Alkyne-vinylidene coupling in the reactions of the alkyne complex $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ with $Me_3SiC{\equiv}CR$ (R = Me, Bu^n). The structure and stereodynamic behavior of clusters $Os_3(CO)_9\{\mu_3\text{-}C(SiMe_3){=}C(Me)C{=}C(SiMe_3)R\}$ containing an osmacyclobutene moiety

A. A. Koridze, A. M. Sheloumov, F. M. Dolgushin, A. I. Yanovsky, P. V. Petrovskii, and O. L. Tok*

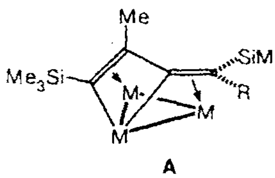
*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: koridz@ineos.ac.ru*

Reactions of the alkyne cluster $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ with alkynes $Me_3SiC{\equiv}CR$ (R = Me, Bu^n) in refluxing hexane result in the formation of clusters $Os_3(CO)_9\{\mu_3\text{-}C(SiMe_3){=}C(Me)C{=}C(SiMe_3)R\}$ (**2a**: R = Me; **3a**: R = Bu^n). The dienediyl ligand in these complexes is formed by alkyne-vinylidene coupling, with vinylidene generated in the course of reaction from the alkyne molecule by the acetylene-vinylidene rearrangement involving a 1,2-shift of the Me_3Si group. The structure of cluster **3a** was determined by X-ray structural analysis. The dienediyl ligand is coordinated to three metal atoms of the cluster framework by two π-ethylene bonds with two osmium atoms and two σ-bonds with the third osmium atom with the formation of the osmacyclobutene moiety. The ^1H and ^{13}C NMR study of ^{13}CO-enriched samples of clusters **2a** and **3a** revealed the stereochemical nonrigidity of these molecules due to the exchange of the hydrocarbon and carbonyl ligands.

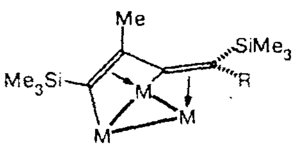
Key words: osmium clusters, silylalkynes, alkyne dimerization; osmacyclobutenes, acetylene-vinylidene rearrangement, intramolecular rearrangements; dynamic ^1H and ^{13}C NMR; crystal and molecular structure.

Previously,[1] in our studies of the dimerization of trimethylsilylpropyne on a triosmium cluster, we have isolated the red cluster $Os_3(CO)_9\{\mu_3\text{-}C(SiMe_3){=}C(Me)C{=}C(SiMe_3)Me\}$ (**2a**) that is the key intermediate of the reaction of the alkyne complex $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ (**1**) with $Me_3SiC{\equiv}CMe$. The composition and spectral characteristics of complex **2a** and the product of its thermolysis indicated that trimethylsilylpropyne undergoes the acetylene-vinylidene rearrangement in the reaction with complex **1** as a result of 1,2-shift of the Me_3Si group.

In principle, there are two possible structures, **A** and **B**, for complex **2a** differing in the mode of bonding of the dienediyl ligand to the metal framework. The structure of type **A** containing the metallacyclobutene moiety has not been described earlier in cluster chemistry. As to the structure of type **B**, it has been determined for the cluster $Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-}PPh_2)\{\mu_3\text{-}CH{=}C(Pr^i)C{=}CH_2\}$ by X-ray structural analysis.[2]



A



B

Since only terminal CO ligands are present in complex **2a** (IR spectral data), the possibility for each Os atom to have the 18-electron shell can only be provided by structure **A**. However, such a uniform electron distribution is not always observed in trimetallic clusters. The structure of cluster **2a** could be unambiguously determined by X-ray structural analysis. Unfortunately, we failed to obtain a single crystal of this compound suitable for an X-ray study. To overcome this difficulty, in this work we used the reaction of complex **1** with $Me_3SiC{\equiv}CBu^n$ to obtain the red complex $Os_3(CO)_9\{\mu_3\text{-}C(SiMe_3){=}C(Me)C{=}C(SiMe_3)Bu^n\}$ (**3a**), which, according to X-ray analysis data, appeared to have structure **A**. We also report the results of investigation of the temperature dependence of the ^1H and ^{13}C NMR spectra of clusters **2a** and **3a**.*

Results and Discussion

The reaction of alkyne complex **1** with trimethylsilylhexyne was carried out in refluxing hexane, *i.e.*, under conditions analogous to those described earlier[1] for the synthesis of complex **2a** (Scheme 1). Separation

