

Reactions of the unsaturated triosmium cluster  
[( $\mu$ -H)Os<sub>3</sub>(CO)<sub>8</sub>(Ph<sub>2</sub>PCH<sub>2</sub>P(Ph)C<sub>6</sub>H<sub>4</sub>)] with HX  
(X = Cl, Br, F, CF<sub>3</sub>CO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub>): X-ray structures  
of [( $\mu$ -H)Os<sub>3</sub>(CO)<sub>7</sub>( $\eta^1$ -Cl)( $\mu$ -Cl)<sub>2</sub>( $\mu$ -dppm)],  
[( $\mu$ -H)<sub>2</sub>Os<sub>3</sub>(CO)<sub>8</sub>(Ph<sub>2</sub>PCH<sub>2</sub>P(Ph)C<sub>6</sub>H<sub>4</sub>)]<sup>+</sup>[CF<sub>3</sub>O]<sup>-</sup>  
and the two isomers of [( $\mu$ -H)Os<sub>3</sub>(CO)<sub>8</sub>( $\mu$ -Cl)( $\mu$ -dppm)]

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## Abstract

Treatment of the electronically unsaturated cluster [( $\mu$ -H)Os<sub>3</sub>(CO)<sub>8</sub>(Ph<sub>2</sub>PCH<sub>2</sub>P(Ph)C<sub>6</sub>H<sub>4</sub>)] (**1**) with HCl gas at ambient temperature in dichloromethane afforded ( $\mu$ -H)Os<sub>3</sub>(CO)<sub>8</sub>( $\mu$ -Cl)( $\mu$ -dppm) (**2**) and [( $\mu$ -H)Os<sub>3</sub>(CO)<sub>7</sub>( $\eta^1$ -Cl)( $\mu$ -Cl)<sub>2</sub>( $\mu$ -dppm)] (**3**). Thermolysis of **2** at 110 °C led to an isomer of **2**, **4**. A similar reaction of **1** with HBr gas gave [( $\mu$ -H)Os<sub>3</sub>(CO)<sub>8</sub>( $\mu$ -Br)( $\mu$ -dppm)] (**5**) as the only product which does not isomerize at 110 °C. In sharp contrast, treatment of **1** with HF gas gave the protonated species [( $\mu$ -H)<sub>2</sub>Os<sub>3</sub>(CO)<sub>8</sub>(Ph<sub>2</sub>PCH<sub>2</sub>P(Ph)C<sub>6</sub>H<sub>4</sub>)]<sup>+</sup> (**6**). Treatment of **1** with CF<sub>3</sub>CO<sub>2</sub>H also gave cation **6** whereas CH<sub>3</sub>CO<sub>2</sub>H yielded [( $\mu$ -H)Os<sub>3</sub>(CO)<sub>8</sub>( $\mu$ - $\eta^2$ -CH<sub>3</sub>CO<sub>2</sub>)( $\mu$ -dppm)] (**7**). Structures of **2**, **3**, **4** and **6** were established crystallographically. In **2**, both the chloride and the hydride ligands simultaneously bridge the same Os–Os edge and the dppm spans another Os–Os bond whereas in **4**, all the three ligands bridge the same Os–Os edge. Compound **3** is comprised of an open Os<sub>3</sub> arrangement in which one chloride bridges the open Os–Os edge, another chloride and a hydride mutually bridge an Os–Os bond and the third chloride is terminally coordinated to one of the Os atoms of the dppm bridged edge. The cation **6** consists of a triangle of osmium atoms in which the shortest Os–Os edge is bridged by a hydride and the metallated phenyl ring and the longest edge is bridged by another hydride and the diphosphine ligand.

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## 1. Introduction

The reactions of triosmium carbonyl clusters with protic acids have been thoroughly investigated and found to exhibit a range of reactivity patterns [1–8].

