Polyhedron 101 (2015) 103–108

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Thermolysis of $Ru_3(CO)_{10}(\mu$-dppm) and $Ru_3(CO)_9(PRPh_2)(\mu$-dppm) (R = Ph, H) in presence of O_2: Synthesis and structure of triruthenium clusters containing a capping-oxo ligand

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ARTICLE INFO

Article history:
Received 9 June 2015
Accepted 7 July 2015
Available online 11 July 2015

Keywords:
Triruthenium clusters
Oxo-capped clusters
Carbonyls
C–P, P–H and C–H bond activation
X-ray structures

ABSTRACT

Thermolysis of $Ru_3(CO)_{10}(\mu$-dppm) [dppm = bis(diphenylphosphino)methane] in boiling xylene in presence of molecular oxygen (O_2) affords the trinuclear oxo-capped cluster $Ru_3(CO)_7(\mu_3$-CO)(μ_3-O)(μ-dppm) (**1**). A similar reaction between $Ru_3(CO)_9(PPh_3)(\mu$-dppm) and O_2 in refluxing benzene also furnishes the oxo-capped $Ru_3(CO)_6(PPh_3)(\mu_3$-CO)(μ_3-O)(μ-dppm) (**2**). Crystal structures of **1** and **2** reveal that both contain a capping oxygen at one face and a triply-bridging carbonyl on the opposite face of the triruthenium plane. In contrast, $Ru_3(CO)_9(PHPh_2)(\mu$-dppm) does not react with O_2 under similar conditions, but undergoes thermal transformations to give $Ru_3(CO)_7(\mu$-H)(μ-PPh_2){μ_3-$PhPCH_2P(C_6H_4)Ph$} (**3**) and $Ru_3(CO)_6(\mu$-CO)(μ-$PPh_2)_2(\mu_3$-CH_2PPh)] (**4**) via C–P, P–H and C–H bond activation. All the new clusters have been characterized by a combination of spectroscopic data and single crystal X-ray diffraction analysis.

1. Introduction

It has been known for some years that zero-valent triruthenium clusters react with elemental sulfur and its heavier congeners to afford chalcogenide-capped clusters [1–4]. In 1979, Johnson and co-workers synthesized $Ru_3(CO)_9(\mu_3$-X)$_2$ and $Ru_3(CO)_9(\mu$-H)$_2(\mu_3$-X) from the reaction of $Ru_3(CO)_{12}$ with X_n (X = S, Se, Te) in presence of CO [3]. In contrast, $Ru_3(CO)_{12}$ does not react with molecular oxygen (O_2) to afford oxo-capped cluster since the triruthenium core is not electron-rich enough to undergo oxidation. One way to increase the electron-richness of the trinuclear core is the substitution of carbonyl(s) by more electron-donating phosphines and the phosphine-substituted derivatives of $Ru_3(CO)_{12}$ such as $Ru_3(CO)_9${$P(C_4H_3S)_3$}(μ-dppm), $Ru_3(CO)_8(\mu$-dppm$)_2$ and $Ru_3(CO)_6$ (μ-dppm$)_3$ have been found to react with O_2 which lead to the formation of oxo-capped clusters (Chart 1) [4–6].

A literature review in this field shows that at least three carbonyls have to be replaced by phosphines from $Ru_3(CO)_{12}$ in order to make it reactive towards O_2 that leads to the formation of oxo-capped cluster [4–6]. In the present work, we have investigated this area further and found that bis(phosphine) substituted cluster $Ru_3(CO)_{10}(\mu$-dppm) also reacts with O_2 to afford oxo-capped cluster, but only at more drastic conditions. The possibility of side reactions when the incorporated phosphine (e.g., diphenylphosphine) is vulnerable to thermal transformation on cluster surface at moderate temperatures have also been examined.

2. Results and discussion

2.1. Reactions of $Ru_3(CO)_{10}(\mu$-dppm) and $Ru_3(CO)_9(PPh_3)(\mu$-dppm) with O_2 – Synthesis of oxo-capped clusters $Ru_3(CO)_7(\mu_3$-CO)(μ_3-O)(μ-dppm) (**1**) and $Ru_3(CO)_6(PPh_3)(\mu_3$-CO)(μ_3-O)(μ-dppm) (**2**)

High temperature reaction between $Ru_3(CO)_{10}(\mu$-dppm) and O_2 in boiling xylene led to the formation of oxo-capped cluster $Ru_3(CO)_7(\mu_3$-CO)(μ_3-O)(μ-dppm) (**1**) in 13% yield (Scheme 1). In contrast, $Ru_3(CO)_9(PPh_3)(\mu$-dppm) afforded the oxo-capped cluster $Ru_3(CO)_6(PPh_3)(\mu_3$-CO)(μ_3-O)(μ-dppm) (**2**) in 18% yield from a similar reaction with O_2 in boiling benzene (Scheme 1). In these reactions face-capping with the oxo-ligand would lead to some level of oxidation of the ruthenium atoms in the resultant clusters. Since the triruthenium core in $Ru_3(CO)_9(PPh_3)(\mu$-dppm) is more basic than that in $Ru_3(CO)_{10}(\mu$-dppm), oxo-capping of the former is expected to be easier than the later. This is evident by the relatively low temperature required in the reaction of O_2 with

