

Preliminary communication

Synthesis of AsMe₂-bridged triosmium clusters: X-ray crystal structures of [Os₃H(CO)₁₁(μ-AsMe₂)] and [Os₃(μ-H)₂(CO)₈(μ-AsMe₂)₂] *

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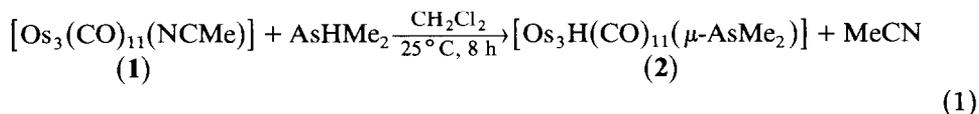
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Abstract

Reactions of the activated clusters [Os₃(CO)_{12-n}(NCMe)_n] (*n* = 1 or 2) with AsHMe₂ give the AsMe₂-bridged triosmium clusters [Os₃(μ-H)(CO)₁₀(μ-AsMe₂)] (**3**) and [Os₃(μ-H)₂(CO)₈(μ-AsMe₂)₂] (**6**), **3** being formed via the novel intermediate [Os₃H(CO)₁₁(μ-AsMe₂)] (**2**) by cleavage and subsequent formation of an Os–Os bond; the X-ray crystal structures of **2** and **6** confirm the presence of μ-AsMe₂ groups.

Compared with the great variety of μ-PR₂-bridged carbonyl clusters, compounds with μ-AsR₂ ligands are surprisingly rare. The few known triosmium clusters containing μ-AsR₂ units have been prepared in low yields by thermolysis of [Os₃(CO)₁₂] in the presence of tertiary arsines AsR₃ [1]. In this communication, we report a high yield synthesis of μ-AsMe₂-bridged triosmium clusters by reaction of the primary arsine AsHMe₂ with the activated clusters [Os₃(CO)_{12-n}(NCMe)_n] (*n* = 1 or 2).

[Os₃(CO)₁₁(NCMe)] (**1**) reacts with AsHMe₂ at room temperature providing the bright yellow cluster [Os₃H(CO)₁₁(μ-AsMe₂)] (**2**), which can be isolated by TLC in greater than 60% yield (eq. 1).



Although **2** can formally be described as a substitution product “Os₃(CO)₁₁-

* Dedicated to Professor Colin Eaborn on the occasion of his 65th birthday.

HAsMe₂”, the spectroscopic data * suggest that the arsine is not coordinated as a terminal ligand via the arsenic lone pair. The chemical shift of $\delta - 7.62$ ppm for the proton in **2** is indicative of a hydride ligand terminally bound to an osmium atom. In the solid state IR spectrum of **2** [2], an absorption at 1914 cm⁻¹ sharpens significantly on cooling to 95 K, and is assigned to the Os–H stretching mode (cf. 1930 cm⁻¹ for the terminal Os–H stretch in [Os₃H₂(CO)₁₁] [3]). The degenerate (OsH) mode is found as a pair of bands at 780 and 772 cm⁻¹; the closeness of these bands rules out any residual As...H interaction.

To establish the molecular geometry of **2**, an X-ray structure analysis was undertaken. The structure ** of **2** is shown in Fig. 1, which includes some important bond parameters. The metals define an open triangle, the long edge of which is bridged by the AsMe₂ ligand. The arsenic atom lies 0.72 Å out of the plane of the Os₃ triangle, and the dihedral angle between the planes defined by Os(1)Os(2)Os(3) and Os(2)Os(3)As(1) is 29.5°. The hydride ligand was not located directly, but the gap in the ligand polyhedron indicates that it is terminal, and occupies an axial site on Os(3) *trans* to C(32)O(32). The long Os...Os edge is somewhat longer than the AsMe₂-bridged edge length of 3.929(5) Å in [Os₃H(CO)₆(C₆H₄)(AsMe₂)] [4]. The two unbridged Os–Os edges in **2** are significantly longer than the average value of 2.877(3) Å found in [Os₃(CO)₁₂] [5], and are more in keeping with the range of values (2.917(1)–2.947(2) Å) observed in the open

