Reaction of alkyne cluster
$Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}Me_3SiC_2Me)$ with $HC{\equiv}CCOOMe$.
Molecular and crystal structures of
$Os_3(CO)_9\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C(SiMe_3)C(Me)C(COOMe)CH\}$ and
$Os_3(CO)_8\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^4{:}\eta^1\text{-}C(SiMe_3)C(Me)C(H)C(COOMe)\}$ complexes

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Reaction of the cluster $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}Me_3SiC_2Me)$ with $HC{\equiv}CCOOMe$ in benzene at 70 °C results in $Os_3(CO)_9\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C(SiMe_3)C(Me)C(COOMe)CH\}$ (**5**), $Os_3(CO)_9\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(COOMe)\}$ (**6**), $Os_3(CO)_9\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^4\text{-}C(SiMe_3)C(Me)C(COOMe)CH\}$ (**7**), and $Os_3(CO)_8\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^4{:}\eta^1\text{-}C(SiMe_3)C(Me)C(H)C(COOMe)\}$ complexes (**8**), containing an osmacyclopentadiene moiety. Complexes **5—8** were characterized by ^1H NMR and IR spectroscopy. The structure of clusters **5** and **8** was confirmed by X-ray analysis. Complex **7** is formed from cluster **5** as a result of a new intramolecular rearrangement and complex **8** is obtained by decarbonylation of compound **6**. Complex **8** adds PPh_3 to give $Os_3(CO)_8(PPh_3)\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^4\text{-}C(SiMe_3)C(Me)C(H)(COOMe)\}$.

Key words: osmium, carbonyl clusters, alkyne dimerization, osmacyclopentadiene complexes, intramolecular rearrangement.

In studies of the mechanism of linear dimerization of silylalkynes and their codimerization with internal alkynes on Ru_3 and Os_3 carbonyl clusters we have shown that it involves the formation of metallacyclobutene derivatives of trimetallic clusters.[1—3] Thus, we established that in the reaction of alkyne cluster $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}Me_3SiC_2Me)$ (**1**) with $Me_3SiC{\equiv}CBu^n$ the second (incoming) alkyne molecule, coupled with the preliminarily coordinated alkyne, undergoes acetylene-vinylidene rearrangement *via* a 1,2-shift of the Me_3Si group. This results in cluster $Os_3(CO)_9\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C(SiMe_3){=}C(Me)C{=}C(SiMe_3)Bu^n\}$ (**2**), containing an osmacyclobutene moiety. The structure of cluster **2** was established by single-crystal X-ray analysis.[3]

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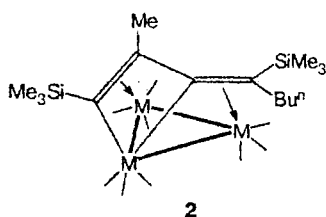
The ability of terminal alkynes to undergo acetylene-vinylidene rearrangement under the action of transition-

metal complexes is well known and most of the studies of the above rearrangements were carried out taking terminal alkynes as examples.[4] Hence it could be expected that in the reactions of cluster **1** with terminal alkynes the latter would undergo a 1,2-hydrogen shift with the formation of corresponding metallacyclobutene derivatives related to cluster **2**. However, as was shown in studies of the reaction of cluster **1** with phenylacetylene[5] (the first example) and ferrocenylacetylene,[6] these alkynes do not undergo acetylene-vinylidene rearrangement under given conditions. The reactions involve alkyne—alkyne coupling and result in triosmium clusters containing an osmacyclopentadiene moiety. At the same time, the structure of $Os_3(CO)_9\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(R)\}$ (**3**: R = Ph,[5] **4**: R = Fc[6]) clusters appeared to be unusual. In these clusters, the dienediyl ligand is bound to three metal atoms and is located above the plane of the Os_3 triangle (structure **A**) in contrast to trimetallic clusters of well known structure **B** with "side-on" or $\mu\text{-}\eta^1{:}\eta^1{:}\eta^4$-coordination of the hydrocarbon ligand.[7]

In a continuation of our studies of heteroalkyne dimerization on Os_3 clusters, in this work we studied the reactions of complex **1** with terminal alkyne $HC{\equiv}CCOOMe$. It was shown that isomeric clusters with structure **A** are primary reaction products; the intramo-

A   **B**
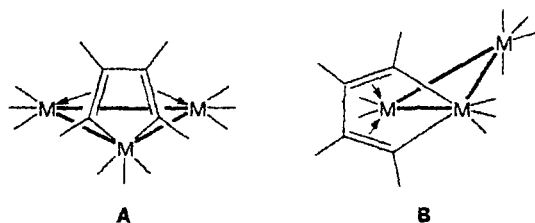
lecular **A** → **B** rearrangement was performed for one of the isomers. Chemical properties of the clusters obtained were also studied.

