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Preliminary communication

$Os_3(CO)_9(\mu_3\text{-}AsC_6H_4CH_3)(\mu_3\text{-}C_6H_3CH_3)$ synthesis and crystal structure

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Abstract

One of the products of the reaction of the activated cluster $Os_3(CO)_{11}(NCMe)$ with As(*p*-tol)$_3$ in refluxing nonane has been shown by spectroscopic and X-ray crystallographic methods to be $Os_3(CO)_9(\mu_3\text{-}AsC_6H_4CH_3)(\mu_3\text{-}C_6H_3CH_3)$, which contains a benzyne moiety bonded asymmetrically from one carbon to one osmium via a σ bond and from a second carbon to form a bridge between the remaining two osmium atoms.

Triosmium clusters containing both μ_3-PR and μ_3-C_6H_4 units have been previously reported [1] but no corresponding osmium-arsenic clusters are known. In this report we present brief details of the synthesis and full characterisation of the new benzyne cluster $Os_3(CO)_9(\mu_3\text{-}AsC_6H_4CH_3)(\mu_3\text{-}C_6H_3CH_3)$ (**1**), which contains such units.

The reaction of $Os_3(CO)_{11}(NCMe)$ with one equivalent of As(*p*-tol)$_3$ in nonane at 150 °C for 1 h resulted in the formation of the air stable yellow compound **1**, which after purification by TLC was obtained in ca. 70% yield. Compound **1** was fully characterised by the usual spectroscopic techniques and single crystal X-ray analysis. The IR for **1** in hexane shows bands at 2085(w), 2065(vs), 2042(vs), 2011(vs), 2004(s), 1994(s), 1990(s), 1972(m) and 1919(m) cm^{-1} in the carbonyl region. The ^1H NMR data showing signals at δ 2.02(s, CH_3), δ 2.42(s, CH_3), δ 6.62(d-d, H^b), δ 7.15(s, H^a), δ 7.26(d, As-tol), δ 7.50(d, As-tol) and δ 7.96(d, H^c) are observed, and the microanalytical data (C, 25.41% and H, 1.02%) are consistent with the structural characterisation of compound **1** see Fig. 1.

The molecular structure of **1**, (Fig. 2) was established by a single crystal X-ray crystallographic study. The metal atom framework can be described as an "open"

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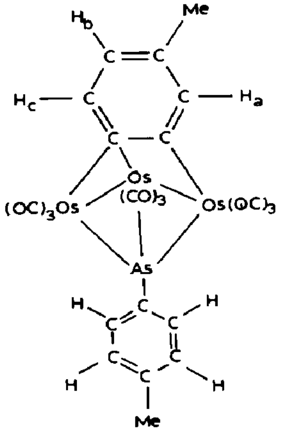


Fig. 1. Structural characterisation of compound **1**.

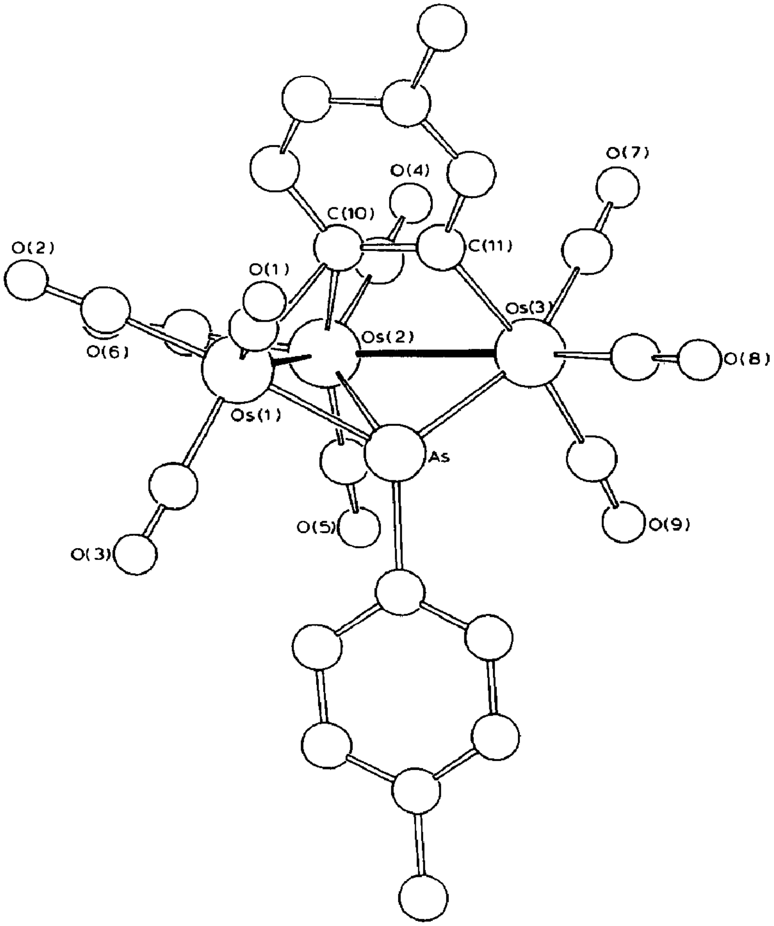
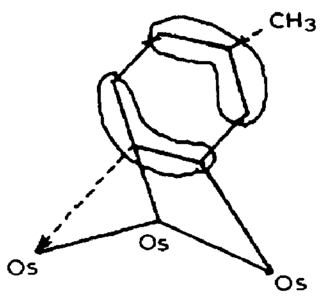


