Reactions of 1,4-diferrocenylbuta-1,3-diyne and 1,4-diphenylbut-1-en-3-yne with $Ru_3(CO)_{12}$. Crystal structure of $Ru_3(CO)_8\{\mu_3-\eta^1-\eta^1-\eta^4-\eta^2-C_4Ph_2(CH=CHPh)_2\}$

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Diyne FcC≡CC≡CFc (Fc is ferrocenyl) reacts with $Ru_3(CO)_{12}$ in boiling hexane to yield binuclear complexes $Ru_2(CO)_6\{C_4Fc_2(C≡CFc)_2\}$ and $Ru_2(CO)_6\{C_4Fc_2(C≡CFc)_2C=O\}$ containing ruthenacyclopentadiene and diruthenacycloheptadienone rings, respectively. The isomerism of the complexes is due to the different ways of coupling of the alkyne fragments of the diyne, namely, "head-to-head", "head-to-tail" or "tail-to-tail". The reaction of enyne PhC≡CCH=CHPh with $Ru_3(CO)_{12}$ under similar conditions gives isomeric binuclear complexes $Ru_2(CO)_6\{C_4Ph_2(CH=CHPh)_2\}$ and trinuclear clusters $Ru_3(CO)_6(\mu-CO)_2\{C_4Ph_2(CH=CHPh)_2\}$ and $Ru_3(CO)_8\{\mu_3-\eta^1-\eta^1-\eta^4-\eta^2-C_4Ph_2(CH=CHPh)_2\}$. The structure of the latter was determined by X-ray diffraction analysis. The Ru_3 triangle coordinates eight terminal CO groups and the organic ligand resulting from the "head-to-head" dimerization of enyne molecules; the ruthenacyclopentadiene moiety is η^4-coordinated to the $Ru(CO)_2$ group, and the third ruthenium atom is η^2-bound to one of the PhCH=CH groups.

Key words: diynes, enynes, dimerization; ruthenium clusters, ruthenium carbonyls, ruthenacycles.

Reactions of alkynes with cluster carbonyls of metals of the iron subgroup have been studied rather extensively;[1] however, only a few studies devoted to the behavior of diynes and enynes in these reactions have been reported.[2-4]

At the same time, the presence of one more unsaturated bond in the molecules of diynes and enynes offers additional possibilities (not existing in the case of ordinary alkynes) for the coordination to metal atoms in a cluster and for the formation of carbon—carbon bonds. In addition, the study of these reactions involving enynes is of special interest, since they are suggested to act as intermediates in oligomerization/cyclization of alkynes under the action of metal complexes.

As a continuation of the systematic research of the interaction of heteroatom-substituted and functionalized alkynes with cluster metal carbonyls,[5-7] we studied the behavior of diynes and enynes in these reactions. In the present work we report on thermal reactions of 1,4-diferrocenylbuta-1,3-diyne and 1,4-diphenylbut-1-en-3-yne with $Ru_3(CO)_{12}$; the transformations of

1,4-diferrocenylbut-1-en-3-yne will be reported in another paper. Some of our results were published as a preliminary communication.[8]

Results and Discussion

1,4-Diferrocenylbuta-1,3-diyne reacts with $Ru_3(CO)_{12}$ in boiling hexane to give a mixture of organoruthenium compounds, from which diruthenium complexes **1a**, **1b**, **2a**, and **2b** (Scheme 1) were isolated in the individual state by column chromatography on silica gel. The compounds obtained were characterized by spectroscopy (IR and ^1H NMR spectra) as well as by elemental and/or X-ray fluorescence analysis (Table 1).

The IR spectra of complexes **1** in the region of the absorption of carbonyl groups are similar to the spectra of binuclear ruthenium complexes of the composition $Ru_2(CO)_6(RC_2R)_2$, containing a ruthenacyclopentadiene ring, for example, $Ru_2(CO)_6(C_4H_2Fc_2)$ (**3**), which was obtained by the reaction of $Ru_3(CO)_{12}$ with ferrocenylacetylene FcC≡CH and characterized by an X-ray structural study.[9]

