)−C(16)	2.197(3)
Ru(1)−C(3)	1.895(3)	Ru(5)−C(17)	2.103(3)
Ru(1)−C(17)	2.113(3)	O(15)−C(15)	1.269(4)
Ru(2)−C(4)	1.923(4)	C(15)−C(16)	1.448(4)
Ru(2)−C(5)	1.898(3)	C(16)−C(17)	1.468(4)

Ru(2)−Ru(1)−Ru(4)	65.47(1)	Ru(1)−Ru(4)−Ru(5)	93.36(1)
Ru(2)−Ru(1)−Ru(3)	63.21(1)	Ru(1)−Ru(4)−Ru(2)	56.35(1)
Ru(4)−Ru(1)−Ru(3)	81.63(1)	Ru(5)−Ru(4)−Ru(2)	90.02(1)
Ru(1)−Ru(2)−Ru(3)	60.01(1)	Ru(3)−Ru(5)−Ru(4)	82.20(1)
Ru(1)−Ru(2)−Ru(4)	58.18(1)	C(15)−O(15)−Ru(3)	114.1(2)
Ru(3)−Ru(2)−Ru(4)	76.95(1)	O(15)−C(15)−C(16)	118.5(3)
Ru(5)−Ru(3)−Ru(1)	92.85(1)	C(15)−C(16)−C(17)	114.8(3)
Ru(5)−Ru(3)−Ru(2)	91.80(1)	C(16)−C(17)−Ru(3)	108.1(2)
Ru(1)−Ru(3)−Ru(2)	56.78(1)	C(17)−Ru(3)−O(15)	79.4(1)

The collected data (experimentally observed stereoisomers, their percentage in the reaction products, and the calculated data on their relative stability) allow establishing the following tendencies for complexes **2**−**4**. The oxygen atom of the carbonyl group of the ligand is the "hardest" ligand in comparison to the nitrogen atom of the amine group. The metalcarbonyl ligand and the carbon atom in the five-membered cycle with a partial furan structure are the "soft" ligands with comparable properties.

The formation of the complexes is controlled by both thermodynamic and kinetic conditions, including the sterical difficulties during the *cis*-arrangement of atoms with bulky substituents. So, in spite of the fact that according to calculations complex **4** is thermodynamically more stable than **3**, in the reaction the yield of complex **4** is 2.5 times less than the yield of complex **3**.

5. Polynuclear Complexes 5−**7.** Minor amounts of the three polynuclear complexes **5**−**7** were also obtained from the reaction of $Ru_3(CO)_{12}$ with **1**. In these complexes $Ru_3(CO)_{12}$ exhibits the ability to form cluster compounds.

According to the X-ray diffraction data (Figure 4, Table 5) the metal core of the pentanuclear complex **5** represents a butterfly framework with an additional ruthenium atom (Ru(5)) bridging the two wingtips (Ru(3) and Ru(4)). In complex 14 terminally bonded carbonyl ligands and two bridging hydrides are present. Complex **5** is the only reaction product, during formation of which the deamination of

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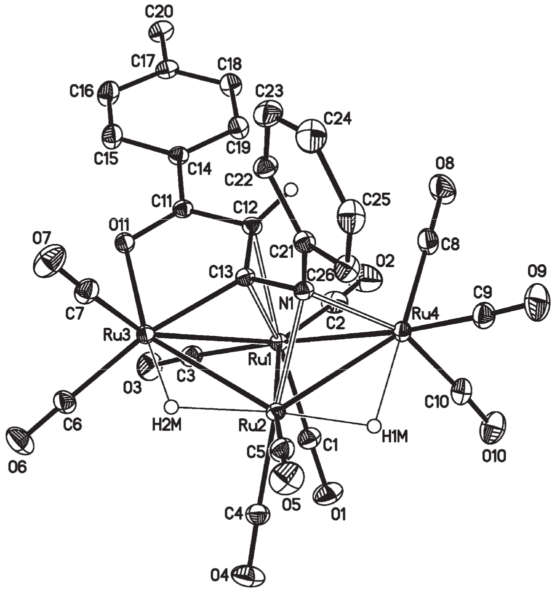

Figure 5. ORTEP drawing of the molecular structure of complex **6** with thermal ellipsoids at the 50% probability level (hydrogen atoms of the phenyl and tolyl substituents have been omitted for clarity).

amino vinyl ketone **1** is observed. The oxadiene fragment of the ligand chelates the Ru(3) atom, forming a five-membered oxaruthenacycle. The olefin group of the oxaruthenacycle participates in π-coordination with the Ru(5) atom. The formation of oxaruthenacycles of similar structure as a result of deamination of amino vinyl ketone has been observed by us earlier in the reaction of Ru$_3$(CO)$_{12}$ with 1-phenyl-3-morpholineprop-2-en-1-one.[14]

The main feature of the oxaruthenacycle in complex **5** consists in the unusual μ_4-coordination of the C(17) atom (the four Ru−C(17) distances are in the range 2.095(3)−2.146(3) Å). The organic ligand is bonded with four of five ruthenium atoms so that the wingtips of the butterfly are bridged only by one atom (C(17)).

