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Mendeleev Commun., 2020, **30**, 374–376

Mendeleev
Communications

Double activation of the diphosphinite pincer proligand by a triosmium carbonyl cluster

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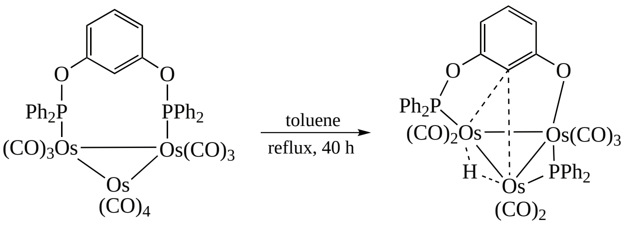
DOI: 10.1016/j.mencom.2020.05.038

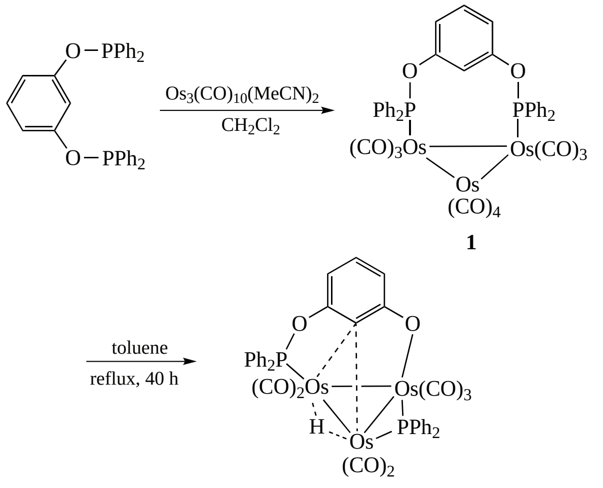
The reaction between 1,3-bis(diphenylphosphinite)benzene and $Os_3(CO)_{10}(MeCN)_2$ affords complex $Os_3(CO)_{10}[1,3\text{-}(PhPO)_2C_6H_4]$. A thermolysis of this cluster in refluxing toluene results in the activation of O–PPh_2 and C–H bonds and the formation of unsaturated triosmium cluster $Os_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7[(C_6H_3(O)(OPPh_2)]$ that possesses a remarkable structure with the pseudo-pincer ligand containing a bridging μ-η^1-aryl group.



Keywords: pincer complexes, pseudo-pincer ligand, osmium cluster, NMR, single crystal X-ray analysis.

In the past thirty years, pincer complexes of transition metals have been attracting considerable interest in the chemical community[1,2] mainly due to the ability of these complexes to activate small molecules and catalyze various reactions involving organic substrates. Among them, the most impressive success has been achieved in the field of homogeneous catalytic dehydrogenation of alkanes.[3–7] Various types of mononuclear pincer complexes based on benzene, pyridine, and other organic molecules have been described.[1,2] Moreover, pincer complexes based on metallocenes, *viz*. ferrocene and ruthenocene, were also synthesized.[8,9] However, the pincer type complexes containing a cluster metal core have never been reported, although attempts to synthesize them were undertaken.[10,11]

Here we report a preparation of triosmium cluster $Os_3(CO)_{10}[1,3\text{-}(Ph_2PO)_2C_6H_4]$ (**1**) by the reaction of 1,3-bis(diphenylphosphinito)benzene with $1,2\text{-}Os_3(CO)_{10}(MeCN)_2$ and a double activation of the organic ligand in **1** under conditions of the cluster thermolysis (Scheme 1). The reaction of $1,3\text{-}(Ph_2PO)_2C_6H_4$ with an equimolar amount of $1,2\text{-}Os_3(CO)_{10}(MeCN)_2$ was carried out in CH_2Cl_2 at room temperature.[†] Light-yellow complex **1** was isolated in 62% yield by column chromatography on silica gel. It was characterized by IR and ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and by single-crystal X-ray diffraction analysis.



