Unusual rearrangement of the $Ru_3(\mu\text{-}CO)_2(CO)_6\{\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{:}\eta^4\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ complex containing an open triruthenium framework to the Ru_3-triangular cluster $Ru_3(CO)_8\{\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{:}\eta^2\text{-}C_4Ph_2(CH{=}CHPh)_2\}$. Reactions of $Ru_3(CO)_8\{\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{:}\eta^2\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ with PPh_3, $P(OPr^i)_3$, CO, and the crystal structure of $Ru_3(CO)_8(PPh_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{-}C_4Ph_2(CH{=}CHPh)_2\}$

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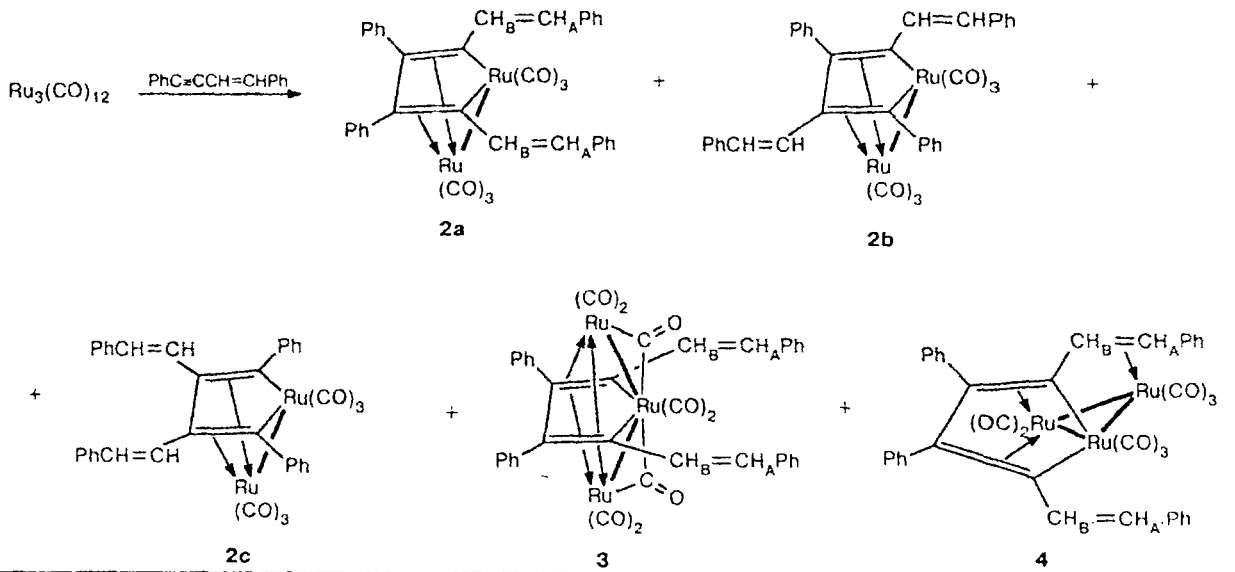
Complex $Ru_3(\mu\text{-}CO)_2(CO)_6\{\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{:}\eta^4\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ containing an open triruthenium framework undergoes rearrangement to the Ru_3-triangular $Ru_3(CO)_8\{\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{:}\eta^2\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ cluster when heated in refluxing hexane. Reactions of the latter complex with PPh_3, $P(OPr^i)_3$, and CO were studied. The structure of one of the reaction products, the $Ru_3(CO)_8(PPh_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ cluster, was established by X-ray structural analysis.

Key words: ruthenium, clusters, alkyne derivatives, rearrangement; Ru_3-triangular clusters, molecular and crystal structure.

Recently,[1] we reported the reaction of $Ru_3(CO)_{12}$ with 1,4-diphenylbut-1-en-3-yne (**1**). Yellow isomeric binuclear complexes of composition $Ru_2(CO)_6\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**2a—c**) as well as orange $Ru_3(\mu\text{-}CO)_2(CO)_6\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**3**) and brown $Ru_3(CO)_8\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**4**) trinuclear clusters are formed in the reaction of ruthenium carbonyl with excess enyne **1** in refluxing hexane (Scheme 1).

Scheme 1



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All the products characterized contain the ruthenacyclopentadiene moiety whose formation involves coupling of the alkyne fragments of the two enyne **1** molecules, which is a typical reaction observed during the conversion of alkynes under the action of carbonyls of the iron subgroup metals.[2] The brown cluster **4** has a rather unusual structure. As was shown by the X-ray study of cluster **4**,[1] the organic ligand obtained by the "head-to-head" coupling of the two enyne molecules forms two σ-bonds with one of the Ru atoms; the diene system of ruthenacyclopentadiene thus formed is π-coordinated on the second Ru atom, while the third metal atom appears to be π-coordinated by one of the alkenyl groups of the enyne dimer. It was of interest to establish the pathways resulting in the formation of cluster **4** and to study its reactivity.

In this work we have shown that cluster **4** is obtained as a result of thermally induced rearrangement of the orange complex **3**. It was also established that compound **4** adds PPh_3, $P(OPr^i)_3$, and CO under mild conditions, which is accompanied by displacement of the alkenyl ligand out of the coordination sphere of the Ru atom.