In complex **5** the seven bonding Ru−Ru distances are present and their values lie in the range 2.7759(4)−3.0337(4) Å, with the shortest distance between Ru(1) and Ru(2) atoms at the hinge of the butterfly. The elongation of the Ru(2)−Ru(3) and Ru(2)−Ru(4) distances is possibly caused by the loosening effect of the bridge hydride ligands, the positions of which are unambiguously established by X-ray diffraction.

Considering the organic ligand in complex **5** as a six-electron donor and taking into account the presence of two hydride ligands and 14 carbonyl ligands, the total number of cluster valence electrons (CVE) is equal to 76, which corresponds to a wingtip-bridged butterfly skeleton.[38] The dihedral angle between the wing planes of the butterfly framework in complex **5** is equal to 92.9°, and the Ru(3)···Ru(4) distance between wingtip atoms is 3.731 Å.

Table 6. Selected Bond Length (Å) and Angles (deg) for Complex 6

Ru(1)−Ru(2)	2.8819(1)	Ru(2)−N(1)	2.1340(9)
Ru(1)−Ru(3)	2.9201(1)	Ru(2)···C(13)	2.524(1)
Ru(1)−Ru(4)	2.8026(1)	Ru(3)−C(6)	1.969(1)
Ru(2)−Ru(3)	2.7867(1)	Ru(3)−C(7)	1.855(1)
Ru(2)−Ru(4)	2.7431(1)	Ru(3)−O(11)	2.1317(8)
Ru(2)−H(1M)	1.72(2)	Ru(3)−C(13)	2.018(1)
Ru(2)−H(2M)	1.79(2)	Ru(4)−C(8)	1.901(1)
Ru(3)−H(2M)	1.66(2)	Ru(4)−C(9)	1.948(1)
Ru(4)−H(1M)	1.85(2)	Ru(4)−C(10)	1.910(1)
Ru(1)−C(1)	1.899(1)	Ru(4)−N(1)	2.1180(9)
Ru(1)−C(2)	1.934(1)	O(11)−C(11)	1.267(1)
Ru(1)−C(3)	1.936(1)	C(11)−C(12)	1.455(1)
Ru(1)−C(12)	2.278(1)	C(12)−C(13)	1.429(1)
Ru(1)−C(13)	2.231(1)	N(1)−C(13)	1.418(1)
Ru(2)−C(4)	1.887(1)	N(1)−C(21)	1.434(1)
Ru(2)−C(5)	1.865(1)		

Ru(2)−Ru(1)−Ru(3)	57.405(3)	O(11)−Ru(3)−Ru(2)	137.22(2)
Ru(4)−Ru(1)−Ru(2)	57.685(3)	C(7)−Ru(3)−Ru(1)	151.19(4)
Ru(4)−Ru(1)−Ru(3)	103.612(4)	C(6)−Ru(3)−Ru(1)	113.98(4)
Ru(3)−Ru(2)−Ru(1)	61.987(3)	O(11)−Ru(3)−Ru(1)	81.89(2)
Ru(4)−Ru(2)−Ru(1)	59.707(3)	C(7)−Ru(3)−H(2M)	88.9(8)
Ru(4)−Ru(2)−Ru(3)	108.866(4)	C(6)−Ru(3)−H(2M)	85.7(8)
Ru(2)−Ru(3)−Ru(1)	60.608(3)	C(13)−Ru(3)−H(2M)	95.0(8)
Ru(2)−Ru(4)−Ru(1)	62.609(3)	O(11)−Ru(3)−H(2M)	174.7(8)
C(13)−Ru(3)−O(11)	79.70(4)	C(13)−N(1)−C(21)	117.79(8)
C(11)−O(11)−Ru(3)	112.00(7)	C(13)−N(1)−Ru(4)	109.08(6)
O(11)−C(11)−C(12)	119.07(9)	C(21)−N(1)−Ru(4)	125.17(7)
C(13)−C(12)−C(11)	113.86(9)	C(13)−N(1)−Ru(2)	88.16(6)
C(12)−C(13)−Ru(3)	111.49(7)	C(21)−N(1)−Ru(2)	125.90(7)
N(1)−C(13)−C(12)	124.62(9)	Ru(4)−N(1)−Ru(2)	80.35(3)
N(1)−C(13)−Ru(3)	123.82(7)		

