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Raft-like osmium- and ruthenium-antimony carbonyl clusters

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This article is dedicated to the late Lord Lewis of Newnham.

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ABSTRACT

The higher nuclearity raft-like cluster $\text{Os}_6(\text{CO})_{20}(\mu\text{-SbPh}_2)_2$, **5-Os**, was isolated from the base hydrolysis of $\text{Os}_3(\text{CO})_{11}(\text{SbPh}_2\text{Cl})$, **1-Os**. The ruthenium analogue, viz., $\text{Ru}_6(\text{CO})_{20}(\mu\text{-SbPh}_2)_2$, **5-Ru**, was obtained from the reduction of $\text{Ru}_3(\text{CO})_{12}$, **7-Ru**, with the benzophenone ketyl radical followed by treatment with SbPh_2Cl . These clusters undergo facile ligand substitution reactions with two-electron donors to afford the mono- and disubstituted derivatives $\text{M}_6(\text{CO})_{20-n}(\mu\text{-SbPh}_2)_2(\text{L})_n$, ($\text{M} = \text{Ru}$ or Os ; $n = 1$ (**8**) or 2 (**9**); $\text{L} = \text{PMe}_3$ (**a**), PPh_3 (**b**), or ${}^t\text{BuNC}$ (**c**)).

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1. Introduction

A great number of high nuclearity homo- or heterometallic Group 8 metal carbonyl clusters have been reported but most of them adopt three-dimensional, polyhedral configurations, such as, the (distorted) octahedron (for hexanuclear clusters) and more complex polyhedra (for heptanuclear and higher nuclearity clusters). Two-dimensional planar or quasi-planar (raft-like), higher nuclearity clusters containing six or more metal atoms are relatively rare. They usually show distinct physical and reactivity properties [1] including some which show interesting magnetic properties [2].

To our knowledge, the only high-nuclearity homometallic osmium clusters with almost planar metal cores are $\text{Os}_6(\text{CO})_{21-n}(\text{NCCH}_3)_n$, ($n = 0, 1$ or 2), and their several phosphine, acetylene, or 2-aldrithiol substitution derivatives [3]; ruthenium analogues are unknown. Heterometallic examples containing osmium or ruthenium include a number of clusters of the general formulae $\text{M}_3(\text{CO})_{12}[\text{M}'(\text{L})]_n$ ($\text{M} = \text{Os}$ or Ru ; $\text{M}' = \text{Pd}$ or Pt ; $\text{L} = \text{P}^t\text{Bu}_3$ or NHC ; $n = 1$ – 3) [1c,4]. The metal cores in the latter group of clusters are rather distorted from planarity and have been referred to simply as “two-dimensional” clusters. Examples containing a

main group metal or metalloid include several with Ge or Sn, obtained via the addition of germylene [5] or Ph_3MH ($\text{M} = \text{Ge}$ or Sn) [6], to $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Os}$ or Ru), or via the pyrolysis of low-nuclearity osmium [7], or ruthenium [8], clusters containing Ge ligands; these clusters tend to be planar.

We have been investigating synthetic routes to osmium-antimony clusters [9], and serendipitously uncovered the almost planar, raft-like, higher nuclearity clusters $\text{M}_6(\text{CO})_{20}(\mu\text{-SbPh}_2)_2$, **5-M** (where $\text{M} = \text{Os}$ or Ru). Our study into their formation and their substitution chemistry is reported here.

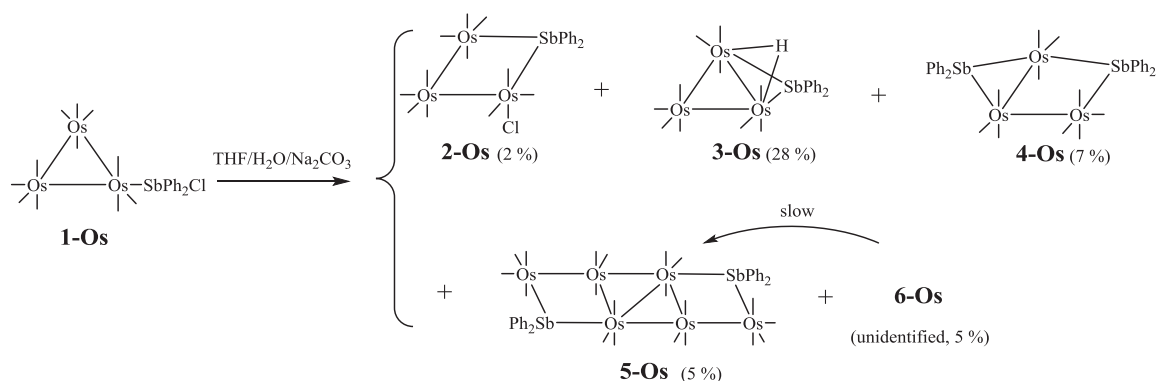
2. Results and discussion

Oxidative addition of the Sb–Cl bond in SbPh_2Cl to $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ occurs via the substitution product $\text{Os}_3(\text{CO})_{11}(\text{SbPh}_2\text{Cl})$, **1-Os**, to eventually form $\text{Os}_3(\text{CO})_{11}(\mu\text{-SbPh}_2)(\text{Cl})$, **2-Os** [10]. During our investigations into the conversion of **1-Os** to **2-Os**, we found that the addition of H_2O and Na_2CO_3 afforded the previously reported clusters **2-Os**, **3-Os** and **4-Os**, and two other clusters, one of which is the new raft-like, higher nuclearity cluster $\text{Os}_6(\text{CO})_{20}(\mu\text{-SbPh}_2)_2$, **5-Os** (Scheme 1).

