

Dimerization of trimethylsilylpropyne on a triosmium cluster. Formation, crystal structure and rearrangement of $\text{Os}_3\text{H}[\mu_3\text{-C}(\text{SiMe}_3)\text{C}(\text{Me})\text{CC}(\text{SiMe}_3)\text{CH}_2](\text{CO})_8$ complex

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Abstract

Trimethylsilylpropyne reacts with $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2$ (C_8H_{14} = cyclooctene) to give $\text{Os}_3(\mu_3\text{-Me}_3\text{SiC}_2\text{Me})(\mu\text{-CO})(\text{CO})_9$ (3). On heating this complex in hydrocarbon solvents, the allenyl compound $\text{Os}_3\text{H}[\mu_3\text{-C}(\text{SiMe}_3)\text{CCH}_2](\text{CO})_9$ (4) is formed. Reaction of the excess $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with the alkyne compound 3 in refluxing hexane first gives the red compound $\text{Os}_3[\text{C}_4(\text{SiMe}_3)(\text{Me})(\text{SiMe}_3)\text{-Me}](\text{CO})_9$ (5), which is then smoothly converted to the yellow compound $\text{Os}_3\text{H}[\mu_3\text{-C}(\text{SiMe}_3)\text{C}(\text{Me})\text{CC}(\text{SiMe}_3)\text{CH}_2](\text{CO})_8$ (6). The reaction of excess $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with the vinyl compound $\text{Os}_3\text{H}(\mu\text{-CH}=\text{CH}_2)(\text{CO})_{10}$ (7), proceeds analogously giving 5 and then 6. Compounds 5 and 6 were characterized by IR and ^1H NMR spectroscopy, and 6 also by X-ray diffraction. Cluster 6 crystallizes in the space group $P2_1/n$, with $a = 9.196(2)$, $b = 29.495(2)$, $c = 10.233(2)$ Å, $\beta = 99.48(2)^\circ$, $Z = 4$. The molecular structure involves a triangular array of osmium atoms and σ , π -coordinated organic ligand, formed by linear coupling of two alkyne molecules. This coupling is accompanied by the dehydrogenation of a methyl group and 1,2 shift of a trimethylsilyl group of one of the alkyne molecules. When the reaction of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with 3 was conducted in refluxing heptane, as well as compound 6, the formation of compound $\text{Os}_3\text{H}[\mu_3\text{-CHC}(\text{SiMe}_3)\text{CC}(\text{Me})\text{CH}(\text{SiMe}_3)](\text{CO})_8$ (8) was indicated. In a separate experiment, it was established that, in refluxing heptane, $6 \rightarrow 8$ rearrangement takes place. Allenyl compound 4, in contrast to alkyne compound 3, does not react with $\text{Me}_3\text{SiC}\equiv\text{CMe}$ in refluxing hexane, and only under more severe conditions in refluxing heptane, does the formation of 6 and 8 take place in very low yields. These results show that compounds 3 and 5 but not 4 are the true intermediates in the reaction of trimethylsilylpropyne dimerization on the triosmium cluster.

Key words: Osmium; Ruthenium

1. Introduction

Recently, we reported the reaction of excess $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with $\text{Ru}_3(\text{CO})_{12}$ in refluxing hexane, which leads to the formation of compounds $\text{Ru}_3(\text{H})[\mu_3\text{-CHC}(\text{SiMe}_3)\text{CC}(\text{Me})\text{CH}(\text{SiMe}_3)](\text{CO})_8$ (1) and $\text{Ru}_3(\text{H})[\mu_3\text{-CHC}(\text{SiMe}_3)\text{CC}(\text{SiMe}_3)\text{CH}(\text{Me})](\text{CO})_8$ (2) [1].

Compounds 1 and 2 contain the novel organic ligand, which is bound to the trimetallic core *via* five carbon atoms of the hydrocarbon chain. Here, we report the results of a detailed study of transformations of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ on the triosmium cluster with the aim

of elucidating the mechanism of dimerization of this alkyne. Some preliminary results of this work have been published [2].

2. Experimental section

All reactions were performed in an argon atmosphere. All column and thin layer chromatographic separations were carried out on SiO_2 in air. IR spectra were recorded in hexane on a Bruker IFS-113v spectrometer, and ^1H NMR spectra in C_6D_6 on a Bruker WP-200SY instrument.

2.1. Reaction of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2$
Trimethylsilylpropyne (0.12 ml) was added to 0.6 g of $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2$ in 40 ml of methylene chloride.

