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Reactions of the face-capped benzothiazolate-substituted clusters $Os_3(CO)_9(\mu_3,\eta^2\text{-}C_7H_3NSR)(\mu\text{-}H)$ (R = H, Me) with PPh_3: Kinetic formation of $Os_3(CO)_9(PPh_3)(\mu,\eta^2\text{-}C_7H_3NSR)(\mu\text{-}H)$ and thermally induced ligand isomerization

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This paper is dedicated to Prof. Richard D. Adams to honor the occasion of his 70th birthday.

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ABSTRACT

The reaction of the benzothiazolate-capped triosmium clusters $Os_3(CO)_9(\mu_3,\eta^2\text{-}C_7H_3NSR)(\mu\text{-}H)$ (**1a**, R = H; **1b**, R = Me) with PPh_3 proceeds readily at room temperature with a $\mu_3,\eta^2 \rightarrow \mu,\eta^2$ hapticity change in the benzothiazolate heterocycle to furnish $Os_3(CO)_9(PPh_3)(\mu,\eta^2\text{-}C_7H_3NSR)(\mu\text{-}H)$ (**2a**, R = H; **2b**, R = Me) in high yields. X-ray crystallography has confirmed the regiospecific nature of this reaction where the PPh_3 ligand is bound to the osmium atom that serves as the coordination site for the hydride and the metalated-carbon atom associated with the edge-bridged benzothiazolate ligand. The thermolysis of **2a** and **2b** in boiling toluene affords several new Os_3 clusters as a result of ligand isomerization, decarbonylation, and ortho metalation of the ancillary PPh_3 ligand. The new products have been isolated and characterized by a combination of spectroscopic methods and X-ray crystallography in the case of **3b**, **4b**, **5b** and **6b**. Clusters **3b** and **4b** are isomers of **2b** and differ in the location of the hydride and PPh_3 ligands relative to the benzothiazolate moiety. Electronic structure calculations on the isomeric clusters **2b**, **3b**, and **4b** confirm that **2b** is the kinetic product of ligand substitution, accounting for its rearrangement to the latter two isomers upon heating. Cluster **5b** contains a face-capping benzothiazolate moiety and is shown by DFT calculations to derive from a site-selective loss of an axial CO group in **4b**. Cluster **6a,b** formed from **5a,b** as a result of further decarbonylation with concomitant ortho metalation of one of the phenyl groups of the coordinated PPh_3 ligand.

1. Introduction

The face-capped triosmium clusters $Os_3(CO)_9(\mu_3,\eta^2$-benzoheterocycle)(μ-H), which are readily obtained from the reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with a wide range of benzoheterocycles containing a pyridinyl nitrogen, remain the subject of numerous studies on cluster-promoted ligand activation and functionalization of heterocyclic substrates [1–26]. These face-capped clusters formally have 46 CVE (cluster valence electron) [18,20,21] and readily react with a variety of two electron donor ligands such as phosphine [5,8], isocyanide [22] etc. at room temperature to form 48-electron adducts. Although the initial reports of these cluster systems focused on modeling the important aspects of catalytic hydrodenitrification at heterogeneous surfaces [4,27–36], ensuing work increasingly shifted towards the selective modification of cluster-tethered benzoheterocyclic moieties *via* treatment with various nucleophiles. The ability of organometallic auxiliaries to effect such transformations serves as the impetus for study by many different research groups [2,3,5,7,15]. The specific product(s) obtained from the reaction of these cluster-activated heterocycles with various nucleophiles depends on the nature of the latter [2,3,5,7,15,17,20–26]. For instance, the reaction with soft nucleophiles such as phosphines and amines results in ligand addition at the metal core, with ligand rearrangements about the cluster

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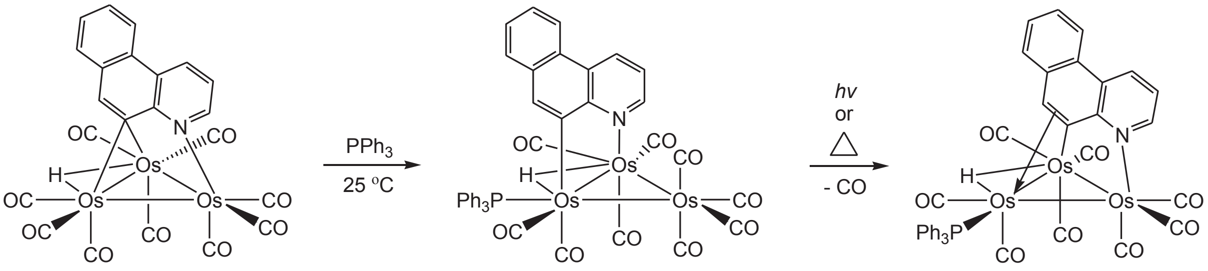
polyhedron typically observed [3,5,6,8,22–25]. In contrast, treatment of the same cluster substrates with hard nucleophiles such as hydrides and carbanions results in ligand attack at the carbocyclic ring of the activated benzoheterocyclic platform [2,3,5,7,15,20,21,26]. While generalizations have been made concerning the mode of ligand reactivity in a few of these systems, additional studies are required before globally trusted reaction patterns can be confidently embraced.