Cluster **5-Os** is stable under ambient conditions over several months and has been fully characterized, including by an X-ray crystallographic analysis. An ORTEP plot depicting its structure is given in Fig. 1. The other unidentified product **6-Os** was found to

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Scheme 1. Base hydrolysis of $\text{Os}_3(\text{CO})_{11}(\text{SbPh}_2\text{Cl})$, **1-Os**.

gradually convert to **5-Os**, especially in a polar solvent such as MeOH, as was evident by monitoring the conversion through ^1H NMR spectroscopy (see [Supplementary data Fig. S3](#)). Its HRMS spectrum showed a similar pattern to that of **5-Os** (see [Supplementary data Fig. S22\(a\)](#) and (b)), suggesting that it was probably an isomer.

We have also carried out some studies into the reaction pathway in the hope of increasing the yield of **5-Os**. As mentioned above, we have shown earlier that **2-Os** resulted from oxidative addition of the Sb–Cl bond in **1-Os** [20]. Cluster **4-Os** was presumably the result of reaction of **3-Os** with SbPh_2Cl , generated from **1-Os** via ligand dissociation or decomposition [11]. On monitoring the base hydrolysis of **1-Os** (in *d*-THF) by ^1H NMR spectroscopy, four metal hydride resonances ($\delta = -8.72, -8.27, -8.97$ and -9.19 ppm) were observed after 8 h (see [Supplementary data Fig. S5](#)).

Treatment of **2-Os** under the same reaction conditions gave **3-Os** as the sole separable product in a much higher yield (*ca.* 75%), albeit with a much longer reaction time (*ca.* 72 h) for completion [12]; no **5-Os** was observed. This suggested that the formation of **5-Os** (and **6-Os**) followed a different reaction pathway from that for clusters **2-Os** to **4-Os**. The ^1H NMR spectrum of this latter reaction showed only two metal hydride resonances ($\delta = -8.27$ and -8.97 ppm) after 24 h (see [Supplementary data Fig. S4](#)). These hydride species probably resulted from a Hieber reaction under the

basic conditions employed. Based on these observations, the proposed reaction pathways to all the products are as given in [Scheme 2](#).

It is suggested that **3-Os** is formed via two competitive pathways (**I** and **II**), through **2-Os** or the intermediate **A**. Presumably, there are two possible isomers of **A**, corresponding to the different relative orientation of the SbPh_2Cl and the terminal H ligands; oxidative addition of the Sb–Cl bond across an Os–Os bond in one leads to **B** and further on to **3-Os** via a chloride elimination, while the other leads to **C** and further on to an electron-deficient cluster **D** via a similar pathway. This latter quickly converts to **5-Os** and **6-Os** through further elimination of H_2 and CO.

The metal hydride resonances at $\delta = -8.27$ and -8.97 ppm may thus be assigned to **B** (and its isomer with the opposite orientation of H) and the other two resonances observed in the reaction of **1-Os** may be assigned to **A** and/or **C**. We have observed through ^1H NMR monitoring of these resonances that the conversion of **B** to **3-Os** (in the hydrolysis of **2-Os**) was more favourable in DCM; the conversion did not occur in THF/ H_2O even after 72 h but upon removal of the solvents and re-dissolution in DCM, the conversion was complete within 5 min. A similar observation was made for the conversion of **C** to **5-Os** and **6-Os** (in the hydrolysis of **1-Os**). These observations are consistent with the more favourable elimination of NaCl (as depicted in the proposed pathways) in DCM than in THF/

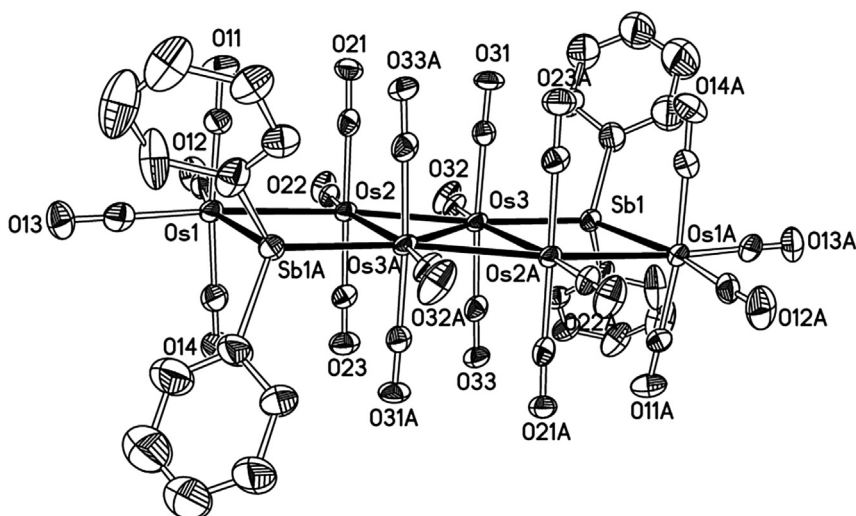


Fig. 1. ORTEP plot of the molecular structure of **5-Os** (one of two asymmetrical molecules) with thermal ellipsoids at the 50% probability level. Organic hydrogen atoms have been omitted for clarity.

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