

Synthesis and X-ray crystal structure of the electron-deficient metal carbonyl cluster $[\text{Os}_3(\text{CO})_5(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$

F.W. Heinemann, H.-C. Böttcher *

Institut für Anorganische Chemie der Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Str. 2, 06120 Halle / Saale, Germany

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Abstract

The reaction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (1) with $^t\text{Bu}_2\text{PH}$ in refluxing diglyme results in the electron-deficient metal cluster complex $[\text{Os}_3(\text{CO})_5(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-dppm})]$ (2) (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) in good yields. The molecular structure of 2 has been established by a single crystal X-ray structure analysis. In contrast to the known homologue $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-dppm})]$ (3), no bridging carbonyl ligand was found in 2. The electronically unsaturated cluster 2 does not react with carbon monoxide under elevated pressure, therefore 2 seems to be coordinatively saturated by reason of the high steric demands of the phosphido ligands.

Keywords: Osmium; Carbonyl; Phosphido-bridged; X-ray structure

1. Introduction

Recently, we reported the synthesis of the electron-deficient metal cluster $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-dppm})]$ (3) by reaction of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ with two equivalents of $^t\text{Bu}_2\text{PH}$ [1]. In this context we were interested in the preparation of analogous iron and osmium compounds. Since the starting material $[\text{Fe}_3(\text{CO})_{10}(\mu\text{-dppm})]$ is still unknown, only the reaction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (1) [2] with $^t\text{Bu}_2\text{PH}$ has been investigated.

2. Results and discussion

Heating of 1 at 130°C for long periods (50 h) afforded the new cluster complex $[\text{Os}_3(\text{CO})_5(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-dppm})]$ (2) in yields of about 50%. The reaction time could be reduced to 20 h by using the solvent diglyme (diethyleneglycoldimethylether) under reflux. (A sample of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (618 mg, 0.5 mmol) was dissolved in 30 ml of diglyme in a Schlenk tube under dry argon. $^t\text{Bu}_2\text{PH}$ (292 mg, 2 mmol) was added and the mixture refluxed for 20 h. After cooling to room temperature and removal of the solvent, the residue was crystallized from dichloromethane/heptane (1:4) to give purple crystals of 2 (yield 347 mg, 50%).)

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The identity and composition of compound 2 were determined by elemental analysis, IR and NMR spectroscopy, and mass spectrometry.

Spectroscopic data for 2. IR (KBr) $\nu(\text{CO})$: 2000s, 1957vs, 1930s, 1898vs and 1878s cm^{-1} . ^1H NMR (CDCl_3): δ 7.36 (m, 20H, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), 4.46 (m, 1H, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), 3.68 (m, 1H, $\text{PPh}_2\text{CH}_2\text{PPh}_2$), 1.68 (d, $^3J(\text{PH}) = 14.6$, 9H, $\mu\text{-P}^t\text{Bu}_2$), 1.58 (d, $^3J(\text{PH}) = 13.3$, 9H, $\mu\text{-P}^t\text{Bu}_2$), 1.19 (d, $^3J(\text{PH}) = 14.2$, 9H, $\mu\text{-P}^t\text{Bu}_2$), 0.96 (d, $^3J(\text{PH}) = 14.6$, 9H, $\mu\text{-P}^t\text{Bu}_2$), -11.57 (m, 1H, $\mu\text{-H}$), -13.12 (m, 1H, $\mu_3\text{-H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 169.25 [ddd, $^2J(\text{PP}) = 97.4$, $^2J(\text{PP}) = 5.8$, $^3J(\text{PP}) = 4.3$, $\mu\text{-P}$], 155.29 [ddd, $^2J(\text{PP}) = 160.6$, $^2J(\text{PP}) = 97.5$, $^3J(\text{PP}) = 2.5$, $\mu\text{-P}$], 19.12 [ddd, $^2J(\text{PP}) = 76.5$, $^2J(\text{PP}) = 5.8$, $^3J(\text{PP}) = 2.5$, $\mu\text{-dppm}$], -15.03 [ddd, $^2J(\text{PP}) = 160.6$, $^2J(\text{PP}) = 76.6$, $^3J(\text{PP}) = 4.1$, $\mu\text{-dppm}$]. Mass spectrum: m/z 1387, M^+ , 1331, $[M-2\text{CO}]^+$, 1303, $[M-3\text{CO}]^+$, 1275, $[M-4\text{CO}]^+$, 1247, $[M-5\text{CO}]^+$. Anal. Found: C, 40.55; H, 4.60. $\text{C}_{46}\text{H}_{60}\text{O}_5\text{Os}_3\text{P}_4$ Calc.: C, 39.82, H, 4.36%.

