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Preliminary communication

Triosmium clusters with μ_3 -AsR group as a building block for hexaosmium-arsenic cluster synthesis. Synthesis and characterisation of $[(\text{CO})_{11}\text{Os}_3\text{As}(\text{Os}_3(\text{CO})_9\text{H}_3)]$ and $[(\text{CO})_9\text{H}_3\text{Os}_3\text{As}(\text{Os}_3(\text{CO})_9\text{H}_3)]$. Crystal structure of $[(\text{CO})_{11}\text{Os}_3\text{As}(\text{Os}_3(\text{CO})_9\text{H}_3)]$

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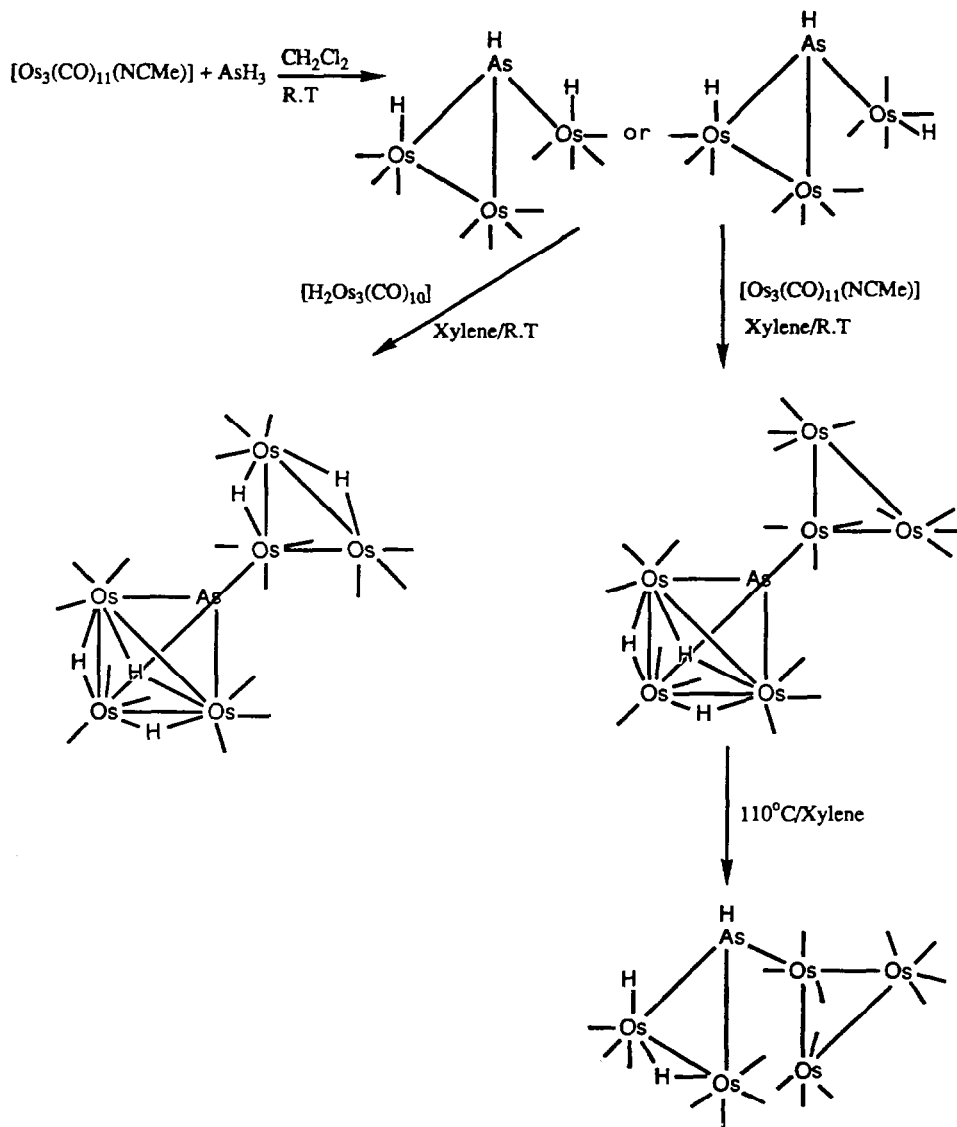
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Abstract