Scheme 1

Its IR spectrum contains absorption bands of the terminal CO groups and is similar to spectra of the known $Os_3(CO)_{10}$(P–P) clusters [where P–P corresponds to 4,6-bis(diphenylphosphinomethyl)-*m*-xylene (dppx), bis(diphenylphosphino)ethane (dppe), and 4,5-bis(diphenylphosphino)-4-cyclopentene-1,1-dione (bpcd)] bearing bridging diphosphorus ligands.[11–14] In the ^{1}H NMR spectrum, protons of the central aromatic ring of ligand appear as three resonances with a relative intensities of 1 : 2 : 1 at δ of 7.135, 6.753, and 6.754, respectively. Phenyl protons of the PPh_2 groups were observed as two multiplets at δ of 7.484 and 7.690. The ^{31}P NMR spectrum of complex **1** contains one signal from the two equivalent phosphorus atoms at δ of 97.08. Its ^{13}C NMR spectrum recorded at room temperature contains two signals at δ of 172.90 and 182.16, which are apparently from the equatorial and axial CO groups of $Os(CO)_4$ moiety since a study of $^{187}Os_3(CO)_{12}$ and $[Os_3(\mu\text{-}H)(CO)_{12}]^+$ species has previously revealed unequivocally that the equatorial and axial ligands in an $Os_3(CO)_{12}$ moiety should correspond to the resonances at δ of 170.4 and 182.3, respectively.[14(*a*)] The remaining six CO groups in **1** undergo a rapid exchange, presumably according to the mechanism involving a pairwise terminal-bridge carbonyl exchange in a plane perpendicular to the Os_3 plane[10,13,14,16] over the two bridged Os atoms.

Cluster **1** contains 48 valence electrons and is electronically saturated *via* the bridging of Os(1) and Os(2) centers by the

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[†] See Online Supplementary Materials for detailed experimental procedures.

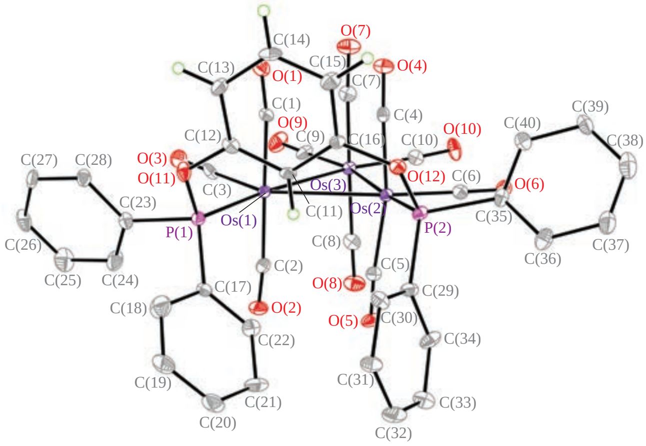

Figure 1 Molecular structure of cluster **1** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms of the phenyl groups of phosphinite moieties are omitted for clarity.

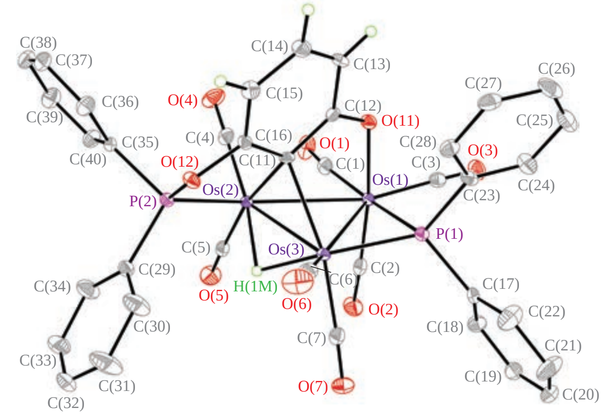

Figure 2 Molecular structure of cluster **2** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms of the phenyl groups of PPh_2 moieties are omitted for clarity.

1,3-bis(diphenylphosphinito)benzene ligand, which has been structurally confirmed. The structure of complex **1** (Figure 1)‡ revealed by the single crystal X-ray diffraction analysis matches the expected one and incorporates two phosphorus atoms in an equatorial position to the adjacent osmium atoms, similarly to that of other triosmium clusters, where the bridging diphosphorus ligand occupies the equatorial *trans*,*trans* positions.[11,14]

Refluxing the suspension of cluster **1** in toluene for 48 h resulted in a color change and formation of an orange-yellow solution, which was evaporated, and chromatography of the residue on a silica gel column afforded yellow complex **2** in 65% yield (see Scheme 1). The composition and structure of complex **2** were determined using element analysis, IR and ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and single-crystal X-ray diffraction analysis.

The IR spectrum of complex **2** contains seven absorption bands of the terminal CO groups, which is equal to their total number in the considered cluster since it does not possess symmetry elements. In agreement with this, in its ^{13}C NMR spectrum, seven signals from the CO groups have also been observed. And the final confirmation for the presence of seven CO groups was provided by the single crystal X-ray diffraction analysis of this cluster (Figure 2).‡ The ^{1}H NMR spectrum contains a hydride signal at δ of –9.331, which undergoes splitting on the two nonequivalent phosphorus nuclei. One of the signals is close to that in cluster **1**, while the second one indicates that a bridging PPh_2 group has been formed.