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http://dx.doi.org/10.1016/j.poly.2015.07.006
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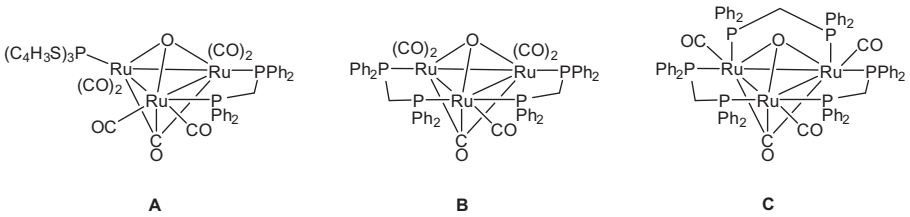
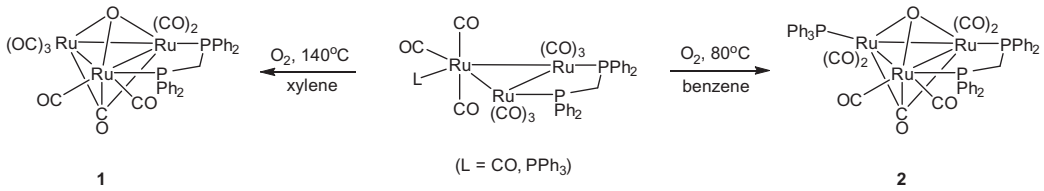


Chart 1. Examples of oxo-capped triruthenium carbonyl cluster.



Scheme 1. Thermolysis of $Ru_3(CO)_{10}(\mu\text{-dppm})$ and $Ru_3(CO)_9(PPh_3)(\mu\text{-dppm})$ in presence of O_2.

$Ru_3(CO)_9(PPh_3)(\mu\text{-dppm})$ compared to that with $Ru_3(CO)_{10}(\mu\text{-dppm})$. Both the new oxo-capped clusters have been adequately characterized in solution by IR, ^1H NMR and $^{31}P\{^1H\}$ NMR spectroscopic data and in the solid-state by single crystal X-ray diffraction analysis.

The solid-state molecular structures of **1** and **2** are depicted in Figs. 1 and 2, respectively, with the captions containing selected bond distances and angles. Both clusters contain a triruthenium core capped with a triply bridging oxo-ligand on one face and a triply bridging carbonyl ligand on the opposite face. They are structurally very similar to the related clusters $Ru_3(CO)_6\{P(C_4H_3S)_3\}(\mu_3\text{-CO})(\mu_3\text{-O})(\mu\text{-dppm})$ (**A**) [4] and $Ru_3(CO)_5(\mu_3\text{-CO})(\mu_3\text{-O})(\mu\text{-dpam})_2$ (**B**) [5] obtained from the reactions of $Ru_3(CO)_9\{P(C_4H_3S)_3(\mu\text{-dppm})$ and $Ru_3(CO)_8(\mu\text{-dpam})_2$ with molecular oxygen respectively. Ruthenium–ruthenium distances in **1**