Fig. 2. Perspective view of compound **1**.



Scheme 1.

Os-triangle (open edge 4.110 Å), which bears on opposite sides a μ_3-As(p-tol) and a μ_3-($C_6H_3CH_3$) ligand. Each Os atom also bears three terminally bound CO ligands. The structure of **1** * is closely related to that of [$Os_3(CO)_9(C_6H_4)(PC_2H_5)$] [1], which contains a similarly bound benzyne ligand. As previously noted, the description of the bonding mode of the organic moieties in **1** and in the corresponding phosphorous species is problematical. If the As(p-tol) entity is regarded as a four-electron donor, then to make a total of 50 valence electrons for an electron precise open triangle the tolyl ligand is required to supply four electrons to the cluster orbitals. Rather than invoking the contribution of two non-equivalent (4-electron or 2-electron donations) ligands to cluster interaction [1], the bonding mode may be described as the result of two σ-interaction [Os(2)–C(10), Os(3)–C(11)] and of a π-interaction between Os(1) and a molecular orbital of appropriate symmetry of the $C_6H_3CH_3$ ligand (see scheme 1).

It is noteworthy that this interaction is not directed towards the mid point of a C–C bonds in the $C_6H_3CH_3$ ligand, but toward a C atom (C(10)) of the ring, and that the Os(1)–C(10) axis is almost orthogonal (97°) to the ligand plane.

The lengthening of all C–C bonds involving the metal-bound C atom (average 1.42(1) Å) with respect to those between the other C atoms of the ring (average 1.38(1) Å) is an indication that the bonding interaction is delocalised over a molecular orbital of the ligand. Furthermore the Os–C(tol) bond lengths are not equivalent. The Os(1)–C(10) bond length (2.323(8) Å) is much longer than the other two, with Os(2)–C(10) (2.191(8) Å) and Os(3)–C(11) (2.113(8) Å). The three Os–As bond lengths are also inequivalent, and span the range 2.406(1) to 2.542(1) Å. The Os–Os bonds are also different, with the one bridged by the C(10)–C(11) system longer (2.936(1) Å) than the other (2.807(1) Å). A similar bond length distribution was observed in [$Os_3(CO)_9(C_6H_4)(PC_2H_5)$] [1]. Altogether it seems that the bonding description of **1** in terms of electron localisation is not appropriate and rather

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* *Crystal data*: $C_{23}H_{13}AsO_9Os_3$
$M = 1084$, monoclinic, space group $P2_1/n$, $a = 13.178(8)$ Å, $b = 11.71(1)$ Å, $c = 16.787(6)$ Å, $\beta = 98.41(4)°$, $U = 2562.0$ Å^3, $Z = 4$, $D_c = 2.81$ gcm^{-3}, $F(000) = 1935$, μ(Mo-K_α) = 155.0 cm^{-1}, θ range 2.5-25°, final R value 2.77%, $R_w = 2.87$% for 3638 out of 3763 absorption corrected independent reflections [$F_o > 4\sigma(F_o)$] transmission range (28–100%). Intensity data were collected at room temperature on an Enraf-Nonius CAD 4 diffractometer by the w-2θ scan method; for all calculations the SHELX 76 [2] package of crystallographic programs was used. A table of atomic coordinates and a full list of bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.

extensive orbital reorganisation of all molecular components is most certainly required in order to achieve even electronic distribution over the three metal centres.

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References

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2 SHELX 76 by G.M. Sheldrick, University of Cambridge, 1976.