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The red solution thus formed was stirred for 0.5 h, then evaporated and the residue was chromatographed on column using a benzene/hexane mixture (3:1) as eluent. Recrystallization of the product from hexane gave 0.44 (81.5%) of red-orange $\text{Os}_3(\mu_3\text{-Me}_3\text{SiC}_2\text{Me})(\mu\text{-CO})(\text{CO})_9$ (**3**). Anal. Found: C, 20.27; H, 1.46; Os, 59.01; Si, 2.86%. $\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{Os}_3\text{Si}$ calcd: C, 19.95; H, 1.26; Os, 59.25; Si, 2.92%. IR: $\nu(\text{CO})$ 2097m, 2074m, 2057vs(br), 2021(sh), 2012vs 2006s, 1997s, 1985(sh), 1848m(br) cm^{-1} . $^1\text{H NMR}$: δ 0.13 (9H, s); 2.36 (3H, s).

2.2. Thermolysis of **3** at 68°C

Compound **3** (0.24 g) was heated in refluxing hexane (50 ml) for 12.5 h, the consumption of **3** being monitored by TLC. The reaction mixture was then evaporated, and the residue was purified on the silica column. Elution with hexane gave 0.20 g (83%) of pale yellow crystals of $\text{Os}_3\text{H}[\mu_3\text{-C}(\text{SiMe}_3)\text{CCH}_2](\text{CO})_9$ (**4**). Anal. Found: C, 19.20; H, 1.44; Os, 61.38; Si, 3.02%. $\text{C}_{15}\text{H}_{12}\text{O}_9\text{Os}_3\text{Si}$ calcd: C, 19.27; H, 1.30; Os, 61.03; Si, 3.00%. IR: $\nu(\text{CO})$ 2098s, 2069vs, 2044s, 2025vs, 2016s, 1996s, 1991m, 1084m, 1977m, 1950vw cm^{-1} . $^1\text{H NMR}$: δ -22.32 (1H, d, $J = 0.6$ Hz); 0.13 (9H, s); 1.87 (1H, dd; $^2J = 1.8$, $^3J = 0.6$ Hz); 3.25 (1H, d, $J = 1.8$ Hz).

2.3. Thermolysis of **4** at 125°C

Compound **4** (0.15 g) in 40 ml of octane was refluxed for 1.5 h. The solvent was removed on a rotary evaporator and the residue was analysed by $^1\text{H NMR}$. Analysis indicated the presence of a mixture of $\text{Os}_3\text{H}(\mu_3\text{-C}\equiv\text{CMe})(\text{CO})_9$ (δ -23.46 (1H), 2.38 (3H)) and **4** in a 3:1 ratio.

2.4. Reaction of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with **3** at 68°C

Alkyne (0.26 g) and compound **3** (0.4 g) were heated in 80 ml of refluxing hexane. After approximately 0.5 h, the colour of the solution changed from orange-yellow to deep red, indicating the formation of $\text{Os}_3[\text{C}_4\text{-}$

$(\text{SiMe}_3)(\text{Me})(\text{SiMe}_3)\text{Me}](\text{CO})_9$ (**5**). This compound was isolated by TLC (eluent hexane). **5**: IR: $\nu(\text{CO})$ 2084s, 2044vs, 2036vs(sh), 2010vs, 1992s, 1976s, 1958vw cm^{-1} . $^1\text{H NMR}$: δ 0.29 (9H, s); 0.44 (9H, s); 1.92 (3H, vbr); 2.04 (3H, s). Further heating of the solution led to a change in colour from red to pale yellow (4 h). Evaporation of the solvent and chromatographic separation gave 0.25 g (54%) of yellow $\text{Os}_3\text{H}[\mu_3\text{-C}(\text{SiMe}_3)\text{-C}(\text{Me})\text{CC}(\text{SiMe}_3)\text{CH}_2](\text{CO})_8$ (**6**). Anal. Found: C, 22.85; H, 2.33; Os, 55.22; Si, 5.55. $\text{C}_{20}\text{H}_{24}\text{O}_8\text{Os}_3\text{Si}_2$ calcd: C, 23.56; H, 2.36; Os, 56.00; Si, 5.51. IR: $\nu(\text{CO})$ 2082s, 2048vs, 2020vs, 1998s, 1990w, 1978m cm^{-1} . $^1\text{H NMR}$: δ -17.04 (1H, d, $J = 0.8$ Hz); 0.06 (9H, s); 0.45 (9H, s); 1.63 (1H, dd, $J = 0.8$, $J = 1.4$ Hz); 2.58 (3H, s); 3.07 (1H, d, $J = 1.4$ Hz).

