Synthesis and the crystal structure of the triosmium cluster with the μ-dehydrobenzene ligand, $Os_3(\mu\text{-}H)_2(CO)_7(\mu\text{-}C_6H_4)\{\mu_3\text{-}Ph_2PCH_2P(C_6H_4)Ph\}$

A. A. Koridze, S. A. Kuklin, P. V. Petrovskii, F. M. Dolgushin, and M. G. Ezernitskaya*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: koridze@ineos.ac.ru

The $Os_3(\mu\text{-}H)_2(CO)_7(\mu\text{-}C_6H_4)\{\mu_3\text{-}Ph_2PCH_2P(C_6H_4)Ph\}$ complex, which was isolated from the products of thermolysis of $Os_3(CO)_{10}(\mu\text{-dppm})$ (dppm is $Ph_2PCH_2PPh_2$) in toluene, was characterized by X-ray diffraction analysis. Protonation of the resulting complex with trifluoroacetic acid afforded the cationic complex $[Os_3(\mu\text{-}H)_3(CO)_7(\mu\text{-}C_6H_4)\{\mu_3\text{-}Ph_2PCH_2P(C_6H_4)Ph\}]^+$.

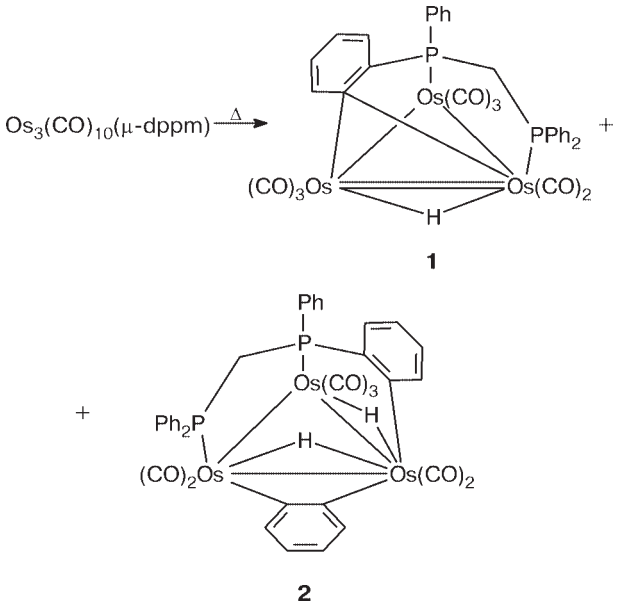
Key words: triosmium clusters, dehydrobenzene complexes, hydrides, carbonylphosphines, protonation, *ortho*-metallation, X-ray diffraction analysis.

The reactions of metal carbonyl clusters are often accompanied[1—3] by the cleavage of the C—H and C—P bonds in the phosphine ligand. These reactions initially afford various complexes in which the aryl group of the phosphine ligand undergoes *ortho*-metallation. Subsequent transformations can involve the cleavage of the C—P bond giving rise to dehydrobenzene complexes[4] or elimination of the benzene molecule (or its derivatives). The data on coupling of dehydrobenzene[1,5] and the phenyl group[6] with other ligands on the cluster surface were reported.

Results and Discussion

As part of continuing studies on the mechanism of formation of coupling products of dehydrobenzene, CO, and enyne in the reaction of $Ru_3(CO)_{10}(\mu\text{-dppm})$ (dppm is $Ph_2PCH_2PPh_2$) with RCH=CHC≡CR (R = Ph [5] or Fc), we attempted to perform an analogous transformation at the trinuclear $Os_3(CO)_{10}(\mu\text{-dppm})$ cluster. When synthesizing the cluster $Os_3(\mu\text{-}H)(CO)_8\{\mu_3\text{-}Ph_2PCH_2(C_6H_4)Ph\}$[7] (**1**), which is the starting complex for the reactions with enynes, by thermolysis of $Os_3(CO)_{10}(\mu\text{-dppm})$ in boiling toluene, we unexpectedly isolated the new yellow complex $Os_3(\mu\text{-}H)_2(CO)_7(\mu\text{-}C_6H_4)\{\mu_3\text{-}Ph_2PCH_2P(C_6H_4)Ph\}$ (**2**) along with compound **1** (Scheme 1).

