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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 $[(CO)_{11}Os_3As(Os_3(CO)_9H_3)]$ and $[(CO)_9H_3Os_3As(Os_3(CO)_9H_3)]$. Crystal structure of $[(CO)_{11}Os_3As(Os_3(CO)_9H_3)]$

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Abstract

Reaction of the activated cluster $[Os_3(CO)_{11}(NCMe)]$ with primary arsine AsH₃ forms the arsinidine compound $[H_2Os_3(\mu_3-AsH)(CO)_{11}]$ (1a, 1b), which on further reaction with $[Os_3(CO)_{11}(NCMe)]$ yields $[(CO)_{11}Os_3As(Os_3(CO)_9H_3)]$ (2) and with $[H_2Os_3(CO)_{10}]$ yields $[H_2Os_3(CO)_9As(Os_3(CO)_9H_3)]$ (3). Similarly $[H_2Os_3(CO)_{10}]$ reacts with AsH₃ at room temperature to afford 3 in good yields. Thermal degradation and rearrangement of 2 gives the pentanuclear cluster $[H_2Os_3(CO)_{17}AsH]$ (4).

The reaction of $[Os_3(CO)_{12}]$ with phosphine RPH₂, 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 $[Os_3(CO)_{12-n}(NCMe)_n]$ (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 $[H_2Os_3(CO)_{11}(\mu_3-AsH)]$ (1) consisting of dinuclear $[H_2Os_2(CO)_7]$ and a mononuclear $[HOs(CO)_4]$ unit held together by a μ_3 -AsR ligand, in which the hydride on the $[HOs(CO)_4]$ 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 $[(CO)_{11}Os_3As(Os_3(CO)_9H_3)]$ (2) and $[H_2(CO)_9Os_3As(Os_3(CO)_9H_3)]$ (3).





Scheme 1. Synthesis of $[{H_3Os_3(CO)_9}As{Os_3(CO)_{11}}]$ and $[H_2Os_5(CO)_{18}(AsH)]$.

Compound 1 reacts by oxidative addition to 1.1 equivalents of unsaturated metal fragment of $[Os_3(CO)_{11}(NCMe)]$ in xylene at room temperature to form the linked compound 2. Similarly 1 reacts with 1.1 equivalent of $[H_2Os_3(CO)_{10}]$ to form 3, and $[H_2Os_3(CO)_{10}]$ reacts with primary arsine AsH₃ 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 $[H_2Os_3(CO)_9AsH]$. Compound 2 undergoes thermal degradation and rearrangement to afford $[H_2Os_2(CO)_7(\mu-AsH)(Os_3-(CO)_{11})]$ (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 $[{H_3Os_3(CO)_9(As)}{H_2Os_3(CO)_9}]$.

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
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Formula	Infrared ν (CO), cm ⁻¹ (n-hexane)	¹ H NMR (CD_2Cl_2)
[H ₂ Os ₃ (CO) ₁₁ AsH] (1a, 1b)	2149(w), 2105(m), 2088(m.br), 2069(s), 2054(s), 2029(v.s), 2022(m) 1999(m.s), 1975(m)	$\begin{array}{l} 0.54 \ (dd) \ (J=8.3/3.0 \ Hz) \\ 0.48 \ (dd) \ (J=3.6 \ Hz) \\ -7.21 \ (d) \ (J=3.5 \ Hz) \\ -7.39 \ (d) \ (J=2.9 \ Hz) \\ -9.42 \ (d) \ (J=3.6 \ Hz) \\ -9.75 \ (d) \ (J=8.4 \ Hz) \end{array}$
[H ₃ Os ₆ (CO) ₂₀ As] (2)	2111(w), 2101(m), 2083(m) 2074(w), 2058(s), 2030(v.s) 2022(sh), 2003(m), 1972(w)	- 21.16 (s)
[H ₂ Os ₃ (CO) ₉ AsH]	2125(w), 2093(w), 2068(s) 2054(s), 2035(v.s), 2014(s)	-
[H ₅ Os ₆ (CO) ₁₈ As] (3)	2125(w), 2093(w), 2055(v.s) 2041(sh), 2019(s)	- 11.58 (s) - 20.61 (s)
[H ₂ Os ₅ (CO) ₁₈ 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)

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Fig. 1. The molecular structure of $[(CO)_{11}Os_3As(Os_3(CO)_9H_3)]$ (2) showing the atom numbering scheme. Selected bond lengths: Os(1)–Os(2), 2.963(2); Os(1)–Os(3), 2.969(2); Os(2)–Os(3), 2.969(2); Os(1)–As(1), 2.489(3); Os(2)–As(1), 2.501(3); Os(3)–As(1), 2.486(3); Os(4)–Os(5), 2.887(2); Os(4)–Os(6), 2.841(2); Os(5)–Os(6), 2.874(2); Os(4)–As(1), 2.457(3) Å. Selected bond angles: Os(2)–Os(1)–Os(3), 60.08(5); Os(1)–Os(2)–Os(3), 60.07(5); Os(1)–Os(3)–Os(2), 59.85(4); As(1)–Os(1)–Os(2), 53.77(8); As(1)–Os(1)–Os(3), 53.31(8); As(1)–Os(2)–Os(1), 53.40(8); As(1)–Os(2)–Os(3), 53.22(8); As(1)–Os(3)–Os(1), 53.42(8); As(1)–Os(3)–Os(2), 53.70(8); Os(1)–As(1)–Os(2), 72.83(9); Os(1)–As(1)–Os(3), 73.3(1); Os(2)–As(1)–Os(3), 73.1(1); Os(1)–As(1)–Os(4), 133.1(1); Os(2)–As(1)–Os(4), 133.3(1); As(1)–Os(4)–Os(5), 107.15(9); Os(5)–Os(4)–Os(6), 60.22(5); Os(4)–Os(5)–Os(6), 59.10(4); Os(4)–Os(6)–Os(5), 60.68(4)°.

the average Os-Os bond [2.877 Å] as observed in case of $[Os_3(CO)_{12}]$; however, they are comparable to the four long bonds observed in case of $[H_4Os_4(CO)_{12}]$ [6] [2.963(2)-2.967(2) Å]. 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 Os(1) and 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_{3v} symmetry of the molecule the third hydride is proposed to bridge Os(1)-Os(2). The Os(4)-As(1) bond distance [2.457(3) Å] is slightly shorter than the Os(1)-As, Os(2)-As or Os(3)-As(1) bond [2.489(3) Å,

^{*} Crystal data: $C_{20}H_{3}O_{20}AsOs_{6}$. M = 1779.35, orthorhombic, space group $P2_{1}2_{1}2_{1}$, $a \ 11.407(2)$ Å, $b \ 16.356(2)$ Å, $c \ 18.070(2)$ Å, $V \ 3371$ Å³, Z = 4, $d_{c} \ 3.51$ g cm⁻³, F(000) = 3088, $\mu(Mo-K_{a}) \ 236.12$ cm⁻¹, 2θ range 2.0-50.0°, 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.

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 $[Os_3(CO)_{12}]$. There is no obvious explanation available for the short Os(4)-Os(6) distance.

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