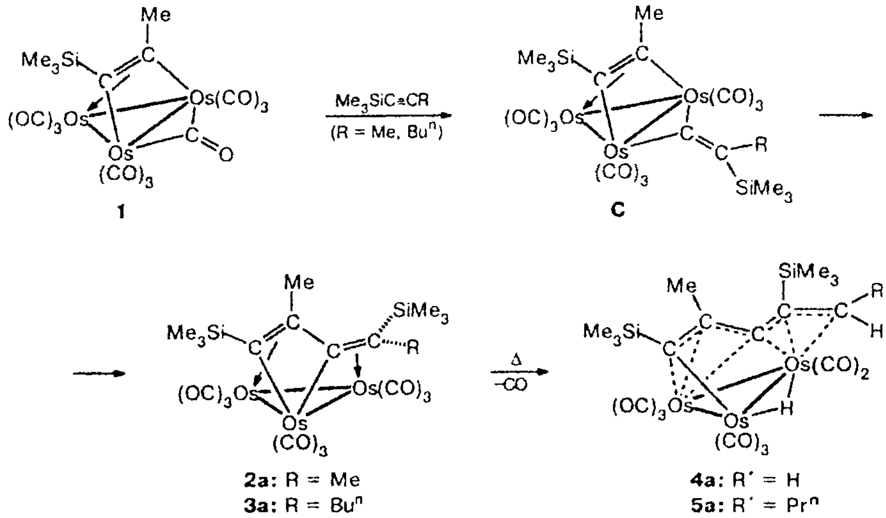
---

* Data reported in this work were published in part as the preliminary communication.[3]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 1024—1029, May, 1998.

1066-5285/98/4705-0995 $20.00 © 1998 Plenum Publishing Corporation

Scheme 1



1

C

2a: R = Me
3a: R = Bu^n

4a: R' = H
5a: R' = Pr^n

of the reaction products by TLC on silica gel afforded the red complex **3a** in 29% yield.

The IR spectrum of cluster **3a** in the region of ν(CO) vibrations indicates the presence of only terminal carbonyl ligands in the molecule and is similar to that of cluster **2a**. The ^{1}H NMR spectrum of compound **3a** contains two signals from nonequivalent Me$_3$Si groups, a singlet corresponding to the methyl group, and a group of signals from protons of the Bu^n substituent. Thermolysis of cluster **3a** in refluxing benzene gave the yellow hydride complex $Os_3(\mu\text{-}H)(CO)_8\{\mu_3\text{-}C(SiMe_3)C(Me)CC(SiMe_3)CH(Pr^n)\}$ (**5a**), whose spectral characteristics (IR and ^{1}H NMR) indicate that its structure is analogous to that of the yellow cluster $Os_3(\mu\text{-}H)(CO)_8\{\mu_3\text{-}C(SiMe_3)C(Me)CC(SiMe_3)CH_2\}$ (**4a**) determined by X-ray structural analysis.[1] These data taken together suggest that complexes **2a** and **3a** have the same structure.

Unlike compound **2a**, cluster **3a** crystallizes from hexane to form single crystals suitable for X-ray study. The molecular structure of compound **3a** is shown in Fig. 1 and the main bond lengths and bond angles are listed in Table 1.

Table 1. Main bond lengths (*d*) and bond angles (ω) in the structure of complex **3a**

Bond	*d*/Å	Bond	*d*/Å
Os(1)—C(1)	1.86(3)	Os(3)—C(7)	1.88(2)
Os(1)—C(3)	1.91(2)	Os(3)—C(9)	1.89(2)
Os(1)—C(2)	1.92(3)	Os(3)—C(8)	1.90(2)
Os(1)—C(12)	2.16(2)	Os(3)—C(12)	2.26(2)
Os(1)—C(10)	2.17(2)	Os(3)—C(13)	2.43(2)
Os(1)—Os(2)	2.798(1)	C(10)—C(11)	1.40(2)
Os(1)—Os(3)	2.841(1)	C(11)—C(24)	1.50(2)
Os(2)—C(5)	1.88(2)	C(11)—C(12)	1.50(2)
Os(2)—C(4)	1.89(2)	C(12)—C(13)	1.43(2)
Os(2)—C(6)	1.92(2)	C(13)—C(14)	1.55(3)
Os(2)—C(10)	2.16(2)	C(14)—C(15)	1.53(3)
Os(2)—C(11)	2.25(2)	C(15)—C(16)	1.55(3)
Os(2)—Os(3)	2.875(1)	C(16)—C(17)	1.42(4)

