

Protonation of triosmium clusters  
 $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CR})$   
and  $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-C}\equiv\text{CR})$   
( $\text{R} = \text{CH}_2\text{OH}, \text{CMe}_2\text{OH}, \text{C}(\text{Me}) = \text{CH}_2$ )

V.V. Krivykh<sup>\*</sup>, O.A. Kizas, E.V. Vorontsov, F.M. Dolgushin, A.I. Yanovsky,  
Yu.T. Struchkov, A.A. Koridze<sup>\*</sup>

*A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str., 28, 117813 Moscow, Russia*

Received 17 March 1995

Abstract

Protonation of  $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CR})$  ( $\text{R} = \text{CH}_2\text{OH}$  (1),  $\text{R} = \text{CMe}_2\text{OH}$  (2), and  $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-C}\equiv\text{CR})$  ( $\text{R} = \text{CH}_2\text{OH}$  (3),  $\text{R} = \text{CMe}_2\text{OH}$  (4),  $\text{R} = \text{C}(\text{Me}) = \text{CH}_2$  (5)) affords cationic complexes with the 5e- and 6e-propargyl ligands  $[\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}3\sigma, \eta^2\text{-HC}\equiv\text{CCR}'_2)]^+$  ( $\text{R}' = \text{H}$  (6),  $\text{R}' = \text{Me}$  (7)) and  $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}2\sigma, 2\eta^2\text{-CCCR}'_2)]^+$  ( $\text{R}' = \text{H}$  (8),  $\text{R}' = \text{Me}$  (9)) respectively. Reactions of the cationic complexes with  $\text{PPh}_3$  were studied. The treatment of solutions of complexes 6–9 with triphenylphosphine leads to the phosphonium derivatives of the  $\text{Os}_3$  clusters  $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CCR}'_2\text{PPh}_3^+)$  ( $\text{R}' = \text{H}$ , (10);  $\text{R}' = \text{Me}$ , (11)) as well as complexes  $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-PPh}_3\text{C}=\text{C}=\text{CR}'_2)$  ( $\text{R}' = \text{H}$  (12),  $\text{R}' = \text{Me}$  (13)) with the novel phosphonium allenyl ligand. The cluster  $\text{Os}_3(\text{CO})_8(\mu\text{-CO})[\text{HC}_2[\text{C}(\text{Me})=\text{CH}_2]\text{COC}[\text{C}(\text{Me})=\text{CH}_2]\text{CH}$  (14) was synthesized and its X-ray study was carried out ( $R = 0.0504$  for 5510 observed reflections). Crystals of 14 are triclinic, at 20°C:  $a = 8.591(2)$ ,  $b = 11.437(2)$ ,  $c = 12.642(3)\text{Å}$ ,  $\alpha = 93.17(2)$ ,  $\beta = 104.67(2)$ ,  $\gamma = 101.83(2)^\circ$ ,  $V = 1168.6(4)\text{Å}^3$ ,  $d_{\text{calc}} = 2.793\text{ g cm}^{-3}$ ,  $Z = 2$ , space group  $P\bar{1}$ .

**Keywords:** Triosmium clusters; Protonation; Six-electronic propargyl ligand; Phosphonium complexes; Phosphonium allenyl ligand; Crystal structure

1. Introduction

Recently, interest has grown in complexes containing the  $\eta^3$ -propargyl ligand coordinated to one [1] or two [2] transition metal atoms. At the same time, there is less information on the coordination of this ligand to three metal atoms. Protonation of compounds containing coordinated propargyl alcohols or vinylacetylenes is known as a route to the synthesis of complexes containing the  $\eta^3$ -propargyl ligand. It is also well known that the acetylenic ligand can coordinate to the  $\text{Os}_3$  cluster in various fashions, namely in the  $\sigma, \eta^2$ -,  $2\sigma$ -,  $\eta^2$ -, and  $\sigma, 2\eta^2$ -modes [3]. Such compounds can be suitable objects for the generation of the propargyl cation and

for the study of its stabilization by the  $\text{Os}_3(\text{CO})_9$  and  $\text{Os}_3(\text{CO})_{10}$  fragments. As early as 1981, some preliminary results of protonation of  $2\sigma, \eta^2$ - and  $\sigma, 2\eta^2$ -coordinated  $\text{HC}\equiv\text{CCMe}_2\text{OH}$  by  $\text{Os}_3$  clusters in  $\text{CF}_3\text{COOH}$  were published [4]. To continue our investigations of  $\eta^3$ -propargyl ligands coordinating mono- and polynuclear species we attempted to study the protonation of  $\text{HC}\equiv\text{CCR}_2\text{OH}$  ( $\text{R} = \text{H}, \text{Me}$ ) bound to the  $\text{Os}_3$  core in more detail. Our preliminary results on the protonation of the  $\text{Os}_3$  clusters containing the  $\text{HC}\equiv\text{CCMe}_2\text{OH}$  and  $\text{HC}\equiv\text{CC}(\text{Me})=\text{CH}_2$  ligands have been reported elsewhere [5].

In the present paper, we report the protonation of  $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CR})$  ( $\text{R} = \text{CH}_2\text{OH}$  (1),  $\text{R} = \text{CMe}_2\text{OH}$  (2) and  $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-C}\equiv\text{CR})$  ( $\text{R} = \text{CH}_2\text{OH}$  (3),  $\text{R} = \text{CMe}_2\text{OH}$  (4),  $\text{R} = \text{C}(\text{Me}) = \text{CH}_2$  (5) clusters, as well as the reactions of generated cationic complexes with triphenylphosphine.

<sup>\*</sup> Corresponding authors.

## 2. Experimental

All reactions were carried out in an argon atmosphere using anhydrous solvents. IR spectra were recorded on a Specord IR-75 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker WP-200 SY instrument at the operation frequency of 200.13 MHz using  $\text{C}_6\text{D}_6$  as a solvent at  $25^\circ\text{C}$  and  $\text{CD}_2\text{Cl}_2$  in the temperature range from  $-60$  to  $-20^\circ\text{C}$ . Chromatography was performed using silica gel of the 40/100 grade (Chechiya) as an adsorbent.

Clusters **2** and **4** were prepared according to the published procedure [4]; cluster **5** was prepared from the  $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$  [5] in 90% yield.