It is interesting to note that a similar pentanuclear cluster, Ru$_5$(CO)$_{14}$(μ-H)$_2$(μ_4-η^1:η^1:η^2:η^2-CCHC(CH$_3$)=O), was synthesized in the reaction of Ru$_3$(CO)$_{12}$ with but-3-yn-2-ol.[39] Despite the difference in the substituents at the carbon atoms, the structure of the cluster is completely identical to that of **5**. It was suggested[39] that but-3-yn-2-ol is oxidized to the corresponding ketone during one of the reaction steps. Therefore, the mechanism of the formation of both complexes can be similar.

The IR spectrum of **5** reveals eight absorption bands of different intensities in the region of stretching vibrations of the terminal carbonyl ligands (Table 1). In ^{1}H NMR spectrum of complex **5** the signal of the proton of the oxaruthenacycle is observed at 5.51 ppm, which is characteristic for the olefin group being σ,π-coordinated to two metal atoms.[20] In addition, there are two high-field doublets at −21.08 and −27.08 ppm ($^2J_{H-H}$ = 1.9 Hz), which correspond to two bridged hydrides. In the ^{13}C NMR spectrum we have found a signal at 323.95 ppm, which can be attributed to the carbido carbon C(17). Similar signals were observed for such μ_4-carbido atoms in polynuclear ruthenium clusters.[39,40] A singlet at 214.14 ppm can be attributed to the carbon atom of the ketone group, C(15). The signals of the metalcarbonyl groups are located at 188.96−199.18 ppm.

According to the X-ray diffraction data the metal framework of the tetranuclear complex **6** has a butterfly structure (Figure 5, Table 6). The oxadiene fragment of the organic ligand chelates the wingtip atom Ru(3) with the formation of a five-membered oxaruthenacycle. The olefin group of the oxaruthenacycle is π-coordinated with the Ru(1) atom in the hinge position (corresponding bond lengths are Ru(1)−C(12) 2.278(1) Å and Ru(1)−C(13) 2.231(1) Å). Such a binuclear fragment with a η^3-coordinated oxaruthenacycle

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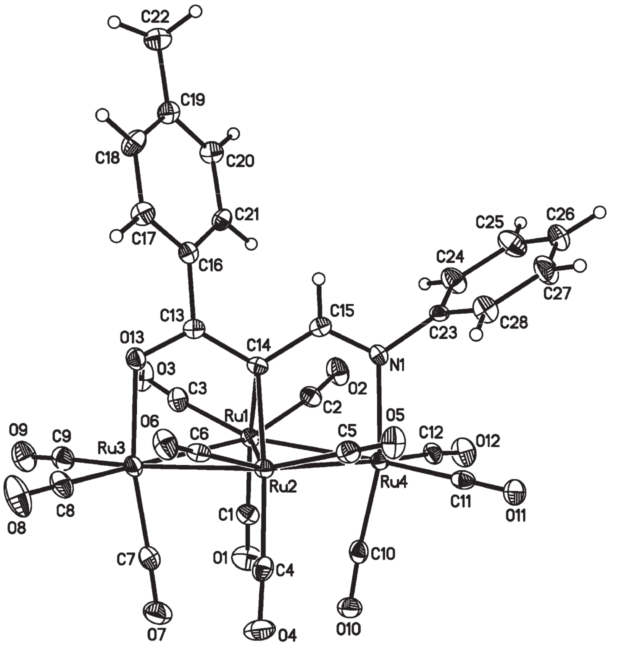

Figure 6. ORTEP drawing of the molecular structure of complex **7** with thermal ellipsoids at the 50% probability level.