2.5. Reaction of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with **7** at 68°C

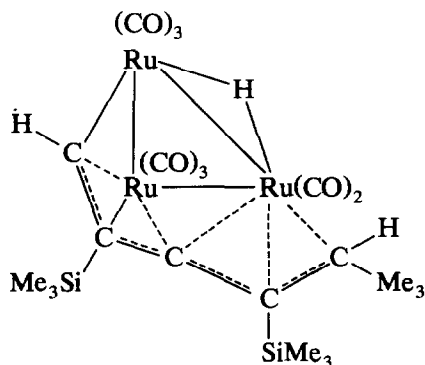
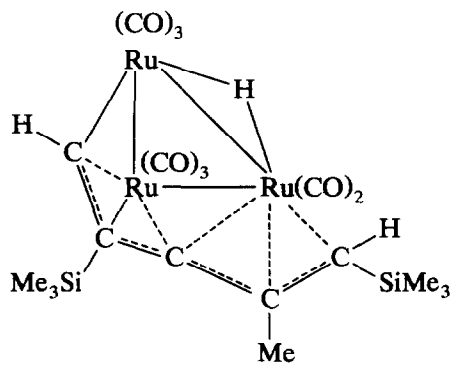
Reaction of excess alkyne with vinyl compound **7** in refluxing hexane proceeds analogously to that with **3**. Compound **6** was isolated in 51% yield. The $\text{Os}_3\text{H}(\mu_3\text{-C}\equiv\text{CMe})(\text{CO})_9$ and $[\text{Os}_3\text{H}_2(\mu_3\text{-C}=\text{C}=\text{CH}_2)(\text{CO})_9]$ (δ -21.78, -18.11, 5.60, 6.11) complexes were also identified in the reaction mixture; there is also an unidentified complex with hydride resonance at -14.69 ppm.

2.6. The **6** \rightarrow **8** isomerization

Compound **6** (30 mg) in 10 ml of heptane was refluxed for 7 h. The solvent was then evaporated and the residue was taken up in C_6D_6 and analysed by $^1\text{H NMR}$. According to the spectrum, the solution contained a mixture of **6** and **8** in the ratio 6:1.

2.7. Reaction of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with **4** at 98°C

Allenyl compound **4** (30 mg) was heated with excess of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ in refluxing heptane for 24 h. The solvent was evaporated the residue was taken in C_6D_6 and analysed by $^1\text{H NMR}$. According to the spectrum, the solution contained a mixture of **4**, **6** and **8** in the ratio 12:7:1.



2.8. X-ray diffraction study of 6

The crystals of **6** were monoclinic, at +20°C, $a = 9.196(2)$, $b = 29.495(7)$, $c = 10.233(2)$ Å, $\beta = 99.48(2)^\circ$, $V = 2737(1)$ Å³, $Z = 4$ (C₂₀H₂₄O₈Os₃Si₂), $d_{\text{calc}} = 2.473$ g cm⁻³, space group $P2_1/n$. The unit cell parameters and intensities of 3754 independent reflections with $I \geq 3\sigma(I)$ were measured with a Siemens P3/PC instrument (+20°C, graphite monochromated Mo-K α radiation, $\lambda = 0.71073$ Å, θ - 2θ scan technique, $2\theta \leq 58.0^\circ$, absorption correction based on Ψ -scans was applied, minimum transmission factor -0.2892). The structure was solved by direct methods using the SHELXTL PLUS programs (PC Version) [3]. Anisotropic least-squares refinement converged at $R = 0.0420$, $R_w = 0.0431$. All H atoms, with the exception of the bridging hydride, were refined in the riding model approximation with a common isotropic temperature factor $U_{\text{iso}} = 0.10(1)$ Å²; the hydride atom was refined in the isotropic approximation. Atomic coordinates are listed in Table 1, bond lengths and angles are given in Tables 2 and 3.

3. Results and discussion

Compounds with the $2\sigma, \pi$ -coordinated organic ligand $M_3(\mu_3\text{-RC}_2\text{R})(\mu\text{-CO})(\text{CO})_9$ ($M = \text{Os}, \text{Ru}$) are formed in the first stage of the reaction of alkynes with triosmium and triruthenium carbonyls. If the internal alkyne has a hydrogen atom in the α -position to the acetylenic carbon atom, thermolysis of the above complexes proceeds with hydrogen transfer and loss of a carbonyl group to give the allenyl compounds $M_3\text{H}[\mu_3\text{-C}(\text{R})=\text{C}=\text{CH}(\text{R}')](\text{CO})_9$. These compounds may rearrange to the thermodynamically more stable $2\sigma, \pi$ -allyl isomers $M_3\text{H}[\mu_3\text{-C}(\text{R})\text{---CH---CR}'](\text{CO})_9$ [4].