### 2.1. Preparation of $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CCH}_2\text{OH})$ (**1**)

$\text{HC}\equiv\text{CCH}_2\text{OH}$  (0.3 g, 5.27 mmol) was added to a solution of  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  (0.5 g, 1.758 mmol) in diethyl ether and stirred at  $25^\circ\text{C}$  until the initial osmium cluster disappeared (chromatography with hexane–ether, 5:1). The solvent was removed in vacuo; the residue was poured into the column. The broad orange band containing a mixture of **1** and the vinyl cluster  $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu_2\text{-}\sigma, \eta^2\text{-HC}=\text{CHCH}_2\text{OH})$  (**15**) was eluted by the solvent mixture mentioned. The reaction products were chromatographed in 0.02 g portions through a layer of silica gel ( $d = 10$  mm,  $l = 550$  mm). Crystallization of the first band from hexane yielded the dark-yellow crystalline compound **1** (0.18 g, 34%). IR (hexane): 2100 w, 2062 vs, 2060 vs, 2021 s, 2008 m, 1848 br  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 1.80 (1H, s, OH), 3.82 (1H, d,  $J(\text{HH}) = 13.5$  Hz, CHH), 4.31 (1H, d,  $J(\text{HH}) = 13.5$  Hz, CHH), 9.31 (1H, s, =CH). The product from the second band was crystallized from hexane to give the orange crystalline compound **15** (0.05 g, 9.4%). IR: 2103 m, 2061 vs, 2052 vs, 2025 vs, 2013 vs, 1992 s, 1982 m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $-19.31$  (1H, s, Os–H–Os), 0.61 (1H, t,  $J(\text{HH}) = 4.6$  Hz, OH), 3.26 (2H, t,  $J(\text{HCCH}) \sim J(\text{HCOH}) \sim 3.9$  Hz, CHH), 4.02 (1H, dt,  $J(\text{HH}) = 13.8$  Hz,  $J(\text{HH}) = 3.6$  Hz, =CHCH<sub>2</sub>), 7.24 (1H, d,  $J(\text{HH}) = 13.8$  Hz).

### 2.2. The reaction of $\text{Os}_3\text{H}_2(\text{CO})_{10}$ with isopropenylacetylene

$\text{HC}\equiv\text{C}(\text{Me})=\text{CH}_2$  (0.005 g, 0.07 mmol) was added to a solution of  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  (0.02 g, 0.023 mmol) in hexane and stirred for about 3 h until the initial cluster disappeared (chromatography with hexane–ether, 5:1). The solvent was removed in vacuo. The column chromatography with a mixture of hexane–ether 5:1 gave two dark yellow crystalline compounds. One of them,  $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu_2\text{-}\sigma, \eta^2\text{-HC}=\text{CHC}(\text{Me})=\text{CH}_2)$  (**16**) was crystallized from hexane (0.01 g, 47%). IR (hexane):

2104 w, 2074 m, 2061 vs, 2052 s, 2031 w, 2022 vs, 2010 s, 1992 m, 1986 w, 1980 w  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $-18.44$  (1H, s, Os–H–Os), 1.43 (3H, s,  $\text{CH}_3$ ), 4.83 (1H, s, =CHH), 5.13 (1H, s, =CHH), 5.16 (1H, d,  $J(\text{HH}) = 14.0$  Hz, =CH), 7.13 (1H, d,  $J(\text{HH}) = 14.0$  Hz, =CH). The other one also crystallized from hexane represents the complex  $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-H}_2\text{C}=\text{C}(\text{Me})\text{-CH}=\text{CH}_2)$  (**17**) [6] (0.01 g, 47%). IR (hexane): 2112 m, 2064 vs, 2032 vs, 2027 s, 2009 s, 1996 w, 1986 m, 1978 sh  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 0.21 (1H, dd,  $J(\text{HH}) = 8.1, 3.0$  Hz, =CHH), 0.56 (1H, d,  $J(\text{HH}) = 3.0$  Hz, MeC=CHH), 2.09 (1H, dd,  $J(\text{HH}) = 6.8$  Hz,  $J(\text{HH}) = 3.0$  Hz, HC=CHH), 2.31 (1H, s, MeC=CHH), 2.68 (3H, s,  $\text{CH}_3$ ), 5.24 (1H, dd,  $J(\text{HH}) = 7.7$  Hz, =CH).

### 2.3. Preparation of $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-C}\equiv\text{CCH}_2\text{OH})$ (**3**)

A solution of complex **1** (0.3 g) in octane (25 ml) was refluxed for 10 min. Octane was removed in vacuo. The column chromatography with a mixture hexane–ether 5:1 gave pale-cream crystalline compound **3** (0.23 g, 80%), which was crystallized from hexane. IR: 2101 m, 2079 vs, 2058 vs, 2023 vs, 2019 s, 1982 m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $-23.30$  (1H, s, Os–H–Os), 2.46 (1H, t,  $J(\text{HH}) = 5.0$  Hz, OH), 5.09 (2H, d,  $J(\text{HH}) = 5.0$  Hz,  $\text{CH}_2$ ).

### 2.4. Preparation of $\text{Os}_3(\text{CO})_8(\mu\text{-CO})\{\text{HC}_2[\text{C}(\text{Me})=\text{CH}_2]\text{COC}[\text{C}(\text{Me})\text{CH}_2]\text{CH}\}$ (**14**)

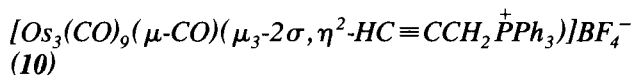
A solution of complex  $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CC}(\text{Me})=\text{CH}_2)$  **19** (0.22 g) in octane (20 ml) was refluxed for 10 min. Octane was removed in vacuo; the residue was column chromatographed, and eluted with heptane. Cluster **5** (90%) was isolated as a major product [5]. The second band contained the orange crystalline compound **14** (0.02 g, 10%). IR (heptane): 2095 s, 2074 w, 2057 vs, 2024 w, 2016 s, 2002 m, 1992 w, 1851 m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 1.80 (3H, s,  $\text{CH}_3$ ), 1.96 (3H, s,  $\text{CH}_3$ ), 5.00 (1H, s, =CH<sub>2</sub>), 5.04 (1H, s, =CH<sub>2</sub>), 5.15 (1H, s, =CH<sub>2</sub>), 5.60 (1H, s, =CH<sub>2</sub>), 7.27 (1H, s, =CH), 8.05 (1H, s, HC=).

### 2.5. Preparation of the phosphonium clusters $[\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CCMe}_2\text{PPh}_3)]\text{BF}_4^-$ (**11**)

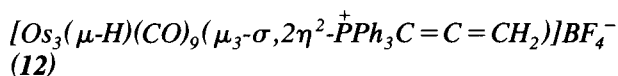
$\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.3 g, 0.04 ml, 0.194 mmol) was added to a solution of cluster **1** (0.06 g, 0.065 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) cooled to  $-60^\circ\text{C}$ . After 5 min, triphenylphosphine (0.02 g, 0.24 mmol) was added, and the mixture was stirred at the mentioned temperature for 20 min. Then the temperature was brought to  $25^\circ\text{C}$ . The phosphonium complex was precipitated from methylene

chloride with ether. The yellow powder **11** was obtained (0.04 g, 66%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2106 m, 2070 vs, 2058 s, 2035 m, 1845 br cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.65 (3H, d, *J*(HP) = 6.8 Hz CH<sub>3</sub>), 1.74 (3H, d, *J*(HP) = 6.8 Hz, CH<sub>3</sub>), 7.71 (15H, m, Ph), 9.29 (1H, s, =CH).