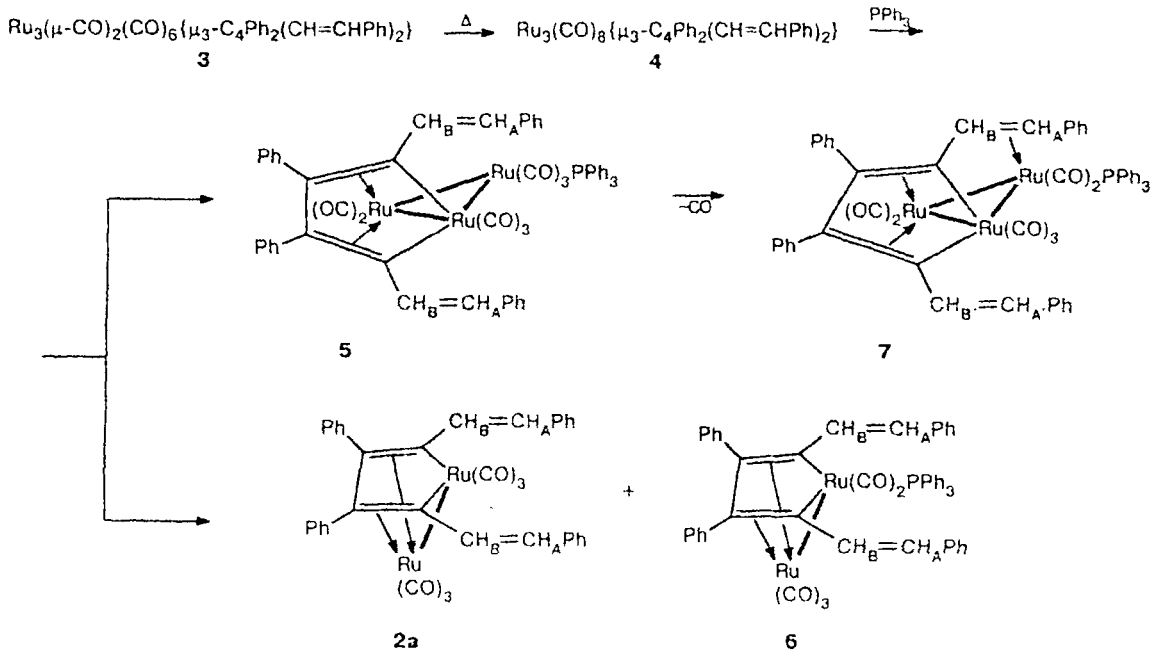
Results and Discussion

In our studies of the pathways of the formation of cluster **4** and its chemical properties we have established that compound **4** is obtained in good yield when isomeric orange complex **3** is heated in refluxing hexane. In this case, the binuclear complex **2a**, a fragmentation product of the trinuclear cluster, is formed in low yield (Scheme 2).

As is known, there are two types of alkyne derivatives of composition $M_3(CO)_8(RC_2R)_2$ in the series of trinuclear iron and ruthenium clusters: the violet (M = Fe, Ru)[3–5] and black (M = Fe)[3] or yellowish-orange (M = Ru).[4,6,7] The derivatives of the first type contain two 2σ,π-coordinated alkyne ligands situated on the opposite sides of the plane of the triangle formed by metal atoms. When heated, these derivatives are converted into isomeric black (M = Fe) or yellowish-orange (M = Ru) complexes. One of the M—M bonds in these clusters is cleaved similarly to that in complex **3** while two alkyne ligands are coupled with the formation of a metallacyclopentadiene moiety. In addition, two of the eight carbonyl ligands are bridging ligands. The isomerization processes mentioned above occur in refluxing benzene. However, there is no information in the literature on further conversion of orange complexes into clusters containing a newly formed Ru_3 triangle, as is observed in the **3** → **4** isomerization. As can be seen, the presence of an alkenyl substituent in the metallacyclopentadiene ring of cluster **3** provides a way for the third isomer of complexes of composition $M_3(CO)_8(RC_2R)_2$ to exist, of the brown complex **4** type.

Although we have shown that the orange complex **3** is the precursor of cluster **4**, the mechanism of this rearrangement remains unclear. Further, we plan to study the reactions of cluster **3** and related "orange isomers" with CO and phosphorus ligands in more detail. The reactions of compounds mentioned above with cluster **4** are considered below.

Scheme 2



Cluster **4** reacts with triphenylphosphine under mild conditions (in benzene at room temperature). In the course of reaction, the starting brown solution turns green. Evaporation of the solvent after stirring for 3.5 h followed by chromatography of the residue on silica gel affords the green complex $Ru_3(CO)_8(PPh_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**5**) and the yellow binuclear complexes **2a** and $Ru_2(CO)_5(PPh_3)\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**6**) (see Scheme 2).

The reaction of cluster **4** with triphenylphosphine in C_6D_6 was monitored by ^1H and ^{31}P NMR spectroscopy. The brown solution turned green. In the case of equimolar amounts of cluster **4** and PPh_3, triphenylphosphine completely reacted after 2 h. The composition of the mixture was found to change with time; first, the green complex **5** was obtained, which then loses the CO or PPh_3 group to give the red cluster $Ru_3(CO)_7(PPh_3)\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**7**) and starting complex **4**, respectively. A signal at 56.26 ppm of a labile complex, probably isomeric compound **5**, with PPh_3 in the alternative equatorial position, is observed in the ^{31}P NMR spectrum. Simultaneously, fragmentation of the triangular cluster occurs resulting in the binuclear complexes **2a** and **6** whose ratio is equal to ~4 : 1 after 7 days.

According to ^1H NMR spectroscopy data, both alkenyl groups in complex **5** are equivalent and not coordinated to the metal atom. The IR spectrum reveals the presence of only terminal CO groups and indicates the cluster nature of the compound. Finally, the ^{31}P NMR spectrum of complex **5** contains a singlet signal at δ 51.3, which indicates the presence of a triphenylphosphine ligand coordinated to the metal atom. These spectroscopic data taken together are evidence for the addition of PPh_3 to cluster **4** accompanied by displacement of the alkenyl group out of the coordination sphere of the Ru atom. This was confirmed by the X-ray structural study of compound **5** (see below).