Scheme 1



The IR spectrum of complex **2** provides evidence for the presence of only terminal CO ligands. The ^{31}P NMR spectrum has two doublets (δ −19.3 and −20.3, $J_{P,P}$ = 79.2 Hz for both doublets), which indicates that two P atoms of the bridging ligand retain the phosphine nature. The ^1H NMR spectrum has two resonances of the hydride ligands at δ −12.74 (br.d, 1 H, J = 10.8 Hz) and −11.97 (dd, 1 H, J = 2.8 Hz and J = 12.0 Hz) and two resonances of the methylene protons at δ 3.82 (m, 1 H) and 5.25 (m, 1 H). The resonances for the aromatic protons are observed at δ 6.59 (t, 1 H, J = 6.4 Hz), 6.75 (t, 1 H, J = 7.4 Hz), 7.50—7.61 (m, 17 H), 7.87 (dd, 1 H, J = 3.2 Hz and J = 7.4 Hz), and 8.05 (d, 1 H, J = 5.6 Hz). The positions and multiplicities of the last two mentioned resonances are indicative of the presence of the

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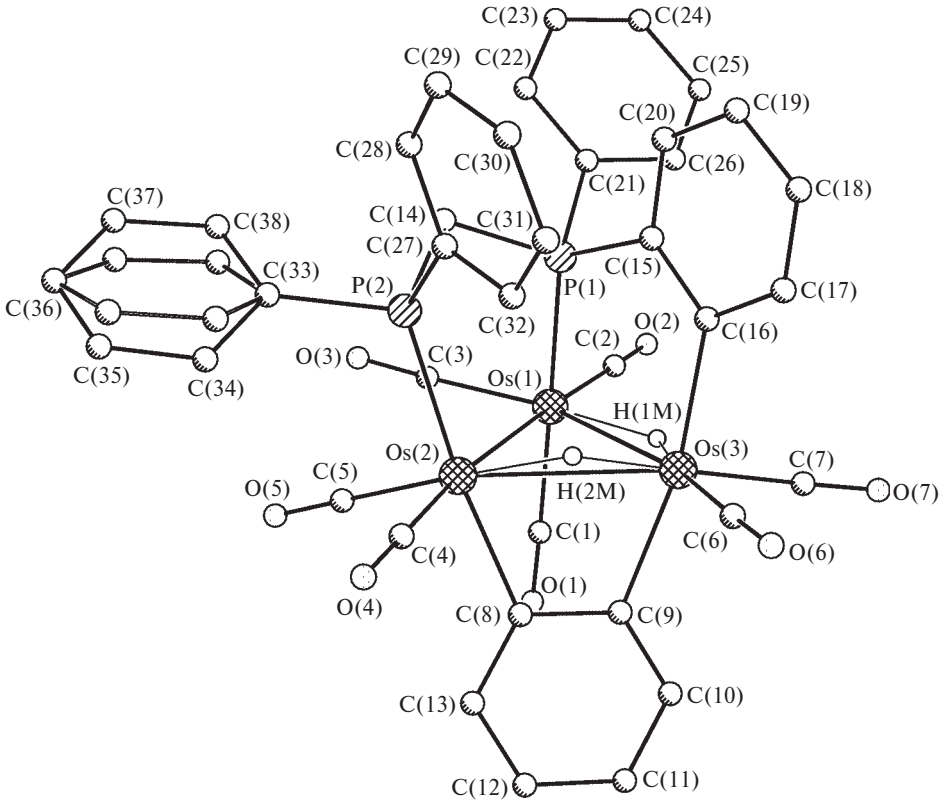


Fig. 1. Molecular structure of complex **2**.

ortho-metallated phenyl group. Finally, two triplets are observed at δ 6.18 (t, 1 H, J = 8.8 Hz) and 6.3 (t, 1 H, J = 7.2 Hz), which are apparently attributable to the dehydrobenzene ligand.

The structure of complex **2** was unambiguously established by single-crystal X-ray diffraction analysis. According to the results of X-ray analysis, molecule **2** (Fig. 1, Tables 1 and 2) contains a triangle of the Os atoms. Two Os atoms, *viz.*, Os(2) and Os(3), each bear two CO ligands, and the Os(1) atom is coordinated by three CO ligands. The Os(1) and Os(2) atoms are bound to the P atoms of the bridging diphosphine ligand. One of the Ph groups of this ligand was subjected to *ortho*-metallation with the Os(3) atom. The μ_3-$Ph_2PCH_2P(C_6H_4)Ph$ ligand is coordinated in such a way that the P(1), P(2), and C(16) atoms occupy axial positions at the Os(1), Os(2), and Os(3) atoms, respectively.