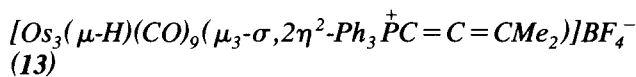
All the protonation reactions followed by the treatment of cationic intermediates with triphenylphosphine and the isolation of the phosphonium compounds were performed under similar conditions. Only in the case of complexes **4** and **5** was a 30% solution of trifluoromethanesulfonic acid in nitromethane used as a protonating agent.



Yellow powder (0.025 g, 65.5%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2105 m, 2070 vs, 2058 vs, 2032 s, 2005 m, 1849 br cm<sup>-1</sup>. <sup>1</sup>H NMR: 3.95 (1H, dd, *J*<sub>av</sub>(HH) (HP) = 15 Hz, CHH), 4.25 (1H, dd, *J*<sub>av</sub>(HH) (HP) = 15.0 Hz, CHH), 7.7 (15H, m, Ph), 8.55 (1H, s, =CH).



White powder (0.05 g, 65.3%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2110 m, 2082 vs, 2060 vs, 2042 s, 2015 s cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): -22.0 (1H, s, Os–H–Os), 2.93 (1H, dd, *J*(HH) ~ *J*(HP) = 2.8 Hz, =CHH), 4.07 (1H, dd, *J*(HH) = 2.5 Hz, *J*(HP) = 3.7 Hz, =CHH), 7.8 (15H, m, Ph).



White powder (0.05 g, 65%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2105 m, 2080 vs, 2059 vs, 2030 s, 2010 m cm<sup>-1</sup>. <sup>1</sup>H NMR: -23.17 (1H, s, Os–H–Os), 1.99 (3H, s, CH<sub>3</sub>), 2.09 (3H, s, CH<sub>3</sub>), 7.8 (15H, m, Ph).

#### 2.6. Preparation of $\bar{O}S_3(\mu-H)(CO)_9(\mu_3-2\sigma, \eta^2-Ph_3\overset{+}{P}C\equiv CCH_2OH)$ (**18**)

HBF<sub>4</sub>·Et<sub>2</sub>O (0.03 g, 0.04 ml, 0.194 mmol) was added to a solution of cluster **3** (0.06 g, 0.068 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at -78°C. After 5 min triphenylphosphine (0.02 g, 0.24 mmol) was added, and the mixture was stirred at this temperature for 1 h. The reaction mixture was slowly brought to 25°C. The solution was chromatographed through a layer of silica gel (*l* = 3 cm, *d* = 1 cm) at -78°C, then washed with methylene chloride at the mentioned temperature. After such treatment, there were no traces of the phosphonium cluster **10** (chromatography with CH<sub>2</sub>Cl<sub>2</sub>–acetone, 5 : 1). The solvent was removed in vacuo, and the residue was crystallized from the ether–hexane mixture. Colourless transparent crystals of the zwitter-ionic cluster **18** were obtained (0.04 g, 50.8%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 3606 br, 2073 s, 2046 vs, 2015 vs, 1993 s, 1968 s, 1944 m cm<sup>-1</sup>. <sup>1</sup>H

Table 1  
Atomic coordinates (× 10<sup>4</sup>) in **14**

	x	y	z
Os(1)	2783(1)	2025(1)	2822(1)
Os(2)	2105(1)	2939(1)	801(1)
Os(3)	5358(1)	3708(1)	2307(1)
O(1)	6462(9)	1600(5)	3162(6)
O(12)	2008(17)	4265(10)	3793(10)
O(13)	4390(15)	1347(11)	5061(8)
O(14)	-518(13)	321(10)	2634(10)
O(15)	-1518(12)	2016(9)	663(10)
O(16)	1535(16)	2557(11)	-1676(9)
O(17)	1678(11)	5546(7)	994(10)
O(18)	5213(12)	3630(8)	-133(8)
O(19)	8708(12)	4674(10)	1907(10)
O(20)	5045(15)	6225(8)	3099(10)
C(1)	2528(13)	1221(8)	1118(8)
C(2)	3952(12)	936(7)	1792(9)
C(3)	5237(12)	1932(8)	2395(8)
C(4)	7369(12)	2558(8)	3962(9)
C(5)	7020(13)	3637(9)	3823(9)
C(6)	4130(14)	-351(8)	1867(10)
C(7)	5401(18)	-669(11)	1444(17)
C(8)	2999(20)	-1145(11)	2280(14)
C(9)	8554(14)	2219(10)	4888(9)
C(10)	9566(20)	3236(12)	5771(11)
C(11)	8711(17)	1085(12)	4942(11)
C(12)	2336(19)	3423(12)	3445(12)
C(13)	3808(14)	1588(10)	4237(9)
C(14)	709(16)	969(11)	2718(10)
C(15)	-155(14)	2380(9)	723(11)
C(16)	1704(16)	2737(11)	-757(10)
C(17)	1889(14)	4594(10)	930(10)
C(18)	4745(14)	3546(9)	654(9)
C(19)	7443(15)	4317(10)	2067(10)
C(20)	5115(16)	5309(9)	2747(11)

NMR (CD<sub>2</sub>Cl<sub>2</sub>): -19.12 (1H, d, *J*(HP) = 3.3 Hz, Os–H–Os), 3.15 (1H, d, *J*(HH) = 13.0 Hz, CHH), 3.79 (1H, d, *J*(HH) = 13.0 Hz, CHH), 7.8 (15H, m, Ph).

#### 2.7. An X-ray study of $Os_3(CO)_8(\mu-CO)\{HC_2[C(Me)=CH_2]COC[C(Me)CH_2]CH\}$ (**14**)

Crystals of **14** are triclinic at 20°C: *a* = 8.591(2), *b* = 11.437(2), *c* = 12.642(3) Å,  $\alpha$  = 93.17(2),  $\beta$  = 104.67(2),  $\gamma$  = 101.83(2)°, *V* = 1168.6(4) Å<sup>3</sup>, *d*<sub>calc</sub> = 2.793 g cm<sup>-3</sup>, *Z* = 2, space group *P* $\bar{1}$ . Unit cell parameters and intensities of 7463 independent reflections were measured on a Siemens P3/PC automatic diffractometer (20°C, Mo K $\alpha$  radiation, graphite monochromator,  $\theta/2\theta$ -scans,  $\theta < 31^\circ$ ).