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Most common is simple protonation to give cationic hydrido species in which the hydride adopts a bridging coordination site [1–5] although cleavage of a metal–carbon [6] or a metal–metal bond [7] are known to occur as well. For example, the parent compound  $[\text{Os}_3(\text{CO})_{12}]$  reacts with concentrated  $\text{H}_2\text{SO}_4$  to give the cationic species  $[(\mu\text{-H})\text{Os}_3(\text{CO})_{12}]^+$  [1]. The protonation of electron rich mono- and diphosphine derivatives occur more readily on treatment with weaker acids such as  $\text{CF}_3\text{CO}_2\text{H}$ . The unsaturated cluster  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$  and its tertiary phosphine substituted derivatives  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{L})]$  ( $\text{L} = \text{PEt}_3$ , or  $\text{PPh}_3$ ) react with  $\text{CF}_3\text{CO}_2\text{H}$  to give the cationic clusters  $[(\mu\text{-H})_3\text{Os}_3(\text{CO})_{10}]^+$  and  $[(\mu\text{-H})_3\text{Os}_3(\text{CO})_9\text{L}]^+$ , respectively [8]. The cyclometallated compound  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-P}(\text{C}_6\text{H}_4)\text{Ph})]$  reacts with Brønsted acids  $\text{HX}$  via a protonation followed by anion coordination to give the addition products  $[(\mu\text{-H})_2\text{Os}_3(\text{X})(\text{CO})_9(\mu\text{-PPh}_2)]$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  or  $\text{CF}_3\text{CO}_2$ ) but with  $\text{HBF}_4$  only the protonated complex  $[(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-P}(\text{C}_6\text{H}_4)\text{Ph})]^+$  is obtained [9]. In some cases, stable polynuclear species where the acid's conjugate base has coordinated to the cluster in place of an organic ligand or a metal–metal bond can be isolated. For example, Shapley and co-workers [6] reported that the triflate compound  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{O}_3\text{SCF}_3)_2]$  reacts with  $\text{CF}_3\text{CO}_2\text{H}$  and  $\text{CH}_3\text{CO}_2\text{H}$  to afford the mixed oxanion ligand clusters  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu, \eta^2\text{-O}_2\text{CCF}_3)_2(\eta^1\text{-O}_3\text{SCF}_3)]$  and  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu, \eta^2\text{-O}_2\text{CCH}_3)_2(\eta^1\text{-O}_3\text{SCF}_3)]$ . We also reported that protonation of  $\mu$ -vinylxy ligand in  $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-OCH}=\text{CH}_2)]$  with  $\text{HX}$  leads to the compounds  $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-X})]$  ( $\text{X} = \text{Cl}, \text{CF}_3\text{CO}_2$ ) with liberation of aldehyde via the intermediate addition species  $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-OCHXCH}_3)]$  [10]. Such acid adducts of the general formula  $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-X})]$  ( $\text{X} = \text{RCO}_2$ , halogen,  $\text{MeO}$ ) are also available from the lightly stabilized cluster  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  [11,12]. A few years ago we reported the first example of direct adduct formation not accompanied by ligand displacement or metal–metal bond cleavage from the reactions of the  $\mu_3$ -imidoyl cluster  $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}=\text{NCH}_2\text{CH}_2\text{CH}_2\text{-})]$  with  $\text{HX}$  to afford  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}=\text{NCH}_2\text{CH}_2\text{CH}_2\text{-})\text{X}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{CF}_3\text{CO}_2, \text{CF}_3\text{SO}_3$ ) [13]. We have recently reported [14] that the electron-deficient quinoline triosmium clusters  $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-XC}_9\text{H}_6\text{N})]$  ( $\text{X} = \text{H}, 5\text{-NH}_2, 6\text{-NH}_2, 3\text{-NH}_2, 5\text{-Br}, 5\text{-CH}_3$ ) all undergo simple protonation with both coordinating ( $\text{CF}_3\text{CO}_2\text{H}$ ) and non-coordinating acids ( $\text{HBF}_4$ ).