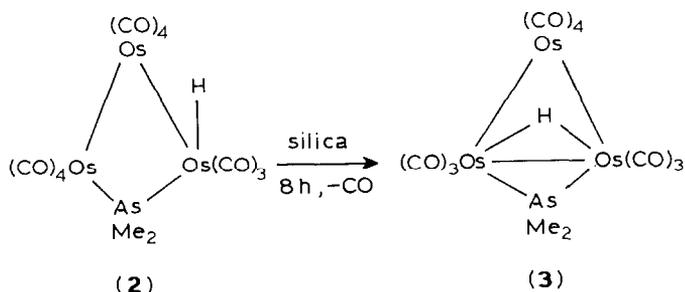
* Spectroscopic and analytical data (IR in hexane; ¹H NMR in CDCl₃ unless otherwise stated): **2** ν (CO): 2118w, 2078s, 2053m, 2047s, 2035vs, 2016m, 2011m, 1992m, 1977m cm⁻¹; ν (OsH) [Csl]: 1914m cm⁻¹, δ (OsH) [Csl]: 780m, 772m cm⁻¹; ¹H NMR: 2.04 (s, CH₃), 1.91 (s, CH₃), -7.62 (s, OsH) ppm; *M*⁺: *m/z* 990 (calc. (¹⁹²Os) for [Os₃H(CO)₁₁AsMe₂]); 990. Anal.: found: C, 15.92; H, 0.78 (calc.: C, 15.86; H, 0.72%). **3** ν (CO): 2102w, 2057vs, 2050m, 2022s, 2006m, 1989m, 1978w cm⁻¹; ¹H NMR: 2.18 (s, CH₃), 1.73 (s, CH₃), -18.94 (s, OsH) ppm; *M*⁺: *m/z* 962 (calc. (¹⁹²Os) for [Os₃H(CO)₁₀AsMe₂]); 962; Anal.: found: C, 14.91; H, 1.10 (calc. C, 15.06; H, 0.74%). **5** ν (CO) [toluene]: 2100w, 2025m, 2008s, 1997vs, 1958m cm⁻¹; **6** ν (CO): 2077m, 2040s, 2022vs, 2004s, 1975m, 1962w cm⁻¹; δ (OsH) [Csl] 725m (as), 715m (s) cm⁻¹; ¹H NMR: 2.07 (s, CH₃), 1.91 (s, CH₃), -18.91 (s, OsH) ppm; *M*⁺: *m/z* 1012 (calc. (¹⁹²Os) for [Os₃H₂(CO)₈(AsMe₂)₂]); 1012; Anal.: found: C, 14.13; H, 1.34 (calc. C, 14.31; H, 1.40%).