Taking into account these well known facts, we carried out a detailed study of the reaction of $\text{Me}_3\text{-SiC}\equiv\text{CMe}$ with the compounds $\text{Os}_3(\mu_3\text{-Me}_3\text{SiC}_2\text{Me})(\mu\text{-CO})(\text{CO})_9$ (**3**) and $\text{Os}_3\text{H}[\mu_3\text{-C}(\text{SiMe}_3)\text{CCH}_2](\text{CO})_9$ (**4**).

Reaction of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with the activated triosmium complex $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2$ in methylene chloride at room temperature gives compound **3** in high yield. Thermolysis of **3** in refluxing hexane leads to compound **4** (Scheme 1). Compounds **3** and **4** were characterized by IR and ¹NMR spectroscopy and elemental analysis.

Trimethylsilylpropyne reacts with **3** in refluxing hexane with formation of the red complex $\text{Os}_3[\text{C}_4(\text{SiMe}_3)(\text{Me})(\text{SiMe}_3)\text{Me}](\text{CO})_9$ (**5**) at the initial stage, this is then converted (in approximately 0.5 h) into the yellow compound $\text{Os}_3\text{H}[\mu\text{-C}(\text{SiMe}_3)\text{C}(\text{Me})\text{CC}(\text{SiMe}_3)\text{-CH}_2](\text{CO})_8$ (**6**) (Scheme 2).

The reaction of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with the vinyl com-

TABLE 1. Atomic coordinates ($\times 10^4$) in **6** and their equivalent isotropic temperature factors (Å² $\times 10^3$)

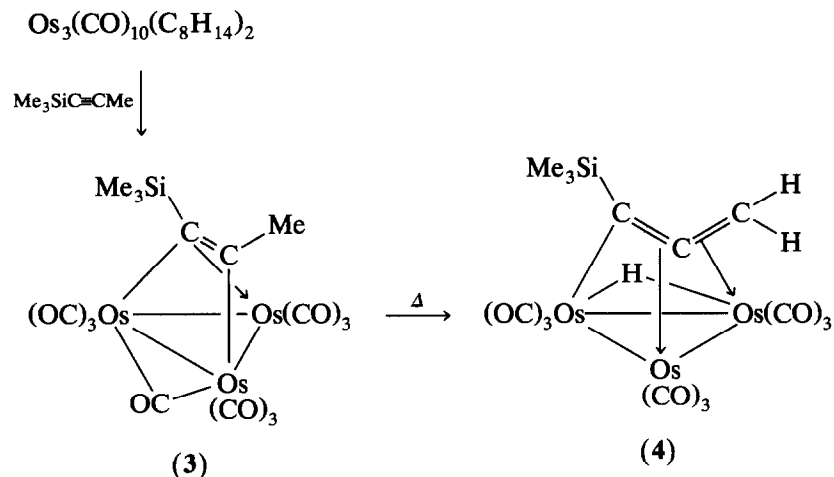
Atom	x	y	z	U_{eq}^a
Os(1)	5469(1)	853(1)	2607(1)	37(1)
Os(2)	8203(1)	925(1)	4271(1)	38(1)
Os(3)	5845(1)	1587(1)	4511(1)	38(1)
Si(1)	8176(4)	824(1)	522(3)	41(1)
Si(2)	7648(4)	2616(1)	3672(3)	48(1)
O(1)	6030(12)	-161(4)	2406(10)	71(4)
O(2)	3715(10)	967(4)	-139(9)	72(4)
O(3)	2801(10)	622(4)	3943(10)	80(5)
O(4)	9592(12)	41(4)	3456(10)	76(5)
O(5)	6777(14)	439(4)	6374(11)	94(5)
O(6)	10927(13)	1207(5)	6183(15)	126(7)
O(7)	3388(13)	2268(5)	3971(12)	98(6)
O(8)	4286(11)	1153(4)	6598(9)	78(5)
C(1)	5840(14)	218(5)	2458(11)	51(5)
C(2)	4353(13)	917(4)	910(11)	43(4)
C(3)	3816(14)	701(5)	3449(12)	55(5)
C(4)	9086(16)	373(5)	3783(12)	56(5)
C(5)	7287(16)	629(5)	5581(13)	61(5)
C(6)	9892(14)	1097(6)	5466(15)	69(6)
C(7)	4336(16)	2010(6)	4213(14)	64(6)
C(8)	4819(14)	1320(6)	5790(12)	58(5)
C(9)	7504(12)	1066(4)	2040(9)	36(4)
C(10)	8307(1)	1443(4)	2662(10)	33(4)
C(11)	7791(11)	1638(4)	3805(10)	33(3)
C(12)	7788(11)	2041(4)	4517(10)	33(3)
C(13)	7519(13)	1968(4)	5841(10)	45(4)
C(14)	10187(14)	684(6)	711(13)	66(6)
C(15)	7698(16)	1262(5)	-761(12)	64(6)
C(16)	7186(16)	294(5)	-103(13)	67(6)
C(17)	9676(14)	1659(5)	2274(12)	55(5)
C(18)	6674(19)	3003(5)	4650(15)	81(7)
C(19)	6621(17)	2556(6)	1970(13)	75(6)
C(20)	9516(16)	2837(6)	3662(14)	75(7)

