



Ligand substitution in the osmium-antimony rings $\text{Os}_3(\mu\text{-SbPh}_2)_2(\text{CO})_{10}$ and $\text{Os}_3(\mu\text{-SbPh}_2)_3(\text{Cl})(\text{CO})_9$



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ABSTRACT

TMNO-activated ligand substitution in the fused ring compounds $\text{Os}_3(\mu\text{-SbPh}_2)_2(\text{CO})_{10}$, **1**, and $\text{Os}_3(\mu\text{-SbPh}_2)_3(\text{Cl})(\text{CO})_9$, **2**, in acetonitrile affords the mono- and disubstituted CH_3CN -derivatives. The initial product of CH_3CN substitution in **1** is an equatorial isomer, which can isomerize to the axial isomer upon heating; they are the first examples in which both isomers have been characterized crystallographically. Subsequent reaction of the CH_3CN -derivatives of **2** with two-electron donor ligands L do not always result in the displacement of the acetonitrile ligands; displacement of a carbonyl ligand can also occur and appears to depend on the stereoelectronic properties of L. This is suggestive of an associative mechanism.

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1. Introduction

For some years now, we have been studying the chemistry of organometallic clusters containing the heavier Group 8 transition metals ruthenium or osmium, and the main group element antimony. What has become apparent is that these show interesting chemistry which are often very different from those of the homologues, arsenic or bismuth. For example, we have previously reported that the clusters $\text{M}_3(\mu\text{-SbPh}_2)_2(\text{CO})_{10}$, where M = Os, **1**, or Ru, **1-Ru**, possess fluxional M–M bonds, and that they undergo Sb–Cl oxidative addition with SbPh_2Cl to give the 3,5-fused rings $\text{M}_3(\mu\text{-SbPh}_2)_3(\text{Cl})(\text{CO})_9$, where M = Os, **2**, or Ru, **2-Ru**. Some osmium-antimony clusters can also undergo cleavage of an M–M bond either via nucleophilic addition of a two-electron donor (such as PPh_3 or $^t\text{BuNC}$) or oxidative addition of a halogen (such as Cl_2 or I_2) [1,2]. TMNO-activated ligand substitution has also been observed with the ruthenium complexes [2]. In this work, we wish to report our study on TMNO-activated ligand substitution in the corresponding osmium complexes **1** and **2**. By virtue of the greater stability of osmium over the corresponding ruthenium complexes [3], this has allowed us to investigate the substitution reaction pathways in greater detail.

2. Results and discussion

2.1. Substitution chemistry of cluster **1**

Cluster **1** failed to react with triorganophosphines (PPh_3 or PMe_3) even on prolonged heating (65 °C). It can, however, be readily activated with TMNO, and in acetonitrile as solvent, to form the CH_3CN -substituted derivatives $\text{Os}_3(\mu\text{-SbPh}_2)_2(\text{CO})_9(\text{NCCH}_3)_2$, **3a**, or $\text{Os}_3(\mu\text{-SbPh}_2)_2(\text{CO})_8(\text{NCCH}_3)_2$, **4a** (Scheme 1).

As it turned out, a single crystal X-ray diffraction study on the monosubstituted derivative shows that it has the CH_3CN ligand in an equatorial position *trans* to the open SbPh_2 bridge (**eq-3a**). It is stable in the presence of CH_3CN but decomposes immediately when the CH_3CN is removed. On heating at 55 °C in acetonitrile, however, **eq-3a** converts almost quantitatively to its axial isomer **ax-3a** which, unlike the equatorial isomer, is stable in common solvents even in the absence of CH_3CN . This axial isomer has also been characterized crystallographically. ORTEP plots showing the molecular structures of both **eq-3a** and **ax-3a** are given in Fig. 1, and selected bond parameters, together with a common atomic numbering scheme, are summarized in Table 1.

A computational study using DFT shows that **eq-3a** lies 30.7 kJ mol⁻¹ above **ax-3a**. Furthermore, the other possible equatorial isomer, *viz.*, **eq-3a'**, in which the CH_3CN ligand is *cis* to the open SbPh_2 bridge, lies a further 16.4 kJ mol⁻¹ above **eq-3a**. Consistent with the latter is that the ¹H NMR spectrum of **eq-3a**

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does not show any evidence for the presence of **eq-3a'** (Fig. S3). The results suggest that **eq-3a** is the kinetic product from the TMNO activation of **1**; the site of TMNO attack which this implies is consistent if the open SbPh₂ bridge has a strong *trans* effect which thereby reduces electron density on the *trans* CO ligand (see also later) [4]. Consistent with this, a natural population analysis (NPA) on **1** shows that C atom carries the highest positive charge among all the carbonyl C atoms (Fig. S45). It may also be inferred that **eq-3a** would be substitutionally more labile, which has indeed been observed to be the case; the ¹H resonance for the CH₃CN ligand in **ax-3a** is observable at room temperature but not that for **eq-3a**, and the reaction of PPh₃ with **eq-3a** proceeds readily at room temperature but only at elevated temperature (≥60 °C) with **ax-3a**.

There are very few clusters for which both the axial and equatorial isomers with the same ligand have been crystallographically characterized; to the best of our knowledge, the only other known pair in osmium carbonyl cluster chemistry is for an isonitrile ligand [1b]. The bond parameters for **eq-3a** and **ax-3a** are consistent with earlier observations that the SbPh₂ group has a comparable *trans* influence to CO [1f,2,5]; for example, as summarized in Table 1, the Os–N bond length is similar whether it is *trans* to SbPh₂ (Os3–L2 = 2.086(8) Å in **eq-3a**) or to a CO (Os3–L3 = 2.092(5) Å in **ax-3a**), but the Os3–Sb1 bond is significantly elongated when it is *trans* to a CO rather than to a CH₃CN (2.6284(7) vs 2.6731(5) Å in **eq-3a** and **ax-3a**, respectively).