Binuclear complexes of the composition $Ru_2(CO)_6\{C_4Fc_2(C≡CFc)_2\}$ can exist as three isomers,
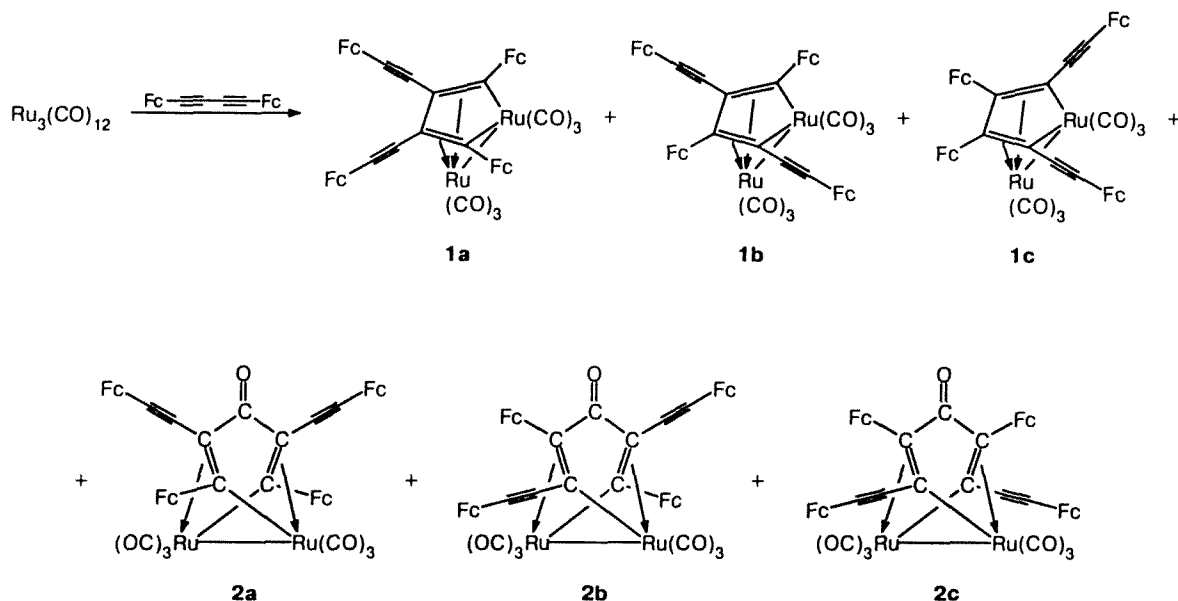
Scheme 1

because the dimerization of two diyne molecules can involve the "head-to-head", "head-to-tail", and "tail-to-tail" type coupling of the alkyne fragments (see Scheme 1, structures 1c, 1b, and 1a, respectively). ^{1}H NMR spectra enable easy identification of complex 1b in which all four ferrocenyl groups are nonequivalent, and the protons of the unsaturated ring of the ferrocene units are manifested as four signals of equal intensities. The second isomer isolated in the individual state apparently has the structure of 1a. This assumption is based on the well-known rule stating that dimerization of acetylenes with the formation of a metallacyclopentadiene ring results in the most bulky substituents being preferably located in the α-position with respect to the metal atom. In addition, the isolation of complex 3, in which ferrocenyl groups occupy the α-positions with respect to the metal of the heterocyclic ring, as one of the major products of the reaction of

Ru₃(CO)₁₂ with ferrocenylacetylene is also consistent with this assignment.[9] The ^{1}H NMR spectra indicate that, along with complexes 1a,b, a third isomer 1c is also formed in the reaction in a very low yield.

Other products isolated upon the reaction of Ru₃(CO)₁₂ with 1,4-diferrocenylbuta-1,3-diyne are binuclear complexes of the composition Ru₂(CO)₆{C₄Fc₂(C≡CFc)₂C=O} (2) containing the diruthenacycloheptadiene system. For complexes 2, like compounds 1, three isomers are possible. Two of them, namely, symmetrical (with the assumed structure 2a) and nonsymmetrical (2b) isomers were isolated from the reaction mixture. The third isomer, presumably 2c, was not detected.

The IR spectra of complexes 2a and 2b in the region of ν(C=O) absorption are similar to the spectra of known complexes of the diruthenacycloheptadienone series;[9,10]

Table 1. Spectral data for the products of the reaction of Ru₃(CO)₁₂ with FcC≡CC≡CFc

Compound	^{1}H NMR,[a] δ	IR,[b] ν/cm⁻¹
1a	4.58 (t, 2 H); 4.48 (t, 4 H); 4.42—4.29 (m, 10 H); 4.41 (s, 10 H); 4.30 (s, 10 H)	2076 s, 2045 s, 2009 s, 1985 m, 1969 m (C≡O); 2215 w (C≡C)
1b	5.63 (t, 1 H); 5.56 (t, 1 H); 5.12 (t, 1 H); 4.63 (m, 2 H); 4.55 (t, 1 H); 4.50 (m, 5 H); 4.37 (m, 5 H); 4.30 (s, 5 H); 4.28 (s, 5 H); 4.24 (s, 5 H); 4.22 (s, 5 H)	2076 s, 2048 s, 2009 s, 1988 m (sh), 1971 m (C≡O); 2212 w, 2185 w (C≡C)
1c	4.46—4.22 (m, 16 H); 4.32 (s, 10 H); 4.21 (s, 10 H)	
2a	5.10 (m, 2 H); 4.58 (m, 2 H); 4.55 (m, 4 H); 4.48 (m, 4 H); 4.35—4.20 (m, 4 H); 4.32 (s, 10 H); 4.29 (s, 10 H)	2086 m, 2066 s, 2049 s, 2026 s (C≡O); 2174 w (C≡C); 1688 (C=O)
2b	5.15 (m, 1 H); 4.93 (m, 1 H); 4.78 (m, 1 H); 4.72 (m, 1 H); 4.68 (m, 1 H); 4.63 (m, 1 H); 4.61 (m, 2 H); 4.53 (m, 1 H); 4.48 (m, 2 H); 4.39 (s, 5 H); 4.38 (s, 5 H); 4.33 (m, 2 H); 4.34 (s, 5 H); 4.31 (m, 2 H); 4.27 (s, 5 H)	2086 m, 2064 s, 2055 w, 2044 w, 2024 s, 2021 s (C≡O); 2176 w (C≡C); 1686 w (S=O)

[a] Recorded in acetone-d₆, except for 1b, for which CDCl₃ was used. [b] In CH₂Cl₂ for complexes 1a and 1b or in heptane for 2a and 2b.