The reactions of the coordinatively unsaturated triosmium cluster  $[(\mu\text{-H})\text{Os}_3(\text{CO})_8(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{-C}_6\text{H}_4)]$  (**1**) with a wide variety of small inorganic and organic ligands such as  $\text{CO}$  [15],  $\text{H}_2$  [16],  $\text{PR}_3$  [17],  $\text{P}(\text{OR})_3$  ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{Bu}$  or  $\text{Ph}$ ) [17],  $\text{PPh}_2\text{H}$  [18],  $\text{RC}\equiv\text{CR}$  ( $\text{R} = \text{Ph}, \text{C}_6\text{H}_4\text{Me}, \text{Me}$  or  $\text{CF}_3$ ) [19],

$[\text{Au}(\text{PPh}_3)]\text{PF}_6$  [20],  $\text{EtSH}$  [21],  $\text{CH}_3\text{CH}(\text{CH}_3)\text{SH}$  [21],  $\text{PhSH}$  [21],  $\text{pySH}$  [22],  $\text{HSCH}_2\text{CH}_2\text{SH}$  [23],  $\text{HSCH}_2\text{CH}_2\text{-CH}_2\text{SH}$  [23], and  $\text{Se}$  [24] that afford many interesting and potentially useful compounds have been investigated. Our recent studies of the reactivity of **1** toward  $\text{CH}_2\text{CN}_2$  [25] and silanes [26] have uncovered some examples of its distinctly different reactivity patterns compared with unsaturated benzoheterocyclic triosmium clusters [27]. Herein, we report our results on the investigations of the reactions of **1** with a series of Brønsted acids. It was of interest to examine whether structurally diverse products would also be accessible in these systems.

## 2. Results and discussion

When  $\text{HCl}$  gas was bubbled through a dichloromethane solution of the electron-deficient cluster **1** at ambient temperature for 2 min, the initial green solution immediately turned orange and two compounds  $[(\mu\text{-H})\text{Os}_3(\text{CO})_8(\mu\text{-Cl})(\mu\text{-dppm})]$  (**2**) and  $[(\mu\text{-H})\text{Os}_3(\text{CO})_7(\eta^1\text{-Cl})(\mu\text{-Cl})_2(\mu\text{-dppm})]$  (**3**) were isolated in 85% and 10% yields, respectively, after chromatographic separation. Both compounds **2** and **3** have been characterized by a combination of spectroscopic data and single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **2** is depicted in Fig. 1, crystal data are given in Table 1 and selected bond distances and bond angles are listed in Table 2. The molecule consists of a triangular cluster of osmium atoms with eight terminal carbonyl groups, one bridging chloride, one bridging hydride and a bridging dppm ligand. Three CO ligands are bound to Os(1) and Os(2) atom while Os(3) bears two carbonyls. The chloride and hydride

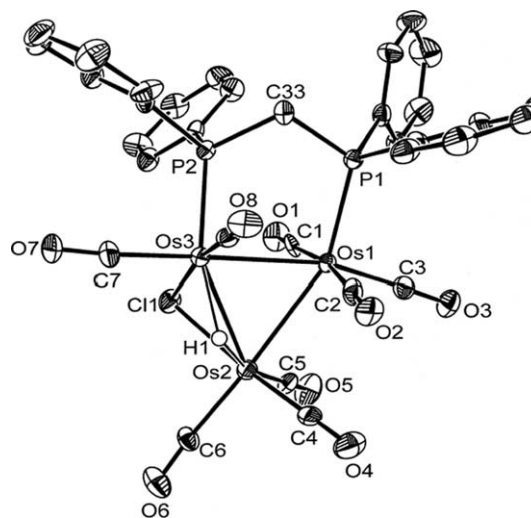


Fig. 1. Molecular structure of  $[(\mu\text{-H})\text{Os}_3(\text{CO})_8(\mu\text{-Cl})(\mu\text{-dppm})]$  (**2**) showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

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