Angle	ω/deg	Angle	ω/deg
C(12)—Os(1)—C(10)	63.0(7)	C(13)—C(12)—C(11)	132(2)
Os(2)—Os(1)—Os(3)	61.29(3)	C(13)—C(12)—Os(1)	133.0(12)
Os(1)—Os(2)—Os(3)	60.09(3)	C(11)—C(12)—Os(1)	94.7(12)
Os(1)—Os(3)—Os(2)	58.61(3)	C(12)—C(13)—C(14)	114(2)
C(11)—C(10)—Si(1)	126.5(14)	C(12)—C(13)—Si(2)	129.5(13)
C(11)—C(10)—Os(1)	97.1(11)	C(14)—C(13)—Si(2)	112.0(12)
Si(1)—C(10)—Os(1)	128.4(9)	C(15)—C(14)—C(13)	114(2)
C(10)—C(11)—C(24)	125(2)	C(14)—C(15)—C(16)	111(2)
C(10)—C(11)—C(12)	103(2)	C(17)—C(16)—C(15)	114(3)
C(24)—C(11)—C(12)	124(2)		

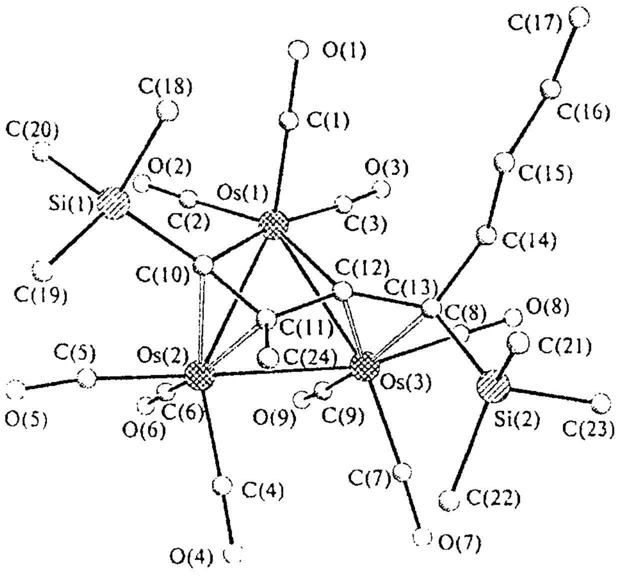


Fig. 1. The molecular structure of complex **3a**.

Molecule **3a** consists of the triosmium triangle, where each of the Os atoms is bonded to three terminal CO groups. The organic ligand is coordinated to three Os atoms: the C(10)=C(11) and C(12)=C(13) double bonds of dienediyl are π-coordinated to the Os(2) and Os(3) atoms, respectively, whereas the third osmium atom, Os(1), forms two σ-bonds with the C(10) and C(12) atoms to give the osmacyclobutene moiety Os(1)C(10)C(11)C(12). The osmacyclobutene ring is nonplanar — the folding angle of the four-membered cycle along the C(10)...C(12) line is equal to 17° and the Os(1)...C(11) distance is equal to 2.73 Å.

The Os—Os distances in the Os_3 triangle are different, which is likely due to the weakest tightening effect of the organic ligand along the Os(2)—Os(3) bond (2.875(1) Å) and its strongest tightening effect along the Os(1)—Os(2) bond (2.798(1) Å).

The alternation of the bond lengths is observed in the chain of the organic ligand: the C(10)—C(11) and C(12)—C(13) distances (1.40(2) and 1.43(2) Å, respectively) are characteristic of π-coordinated olefinic bond, whereas the length of the C(11)—C(12) bond (1.50(2) Å) indicates its ordinary character. It should also be noted that the geometry of the environment of the C(10), C(11), and C(13) atoms deviates slightly from planar geometry (the sums of the bond angles at these atoms are equal to 352°, 352°, and 356°, respectively). This is in agreement with the well-known fact that the substituents in the olefinic fragment deviate in the opposite direction from the metal atom upon coordination. In this case, the sum of the bond angles at the C(12) atom is equal to 360°, which indicates that this atom has a planar environment.

The midplane of the osmacyclobutene fragment makes a dihedral angle of 51° with the plane of the Os_3-triangle; the Bu^n substituent has a planar zigzag structure: the C(13), C(14), C(15), C(16), and C(17) atoms are in the same plane (the maximum deviation from the midplane passing through these atoms is 0.06 Å).

Thus, each osmium atom in molecule **3a** has the 18-electron shell and the organic ligand is the six-electron donor; as a result, cluster **3a** becomes a 48-electron cluster having the structure of the type **A**.