Scheme 2
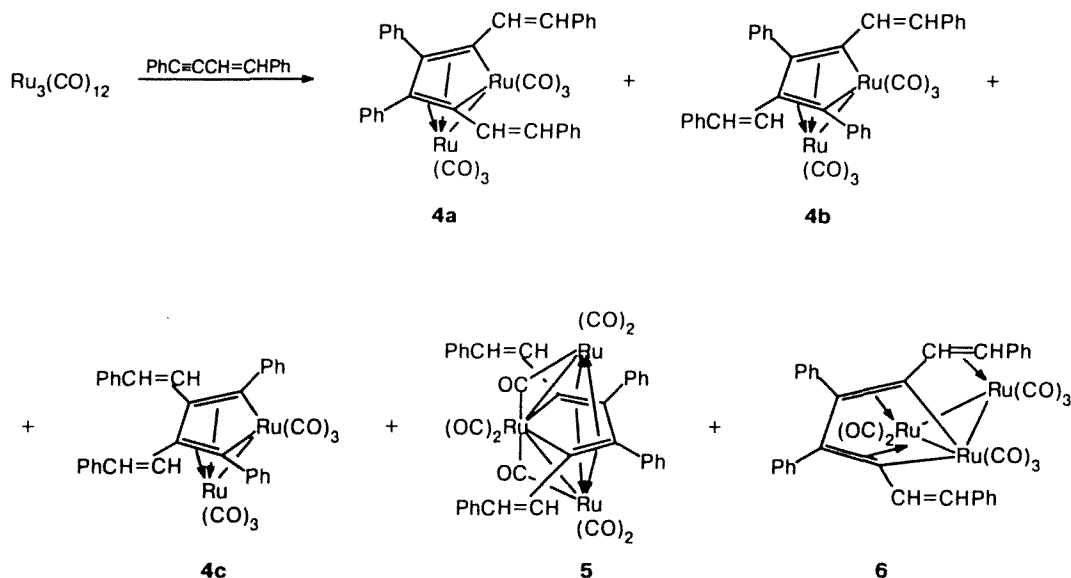
they exhibit bands at 1688 and 1686 cm^{-1}, respectively, which are typical of an oxo group, and also weak bands at 2174 and 2176 cm^{-1}, corresponding to noncoordinated $C\equiv C$ bonds.

Thus, the reaction of 1,4-diferrocenylbutadiyne with $Ru_3(CO)_{12}$ in boiling hexane affords binuclear complexes with metallacyclopentadiene and dimetallacycloheptadienone fragments. During the formation of each of these complexes only one triple bond of the starting diyne participates in the coupling and in the subsequent coordination to the Ru atoms.

We also carried out the reaction of $Ru_3(CO)_{12}$ with the enyne $PhC\equiv CCH=CHPh$ under similar conditions. The products of this reaction (Scheme 2) were isolated by chromatography on silica gel. Table 2 presents spectroscopic characteristics of the resulting compounds.

As the reaction of $Ru_3(CO)_{12}$ with 1,4-diferrocenylbuta-1,3-diyne, the reaction with the enyne yields binuclear ruthenacyclopentadiene complexes. The yellow-colored complex $Ru_2(CO)_6\{C_4Ph_2(CH=CHPh)_2\}$ (**4b**) was isolated in 40% yield. The asymmetrical character of the complex is indicated by the presence of four doublet signals at δ 5.96 and 6.35 with $J = 16.7$ Hz and at δ 6.71 and 6.92 with $J = 15.6$ Hz, corresponding to the protons of two alkenyl groups, in its ^1H NMR spectrum. The symmetrical isomer $Ru_2(CO)_6\{C_4Ph_2(CH=CHPh)_2\}$ (**4a**) was isolated in a yield of only 3%.

The structures of the symmetrical isomers of $Ru_2(CO)_6\{C_4Ph_2(CH=CHPh)_2\}$, unlike those of symmetrical isomers **1a** and **1c**, can be assigned rather reliably. This is provided by the presence of alkenyl groups in these compounds and by the known rule that the $J_{H,H}$

Table 2. Spectral data for the products of the reaction of $Ru_3(CO)_{12}$ with $PhC\equiv CCH=CHPh$