^a Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $U_{i,j}$ tensor.

pound $\text{Os}_3\text{H}(\mu\text{-CH}=\text{CH}_2)(\text{CO})_{10}$ (**7**) proceeds analogously affording **5** and then **6**; obviously, in this case, reaction of excess $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with vinyl compound **7** proceeds *via* intermediate formation of **3**.

TABLE 2. Bond lengths (Å) in molecule **6**

Os(1)-Os(2)	2.802(1)	Os(3)-C(7)	1.85(2)	O(1)-C(1)	1.14(2)
Os(1)-Os(3)	2.896(1)	Os(3)-C(8)	1.91(1)	O(2)-C(2)	1.14(1)
Os(1)-C(1)	1.91(2)	Os(3)-C(11)	2.04(1)	O(3)-C(3)	1.16(2)
Os(1)-C(2)	1.87(1)	Os(3)-C(12)	2.23(1)	O(4)-C(4)	1.16(2)
Os(1)-C(3)	1.92(1)	Os(3)-C(13)	2.19(1)	O(5)-C(5)	1.15(2)
Os(1)-C(9)	2.14(1)	Si(1)-C(9)	1.90(1)	O(6)-C(6)	1.15(2)
Os(2)-Os(3)	2.959(1)	Si(1)-C(14)	1.87(1)	O(7)-C(7)	1.15(2)
Os(2)-C(4)	1.92(2)	Si(1)-C(15)	1.84(1)	O(8)-C(8)	1.14(2)
Os(2)-C(5)	1.91(2)	Si(1)-C(16)	1.87(2)	C(9)-C(10)	1.43(2)
Os(2)-C(6)	1.88(1)	Si(2)-C(12)	1.90(1)	C(10)-C(11)	1.45(2)
Os(2)-C(9)	2.305(9)	Si(2)-C(18)	1.84(2)	C(10)-C(17)	1.52(2)
Os(2)-C(10)	2.26(1)	Si(2)-C(19)	1.85(1)	C(11)-C(12)	1.39(2)
Os(2)-C(11)	2.18(1)	Si(2)-C(20)	1.84(2)	C(12)-C(13)	1.43(2)



Scheme 1.

Compounds **5** and **6** have been isolated in individual form by chromatography on silica, and characterized by IR and ^1H NMR spectroscopy, and compound **6** also by a single crystal X-ray diffraction study.

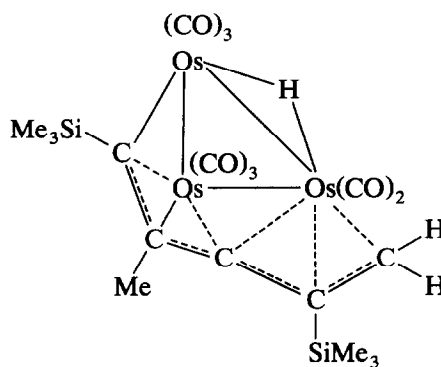
The ^1H NMR spectrum of compound **5** at room temperature contains two pairs of resonances of non-equivalent Me_3Si and Me groups at δ 0.29, 0.44, 1.92 and 2.04 ppm; the resonance of the methyl group at 1.92 ppm is very broad. When a solution of **5** in CD_2Cl_2 was cooled to -60°C , this resonance became narrow, but no other changes were detected in the spectrum, either in the low field or in the high field hydride region. Unfortunately, numerous attempts to obtain a single crystal of **5** suitable for X-ray analysis were unsuccessful. Therefore, the structure of **5** and the nature of the dynamic process in this compound are still uncertain. The temperature dependence of the ^1H NMR spectrum of compound **5** is probably due to



(3)



(5)



(6)

the rapid reversible cleavage of one of the C–H bonds of the methyl group, which forms an agostic bond with the osmium atom.