The structure was solved by direct methods and refined by the full-matrix least squares technique, first in the isotropic and then in the anisotropic approximation. The hydrogen atoms were not located. The correction for absorption ( $\mu$  = 163 cm<sup>-1</sup>) was based on the azimuthal scans (*T*<sub>min</sub> = 0.270). The final discrepancy factors *R* = 0.0504, *R*<sub>w</sub> = 0.0506 for 5510 reflections with *I* ≥ 3σ (*I*). All calculations were carried out with

the SHELXTL PLUS programs (PC version) [7] on an IBM PC. Coordinates of non-hydrogen atoms are given in Table 1. A table of thermal parameters and a complete list of bond lengths and angles has been deposited at the Cambridge Crystallographic Data Centre.

### 3. Results and discussion

#### 3.1. The synthesis of clusters with acetylenic ligands

Cluster  $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CCH}_2\text{OH})$  (**1**) was obtained as a hard-to-separate mixture with the vinyl derivative  $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu_2\text{-}\sigma, \eta^2\text{-HC}=\text{CHCH}_2\text{OH})$  (**15**) by the treatment of osmium carbonylhydride with propargyl alcohol in ether at 25°C. Column chromatography of this mixture in small batches and recrystallization gave clusters **1** and **15** in the 34.0% and 9.4% yields respectively. In the IR spectrum of **1**, there are six CO bands of the terminal CO groups and a band at 1848  $\text{cm}^{-1}$  of the bridging carbonyl group. In the  $^1\text{H}$  NMR spectrum, there is a broad signal at 1.8 ppm associated with the hydroxyl group, two signals at 3.8 and 4.3 ppm with  $J_{\text{AB}} = 13.5$  Hz associated with the magnetically non-equivalent protons of the  $\text{CH}_2$  group, and a low-field signal at 9.3 ppm of the methyne proton. Thus, spectral characteristics are in accord with the proposed structure of cluster **1**.

All attempts to obtain cluster  $\text{Os}_3(\mu\text{-CO})(\text{CO})_9(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CC}(\text{Me})=\text{CH}_2)$  (**19**) using the same method were unsuccessful. The treatment of  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  with vinylacetylene in a 1:1 ratio provided the vinyl compound  $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-}\sigma, \eta^2\text{-HC}=\text{CHC}(\text{Me})=\text{CH}_2)$  (**16**) and the product of the selective enyne hydrogenation, namely the diene cluster  $\text{Os}_3(\text{CO})_{10}(\eta^4\text{-H}_2\text{C}=\text{C}(\text{CH}_3)\text{-CH}=\text{CH}_2)$  (**17**), which was obtained earlier [6] directly from 2-methyl-1,3-butadiene and  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ . After crystallization, clusters **16** and **17** were each obtained in 47% yield. In the IR spectrum of the vinyl compound **16**, there are ten bands of the terminal CO groups; in the  $^1\text{H}$  NMR spectrum, there are the following signals: –18.44 of the bridging hydride, a singlet at 1.43 ppm of the methyl group protons, and the other signals corresponding to the structure of **16**, namely two signals at 4.83 and 5.15 ppm ( $=\text{CH}_2$ ), and two doublets at 5.16 and 7.13 ppm with  $J = 14.0$  Hz ( $\text{HC}=\text{CH}$ ). In the IR spectrum of the diene cluster **17**, there are eight bands of the terminal CO groups. The  $^1\text{H}$  NMR spectrum contains the signals: 0.21 (dd,  $J(\text{HH}) = 8.1, 3.0$  Hz,  $\text{CHH}$ ), 0.56 (1H, d,  $J(\text{HH}) = 3.0$  Hz,  $\text{MeC}=\text{CHH}$ ), 2.68 (1H, s,  $\text{CH}_3$ ), and 5.24 (1H, dd,  $J(\text{HH}) = 7.7$  Hz,  $\text{HC}=\text{CH}$ ).

Cluster **19** was obtained in high yield (85%) by the treatment of  $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$  with isopropenylacetylene in an ether solution at 25°C [5].

The thermolysis of **1** and **19** in boiling octane yielded

the clusters with the five electron acetylide ligands  $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-C}\equiv\text{CCH}_2\text{OH})$  (**3**) and  $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-C}\equiv\text{CC}(\text{Me})=\text{CH}_2)$  (**5**) in high yield (90%). IR spectra of both compounds contain the bands of the terminal carbonyl groups; in  $^1\text{H}$  NMR spectra, there are signals of the bridging hydrogen ligands at –23.30 and –23.43 ppm, which are characteristic of clusters with the  $\mu_3\text{-}\sigma, 2\eta^2$ -acetylide ligands.

The thermolysis of complex **19** provides, along with **5**, another compound **14** in low yield (10%), the IR spectrum of which has, apart from seven bands of the terminal CO groups, a band at 1850  $\text{cm}^{-1}$  of the bridging carbonyl group. The  $^1\text{H}$  NMR spectrum contains two singlets of the methyl groups at 1.80 and 1.96 ppm, four singlets at 5.00, 5.04, 5.15 and 5.60 ppm associated with two  $=\text{CH}_2$  groups as well as two singlets at 7.27 and 8.05 ppm associated with two fragments of  $=\text{CH}$ . The spectral data allowed to assign the formula of  $\text{Os}_3(\text{CO})_8(\mu\text{-CO})\{\text{HC}_2[\text{C}(\text{Me})=\text{CH}_2]\text{-COC}[\text{C}(\text{Me})\text{CH}_2]\text{CH}\}$  to this compound. Its structure was unambiguously established by an X-ray study. The compound has a complex ligand formed by a combination of the allyl fragment and the oxygen-containing five-membered metallacycle and is analogous both to complex  $\text{Os}_3(\text{CO})_8(\mu\text{-CO})\{\text{H}_2\text{CPhCOCPhCH}\}$  reported in Ref. [8] and cluster  $\text{Os}_3(\text{CO})_8(\mu\text{-CO})\{\text{H}_2\text{CFcCOCFcCH}\}$ , which we described earlier [9]. The thermolysis of clusters containing a terminal alkyne and the bridging carbonyl group as ligands, usually proceeds via the decarbonylation followed by the oxidative addition of the C–H bond to the metal atom, thus changing the ligand coordination mode from  $2\sigma, \eta^2$  to  $\sigma, 2\eta^2$  and yielding acetylide clusters.

However, as seen from the examples cited, in a number of cases, complexes of the same type as **14** are formed (the mechanism is still uncertain) in which the bridging carbonyl group is retained and a complex organic ligand involving the former terminal CO group is formed.