Table 7. Selected Bond Length (Å) and Angles (deg) for Complex 7

Ru(1)−Ru(2)	2.7007(5)	Ru(3)−C(7)	1.885(4)
Ru(1)−Ru(3)	2.8124(4)	Ru(3)−C(8)	1.924(4)
Ru(1)−Ru(4)	2.8154(4)	Ru(3)−C(9)	1.914(4)
Ru(2)−Ru(3)	2.7458(4)	Ru(3)−O(13)	2.121(3)
Ru(2)−Ru(4)	2.7796(4)	Ru(4)−C(10)	1.887(4)
Ru(1)−C(1)	1.908(4)	Ru(4)−C(11)	1.919(4)
Ru(1)−C(2)	1.926(4)	Ru(4)−C(12)	1.906(4)
Ru(1)−C(3)	1.917(4)	Ru(4)−N(1)	2.135(3)
Ru(1)−C(14)	2.207(4)	O(13)−C(13)	1.269(4)
Ru(2)−C(4)	1.914(4)	N(1)−C(15)	1.292(4)
Ru(2)−C(5)	1.919(4)	N(1)−C(23)	1.445(4)
Ru(2)−C(6)	1.904(4)	C(13)−C(14)	1.434(5)
Ru(2)−C(14)	2.199(3)	C(14)−C(15)	1.441(5)
Ru(2)−Ru(1)−Ru(3)	59.70(1)	C(13)−O(13)−Ru(3)	117.5(2)
Ru(2)−Ru(1)−Ru(4)	60.48(1)	C(15)−N(1)−C(23)	118.9(3)
Ru(3)−Ru(1)−Ru(4)	119.47(1)	C(15)−N(1)−Ru(4)	117.9(2)
Ru(1)−Ru(2)−Ru(3)	62.17(1)	C(23)−N(1)−Ru(4)	123.2(2)
Ru(1)−Ru(2)−Ru(4)	61.81(1)	O(13)−C(13)−C(14)	122.5(3)
Ru(3)−Ru(2)−Ru(4)	123.21(2)	C(13)−C(14)−C(15)	117.6(3)
Ru(2)−Ru(3)−Ru(1)	58.13(1)	C(13)−C(14)−Ru(2)	116.9(2)
Ru(2)−Ru(4)−Ru(1)	57.72(1)	C(15)−C(14)−Ru(2)	114.1(2)
O(2)−C(2)−Ru(1)	170.7(4)	C(13)−C(14)−Ru(1)	110.0(2)
O(3)−C(3)−Ru(1)	170.7(3)	C(15)−C(14)−Ru(1)	115.6(2)
O(5)−C(5)−Ru(2)	168.0(3)	Ru(2)−C(14)−Ru(1)	75.6(1)
O(6)−C(6)−Ru(2)	169.9(3)	N(1)−C(15)−C(14)	121.7(3)

is typical for the complexes obtained in the reactions of $Ru_3(CO)_{12}$ with oxadienes.[20]

It should be noted that C(13) and Ru(2) atoms in complex **6** are brought together to a distance of 2.524(1) Å; however from our point of view this is rather a forced contact than an attractive interaction. This is confirmed by the ^{13}C NMR spectrum of the complex. A signal attributed to the C(13) atom is located at 162.24 ppm. In binuclear complex $Ru_2(CO)_6(\mu\text{-}H)(O{=}C(Tol)CH{=}\mathit{C}Ph)$, also containing a η^3-coordinated oxaruthenacycle, the corresponding carbon atom has a closely located signal at 152.33 ppm.[20]

The deprotonated nitrogen atom bridges Ru(2) and Ru(4) atoms in an almost symmetrical manner (Ru(2)−N(1) 2.134(1) and Ru(4)−N(1) 2.118(1) Å). As a result, the C(13)−N(1) bond is considerably elongated (1.418(1) Å), in comparison to the similar bond in mononuclear complexes **3** and **4**. Thus, in complex **6** the nitrogen atom is out of conjugation with the oxadiene fragment, which is also confirmed by the orientation of the phenyl substituent (torsion angle C(12)−C(13)−N(1)−C(21) is 90.0°). As a result, the olefin group participates in π-coordination with the ruthenium atom. This coordination is not typical for amino vinyl ketones in which the olefin group is deactivated by the donor influence of the amino group.

It is surprising that in complex **6** among five bonding Ru−Ru distances the shortest ones are Ru(2)−Ru(3) (2.7867(1) Å) and Ru(2)−Ru(4) (2.7431(1) Å), along which the μ-hydride ligands were unambiguously localized by the X-ray analysis. Such shortening of these Ru−Ru bonds is in contrast to the well-known loosening effect of the bridging hydrides. Possibly, in complex **6** this effect is decreased by the tightening action of the organic ligand that bridges all four ruthenium atoms and its coordination is formally described as μ_4-η^1:η^1:η^2:η^2. Unlike **5**, in complex **6**, the wingtip ruthenium atoms are bridged by the two-atom C−N fragment of the ligand. The dihedral angle between the wing planes of the butterfly framework in complex **6** is equal to 137.3°, and the Ru(3)···Ru(4) distance between the wingtip atoms is 4.498 Å.

