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Communication

Convenient route to an electron-deficient Tetraosmium(I) Carboxylate chain

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ABSTRACT

Refluxing the dinuclear complex $[Os_2(CO)_6(\mu\text{-}OOC^tBu)_2]$ in acetonitrile affords the substituted derivative $[Os_2(CO)_4(\mu\text{-}OOC^tBu)_2(NCMe)_2]$. Their reaction with PPh_3 in a 2:1 ($Os:PPh_3$) ratio represents a convenient route to the 64-electron, tetraosmium chain $[Os_4(CO)_8(\mu\text{-}OOC^tBu)_4(PPh_3)_2]$.

1. Introduction

The reaction of $[Os_3(CO)_{12}]$ (**1**) with various carboxylic acids at elevated temperatures is known to afford dinuclear complexes $[Os_2(CO)_6(\mu\text{-}OOCR)_2]$ [1,2]. A more convenient synthesis via microwave irradiation in 1,2-dichlorobenzene has also been reported recently [3]. These complexes have a sawhorse geometry, similar to that of their ruthenium analogues, in which the diosmium unit is bridged by two *cis* carboxylate groups, with two radial and an axial CO ligands on each osmium atom. The axial CO ligands are labile and can be substituted by other two-electron donors like phosphanes, pyridine and acetonitrile (Scheme 1).

In contrast to the significant number of tetranuclear ruthenium chains known [4,5], only one tetraosmium chain complex has been reported to-date; the 64-electron species $[\{Os_2(CO)_5(thd)_2\}_2]$ obtained from the reaction of **1** with thdH (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate). This dark red complex contains three unsupported Os—Os bonds, with a short-long-short alternation in the Os—Os bond lengths. An EHMO calculation revealed that the HOMO is delocalized over the entire Os_4 chain, making them of interest as molecular wires [6,7]. We have recently shown that the tetraruthenium carboxylate chains may be viewed as dimers of the diruthenium unit [4,8]. It therefore seems reasonable that the diosmium carboxylate species may also act as a precursor for the tetraosmium carboxylate. Our findings are reported here.

2. Results and discussion

The diosmium carboxylate $[Os_2(CO)_6(\mu\text{-}OOC^tBu)_2]$ (**3**) is obtained as a white solid from the reaction of **1** with pivalic acid ^tBuCOOH (**2**). Its IR spectrum in the carbonyl stretch region is characteristic of the $Os_2(CO)_6$ sawhorse structure, like that found in the known analogues $[Os_2(CO)_6(\mu\text{-}OOCR)_2]$ (where R = H, Me, Et, iPr, Ph) [1–3]. Complex **3** converts quantitatively to $[Os_2(CO)_4(\mu\text{-}OOC^tBu)_2(NCMe)_2]$ (**4**) upon reflux in acetonitrile, the IR spectrum showing the characteristic pattern in the ν_{CO} region expected for *ax*-$[Os_2(CO)_4(\mu\text{-}OOC^tBu)_2(NCMe)_2]$ and the ^1H NMR spectrum exhibiting a resonance at δ 0.93 ppm for the acetonitrile ligands; the ethanoate analogue has been reported earlier [2].

Removal of the solvent gives a purple solid which re-dissolves readily in MeCN to reform **4** as a colourless solution. In less coordinating solvents such as DCM or toluene, purple solutions are obtained initially which gradually turns brown, from which the purple solid cannot be recovered by solvent removal. Attempts to characterize the purple compound directly are unsuccessful as it readily decomposes in both the solid state and in solution. In analogy with the ruthenium system, we believe that the purple solid is probably a tetraosmium chain, i.e., it is a "dimer of dimers" comprising two $[Os_2(CO)_4(\mu\text{-}OOC^tBu)_2(S)]$ units linked via an

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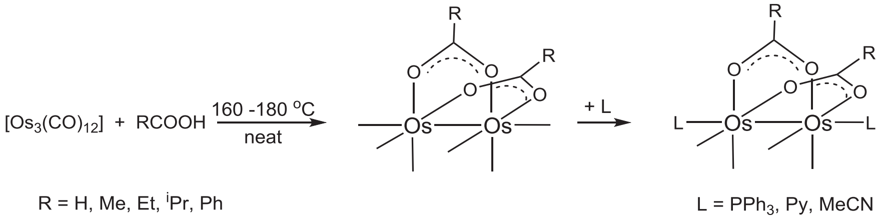


Scheme 1.

unsupported Os–Os bond, with weakly bound solvent or acid molecules (S) occupying the two axial positions. Tetraosmium ion fragments can also be observed in the mass spectrum of **4**, and consistent with this is the observation that while **4** reacts with excess PPh_3 to afford pale yellow $[Os_2(CO)_4(\mu\text{-OOC}^tBu)_2(PPh_3)_2]$ (**5**), it reacts in a 2:1 ratio of Os:PPh_3 to afford the pink tetraosmium chain $[Os_4(CO)_8(\mu\text{-OOC}^tBu)_4(PPh_3)_2]$ (**6**) (Scheme 2).