The molecule of compound **6** (Fig. 1) involves an osmium triangle and a hydrocarbon chain bound to the trimetallic core in the same fashion observed earlier for the ruthenium compound **1** in crystal form [1]: the C(9) forms a σ -bond with the Os(1) atom, and the C(9)C(10)C(11) and C(11)C(12)C(13) groups are π -coordinated with the Os(2) and Os(3) atoms, respectively. The bonding of the C(9)–C(10) fragment to the Os(1) and Os(2) atoms may be regarded as σ,π -alkenyl, and the C(11)C(12)C(13) group represents a π -allyl system coordinated to the Os(3) atom. The delocalization of the π -electron density in the organic ligand is manifested in almost equal bond lengths, all of which fall within the range 1.39–1.45 Å. These bond lengths are in good agreement with the value of 1.41 Å typical for

Scheme 2.

π -coordinated allyl groups (e.g. in [5]). The dihedral angle formed by the C(9)C(10)C(11) and C(11)C(12)C(13) planes is equal to 44(1)°, which almost excludes the possibility of significant conjugation over the full

TABLE 3. Bond angles (°) in molecule 6

Os(2)Os(1)Os(3)	62.5(1)	C(7)Os(3)C(12)	100.0(6)
Os(2)Os(1)C(1)	88.2(3)	C(8)Os(3)C(12)	137.1(5)
Os(3)Os(1)C(1)	141.5(3)	C(11)Os(3)C(12)	37.7(4)
Os(2)Os(1)C(2)	148.7(4)	Os(1)Os(3)C(13)	142.7(3)
Os(3)Os(1)C(2)	122.3(4)	Os(2)Os(3)C(13)	86.6(3)
C(1)Os(1)C(2)	95.9(5)	C(7)Os(3)C(13)	100.8(6)
Os(2)Os(1)C(3)	116.2(3)	C(8)Os(3)C(13)	99.3(5)
Os(3)Os(1)C(3)	83.5(4)	C(11)Os(3)C(13)	67.3(4)
C(1)Os(1)C(3)	88.4(6)	C(12)Os(3)C(13)	37.8(4)
C(2)Os(1)C(3)	94.9(5)	C(9)Si(1)C(14)	116.5(5)
Os(2)Os(1)C(9)	53.6(2)	C(9)Si(1)C(15)	104.3(6)
Os(3)Os(1)C(9)	87.1(3)	C(14)Si(1)C(15)	110.1(7)
C(1)Os(1)C(9)	95.2(5)	C(9)Si(1)C(16)	112.9(6)
C(2)Os(1)C(9)	95.1(5)	C(14)Si(1)C(16)	105.6(7)
C(3)Os(1)C(9)	168.9(4)	C(15)Si(1)C(16)	107.3(6)
Os(1)Os(2)Os(3)	60.3(1)	C(12)Si(2)C(18)	107.9(6)
Os(1)Os(2)C(4)	98.8(4)	C(12)Si(2)C(19)	109.3(6)
Os(3)Os(2)C(4)	158.1(4)	C(18)Si(2)C(19)	110.6(7)
Os(1)Os(2)C(5)	86.4(4)	C(12)Si(2)C(20)	109.1(6)
Os(3)Os(2)C(5)	80.2(5)	C(18)Si(2)C(20)	108.7(7)
C(4)Os(2)C(5)	92.8(6)	C(19)Si(2)C(20)	111.2(7)
Os(1)Os(2)C(6)	167.7(5)	Os(1)C(1)O(1)	177.4(11)
Os(3)Os(2)C(6)	107.8(5)	Os(1)C(2)O(2)	177.2(12)
C(4)Os(2)C(6)	93.4(6)	Os(1)C(3)O(3)	178.0(13)
C(5)Os(2)C(6)	94.6(6)	Os(2)C(4)O(4)	178.1(9)
Os(1)Os(2)C(9)	48.4(3)	Os(2)C(5)O(5)	177.5(13)
Os(3)Os(2)C(9)	82.8(3)	Os(2)C(6)O(6)	179.0(15)
C(4)Os(2)C(9)	87.5(5)	Os(3)C(7)O(7)	177.1(12)
C(5)Os(2)C(9)	134.1(5)	Os(3)C(8)O(8)	175.9(11)
C(6)Os(2)C(9)	131.3(6)	Os(1)C(9)Os(2)	78.0(3)
Os(1)Os(2)C(10)	75.5(2)	Os(1)C(9)Si(1)	121.7(5)
Os(3)Os(2)C(10)	74.5(3)	Os(2)C(9)Si(1)	131.7(6)
C(4)Os(2)C(10)	108.2(5)	Os(1)C(9)C(10)	121.3(8)
C(5)Os(2)C(10)	153.9(5)	Os(2)C(9)C(10)	70.1(5)
C(6)Os(2)C(10)	99.3(6)	Si(1)C(9)C(10)	116.3(8)
C(9)Os(2)C(10)	36.4(4)	Os(2)C(10)C(9)	73.5(6)
Os(1)Os(2)C(11)	80.4(3)	Os(2)C(10)C(11)	67.8(6)
Os(3)Os(2)C(11)	43.7(3)	C(9)C(10)C(11)	117.1(10)
C(4)Os(2)C(11)	145.8(5)	Os(2)C(10)C(11)	127.6(7)
C(5)Os(2)C(11)	121.0(5)	C(9)C(10)C(17)	126.9(10)
C(6)Os(2)C(11)	88.6(6)	C(11)C(10)C(17)	116.0(9)
C(9)Os(2)C(11)	66.3(4)	Os(2)C(11)Os(3)	89.0(4)
C(10)Os(2)C(11)	38.1(4)	Os(2)C(11)C(10)	74.0(6)
Os(1)Os(3)Os(2)	57.2(1)	Os(3)C(11)C(10)	132.6(7)
Os(1)Os(3)C(7)	112.9(4)	Os(2)C(11)C(12)	136.4(8)
Os(2)Os(3)C(7)	165.9(4)	Os(3)C(11)C(12)	78.5(6)
Os(1)Os(3)C(8)	97.8(4)	C(10)C(11)C(12)	142.0(11)
Os(2)Os(3)C(8)	103.7(5)	Os(3)C(12)Si(2)	122.7(5)
C(7)Os(3)C(8)	87.1(7)	Os(3)C(12)C(11)	63.8(6)
Os(1)Os(3)C(11)	80.3(3)	Si(2)C(12)C(11)	121.9(8)
Os(2)Os(3)C(11)	47.4(3)	Os(3)C(12)C(13)	69.5(6)
C(7)Os(3)C(11)	124.6(6)	Si(2)C(12)C(13)	123.8(8)
C(8)Os(3)C(11)	146.7(5)	C(11)C(12)C(13)	112.5(10)
Os(1)Os(3)C(12)	117.2(3)	Os(3)C(13)C(12)	72.7(6)
Os(2)Os(3)C(12)	78.4(3)		