One of the 10 metalcarbonyl groups considerably deviates from a linear structure (angle O(3)−C(3)−Ru(1) is 168.6(1)°), and apparently it participates in the semibridging interaction with the Ru(3) atom (Ru(3)···C(3) distance is 2.849 Å).

Considering the organic ligand in complex **6** as an eight-electron donor and taking into account the presence of two hydride ligands and 10 metalcarbonyl ligands, the total number of CVEs is equal to 62, which is in agreement with a butterfly skeleton.

The spectral data for complex **6** are in a good agreement with the X-ray data. In the ^{1}H NMR spectra the signals of the hydrides are present as two doublets at −14.44 and −14.02 ppm ($^2J_{H-H}$ = 2.3 Hz).

According to X-ray data the metal core of complex **7** has a flattened butterfly geometry (Figure 6, Table 7). Unlike all other complexes, the organic ligand in **7** has an unusual open-chain structure in the keto-imine tautomeric form. The bond lengths O(13)−C(13) 1.269(4) and N(1)−C(15) 1.292(4) Å are close to those for the double bonds, but slightly elongated due to the coordination with the metal atom. The nitrogen and oxygen atoms are bonded with the wingtip ruthenium atoms and the sp^3-hybridized C(14) atom is coordinated by two σ-bonds with the ruthenium atoms at the hinge of the butterfly framework. The imine nature of the ligand is confirmed by the ^{1}H NMR spectrum of the complex. A signal attributed to the proton at the C(15) atom is located at 9.90 ppm, which corresponds to a proton at the double CH=N bond.

The wingtip ruthenium atoms are bridged by the five-atom fragment O(13)C(13)C(14)C(15)N(1). Such coordination not only flattens the geometry of the butterfly but even leads to the opening of the wings of the butterfly by almost 10° outward, in the opposite direction from the coordinated ligand. The dihedral angle between the wing planes of the butterfly framework in complex **7** is equal to 170.3°, and the Ru(3)···Ru(4) distance between the wingtip atoms is 4.861 Å.

The bridging fragment (O(13)C(13)C(14)C(15)N(1)) slightly deviates from a planar structure (the maximum deviation from an average plane for these five atoms is 0.067 Å). The plane of this fragment is perpendicular to the average plane of the quasiplanar metal framework (the dihedral angle between these planes is 84.5°). The asymmetry of the organic ligand does not affect the general symmetry of the complex. It is manifested in the equalization of the Ru(3)−O(13) (2.121(3) Å) and Ru(4)−N(1) (2.135(3) Å) distances, as well as in the positions of the signals of the carbon atoms C(13) and C(15) in the ^{13}C NMR spectrum (at 199.20 (C=O) and 196.23 (*C*H=N) ppm, respectively). It is interesting to notice that the general symmetry of the complex is observed also in the equivalence of the Ru−CO distances with the metalcarbonyl groups located in *trans*-positions to the oxygen and nitrogen atoms of the organic ligand (Ru(3)−C(7) 1.885(4) and Ru(4)−C(10) 1.887(4) Å, respectively). This also points to an almost equal *trans*-influence of the carbonyl and the imine groups.

The equatorial metalcarbonyl groups at the ruthenium atoms at the hinge of the butterfly are semibridging with respect to the wingtip ruthenium atoms (the deviation from a linear structure for these metalcarbonyl groups is 10° on average). All Ru−Ru distances in **7** are considerably shortened in comparison to the complexes **5** and **6** and are in a narrow interval of values (2.7007(5)−2.8154(4) Å).

In the reaction of $Ru_3(CO)_{12}$ with **1** a considerable amount of tetrahedral hydrides $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ is formed. Formally, the M_4 species in which the metal framework has a butterfly configuration derive from the tetrahedral metal clusters by the cleavage of one metal−metal bond.[41] Therefore one can assume that these tetrahedral hydrides are the precursors for complexes **5**−**7**. In order to prove this assumption, we have carried out separate reactions in which the tetrahedral hydrides have been boiled in heptane with an excess of ligand **1** under the same conditions as the title reaction. It was shown that tetrahedral hydrides $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ do not react with **1**.[42] This fact confirms that exactly $Ru_3(CO)_{12}$ is the precursor for complexes **5**−**7**.