The data acquired by single-crystal X-ray diffraction analysis for cluster **2** are totally consistent with the spectroscopic data. The Os_3 metal triangle was preserved upon formation of cluster **2** (see Figure 2), whereas starting cluster **1** has lost three CO groups. The organic ligand underwent a significant transformation: the hydride Os(2)–H–Os(3) and phosphide Os(1)–PPh_2–Os(3) bridging ligands formed upon the double activation, cleavage of C–H bond at the central benzene ring, and cleavage of O–PPh_2 bond of the phosphinite ligand. The phosphinite ligand is coordinated with all the three osmium atoms, one of the phosphinite groups has retained the P(2)–Os(2) bond, and the O(11) oxygen atom belonging to the second cleaved phosphinite group is σ-bound with the Os(1) atom, while the metallated C(11) carbon atom forms a bridge between the Os(2) and Os(3) atoms.

The electron counting shows that cluster **2** contains 46 electrons, representing a rare example of the electron-deficient triosmium complex. A formation of the electron-unsaturated orthometallic complex $Os_3(\mu\text{-}H)(CO)_8[\mu\text{-}PhP(C_6H_4\text{-}\mu_2\eta^1)CH_2PPh_2]$ during a thermolysis of the $Os_3(CO)_{10}$(dppm) bearing a bridged diphosphine ligand has been previously observed.[17] Another feature of cluster **2** is the presence of bridging aryl group: the C(11) atom of central benzene ring of the organic ligand forms a bridge between the two metal atoms with the Os(2)–C(11) and Os(3)–C(11) distances of 2.183(3) and 2.293(3) Å, respectively. These distances are close to those found earlier in the triosmium clusters containing bridged phenyl ligands, $Os_3(CO)_8(\mu\text{-}Ph)(\mu\text{-}PPh_2)(\mu\text{-}PPhC_6H_4)$ (2.19 and 2.39 Å)[18] and $Os_3(CO)_{10}(\mu\text{:}\eta^1\text{-}Ph)(\mu\text{-}AuPPh_3)$ (2.19 and 2.336 Å).[19]

In conclusion, the reported formation of cluster **2** is the first example of double activation of a pincer diphosphorus proligand by a cluster complex occurred due to the cleavage of C–H and O–PPh_2 bonds in the organic ligand. An electron-deficient 46-electron triosmium cluster bearing a ligand of the pseudo-pincer type was isolated and characterized by the single crystal X-ray crystallography. The unsaturated nature of cluster **2** is of interest in the context of further studies on the reversibility of cleavage of the chemical bonds over the surface of a metal cluster.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation and performed using the equipment of Center for Molecular Composition Studies at the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.038.

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‡ Crystal data were acquired using a Bruker SMART APEX II diffractometer [λ(MoKα) = 0.71073 Å]. All the calculations were performed using SHELXL program package.[15]

Crystal data for **1**. $0.8(C_6H_{14})\cdot 0.2(CHCl_3):C_{45}H_{35.4}Cl_{0.6}O_{12}Os_3P_2$, M = 1421.94, orange crystals, monoclinic, space group $P2_1/c$, a = 15.8069(8), b = 21.3695(11) and c = 13.4618(7) Å, β = 100.117(1)°, V = 4476.5(4) Å^3, d_{calc} = 2.110 g cm^{-3}, Z = 4, μ(MoKα) = 86.64 cm^{-1}, T = 120(2) K, $2\theta_{\text{max}}$ = 60°, R_1 = 0.0554 for 9433 reflections with $I > 2\sigma(I)$, and wR_2 = 0.0968 for all the 13055 unique reflections (R_{int} = 0.0979).

Crystal data for **2**. $0.5(CH_2Cl_2):C_{37.5}H_{25}ClO_9Os_3P_2$, M = 1287.56, yellow crystals, monoclinic, space group $C2/c$, a = 32.4629(12), b = 9.3492(4) and c = 24.4456(9) Å, β = 90.037(1)°, V = 7419.3(5) Å^3, d_{calc} = 2.305 g cm^{-3}, Z = 8, μ(MoKα) = 104.63 cm^{-1}, T = 100(2) K, $2\theta_{\text{max}}$ = 64°, R_1 = 0.0267 for 10753 reflections with $I > 2\sigma(I)$, and wR_2 = 0.0527 for all the 12875 unique reflections (R_{int} = 0.0503).

CCDC 1955633 and 1955634 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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Received: 10th October 2019; Com. 19/6039