Reaction of the activated cluster $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ with primary arsine AsH_3 forms the arsinidine compound $[\text{H}_2\text{Os}_3(\mu_3\text{-AsH})(\text{CO})_{11}]$ (**1a**, **1b**), which on further reaction with $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ yields $[(\text{CO})_{11}\text{Os}_3\text{As}(\text{Os}_3(\text{CO})_9\text{H}_3)]$ (**2**) and with $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ yields $[\text{H}_2\text{Os}_3(\text{CO})_9\text{As}(\text{Os}_3(\text{CO})_9\text{H}_3)]$ (**3**). Similarly $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ reacts with AsH_3 at room temperature to afford **3** in good yields. Thermal degradation and rearrangement of **2** gives the pentanuclear cluster $[\text{H}_2\text{Os}_5(\text{CO})_{17}\text{AsH}]$ (**4**).

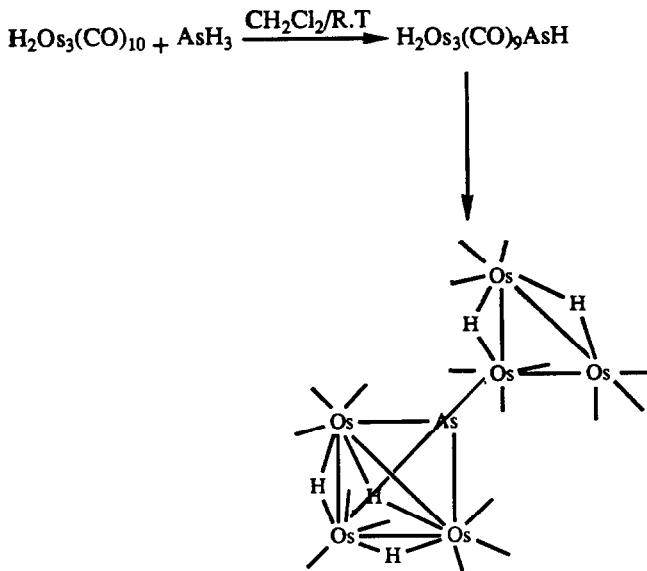
The reaction of $[\text{Os}_3(\text{CO})_{12}]$ with phosphine RPH_2 , has proved to be a reliable method for obtaining μ_3 -PR bridged clusters [1,2]. Mullner and Vahrenkamp [3] for example have demonstrated that dinuclear complexes with a bridging μ -PRH phosphido moiety will add oxidatively to sources of unsaturated metal fragments to give μ_3 -PR phosphinidine capped clusters. It is also known that the weakly ligated triosmium cluster $[\text{Os}_3(\text{CO})_{12-n}(\text{NCMe})_n]$ ($n = 1, 2$) readily reacts with compounds containing acidic hydrogen to give addition products [4,5]. With this in mind we have explored the possibility that the μ -AsR may serve as a building block in cluster synthesis.

In this communication we report the reaction of the activated cluster gives the open cluster $[\text{H}_2\text{Os}_3(\text{CO})_{11}(\mu_3\text{-AsH})]$ (**1**) consisting of dinuclear $[\text{H}_2\text{Os}_2(\text{CO})_7]$ and a mononuclear $[\text{HOs}(\text{CO})_4]$ unit held together by a μ_3 -AsR ligand, in which the hydride on the $[\text{HOs}(\text{CO})_4]$ spike can adopt a *cis* (**1a**) or a *trans* (**1b**) position with respect to the arsenic atom resulting in the formation of two isomers in a ratio of approximately 1 : 1. We also report the synthesis of the new hexaosmium-arsenic clusters $[(\text{CO})_{11}\text{Os}_3\text{As}(\text{Os}_3(\text{CO})_9\text{H}_3)]$ (**2**) and $[\text{H}_2(\text{CO})_9\text{Os}_3\text{As}(\text{Os}_3(\text{CO})_9\text{H}_3)]$ (**3**).