In contrast to 3, we observed for 2 only $\nu(\text{CO})$ absorption bands in the region characteristic of terminal carbonyl ligands. Therefore, we assumed that both clusters do not possess the same structural arrangement of ligands, and it was desirable to determine the molecular structure of compound 2.

* Corresponding author.

Purple crystals of **2** suitable for single crystal X-ray analysis were grown by slow diffusion of di-*n*-butylether into THF solution at room temperature.

Crystal data for **2**. $[\text{Os}_3(\text{CO})_5(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$, $\text{C}_{46}\text{H}_{60}\text{O}_5\text{Os}_3\text{P}_4$, $M = 1387.42$, monoclinic, space group $P2_1/c$ (No. 14), $a = 22.967(5)$, $b = 10.269(2)$, $c = 23.177(5)$ Å, $\beta = 114.71(3)^\circ$, $V = 4966(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.856$ g cm⁻³, $F(000) = 2656$, Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), $2\theta_{\text{max}} = 48.1^\circ$, temperature 293 K, $\mu(\text{Mo } K\alpha) = 7.83$ mm⁻¹, red-violet rhombus $0.27 \times 0.27 \times 0.11$ mm³, Stoe IPDS, 7808 unique and 6339 observed [$F_o \geq 4.0\sigma(F)$] data. Structure solved by direct methods [3,4] and Fourier difference techniques, refined by full-matrix least-squares analysis on F^2 . All non-hydrogen atoms anisotropic. Goodness-of-fit on F^2 1.037. $R_1 = 0.0500$, $wR_2 = 0.1284$, $w = 1/[\sigma^2(F_o^2) + (0.0815P)^2]$, $P = (F_o^2) + 2F_c^2/3$. Maximum residual electron density $\Delta\rho = 3.876$ e Å⁻³ (close to Os). The hydride H atom (H1) was located in a difference Fourier map, no further refinement for this atom has been carried out. All other hydrogen atoms are geometrically positioned. The molecular structure and selected bond parameters for **2** are given in Fig. 1, see also Supplementary material.

As a remarkable difference to the structure of **3**, we observed that the dppm-bridged Os–Os bond in **2** is not bridged by a carbonyl group. The atom Os(2) bears two terminal carbonyl ligands whereas Os(3) exhibits only one carbonyl group in a terminal coordination mode. The lack of bridging carbonyls in **2** confirms the tendency of the carbonyl-bridging ability of the higher elements to decrease; therefore the Os(3) center is electronically unsaturated (in **3** this is not so obvious).

The metal framework of **2** is closely related to the metal core of the triruthenium cluster **3**, e.g. also in **2** a μ_3 -capping hydride was found. In contrast to **3**, the location of the second hydride ligand could not be elucidated during the X-ray structure determination. However, the ¹H NMR spectra suggest the presence of two different hydrides and in comparison with the structural data of **3** we assume that also **2** contains a μ_2 - and a μ_3 -hydride. Furthermore, this fact is indicated by the unsymmetrical arrangement of the trimetal core. For **2** (as for **3**) three very different metal–metal distances were observed: Os(2)–Os(3) 2.8917(12) [2.8933(4)], Os(1)–Os(3) 2.7046(7) [2.7295(4)] and Os(1)–Os(2) 3.0551(11) [3.1592(4)] Å. In analogy to **3**, we assume a bridging hydride between Os(1) and Os(3) in **2**, since the Os(3) is electronically unsaturated (formally), therefore a saturation in the coordinative sense by this metal center is sought. However, the bridging position between Os(1) and Os(2) cannot be ruled out with certainty, because the spectroscopic data do not permit an unequivocal assignment. In contrast, cluster **2** is somewhat comparable with the 46 v.e. triosmium complex