** *Crystal data for 2*. C₁₃H₇AsO₁₁Os₃, *M* = 984.71, monoclinic, space group *P*2₁/*c* (No. 14), *a* 14.020(3), *b* 9.219(1), *c* 15.803(2) Å, β 96.55(1)°, *V* 2029.2 Å³, *D*_c 3.222 g cm⁻³, *Z* = 4, *F*(000) = 1736, λ (Mo-*K* α) 0.71069 Å, μ (Mo-*K* α) 203.98 cm⁻¹. Yellow multifaceted blocks, crystal dimensions: 0.10 × 0.20 × 0.22 mm. 2980 data measured on a Stoe-Siemens four-circle diffractometer (5.0 ≤ 2 θ ≤ 45.0°), corrected for absorption, 2102 unique observed reflections with $|F_o| > 4\sigma(F_o)$. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least squares with all non-hydrogen atoms assigned anisotropic thermal parameters. The weighting scheme employed was 1.113/[$\sigma^2(F_o) + 0.001F_o^2$]. The final residuals were *R* = 0.056 and *R*_w = 0.055. *Crystal data for 6*. C₁₂H₁₄As₂O₈Os₂, *M* = 1006.67, triclinic, space group *P* $\bar{1}$ (No. 2), *a* 8.777(1), *b* 9.724(1), *c* 14.147(1) Å, α 70.61(1), β 76.74(1), γ 66.99(1)°, *V* 1041.4 Å³, *D*_c 3.209 g cm⁻³, *Z* = 2, *F*(000) = 888, λ (Mo-*K* α) 0.71069 Å, μ (Mo-*K* α) 214.35 cm⁻¹. Yellow platelets, crystal dimensions: 0.14 × 0.19 × 0.26 mm. 3220 data measured on a Stoe-Siemens four-circle diffractometer (5.0 ≤ 2 θ ≤ 47.5°), corrected for absorption, 2685 unique observed reflections with $|F_o| > 4\sigma(F_o)$. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least squares, with Os, As, and O atoms assigned anisotropic thermal parameters. The weighting scheme employed was 2.164/[$\sigma^2(F_o) + 0.001F_o^2$]. The final residuals were *R* = 0.050 and *R*_w = 0.053. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

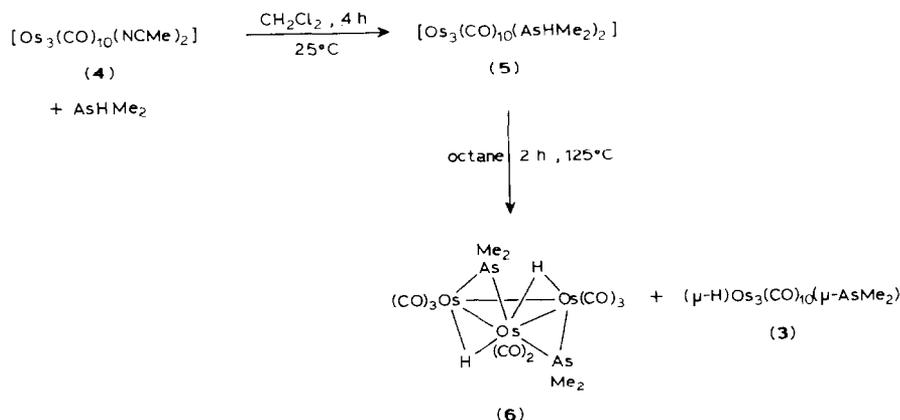
triangular framework in $[\text{Os}_3(\text{CO})_{11}(\text{C}_3\text{H}_4)]$ [6]. The $\text{Os}(3)\text{--Os}(1)\text{--Os}(2)$ angle is also similar to that of $82(1)^\circ$ found for the equivalent parameter in $[\text{Os}_3(\text{CO})_{11}(\text{C}_3\text{H}_4)]$ [6]. The bridging AsMe_2 group shows some asymmetry, with the shorter $\text{Os}\text{--As}$ distance associated with the osmium atom which is also coordinated to the terminal hydride ligand. This shorter bond lengths is similar to the average value of $2.483(4)$ Å for the symmetric AsMe_2 bridging group in $[\text{Os}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_4)(\text{AsMe}_2)]$ [4]. The $\text{Os}(3)\text{--As}(1)\text{--Os}(2)$ angle in **2** corresponds more closely to the idealised tetrahedral angle than does the equivalent angle of $104.6(2)^\circ$ in the benzyne complex.

When the opened cluster (**2**) is adsorbed onto silica TLC plates and exposed to light, it is readily converted in greater than 90% yield with loss of CO, to the hydrido-arsenido-bridged compound $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-AsMe}_2)]$ (**3**), which is characterised by its spectroscopic and analytical data:

The $\nu(\text{CO})$ bands in the IR spectrum of **3** are very similar to those observed for the corresponding phosphido cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-PR}_2)]$ [7].



The reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ (**4**) with AsHMe_2 in CH_2Cl_2 affords in a first step the cluster $[\text{Os}_3(\text{CO})_{10}(\text{AsHMe}_2)_2]$ (**5**), which has not been isolated. Its IR spectrum indicates the presence of a simple substitution product of the type $[\text{Os}_3(\text{CO})_{10}\text{L}_2]$, and rules out a structure similar to that of **2** with a cleaved $\text{Os}\text{--Os}$ bond. Thermolysis of (**5**) in boiling octane gives the doubly- AsMe_2 -bridged cluster $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_8(\mu\text{-AsMe}_2)_2]$ (**6**) in 35% yield and the singly- AsMe_2 -bridged compound $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-AsMe}_2)]$ (**3**) as a minor product (8% yield) (Scheme 1).



Scheme 1.

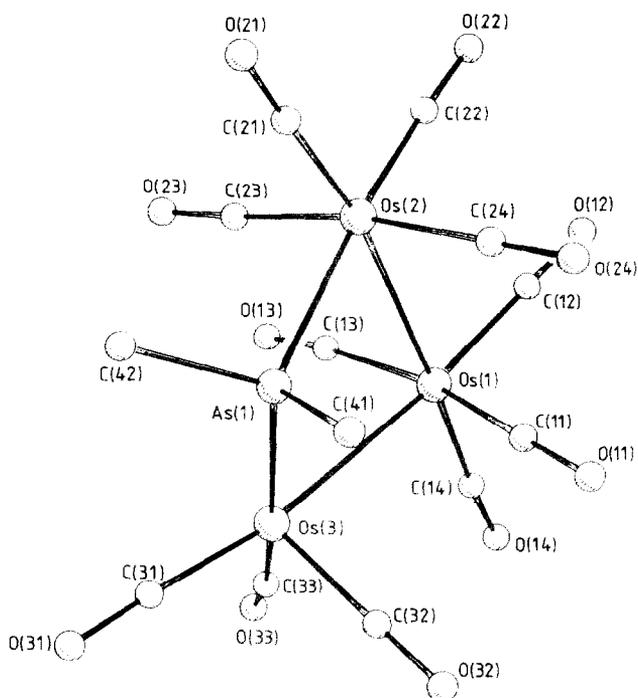


Fig. 1. The molecular structure of $[\text{Os}_3\text{H}(\text{CO})_{11}(\mu\text{-AsMe}_2)]$ (**2**). Selected bond parameters are: Os(2)–Os(1), 2.982(1); Os(3)–Os(1), 2.951(1); Os(3)–Os(2), 4.072(1); As(1)–Os(2), 2.523(2); As(1)–Os(3), 2.480(3) Å; Os(3)–Os(1)–Os(2), 86.7(1); As(1)–Os(2)–Os(1), 78.4(1); As(1)–Os(3)–Os(1), 79.6(1); Os(3)–As(1)–Os(2), 109.0(1)°.