Molecule **2** contains the dehydrobenzene ligand, which is bound only to two metal atoms of cluster **2**, *viz.*, Os(2) and Os(3). The Os(2)—C(8) and Os(3)—C(9) σ-bond lengths (2.115(7) and 2.146(6) Å, respectively) are close to the Os—C bond lengths found in other triosmium dehydrobenzene complexes.[8—10] The dehydrobenzene ring is planar and the dihedral angle between the Os(1)Os(2)Os(3) and Os(2)Os(3)C(8)C(9) planes is 82.3°. The C(8)—C(9) distance is 1.362(9) Å. In the C_6H_4 ring, no essential alternation is observed in the C—C bond lengths (the average length is 1.375 Å).

The hydride ligands, which were located from electron density syntheses, are bridging ligands at the

Table 1. Selected bond lengths (d) in cluster **2**

Bond	d/Å	Bond	d/Å
Os(1)—Os(2)	2.9178(5)	P(1)—C(14)	1.811(7)
Os(1)—Os(3)	3.0442(5)	P(1)—C(15)	1.812(7)
Os(2)—Os(3)	2.9715(5)	P(1)—C(21)	1.825(7)
Os(1)—H(1M)	1.73(17)	P(2)—C(14)	1.844(7)
Os(3)—H(1M)	1.56(17)	P(2)—C(27)	1.837(7)
Os(2)—H(2M)	1.73(10)	P(2)—C(33)	1.829(7)
Os(3)—H(2M)	1.73(10)	C(8)—C(9)	1.362(9)
Os(1)—P(1)	2.364(2)	C(8)—C(13)	1.399(10)
Os(2)—P(2)	2.381(2)	C(9)—C(10)	1.345(8)
Os(1)—C(1)	1.949(8)	C(10)—C(11)	1.375(10)
Os(1)—C(2)	1.915(8)	C(11)—C(12)	1.396(11)
Os(1)—C(3)	1.912(7)	C(12)—C(13)	1.372(10)
Os(2)—C(4)	1.884(7)	C(15)—C(20)	1.397(10)
Os(2)—C(5)	1.900(7)	C(15)—C(16)	1.412(9)
Os(2)—C(8)	2.115(7)	C(16)—C(17)	1.414(10)
Os(3)—C(6)	1.874(7)	C(17)—C(18)	1.375(10)
Os(3)—C(7)	1.867(7)	C(18)—C(19)	1.390(11)
Os(3)—C(9)	2.146(6)	C(19)—C(20)	1.377(10)
Os(3)—C(16)	2.125(7)		

Table 2. Selected bond angles (ω) in cluster **2**

Angle	ω/deg	Angle	ω/deg
Os(2)—Os(1)—Os(3)	59.745(11)	C(33)—P(2)—C(14)	103.8(3)
Os(1)—Os(2)—Os(3)	62.240(9)	C(27)—P(2)—C(14)	101.6(3)
Os(2)—Os(3)—Os(1)	58.015(11)	C(33)—P(2)—Os(2)	114.3(2)
C(3)—Os(1)—Os(2)	85.8(2)	C(27)—P(2)—Os(2)	119.7(2)
C(2)—Os(1)—Os(3)	115.6(2)	C(14)—P(2)—Os(2)	114.2(2)
C(5)—Os(2)—Os(1)	91.1(2)	C(9)—C(8)—C(13)	118.2(6)
C(4)—Os(2)—Os(3)	113.4(2)	C(9)—C(8)—Os(2)	113.6(5)
C(8)—Os(2)—Os(3)	67.73(19)	C(13)—C(8)—Os(2)	128.2(5)
C(6)—Os(3)—Os(2)	106.8(2)	C(10)—C(9)—C(8)	121.2(6)
C(9)—Os(3)—Os(2)	67.87(15)	C(10)—C(9)—Os(3)	127.9(5)
C(7)—Os(3)—Os(1)	105.9(2)	C(8)—C(9)—Os(3)	110.8(4)
C(14)—P(1)—C(15)	106.5(3)	P(1)—C(14)—P(2)	108.3(4)
C(14)—P(1)—C(21)	102.4(3)	C(20)—C(15)—C(16)	122.5(6)
C(15)—P(1)—C(21)	102.1(3)	C(20)—C(15)—P(1)	115.7(5)
C(14)—P(1)—Os(1)	110.6(2)	C(16)—C(15)—P(1)	121.8(5)
C(15)—P(1)—Os(1)	117.4(2)	C(15)—C(16)—C(17)	113.8(6)
C(21)—P(1)—Os(1)	116.3(2)	C(15)—C(16)—Os(3)	124.6(5)
C(33)—P(2)—C(27)	101.1(3)	C(17)—C(16)—Os(3)	121.4(5)