Results and Discussion

The reaction of complex **1** with methyl propiolate in benzene (70 °C, 6 h) resulted in four new compounds isolated by chromatography on silica gel (Scheme 1). Clusters $Os_3(CO)_9\{\mu_3-\eta^1:\eta^1:\eta^2:\eta^2-C(SiMe_3)C(Me)C(COOMe)CH\}$ (**5**), $Os_3(CO)_9\{\mu_3-\eta^1:\eta^1:\eta^2:\eta^2-C(SiMe_3)C(Me)C(H)C(COOMe)\}$ (**6**), $Os_3(CO)_9\{\mu-\eta^1:\eta^1:\eta^4-C(SiMe_3)C(Me)C(COOMe)CH\}$ (**7**), and $Os_3(CO)_8\{\mu_3-\eta^1:\eta^1:\eta^4:\eta^1-C(SiMe_3)C(Me)—C(H)C(COOMe)\}$ (**8**) were obtained in 16, 29, 40, and 9% yields, respectively. They were characterized by ^{1}H NMR and IR spectroscopy and the structure of complexes **5** and **8** was also confirmed by X-ray analysis.

IR spectra of clusters **5** and **6** in the region of $v(C=O)$ absorption are similar to those of compounds **3** and **4**.[3] This indicates that they have structure **A**. On the contrary, IR spectroscopy data show that cluster **7** has structure of type **B**. Isomerism of compounds **5** and **6** should be a consequence of different modes of coupling of asymmetric alkynes. ^{1}H NMR spectra make it possible to choose between isomeric structures of clusters **5** and **6**. Thus, although the ^{1}H NMR spectra of both clusters contain four singlets with the ratio of relative

integral intensities 9 : 3 : 3 : 1 (due to Me_3Si, Me, OMe, and H, respectively), the chemical shifts of the signal with the relative integral intensity of 1 are strongly different: the δ value is 10.35 and 6.69 for cluster **5** and **6**, respectively. Strong deshielding of the above signal in the spectrum of cluster **5** may indicate that, in contrast to complexes **3**, **4**, and **6**, in this compound the hydrogen atom is at the σ,π-coordinated carbon atom (α-position of the osmacyclopentadiene moiety). This assignment was confirmed by the data of X-ray study of compound **5**.

The molecular structure of cluster **5** is shown in Fig. 1 and the main bond lengths and bond angles are listed in Table 1. Molecule **5** is an osmacyclopentadiene derivative of the triosmium cluster and is similar to complexes **3** and **4** studied previously.[5,6] In contrast to **3** and **4**, the coupling of terminal alkyne with silyl-substituted alkyne, resulting in cluster **5**, occurs in such a way that the hydrogen atom appears to be attached to the α-C atom of the osmacyclopentadiene moiety. The latter is nonplanar and has an envelope conformation: the angle of folding along the C(10)...C(13) line is 25°. The angle between the Os_3 and C(10)Os(1)C(13) planes is 60° and the angle between the Os_3 and C(10)C(11)C(12)C(13) diene fragment is 36°. As in previously studied clusters **3** and **4**, asymmetry of the π-bonds of the Os(2) and Os(3) atoms with olefin fragments of the metallacyclopentadiene moiety is observed in the structure of molecule **5**. Thus, the Os—C distances for one π-bond appreciably differ (Os(2)—C(10) 2.167 and Os(2)—C(11) 2.441 Å) from those for the other π-bond (Os(3)—C(12) 2.277 and Os(3)—C(13) 2.178 Å).

The ^{1}H NMR spectra of clusters **6** and **8** are rather similar, while the IR spectrum of the latter contains a weak absorption band at 1571 cm^{−1}, which can be assigned to the coordinated acyl group.[8,9] In addition, the IR spectrum of compound **8** in the region of stretching $v(C=O)$ vibrations is similar to that of