As is known, all metallacyclobutene complexes characterized previously are mononuclear.[4] The methods for the synthesis of such complexes include reactions of metal carbene derivatives with alkynes, insertion of a metal atom into the carbon-carbon bond of cyclopropenes, and the perfluoroalkyne-CO and alkyne-isonitrile coupling in carbonyl and alkyne complexes, respectively. As to cluster metallacyclobutene complexes, the coordinatively unsaturated $Os_3(CO)_9\{\mu\text{-}C(Ph){=}C(Ph)CH_2\}$ was assumed to be involved in the formation of $2\sigma,\pi$-allylic derivative $Os_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}C(Ph)C(Ph)CH\}$ from the alkynecarbene complex $Os_3(CO)_9(\mu_3\text{-}PhC_2Ph)(\mu\text{-}CH_2)$ and in the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1,2-diphenylcyclopropene.[5] In addition, a short communication[6] concerning the synthesis of cluster $Os_3(CO)_9\{\mu_3\text{-}Fe[C_5H_4(C_2SiMe_3)]_2\}$ related to compounds **2a** and **3a** has appeared after this work was finished.

The isolation of complexes **2a** and **3a** safely suggests that linear dimerization of alkynes on trimetallic clusters occurs *via* the alkyne-vinylidene coupling (see intermediate **C** in Scheme 1). In addition, the structure of cluster **3a** and the products of heteroalkyne linear co-dimerization we studied earlier[7] points to the fact that it is just the second molecule participating in the coupling with the μ_3-coordinated alkyne that undergoes the acetylene-vinylidene rearrangement by a 1,2-shift of the Me_3Si group. As a result, the coupling of the μ_3-coordinated trimethylsilylpropyne ligand with carbene $C{=}C(SiMe_3)Me$ and $C{=}C(SiMe_3)Bu^n$ ligands on the triosmium cluster results in complexes **2a** and **3a**, respectively.

Noteworthy is the fact that the first silylalkyne molecule does not undergo the acetylene-vinylidene rearrangement upon coordination on the Os_3-cluster even when complex **1** is heated in refluxing heptane; the hydride cluster $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}Me_3SiC{=}C{=}CH_2)$ with the allenyl ligand is formed in this case.[1] This is the difference between complex **1** and the related heteronuclear complex $RuCo_2(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ that undergoes isomerization into a thermodynamically more stable vinylidene complex $RuCo_2(CO)_9\{\mu_3\text{-}C{=}C(SiMe_3)Me\}$ already at room temperature.[8]

The ^1H and ^{13}C NMR data for complexes **2a** and **3a** are consistent with the structure of type **A** determined for compound **3a** in the crystal. As has been reported earlier,[1] the ^1H NMR spectrum of complex **2a** is temperature-dependent, which indicates a dynamic process. The temperature dependence manifests itself as a reversible change in the linewidth of the signal of one of the methyl groups at δ 1.93: being very broad at 25 °C, this signal is narrowed as the solution is cooled, while other signals at δ 2.01 (3 H), 0.42 (9 H), and 0.28 (9 H) remain unchanged in the temperature interval from −60 to +40 °C (conversion of complex **2a** into hydride **4a** begins at higher temperatures).

The ^{13}C NMR spectrum of the ^{13}CO-enriched sample of cluster **2a** was investigated in the temperature interval from −80 to +40 °C. The hydrocarbon region of the spectrum (CD_2Cl_2, −45 °C) contains signals at δ 0.57 (3), 2.47 (3), 31.23 (1), 33.25 (1), 51.53 (1), 71.87 (1), 126.33 (1) and 127.08 (1) (hereinafter the relative integrated intensity of the signal is given in parentheses); some broadening of the signals of methyl and trimethylsilyl groups (at δ 33.25 and 0.57, respectively) is observed as the temperature decreases.

Seven signals at δ 181.55 (1), 177.86 (1), 175.77 (3), 174.94 (1), 173.11 (1), 170.78 (1), and 170.15 (1) are observed in the carbonyl region of the spectrum of complex **2a** at −45 °C; the triple relative integrated intensity of the signal at δ 175.77 indicates a localized exchange of three CO groups at one of the Os atoms. The carbonyl region of the spectrum remains unchanged down to −80 °C; raising the temperature from approximately −25 °C results in broadening of six signals of equal intensity. This broadening occurs at equal apparent rate for six signals, and it can only be seen in the spectrum obtained at 0 °C that the signals at δ 173.11 and 170.78 are broader than other signals. At a temperature about 10 °C, the six signals become broadened to an extent that they melt into the background and are no longer visible. The signal at δ 175.77 with the triple relative integrated intensity remains unchanged and becomes somewhat broader only at 35 °C.

