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- Short communication

X-RAY CRYSTAL STRUCTURE OF [(μ-H)Os_2(CO)$_4$($SnPh_3$)$_2$(μ-HSnPh_2)(μ-dppf)] (dppf = 1,1´-BIS (DIPHENYLPHOSPHINO) FERROCENE

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ABSTRACT

The solid-state molecular structure determination of the bimetallic osmium-tin compound [(μ-H)$Os_2(CO)_4(SnPh_3)_2$(μ-$HSnPh_2$)(μ-dppf)] (1) was carried out to determine the relative orientation of the coordinated ligands. Compound 1 crystallizes in the monoclinic space group $P\ 2_1/c$ with a = 22.366(7), b = 14.217(4), c = 25.213(8) Å, β = 98.865(7)°, Z = 8 and V = 7921(4) Å^3. It is a 34-electron bimetallic cluster with the Os-Os edge concomitantly bridged by a dppf and two $HSnPh_2$ ligands,

Key words: Bimetallic, Osmium-tin cluster, Diphosphine, Crystal structure

Transition metal complexes bearing diphosphine ligands have attracted considerable attention because of their ability to promote organic transformations (Miyake *et al.* 2007), their propensity to act as templates for the synthesis of metal-metal bonds by bridge-assisted reactions (Fan *et al.* 2004), and their versatile application in homogeneous catalysis (Kuiper *et al.* 2004, Marr *et al.* 2007). This versatility is highly prominent in the case of the flexible diphosphine, 1,1'-bis(diphenylphosphino)ferrocene (dppf) (Fairlamb *et al.* 2007, Ng *et al.* 2007), due to its ability to adopt various coordination modes that can match the steric requirements of the molecular environment during catalysis (Ohs *et al.* 2004, Lu *et al.* 2003). Presently, there is extensive interest in the chemistry of transition metal-tin compounds. This is because tin is often used as a modifier in bimetallic catalysts and whose presence leading to increased selectivity in a variety of chemical transformations (Santos *et al.* 2004, Huber *et al.* 2003). Group 14 metals can be incorporated into transition-metal clusters in a number of ways. Quite a few osmium-tin clusters have been prepared using these methods (Adams *et al.* 2006, Hasan *et al.* 2007). Recently the authors reported that the title compound [(μ-H)$Os_2(CO)_4(SnPh_3)_2$(μ-$HSnPh_2$)(μ-dppf)] (5) was obtained in 12% yield together with four osmium complexes [$HOs(CO)_4(SnPh_3)$] (2), [$Os_3(CO)_8$(μ-$OH)_2$(μ-dppf)] (3), [$Os_2(CO)_6(SnPh_3)_2$(μ-$SnPh_2)_2$] (4) and [H(μ-H)$_2Os_3(CO)_8(SnPh_3)$(μ-dppf)] (6) from the reaction between [$Os_3(CO)_8$(μ-

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dppf)(μ-H)$_2$] (1) with Ph_3SnH (Scheme 1) (Sarker *et al.* 2013). Previously cluster 5 was characterized by spectroscopic data only and, now X-ray diffraction analysis of it has been described in this paper.