Scheme 1
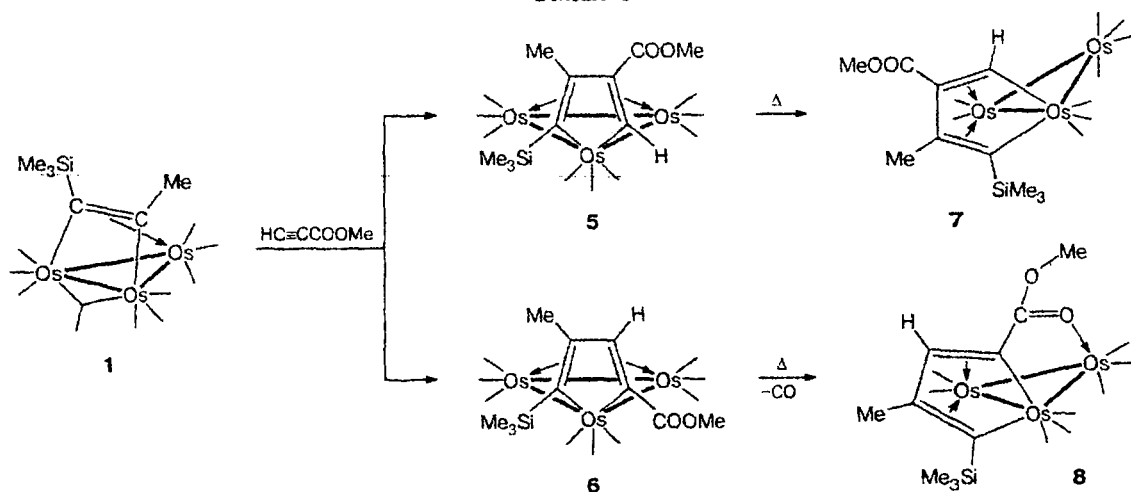
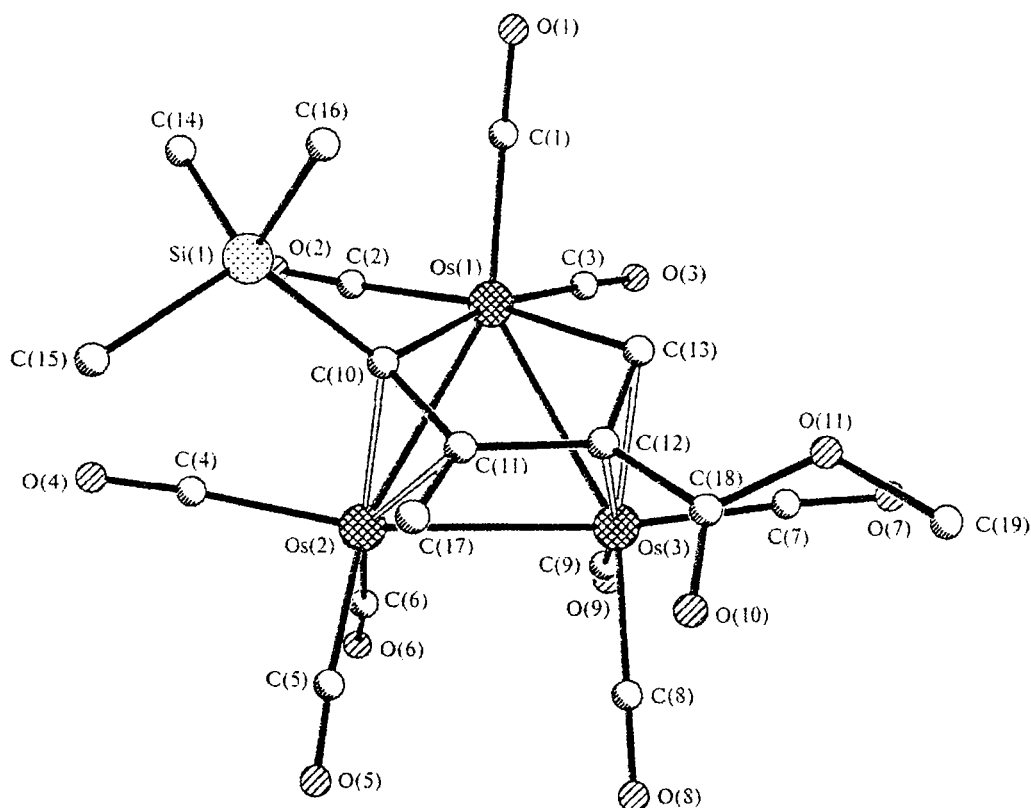**Fig. 1.** Molecular structure of complex Os₃(CO)₉{µ₃-η¹:η¹:η²:η²-C(SiMe₃)C(Me)C(COOMe)CH} (5).

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

Bond	$d/\text{Å}$	Bond	$d/\text{Å}$	Bond	$d/\text{Å}$
Os(1)—Os(2)	2.8248(7)	Os(3)—C(12)	2.277(9)	C(11)—C(12)	1.486(12)
Os(1)—Os(3)	2.8254(7)	Os(3)—C(13)	2.178(8)	C(11)—C(17)	1.520(12)
Os(2)—Os(3)	2.7932(7)	O(10)—C(18)	1.185(11)	C(12)—C(13)	1.422(11)
Os(1)—C(10)	2.174(7)	O(11)—C(18)	1.355(11)	C(12)—C(18)	1.489(11)
Os(1)—C(13)	2.099(8)	O(11)—C(19)	1.466(11)	Os—C(O) (aver.)	1.890(9)—1.933(9)
Os(2)—C(10)	2.167(9)	C(10)—C(11)	1.424(11)	C—O (aver.)	1.088(13)—1.156(12)
Os(2)—C(11)	2.441(9)				

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Os(2)—Os(1)—Os(3)	59.25(1)	Si(1)—C(10)—Os(1)	124.4(4)	C(18)—C(12)—C(11)	120.7(7)
Os(3)—Os(2)—Os(1)	60.38(1)	C(10)—C(11)—C(12)	116.7(7)	C(12)—C(13)—Os(1)	112.0(5)
Os(2)—Os(3)—Os(1)	60.36(2)	C(10)—C(11)—C(17)	123.6(8)	O(10)—C(18)—O(11)	122.6(8)
C(13)—Os(1)—C(10)	79.4(3)	C(12)—C(11)—C(17)	117.7(8)	O(10)—C(18)—C(12)	127.1(9)
C(11)—C(10)—Os(1)	109.4(5)	C(13)—C(12)—C(18)	122.1(7)	O(11)—C(18)—C(12)	110.1(7)
C(11)—C(10)—Si(1)	119.5(6)	C(13)—C(12)—C(11)	115.1(6)	O—C—Os (aver.)	174.2(12)—178.8(8)

the octacarbonyl triosmium cluster Os₃(CO)₈{µ₃-η¹:η¹:η⁴:η¹-(1,2-C₆H₄CPh)CCOOMe} (9) obtained using a complex procedure.[10] The presence of an ester group in α-position of the osmacyclopentadiene moiety of cluster 6 suggested that decarbonylation of cluster 6 will result in compound 8. A separate experiment showed that it does occur: cluster 8 appeared to be the only product of thermolysis of cluster 6 in boiling benzene.