Other complexes formed in the reaction between cluster **4** and PPh_3 were characterized by IR and ^1H and ^{31}P NMR spectroscopy and elemental analysis. The ^1H NMR spectrum of red cluster **7** similar to that of brown cluster **4** and indicating π-coordination of one of the alkenyl groups to the metal is particularly informative. The coordination of the PPh_3 group to the metallacyclopentadiene Ru atom in complex **6** is suggested by analogy with the known structure of the $Fe_2(CO)_5(PPh_3)(\mu\text{-}C_4Ph_4)$ complex.[8] Recently, we have proved the validity of this assumption when studying an analog of complex **6** obtained from the asymmetric binuclear derivative **2b** (this will be reported in detail in our next publication).

The structure of complex **5** was established by the X-ray structural study of the $5 \cdot C_6H_{14} \cdot CH_2Cl_2$ crystal solvate obtained by slow crystallization from a hexane—CH_2Cl_2 mixture at −5 °C. The molecular structure of cluster is shown in Fig. 1, and the main bond lengths and bond angles are listed in Table 1.

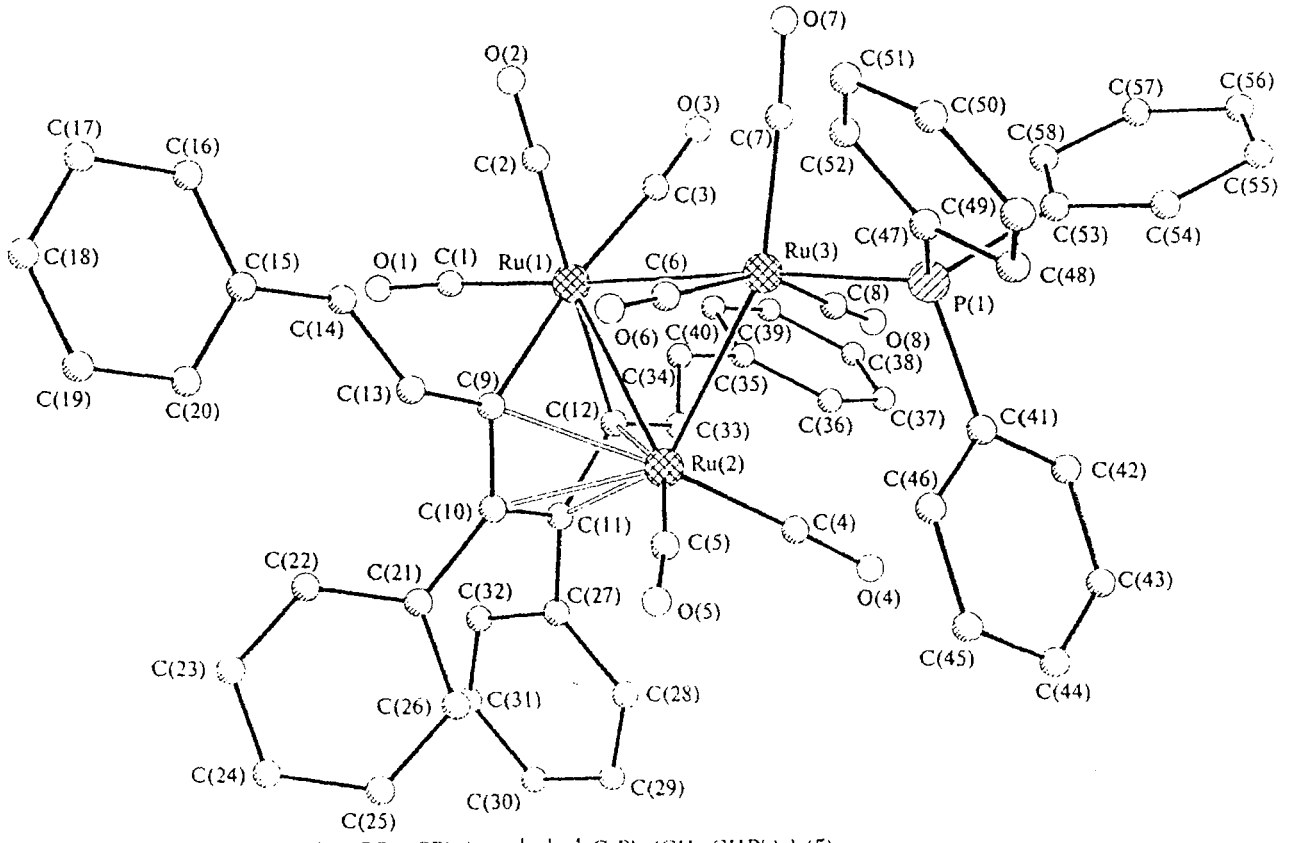


Fig. 1. Molecular structure of $Ru_3(CO)_8(PPh_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**5**).