The polynuclear clusters **5**−**7** show unprecedented variation of the butterfly geometry; namely, the dihedral angle between the wings varies from 93° in **5** to 170° in **7**. It has been shown that the electron donation from the ligands can play a major role in influencing the butterfly geometry with higher electron counts (64 CVE instead of 62 CVE for the electron-precise butterfly clusters), favoring larger dihedral angles and Ru−Ru bond elongation.[43a,b] Besides electron-rich butterfly clusters, several electron-precise flattened butterfly clusters were also observed.[43b−e] All these complexes as well as complex **7** are characterized by the shortened Ru−Ru bond lengths. Whereas the complexes **5**−**7** are the electron-precise clusters, it can be noted that the butterfly geometry does not depend on the electronic properties of the ligands. Such considerable changes in the values of the dihedral angle between the wings are caused, first of all, by the length of the organic chain bridging the wingtip atoms (one atom in **5**, two-atom fragment in **6**, and five-atom fragment in **7**). The elongation of the chain connecting the wingtip atoms leads to the increase in the dihedral angle between the "wing" planes of the butterfly framework. It indicates the lability of the Ru_4 metal core, which is capable of adjusting to both the electronic and spatial peculiarities of the organic molecule.

Conclusion

Unlike iron carbonyls, $Ru_3(CO)_{12}$ exhibits activity in reactions with amino vinyl ketones. This is explained by the ability of ruthenium to form metal chelates due to the preferable coordination with the electron lone pairs of the heteroatoms, instead of the π-systems of the olefin and carbonyl groups, which is most frequently observed for iron. As a result, the main products of the reaction of $Ru_3(CO)_{12}$ with **1** are the mononuclear chelate complexes **2**−**4**. Along with the six-membered chelate cycles the five-membered ones are formed. This points to an alternative coordination of ruthenium to N−H and C_β−H bonds. Earlier the formation of the five-membered chelate cycles in the reactions of amino vinyl ketones with transition metals was not observed. Among the products of the reaction only complex **7**, with open-chain coordination of the ligand, is isolated. This complex is formed as a result of the N−H and C_α−H bond activation. The reaction is accompanied by the deprotonation of the ligand and requires the presence of a hydrogen acceptor in the reaction mixture.

All possible tautomeric forms of amino vinyl ketone **1** are realized as a result of the coordination with the metal atoms. In the organic ligand of the mononuclear chelate complexes **2**−**4**, the delocalized system is observed with the main contribution of the imine-enol form. In the butterfly clusters **6** and **7**, the ligand is present in the keto-enamine and the keto-imine forms, respectively.

Comparing the complexes and their ratio in the reaction products, it is possible to order the relative reactivity of the functional groups of 1-(4-tolyl)-3-phenylaminoprop-2-en-1-one in the conditions of the thermal reaction with $Ru_3(CO)_{12}$ as follows: O: > N−H > C−H > N:, C=C.

Unlike earlier studied amino vinyl ketone with tertiary amino group (1-phenyl-2-methyl-3-morpholinoprop-2-en-1-one),[14] the deamination is not a characteristic feature for the amino vinyl ketone **1**, with a secondary amino group. The deamination of the ligand is observed only in one of the minor products of the reaction (complex **5**). Further study of the influence of the substituents in β-amino vinyl ketones in the course of the thermal reactions with $Ru_3(CO)_{12}$ and of the structure of the forming products is in progress.

Experimental Section

All reactions were carried out in Schlenk equipment under an atmosphere of dry argon using standard Schlenk techniques.

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(42) A mixture of $H_4Ru_4(CO)_{12}$ and **1** in heptane (50 mL) was refluxed for 5 h. The course of the reaction was monitored by IR spectra in the region of valence vibrations of the metal carbonyl groups. No changes in the IR spectrum were detected. A mixture of $H_2Ru_4(CO)_{13}$ and **1** in heptane (50 mL) was refluxed for 1 h. After 30 min of heating in the IR spectrum the signals corresponding to $H_4Ru_4(CO)_{12}$ were fixed. After 60 min of heating in solution only $H_4Ru_4(CO)_{12}$ was detected, and any further changes in the IR spectrum were not observed.