X-ray study of a single crystal of cluster 8 confirmed the assumed structure.

The molecular structure of cluster 8 is shown in Fig. 2 and the main bond lengths and bond angles are listed in Table 2. Molecule 8 is an Os₃ cluster in which the metal atoms are at the vertices of a nearly equilateral triangle. The SiMe₃ and COOMe substituents are in α-positions of the osmacyclopentadiene moiety of com-
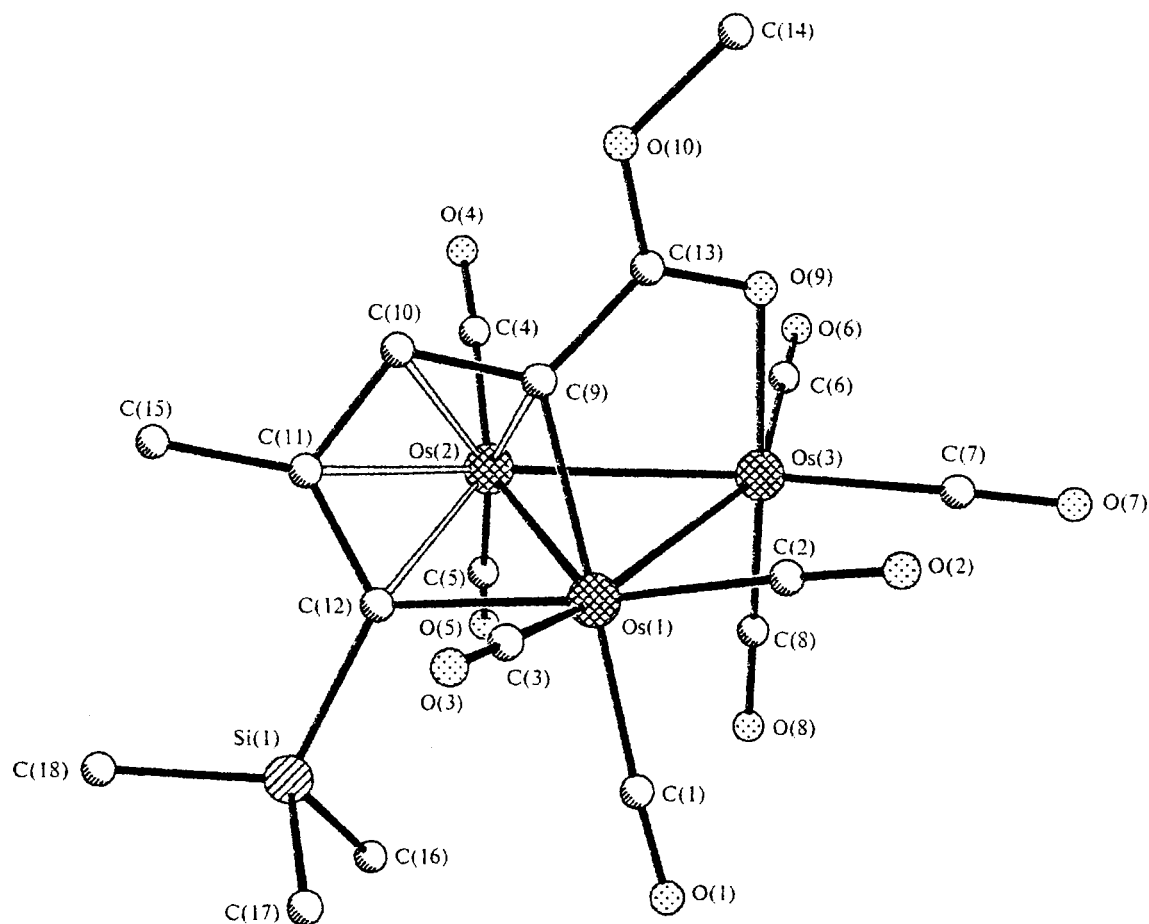
Fig. 2. Molecular structure of complex $Os_3(CO)_8\{\mu_3-\eta^1:\eta^1:\eta^4:\eta^1-C(SiMe_3)C(Me)C(H)C(COOMe)\}$ (8).