Compound[a]	^1H NMR (acetone-d_6), δ	IR,[b] v/cm^{-1}
4a	7.13—7.31 (m, 20 H); 6.88 (d, 2 H, $J = 15.6$ Hz); 6.58 (d, 2 H, $J = 15.6$ Hz)	2082 s, 2050 s, 2017 s, 2005 s, 1987 m, 1962 m
4b	6.82—7.83 (m, 20 H); 6.93 (d, 1 H, $J = 15.6$ Hz); 6.70 (d, 1 H, $J = 15.6$ Hz); 6.35 (d, 1 H, $J = 16.7$ Hz); 5.96 (d, 1 H, $J = 16.7$ Hz)	2080 s, 2050 s, 2015 s, 2007 s, 1998 s, 1970 sh
5	7.02—7.82 (m, 20 H); 5.95 (d, 2 H, $J = 15.3$ Hz); 5.81 (d, 2 H, $J = 15.3$ Hz)	2066 m, 2027 s, 2006 s, 1977 m, 1876 w, 1848 w
6	7.10—7.40 (m, 20 H); 7.28 (d, 1 H, $J = 15.7$ Hz); 6.87 (d, 1 H, $J = 15.7$ Hz); 5.32 (d, 1 H, $J = 12.3$ Hz); 5.13 (d, 1 H, $J = 12.3$ Hz)	2071 s, 2043 s, 2030 sh, 2009 s, 1990 s
7	7.17—7.71 (m, 20 H); 5.29 (d, 1 H, $J = 10.6$ Hz); 4.50 (d, 1 H, $J = 10.6$ Hz)	2065 s, 2028 m, 2018 m, 1977 w (br), 1945 m (br)

[a] Isomer **4s** was identified in the fraction containing **4a** and **4b**; its vinylic protons are exhibited at δ 7.02 and 6.70 ($J = 16.5$ Hz). [b] In hexane for complexes **4a**, **4b**, and **7** and in CH_2Cl_2 for compounds **5** and **6**.

spin-spin coupling constant in *trans*-disubstituted alkenes depends on the electronic properties of the substituent at the double bond. For example, it has been shown that the $J_{H,H}$ constants in *trans*-ferrocenylethylenes FcCH=CHCOMe, FcCH=CHCN, and FcCH=CHNO$_2$ decrease continuously with an increase in the electron-withdrawing ability of the substituent and amount to 16.0, 15.6, and 13.5 Hz, respectively.[11]

As noted above, the $J_{H,H}$ values for the ethylene protons of the two alkenyl groups in the asymmetrical complexe **4b** are 15.6 and 16.7 Hz. We believe that the lower value (15.6 Hz) refers to the alkenyl substituent located in the α-position with respect to the electron-withdrawing Ru(CO)$_3$ group in the ruthenacycle. Therefore, we attribute the structure **4a**, in which the alkenyl groups occupy the α- and α'-positions with respect to the Ru(CO)$_3$ group in the heterocyclic ring, to the symmetrical isomer Ru$_2$(CO)$_6$\{C$_4$Ph$_2$(CH=CHPh)$_2$\} with $J_{H,H}$ = 15.6 Hz for the ethylene protons.*

The same reasoning was used to determine the structures of other organoruthenium compounds, obtained in the reaction of Ru$_3$(CO)$_{12}$ with 1,4-diphenylbut-1-en-3-yne; its validity was confirmed by an X-ray structural study of cluster **6**.

A fraction containing three organoruthenium compounds in an overall yield of 40 % was also obtained in this reaction. This mixture was virtually inseparable by chromatography; however, after crystallization from hexane, orange (**5**), brown (**6**), and yellow-orange (**7**) crystalline products could be separated mechanically.

The IR spectrum of compound **5** (orange-colored) exhibits absorption bands at 1876 and 1848 cm^{-1} corresponding to the bridging CO ligands, and in general, it is similar to the spectra of "orange" isomers of ruthenium complexes of the composition Ru$_3$(CO)$_6$(μ-CO)$_2$(RC$_2$R)$_2$, the structure of which is known.[12,13] In the ¹H NMR spectrum of complex **5**, the signals of the ethylene protons of the two equivalent alkenyl groups have a spin-spin coupling constant $J_{H,H}$ of 15.3 Hz. Based on the spectral data we attributed the structure Ru$_3$(CO)$_6$(μ-CO)$_2$\{C$_4$Ph$_2$(CH=CHPh)$_2$\} to the orange cluster **5** (see Scheme 2).

Complex **6** (brown-colored) has the same composition, however, its IR spectrum differs from that of the orange complex **5** and indicates that only terminal CO groups are present. In addition, the ¹H NMR spectrum attests that one of the alkenyl groups is coordinated to the Ru atom: the two doublets corresponding to the protons of this group are exhibited in a substantially higher field (δ 5.13 and 5.32) and are split with a markedly lower spin-spin coupling constant ($J_{H,H}$ = 12 Hz) than those corresponding to the noncoordinated alkenyl group (δ 6.87 and 7.28, $J_{H,H}$ = 15.7 Hz).

* Isomer **4c** was not isolated in the individual state. It was identified in a mixture containing **4a** and **4b** on the basis of the ¹H NMR spectrum (see Table 2).

The structure of cluster **6** was established by an X-ray structural study of its single crystal. The molecular structure of **6** is presented in Fig. 1 and the main bond lengths and angles are presented in Table 3.