The molecular structure of **14** is shown in Fig. 1. Selected bond distances and angles in **14** are listed in Tables 2 and 3. The structure is identical with that of the complex with the phenyl substituents reported earlier [8]. Three osmium atoms form a triangle with the  $\text{Os}(1)\text{-Os}(2)$ ,  $\text{Os}(1)\text{-Os}(3)$ ,  $\text{Os}(2)\text{-Os}(3)$  distances equal to 2.785(1), 2.854(1) and 2.885(1) Å respectively (the corresponding distances in  $\text{Os}_3(\text{CO})_8(\mu\text{-CO})\{\text{H}_2\text{-CPhCOCPhCH}\}$  [8], are 2.794, 2.857 and 2.880 Å).

Like the complex with the phenyl substituents, the dimerized acetylene ligand is bound to the triosmium core by three  $\sigma$ -bonds  $\text{Os}(2)\text{-C}(1)$ ,  $\text{Os}(3)\text{-C}(3)$  and  $\text{Os}(3)\text{-C}(5)$  and its allyl moiety  $\text{C}(1)\text{C}(2)\text{C}(3)$  is  $\pi$ -coordinated by the  $\text{Os}(1)$  atom. Two five-membered cycles  $\text{Os}(2)\text{C}(1)\text{C}(2)\text{C}(3)\text{Os}(3)$  and  $\text{Os}(3)\text{C}(3)\text{O}(1)\text{C}(4)\text{C}(5)$  are fused via the  $\text{Os}(3)\text{-C}(3)$  bond and do not show considerable deviations from planarity (maximum devi-

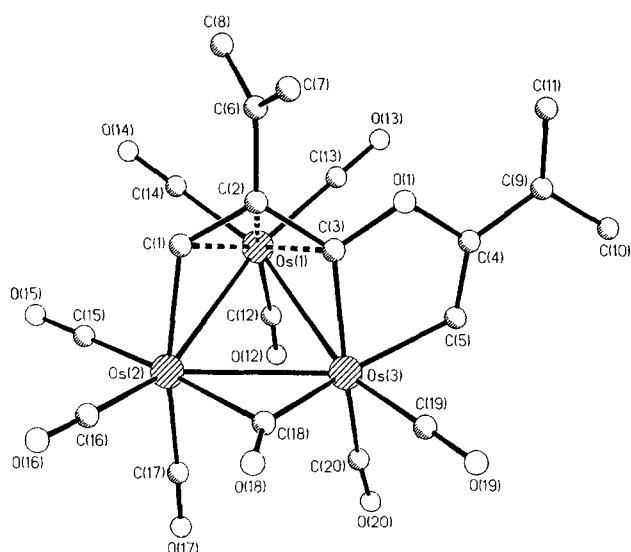


Fig. 1. The molecular structure of  $\text{Os}_3(\text{CO})_9(\mu\text{-CO})\text{-}(\text{HC}_2[\text{C}(\text{Me})=\text{CH}_2]\text{COC}[\text{C}(\text{Me})=\text{CH}_2]\text{CH})$  (**14**).

ations from their mean planes are 0.03 and 0.11 Å respectively); the dihedral angle formed by their planes is equal to  $20^\circ$  (the same value was found for the phenyl analog).

It should be noted that the isopropenyl substituents in **14** are non-equivalent. In one of them, which is bound to the oxygen-containing chelate metallacycle, there is a distinct difference in the double  $\text{C}(9)=\text{C}(11)$  bond (1.33(2) Å) and the ordinary  $\text{C}(9)-\text{C}(10)$  bond (1.52(2) Å) lengths. Moreover, this substituent is trans-conjugated with the  $\text{C}(4)=\text{C}(5)$  double bond (1.34(1) Å) of the metallacycle; the torsion angle  $\text{C}(11)\text{C}(9)\text{C}(4)\text{C}(5)$  is equal to  $176^\circ$ . In contrast, the isopropenyl group bound to the allenyl fragment of the other metallacycle has almost equal  $\text{C}(6)-\text{C}(7)$  and  $\text{C}(6)-\text{C}(8)$  bond lengths (1.43(2) and 1.41(2) Å respectively). However, this feature most probably does not have any chemical implications and should be attributed to the effect of a disorder in the crystal. The dihedral angle formed by the planes of the isopropenyl and allyl groups in this case is equal to  $64^\circ$ . The lack of the conjugation in this system

Table 2  
Selected bond lengths (angstroms) in **14**

Os(1)–Os(2)	2.785(1)	Os(1)–Os(3)	2.854(1)
Os(1)–C(1)	2.235(10)	Os(1)–C(2)	2.291(11)
Os(1)–C(3)	2.325(11)	Os(2)–Os(3)	2.885(1)
Os(2)–C(1)	2.112(10)	Os(2)–C(18)	2.289(12)
Os(3)–C(3)	2.023(9)	Os(3)–C(5)	2.097(10)
Os(3)–C(18)	2.009(11)	O(1)–C(3)	1.371(12)
O(1)–C(4)	1.399(10)	O(18)–C(18)	1.166(16)
C(1)–C(2)	1.412(14)	C(2)–C(3)	1.435(11)
C(2)–C(6)	1.517(13)	C(4)–C(5)	1.339(14)
C(4)–C(9)	1.472(15)	C(6)–C(7)	1.432(23)
C(6)–C(8)	1.410(20)	C(9)–C(10)	1.519(15)
C(9)–C(11)	1.334(18)		

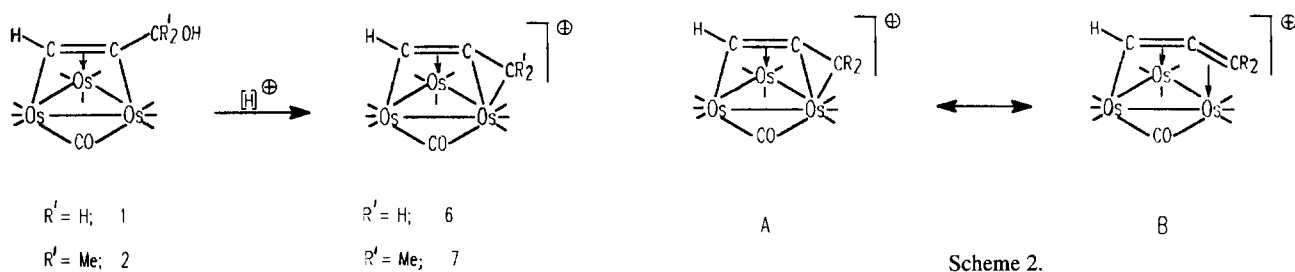
Table 3  
Selected bond angles (deg) in **14**