Table 1. Main bond lengths (d) and bond angles (ω) in complex **5**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Ru(1)—C(1)	1.897(7)	C(1)—Ru(1)—C(2)	99.0(3)	C(7)—Ru(3)—Ru(1)	96.9(2)
Ru(1)—C(2)	1.950(7)	C(1)—Ru(1)—C(3)	98.7(3)	C(6)—Ru(3)—Ru(1)	86.9(2)
Ru(1)—C(3)	1.961(7)	C(2)—Ru(1)—C(3)	88.8(3)	C(8)—Ru(3)—Ru(1)	83.5(2)
Ru(1)—C(9)	2.128(6)	C(1)—Ru(1)—C(9)	85.3(3)	P(1)—Ru(3)—Ru(1)	174.91(5)
Ru(1)—C(12)	2.137(7)	C(2)—Ru(1)—C(9)	96.3(3)	Ru(2)—Ru(3)—Ru(1)	58.19(2)
Ru(1)—Ru(2)	2.7571(10)	C(3)—Ru(1)—C(9)	173.0(3)	C(41)—P(1)—C(47)	103.8(3)
Ru(1)—Ru(3)	2.9274(9)	C(1)—Ru(1)—C(12)	86.7(3)	C(41)—P(1)—C(53)	103.4(3)
Ru(2)—C(5)	1.864(7)	C(2)—Ru(1)—C(12)	171.5(2)	C(47)—P(1)—C(53)	104.0(3)
Ru(2)—C(4)	1.895(7)	C(3)—Ru(1)—C(12)	96.6(3)	C(41)—P(1)—Ru(3)	112.1(2)
Ru(2)—C(11)	2.245(6)	C(9)—Ru(1)—C(12)	77.7(2)	C(47)—P(1)—Ru(3)	116.1(2)
Ru(2)—C(10)	2.248(6)	C(1)—Ru(1)—Ru(2)	124.5(2)	C(53)—P(1)—Ru(3)	116.0(2)
Ru(2)—C(12)	2.254(6)	C(2)—Ru(1)—Ru(2)	118.5(2)	O(1)—C(1)—Ru(1)	176.5(6)
Ru(2)—C(9)	2.263(6)	C(3)—Ru(1)—Ru(2)	119.9(2)	O(2)—C(2)—Ru(1)	175.5(6)
Ru(2)—Ru(3)	2.7319(9)	C(1)—Ru(1)—Ru(3)	176.5(2)	O(3)—C(3)—Ru(1)	175.8(6)
Ru(3)—C(7)	1.871(7)	C(2)—Ru(1)—Ru(3)	77.6(2)	O(4)—C(4)—Ru(2)	176.4(6)
Ru(3)—C(6)	1.941(7)	C(3)—Ru(1)—Ru(3)	82.1(2)	O(5)—C(5)—Ru(2)	173.6(6)
Ru(3)—C(8)	1.956(7)	C(9)—Ru(1)—Ru(3)	94.2(2)	O(6)—C(6)—Ru(3)	175.2(6)
Ru(3)—P(1)	2.324(2)	C(12)—Ru(1)—Ru(3)	96.7(2)	O(7)—C(7)—Ru(3)	175.6(6)
P(1)—C(41)	1.820(6)	Ru(2)—Ru(1)—Ru(3)	57.35(2)	O(8)—C(8)—Ru(3)	178.1(6)
P(1)—C(47)	1.838(6)	C(5)—Ru(2)—C(4)	92.8(3)	C(10)—C(9)—C(13)	117.4(6)
P(1)—C(53)	1.844(7)	C(5)—Ru(2)—Ru(3)	99.7(2)	C(10)—C(9)—Ru(1)	115.0(4)
O(1)—C(1)	1.131(8)	C(4)—Ru(2)—Ru(3)	92.2(2)	C(13)—C(9)—Ru(1)	126.1(5)
O(2)—C(2)	1.148(8)	C(5)—Ru(2)—Ru(1)	135.3(2)	C(9)—C(10)—C(11)	116.2(6)
O(3)—C(3)	1.129(8)	C(4)—Ru(2)—Ru(1)	127.4(2)	C(9)—C(10)—C(21)	122.0(5)
O(4)—C(4)	1.128(8)	Ru(3)—Ru(2)—Ru(1)	64.46(3)	C(11)—C(10)—C(21)	121.5(5)
O(5)—C(5)	1.150(8)	C(7)—Ru(3)—C(6)	102.5(3)	C(12)—C(11)—C(10)	115.5(6)
O(6)—C(6)	1.144(8)	C(7)—Ru(3)—C(8)	98.4(3)	C(12)—C(11)—C(27)	123.6(6)
O(7)—C(7)	1.159(8)	C(6)—Ru(3)—C(8)	157.9(3)	C(10)—C(11)—C(27)	120.3(5)
O(8)—C(8)	1.135(8)	C(7)—Ru(3)—P(1)	88.1(2)	C(11)—C(12)—C(33)	119.3(6)
C(9)—C(10)	1.409(9)	C(6)—Ru(3)—P(1)	93.0(2)	C(11)—C(12)—Ru(1)	114.3(5)
C(9)—C(13)	1.465(9)	C(8)—Ru(3)—P(1)	94.8(2)	C(33)—C(12)—Ru(1)	125.8(4)
C(10)—C(11)	1.438(9)	C(7)—Ru(3)—Ru(2)	155.1(2)	C(14)—C(13)—C(9)	126.3(6)
C(10)—C(21)	1.504(9)	C(6)—Ru(3)—Ru(2)	77.6(2)	C(13)—C(14)—C(15)	127.3(7)
C(11)—C(12)	1.428(9)	C(8)—Ru(3)—Ru(2)	80.5(2)	C(34)—C(33)—C(12)	125.0(6)
C(11)—C(27)	1.507(9)	P(1)—Ru(3)—Ru(2)	116.83(5)	C(33)—C(34)—C(35)	125.8(6)
C(12)—C(33)	1.474(9)				
C(13)—C(14)	1.336(9)				
C(14)—C(15)	1.464(9)				
C(33)—C(34)	1.341(9)				
C(34)—C(35)	1.464(9)				