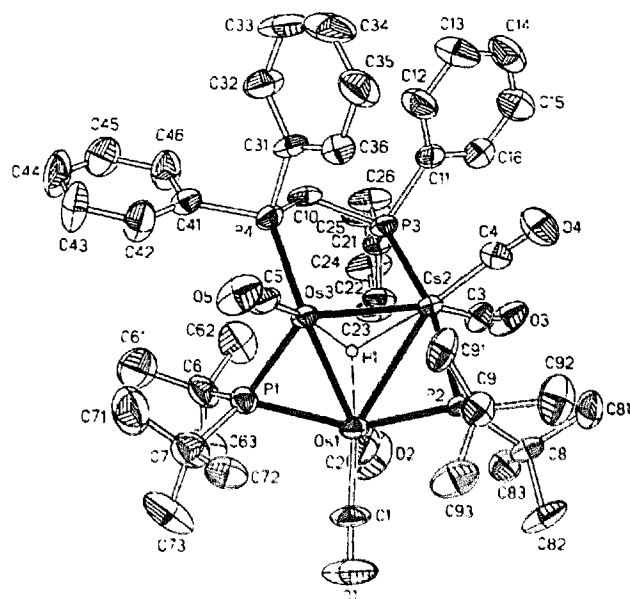


Fig. 1. The molecular structure of $[\text{Os}_3(\text{CO})_5(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-dppm})]$ (**2**) showing the atomic numbering scheme. Selected bond distances (Å) and angles ($^\circ$): Os(1)–Os(3) 2.7046(7), Os(1)–Os(2) 3.0551(11), Os(2)–Os(3) 2.8917(12), Os(1)–C(1) 1.863(11), Os(1)–C(2) 1.889(14), Os(2)–C(3) 1.897(11), Os(2)–C(4) 1.873(11), Os(3)–C(5) 1.854(11), Os(1)–P(2) 2.378(3), Os(1)–P(1) 2.392(3), Os(2)–P(2) 2.385(2), Os(2)–P(3) 2.403(3), Os(3)–P(4) 2.293(3), Os(3)–P(1) 2.332(3), Os(1)–C(1) 1.158(14), Os(2)–C(2) 1.14(2), Os(3)–C(3) 1.132(13), Os(4)–C(4) 1.143(13), Os(5)–C(5) 1.147(13), Os(3)–Os(1)–Os(2) 59.90(2), Os(3)–Os(2)–Os(1) 54.02(3), Os(1)–Os(3)–Os(2) 66.08(2), Os(3)–P(1)–Os(1) 69.83(8), Os(1)–P(2)–Os(2) 79.81(8), P(3)–C(10)–P(4) 113.6(5), C(10)–P(4)–Os(3) 111.7(3), C(10)–P(3)–Os(2) 121.8(3), Os(1)–H(1) 1.62, Os(2)–H(1) 1.96, Os(3)–H(1) 1.44.

$[\text{Os}_3(\text{CO})_6(^t\text{Bu}_2\text{PH})(\mu\text{-H})_2(\mu\text{-P}^t\text{Bu}_2)_2]$, in which the longest metal–metal bond without bridging hydride is assumed [5]. The question of multiple metal–metal bonding character for **2** can also be ruled out with some confidence (average Os–Os bonds 2.8838 Å). The dppm-bridged Os–Os bond is comparable with other bond lengths of such type, for instance in $[\text{Os}_3(\text{CO})_8(\mu\text{-dppm})_2]$ [6]: 2.860(1) and 2.854(1) Å respectively vs. 2.8917(12) Å in **2**.

In contrast to other electron-deficient trimetallic osmium species, like for instance $[\text{Os}_3(\text{CO})_8(\text{H})(\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)]$ [7], $[\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-}\eta^2\text{-C}_6\text{H}_5(4\text{-CH}_3)\text{N})]$ [8] and $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2\text{-}(\text{Si}(\text{OMe})_3)(\mu\text{-PMe}_2(\text{C}_6\text{H}_4))]$ [9], **2** exhibits a low reactivity towards small molecules. The first mentioned clusters react spontaneously in addition reactions with carbon monoxide, whereas for **2** even at elevated pressure (50 bar CO, THF, 25 °C, 5 h) no reaction with CO can be observed. Even the more closely related 46 v.e. complex $[\text{Os}_3(\text{CO})_6(^t\text{Bu}_2\text{PH})(\mu\text{-H})_2(\mu\text{-P}^t\text{Bu}_2)_2]$ reacts to the electronically saturated metal cluster $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-P}^t\text{Bu}_2)_2]$ by simple bubbling of carbon monoxide through a solution of this compound [5]. Therefore, we assume the lack of two cluster valence

electrons in **2** exclusively by reason of steric demands of the coordination sphere.

3. Supplementary material available

Additional material to this paper can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository number CSD-405151, the names of the authors and the journal citation.

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