# Triosmium clusters with $\mu_{3}$-AsR group as a building block for hexaosmium-arsenic cluster synthesis. Synthesis and characterisation of $\left[(\mathrm{CO})_{11} \mathrm{Os}_{3} \mathrm{As}_{( }\left(\mathrm{Os}_{3}(\mathrm{CO})_{9} \mathrm{H}_{3}\right)\right]$ and $\left[(\mathrm{CO}){ }_{9} \mathrm{H}_{3} \mathrm{Os}_{3} \mathrm{As}\left(\mathrm{Os}_{3}(\mathrm{CO})_{9} \mathrm{H}_{3}\right)\right]$. Crystal structure of $\left[(\mathrm{CO})_{11} \mathrm{Os}_{3} \mathrm{As}\left(\mathrm{Os}_{3}(\mathrm{CO})_{9} \mathrm{H}_{3}\right)\right]$ 

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#### Abstract

Reaction of the activated cluster $\left[\mathrm{Os}_{3}(\mathrm{CO})_{11}(\mathrm{NCMe})\right]$ with primary arsine $\mathrm{AsH}_{3}$ forms the arsinidine compound $\left[\mathrm{H}_{2} \mathrm{Os}_{3}\left(\mu_{3}-\mathrm{AsH}\right)(\mathrm{CO})_{11}\right](1 \mathrm{a}, \mathbf{1 b})$, which on further reaction with $\left[\mathrm{Os}_{3}(\mathrm{CO})_{11}(\mathrm{NCMe})\right]$ yields  Similarly $\left[\mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{10}\right]$ reacts with $\mathrm{AsH}_{3}$ at room temperature to afford 3 in good yields. Thermal degradation and rearrangement of 2 gives the pentanuclear cluster $\left[\mathrm{H}_{2} \mathrm{Os}_{5}(\mathrm{CO})_{17} \mathrm{AsH}\right]$ (4).


The reaction of $\left[\mathrm{Os}_{3}(\mathrm{CO})_{12}\right]$ with phosphine $\mathrm{RPH}_{2}$, has proved to be a reliable method for obtaining $\mu_{3}$-PR bridged clusters [1,2]. Mullner and Vahrenkamp [3] for example have demonstrated that dinuclear complexes with a bridging $\mu$-PRH phosphido moiety will add oxidatively to sources of unsaturated metal fragments to give $\mu_{3}$-PR phosphinidine capped clusters. It is also known that the weakly ligated triosmium cluster $\left[\mathrm{Os}_{3}(\mathrm{CO})_{12-n}(\mathrm{NCMe})_{n}\right](n=1,2)$ readily reacts with compounds containing acidic hydrogen to give addition products [4,5]. With this in mind we have explored the possibility that the $\mu$-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 $\left[\mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{11}\left(\mu_{3}-\mathrm{AsH}\right)\right]$ (1) consisting of dinuclear $\left[\mathrm{H}_{2} \mathrm{Os}_{2}(\mathrm{CO})_{7}\right]$ and a mononuclear $\left[\mathrm{HOs}(\mathrm{CO})_{4}\right]$ unit held together by a $\mu_{3}$-AsR ligand, in which the hydride on the $\left[\mathrm{HOs}(\mathrm{CO})_{4}\right]$ 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 $\left[(\mathrm{CO})_{11} \mathrm{Os}_{3} \mathrm{As}\left(\mathrm{Os}_{3}(\mathrm{CO})_{9} \mathrm{H}_{3}\right)\right]$ (2) and $\left[\mathrm{H}_{2}(\mathrm{CO})_{9} \mathrm{Os}_{3} \mathrm{As}_{( }\left(\mathrm{Os}_{3}(\mathrm{CO})_{9} \mathrm{H}_{3}\right)\right]$ (3).






Scheme 1. Synthesis of $\left[\left\{\mathrm{H}_{3} \mathrm{Os}_{3}(\mathrm{CO})_{9}\right\} \operatorname{As}\left\{\mathrm{Os}_{3}(\mathrm{CO})_{11}\right\}\right]$ and $\left[\mathrm{H}_{2} \mathrm{Os}_{5}(\mathrm{CO})_{18}(\mathrm{AsH})\right]$.

Compound 1 reacts by oxidative addition to 1.1 equivalents of unsaturated metal fragment of $\left[\mathrm{Os}_{3}(\mathrm{CO})_{11}(\mathrm{NCMe})\right]$ in xylene at room temperature to form the linked compound 2. Similarly 1 reacts with 1.1 equivalent of $\left[\mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{10}\right]$ to form 3 , and $\left[\mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{10}\right.$ ] reacts with primary arsine $\mathrm{AsH}_{3}$ 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 $\left[\mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{9} \mathrm{AsH}\right]$. Compound 2 undergoes thermal degradation and rearrangement to afford $\left[\mathrm{H}_{2} \mathrm{Os}_{2}(\mathrm{CO})_{7}(\mu-\mathrm{AsH})\left(\mathrm{Os}_{3}-\right.\right.$ $\left.\left.(\mathrm{CO})_{11}\right)\right](4)$ 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 $\mathbf{2}$ a single-crystal

## $\mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{10}+\mathrm{AsH}_{3} \xrightarrow{\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{R} . \mathrm{T}} \mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{9} \mathrm{AsH}$



Scheme 2. Synthesis of $\left[\left\{\mathrm{H}_{3} \mathrm{Os}_{3}(\mathrm{CO})_{9}(\mathrm{As})\right\}\left\{\mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{9}\right\}\right]$.