Table 3. The main bond lengths (*d*) and angles (ω) in the structure of **6**

Bond	*d*/Å	Angle	ω/deg
Ru(1)—C(1)	1.904(7)	C(1)—Ru(1)—C(3)	93.5(3)
Ru(1)—C(3)	1.938(6)	C(1)—Ru(1)—C(2)	98.6(3)
Ru(1)—C(2)	1.967(6)	C(3)—Ru(1)—C(2)	88.0(2)
Ru(1)—C(12)	2.082(5)	C(12)—Ru(1)—C(9)	77.5(2)
Ru(1)—C(9)	2.146(5)	C(1)—Ru(1)—Ru(2)	124.4(2)
Ru(1)—Ru(2)	2.7332(10)	C(3)—Ru(1)—Ru(2)	133.5(2)
Ru(1)—Ru(3)	2.8231(7)	C(2)—Ru(1)—Ru(2)	109.1(2)
Ru(2)—C(5)	1.877(6)	C(1)—Ru(1)—Ru(3)	147.7(2)
Ru(2)—C(4)	1.878(6)	C(3)—Ru(1)—Ru(3)	73.0(2)
Ru(2)—C(9)	2.137(5)	C(2)—Ru(1)—Ru(3)	109.8(2)
Ru(2)—C(10)	2.271(5)	Ru(2)—Ru(1)—Ru(3)	60.54(2)
Ru(2)—C(12)	2.281(5)	C(5)—Ru(2)—C(4)	86.1(3)
Ru(2)—C(11)	2.300(5)	C(5)—Ru(2)—Ru(1)	111.6(2)
Ru(2)—Ru(3)	2.8018(7)	C(4)—Ru(2)—Ru(1)	158.3(2)
Ru(3)—C(8)	1.894(6)	C(5)—Ru(2)—Ru(3)	107.5(2)
Ru(3)—C(7)	1.898(6)	C(4)—Ru(2)—Ru(3)	102.3(2)
Ru(3)—C(6)	1.900(6)	Ru(1)—Ru(2)—Ru(3)	61.32(2)
Ru(3)—C(33)	2.337(5)	C(8)—Ru(3)—C(7)	95.9(3)
Ru(3)—C(34)	2.397(5)	C(8)—Ru(3)—C(6)	94.3(3)
O(1)—C(1)	1.129(8)	C(7)—Ru(3)—C(6)	92.6(3)
O(2)—C(2)	1.115(7)	C(8)—Ru(3)—Ru(2)	72.5(2)
O(3)—C(3)	1.125(7)	C(7)—Ru(3)—Ru(2)	162.7(2)
O(4)—C(4)	1.127(8)	C(6)—Ru(3)—Ru(2)	100.9(2)
O(5)—C(5)	1.150(7)	O(8)—Ru(3)—Ru(1)	84.6(2)
O(6)—C(6)	1.126(8)	C(7)—Ru(3)—Ru(1)	109.0(2)
O(7)—C(7)	1.131(7)	C(6)—Ru(3)—Ru(1)	158.4(2)
O(8)—C(8)	1.135(7)	Ru(2)—Ru(3)—Ru(1)	58.14(2)
C(9)—C(10)	1.432(7)	O(1)—C(1)—Ru(1)	177.3(8)
C(9)—C(13)	1.467(7)	O(2)—C(2)—Ru(1)	177.1(6)
C(10)—C(11)	1.443(7)	O(3)—C(3)—Ru(1)	171.3(5)
C(10)—C(21)	1.501(7)	O(4)—C(4)—Ru(2)	175.2(6)
C(11)—C(12)	1.430(7)	O(5)—C(5)—Ru(2)	177.5(6)
C(11)—C(27)	1.498(7)	O(6)—C(6)—Ru(3)	176.8(6)
C(12)—C(33)	1.474(7)	O(7)—C(7)—Ru(3)	178.8(6)
C(13)—C(14)	1.329(8)	O(8)—C(8)—Ru(3)	168.5(5)
C(14)—C(15)	1.457(8)	C(10)—C(9)—C(13)	118.7(5)
C(33)—C(34)	1.377(7)	C(10)—C(9)—Ru(1)	113.7(3)
C(34)—C(35)	1.488(7)	C(13)—C(9)—Ru(1)	123.4(4)
		C(9)—C(10)—C(11)	114.6(4)
		C(9)—C(10)—C(21)	122.0(5)
		C(11)—C(10)—C(21)	123.3(5)
		C(12)—C(11)—C(10)	115.0(4)
		C(12)—C(11)—C(27)	123.7(4)
		C(10)—C(11)—C(27)	121.3(5)
		C(11)—C(12)—C(33)	118.3(5)
		C(11)—C(12)—Ru(1)	116.2(3)
		C(33)—C(12)—Ru(1)	124.8(4)
		C(14)—C(13)—C(9)	126.0(6)
		C(13)—C(14)—C(15)	126.6(6)
		C(34)—C(33)—C(12)	123.5(5)
		C(33)—C(34)—C(35)	126.4(5)

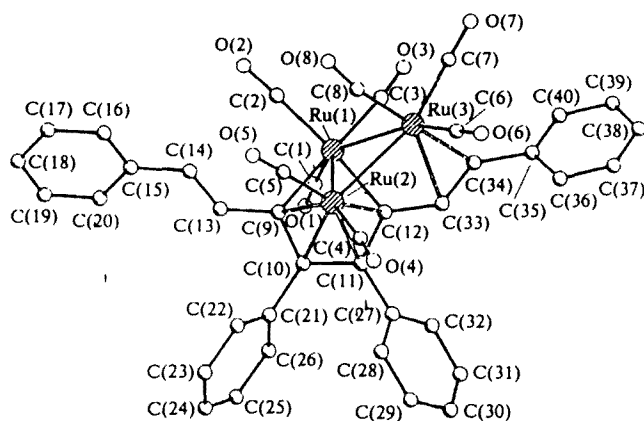Fig. 1. Molecular structure of complex 6.