C(1)–Os(1)–C(2)	36.3(4)	C(1)–Os(1)–C(3)	64.1(3)
C(2)–Os(1)–C(3)	36.2(3)	C(1)–Os(2)–C(18)	90.0(4)
C(3)–Os(3)–C(5)	75.7(4)	C(3)–Os(3)–C(18)	94.2(4)
C(5)–Os(3)–C(18)	150.7(5)	C(3)–O(1)–C(4)	111.7(7)
Os(1)–C(1)–Os(2)	79.6(3)	Os(1)–C(1)–C(2)	74.0(6)
Os(2)–C(1)–C(2)	128.1(6)	Os(1)–C(2)–C(1)	69.7(6)
Os(1)–C(2)–C(3)	73.2(6)	C(1)–C(2)–C(3)	116.4(8)
Os(1)–C(2)–C(6)	127.8(8)	C(1)–C(2)–C(6)	122.0(7)
C(3)–C(2)–C(6)	121.5(9)	Os(1)–C(3)–Os(3)	81.7(4)
Os(1)–C(3)–O(1)	119.0(7)	Os(3)–C(3)–O(1)	118.1(5)
Os(1)–C(3)–C(2)	70.6(6)	Os(3)–C(3)–C(2)	128.1(7)
O(1)–C(3)–C(2)	113.6(8)	O(1)–C(4)–C(5)	117.5(9)
O(1)–C(4)–C(9)	114.2(8)	C(5)–C(4)–C(9)	128.3(9)
Os(3)–C(5)–C(4)	114.3(7)	C(2)–C(6)–C(7)	115.8(10)
C(2)–C(6)–C(8)	118.6(12)	C(7)–C(6)–C(8)	125.5(11)
C(4)–C(9)–C(10)	115.7(10)	C(4)–C(9)–C(11)	121.6(9)
C(10)–C(9)–C(11)	122.6(11)	Os(2)–C(18)–Os(3)	84.0(5)
Os(2)–C(18)–O(18)	129.3(8)	Os(3)–C(18)–O(18)	146.7(9)

seems to be associated with the strong electron density transfer from the  $\pi$ -system of the allyl fragment to the coordinating metal atom. However, the atomic coordinates for the phenyl substituted complex are not available, either in the original paper [8] or in the Cambridge Structural Database, so that we could not check whether the same is true in the case of phenyl derivative. However, as can be seen from the figure given in Ref. [8], one may anticipate the same effect in the structure of phenyl derivative.

### 3.2. Protonation of clusters $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma, \eta^2\text{-HC}\equiv\text{CCR})$ ( $R = \text{CH}_2\text{OH}$ (**1**), $R = \text{CMe}_2\text{OH}$ (**2**)) and $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-C}\equiv\text{CR})$ ( $R = \text{CH}_2\text{OH}$ (**3**), $R = \text{CMe}_2\text{OH}$ (**4**), $R = \text{C}(\text{Me})=\text{CH}_2$ (**5**))

If one drop of  $\text{CF}_3\text{COOH}$  is added to a solution of **1** in  $\text{CD}_2\text{Cl}_2$  at  $-50^\circ\text{C}$ , the  $^1\text{H}$  NMR spectrum is changed in the following way. The signal of the OH group at 1.8 ppm is shifted low-field, and two broad signals appear corresponding to the slowly exchanging OH and  $\text{CF}_3\text{COOH}$ . The signals of two non-equivalent protons of the  $\text{CH}_2$  group at 3.80 and 4.30 ppm are drawn closer together (3.95, 4.25 ppm) with the coupling constant being retained ( $J_{\text{AB}} = 13.5$  Hz), although the high field component already contains an additional splitting with  $J^2 = 3.5$  Hz. At the same time, the low-field signal at 9.3 ppm is practically unchanged. The addition of five more drops of trifluoroacetic acid leads to the collapse of the AB system components and to the appearance of a new singlet at 4.3 ppm, but only on addition of two drops of trifluoromethanesulfonic acid; the latter signal transforms to two doublets at 3.70 and 4.93 ppm with  $J = 5.0$  Hz, thus evidencing for the formation of the cationic complex **6**.



Scheme 1.

Scheme 2.

The proton signal at 9.3 ppm is 0.5 ppm down-shifted. In this case, the previous set of signals is still observed, which corresponds to a high concentration of  $\text{CF}_3\text{COOH}$  in the ratio 1 : 1. Protonation of **1** was carried out within the temperature range  $-50$ – $-20^\circ\text{C}$ . As the temperature is increased, the signals of decomposition products appear in the spectrum. At  $17^\circ\text{C}$ , the reversible broadening of the  $\text{CH}_2$  group signals was observed, but a further increase in the temperature caused the degradation of the cationic cluster **6**. Spectral changes occurring upon the gradual additions of acids to **1** might be rationalized as follows. Trifluoroacetic acid forms a solvate with cluster **1** resulting in an additional signal with  $J = 3.5$  Hz due to the interaction of the  $\text{CH}_2\text{OH}$  group with  $\text{CF}_3\text{COOH}$  through the oxygen atom. An increase in the acid concentration facilitates the exchange process bringing the signals of the  $\text{CH}_2$  group protons together and finally causing the collapse of these signals; only the addition of a stronger acid leads to the cationic complex **6**. The structure of this complex can be described as a resonance hybrid of structures **A** and **B** (Scheme 2).

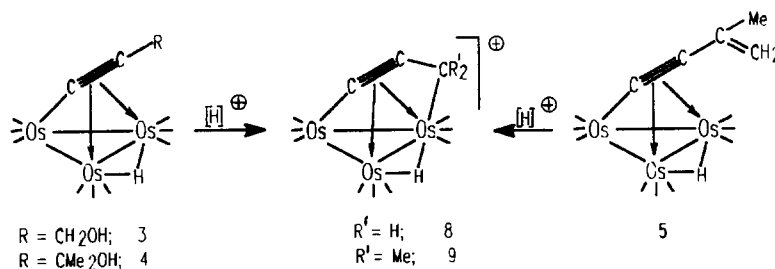
Protonation of  $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}2\sigma,\eta^2\text{-HC=CCMe}_2\text{OH})$  (**2**) was studied earlier by the  $^1\text{H}$  NMR method [4]. We studied the protonation of **2** by the  $^{13}\text{C}$  NMR method. Comparison of the  $^{13}\text{C}$  NMR spectra of the initial **2** (29.49 (q,  $J(\text{CH}) = 127$  Hz, Me), 33.40 (q,  $J(\text{CH}) = 127$  Hz, Me), 79.53 (s,  $\text{C-Me}_2$ ), 117.0 (d,  $J(\text{CH}) = 163$  Hz,  $=\text{CH}$ ), 168.52 (s,  $=\text{C}$ ), 171.8, 174.43, 176.0 (br), 179.38, 179.86 (CO), 202.85 ( $\mu\text{-CO}$ )) and its protonated form after the addition of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  in a  $\text{CD}_2\text{Cl}_2$  solution at  $-60^\circ\text{C}$  (14.0 (s, Me), 19.92 (s, Me), 110.24 (d,  $J(\text{CH}) = 162$  Hz,  $\text{HC}=\text{C}$ ), 117.02 (s,  $\text{C-Me}_2$ ), 152.99 (s,  $=\text{C}$ ), 158.97, 174.02,