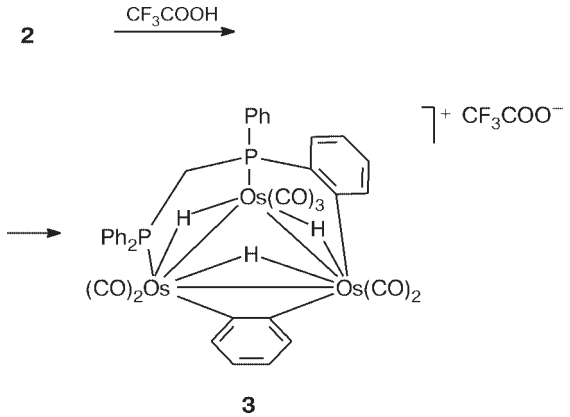
Os(1)—Os(3) and Os(2)—Os(3) edges. The positions of the μ-hydride ligands are confirmed by elongation of the corresponding Os—Os bonds (3.0442(5) and 2.9715(5) Å) compared to the Os(1)—Os(2) bond (2.9178(5) Å) and by the larger CO—Os—CO angles involving the equatorial carbonyl ligands (C(2)—Os(1)—Os(3), 115.6(2)°; C(7)—Os(3)—Os(1), 105.9(2)°; C(4)—Os(2)—Os(3), 113.4(2)°; and C(6)—Os(3)—Os(2), 106.8(2)°) compared to the analogous angles at the Os(1)—Os(2) bond (C(3)—Os(1)—Os(2), 85.8(2)°; and C(5)—Os(2)—Os(1), 91.2(2)°).

Taking into account the nature and the number of donated electrons, cluster **2** would be expected to belong to 47-electron compounds. However, neither broadening or shifts of the resonances characteristic of paramagnetic complexes is observed in the ^{1}H and ^{31}P NMR spectra. In addition, a resonance of the unpaired electron is absent in the ESR spectrum. The reasons for this inconsistency remain unclear. It can be assumed that the Os(2)—C(8) and Os(3)—C(9) bonds are one-and-a-half bonds due to which the μ-C_6H_4 ligand donates three rather than two electrons to the cluster. It is also conceivable that the charges in the cluster are separated, the negative charge being localized on the Os_3 core.

In addition, complex **2** is distinguished by μ-coordination of the dehydrobenzene ligand,[8] which is very untypical of trimetallic clusters (generally, the C_6H_4 ligand forms two σ-bonds and one π-bond and is coordinated to three metal atoms), and by the arrangement of two P atoms of the diphosphine ligands in the axial positions in the cluster (as a rule, the bulky phosphorus-containing ligands occupy sterically less hindered equatorial positions).

The reaction of CF_3COOH with a solution of cluster **2** in CD_2Cl_2 (an NMR tube, low temperature) afforded the trihydride cationic complex $[Os_3(\mu\text{-}H)_3(CO)_7(\mu\text{-}C_6H_4)\{\mu_3\text{-}Ph_2PCH_2P(C_6H_4)Ph\}]^+$ (**3**) (Scheme 2). The hydride region of the ^{1}H NMR spectrum shows resonances at δ −11.99 (dd, J = 3.5 Hz and J = 15.5 Hz), −14.23 (d, J = 10.2 Hz), and −18.04 (br. pseudotriplet, $J \approx 7$ Hz). The character of the last-mentioned resonance indicates that the hydride ligand is bridging between the Os(1) and Os(2) atoms, each atom being coordinated to the P atom of diphosphine. This is additional supporting evidence for the fact that the μ-H ligands in the starting cluster **2** are located at the Os(1)—Os(3) and Os(2)—Os(3) edges.

Scheme 2



Experimental

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 and 161.98 MHz, respectively). The IR spectra were measured on a Bruker IFS 113v instrument.

The reactions were carried out under argon. Chromatographic separation was performed in air. Preparative separation was carried out using silica gel L(100/160 μm) (Chemapol). Organic solvents were distilled under argon over the corresponding drying agents. The $Os_3(CO)_{10}$(μ-dppm) complex was prepared according to a known procedure[11] and recrystallized from an acetone—EtOH mixture.