Molecule **5** is a Ru_3-triangular cluster; in contrast to its precursor (cluster **4**), the previously coordinated alkenyl group in complex **5** is substituted in the coordination sphere of the Ru atom by the triphenylphosphine ligand. As is known, the phosphine ligands in trimetallic carbonyl clusters are in sterically less hindered equatorial positions.[9,10] This is precisely observed in complex **5**, where PPh_3 occupies one of the equatorial positions at the Ru(3) atom, in *trans*-position to the Ru(1)—Ru(3) bond. The coordination of the Ru(2) and Ru(3) atoms in complex **5** is similar to that in structure **4**: one of the metal atoms is bonded to three while the other is bonded to two carbonyl ligands. The metallacyclopentadiene moiety in cluster **5** is in symmetric position with respect to the Ru_3 plane: the central nucleus of the molecule, except for the phenyl substituents, has its proper symmetry pseudoplane passing through the midpoint of the C(10)—C(11) bond of the diene ligand and the Ru(1), Ru(2), Ru(3), and P(1) atoms; the dihedral angle formed by the C(9)Ru(1)C(12) plane and the Ru_3 plane is equal to 88.3°. This is just the difference between cluster **5** and molecule **4** where the five-membered heterocycle is tilted with respect to the Ru_3 plane due to the tightening effect of the coordinated alkenyl group, and the dihedral angle made by the C(9)Ru(1)C(12) plane and the Ru_3 plane in complex **4** is equal to 54.1°.

The redistribution of the Ru—Ru bond lengths in structure **5** as compared to molecule **4** has engaged our attention. The metal atoms in complex **4** are located at the vertices of an isosceles triangle with two longer sides (the Ru(1)—Ru(3)* and Ru(2)—Ru(3) distances are equal to 2.8018(7) Å and 2.8231(7) Å, respectively) and one

* Numbering of metal atoms in complex **4** corresponds to that in Fig. 1.

shorter side (the Ru(1)—Ru(2) distance is equal to 2.7332(10) Å), whereas the Ru_3 triangle in molecule **5** has two short edges (the Ru(1)—Ru(2) and Ru(2)—Ru(3) distances are equal to 2.7571(10) Å and 2.7319(9) Å, respectively) and one longer edge (the Ru(1)—Ru(3) distance is equal to 2.9274(9) Å). The lengthening of the Ru(1)—Ru(3) bond might be associated with the effect of the phosphine ligand in *trans*-position to this bond.

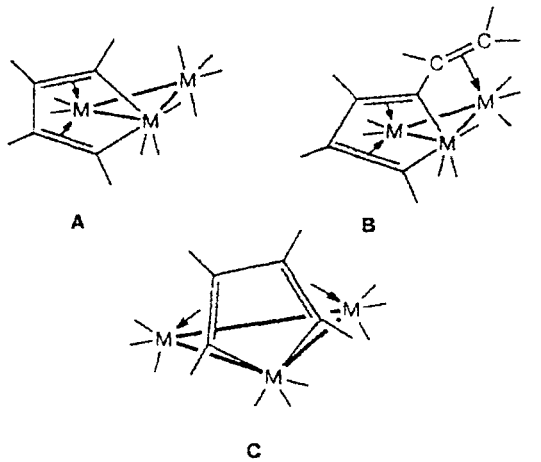
The C—C and Ru—C distances in the hydrocarbon ligand of complex **5** are nearly the same as those in its precursor **4**.

The ruthenacyclopentadiene ring has the conformation of a flattened envelope: the folding angle along the C(9)...C(12) line is equal to 9.6°, which is somewhat smaller than that found for complex **4** (14.6°).

Similarly to the reaction with triphenylphosphine, cluster **4** reacts with triisopropyl phosphite in benzene at room temperature with the formation of the green complex $Ru_3(CO)_8\{P(OPr^i)_3\}(\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**8**), which is a phosphite analog of cluster **5**. This complex is somewhat more stable towards fragmentation than its triphenylphosphine analog. Only a small amount of complex **2a** was found among the reaction products. It is likely that the stability of clusters **5** and **8** towards fragmentation is affected by the Tolman cone angle of the phosphorus ligands in these complexes (145° and 130° for PPh_3 and $P(OPr^i)_3$, respectively). Earlier,[11] it was shown that the related triosmium cluster $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ (**9**) with the osmacyclopentadiene moiety reacts with the P-donor nucleophiles with the preferable formation of substitution products of $Os_3(CO)_8(PR_3)(\mu\text{-}C_4Ph_4)$ if the cone angles of nucleophiles are not larger than 145°; if the cone angles of reacting nucleophiles are larger than 145°, then fragmentation of the cluster with the formation of the pair products $Os(CO)_4PR_3$ and $Os_2(CO)_5(PR_3)(\mu\text{-}C_4Ph_4)$, and $Os(CO)_3(PR_3)_2$ and $Os_2(CO)_6(\mu\text{-}C_4Ph_4)$ is observed.

When carbon monoxide is bubbled through a benzene solution of cluster **4**, the starting brown solution gradually turns yellow because of the presence of the binuclear complex **2a**. We believe that CO as well as phosphorus ligands replace the alkenyl group in the coordination sphere of the Ru atom in complex **4**; however, the nonacarbonyl cluster $Ru_3(CO)_9\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**10**) formed in this case undergoes fragmentation under the reaction conditions to give the binuclear complex **2a**. In this regard, the behavior of cluster **10** is similar to that of the related triosmium cluster **9**, whose fragmentation under the action of CO results in complexes $Os_2(CO)_6(\mu\text{-}C_4Ph_4)$ and $Os(CO)_5$.[12]

Thus, the reversible dissociation of the π-coordinated alkenyl group in the triruthenium cluster has been demonstrated in this work; the transformations **4** → **5** → **7** are accompanied by migration of the metallacyclopentadiene fragment with respect to the Ru_3 plane. Thus, the metallacyclopentadiene ring in cluster **4** is tilted to the Ru_3 plane (structure **B**) and is in an intermediate position between the well-known structure **A** found earlier[13–15] for the triosmium cluster **9** and currently for the triruthenium cluster **5** (the "side-on" or $\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4$-coordination) and structure **C** recently established[16,17] for the triosmium clusters $Os_3(CO)_9\{\mu_3\text{-}C(SiMe_3)C(Me)CHC(R)\}$ (R = Ph and ferrocenyl) (the "face-on" or $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2$-coordination).