Molecule 6 is a trinuclear ruthenium cluster in which the metal atoms are located at the vertices of a triangle with one short side [Ru(1)—Ru(2), 2.7332(7) Å] and two long sides [Ru(2)—Ru(3), 2.8018(3) Å and Ru(1)—Ru(3), 2.8231(7) Å]. The metallic framework coordinates eight terminal CO groups and the organic ligand resulting from the "head-to-head" coupling of two enyne molecules. The organic ligand is linked to one of the Ru atoms through two σ-bonds thus forming a ruthenacyclopentadiene ring and is linked to the other metal atom through a diene π-bond. Such a "side" or μ_2-η^1-η^1-η^4-bonding of the metallacyclopentadiene moiety is usual in the series of trimetallic clusters of osmium,[14] ruthenium,[15] and iron.[16] Only recently[17] we found for the first time an alternative "face", μ_3-η^1-η^1-η^2-η^2-bonding of this moiety in the $Os_3(CO)_9\{\mu_3$-η^1-η^1-η^2-η^2-$C(SiMe_3)C(Me)C(H)C(Ph)\}$ cluster. An interesting feature of the structure of compound 6 is that one of the alkenyl groups bound to the metallacyclopentadiene ring forms a π-bond with the third Ru atom. The data of ¹H NMR spectroscopy indicate that this interaction is also retained in solutions of complex 6. Thus, the organic ligand in cluster 6 as a whole is a donor of eight electrons.

The Ru(1)C(9)C(10)C(11)C(12) ruthenacyclopentadiene ring in the structure of 6 has a flattened envelope conformation: the Ru(1) atom emerges from the plane (accurate to 0.02 Å) of the remaining four atoms of the ring by 0.41 Å, the inflection angle along the C(9)···C(12) line is 14.6°. The dihedral angle formed by the C(9)Ru(1)C(12) plane and the Ru₃ plane is 125.9°.

All the bonds in the C(9)C(10)C(11)C(12) diene fragment are virtually equal [C(9)—C(10), 1.432(7) Å; C(10)—C(11), 1.443(7) Å; C(11)—C(12), 1.432(7) Å]. A notable feature of the geometry of the complex, which is obviously caused by its general asymmetry, is that the lengths of the Ru(1)—C(9) [2.146(5) Å] and Ru(1)—C(12) [2.082(5) Å] σ-bonds are substantially dissimilar. Naturally, the lengths of the free and coordinated ethylene bonds are markedly different [C(13)—C(14), 1.329(8) Å; C(33)—C(34), 1.377(7) Å], whereas the lengths of the single bonds adjacent to them, C(9)—C(13)

[1.467(7) Å] and C(12)—C(13) [1.474(7) Å], are almost identical.

The molecular structure of complex 6 is similar to those found for complexes $Fe_3(CO)_8\{C_4Me(NEt_2)_2\}$ [16] (8) and $Ru_3(CO)_8\{C_4Ph_2MeCH_2NMe_2\}$ [18] (9), which also contain metallacyclopentadiene fragment with the "side" coordination; however, the third metal atom in these clusters coordinates the N atom of the amino group.
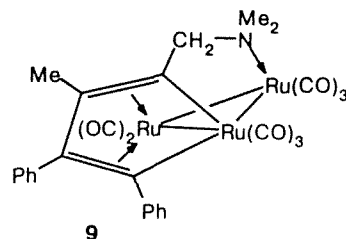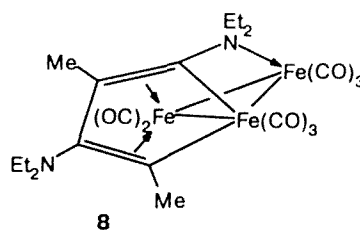
The ¹H NMR spectrum of compound 7 (yellow-orange colored) is rather simple and contains two doublets at δ 5.40 and 5.29 ($J_{H,H}$ = 10.6 Hz in both cases) and a complex multiplet for the phenyl groups in the region of δ 7.17—7.70. The upfield shift of the ethylene protons with respect to the signals of the noncoordinated alkenyl group and the small $J_{H,H}$ value indicate that this group is coordinated to the Ru atom. The region of the absorption of carbonyl groups in the IR spectrum of complex 7 contains bands at 2065, 2028, 2018, 1977, and 1945 cm⁻¹.

In some experiments, black-colored cluster 10 has been obtained in a very low yield. The ¹H NMR spectrum of this compound, along with the broad multiplet due to the aromatic protons, exhibits four doublets, two of which recorded at δ 6.26 and 5.60 and having a spin-spin coupling constant $J_{H,H}$ of 16.4 Hz correspond to the noncoordinated alkenyl group; the two other signals at δ 4.97 and 4.78 are split with $J_{H,H}$ = 10.8 Hz and should be assigned to the π-coordinated group. The IR spectrum of this complex exhibits nine absorption bands due to the terminal CO groups and a band at 1670 cm⁻¹.