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, $\mathrm{Os}(1)-\mathrm{Os}(2)-\mathrm{Os}(3)$ and $\mathrm{Os}(4)-\mathrm{Os}(5)-\mathrm{Os}(6)$ that are linked by an arsenido group coordinated axially to $\mathrm{Os}(4)$ and via $\mu_{3}$-bridge to $\mathrm{Os}(1)$ -$\mathrm{Os}(2)-\mathrm{Os}(3)$ thus forming a distorted tetrahedron $\mathrm{Os}(1)-\mathrm{Os}(2)-\mathrm{Os}(3)-\mathrm{As}$. The three Os-Os bonds in triangle $\mathrm{Os}(1)-\mathrm{Os}(2)-\mathrm{Os}(3)$ are longer $[2.963(3)-2.969(3) \AA$ ] than

Table 1
Spectroscopic data for compounds 1 to 4

| Formula | Infrared $\nu(\mathrm{CO}), \mathrm{cm}^{-1}$ ( n -hexane) | ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$ |
| :---: | :---: | :---: |
| $\left[\mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{11} \mathrm{AsH}\right]$ | 2149(w), 2105(m), 2088(m.br), | 0.54 (dd) ( $J=8.3 / 3.0 \mathrm{~Hz}$ ) |
| (1a, 1b) | 2069(s), 2054(s), 2029(v.s), 2022(m) | 0.48 (dd) ( $J=3.6 \mathrm{~Hz}$ ) |
|  | 1999(m.s), 1975(m) | -7.21 (d) ( $J=3.5 \mathrm{~Hz}$ ) |
|  |  | -7.39 (d) ( $J=2.9 \mathrm{~Hz}$ ) |
|  |  | -9.42 (d) ( $J=3.6 \mathrm{~Hz}$ ) |
|  |  | -9.75 (d) ( $J=8.4 \mathrm{~Hz}$ ) |
| $\left[\mathrm{H}_{3} \mathrm{Os}_{6}(\mathrm{CO})_{20} \mathrm{As}\right]$ | 2111(w), 2101(m), 2083(m) | -21.16 (s) |
| (2) | 2074(w), 2058(s), 2030(v.s) |  |
|  | 2022(sh), 2003(m), 1972(w) |  |
| $\left[\mathrm{H}_{2} \mathrm{Os}_{3}(\mathrm{CO})_{9} \mathrm{AsH}\right]$ | 2125(w), 2093(w), 2068(s) | - |
|  | 2054(s), 2035(v.s), 2014(s) |  |
| $\left[\mathrm{H}_{5} \mathrm{Os}_{6}(\mathrm{CO})_{18} \mathrm{As}\right]$ | 2125(w), 2093(w), 2055(v.s) | -11.58(s) |
| (3) | 2041(sh), 2019(s) | -20.61 (s) |
| $\left[\mathrm{H}_{2} \mathrm{Os}_{5}(\mathrm{CO})_{18} \mathrm{AsH}\right]$ | 2092(w), 2075(s), 2063(s), 2025(v.s) | 0.170 (d) ( $J=3.7 \mathrm{~Hz}$ ) |
| (4) | 2010(s), 1989(w), 1944(v.w) | -9.17 (d) ( $J=4.1 \mathrm{~Hz}$ ) |
|  | 1915(w) | -16.47 (s) |