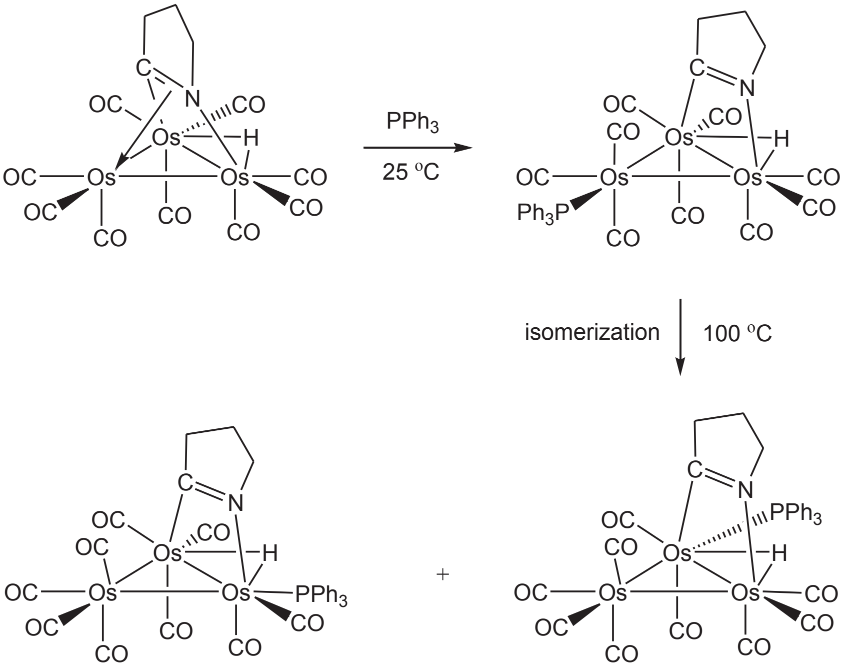
We have previously shown that several $Os_3(CO)_9(\mu_3,\eta^2$-benzoheterocycle)(μ-H) clusters rapidly react with different monodentate PR_3 donors at room temperature to afford the saturated clusters $Os_3(CO)_9(PR_3)(\mu_3,\eta^2$-benzoheterocycle)(μ-H), where the PR_3 ligand always occupies an equatorial site at the carbon-bound osmium atom [3,5,8,23]. Photolysis or thermolysis of these phosphine adducts usually leads to nonspecific decomposition or phosphine ligand dissociation to give the phosphine-free nona- and decacarbonyl clusters $Os_3(CO)_9(\mu_3,\eta^2$-benzoheterocycle)(μ-H) and $Os_3(CO)_{10}(\mu,\eta^2$-benzoheterocycle)(μ-H) [3,8]. However, in the case of the metalated 5,6-benzoquinolate cluster, both photolysis and thermolysis lead to the formation of an electron-precise σ-π vinyl complex *via* carbonyl dissociation (Scheme 1) [8].

In contrast, the related triosmium cluster $Os_3(CO)_9(PPh_3)\{\mu,\eta^2$-$C{=}N(CH_2)_3\}(\mu$-H), which was synthesized from the reaction of the labile cluster $Os_3(CO)_9\{\mu_3,\eta^2$-$C{=}N(CH_2)_3\}(\mu$-H) with PPh_3, undergoes rearrangement *via* phosphine migration upon thermolysis in *n*-heptane to give two isomeric products (Scheme 2) [37]. All three phosphine derivatives based on $Os_3(CO)_9(PPh_3)\{\mu,\eta^2$-$C{=}N(CH_2)_3\}(\mu$-H) undergo decarbonylation in boiling *n*-octane to yield a single isomer of $Os_3(CO)_8(PPh_3)\{\mu,\eta^2$-$C{=}N(CH_2)_3\}(\mu$-H) as the observable product [37].

Recently, we reported that the benzothiazolate-capped cluster $Os_3(CO)_9(\mu_3,\eta^2$-$C_7H_3NSCH_3)(\mu$-H) (**1b**) readily reacts with ^tBuNC at room temperature to give the adduct $Os_3(CO)_9(^tBuNC)(\mu,\eta^2$-$C_7H_3NSCH_3)(\mu$-H) that contains an axial isonitrile ligand at the non-hydride-bridged Os-Os vector. This product undergoes decarbonylation in refluxing toluene to afford $Os_3(CO)_8(^tBuNC)(\mu_3,\eta^2$-$C_7H_3NSCH_3)(\mu$-H) (Scheme 3) [22]. This reactivity of the isonitrile-substituted cluster was unusual vis-à-vis the phosphine adducts of $Os_3(CO)_8(PR_3)(\mu_3,\eta^2$-benzoheterocycle)(μ-H), prompting us to investigate the reaction of clusters $Os_3(CO)_9(\mu_3,\eta^2$-$C_7H_3NSR)(\mu$-H) (**1a**, R = H; **1b**, R = Me) with PPh_3. The substitution products **2a** and **2b** have been isolated and the locus of the PPh_3 ligand in each cluster established by X-ray crystallography. The reactivity of the products at elevated temperature has been investigated in order to better understand the effect, if any, that the heterocyclic auxiliary exerts on the ensuing ligand isomerization and bond-activation sequences.



Scheme 1. Reactivity of $Os_3(CO)_9(\mu_3,\eta^2$-$C_{13}H_8N)(\mu$-H) with PPh_3 [8].



Scheme 2. Reactivity of $Os_3(CO)_9\{\mu_3,\eta^2$-$C{=}N(CH_2)_3\}(\mu$-H) towards PPh_3 [37].

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