Further study of the clusters described in this work and related clusters with the metallacyclopentadiene moiety may help to elucidate the possibility of interconversions between the isomers of structure **A** and **C**.

Experimental

The reactions were carried out under an argon atmosphere and chromatographic separation of the products was performed in the air using the L100/160 μ and 100/400 μ (Chemapol) silica gel as adsorbent.

^1H and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 and 161.98 MHz for ^1H and ^{31}P, respectively). IR spectra were recorded on a Bruker IFS-113v spectrometer.

Thermolysis of $Ru_3(\mu\text{-}CO)_2(CO)_6\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (3). A solution of compound **3** (30 mg) in hexane (20 mL) was refluxed for 12 h to obtain a 2.5 : 1.0 mixture of the $Ru_3(CO)_8\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**4**) and $Ru_2(CO)_6\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**2a**) complexes, identified by ^1H NMR spectroscopy.

Reaction of $Ru_3(CO)_8\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (4) with PPh_3. *A.* Compound **4** (90 mg, 0.096 mmol) and PPh_3 (30 mg, 0.120 mmol) were stirred in 60 mL of benzene for 3.5 h at 20 °C. In this period, the brown solution turned green. The solvent was evaporated on a rotary evaporator, and the residue was separated by TLC on Silufol. Elution of the mixture with petroleum ether (b.p. 40—70 °C) gave three bands, an orange-brown band (the starting complex **4**), a yellow band, and a green band. The yellow band afforded 20 mg (20.5%) of bright-yellow complex $Ru_2(CO)_5(PPh_3)(\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**6**). Found (%): C, 65.48; H, 4.41. $C_{55}H_{39}O_5PRu_2$. Calculated (%): C, 65.21; H, 3.88. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2054 s, 2039 s, 2009 s, 1970 s, 1886 w.br. ^1H NMR (C_6D_6), δ: 6.57 (d, 2 H, H_A, J = 15.7 Hz); 6.96 (d, 2 H, H_B, J = 15.7 Hz); 6.9—7.7 (m, 35 H, Ph). ^{31}P NMR (C_6D_6), δ: 46.2 (s). The green band afforded 50 mg (43.5%) of compound

Table 2. Atomic coordinates ($\times 10^4$) and their equivalent isotropic thermal parameters ($U_{eq} \times 10^3$) in the structure of 5

