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Os₃(CO)₁₁(BiPh₃): The Missing Link in Osmium-Bismuth Cluster Chemistry

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Abstract

The room temperature reaction of Os₃(CO)₁₁(NCCH₃) with BiPh₃ afforded the substituted derivative Os₃(CO)₁₁(BiPh₃) which decomposed rapidly. The X-ray crystallographic study is reported, together with that of the stibine and arsine analogues.

1. Introduction

Heteronuclear clusters containing a main group element with a transition metal are of interest because of the very different chemistry exhibited by the components. We have, for many years now, been interested in osmium carbonyl clusters containing the heavier group 15 elements. In particular, we have uncovered a lot of novel reactivity associated with osmium-antimony clusters. The elements in group 15 exhibit characters ranging from the non-metallic (N and P) through metalloid (As and Sb) to metallic (Bi), and we believe that the interesting chemistry of osmium-antimony clusters may be related to this increasing metallic character as we go down group 15.¹ It is thus reasonable to expect that moving on to bismuth should yield even more contrasting chemistry.

The first report on the synthesis of osmium-bismuth clusters appeared almost 30 years ago,² and it took a pause of more than two decades before their chemistry was

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looked at again.³ In the latter work, it was reported that the reaction of the lightly-stabilised cluster $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$, **1a**, with BiPh_3 , **2d**, afforded five clusters, viz., $\text{Os}_2(\text{CO})_8(\mu\text{-BiPh})$, $\text{Os}(\text{CO})_4\text{Ph}_2$, $\text{Os}_4(\text{CO})_{14}(\mu\text{-}\eta^3\text{-OCC}_6\text{H}_5)(\mu_4\text{-Bi})$, $\text{Os}_4(\text{CO})_{15}\text{Ph}(\mu_4\text{-Bi})$ and $\text{Os}_5(\text{CO})_{19}\text{Ph}(\mu_4\text{-Bi})$, via Bi-C bond cleavage and cluster fragmentation. Significantly, no cluster containing an intact BiPh_3 ligand was observed,^{3a} even though it was expected that the initial reaction product ought to be the substitution product $\text{Os}_3(\text{CO})_{11}(\text{BiPh}_3)$, **3d**. We wish to report here that we have been able to isolate **3d** from the reaction and characterise it crystallographically.

2. Results and Discussion

The cluster **3d** can be isolated in low yields, and in an impure form, from the reaction of **1a** with **2d**. A similar result was obtained using $\text{Os}_3(\text{CO})_{11}(\text{COE})$, **1b**, in place of **1a**. Cluster **3d** is thermally not very stable; solutions decomposed slowly even at and below ambient temperatures, although the solid could be stored for several days at 0 °C. Although we were able to obtain a reasonable clean IR spectrum of the product, a pure sample eluded us despite numerous attempts over several years! Fortuitously, we were able to obtain a diffraction quality crystal during an attempt at recrystallisation; an ORTEP plot showing the molecular structure is given in Figure 1.

Figure 1. ORTEP plot of **3d**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

The single-crystal structural study of the phosphine derivative, *viz.*, $\text{Os}_3(\text{CO})_{11}(\text{PPh}_3)$, **3a**, has already been reported in a landmark study by Bruce, *et. al.*⁴ Although aspects of the chemistry of the arsine,⁵ and stibine,^{5a,6} analogues have been reported, their solid-state structures have not been determined. We have thus determined the structures of these arsine and stibine analogues, **3b** and **3c**, respectively, as well. To the best of our knowledge, this represents the first complete series of an organometallic cluster containing a group 15 ligand which has been structurally characterized. Selected bond parameters for all four clusters are collected in Table 1.

Clusters **3a-c** are isomorphic and isostructural; they all crystallize in the monoclinic space group $C2/c$ with essentially similar unit cell parameters. The crystal of **3d** differs by virtue of its containing a dichloromethane solvate. Otherwise, the molecular parameters of **3a-d** show trends which are nicely consistent with the identity of the group 15 element (E), and the observations which have been made earlier by Bruce *et. al.* in their study on the phosphine and arsine derivatives. For example, the

Os2-Os1-E bond angle decreases as we move from E = P to E = Bi, and the Os1-Os2 bond which is *cis* to the group 15 ligand (**2x**) is the longest of the three Os-Os bonds in each case. All the structures are also of the “*E*” conformation defined by Pomeroy et al.⁷

Table 1. Common atomic labelling scheme and selected bond lengths (Å) and angles (°) for clusters **3a-d**.

Cluster	3a [†]	3b	3c	3d
E	P	As	Sb	Bi
Os1-Os2	2.9183(7)	2.9148(7)	2.9176(4)	2.9050(6)
Os2-Os3	2.8861(7)	2.8871(6)	2.8955(4)	2.8837(7)
Os3-Os1	2.8905(8)	2.8727(9)	2.8682(3)	2.8468(5)
Os1-E	2.370(2)	2.4670(9)	2.6054(5)	2.6909(6)
Os2-Os1-Os3	59.58(1)	59.842(8)	60.053(9)	60.170(15)
Os1-Os2-Os3	59.73(2)	59.355(18)	59.127(9)	58.914(15)
Os1-Os3-Os2	60.69(2)	60.802(19)	60.820(9)	60.916(15)
Os2-Os1-E	102.59(6)	100.596(18)	97.762(13)	96.497(19)
Dihedral angle [‡]	8.4	8.4	6.8	9.8

[†]Data obtained from reference [4].