The broadening of several signals of the hydrocarbon ligand in the ^{1}H and ^{13}C NMR spectra of cluster **2a** suggests the presence of at least two isomers undergoing interconversion in solution. However, the concentration of isomer involved in exchange with complex **2a** is so low that it cannot be detected by NMR spectroscopy most likely because of a fast "hidden partner" exchange process.[9,10]

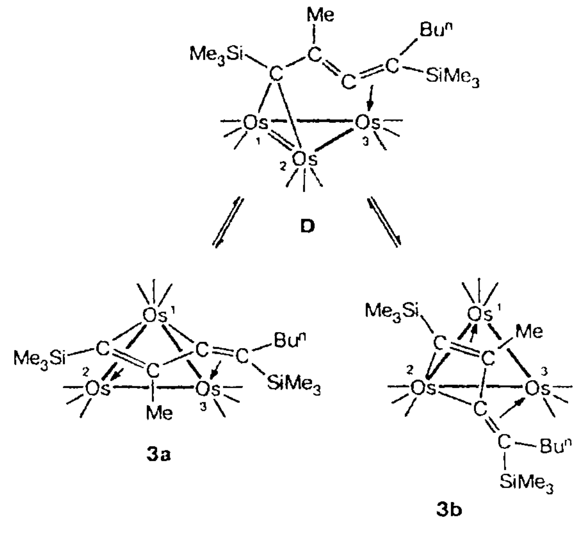
The results of NMR investigation of complex **3a** appeared to be more informative. The NMR spectra of this compound in CD_2Cl_2 (or $CDCl_3$) were recorded in the temperature interval from −75 to +30 °C. The ^{1}H NMR spectrum (CD_2Cl_2, at 25 °C) contains signals from the Me_3Si groups at δ 0.33 and 0.45 (the latter signal is somewhat broadened), a triplet at δ 0.88 corresponding to the methyl protons of the Bu^n group, multiplets from the methylene protons of the same group in the δ interval 1.20—1.67, and a single broadened signal of the Me group at δ 1.97. A decrease in temperature leads to narrowing of the signal at δ 1.97 and gradual broadening of the signal from one of the Me_3Si groups at δ 0.33, whose width ($\Delta\nu_{1/2}$) reaches 17 Hz at −60 °C.

Seven signals at δ 181.39, 177.14, 176.25, 174.84, 173.44, 172.84, and 171.51 with the ratio of relative integrated intensities 1 : 3 : 1 : 1 : 1 : 1 : 1 are observed in the carbonyl region of the spectrum of complex **3a** at −60 °C. This resembles the spectral pattern for complex **2a**. The widths of the signals with equal intensities are obviously different, which indicates the onset of an exchange process that leads to pairwise averaging of these signals. Along with the signals from complex **3a**, there are signals of weaker intensity in the spectrum; we assume that they correspond to the isomeric complex **3b**. According to the signal intensities, the ratio of isomers **3a** and **3b** is approximately equal to 5 : 1 at −60 °C. Due to the low content of complex **3b** in solution and broadening of signals caused by the exchange process, it was possible to reliably identify only several signals of complex **3b** at δ 178.39 (1), 177.55 (3), 172.84 (1), and 169.06 (1). The signals of the carbonyl groups of isomers **3a** and **3b** are broadened in a still greater extent as the solution temperature decreases to −75 °C; therefore, no further cooling of the solution was carried out.

The signals of isomer **3b** are broadened as the temperature of the same solution increases from approximately −60 °C and melt into the background at −47 °C, whereas pairwise averaging of the six signals of complex **3a** of equal intensity (at δ 174.84 and 176.25, at δ 172.84 and 173.44, and at δ 171.51 and 181.39) begins. At 22 °C, they merge into one broadened signal (δ 174.95). The signal at δ 177.14 with the triple relative integrated intensity remains narrow up to 0 °C and its gradual broadening begins only with further increasing the temperature. Finally, two broad signals from the carbonyl groups at δ 177.08 and 174.95 with a ratio of integrated intensities of 1 : 2 are observed at 22 °C, and the latter signal is somewhat broader than the former one. Raising the temperature up to 30 °C only results in additional broadening of signals mentioned above.

The observed temperature dependence of the ^{13}C NMR spectrum of complex **3a** can be explained as follows. Several exchange processes occur in the molecule. A localized exchange of three CO groups at one of the Os atoms is one of these processes and we believe that it occurs at the Os(3) atom (Scheme 2). This process cannot be "frozen" even at −60 °C. The exchange of the hydrocarbon ligand resulting in isomerization **3a** ⇌ **3b** is the second process.