Fig. 1. The molecular structure of $\left.\left[(\mathrm{CO})_{11} \mathrm{Os}_{3} \mathrm{As}^{\left(\mathrm{Os}_{3}(\mathrm{CO})\right.}{ }_{9} \mathrm{H}_{3}\right)\right]$ (2) showing the atom numbering scheme. Selected bond lengths: $\operatorname{Os}(1)-\operatorname{Os}(2), 2.963(2) ; \operatorname{Os}(1)-\operatorname{Os}(3), 2.969(2) ; \operatorname{Os}(2)-\mathrm{Os}(3), 2.969(2) ; \operatorname{Os}(1)-\mathrm{As}(1)$, $2.489(3) ; \mathrm{Os}(2)-\mathrm{As}(1), 2.501(3) ; \mathrm{Os}(3)-\mathrm{As}(1), 2.486(3) ; \mathrm{Os}(4)-\mathrm{Os}(5), 2.887(2) ; \mathrm{Os}(4)-\mathrm{Os}(6), 2.841(2) ;$ $\mathrm{Os}(5)-\mathrm{Os}(6), 2.874(2) ; \mathrm{Os}(4)-\mathrm{As}(1), 2.457(3) \AA$. Selected bond angles: $\mathrm{Os}(2)-\mathrm{Os}(1)-\mathrm{Os}(3), 60.08(5)$; $\mathrm{Os}(1)-\mathrm{Os}(2)-\mathrm{Os}(3), 60.07(5) ; \mathrm{Os}(1)-\mathrm{Os}(3)-\mathrm{Os}(2), 59.85(4) ; \mathrm{As}(1)-\mathrm{Os}(1)-\mathrm{Os}(2), 53.77(8) ; \mathrm{As}(1)-\mathrm{Os}(1)-$ $\mathrm{Os}(3), 53.31(8) ; \mathrm{As}(1)-\mathrm{Os}(2)-\mathrm{Os}(1), 53.40(8) ; \mathrm{As}(1)-\mathrm{Os}(2)-\mathrm{Os}(3), 53.22(8) ; \mathrm{As}(1)-\mathrm{Os}(3)-\mathrm{Os}(1), 53.42(8)$; $\mathrm{As}(1)-\mathrm{Os}(3)-\mathrm{Os}(2), 53.70(8) ; \mathrm{Os}(1)-\mathrm{As}(1)-\mathrm{Os}(2), 72.83(9) ; \mathrm{Os}(1)-\mathrm{As}(1)-\mathrm{Os}(3), 73.3(1) ; \mathrm{Os}(2)-\mathrm{As}(1)-$ $\mathrm{O}(3)$, 73.1(1); $\mathrm{Os}(1)-\mathrm{As}(1)-\mathrm{Os}(4), 133.1(1) ; \mathrm{Os}(2)-\mathrm{As}(1)-\mathrm{Os}(4), 133.3(1) ; \mathrm{As}(1)-\mathrm{Os}(4)-\mathrm{Os}(5), 107.15(9)$; $\mathrm{Os}(5)-\mathrm{Os}(4)-\mathrm{Os}(6), 60.22(5) ; \mathrm{Os}(4)-\mathrm{Os}(5)-\mathrm{Os}(6), 59.10(4) ; \mathrm{Os}(4)-\mathrm{Os}(6)-\mathrm{Os}(5), 60.68(4)^{\circ}$.
the average $\mathrm{Os}-\mathrm{Os}$ bond $\left[2.877 \AA\right.$ ] as observed in case of $\left[\mathrm{Os}_{3}(\mathrm{CO})_{12}\right]$; however, they are comparable to the four long bonds observed in case of $\left[\mathrm{H}_{4} \mathrm{Os}_{4}(\mathrm{CO})_{12}\right.$ [6] $[2.963(2)-2.967(2) \AA]$. This is consistent with the view that the three hydrides bridge three Os-Os edges. Two hydrogen atoms were located by difference map, but the third hydrogen atom between $\mathrm{Os}(1)$ and $\mathrm{Os}(2)$ has not been fully located from the X-ray data. However, from other spectroscopic analysis data, the three hydrides are equivalent. In order to retain the $C_{30}$ symmetry of the molecule the third hydride is proposed to bridge $\mathrm{Os}(1)-\mathrm{Os}(2)$. The $\mathrm{Os}(4)-\mathrm{As}(1)$ bond distance $[2.457(3) \AA]$ is slightly shorter than the $\mathrm{Os}(1)-\mathrm{As}, \mathrm{Os}(2)-\mathrm{As}$ or $\mathrm{Os}(3)-\mathrm{As}(1)$ bond $[2.489(3) \AA$,

[^0]2.501 (3) $\AA, 2.486(3) \AA$; this can be asserted to the formation of a relative strong donor bond. The triangle $\mathrm{Os}(4)-\mathrm{Os}(5)-\mathrm{Os}(6)$ shows bond lengths and bond angles comparable to those observed for $\left[\mathrm{Os}_{3}(\mathrm{CO})_{12}\right]$. There is no obvious explanation available for the short $\mathrm{Os}(4)-\mathrm{Os}(6)$ distance.

## References

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[^0]:    * Crystal data: $\mathrm{C}_{20} \mathrm{H}_{3} \mathrm{O}_{20} \mathrm{AsOs}_{6}$. $M=1779.35$, orthorhombic, space group $P 2_{1} 2_{1} 2_{1}, a 11.407(2) \AA, b$ $16.356(2) \AA, c 18.070(2) \AA, V 3371 \AA^{3}, Z=4, d_{c} 3.51 \mathrm{~g} \mathrm{~cm}^{-3}, \Gamma(000)-3088, \mu\left(\mathrm{Mo}-K_{\alpha}\right) 236.12$ $\mathrm{cm}^{-1}, 2 \theta$ range $2.0-50.0^{\circ}$, final $R=4.5 \%, R_{w}=5.3 \%$, for 2488 out of 3505 absorption corrected independent reflections ( $I>3 \sigma I$ ), transmission range ( $55-100 \%$ ). Intensity data were collected at room temperature on an Enraf-Nonius CAD 4 diffractometer by $\omega-2 \theta$ scan method; for all calculations the 1985 CRYSTALS user manual was used [7]. A table of atomic coordinates and full list of bond lengths and angles is deposited with the Cambridge Crystallographic Data Centre. Any request should be accompanied by full literature caption for this communication. No attempts were made to determine the absolute structure.