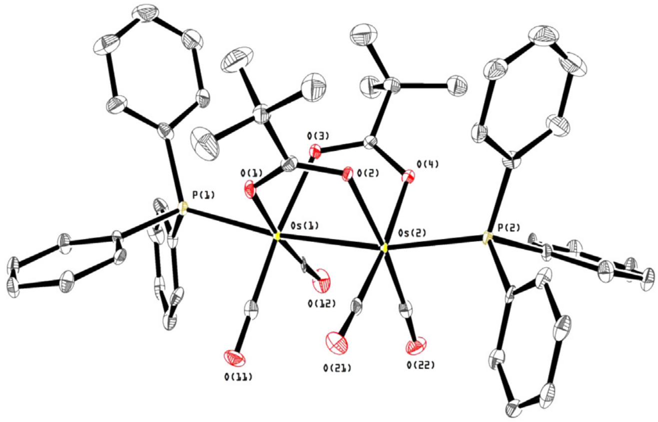
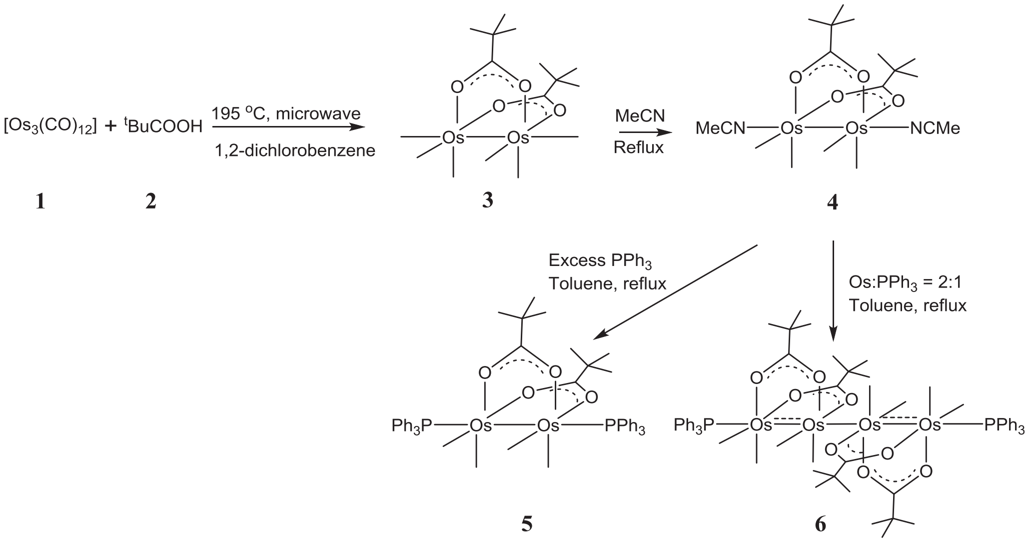


Fig. 1. Thermal ellipsoid representation of complex **5**. Selected bond lengths (Å) and angles (°): Os(1)-Os(2) = 2.7198(3), Os(1)-P(1) = 2.4020(15), Os(2)-P(2) = 2.4061(14), Os(1)-O(1) = 2.118(4), Os(1)-O(3) = 2.148(4), Os(2)-O(2) = 2.155(4), Os(2)-O(4) = 2.111(4); Os(1)-Os(2)-O(2) = 82.00(10), Os(1)- Os(2)-O(4) = 82.90(11), Os(2)-Os(1)-O(1) = 82.35(11), Os(2)-Os(1)-O(3) = 81.71(11), Os(1)-Os(2)-P(2) = 167.29(4), Os(2)-Os(1)-P(1) = 167.93(4), O(1)-Os(1)-O(3) = 83.62(16), O(2)-Os(2)-O(4) = 83.26(15).

Both **5** and **6** have been characterised by single crystal X-ray crystallographic studies; ORTEP plots depicting their molecular structures, together with selected bond parameters, are shown in Figs. 1 and 2, respectively. With a total valence electron count of 34, complex **5** is electron-precise. The Os–Os single bond length of 2.7198(3) Å is close to the 2.731(2) Å reported for $[Os_2(CO)_6(\mu\text{-OOCCH}_3)_2]$ [9]. The crystals of **6** are dichroic (pink/green). The molecular structure of **6** can be viewed as comprising two $[Os_2(CO)_4(\mu\text{-OOC}^tBu)_2(PPh_3)]$ units linked through an Os–Os bond, similar to that of its ruthenium analogue [4,8]. With a total valence electron count of 64, complex **6** is electron-deficient. The Os–Os bond lengths show an alternating short-long-short pattern; the outer and central Os–Os bond lengths are 2.7293(3) and 2.8402(4) Å, respectively, although both are appreciably shorter than the corresponding lengths in $[\{Os_2(CO)_5(thd)_2\}_2]$ (2.7683(4) and 2.9778(6) Å, respectively) [6,7]. As depicted in Scheme 2, these bonds may be regarded as having bond orders of 1.5 and 1.0, respectively. This is also supported by an NBO analysis at the B3LYP/LANL2DZ level of theory, carried out on a simplified model **6**′ in which both the ^{t}Bu and Ph groups are replaced by methyl groups (Fig. S1); the Wiberg bond indices are 0.52 and 0.37 for the outer and central Os–Os bonds, respectively, similar to what was found for the ruthenium analogue [4]. While the HOMO is bonding along the outer Os–Os vectors and anti-bonding along the central Os–Os vector, the LUMO is concentrated at the central Os–Os vector (Fig. S2). This suggests that it will tend to undergo nucleophilic cleavage at the central Os–Os bond, and is consistent with the observation that while a concentrated solution of **6** in less coordinating solvents (benzene, toluene or DCM) is a dark purple, dilution leads to a change in colour to red through orange and finally pale



Scheme 2.