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Axial and equatorial isomers in an isonitrile-substituted osmium–antimony cluster

Guizhu Chen, Weng Kee Leong *

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, Singapore

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Abstract

The reaction of ^{t}BuNC with the osmium–antimony cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}SbPh_2)$ (**1**) proceeded via Os–Os bond cleavage to give $HOs_3(CO)_{10}(\mu\text{-}SbPh_2)(CNBu^t)$ (**2**) in which the ^{t}BuNC ligand was added onto one of the osmium atoms bridged by the antimony. Cluster **2** exists in isomeric forms, where the ^{t}BuNC ligand occupies either an *axial* (*a*-**2**) or an *equatorial* (*e*-**2**) position with respect to the Os_3Sb plane. In solution, *e*-**2** was found to occur as a mixture of isomers in which the isonitrile was presumably either *cis* to the unique osmium or to the antimony. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Osmium; Antimony; Clusters; Isomers

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1. Introduction

Compounds containing μ-SbR_2 ligands are very rare; the only triosmium cluster containing a μ-SbR_2 ligand reported to date is $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}SbPh_2)$ (**1**) [1]. Cluster **1** undergoes nucleophilic addition reactions with either EPh_3 (E = P, As, Sb) or CO via an Os–Os bond cleavage. In these adducts, the ligands occupy an equatorial position with respect to the Os_3Sb plane [2]. This stereochemistry of substitution was consistent with that observed previously in triosmium cluster chemistry; it has been established that N and C donor ligands which are rod-like, such as cyanides and isonitriles, tend to occupy *axial* positions and this has been attributed to electronic reasons [3]. In this paper we report that the *tert*-butylisonitrile adduct of **1** does not show such an electronic preference for an *axial* site.

2. Results

The reaction of **1** with an excess of ^{t}BuNC proceeded at room temperature to give isomers of the adduct $HOs_3(CO)_{10}(\mu\text{-}SbPh_2)(CNBu^t)$ (**2**) via the cleavage of an Os–Os bond. The adduct **2** was separated by column chromatography into two bands, both of which were found to have the isonitrile ligand on one of the antimony-bridged osmiums, and differed only in that in one, the isonitrile occupied an *axial* coordination site (*a*-**2**), and in the other, an *equatorial* coordination site (*e*-**2**) (with respect to the Os_3Sb plane). The molecular geometries of the adducts **2** were confirmed by single-crystal X-ray structural studies (Figs. 1 and 2). The terminal metal hydrides were located in the crystallographic studies and confirmed by ^{1}H-NMR spectroscopy. The spectra of both compounds showed resonances at about -8 ppm, consistent with the presence of a terminal OsH. Furthermore, the ^{1}H-NMR spectrum of *e*-**2** showed two resonances, indicating the presence of isomers which differed in the arrangement of the equatorial isonitrile relative to the antimony atom (Fig. 3). There was no spectroscopic evidence that *a*-**2** existed as a mixture of isomers.

To our knowledge, this is the first example of a substituted triosmium cluster which exists as both *axial* and *equatorial* isomers, which are separable, and which

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* Corresponding author. E-mail: chmlwk@nus.edu.sg