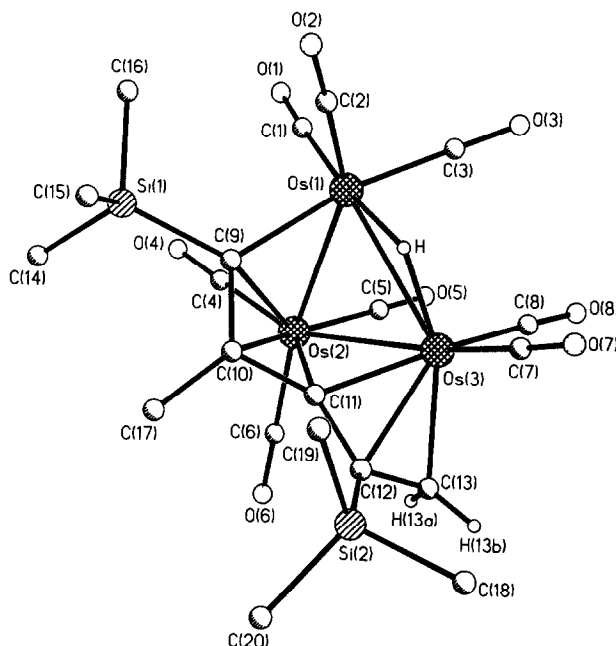
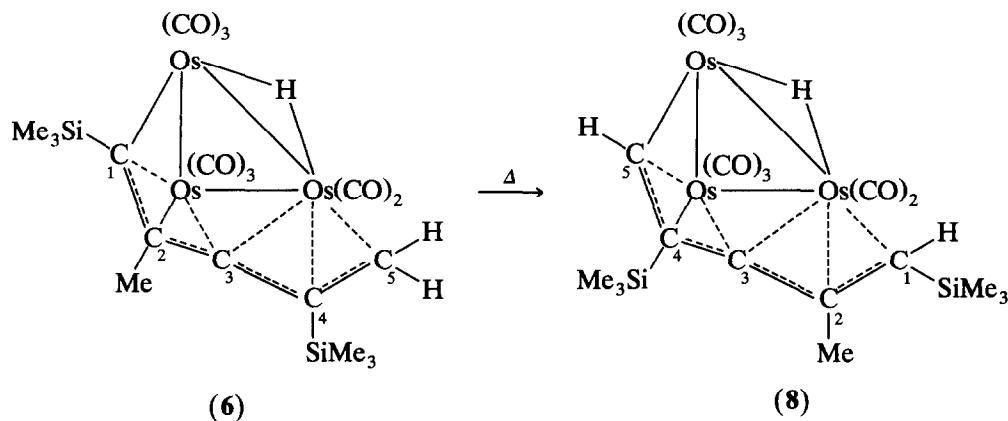