Atom	x	y	z	$U_{eq}/Å^2$	Atom	x	y	z	$U_{eq}/Å^2$
Ru(1)	3155(1)	11972(1)	9633(1)	16(1)	C(51)	1643(3)	8990(6)	7814(3)	36(2)
Ru(2)	3768(1)	11327(1)	9190(1)	17(1)	C(52)	2024(3)	9125(5)	8204(2)	29(2)
Ru(3)	3009(1)	10168(1)	9169(1)	18(1)	C(53)	2907(2)	7688(4)	9106(2)	21(1)
P(1)	2962(1)	8751(1)	8796(1)	18(1)	C(54)	2864(3)	6812(5)	8899(2)	32(2)
O(1)	3257(2)	13886(3)	10066(2)	34(1)	C(55)	2849(3)	5999(5)	9134(3)	33(2)
O(2)	2038(2)	11996(3)	9168(2)	30(1)	C(56)	2863(3)	6060(5)	9567(3)	31(2)
O(3)	2946(2)	10786(3)	10364(2)	31(1)	C(57)	2910(3)	6898(5)	9775(2)	30(2)
O(4)	4514(2)	9772(4)	9475(2)	38(1)	C(58)	2925(3)	7726(5)	9546(2)	29(2)
O(5)	3740(2)	11297(4)	8238(2)	44(1)	Cl(1)	3434(1)	16431(2)	7703(1)	62(1)
O(6)	2586(2)	11240(3)	8289(2)	34(1)	Cl(2)	3626(2)	16754(3)	6879(1)	110(1)
O(7)	2098(2)	9652(4)	9389(2)	37(1)	C(59)	3427(4)	17233(7)	7294(3)	59(3)
O(8)	3762(2)	9449(4)	10034(2)	34(1)	C(60)	4353(4)	16105(8)	6046(3)	74(3)
C(1)	3210(2)	13163(5)	9912(2)	22(1)	C(61)	4242(4)	15033(10)	5903(4)	83(4)
C(2)	2455(3)	11969(4)	9326(2)	21(1)	C(62)	4091(4)	14395(10)	6221(5)	97(5)
C(3)	3040(2)	11204(5)	10101(2)	22(1)	C(63)	3955(6)	13345(13)	5983(5)	121(6)
C(4)	4225(3)	10332(5)	9360(2)	24(2)	C(64)	3684(8)	12660(16)	6177(6)	145(7)
C(5)	3741(3)	11256(5)	8599(2)	26(2)	C(65)	3561(6)	11683(12)	5968(5)	106(5)
C(6)	2749(3)	10879(5)	8625(2)	25(2)	C(66)	4848(5)	6937(10)	7719(5)	28(3)
C(7)	2444(3)	9817(5)	9295(2)	25(2)	C(67)	5000	6335(37)	7500	278(22)
C(8)	3491(2)	9724(5)	9715(2)	24(2)	C(68)	5107(4)	5050(8)	7519(5)	21(3)
C(9)	3354(2)	12694(4)	9132(2)	18(1)	C(69)	4737(13)	2528(28)	7366(14)	147(14)
C(10)	3855(2)	12896(4)	9239(2)	18(1)	C(70)	4529(7)	2202(14)	7562(6)	53(5)
C(11)	4170(2)	12481(4)	9639(2)	18(1)	H(13)	3144(26)	13243(51)	8510(25)	32(20)
C(12)	3933(2)	11914(4)	9879(2)	21(1)	H(14)	2506(22)	13497(43)	8917(21)	6(16)
C(13)	3019(2)	13168(5)	8746(2)	19(1)	H(16)	1716(31)	14157(63)	8559(29)	53(27)
C(14)	2597(3)	13580(5)	8725(2)	25(2)	H(17)	1307(41)	15182(82)	8064(38)	81(42)
C(15)	2298(2)	14192(4)	8374(2)	21(1)	H(18)	1576(23)	15924(45)	7534(21)	15(16)
C(16)	1828(3)	14436(5)	8371(3)	31(2)	H(19)	2286(33)	15502(64)	7587(31)	52(29)
C(17)	1549(3)	15073(7)	8066(3)	44(2)	H(20)	2729(32)	14443(63)	8055(29)	50(28)
C(18)	1728(3)	15474(6)	7758(3)	41(2)	H(22)	3720(23)	14670(44)	9140(22)	13(17)
C(19)	2189(3)	15242(6)	7754(3)	35(2)	H(23)	3955(30)	15866(62)	8729(27)	48(24)
C(20)	2467(3)	14612(5)	8055(2)	30(2)	H(24)	4460(25)	15336(51)	8317(23)	26(19)
C(21)	4044(2)	13585(5)	8975(2)	20(1)	H(25)	4700(27)	13882(50)	8335(24)	30(21)
C(22)	3883(3)	14506(5)	8944(2)	32(2)	H(26)	4442(22)	12769(47)	8725(20)	9(16)
C(23)	4038(3)	15162(6)	8702(3)	41(2)	H(28)	5026(31)	11562(65)	9562(29)	57(26)
C(24)	4354(3)	14906(6)	8476(3)	47(2)	H(29)	5761(32)	12231(61)	9791(28)	49(26)
C(25)	4516(3)	14000(7)	8501(3)	41(2)	H(30)	5934(36)	13571(65)	10188(30)	58(29)
C(26)	4366(3)	13341(6)	8750(2)	31(2)	H(31)	5390(30)	14532(62)	10383(28)	51(24)
C(27)	4700(2)	12752(5)	9814(2)	22(1)	H(32)	4621(29)	13825(55)	10141(26)	34(24)
C(28)	5068(3)	12236(5)	9725(3)	34(2)	H(33)	4619(28)	11090(52)	10334(24)	40(22)
C(29)	5544(3)	12567(7)	9879(3)	42(2)	H(34)	3820(23)	11800(43)	10653(20)	12(16)
C(30)	5654(3)	13394(6)	10106(3)	43(2)	H(36)	4717(19)	9930(37)	10791(19)	0(13)
C(31)	5292(3)	13898(6)	10206(3)	41(2)	H(37)	5104(33)	9227(65)	11417(29)	52(28)
C(32)	4819(3)	13579(6)	10054(3)	34(2)	H(38)	5079(26)	9683(50)	12131(25)	30(19)
C(33)	4228(2)	11459(5)	10294(2)	22(1)	H(39)	4593(28)	10990(54)	12051(25)	21(23)
C(34)	4113(2)	11435(5)	10669(2)	25(2)	H(40)	4152(24)	11822(48)	11514(21)	19(17)
C(35)	4384(2)	10934(5)	11074(2)	25(2)	H(42)	3820(23)	7629(46)	9170(22)	20(17)
C(36)	4667(3)	10158(6)	11062(2)	32(2)	H(43)	4512(31)	7382(60)	8976(28)	46(25)
C(37)	4924(3)	9701(7)	11453(3)	46(2)	H(44)	4596(25)	8196(45)	8408(21)	9(18)
C(38)	4895(3)	10005(7)	11858(3)	49(2)	H(45)	4058(25)	9183(50)	7962(24)	26(19)
C(39)	4613(3)	10768(8)	11865(3)	44(2)	H(46)	3352(28)	9436(55)	8127(25)	35(21)
C(40)	4348(3)	11236(7)	11479(2)	37(2)	H(48)	2763(28)	7649(53)	7960(24)	32(21)
C(41)	3507(2)	8527(4)	8643(2)	20(1)	H(49)	2132(24)	7542(49)	7356(23)	20(18)
C(42)	3878(3)	7952(5)	8911(2)	27(2)	H(50)	1452(26)	8405(48)	7223(24)	24(19)
C(43)	4306(3)	7826(5)	8809(3)	32(2)	H(51)	1396(25)	9268(46)	7793(21)	13(17)
C(44)	4362(3)	8280(6)	8445(3)	34(2)	H(52)	2008(19)	9585(40)	8403(18)	0(13)
C(45)	4002(3)	8861(5)	8185(3)	32(2)	H(54)	2832(26)	6769(51)	8595(26)	31(20)
C(46)	3573(3)	8984(5)	8282(2)	26(2)	H(55)	2873(30)	5442(63)	8969(28)	50(25)
C(47)	2462(2)	8643(4)	8270(2)	21(1)	H(56)	2884(22)	5557(48)	9707(21)	13(16)
C(48)	2498(3)	8028(5)	7940(2)	26(2)	H(57)	2951(23)	6988(44)	10099(22)	18(17)
C(49)	2109(3)	7905(6)	7557(2)	31(2)	H(58)	2940(26)	8275(55)	9683(24)	29(20)
C(50)	1680(3)	8382(6)	7495(3)	34(2)					

$Ru_3(CO)_8(PPh_3)\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**5**) as dark-green crystals. Found (%): P, 2.28. $C_{58}H_{39}O_8PRu_3$. Calculated (%): P, 2.59. IR (hexane), ν(CO)/cm^{-1}: 2077 s, 2062 m, 2041 s, 1998 vs, 1975 s, 1944 m, 1927 m. ^{1}H NMR (C_6D_6), δ: 7.90 (d, 2 H, H_B, J = 15.5 Hz); 6.8—7.7 (m, 37 H, Ph+H_A). ^{31}P NMR ($CDCl_3$), δ: 52.3 (s).