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **8**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Os(1)—Os(2)	2.7177(6)	Os(2)—C(11)	2.301(9)	C(9)—C(13)	1.457(9)
Os(1)—Os(3)	2.8540(7)	Os(2)—C(12)	2.199(8)	C(10)—C(11)	1.458(10)
Os(2)—Os(3)	2.7216(6)	Os(3)—O(9)	2.173(4)	C(11)—C(12)	1.440(10)
Os(1)—C(9)	2.108(6)	O(9)—C(13)	1.249(8)	C(11)—C(15)	1.524(10)
Os(1)—C(12)	2.202(6)	O(10)—C(13)	1.312(7)	Os—C(O) (aver.) 1.844(7)—1.936(7)	
Os(2)—C(9)	2.224(6)	O(10)—C(14)	1.453(8)	C—O (aver.) 1.126(9)—1.188(11)	
Os(2)—C(10)	2.261(8)	C(9)—C(10)	1.401(9)		

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Os(2)—Os(1)—Os(3)	58.42(2)	C(10)—C(9)—Os(1)	117.5(5)	C(11)—C(12)—Os(1)	113.5(4)
Os(1)—Os(2)—Os(3)	63.30(2)	C(13)—C(9)—Os(1)	121.1(4)	Si(1)—C(12)—Os(1)	119.2(3)
Os(2)—Os(3)—Os(1)	58.28(2)	C(9)—C(10)—C(11)	116.1(6)	O(9)—C(13)—O(10)	121.6(6)
C(9)—Os(1)—C(12)	76.5(2)	C(12)—C(11)—C(10)	114.2(6)	O(9)—C(13)—C(9)	120.9(5)
C(13)—O(9)—Os(3)	113.9(4)	C(12)—C(11)—C(15)	127.9(7)	O(10)—C(13)—C(9)	117.5(6)
C(13)—O(10)—C(14)	116.5(6)	C(10)—C(11)—C(15)	117.9(7)	O—C—Os (aver.) 171.8(8)—178.0(6)	
C(10)—C(9)—C(13)	121.3(6)	C(11)—C(12)—Si(1)	125.1(5)		

plex **8**, as we suggested for compound **6**, a precursor of complex **8**. In contrast to structure **6**, the dienediyl ligand in molecule **8** is bonded only to two osmium atoms, by two σ-bonds to the Os(1) atom and by a η^4-diene bond to the Os(2) atom; in this case, the metal atoms coordinate respectively three and two CO ligands.

The third metal atom, Os(3), coordinates two equatorial CO groups and one axial CO group; the oxygen atom of the acyl group is in *trans*-position to the latter (the Os(3)—O(9) distance is 2.173(4) Å). The C(13)—O(9) distance in this group is 1.249(8) Å and coincides with the value 1.247(5) Å found for the acyl group coordinated to the ruthenium atom in cluster Ru₃(μ-H)₂(CO)₉(μ₃-CHCOOMe).[8]

Carbonyl ligands have conventional geometric parameters, except for the nonlinear C(2)O(2) group at the Os(1) atom (the Os(1)—C(2)—O(2) angle is 171.8(8)°), which can be considered as a semibridging group (the C(2)...Os(3) distance is 2.935 Å).

The five-membered metallacycle in molecule **8** has an envelope conformation: the Os(1) atom deviates from the C(9)C(10)C(11)C(12) plane by 0.367 Å and the angle of folding along the C(9)...C(12) line is 12.5°. The angle between the plane of the Os₃ triangle and the mean plane of the five-membered metallacycle is 64.7°. Such a tilt of the metallacyclopentadiene ring with respect to the plane of the metal triangle was also reported for related clusters where the metallacyclopentadiene ring has an intermediate position between structures A and B because of the tightening effect of the α-substituent due to its coordination to the metal atom. The structures of hydride complex Os₃(μ-H)(CO)₈{μ₃-η¹:η¹:η⁴:η¹-C₄Ph₃(C₆H₄)}[11] (**10**) with the *ortho*-metallated phenyl substituent and the complex Ru₃(CO)₈{μ₃-η¹:η¹:η⁴:η²-C₄Ph₂(CH=CHPh)₂}[12] (**11**), in which one of the alkenyl groups is coordinated to the ruthenium atom not participating in the bonding with the ruthenacyclopentadiene moiety, can be taken as examples. According to data of ¹H NMR and IR spectroscopy, hydride clusters Os₃(μ-H)(CO)₈{μ₃-η¹:η¹:η⁴:η¹-C(SiMe₃)C(Me)C(H)C(R')} (**12**: R' = C₆H₄; **13**: R' = C₅H₃FeC₅H₅), obtained[5,6] on heating respectively complexes **3** and **4** in benzene, have a structure similar to that found for compound **10**.

Since neither a group capable of undergoing *ortho*-metallation nor a functional substituent capable of coordinating the metal atom is attached to the α-position of the metallacyclopentadiene moiety of cluster **5**, it should be expected that this cluster can undergo intramolecular A → B rearrangement and, hence, is a precursor of cluster **7**. It turned out that thermal isomerization **5** → **7** does occur under mild conditions: heating a solution of complex **5** in CDCl₃ or C₆D₆ in an NMR tube at 45—50 °C results in its isomerization into complex **7**.[13] This intramolecular rearrangement never observed previously involves changes in the dienediyl ligand coordination from μ₃-η¹:η¹:η²:η² to μ-η¹:η¹:η¹:η⁴ and internuclear migration of one of the CO groups. Thus, we showed that the trimetallic cluster of type A, in which the hydrocarbon ligand forms η²-bonds with two metal atoms, is thermodynamically less stable as compared to isomer **B**, in which the same ligand forms a diene η⁴-bond with one metal atom. We believe this fact can

explain why complexes of type **A** have remained elusive for such a long time.