Scheme 2



Isomerization consists in the 2σ,π ⇌ π,2σ exchange of the organic ligand between the Os(1) and Os(2) atoms and can occur with the intermediate formation of an unsaturated 46-electron cluster **D**. If the substituents at its exocyclic ethylene carbon atom are excluded from consideration, then this cluster can be considered as having a symmetry pseudoplane passing through the midpoint of the Os(1)—Os(2) bond and four carbon atoms of the hydrocarbon ligand; the nonequivalent Bu^n and Me_3Si substituents at the terminal carbon atom are sufficiently distant from the CO ligands at the Os(1) and Os(2) atoms. However, in the absence of the process leading to the exchange of the positions of the substituents indicated, even when the exchange of the hydrocarbon ligand shown in Scheme 2 in combination with the localized exchange of three CO groups at tge Os(1) and Os(2) atoms occurs, these groups should appear as two signals with equal intensities. The broadening of the singlet signal from three CO groups at the Os(3) atom observed as temperature exceeds 22 °C may be a result of a new process averaging all nine CO groups; this process can involve the internuclear exchange[11] of carbonyl ligands through formation of intermediates with bridging CO groups.

The exchange processes considered do not rule out a rearrangement through the $\sigma,\pi \rightleftharpoons \pi,\sigma$ exchange of the hydrocarbon ligand between the Os(1) and Os(2) atoms resulting in isomerization of clusters with structures **A** and **B**. However, it should be remembered that in this case the Os atoms mentioned above will not retain their 18-electron shells in the structure **B** thus generated. In addition, the spectral changes observed, namely, the pairwise averaging of the signals of three pairs of CO groups and further averaging of the signals of these six CO groups, cannot be explained only by the $\sigma,\pi \rightleftharpoons \pi,\sigma$ exchange of the hydrocarbon ligand. For this reason, the $\sigma,\pi \rightleftharpoons \pi,\sigma$ exchange leading to isomerization **A** $\rightleftharpoons$ **B** can only be considered as one of the possible stages of the $2\sigma,\pi \rightleftharpoons \pi,2\sigma$ exchange of the hydrocarbon ligand.

In conclusion, in this study we were able to establish that complexes containing a metallacyclobutene moiety are the key intermediates of the processes of linear dimerization of silylalkynes and their co-dimerization with other alkynes on trimetallic metal carbonyl clusters and that the organic ligands in these complexes are formed *via* the alkyne-vinylidene coupling. The dienediyl ligand in triosmium clusters has been shown to be fluxional. In the future, we plan to study the reactivity of clusters containing metallacyclobutene fragments, in particular, under conditions of reductive elimination involving the formation of corresponding cyclopropene hydrocarbons; the structure of dimerization products of trimethylsilylpropyne on the triruthenium cluster[12] suggests that cyclopropenes are generated in the course of reaction.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 and 100.61 MHz, respectively). IR spectra were recorded on a Bruker IFS-113v spectrometer. 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 silica gel (Chemapol) as adsorbent.

The samples of complexes **2a** and **3a** enriched with ^{13}CO were synthesized from $Os_3(^{13}CO)_{10}(NCMe)_2$; the degree of enrichment in its precursor, osmium carbonyl $Os_3(^{13}CO)_{12}$, was approximately equal to 40%.

Reaction of $Os_3(\mu\text{-}^{13}CO)(^{13}CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ with $Me_3SiC{\equiv}CMe$. The reaction was carried out under conditions described for obtaining a non-enriched sample of complex **2a**.[1]

$^{13}C\{^1H\}$ NMR spectrum of complex $Os_3(^{13}CO)_9\{\mu_3\text{-}C(SiMe_3){=}C(Me)C{=}C(SiMe_3)Me\}$ ($CDCl_3$, −45 °C), δ: 0.57 ($Si(CH_3)_3$); 2.47 ($Si(CH_3)_3$); 31.23 (CH_3); 33.25 (CH_3); 51.53 ($\underline{C}CH_3$); 71.87 ($\underline{C}(CH_3)SiMe_3$); 126.33 (>C=); 127.08 (>C=); 170.15 (CO); 170.78 (CO); 173.11 (CO); 174.94 (CO); 175.78 (3 CO); 177.86 (CO); 181.55 (CO).

Reaction of $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ with $Me_3SiC{\equiv}CBu^n$. Trimethylsilylhexyne (92 mg, 36 mmol) was added to a solution of $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ (172 mg, 17 mmol) in 30 mL of hexane and the mixture was refluxed for 0.5 h. The starting yellow-orange solution turned red. 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. Three main fractions were separated: a red fraction containing complex $Os_3(CO)_9\{\mu_3\text{-}C(SiMe_3){=}C(Me)C{=}C(SiMe_3)Bu^n\}$ (**3a**) (yield 56 mg, 29%), an orange fraction containing the starting complex $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ (**1**), and a yellow fraction containing the hydride complex $Os_3(\mu\text{-}H)(CO)_8\{\mu_3\text{-}C(SiMe_3)C(Me)CC(SiMe_3)CH(Pr^n)\}$ (**5a**) (yield 29 mg, 15.3%).