Scheme 1. Synthesis of $[\{\text{H}_3\text{Os}_3(\text{CO})_9\}\text{As}\{\text{Os}_3(\text{CO})_{11}\}]$ and $[\text{H}_2\text{Os}_5(\text{CO})_{18}(\text{AsH})]$.

Compound **1** reacts by oxidative addition to 1.1 equivalents of unsaturated metal fragment of $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ in xylene at room temperature to form the linked compound **2**. Similarly **1** reacts with 1.1 equivalent of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ to form **3**, and $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ reacts with primary arsine AsH_3 in dichloromethane at room temperature to yield as a final product cluster **3** in high yield (60%). This reaction proceeds through the formation of a reactive intermediate which has not been isolated but is tentatively formulated as $[\text{H}_2\text{Os}_3(\text{CO})_9\text{AsH}]$. Compound **2** undergoes thermal degradation and rearrangement to afford $[\text{H}_2\text{Os}_2(\text{CO})_7(\mu\text{-AsH})(\text{Os}_3\text{-}(\text{CO})_{11})]$ (**4**) as shown in Schemes 1 and 2. Spectroscopic data for compounds **1–4** are given in Table 1. In order to establish the molecular geometry of **2** a single-crystal

Scheme 2. Synthesis of $[(\text{H}_3\text{Os}_3(\text{CO})_9(\text{As}))\{\text{H}_2\text{Os}_3(\text{CO})_9\}]$.

X-ray diffraction study was undertaken *. The molecular structure of **2** with atomic numbering is shown in Fig. 1. The six osmium atoms define two approximately perpendicular triangles, Os(1)–Os(2)–Os(3) and Os(4)–Os(5)–Os(6) that are linked by an arsenido group coordinated axially to Os(4) and via μ_3 -bridge to Os(1)–Os(2)–Os(3) thus forming a distorted tetrahedron Os(1)–Os(2)–Os(3)–As. The three Os–Os bonds in triangle Os(1)–Os(2)–Os(3) are longer [2.963(3)–2.969(3) Å] than

Table 1
Spectroscopic data for compounds **1** to **4**

Formula	Infrared $\nu(\text{CO})$, cm^{-1} (n-hexane)	^1H NMR (CD_2Cl_2)
$[\text{H}_2\text{Os}_3(\text{CO})_{11}\text{AsH}]$ (1a , 1b)	2149(w), 2105(m), 2088(m.br), 2069(s), 2054(s), 2029(v.s), 2022(m) 1999(m.s), 1975(m)	0.54 (dd) ($J = 8.3/3.0$ Hz) 0.48 (dd) ($J = 3.6$ Hz) – 7.21 (d) ($J = 3.5$ Hz) – 7.39 (d) ($J = 2.9$ Hz) – 9.42 (d) ($J = 3.6$ Hz) – 9.75 (d) ($J = 8.4$ Hz)
$[\text{H}_3\text{Os}_6(\text{CO})_{20}\text{As}]$ (2)	2111(w), 2101(m), 2083(m) 2074(w), 2058(s), 2030(v.s) 2022(sh), 2003(m), 1972(w)	– 21.16 (s)
$[\text{H}_2\text{Os}_3(\text{CO})_9\text{AsH}]$	2125(w), 2093(w), 2068(s) 2054(s), 2035(v.s), 2014(s)	–
$[\text{H}_5\text{Os}_6(\text{CO})_{18}\text{As}]$ (3)	2125(w), 2093(w), 2055(v.s) 2041(sh), 2019(s)	– 11.58 (s) – 20.61 (s)
$[\text{H}_2\text{Os}_5(\text{CO})_{18}\text{AsH}]$ (4)	2092(w), 2075(s), 2063(s), 2025(v.s) 2010(s), 1989(w), 1944(v.w) 1915(w)	0.170 (d) ($J = 3.7$ Hz) – 9.17 (d) ($J = 4.1$ Hz) – 16.47 (s)

2.501(3) Å, 2.486(3) Å]; this can be asserted to the formation of a relative strong donor bond. The triangle Os(4)–Os(5)–Os(6) shows bond lengths and bond angles comparable to those observed for [Os₃(CO)₁₂]. There is no obvious explanation available for the short Os(4)–Os(6) distance.

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