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Table 8. Crystal Data, Data Collection, and Structure Refinement Parameters for Complexes 2−7

	2	**3**	**“4 + 1”**
formula	$C_{34}H_{28}N_2O_4Ru$	$C_{34}H_{28}N_2O_4Ru$	$C_{34}H_{28}N_2O_4Ru_4 \cdot C_{16}H_{15}NO$
molecular weight	629.65	629.65	866.94
cryst color, habit	yellow plate	yellow prism	yellow prism
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	9.749(2)	11.294(2)	10.256(6)
b, Å	10.453(2)	14.256(2)	27.132(15)
c, Å	14.587(3)	18.749(3)	15.157(9)
α, deg	81.119(4)	88.756(4)	90
β, deg	78.646(4)	82.519(4)	91.619(8)
γ, deg	78.244(4)	77.315(4)	90
V, Å^3	1416.8(5)	2919.9(8)	4216(4)
Z	2	4	4
d(calc), g cm^{-3}	1.476	1.432	1.366
θ_{max}, deg	28.0	24.0	24.0
μ (Mo Kα, λ = 0.71073 Å), cm^{-1}	5.95	5.78	4.23
transmn factors, T_{min}/T_{max}	0.825/0.971	0.878/0.982	0.830/0.959
no. unique reflns (R_{int})	6788 (0.0564)	9129 (0.0862)	6569 (0.1608)
no. obsd reflns ($I > 2\sigma(I)$)	5174	4274	2734
R_1 (on F for obsd reflns)	0.0423	0.0580	0.0749
wR_2 (on F^2 for all reflns)	0.0853	0.1164	0.1537
GOF	0.979	0.873	0.834
largest diff peak/hole, e Å^{-3}	0.605/-0.879	0.816/-0.484	0.547/-0.630

	5	**6**	**7**
formula	$C_{24}H_{10}O_{15}Ru_5$	$C_{26}H_{15}NO_{11}Ru_4$	$C_{28}H_{13}NO_{13}Ru_4 \cdot 0.5(C_6H_{14})$
molecular weight	1043.67	921.67	1018.76
cryst color, habit	orange prism	red prism	brown plate
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.9357(8)	9.1494(2)	11.3344(6)
b, Å	10.210(1)	12.2864(3)	12.2030(7)
c, Å	16.755(2)	13.4511(3)	14.060(1)
α, deg	99.856(2)	104.050(1)	105.416(1)
β, deg	98.711(2)	91.887(1)	95.563(1)
γ, deg	92.187(2)	91.709(1)	111.685(1)
V, Å^3	1485.4(2)	1464.93(6)	1700.2(2)
Z	2	2	2
d(calc), g cm^{-3}	2.334	2.089	1.990
θ_{max}, deg	30.0	43.0	30.0
μ(Mo Kα, λ = 0.71073 Å), cm^{-1}	25.54	20.81	18.08
transmn factors, T_{min}/T_{max}	0.588/0.862	0.653/0.851	0.782/0.948
no. unique reflns (R_{int})	8647 (0.0285)	21483 (0.0354)	9876 (0.0567)
no. obsd reflns ($I > 2\sigma(I)$)	7105	17869	7054
R_1 (on F for obsd reflns)	0.0290	0.0247	0.0371
wR_2 (on F^2 for all reflns)	0.0666	0. 0540	0.0814
GOF	1.022	1.020	0.990
largest diff peak/hole, e Å^{-3}	2.077/−0.838	1.372/−1.040	1.188/−0.997

All solvents were dried according to standard procedures. Column chromatography was performed with Aldrich silica gel (70−230 mesh). Amino vinyl ketone **1** was prepared by a published method.[44] Elemental analyses were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS. The IR spectra were recorded in solution on a Specord 75-IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker Avance-400 spectrometer (400.13 and 100.61 MHz, respectively) and Avance-600 spectrometer (600.22 and 150.93 MHz, respectively). The ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual protons in the deuterated solvents ($CDCl_3$, 7.25 ppm; C_6D_6, 7.26 ppm; all vs Me_4Si). The ^{1}H and $^{13}C\{^1H\}$ NMR and 2D experiments (COSY for **1** and HMQC for **1** and **7**) were performed at 298 K using standard pulse sequences from the Bruker library.

Preparation of Complexes 2−7 from $Ru_3(CO)_{12}$ and 1. A mixture of $Ru_3(CO)_{12}$ (178 mg, 0.28 mmol) and **1** (200 mg, 0.84 mmol) flushed with argon was added in 150 mL of heptane, and the resulting suspension was refluxed for 5 h. After cooling to 20 °C, the reaction mixture was filtered, partly concentrated, and then treated by column chromatography on silica gel. Elution with a hexane yielded $H_4Ru_4(CO)_{12}$ (30 mg, 15.4%), $Ru_3(CO)_{12}$ (10 mg), and $H_2Ru_4(CO)_{13}$ (14 mg, 6.9%), all of which were identified by IR spectroscopy;[45] complexes **5** (13.5 mg, 4.9%), **6** (10.2 mg, 4.2%), and **7** (10.0 mg, 3.8%) were separated next. These were recrystallized from *n*-hexane, affording analytically pure samples **5**−**7**, which were characterized by analytical and spectral data (Table 1). **5**: Anal. Calcd for $Ru_5C_{24}H_{10}O_{15}$: C, 27.20; H, 0.99. Found: C, 27.35; H, 1.03. **6**: Anal. Calcd for $Ru_4C_{26}H_{15}NO_{11}$: C, 34.15; H, 1.59. Found: C, 34.30; H, 1.65. **7**: Anal. Calcd for $Ru_4C_{28}H_{13}NO_{13}$: C, 34.47; H, 1.34. Found: C, 34.60; H, 1.42.