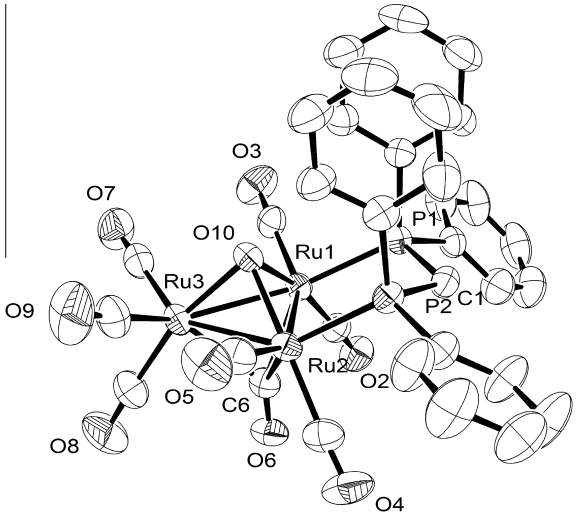


Fig. 1. The solid-state molecular structure of $Ru_3(CO)_7(\mu_3\text{-CO})(\mu_3\text{-O})(\mu\text{-dppm})$ (**1**) showing 50% probability thermal ellipsoid. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.7302(7), Ru(1)–Ru(3) 2.7238(7), Ru(2)–Ru(3) 2.7084(7), Ru(1)–P(1) 2.3358(16), Ru(2)–P(2) 2.3310(17), Ru(1)–O(10) 2.059(4), Ru(2)–O(10) 2.055(4), Ru(3)–O(10) 2.047(4), Ru(1)–C(6) 2.158(6), Ru(2)–C(6) 2.131(6), Ru(3)–C(6) 2.228(7), Ru(3)–Ru(1)–Ru(2) 59.548(19), Ru(3)–Ru(2)–Ru(1) 60.107(18), Ru(2)–Ru(3)–Ru(1) 60.345(18), Ru(3)–O(10)–Ru(2) 82.65(15), Ru(3)–O(10)–Ru(1) 83.13(15), Ru(2)–O(10)–Ru(1) 83.17(16), Ru(2)–C(6)–Ru(1) 79.1(2), Ru(2)–C(6)–Ru(3) 76.8(2), Ru(1)–C(6)–Ru(3) 76.8(2), P(2)–C(1)–P(1) 109.2(3).

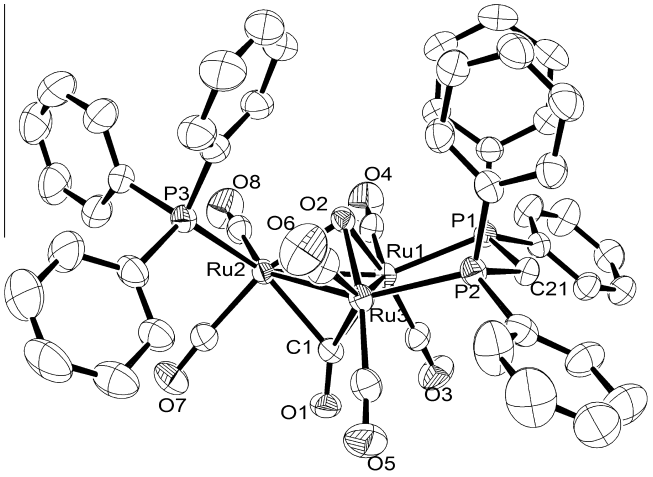


Fig. 2. The solid-state molecular structure of $Ru_3(CO)_6(PPh_3)(\mu_3\text{-CO})(\mu_3\text{-O})(\mu\text{-dppm})$ (**2**) showing 50% probability thermal ellipsoid. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.7218(5), Ru(1)–Ru(3) 2.7501(5), Ru(2)–Ru(3) 2.7415(5), Ru(1)–P(1) 2.3229(10), Ru(2)–P(3) 2.3595(10), Ru(3)–P(2) 2.3607(10), Ru(1)–O(2) 2.037(2), Ru(2)–O(2) 2.049(2), Ru(3)–O(2) 2.066(2), Ru(3)–C(1) 2.132(4) Ru(1)–C(1) 2.170(4), Ru(2)–C(1) 2.178(4); Ru(2)–Ru(1)–Ru(3) 60.132(13), Ru(1)–Ru(2)–Ru(3) 60.447(12), Ru(2)–Ru(3)–Ru(1) 59.421(13), Ru(1)–O(2)–Ru(2) 83.53(8), Ru(1)–O(2)–Ru(3) 84.18(9), Ru(2)–O(2)–Ru(3) 83.55(9), Ru(3)–C(1)–Ru(1) 79.46(13), Ru(3)–C(1)–Ru(2) 78.98(13), Ru(1)–C(1)–Ru(2) 77.50(12).

[Ru–Ru 2.7084(7)–2.7302(7) Å] and **2** [Ru–Ru 2.7218(5)–2.7501(5) Å] are comparable to those found in related oxo-capped clusters **A** [Ru–Ru 2.7069(5)–2.7462(5) Å] [4] and **B** [Ru–Ru 2.670(2)–2.750(2) Å] [5], but are significantly shorter than those observed in the parent clusters $Ru_3(CO)_8(\mu\text{-dppm})$ [Ru–Ru 2.834(1)–2.860(1) Å] [7] and $Ru_3(CO)_9(PPh_3)(\mu\text{-dppm})$ [Ru–Ru 2.8523(3)–2.8938(3) Å] [8] which indicate some level of oxidation of the ruthenium atoms in both **1** and **2**. The ruthenium–oxygen bond distances in both of them [Ru–O 2.047(4)–2.059(4) Å (in **1**) and 2.037(2)–2.066(2) Å (in **2**)] are also comparable to those found in related **A** and **B** [Ru–O 2.051(3)–2.057(3) Å (in **A**) and 2.06(1)–2.11(1) Å (in **2**)] [4,5]. In addition, all three Ru–O bond lengths are almost similar within the experimental error in both **1** and **2**. This suggests that they may have delocalized electronic states with an averaged ruthenium oxidation number. In order to check this assumption, we compare the ruthenium–oxygen bond distances