One more indication of relative stability of isomers of type **B** is the formation of the above complexes and their phosphine derivatives under the action of carbon monoxide[14] and triphenylphosphine[2,14] on hydride clusters **10** and **12**. These reactions result in Os₃(CO)₉₋ₙLₙ(μ-η¹:η¹:η⁴-C₄Ph₄) (L = CO, n = 0; L = PPh₃, n = 1) and Os₃(CO)₈(PPh₃){μ-η¹:η¹:η⁴-C(SiMe₃)C(Me)C(H)C(Ph)} complexes. We found that complex **8** behaves analogously and adds PPh₃ at room temperature to replace the acyl group from the coordination sphere of the Os atom and to give the carbonylphosphine derivative Os₃(CO)₈(PPh₃){μ-η¹:η¹:η⁴-C(SiMe₃)C(Me)C(H)C(COOMe)} (**14**) (Scheme 2). It is assumed that the structure of complex **14** is similar to that found recently[12] for the triruthenium cluster Ru₃(CO)₈(PPh₃){μ-η¹:η¹:η⁴-C₄Ph₂(CH=CHPh)₂}, with a phosphine ligand in the equatorial position, in *trans*-position with respect to the (OC)₃Ru—Ru(CO)₃PPh₃ bond.

Scheme 2

One more indication of relative stability of isomers
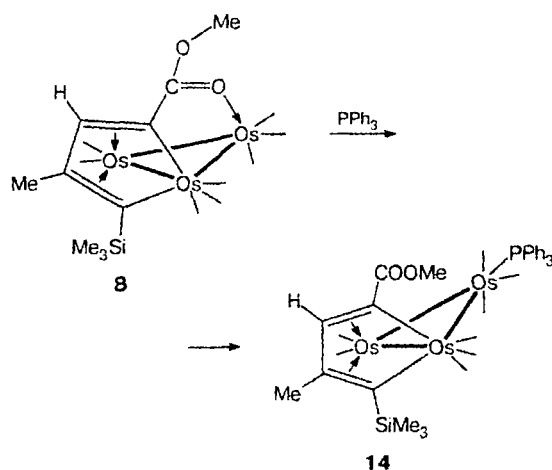
Experimental

¹H and ³¹P NMR spectra were recorded on a Bruker AMX-400 spectrometer and IR spectra were recorded on a Bruker IFS-113v instrument. The reactions were carried out in an Ar atmosphere and chromatographic separation was performed in air. Chemapol L 100/160 μm silica gel was used for preparative chromatographic separations of the reaction products.

Reaction of complex Os₃(μ-CO)(CO)₉(μ₃-Me₃SiC₂Me) (1) with HC≡CCOOMe. To a solution of Os₃(μ-CO)(CO)₉(μ₃-Me₃SiC₂Me) (135 mg, 0.14 mmol) in benzene, HC≡CCOOMe (59 mg, 0.7 mmol) was added, the mixture was stirred for 6 h at 65—70 °C, and the orange solution turned red-brown. The reaction was monitored by TLC. After evaporation of the

solvent, the reaction products were separated by column chromatography on silica gel. Four fractions were isolated. First, a light-yellow fraction and a yellow fraction were eluted with hexane. The starting complex $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ (1) and 13 mg (9%) of complex $Os_3(CO)_8\{\mu_3\text{-}\eta^1:\eta^1:\eta^4:\eta^1\text{-}C(SiMe_3)C(Me)C(H)C(COOMe)\}$ (8) were isolated from the light-yellow and yellow fractions, respectively. Then, a red-brown fraction containing 55 mg (40%) of complex $Os_3(CO)_9\{\mu_3\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}C(SiMe_3)C(Me)C(COOMe)CH\}$ (5) and 22 mg (16%) of complex $Os_3(CO)_9\{\mu\text{-}\eta^1:\eta^1:\eta^4\text{-}C(SiMe_3)C(Me)C(COOMe)CH\}$ (7) in a 2.5 : 1.0 ratio was eluted with a hexane—benzene (5 : 1) mixture. Further elution of the red-brown fraction with a hexane—benzene (5 : 1) mixture gave 40 mg (29%) of complex $Os_3(CO)_9\{\mu_3\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(COOMe)\}$ (6).

1,1,1,2,2,3,3,3-Octacarbonyl-μ_3-[(2-η^4-1'-trimethylsilyl-2'-methyl-4'-carboxymethyl-1',3'-butadiene-1',4'-diyl-1,1)-3-η^1-O=C]-*triangulo*-triosmium (8) is an orange-red crystalline substance. Found (%): C, 21.15; H, 1.65; Os, 60.25; Si, 3.40. $C_{18}H_{16}O_{10}Os_3Si$. Calculated (%): C, 21.82; H, 1.63; Os, 57.58; Si, 2.83. IR (hexane), $\nu(CO)/cm^{-1}$: 2084 vs, 2049 vs, 2005 vs, 2001 vs, 1990 s, 1984 sh, 1969 w, 1933 m. ^1H NMR (CDCl$_3$, 25 °C), δ: 0.33 (s, 9 H, Si(CH$_3$)$_3$); 2.67 (s, 3 H, CH$_3$); 3.83 (s, 3 H, OCH$_3$); 6.62 (s, 1 H, CH).