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did not readily interconvert. It provided an opportunity for us to assess the influence of *axial* versus *equatorial* substitution on the molecular geometry. A comparison of the structures of *a*-**2** and *e*-**2** showed that the largest differences in bond parameters were, as to be expected, associated with Os(1) to which the isonitrile ligand was bonded. For example, the two axial CO ligands on Os(1) in *e*-**2** were slightly bent away from a mutually *trans* arrangement (∠C(11)–Os(1)–C(13) = 170.9(3)°) while the axial CO and ^{t}BuNC ligands in *a*-**2** were closer to being mutually *trans* (∠C(11)–Os(1)–C(13) = 178.3(3)°). In addition, the Os(1)–Sb(4) bond length was longer in *a*-**2** (2.6790(5) and 2.6674(5) Å for *a*-**2** and *e*-**2**, respectively). Both these differences may be explained on the basis that π-bonding effects are dominant and that the π-accepting ability was in the order: CO > ^{t}BuNC > SbPh$_2$. Thus, the two strong π-accepting CO ligands in *e*-**2** deviated from linearity to avoid a mutually *trans* arrangement—the 'umbrella' effect [4]; and the strongly π-accepting CO *trans* to Sb(4) in *a*-**2** weakened the Os → Sb π back-bonding thus lengthening the Os(1)–Sb(4) bond as compared with the case in *e*-**2** where ^{t}BuNC was *trans* to Sb(4). Steric factors influence the effect of the ^{t}BuNC ligand on the Os(1)–Os(3) bond. In both isomers, the ^{t}BuNC was *cis* to the Os(1)–Os(3) bond. The CO ligand on Os(3) *cis* to the ^{t}BuNC ligand in both isomers were similarly disposed (∠C(33)–Os(3)–Os(1) = 86.6(2)° in *a*-**2**, (∠C(34)–Os(3)–Os(1) = 85.8(2)° in *e*-**2**), while the ^{t}BuNC ligand itself was bent more towards the Os(1)–Os(3) bond in *a*-**2** (∠Os(3)–Os(1)–C(13) = 90.6(2)°) than in *e*-**2** (∠Os(3)–Os(1)–C(14) = 94.5(2)°). The closer contact for *e*-**2** gave rise to a longer Os(1)–Os(3) bond (3.0035(4) and 2.9965(4) Å, respectively, for *a*-**2** and *e*-**2**).

3. Experimental section

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. Infrared spectra were recorded as hexane solutions. ^{1}H-NMR spectra were recorded as d$_8$-toluene solutions on a Bruker ACF-300 FT-NMR spectrometer. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore.

Cluster **1** (34 mg, 0.030 mmol) and excess ^{t}BuNC (0.2 ml) were stirred in hexane (20 ml) at room temperature for 10 h. The solvent and volatile compounds were removed in vacuo and the residue separated by column chromatography on silica gel. Elution with dichloromethane–hexane (10:90, v/v) gave two bands.

Band 1 gave *e*-**2** (20 mg, 55%). Found: C, 26.80; H, 1.83; N, 1.11. Calc. for C$_{27}$H$_{20}$NO$_{10}$Os$_3$Sb: C, 26.78; H, 1.65; N, 1.16. ν(CO): 2088m, 2056s, 2042m, 2022vs, 2003m, 1996m, 1982m, 1967m cm^{-1}; ν(CN): 2195w cm^{-1}; δ_H 1.57 (s, ^{t}BuNC), −8.28 (s, OsH), −8.75 (s, OsH).

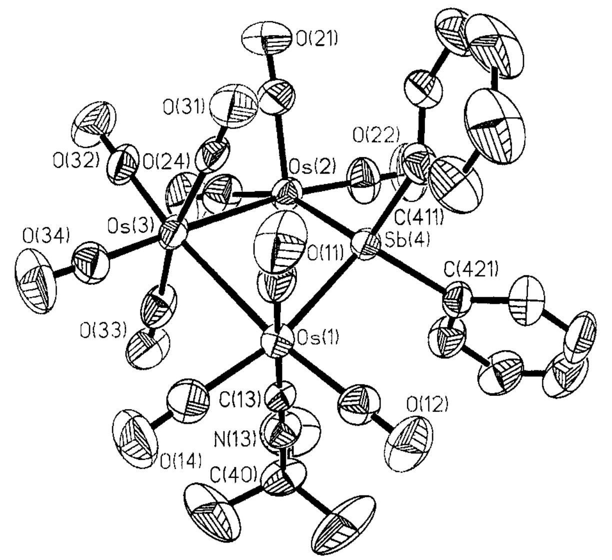

Fig. 1. ORTEP diagram of *a*-**2** (50% probability thermal ellipsoids). Os(1)–Os(3) = 3.0035(4); Os(2)–Os(3) = 2.9710(4); Os(1)–Sb(4) = 2.6790(5); Os(2)–Sb(4) = 2.6333(5) Å; Os(3)–Os(1)–Sb(4) = 76.488(13); Os(3)–Os(2)–Sb(4) = 77.738(13); Os(1)–Os(3)–Os(2) = 90.235(10); Os(1)–Os(3)–C(33) = 86.6(2); Os(3)–Os(1)–C(13) = 90.6(2); C(11)–Os(1)–C(13) = 178.3(3)°.