Table 2. Atomic coordinates (×10^4) and their equivalent isotropic thermal parameters (U_{eq}×10^3) in structure **3a**

Atom	x	y	z	U_{eq}/Å^2
Os(1)	2870(1)	3276(1)	3722(1)	34(1)
Os(2)	955(1)	2880(1)	3030(1)	34(1)
Os(3)	2305(1)	4185(1)	2279(1)	33(1)
Si(1)	2138(5)	884(3)	4031(4)	49(1)
Si(2)	3606(5)	2763(4)	750(3)	41(1)
O(1)	4790(15)	2340(14)	4380(15)	95(7)
O(2)	1850(18)	3640(14)	5350(11)	89(6)
O(3)	3932(20)	5145(12)	3873(14)	104(8)
O(4)	−164(14)	2769(12)	1457(9)	65(4)
O(5)	−561(12)	1578(12)	3805(14)	77(6)
O(6)	−358(17)	4344(13)	3848(15)	94(7)
O(7)	1268(15)	4559(11)	697(12)	71(5)
O(8)	3947(14)	5614(9)	1919(12)	68(5)
O(9)	985(15)	5666(10)	3049(13)	78(6)
C(1)	4035(22)	2690(17)	4116(15)	66(7)
C(2)	2209(22)	3501(14)	4738(16)	61(6)
C(3)	3504(23)	4450(15)	3790(16)	72(8)
C(4)	266(18)	2816(15)	2033(17)	59(6)
C(5)	65(14)	2058(15)	3546(15)	52(6)
C(6)	147(20)	3795(14)	3563(16)	59(7)
C(7)	1669(18)	4394(12)	1284(13)	45(5)
C(8)	3359(16)	5051(11)	2055(14)	44(5)
C(9)	1444(20)	5090(12)	2741(15)	57(6)
C(10)	2167(13)	1972(11)	3418(11)	36(4)
C(11)	2289(12)	2038(11)	2583(11)	32(4)
C(12)	3042(12)	2810(10)	2498(11)	33(4)
C(13)	3637(14)	3131(11)	1835(11)	34(4)
C(14)	4701(13)	3531(11)	2077(14)	40(4)
C(15)	5539(16)	2805(17)	2192(20)	71(8)
C(16)	6540(19)	3243(17)	2531(25)	97(13)
C(17)	7389(19)	2637(26)	2581(35)	154(23)
C(18)	3461(16)	408(15)	4006(20)	71(9)
C(19)	1224(19)	−12(15)	3640(21)	81(9)
C(20)	1781(30)	1107(17)	5096(19)	94(11)
C(21)	4339(23)	1675(17)	549(17)	81(9)
C(22)	2304(20)	2622(20)	272(18)	79(8)
C(23)	4246(34)	3726(17)	153(16)	110(15)
C(24)	2211(17)	1258(11)	2006(14)	51(5)

Complex 3a is a dark-red crystalline substance. Found (%): C, 26.38; H, 2.91; Os, 52.82; Si, 5.10. $C_{24}H_{30}O_9Os_3Si_2$. Calculated (%): C, 26.46; H, 2.77; Os, 52.38; Si, 5.16. IR (hexane), ν(CO)/cm^{-1}: 2084 s, 2044 s, 2036 vs, 2010 s, 1996 sh, 1990 s, 1976 m, 1962 w. ^1H NMR ($CDCl_3$, 25 °C), δ: 0.31 (s, 9 H, $Si(CH_3)_3$); 0.43 (s, 9 H, $Si(CH_3)_3$); 0.88 (t, 3 H, $CH_2CH_2CH_2C\underline{H}_3$, J = 7.2 Hz); 0.90—1.67 (m, 6 H, $C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$); 1.93 (br.s, 3 H, CH_3). ^{13}C NMR (CD_2Cl_2, −30 °C), δ: 2.12 (3 C, $Si(CH_3)_3$); 3.24 (br., 3 C, $Si(CH_3)_3$); 13.72 (1 C, $CH_2CH_2CH_2\underline{C}H_3$); 23.29 (1 C, $CH_2CH_2\underline{C}H_2CH_3$); 39.37 (1 C, $CH_2\underline{C}H_2CH_2CH_3$); 36.92 (1 C, $\underline{C}H_2CH_2CH_2CH_3$); 49.21 (1 C, $=\underline{C}(Me)$—); 84.90 (1 C, $=\underline{C}(SiMe_3)Bu^n$); 121.27 (1 C, $=\underline{C}(SiMe_3)$); 136.20 (1 C, >C=); ^{13}C NMR (CD_2Cl_2, −60 °C), δ: 181.39 (CO); 177.14 (3 CO); 176.25 (CO); 174.84 (CO); 173.44 (CO); 172.84 (CO); 177.51 (CO).