In order to determine the structures of complexes 7 and 10, we are trying to prepare single crystals of these compounds suitable for X-ray diffraction analysis.

Experimental

The reactions were carried out in an argon atmosphere, while the chromatographic separation of reaction products was carried out in air. The L 100/160 μ silica gel (Chemapol) was

Table 4. Coordinates of atoms ($\times 10^4$) and their isotropic equivalent temperature factors ($\times 10^3$) in the structure of **6**

Atom	x	y	z	$U_{eq}/\text{Å}^2$
Ru(1)	1342(1)	4796(1)	1054(1)	35(1)
Ru(2)	2254(1)	4865(1)	2315(1)	35(1)
Ru(3)	1407(1)	5823(1)	1985(1)	36(1)
O(1)	1664(4)	4210(3)	−539(3)	112(3)
O(2)	100(2)	4047(2)	1546(3)	70(1)
O(3)	306(3)	5605(2)	231(3)	65(1)
O(4)	3331(3)	5344(3)	3439(3)	85(2)
O(5)	1726(3)	4271(2)	3817(3)	78(2)
O(6)	1952(4)	6695(2)	3199(3)	94(2)
O(7)	171(3)	6578(3)	1601(4)	89(2)
O(8)	628(2)	5176(2)	3271(3)	64(1)
C(1)	1528(4)	4423(3)	54(4)	62(2)
C(2)	545(3)	4328(2)	1384(3)	46(1)
C(3)	701(3)	5343(3)	572(3)	46(1)
C(4)	2927(3)	5187(3)	3000(4)	50(1)
C(5)	1911(3)	4499(3)	3241(3)	50(1)
C(6)	1763(4)	6375(3)	2732(4)	55(2)
C(7)	631(3)	6293(3)	1737(4)	56(2)
C(8)	967(3)	5371(3)	2787(3)	46(1)
C(9)	2065(3)	4164(2)	1496(3)	39(1)
C(10)	2768(3)	4316(2)	1353(3)	39(1)
C(11)	2878(3)	4917(2)	1143(3)	37(1)
C(12)	2265(3)	5255(2)	1049(3)	35(1)
C(13)	1890(3)	3551(2)	1626(4)	49(1)
C(14)	1430(3)	3350(2)	2145(4)	50(1)
C(15)	1250(3)	2743(3)	2281(5)	61(2)
C(16)	871(5)	2597(4)	2956(5)	82(2)
C(17)	718(6)	2016(5)	3112(7)	114(4)
C(18)	935(7)	1585(5)	2604(10)	134(6)
C(19)	1309(6)	1726(4)	1948(10)	135(5)
C(20)	1467(5)	2301(3)	1792(7)	95(3)
C(21)	3333(3)	3870(3)	1365(4)	53(2)
C(22)	3519(4)	3589(4)	2074(6)	84(3)
C(23)	4020(6)	3154(5)	2067(9)	126(5)
C(24)	4320(6)	3002(5)	1335(9)	127(5)
C(25)	4126(5)	3274(4)	626(7)	107(4)
C(26)	3637(4)	3718(3)	655(5)	68(2)
C(27)	3588(3)	5156(2)	1028(3)	42(1)
C(28)	4132(3)	5037(3)	1533(4)	55(2)
C(29)	4784(3)	5244(3)	1371(5)	67(2)
C(30)	4897(4)	5578(3)	696(5)	68(2)
C(31)	4370(4)	5686(3)	181(5)	68(2)
C(32)	3703(3)	5478(2)	324(4)	51(1)
C(33)	2323(3)	5894(2)	1086(3)	37(1)
C(34)	1833(3)	6266(2)	779(3)	41(1)
C(35)	1861(3)	6913(2)	788(3)	43(1)
C(36)	2349(3)	7225(3)	1208(4)	55(2)
C(37)	2333(4)	7831(3)	1206(5)	68(2)
C(38)	1837(4)	8117(3)	772(5)	69(2)
C(39)	1361(5)	7818(3)	356(5)	75(2)
C(40)	1365(4)	7216(3)	346(4)	62(2)

used as the adsorbent. 1,4-Diferrocenylbuta-1,3-diyne and 1,4-diphenylbut-1-en-3-yne were synthesized by known procedures.[19,20]

^{1}H NMR spectra were recorded on a Bruker WP-SY instrument (200.13 MHz). IR spectra were obtained on a Bruker IFS-113v instrument.