In order to confirm the spectroscopic assignment, an X-ray analysis of **6** was carried out, and the structure is shown in Fig. 2, together with some important bond parameters. The molecule is isostructural with the phosphido-bridged analogues $[\text{M}_3(\mu\text{-H})_2(\text{CO})_8(\mu\text{-PPh}_2)_2]$ (Me = Fe, Ru or Os) [8], with two edges of the closed-Os₃ triangle bridged by both hydride and AsMe₂ ligands, and with the two AsMe₂ groups lying on opposite sides of the trimetal plane. The dihedral angles between the Os(1)Os(2)Os(3) plane and the Os(1)Os(2)As(1) and the Os(2)Os(3)As(2) planes are 67.8° and 112.4°, respectively. In the case of **6**, the bridging hydrides were not located directly, but the distribution of carbonyl ligands is consistent with them bridging the Os(1)–Os(2) and Os(2)–Os(3) edges. As with the phosphido cluster $[\text{Os}_3\text{H}_2(\text{CO})_8(\mu\text{-PPh}_2)_2]$ [8], the unbridged Os(1)–Os(3) edge in **6** is significant longer than the average value of 2.923(2) Å for the two bridged edges. However, a detailed comparison shows that the Os(1)–Os(3) distance is ca. 0.02 Å shorter than the value of 2.960(1) Å in the phosphido cluster and the bridged Os(1)–Os(2) and Os(2)–Os(3) edges are ca. 0.03 Å longer than the average distance of 2.890(3) Å in the lighter analogue [8]. This presumably reflects the fact that while for each “Os₂HP” and “Os₂HAS” unit electrons are entering molecular orbitals which are metal–metal bonding in character, the larger steric requirement of the bridgehead arsenic atom prevents a shorter Os–Os contact. In **6**, the Os–As–Os bridges show asymmetry, with the shorter Os–As distance associated with Os(2), which is

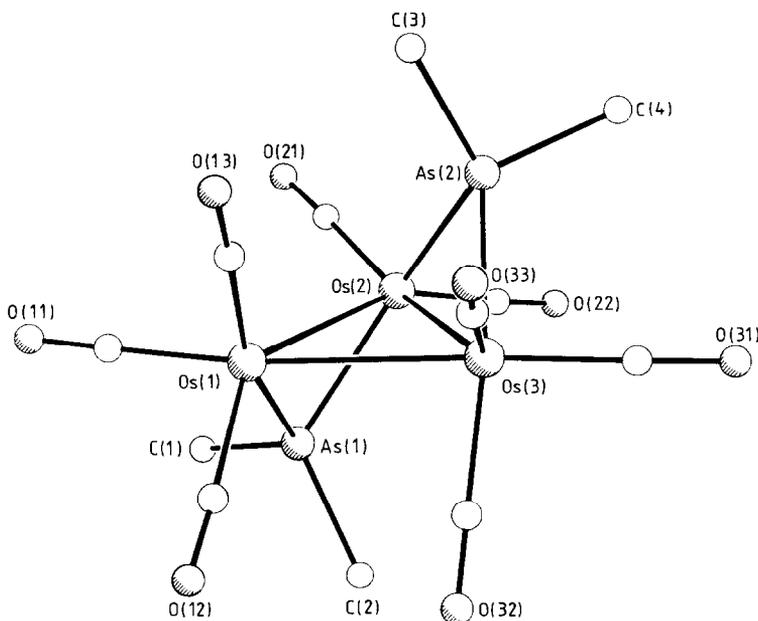


Fig. 2. The molecular structure of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_8(\mu\text{-AsMe}_2)_2]$ (**6**). Selected bond parameters are: Os(2)–Os(1), 2.920(1); Os(3)–Os(1), 2.943(1); Os(3)–Os(2), 2.926(1); As(1)–Os(1), 2.502(2); As(1)–Os(2), 2.428(2); As(2)–Os(2), 2.428(2); As(2)–Os(3), 2.501(2) Å; Os(3)–Os(1)–Os(2), 59.9(1); Os(3)–Os(2)–Os(1), 60.4(1); Os(2)–Os(3)–Os(1), 59.7(1); Os(2)–As(1)–Os(1), 72.6(1); Os(3)–As(2)–Os(2), 72.8(1)°.

coordinated to both hydrides and both AsMe_2 groups. The range of Os–As distances in **6** (2.428(2)–2.502(1) Å) is greater than that observed in **2** (2.480(3)–2.532(2) Å), but a range of 0.07 Å is also observed for the Os–P distances (2.341(3)–2.413(2) Å) in $[\text{Os}_3\text{H}_2(\text{CO})_8(\mu\text{-PPh}_2)_2]$ [8].

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