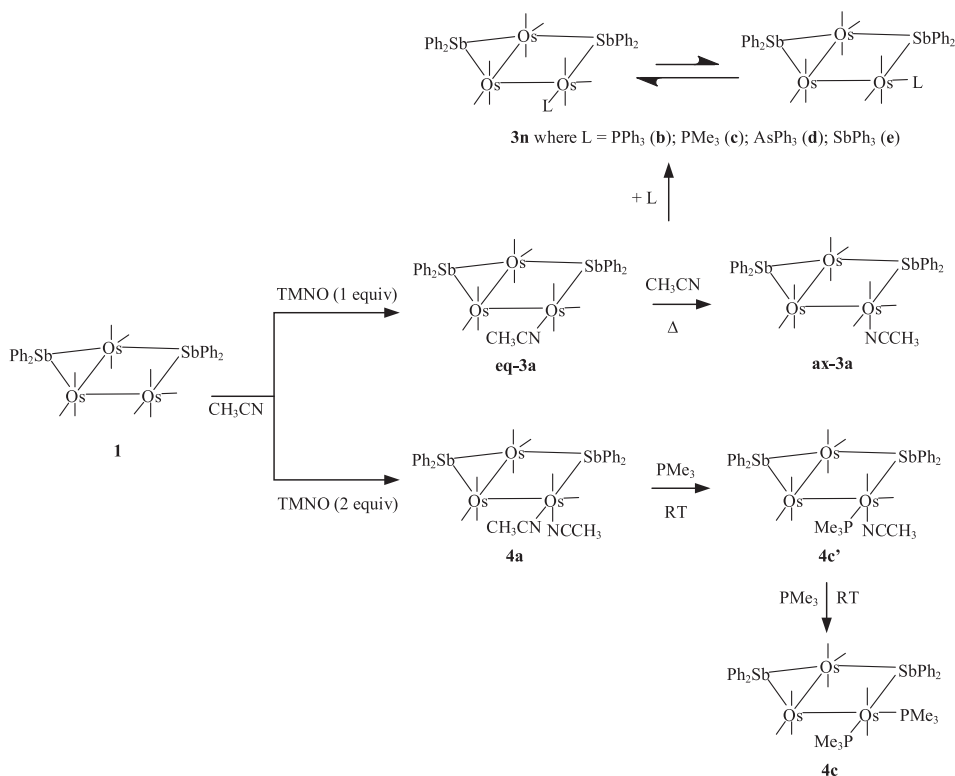
As mentioned above, the treatment of **eq-3a** with other two-electron donors L afforded the substitution products Os₃(μ-SbPh₂)₂(CO)₉(L), where L = PPh₃, **3b**; PMe₃, **3c**; AsPh₃, **3d** or SbPh₃, **3e** (Scheme 1). All these products are stable, and they have been fully characterized, including by X-ray crystallographic analyses; the ORTEP diagrams showing the molecular structures of **3b** and **3c** are given in Fig. 2. The PPh₃ ligand in **3b** is oriented differently from the substitution ligands in **3c-e**; it is *cis* to the adjacent (open)

bridging SbPh₂ group, while the group 15 ligands in **3c-e** are *trans*. Interestingly, this conformation for **3d** and **3e** is different from that of their corresponding ruthenium analogues (*cis*) [2]. But we believe that like in the latter, they exist as two isomers in solution, in a ratio that depends on the stereoelectronic properties of the ligand. DFT calculations of the free energies for these pairs of isomers reveal that the *trans* configuration is the more stable isomer for all of them, with ΔE_{*cis-trans*} of 1.6, 15.7, 3.7 and 7.6 kJ mol⁻¹ for **3b-e**, respectively. Thus although the structure of **3b** observed in the solid state corresponds to the less stable isomer, this is not surprising given the very small energy difference between its two isomers.

As in the ruthenium analogue, V-T NMR and ³¹P NOESY experiments carried out on **3b** suggests the presence of a “turnstile” isomerization process (Figs. S8–10). However, while coalescence of the two ³¹P resonances in the ruthenium analogue **3b-Ru** occurred at -25 °C, this was not observed with **3b** even up to 85 °C, indicating a much slower isomerization for the osmium system.

The disubstituted CH₃CN derivative **4a** is also unstable, decomposing upon removal of the solvent. Its ¹H NMR spectrum shows no resonance ascribable to the CH₃CN ligands, presumably due to fast exchange with the CD₃CN solvent. Attempts at growing diffraction quality crystals were unsuccessful, hence the configuration of the two CH₃CN ligands could not be confirmed. On the basis of DFT calculations, however, the lowest energy isomer has the structure depicted, i.e., the CH₃CN ligands occupy an equatorial and an axial position (Table S2).

The room temperature reaction of **4a** with PMe₃ in a DCM/ACN mixture leads to the substitution of one acetonitrile ligand to afford Os₃(μ-SbPh₂)₂(CO)₈(CH₃CN)(PMe₃), **4c'**; mild heating is required if the reaction is carried out in ACN as the solvent. Cluster **4c'** has been crystallographically characterized; the ORTEP plot showing its molecular structure is given in Fig. 3. Unlike in **3b-e**, the ¹H and ³¹P



Scheme 1. Substitution reactions of cluster **1**.

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