[‡]Dihedral angle between the C_{ax}-Os2-C_{ax}-Os3 and C_{ax}-Os3-C_{ax}-Os2 planes of the Os₂(CO)₈ unit as defined in reference [7].

The Os-E bond lengths are correlated to the covalent radii of E (1.06, 1.20, 1.40 and 1.46 Å for P, As, Sb and Bi, respectively), but otherwise, there is no obvious correlation between the length of the Os-E bond with the stability of the clusters **3x** since the increase in this length is the least in going from Sb to Bi. We have therefore sought to gain some insight through a computation of the free energy change (ΔG°) for

the formation of **3x** from **1a** and **2x** using density functional theory (Table 2). The trend is very clear; the reaction is less favoured going from P to Bi. In fact, the free energy suggests that the formation of **3d** is highly disfavoured.⁸ It is therefore plausible that **3d** may easily dissociate to, for example, an “Os₃(CO)₁₁” fragment. Such a fragment could readily insert into a Bi-C bond, and may account for the reaction products observed by Adams, *et. al*.³ thermolysis of a sample of **3d** which was slightly contaminated with **2d** afforded a number of products, among which were the clusters Os₄(CO)₁₄(μ-η³-OCC₆H₅)(μ₄-Bi) and Os₄(CO)₁₅Ph(μ₄-Bi) and Os₅(CO)₁₉Ph(μ₄-Bi) reported earlier.^{3a}

Table 2. Computed ΔG° for the reaction of **1** and **2x** to form **3x**.

x	a	b	c	d
ΔG°, kJ mol ⁻¹	-4.9	-3.4	+8.4	+38.2

3. Experimental

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. Solvents were purified, dried, distilled, and stored under nitrogen prior to use. Routine NMR spectra were acquired as CDCl₃ solutions on a Bruker ACF300 NMR spectrometer. Chemical shifts reported are referenced to that for the residual proton of the solvent. ESI mass spectra were obtained on a Finnigan MAT95XL-T spectrometer, at 50 °C, using methanol with sodium methoxide. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The clusters **1a** and **1b** were prepared according to the literature methods.^{9,10} All other reagents were from commercial sources and used as

supplied. The clusters **3b** and **3c** were prepared from the reaction of **1a** with **2b** and **2c**, respectively.

3.1. Synthesis of $Os_3(CO)_{11}(BiPh_3)$, **3d.** A sample of **1a** (88 mg, 96 μ mol) and $BiPh_3$, **2d**, (43 mg, 98 μ mol) dissolved in toluene (10 ml) was placed in a Carius tube, degassed by three cycles of freeze-pump-thaw, and then heated in an oil bath at 40 °C for 20 min, during which the color changed from orange yellow to brown. After solvent removal, the crude was extracted with hexane and **3d** crystallized out at low temperature.

Similarly, a mixture of **1b** (40 mg, 40 μ mol) and **2d** (100 mg, 0.20 mmol) in DCM (20 ml) stirred at room temperature for 12 h afforded a brown-yellow suspension. Removal of the solvent followed by TLC separation with DCM/Hex (1:3, v/v) as eluent afforded unreacted $BiPh_3$ as the first colorless band, followed by a yellow band which comprised a mixture of **2d** and **3d** (R_f = 0.60).

3d: IR (CH_2Cl_2) $\nu(CO)$: 2109m, 2058s, 2033 s, 2021s, 1991w, 1977w, 1953w cm^{-1} ; ^1H NMR (C_6D_6) δ 7.56 (dd, 6H, PhH), 7.06 (t, 6H, PhH), 7.00 (t, 3H, PhH).

3.2. X-ray crystal structure determinations. Crystals were mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo $K\alpha$ radiation, with the SMART suite of programs.¹¹ Data were processed and corrected for Lorentz and polarisation effects with SAINT,¹² and for absorption effects with SADABS.¹³ Structural solution and refinement were carried out with the SHELXTL suite of programs.¹⁴ Crystal and refinement data are summarised in Table S1.

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. In **3d**, a disordered dichloromethane solvate was found. The disorder was modelled with two alternative sites, with occupancies summed to unity, and appropriate restraints on bond and thermal parameters applied. Organic hydrogen atoms were placed in calculated positions and

refined with a riding model. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model.

3.3. Computational studies. Geometry optimizations were carried out by DFT utilizing the MPW1PW91,¹⁵ or M06 density-functionals.¹⁶ The LANL2DZ (Los Alamos effective core potential double- ζ) basis set, together with polarization functions,¹⁷ were employed for the heavy atoms, viz., Os, P, As, Sb and Bi; the 6-311+G(2d,p) basis set was used for all the other atoms. Spin-restricted calculations were used for geometry optimization, and harmonic frequencies were then calculated to characterize the stationary points as equilibrium structures with all real frequencies, and to evaluate zero-point energy (ZPE) corrections. All calculations were performed using the Gaussian 09 suite of programs.¹⁸

Supplementary Material: Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1033893-5. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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