174.74, 175 (br), 175.23, 178.82, (CO), 207.15 ( $\mu\text{-CO}$ )), shows that the formation of the cationic complex causes a low-field shift of the carbon signal of  $\text{CMe}_2$  group by 37 ppm. The other signals of the  $\text{C}_3$  ligand are only slightly shifted, thus indicating the retention, to a great extent, of the  $2\sigma,\eta^2$ -bonding mode in the fragment  $\text{H-C}=\text{C}$  (structure **A**) though the contribution of the

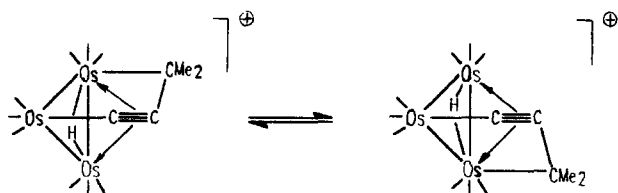
structure **B** should also be taken into account. It is remarkable that the signal of the bridging CO group is retained although it is shifted low-field by 4 ppm. Hence the protonation of the complexes with four electron acetylene ligands, such as propargyl alcohol and its derivatives, coordinated to the  $\text{Os}_3$  cluster in the  $2\sigma,\eta^2$  fashion, gives the cationic complexes with the five electron propargyl ligand.

We were successful in detecting the formation of the cationic cluster with the six-electron propargyl ligand on protonation of clusters containing the acetylide ligand coordinated in the  $\sigma,2\eta^2$ -fashion (Scheme 3)

If a solution of trifluoromethanesulfonic acid in  $\text{CD}_3\text{NO}_2$  is added to solutions of complexes **4** and **5** in  $\text{CD}_2\text{Cl}_2$  at  $-50^\circ\text{C}$  [5], the  $^1\text{H}$  NMR spectra are changed in the following way: the hydride signals at  $-23.5$  ppm **4** and  $-23.34$  ppm **5** gradually disappear and a new signal at  $-22.9$  ppm appears. In the low-field range of the spectra the following signals disappear: the singlet of the magnetically equivalent methyl groups at 1.8 ppm for **4** and the signal of the methyl group at 2.19 ppm for **5**, as well as the signals in the range of 5.0–5.3 ppm, responsible for the protons of the  $=\text{CH}_2$  group in **5**. In both cases, the same set of signals appears, namely the signal of the  $\mu$ -hydride at  $-22.9$  ppm and two signals of two magnetically non-equivalent methyl groups at 2.24 and 2.64 ppm, the spectral pattern evi-



Scheme 3.



Scheme 4.

dences for the formation of the cationic cluster **9** in the solution. With an increase in the temperature, the signals of the methyl groups are gradually broadened; they coalesce at 17°C and a further temperature increase leads to the sharpening of the signal. Temperature changes in the spectrum may be interpreted in the following way. The protonation of **4** or **5** generates the carbenium ion in the  $\alpha$ -position, with respect to the triple bond. The cation is stabilized due to the direct interaction of the carbocationic center with one of the osmium atoms bearing the hydrogen bridge (Scheme 4) (the same situation takes place in mono-[1a] and binuclear [2a,b,c] propargyl complexes). Such direct participation of the metal atom in the stabilization of the  $\alpha$ -cationic center is a general property for  $\alpha$ -metallocenylcarbenium ions and related cationic complexes [10]. Since the probability of bonding to both osmium atoms mentioned is equal, the degenerate exchange process takes place resulting in the observed temperature dependence. The free activation energy of this process is  $G_{290\text{ K}}^* = 13.3 \pm 0.3 \text{ kcal mol}^{-1}$ . Recently, a similar exchange process has been observed in the neutral complex  $\text{CpWRe}_2(\text{CO})_8(\text{OR})(\text{C}_3\text{Me}_2)$  [11]. The cationic cluster **9** is not stable enough for isolation; moreover, as the temperature of a solution of **9** is increased to 25°C, another set of signals appears in the spectrum, namely two singlets in the range of the methyl groups at 2.23 and 2.47 ppm, and the hydride signal at -19.5 ppm. The chemical shift value of the hydride signal is not in line with that for similar clusters with the five-electron acetylide ligand of the  $\sigma, 2\eta^2$  type. The intensities of these signals depend on the exposure time of the solution of **9**. These signals seem to have been observed earlier [4] upon dissolving of **4** in  $\text{CF}_3\text{COOH}$  at room temperature.

If the protonation is carried out at low temperatures, a different spectrum is observed. At -10°C, the  $^1\text{H}$  spectrum contains the following signals: the singlet at 2.13 ppm of two methyl groups, the signal of the hydride ligand at -23.62 ppm as well as another signal set of two methyl groups and the corresponding signal of the hydride ligand at -23.52 ppm in the ratio of 5:1. An increase in the acid concentration leads to a change in the intensity ratio of the signal sets to 1:2. An addition of one drop of trifluoromethanesulfonic acid in nitromethane to this solution causes the appearance of the signals of the cationic cluster **9**: 2.28 (1H, s,

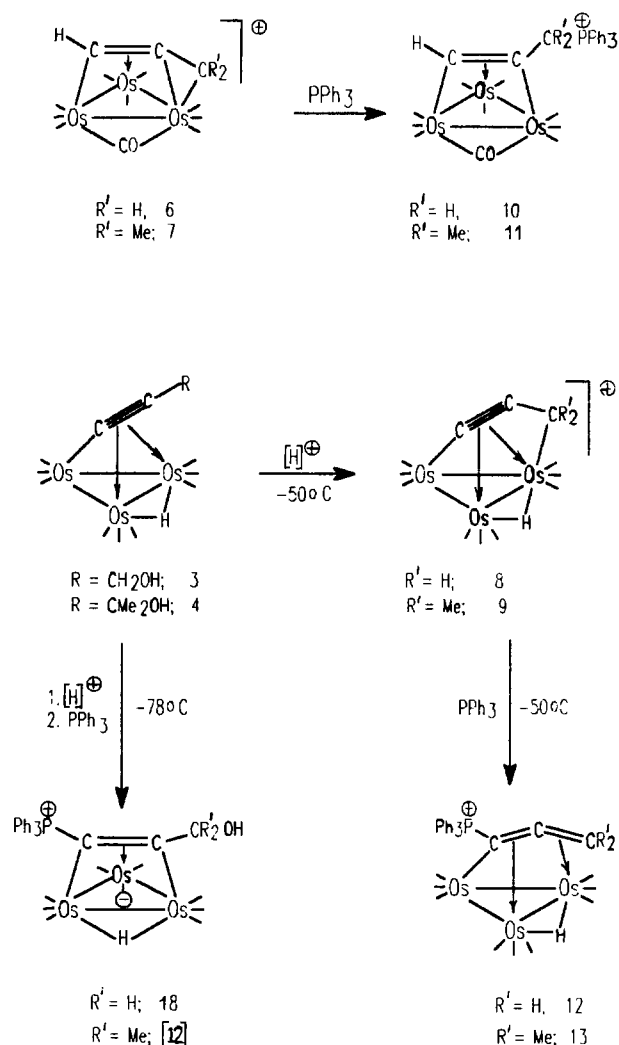
$\text{CH}_3$ ), 2.68 (1H, s,  $\text{CH}_3$ ), and -22.99 (1H, s, Os-H-Os), the signals at -23.52 (Os-H-Os) and 2.09 of the methyl groups still being observed in the spectrum in the ratio of 3:1. At low temperatures, trifluoroacetic acid does not seem to generate the cationic complex **9** but only  $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-C}\equiv\text{CCMe}_2\text{OCOCF}_3)$  (**19**) is formed showing the signals at -23.52 ppm and 2.13 ppm of the methyl groups.