Fig. 1. The molecular structure of 6. Methyl H atoms are omitted for clarity.

length of the pentacarbon chain. At the same time, the C(10), C(11), C(12) atoms form a distorted allene unit, whose central C(11) atom is simultaneously coordinated to the Os(2) and Os(3) atoms, which results in its strongly distorted pseudo-tetrahedral environment (in particular, the C(10)C(11)C(12) bond angle is equal to 142° and the C(10)C(11)C(12) and Os(2)C(11)Os(3) planes form the dihedral angle of 45°). It is noteworthy that a very similar geometry of the coordinated pentacarbon ligand has been observed in the Ru complex 1 [1].

The hydrocarbon ligand donates seven electrons to the cluster, providing 6 (along with eight carbonyl groups and a hydride ligand) with a 48e configuration typical of organometallic triosmium clusters. ¹H NMR spectral data for 6 are in accordance with the X-ray crystal structure.

When the reactions of trimethylsilylpropyne with 3 or 7 were performed under more severe conditions in refluxing heptane, the complex Os₃H[μ₃-CHC(SiMe₃)CC(Me)C(SiMe₃)H](CO)₈ (8) was formed along with 6. According to the ¹H NMR spectrum, compound 8 is the osmium analogue of the ruthenium complex 1. An unidentified compound with hydride resonance at δ -14.63 a dihydride complex with the tentative structure of [Os₃H₂(μ₃-C=C=CH₂)(CO)₉] (δ -21.78, -18.11, 5.60, 6.11), and the known [6] acetylide compound Os₃H(μ₃-C≡CMe)(CO)₉ were detected by means of ¹H NMR spectroscopy together with 6 and 8 in the reaction mixture. Formation of the acetylide



complex was previously observed in the reactions of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with triosmium clusters under severe conditions, as well as in an unsuccessful attempt to isomerize **4** into the $2\sigma,\pi$ -allyl compound $\text{Os}_3\text{H}[\mu_3\text{-C}(\text{SiMe}_3)\text{CHCH}](\text{CO})_9$ in refluxing heptane or octane.

Allenyl compound **4**, in contrast to **3**, does not react with $\text{Me}_3\text{SiC}\equiv\text{CMe}$ in refluxing hexane, and the formation of **6** and **8** in low yields was observed only after prolonged heating of **4** and alkyne in refluxing heptane. Therefore, compound **4** may not be considered as intermediate in the formation of dimerization products of trimethylsilylpropyne.

Isolation of **6** in the reactions of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ with triosmium clusters and comparison of the structures of organic ligands in **6** and **8** show that these ligands may be interconverted by a formal 1,5 shift of the hydrogen atom. Indeed, we found that when heated in refluxing heptane for 7 h, compound **6** yields a mixture of **6** and **8** in the ratio 6:1.

This rearrangement of the organic ligand, including exchange of hydrogen atoms between the metallic core and hydrocarbon ligand (accompanied by internuclear migration of CO group), may be considered as one of the homogeneous models for rearrangements that proceed on metal surfaces.

Thus, the present study shows that dimerization of $\text{Me}_3\text{SiC}\equiv\text{CMe}$ on triosmium cluster includes the formation $\text{Os}_3[\mu_3\text{-Me}_3\text{SiC}_2\text{Me}](\mu\text{-CO})(\text{CO})_9$ (**3**), $\text{Os}_3[\text{C}_4\text{-}$

$(\text{SiMe}_3)(\text{Me})(\text{SiMe}_3)\text{Me}](\text{CO})_9$ (**5**) and $\text{Os}_3\text{H}[\mu_3\text{-C}(\text{SiMe}_3)\text{C}(\text{Me})\text{CC}(\text{SiMe}_3)\text{CH}_2](\text{CO})_8$ (**6**) clusters as direct intermediates; there is still uncertainty about the structure of the red compound **5** and the stage at which the 1,2-shift of the trimethylsilyl group and coupling of the two hydrocarbon (alkyne) ligands takes place.

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