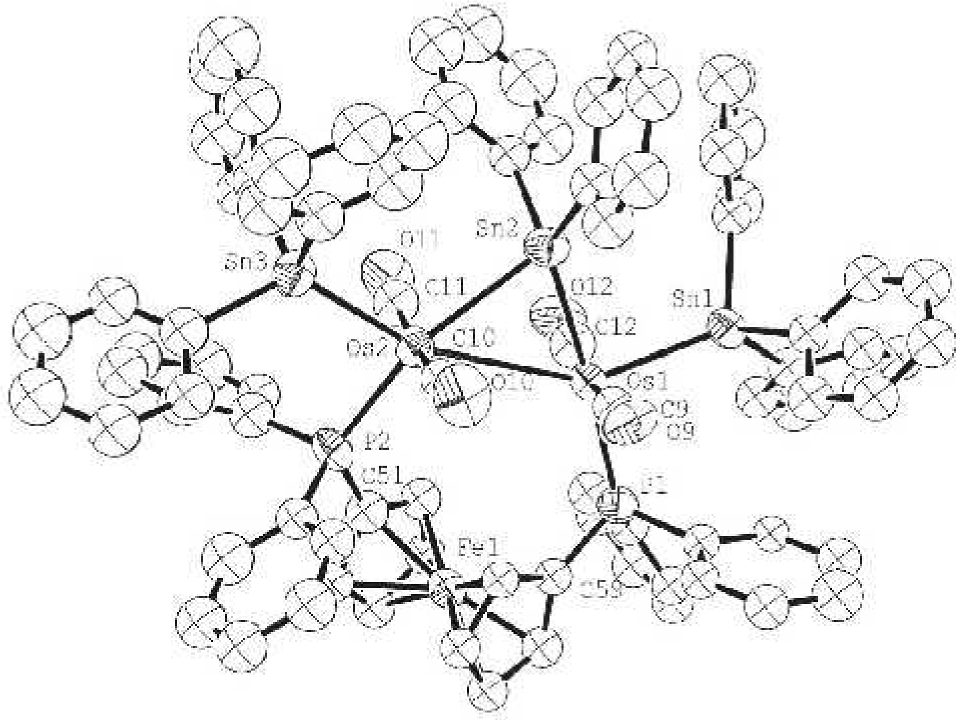

Fig. 1. ORTEP diagram of the molecular structure of [(μ-H)$Os_2(CO)_4(SnPh_3)_2$(μ-$HSnPh_2$)(μ-dppf)] (**5**) at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Os(1)-Os(2) 3.35(5), Os(1)-P(1) 2.415(6), Os(1)-Sn(2) 2.6609(19), Os(1)-Sn(1) 2.7241(17), Os(2)-P(2) 2.449(6), Os(2)-Sn(3) 2.763(2), Os(2)-Sn(2) 2.9587(19), P(2)-Os(2)-Sn(3) 91.20(16), Sn(3)-Os(2)-Sn(2) 110.27(5), Os(1)-Sn(2)-Os(2) 72.98(4), Sn(2)-Os(1)-Sn(1) 89.36(5), C(12)-Os(1)-Sn(2) 87.2(6), C(12)-Os(1)-Sn(1) 84.5(7), P(1)-Os(1)-Sn(1) 95.37(14), C(11)-Os(2)-Sn(2) 81.4(5), C(10)-Os(2)-Sn(2) 91.4(5), C(10)-Os(2)-Sn(3) 81.5(5), C(10)-Os(2)-P(2) 101.7(5), C(11)-Os(2)-P(2) 87.3(5), C(12)-Os(1)-P(1) 97.0(7), C(9)-Os(1)-P(1) 89.6(5), P(2)-Os(2)-Sn(2) 156.41(15).

An ORTEP diagram of the structure of 5 is shown in Fig. 1 and selected bond distances and angles are listed in the caption. The solid-state structure reveals that each osmium atom contains one σ-bonded $SnPh_3$ ligand [Os(1)-Sn(1) 2.722(2), Os(2)-Sn(3) 2.761(2) Å] and two linear carbonyl groups. The Os-$SnPh_3$ distances in 5 are very similar in length to the Os-$SnPh_3$ distances in [$Os_2(CO)_6(SnPh_3)_2$(μ-$SnPh_2$)$_2$] [2.7253(2) Å] (Adams *et al.* 2006) and these same groups display an overall *cis* geometry with respect to the Os-Os bond. The molecule possesses two non-hydrogen bridging ligands, one Ph_2Sn and one dppf, that serve to tether the Os(1)-Os(2) vector. Missing from the diffraction structure were the two bridging hydride ligands that are associated with the Os(1)-Os(2) and Os(2)-Sn(2) vectors, which were found in the DFT-optimized structure (Sarker *et al.* 2013). The Os-Os distance [3.35(2) Å] is considerably longer than the Os-Os distance in $[Os_2(CO)_6(SnPh_3)_2(\mu\text{-}SnPh_2)_2]$ [3.1471(2) Å] (Adams *et al.* 2006). Compound 5 contains 34 valence electrons and is coordinatively saturated, assuming that the Ph_3Sn and hydride ligands serve as one-electron donors and the bridging stannylene moiety functions as a two-electron donor moiety.

Single crystals of cluster 5, prepared according to the published procedure from the reaction between $[Os_3(CO)_8(\mu\text{-dppf})(\mu\text{-}H)_2]$ and Ph_3SnH at 110°C, suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution at 4°C. All geometric and crystallographic data were collected on a Rigaku XtaLab Mini sealed-tube diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data collection, indexing, and initial cell refinements were all carried out using CrystalClear-SM Expert 2.0 r15 (Rigaku 2011). Frame integration and final cell refinements were carried out using CrystalClear-SM Expert 2.0 r15 (Rigaku 2011) as well. The data were corrected for Lorentz, polarization and absorption effects. The structures were solved using the direct methods and difference Fourier techniques (SHELXTL, V6.12) (Sheldrick 2008). Due to poor quality of the crystal, the thermal ellipsoids of some of the carbon atoms would become NPDs during refinements. So, all the carbon atoms were refined isotropically but other non hydrogen atoms were refined anisotropically. The hydride ligands in 5 could not be crystallographically located. Scattering factors and anomalous dispersion corrections are taken from the International Tables for X-ray crystallography (Wilson 1992). Structure solution, refinement, graphics, and generation of publication materials were performed by using WinGX (Farrugia 1999) software.

Temperature 293(2) K, dimensions 0.33 x 0.14 x 0.07 mm^3, monoclinic, space group $P\ 2_1/c$, $a = 22.366(7)$, $b = 14.217(4)$, $c = 25.213(8)$ Å, $\beta = 98.865(7)°$, $V = 7921(4)$ $Å^3$, Z = 8, F(000) 3904, $d_{calc} = 1.695$ g/cm^3, $\mu = 4.393/mm$. 27873 reflections were collected, independent reflections (R_{int}) = 7347 (0.1980). At convergence, $R_1 = 0.0937$, $wR_2 = 0.2034$ [$I > 2.0\sigma(I)$] and $R_1 = 0.1545$, $wR_2 = 0.2475$ (all data), for 461 parameters.

CCDC 890662 contains supplementary crystallographic data for **5**. These data may be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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