Reaction of 1,4-diferrocenylbuta-1,3-diyne with Ru₃(CO)₁₂. A mixture of diyne (0.21 g, 0.50 mmol) and Ru₃(CO)₁₂ (0.14 g, 0.22 mmol) in 60 mL of hexane was boiled for 2 h. The solvent

was evaporated on a rotary evaporator, and the residue was chromatographed on a column with silica gel. A light yellow band was eluted with petroleum ether (40—70 °C); 0.02 g (14 %) of ruthenium carbonyl was recovered from this fraction. Red-brown and then the crimson-colored bands were eluted with a petroleum ether—benzene (1 : 1) mixture. The repeated chromatographing of the red-brown fraction on a column with silica gel (a petroleum ether—benzene mixture (5 : 1), as the eluent) gave 0.09 g (34 %) of complex **1a**. The repeated chromatographing of the crimson-colored fraction (a petroleum ether—benzene mixture (5 : 1), as the eluent) resulted in an orange band and two crimson bands; 0.03 g (11 %) of complex **1b** were isolated from the orange band, 0.02 g (7 %) of complex **2a** was isolated from the first crimson band, and 0.03 g (11 %) of complex **2b** was obtained from the second crimson band.

Ru₂(CO)₆{C₄Fc₂(C≡CFc)₂} (**1a**). Red crystals, m.p. 203—205 °C. Found (%): C, 53.74; H, 3.01; Ru, 16.15. C₅₄H₃₆Fe₄O₆Ru₂. Calculated (%): C, 53.73; H, 2.98; Ru, 16.74.

Ru₂(CO)₆{C₄Fc₂(C≡CFc)₂} (**1b**). Red-orange crystals, m.p. 231—234 °C (decomp.) (from a hexane—CH₂Cl₂ mixture). Found (%): C, 53.72; H, 3.42. C₅₄H₃₆Fe₄O₆Ru₂. Calculated (%): C, 53.73; H, 2.98. Data of X-ray fluorescence analysis: Fe/Ru = 2 : 1.

Ru₂(CO)₆{C₄Fc₂(C≡CFc)₂C=O} (**2a**). Dark red crystals, m.p. 225—227 °C (decomp.). Found (%): C, 53.87; H, 2.92. C₅₅H₃₆Fe₄O₇Ru₂. Calculated (%): C, 53.53; H, 2.92. Data of X-ray fluorescence analysis: Fe/Ru = 2 : 1.

Ru₂(CO)₆{C₄Fc₂(C≡CFc)₂C=O} (**2b**). Dark-crimson-colored crystals, decomp. at 200 °C (from pentane). Found (%): C, 54.38; H, 3.65. C₅₅H₃₆Fe₄O₇Ru₂. Calculated (%): C, 53.53; H, 2.92. Data of X-ray fluorescence analysis: Fe/Ru = 2.3 : 1.0.

Reaction of 1,4-diphenylbut-1-en-3-yne with Ru₃(CO)₁₂. A mixture of enyne (0.20 g, 0.98 mmol) and Ru₃(CO)₁₂ (0.21 g, 0.33 mmol) in 30 mL of hexane was boiled for 2 h. The reaction mixture was filtered off, the solvent was evaporated on a rotary evaporator, and the residue was chromatographed on a column. A light-yellow band was eluted with petroleum ether; 0.01 g (5 %) of ruthenium carbonyl was recovered from this fraction; 0.11 g (42 %) of compound **4b** was obtained from the following bright-yellow band, and the next brown band contained 0.01 g (3 %) of compound **4a**. A broad dark-red band was eluted with a petroleum ether—benzene (5 : 1) mixture; this fraction afforded 0.12 g (39 %) of a mixture of three-nuclear clusters. Crystallization of this mixture from hexane gave orange (**5**) and brown (**6**) complexes both having the same composition Ru₃(CO)₈(PhC₂CH=CHPh)₂, as well as yellow-orange complex **7**.

Ru₂(CO)₆{C₄Ph₂(CH=CHPh)₂} (**4b**). Bright-yellow crystals. Found (%): C, 58.25; H, 3.34. C₃₈H₂₄O₆Ru₂. Calculated (%): C, 58.62; H, 3.08.

Ru₃(CO)₈{C₄Ph₂(CH=CHPh)₂} (**6**). Brown crystals. Found (%): C, 51.31; H, 2.40. C₄₀H₂₄O₈Ru₃. Calculated (%): C, 51.33; H, 2.59.

X-ray structural study of complex 6. Crystals of **6** are monoclinic; at 20 °C $a = 19.433(4)$ Å, $b = 23.003(5)$ Å, $c = 16.566(3)$ Å, $\beta = 90.44(3)°$, $V = 7405(3)$ Å³, $d_{calc} = 1.679$ g cm⁻³, $Z = 8$, space group $C2/c$. Unit cell parameters and intensities of 7639 independent reflections were measured on a CAD-4 Enraf-Nonius automatic diffractometer (20 °C, Mo-Kα-radiation, graphite monochromator, θ-5/3θ-scanning, θ ≤ 26.48°).

The structure was solved by the direct method and refined by the full-matrix least-squares method in the isotropic and then in the anisotropic approximations. Hydrogen atoms were arranged geometrically and included in the refinement in terms of the "rider" model with the common temperature factor being refined $U_{iso} = 0.086(5)$ Å². The final residual factors: $R_1 = 0.0433$ (over

F for 6009 observed reflections with $I > 2\sigma(I)$), $wR_2 = 0.1516$ (over F^2 for all the 7566 independent reflections used in the refinement). All the calculations were carried out using the SHELXL-93 program on IBM PC. The coordinates of nonhydrogen atoms are listed in Table 4.

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