1,1,1,2,2,2,3,3,3-Nonacarbonyl-μ_3-(2-η^2-3-η^2-1'-trimethylsilyl-2'-methyl-3'-carboxymethyl-1',3'-butadiene-1',4'-diyl-1,1)-*triangulo*-triosmium (5) is a yellow-red crystalline substance. IR (hexane), $\nu(CO)/cm^{-1}$: 2090 m, 2051 vs, 2029 vw, 2015 m, 2000 w, 1992 w, 1986 w, 1894 br. ^1H NMR (CDCl$_3$, 25 °C), δ: 0.33 (s, 9 H, Si(CH$_3$)$_3$); 2.47 (s, 3 H, CH$_3$); 3.76 (s, 3 H, OCH$_3$); 10.35 (s, 1 H, CH).

1,1,1,2,2,3,3,3,3-Nonacarbonyl-1,2-μ-(2-η^4-1'-trimethylsilyl-2'-methyl-3'-carboxymethyl-1',3'-butadiene-1',4'-diyl-1,1)-*triangulo*-triosmium (7) is a dark-red crystalline substance. IR (hexane), $\nu(CO)/cm^{-1}$: 2109 s, 2057 vs, 2035 s, 2031 vs, 2013 vs, 1998 s, 1988 m, 1985 sh, 1942 m. ^1H NMR (CDCl$_3$, 25 °C), δ: 0.37 (s, 9 H, Si(CH$_3$)$_3$); 2.80 (s, 3 H, CH$_3$); 3.85 (s, 3 H, OCH$_3$); 8.32 (s, 1 H, CH).

1,1,1,2,2,2,3,3,3-Nonacarbonyl-μ_3-(2-η^2-3-η^2-1'-trimethylsilyl-2'-methyl-4'-carboxymethyl-1',3'-butadiene-1',4'-diyl-1,1)-*triangulo*-triosmium (6) is a red crystalline substance. IR (hexane), $\nu(CO)/cm^{-1}$: 2090 m, 2055 vs, 2050 vs, 2016 s, 2001 m, 1991 m, 1988 sh, 1896 br. ^1H NMR (CDCl$_3$, 25 °C), δ: 0.35 (s, 9 H, Si(CH$_3$)$_3$); 2.32 (s, 3 H, CH$_3$); 3.79 (s, 3 H, OCH$_3$); 6.69 (s, 1 H, CH).

Thermolysis of complex $Os_3(CO)_9\{\mu_3\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(COOMe)\}$ (6). A solution of complex 6 (40 mg, 0.039 mmol) in 50 mL of benzene was heated for 6.5 h at 70 °C with stirring and the yellow-orange solution turned pale-yellow. The reaction was monitored by TLC. After evaporation of the solvent, the reaction mixture was separated by TLC on silica gel (with hexane as eluent). Two fractions were isolated, a red fraction containing the starting complex $Os_3(CO)_9\{\mu_3\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(COOMe)\}$ (6) and a yellow fraction containing 16 mg (40%) of complex $Os_3(CO)_8\{\mu_3\text{-}\eta^1:\eta^1:\eta^4:\eta^1\text{-}C(SiMe_3)C(Me)C(H)C(COOMe)\}$ (8).

Reaction of complex $Os_3(CO)_8\{\mu_3\text{-}\eta^1:\eta^1:\eta^4:\eta^1\text{-}C(SiMe_3)C(Me)C(H)C(COOMe)\}$ (8) with PPh$_3$. To a solution of complex 8 (40 mg, 0.0403 mmol) in 50 mL of benzene, PPh$_3$ (10 mg, 0.038 mmol) was added. The mixture was stirred for 45 h at ~20 °C and the light-yellow solution turned dark-green. The reaction was monitored by TLC. The reaction product was recrystallized from a hexane—CH$_2$Cl$_2$ (4 : 1) mixture to give dark-green crystals of complex 1,1,1,2,2,3,3,3-octacarbonyl-3-triphenylphosphine-μ-(2-η^4-1'-trimethylsilyl-2'-methyl-4'-carboxymethyl-1',3'-butadiene-

1',4'-diyl-1,1)-*triangulo*-triosmium, $Os_3(CO)_8(PPh_3)\{\mu\text{-}\eta^1:\eta^1:\eta^4\text{-}C(SiMe_3)C(Me)C(H)(COOMe)\}$ (14, the yield was 43 mg, 85%). Found (%): C, 35.07; H, 2.74; Os, 45.01. $C_{36}H_{31}O_{10}Os_3SiP$. Calculated (%): C, 34.50, H, 2.49; Os, 45.53. IR (hexane), $\nu(CO)/cm^{-1}$: 2073 m, 2041 s, 2007 s, 2000 sh, 1994 vs, 1975 s, 1937 vw, 1923 m. ^1H NMR (CDCl$_3$, 25 °C), δ: 0.34 (s, 9 H, Si(CH$_3$)$_3$); 2.64 (s, 3 H, CH$_3$); 3.74 (s, 3 H, OCH$_3$); 7.41 (s, 1 H, CH). ^{31}P NMR (CDCl$_3$, 25 °C), δ: 20.60 (s).