Further elution with a 1:1 *n*-hexane/benzene mixture yielded 102 mg of a mixture of the complexes **2**−**4**. The obtained 102 mg of the mixture **2**−**4** was separated by repeated column chromatography on silica gel (eluent benzene) to give pure fractions of complex **2** (49.6 mg, 29.9%), **3** (16.5 mg, 10.0%), and **4** (6.6 mg, 4.0%). The NMR and IR data for complexes **2**−**7** are given in Table 1. **2**: Anal. Calcd for $RuC_{34}H_{28}N_2O_4$: C, 64.86; H, 4.45; N,

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4.45. Found: C, 64.73; H, 4.42; N, 4.41. **3**: Anal. Calcd for $RuC_{34}H_{28}N_2O_4$: C, 64.86; H, 4.45; N, 4.45. Found: C, 64.62; H, 4.57; N, 4.38. **4**: Anal. Calcd for $RuC_{34}H_{28}N_2O_4$: C, 64.86; H, 4.45; N, 4.45. Found: C, 64.71; H, 4.41; N, 4.35. In all cases, crystals suitable for X-ray analysis were obtained by slow crystallization of **2**−**7** from *n*-hexane.

High-Temperature ^{1}H NMR Spectra of 1. High-temperature ^{1}H NMR spectra of **1** were obtained with a Bruker Avance-600 spectrometer at 323, 343, and 363 K in nonane (internal standard DMSO-D_6). The presence of the *trans*-conformation of **1** at 363 K was not observed. The spin−spin coupling constant between the amino group proton and the proton at the β-carbon atom, $^3J_{H-H} = 12.0$ (at 293 K) and 11.4 Hz (at 363 K), shows that at 363 K the intramolecular hydrogen bond is not broken. ^{1}H NMR of **1** (nonane, 293 K): 2.28 (s, 3H, Me); 5.85 (d, 1H, C*H*=CH, $^3J_{H-H} = 8.0$); 6.86 (t, 1H, *p*-Ph, $^3J_{H-H} = 7.3$); 6.91 (d, 2H, *o*-Ph, $^3J_{H-H} = 8.0$); 7.06 (d, 2H, Tol, $^3J_{H-H} = 8.2$); 7.14 (dd, 2H, *m*-Ph, $^3J_{H-H} = 7.3$, 8.0); 7.27 (dd, 1H, NH-C*H*=CH, $^3J_{H-H} = 8.0$, 12.0); 7.75(d, 2H, Tol, $^3J_{H-H} = 8.2$); 12.33 (d, 1H, NH, $^3J_{H-H} = 12.0$). ^{1}H NMR of **1** (nonane, 363 K): 2.33 (s, 3H, Me); 5.88 (d, 1H, C*H* = CH, $^3J_{H-H} = 8.0$); 6.91 (t, 1H, *p*-Ph, $^3J_{H-H} = 7.3$); 6.96 (d, 2H, *o*-Ph, $^3J_{H-H} = 8.0$); 7.11 (d, 2H, Tol, $^3J_{H-H} = 8.2$); 7.20 (dd, 2H, *m*-Ph, $^3J_{H-H} = 7.3$, 8.0); 7.29 (dd, 1H, NH-C*H*=CH, $^3J_{H-H} = 8.0$, 11.4); 7.79 (d, 2H, Tol, $^3J_{H-H} = 8.2$); 12.25 (d, 1H, NH, $^3J_{H-H} = 11.4$).

X-ray Diffraction Study of 2−7. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, ω-scan technique, $T = 100(2)$ K). The APEX II software[46] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling, and absorption correction, and SHELXTL[47] 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 anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of hydride ligands in structures **5** and **6** were located in difference Fourier synthesis. The rest of the hydrogen atoms in the structures **2**−**7** were placed geometrically and included in the structure factor calculations in the riding motion approximation. The principal experimental and crystallographic parameters are presented in Table 8.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths and angles for **2**−**7** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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