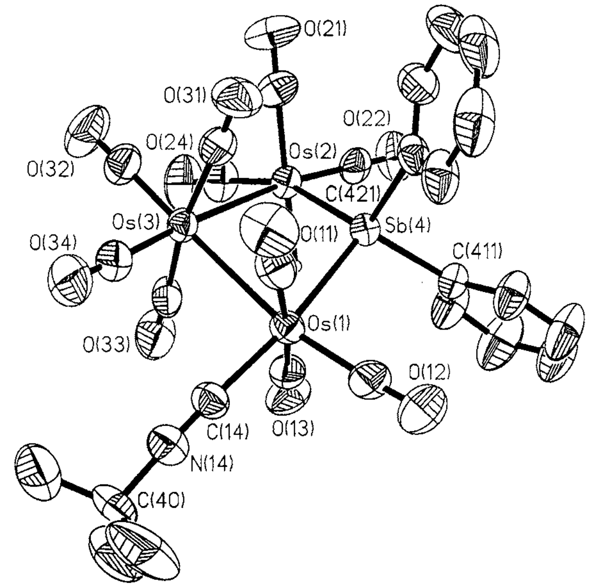

Fig. 2. ORTEP diagram of *e*-**2** (50% probability thermal ellipsoids). Os(1)–Os(3) = 2.9965(4); Os(2)–Os(3) = 2.9759(4); Os(1)–Sb(4) = 2.6674(5); Os(2)–Sb(4) = 2.6341(5) Å; Os(3)–Os(1)–Sb(4) = 76.221(12); Os(3)–Os(2)–Sb(4) = 77.070(12); Os(1)–Os(3)–Os(2) = 90.103(10); Os(1)–Os(3)–C(34) = 85.8(2); Os(3)–Os(1)–C(14) = 94.5(2); C(11)–Os(1)–C(13) = 170.9(3)°.

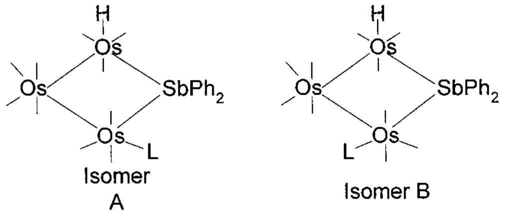

Fig. 3. Two isomers of *e*-**2**.

Crystal data for *e*-**2**: $C_{20}H_{10}NO_{10}Os_3Sb$, $M = 1210.79$, orthorhombic, space group *Pbca*, $a = 12.8615(1)$, $b = 17.7514(3)$, $c = 28.8072(4)$ Å; $U = 6577.0(2)$ Å^3; $Z = 8$; $\rho_c = 2.446$ mg m^{-3}; μ(Mo–K$_\alpha$) = 12.418 mm^{-1}, $T = 298$ K, 38701 reflections collected, 7764 unique reflections, final $R = 6.63\%$, $wR = 6.72\%$ for all data and 396 parameters.

Band 2 gave *a*-**2** (10 mg, 28%). Found: C, 26.92; H, 1.90; N, 1.02. Calc. for $C_{27}H_{20}NO_{10}Os_3Sb$: C, 26.78; H, 1.65; N, 1.16. ν(CO): 2090w, 2062m, 2042m, 2020vs, 1996m, 1982m, 1966m cm^{-1}; ν(CN): 2178w cm^{-1}; δ_H 1.57 (s, ^{t}BuNC), −8.21 (s, OsH).

Crystal data for *a*-**2**: $C_{20}H_{10}NO_{10}Os_3Sb$, $M = 1210.79$, triclinic, space group *P*1, $a = 9.5713(1)$, $b = 10.0990(2)$, $c = 18.8008(2)$ Å, $\alpha = 84.771(1)$, $\beta = 75.328(1)$, $\alpha = 69.829(1)°$; $U = 1650.20(4)$ Å^3; $Z = 2$; $\rho_c = 2.437$ mg m^{-3}; μ(Mo–K$_\alpha$) = 12.373 mm^{-1}, $T = 298$ K, 12990 reflections collected, 7235 unique reflections, final $R = 5.13\%$, $wR = 8.35\%$ for all data and 386 parameters.

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