X-ray study of complexes 5 and 8. Single crystals of complexes 5 and 8 suitable for X-ray study were obtained by recrystallization from hexane and a hexane—CH$_2$Cl$_2$ (5 : 1) mixture, respectively. Crystallographic data and main parameters of the refinement for compounds 5 and 8 are listed in Table 3. Both structures were solved by direct methods. The positions and thermal parameters of non-hydrogen atoms were refined isotropically and then anisotropically by the full-matrix least squares method. The calculated positions of hydrogen atoms were included in the refinement using the "riding" model. In both cases, the absorption correction was introduced using the experimental curves of azimuthal scanning. All calculations were performed on a personal computer using the SHELXTL PLUS 5 program package.[15]

Table 3. Crystallographic data, conditions of X-ray experiment, and refinement parameters for compounds 5 and 8

Parameter	5	8
Molecular formula	$C_{19}H_{16}O_{11}SiOs_3$	$C_{18}H_{16}O_{10}SiOs_3$
Molecular weight	1019.01	991.00
Space group	$P2_1/c$	$P2_1/c$
Temperature/K	293(2)	293(2)
a/Å	12.082(2)	9.232(2)
b/Å	13.381(3)	17.102(3)
c/Å	16.009(3)	15.206(3)
α/deg	—	—
β/deg	105.02(2)	95.46(3)
γ/deg	—	—
$V/Å^3$	2499.7(9)	2389.9(8)
Z	4	4
d_{calc}/g cm^{-3}	2.708	2.754
Diffractometer	CAD-4	
Radiation (λ/Å)	Mo-Kα (λ = 0.71073 Å)	
μ/cm^{-1}	153.13	160.09
Absorption correction	ψ-curves	
T_{min}/T_{max}	0.085/0.532	0.059/0.406
Scanning type	θ/(5/3)θ	θ/(5/3)θ
$2\theta_{max}$/deg	54	60
Number of independent reflections	5140	5930
R_1 (*F*-refinement for reflections with $I > 2\sigma(I)$)	0.0456 (4462 reflections)	0.0306 (4436 reflections)
wR_2 (*F^2*-refinement for all reflections)	0.1435	0.0973
Number of refined parameters	307	289
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = 1/3(F_o^2 + 2F_c^2)$	
a	0.0981	0.0466
b	2.9234	0

References

1. A. A. Koridze, N. M. Astakhova, A. I. Yanovsky, and Yu. T. Struchkov, *Metalloorg. Khim.*, 1992, **5**, 886 [*Organomet. Chem. USSR*, 1992, **5** (Engl. Transl.)].
2. A. A. Koridze, N. M. Astakhova, P. V. Petrovskii, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1994, **481**, 247.
3. A. A. Koridze, A. M. Sheloumov, F. M. Dolgushin, A. I. Yanovsky, P. V. Petrovskii, and O. L. Tok, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1024 [*Russ. Chem. Bull.*, 1998, **47**, 995 (Engl. Transl.)].
4. M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197.
5. A. A. Koridze, N. M. Astakhova, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, and P. V. Petrovskii, *Organometallics*, 1995, **14**, 2167.
6. A. A. Koridze, A. M. Sheloumov, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, and P. V. Petrovskii, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 741 [*Russ. Chem. Bull.*, 1996, **45**, 702 (Engl. Transl.)].
7. G. Ferraris and G. Gervasio, *J. Chem. Soc., Dalton Trans.*, 1974, 1813.
8. M. R. Churchill, T. S. Janik, T. P. Duggan, and J. B. Keister, *Organometallics*, 1987, **6**, 799.
9. K. A. Azam, A. J. Deeming, and I. P. Rothwell, *J. Chem. Soc., Dalton. Trans.*, 1981, 91.
10. W.-Y. Yeh, J. R. Shapley, J. W. Ziller, and M. R. Churchill, *Organometallics*, 1986, **5**, 1757.
11. G. Ferraris and G. Gervasio, *J. Chem. Soc., Dalton Trans.*, 1972, 1057.
12. A. A. Koridze, V. I. Zdanovich, V. Yu. Lagunova, M. G. Ezernitskaya, P. V. Petrovskii, F. M. Dolgushin, and A. I. Yanovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1017 [*Russ. Chem. Bull.*, 1998, **47**, 988 (Engl. Transl.)].
13. A. A. Koridze, A. M. Sheloumov, P. V. Petrovskii, and O. L. Tok, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1026 [*Russ. Chem. Bull.*, 1999, **48**, (Engl. Transl.)].
14. O. Gambino, G. A. Vaglio, R. P. Ferrari, and G. Cetini, *J. Organomet. Chem.*, 1971, **30**, 381.
15. G. M. Sheldrick, *SHELXTL. Version 5, Software Reference Manual*, Siemens Industrial Automation, Inc., Madison, 1994.