Thermolysis of $Os_3(CO)_{10}$(μ-dppm). A solution of the $Os_3(CO)_{10}$(μ-dppm) complex (240 mg, 0.193 mmol) in toluene (25 mL) was stirred at 110 °C for 10 h. The color of the solution changed from orange to green. Then the reaction mixture was concentrated and the residue was chromatographed on a column with silica gel (a 1 : 3 CH_2Cl_2—hexane mixture as the eluent). Three fractions were taken (in order of elution), *viz.*, orange (the starting $Os_3(CO)_{10}$(μ-dppm) complex), yellow (complex **2**), and green (complex **1**) fractions. After recrystallization from a 1 : 2 CH_2Cl_2—*n*-hexane mixture, complex **1** was isolated as green crystals in a yield of 65 mg (30.1%). After recrystallization from acetone, complex **2** was obtained in a yield of 42 mg (18%). IR (CH_2Cl_2), ν/cm^{-1}: 2087 v.w, 2062 s, 2020 v.s, 1997 v.s, 1971 w, 1948 m, 1935 sh. (CO). ^{1}H NMR ($CDCl_3$, 25 °C), δ: −12.74 (br.d, 1 H, J = 10.8 Hz); −11.97 (dd, 1 H, J = 2.8 Hz, J = 12.0 Hz); 3.82 and 5.25 (both m, 1 H each); 6.59 (t, 1 H, J = 6.4 Hz); 6.75 (t, 1 H, J = 7.4 Hz); 7.50—7.61 (m, 17 H); 7.87 (dd, 1 H, J = 3.2 Hz, J = 7.4 Hz); 8.05 (d, 1 H, J = 5.6 Hz). ^{31}P NMR ($CDCl_3$, 25 °C), δ: −20.3, −19.3 (both d, J = 79.2 Hz).

Protonation of 1,1,2,2,3,3,3-heptacarbonyl-1,2-μ-dehydrobenzene-μ$_3$-{*o*-[(diphenylphosphino)methyl(phenylphosphino)]phenyl-C^1(Os^1)P^1(Os^3)P^2(Os^2)}-1,2:1,3-di-μ-hydrido-*triangulo*-triosmium, $Os_3(\mu\text{-}H)_2(CO)_7(\mu\text{-}C_6H_4)\{\mu_3\text{-}Ph_2PCH_2P(C_6H_4)Ph\}$ (2). A solution of complex **2** (20 mg, 0.013 mmol) in CD_2Cl_2 was placed in an NMR tube and cooled to −70 °C. Then three—four drops of CF_3COOH were added. ^{1}H NMR (CD_2Cl_2), δ: −18.04 (br. pseudotriplet, 1 H, $J \approx 7$ Hz); −14.23 (d, 1 H, J = 10.2 Hz); −11.99 (dd, 1 H, J = 3.5 Hz, J = 15.5 Hz); 6.19 and 6.42 (both m, 1 H each); 6.90—7.75 (m, 17 H); 7.90 (m, 1 H); 8.35 (d, 1 H, J = 5.4 Hz).

X-ray diffraction study of complex 2. Single crystals of complex **2** suitable for X-ray diffraction analysis were obtained by crystallization from acetone. The crystals of $C_{41}H_{33}O_8P_2Os_3$ (**2**·Me_2CO) are monoclinic, space group $P2_1/c$, at 110 K a = 11.104(2), b = 12.789(2), c = 28.643(4) Å, β = 92.544(3)°, V = 4063(1) Å^3, Z = 4, M = 1286.21, d_{calc} = 2.103 g cm^{-3}, μ(Mo-Kα) = 94.87 cm^{-1}, F(000) = 2404. The intensities of 11798 independent reflections (R_{int} = 0.0411) were measured on an automated Bruker SMART 1000 CCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator, T = 110 K, $2\theta_{max}$ = 60°, the scan step was 0.3°, frames were exposed for 10 s). The X-ray diffraction data were processed with the use of the SAINT program.[12] The empirical absorption correction was applied based on repeated measurements of the intensities of equivalent reflections (the SADABS program[13]). The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms, except for the disordered C(34), C(35), C(37), and C(38) atoms of one of the phenyl substituents and the acetone molecule of solvation. The positions of the H atoms of the bridging hydride ligands were revealed from electron density syntheses and refined isotropically; the remaining H atoms were placed in geometrically calculated positions and refined using the riding model. The final reliability factors were as follows: R_1 = 0.0472 (based on F for 10090 observed reflections with $I > 2\sigma(I)$) and wR_2 = 0.0988 (based on F^2 for all reflections) for 507 refinable parameters. All calculations were carried out using the SHELXTL-97 program package.[14]

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