B. Compound **4** (20 mg, 0.021 mmol) and PPh_3 (7 mg, 0.026 mmol) were stirred in 15 mL of benzene for 40 h at 20 °C. The solvent was evaporated, and the residue was separated by TLC on Silufol. Elution of the reaction mixture with a petroleum ether—benzene (5 : 1) mixture resulted in four bands (listed in order of decreasing R_f), a light-yellow band (complex **2a**), an orange-brown band (the starting cluster **4**), a very narrow green band (cluster **5**), and a broad red band, from which compound $Ru_3(CO)_7(PPh_3)\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**7**) was obtained as dark-red crystals. Found (%): P, 2.50. $C_{57}H_{39}O_7PRu_3$. Calculated (%): P, 2.65. IR (hexane), ν(CO)/cm^{-1}: 2058 s, 2023 m, 2009 s, 1985 s. NMR ^{1}H (acetone-d_6), δ: 4.92 (d, 1 H, H_B, J = 12.8 Hz); 5.24 (d, 1 H, H_A, J = 12.8 Hz); 6.67 (d, 1 H, $H_{A'}$, J = 15.5 Hz); 6.65—7.95 (m, 36 H, Ph + $H_{B'}$). ^{31}P NMR (C_6D_6), δ: 46.2 (s).

Reaction of $Ru_3(CO)_8\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (4) with $P(OPr^i)_3$. Triisopropyl phosphite (0.08 mL, 0.328 mmol) was added using a pipette to a solution of compound **4** (230 mg, 0.245 mmol) in 100 mL of benzene. The solution was stirred for 2.5 h at 20 °C and gradually turned green. The solvent was evaporated, and the residue was chromatographed on a column with silica gel. First, a yellow band and a brown band were eluted with a petroleum ether—benzene (5 : 1) mixture, and then a green band was eluted with a 1 : 3 mixture of the same solvents. The yellow band afforded compound **2a** (20 mg, 10.5%) as yellow crystals. The brown band contained the starting complex **4**, and the green band afforded 100 mg (35.7%) of cluster $Ru_3(CO)_8\{P(OPr^i)_3\}\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$. Found (%): P, 2.57. $C_{49}H_{45}O_{11}PRu_3$. Calculated (%): P, 2.71. IR (hexane), ν(CO)/cm^{-1}: 2080 s, 2065 s, 2047 s, 2032 s, 2015 s, 2000 s, 1970 s, 1923 m. ^{1}H NMR (C_6D_6), δ: 0.98 (d, 3 H, CH_3, J = 7.1 Hz); 1.02 (d, 3 H, CH_3, J = 7.1 Hz); 1.92 (m, 1 H, CH); 6.8—7.6 (m, 22 H, Ph + H_A); 7.89 (d, 2 H, H_B, J = 15.5 Hz).

Reaction of $Ru_3(CO)_8\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (4) with CO. Carbon monoxide was slowly bubbled through a solution of compound **4** (90 mg, 0.096 mmol) in 60 mL of benzene for 5 h at 20 °C. The brown solution gradually turned yellow. Evaporation of the solvent afforded yellow crystals of compound $Ru_2(CO)_6\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**2a**), whose spectral (IR and ^{1}H NMR) characteristics were identical with those of an authentic sample.[1]

X-ray structural study of complex 5. Crystals of $C_{58}H_{39}O_8PRu_3 \cdot C_6H_{14} \cdot CH_2Cl_2$ are monoclinic; at −125 °C, a = 28.945(9) Å, b = 14.238(4) Å, c = 31.888(10) Å, β = 108.66(2)°, V = 12451(6) Å^3, d_{calc} = 1.493 g cm^{-3}, Z = 8, space group $C2/c$. The unit cell parameters and intensities of 12284 independent reflections were measured on an automatic Siemens P3/PC diffractometer (−125 °C, Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scan, $\theta \le 26.5°$).

The structure was solved by direct methods. Fourteen peaks were located in the difference synthesis calculated using all atoms of the complex; nine of them were identified and refined as solvate molecules of *n*-hexane and methylene chloride. Five peaks located near the axis *2* far from all other atoms of the structure (the distances are approximately equal to the sum of the van der Waals radii) evidently correspond to another disordered solvent molecule. Attempts to elucidate the chemical nature of this molecule failed. However, the final refinement resulted in an appreciable decrease in the R factor and in a some increase in the accuracy of determination of geometric parameters when the C(66)—C(70) atoms were included with halved population factors. The refinement was carried out by the full-matrix least squares method first isotropically and then anisotropically (the atoms C(66)—C(70) were refined isotropically). All hydrogen atoms in complex **5** were located unequivocally and included in the isotropic refinement. The calculated positions of the hydrogen atoms of the solvate molecules of *n*-hexane and methylene chloride were included in the final refinement using the riding model. The final reliability factors are R_1 = 0.0637 (F for 7684 observed reflections with $I > 2\sigma(I)$) and wR_2 = 0.1874 (F^2 for all 12164 reflections used in the refinement); the number of refined parameters was 886. All calculations were performed using the SHELXTL PLUS 5 program package.[18] The atomic coordinates are listed in Table 2.

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