Complex 5a is a yellow crystalline substance. ^1H NMR (C_6D_6), δ: −17.09 (s, 1 H, Os_2H); 0.20 (s, 9 H, $SiMe_3$); 0.46 (s, 9 H, $SiMe_3$); 1.01 (t, 3 H, $CH_2CH_2C\underline{H}_3$, J = 7.1 Hz); 1.57 (m, 1 H, $CH_2C\underline{H}_AH_BCH_3$); 1.71 (m, 1 H, $CH_2CH_A\underline{H}_BCH_3$); 2.19 (m, 1 H, $C\underline{H}_CH_DCH_2CH_3$); 2.45 (m, 1 H, $CH_C\underline{H}_DCH_2CH_3$); 2.53 (t, 1 H, CH, J = 7.0 Hz); 2.63 (s, 3 H, Me).

X-ray study of complex 3a. Crystals of 3a ($C_{24}H_{30}O_9Os_3Si_2$, M = 1089.26) are orthorhombic; at 20 °C, a = 12.965(5) Å, b = 14.625(4) Å, c = 16.644(7) Å, V = 3156(2) $Å^3$, d_{calc} = 2.292 g cm^{-3}, Z = 4, space group $P2_12_12_1$. The unit cell parameters and intensities of 5375 independent reflections were measured on a Siemens P3/PC automatic diffractometer (20 °C, Mo-Kα radiation, graphite monochromator, θ/2θ scan, θ ≤ 32°).

The structure was solved by direct methods. The refinement was carried out by the full-matrix least squares method first isotropically and then anisotropically. The absorption correction (μ(Mo-Kα) = 121.7 cm^{-1}) was introduced using the experimental curves of azimuthal scan (25 reflections, $0 < \Psi < 360°$ with an interval of 10°, T_{min} = 0.097, and T_{max} = 0.621). The calculated positions of hydrogen atoms were included in the final refinement using the riding model. The final reliability factors are: R_1 = 0.0733 (the F-refinement for 3492 observed reflections with $I > 2\sigma(I)$) and wR_2 = 0.1359 (the F^2-refinement for all 5320 reflections used in the procedure, the weight scheme used was $w^{-1} = \sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P$, where $P = (F_0^2 + 2F_c^2)/3$, a = 0.0548, and b = 12.4721); and the number of refined parameters was equal to 344. All calculations were carried out using the SHELXTL PLUS 5 programs[13] on an IBM PC computer. The atomic coordinates are listed in Table 2.

The authors express their gratitude to V. S. Khotimsky for providing the trimethylsilylhexyne.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-32929a and 97-03-33783a).

References

1. 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.
2. D. Nucciarone, N. J. Taylor, A. J. Carty, A. Tiripicchio, M. Tiripicchio Camellini, and E. Sappa, *Organometallics*, 1988, 7, 118.
3. A. M. Sheloumov, F. M. Dolgushin, A. I. Yanovsky, P. V. Petrovskii, and A. A. Koridze, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1418 [*Russ. Chem. Bull.*, 1997, **46**, 1361 (Engl. Transl.)].
4. P. W. Jennings and L. L. Johnson, *Chem. Rev.*, 1994, **94**, 2241.
5. A. D. Clauss, J. R. Shapley, and S. R. Wilson, *J. Am. Chem. Soc.*, 1981, **103**, 7387.
6. L. P. Clarke, J. E. Davies, P. R. Raithby, and G. P. Shields, *J. Chem. Soc., Dalton Trans.*, 1996, 4147.
7. A. A. Koridze, in *The Synergy Between Dynamics and Reactivity at Clusters and Surfaces*, Ed. L. J. Farrugia, Kluwer Acad. Publishers, Dodrecht, 1995, 351.
8. H. Bantel, A. K. Powell, and H. Vahrenkamp, *Chem. Ber.*, 1990, **123**, 661.
9. D. Nucciarone, N. J. Taylor, and A. J. Carty, *Organometallics*, 1988, 7, 127.
10. N. Okazawa and T. S. Sorensen, *Can. J. Chem.*, 1978, **56**, 2355.
11. A. A. Koridze, O. A. Kizas, N. M. Astakhova, P. V. Petrovskii, and Yu. K. Grishin, *J. Chem. Soc., Chem. Commun.*, 1981, 853.
12. 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.)].
13. G. M. Sheldrick, *SHELXTL. Version 5, Software Reference Manual*, Siemens Industrial Automation, Inc., Madison, 1994.

Received December 19, 1997