Protonation of **3** yields the cationic cluster  $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}2\sigma, 2\eta^2\text{-C}\equiv\text{CCH}_2)]^+$  (**8**), which appeared to be even less stable than **9**. The addition of  $\text{CF}_3\text{COOH}$  in  $\text{CD}_3\text{NO}_2$  to a solution of **3** in  $\text{CD}_2\text{Cl}_2$  at -50°C results in the features of **8** in the  $^1\text{H}$  NMR spectrum, that is the signals at -21.99 ppm and two singlets of the magnetically non-equivalent protons of the  $\text{CH}_2$  group at 5.14 and 6.07 ppm. The ratio of the neutral and cationic clusters is 5:1. The addition of two more and then three more drops of trifluoromethanesulfonic acid changes this ratio from 1:1 to 1:3 respectively. In the latter case, the spectrum indicates the degradation products. At -20°C, the initial complex **3** gradually disappears, and on further temperature increase (20°C), the cationic cluster **8** is completely decomposed.

### 3.3. Preparation of phosphonium clusters

The treatment of solutions of the cationic clusters **6–9** with triphenylphosphine in the temperature range -50–-60°C gives new phosphonium derivatives of the  $\text{Os}_3$  clusters. The cationic complexes **6** and **7** yield  $2\sigma, \eta^2$ -coordinated derivatives **10** and **11** respectively with four-electron acetylene ligands, while the treatment of cations **8** and **9** with phosphine allowed clusters **12** and **13** respectively to be obtained with the new five-electron phosphonium allenyl ligand (Scheme 5).

IR spectra of **10** and **11** in the carbonyl region exhibit the bands at 1849 and 1845  $\text{cm}^{-1}$ , respectively, characteristic of the bridging carbonyl groups. The  $^1\text{H}$  NMR spectrum of **10** at -20°C exhibits two doublets of doublets at 3.95 and 4.25 ppm with  $J(\text{HH}) \sim J(\text{HP}) \sim 15 \text{ Hz}$  belonging to the protons of the  $\text{CH}_2$  group, the multiplet of the phenyl substituent at 7.7 ppm, and the low-field singlet signal of the methyne proton at 8.55 ppm. The  $^1\text{H}$  NMR spectrum of **11** at -20°C shows two doublets of the methyl group at 1.65 and 1.74 ppm, with  $J(\text{HP}) = 6.8 \text{ Hz}$ , the multiplet of the phenyl group, and the low-field singlet signal at 9.29 ppm. With an increase in the temperature to 17°C, two doublet signals of the methyl groups collapse into one broad signal, probably, due to the migration of the  $\text{C}_3$  ligand relative to the metal core of the cluster. Similar processes were reported for alkyne complexes [4,12]. The addition of triphenylphosphine to solutions of **8** and **9** at -50°C generates the phosphoniumallenyl clusters  $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\sigma, 2\eta^2\text{-Ph}_3\text{PC}=\text{C}=\text{CR}'_2)$  ( $\text{R}' = \text{H}$  (**12**)) and ( $\text{R}' = \text{Me}$  (**13**)). The site of the nucleophilic



Scheme 5.

attack of the six-electron propargyl ligand can be derived from the  $^1\text{H}$  NMR spectra of complexes **12** and **13**. In the case of **12**, the protons of the  $=\text{CH}_2$  group give rise to two double doublets with  $J(\text{HH}) \sim J(\text{HP}) \sim 2.8$  Hz,  $J(\text{HH}) = 2.5$  Hz,  $J(\text{HP}) = 3.7$  Hz, and the hydride ligand gives rise to singlet at  $-22.0$  ppm. The same picture is observed in the case of **13**. The  $^1\text{H}$  NMR spectrum exhibits two singlets at 1.99 and 2.09 ppm of the methyl groups and a singlet at  $-23.17$  ppm of the hydride ligand. A small  $J$  value for 'H'–'P' interaction in **12**, as well as the lack of the 'H'–'P' interaction in **13**, evidence for the attack of the  $\alpha$ -carbon atom of the ligand by phosphine which is in accord with the structure involving the phosphonium allenyl ligand proposed for **12** and **13**.

If the reaction of **3** or **4** with an acid is performed at  $-78^\circ\text{C}$ , the ionization does not take place and, therefore, the cationic complexes **8** and **9** are not formed. However, a known reaction of phosphine addition to acetylenic ligands takes place, that is the interaction of the neutral cluster with the neutral nucleophile to form

zwitter-ionic derivatives [12]. In our case, compounds  $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}2\sigma, \eta^2\text{-Ph}_3\text{PC}\equiv\text{CCR}'_2\text{OH})$  ( $R' = \text{H}$  (**18**)) and ( $R' = \text{Me}$  [12]) were obtained.

Thus, in the present paper, protonation of the  $\text{Os}_3$  clusters coordinated to propargyl alcohol and its derivatives in the  $2\sigma, \eta^2$ - and  $\sigma, 2\eta^2$ -fashion has been studied. Labile cationic complexes with 5e- and 6e-propargyl ligands were generated and studied by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

In conclusion, we may state that depending on the nuclearity and coordination mode of the propargyl ligand, the nucleophilic attack can be selectively directed to  $\text{C}_1$ ,  $\text{C}_2$ , or  $\text{C}_3$  ligand atoms.

### Acknowledgment

The authors are deeply grateful to Professor V.I. Bakhmutov for help in measuring and interpreting the NMR spectra. This work was in part supported by the Russian Foundation for Basic Research (project No. 94-03-08167 and 94-03-08338) and the International Science Foundation (grant No. M04300).

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