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The thermolysis products of $Os_3(CO)_{11}(AsPh_3)$

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Abstract

Thermolysis of the substituted triosmium cluster $Os_3(CO)_{11}(AsPh_3)$ in refluxing nonane gave four major products: $Os_3(\mu_3\text{-}AsPh)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9$, $Os_3(\mu\text{-}H)(\mu\text{-}AsPh_2)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9$, $Os_3(\mu\text{-}AsPh_2)_2(\mu_3,\eta^2\text{-}C_6H_4)(CO)_7$ and $Os_3(\mu_3\text{-}AsPh)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_8(AsPh_3)$. All the new clusters have been characterised by spectroscopy and single-crystal X-ray crystallographic studies. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Osmium; Arsenic; Clusters

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1. Introduction

The direct reaction between $Os_3(CO)_{12}$ and $AsPh_3$ resulted in mainly the substituted derivatives [1]. Deeming and coworkers demonstrated that controlled thermolyses through the use of $Os_3(CO)_{11}(AsMe_2Ar)$ (where Ar is an aryl group) gave as the major product the clusters $Os_3(\mu\text{-}H)(\mu\text{-}AsMe_2)(\mu_3,\eta^2\text{-aryne})(CO)_9$ [2]. In contrast, the reaction of $Os_3(CO)_{11}(CH_3CN)$ with $As(p\text{-tolyl})_3$ in refluxing nonane, which presumably proceeded via $Os_3(CO)_{11}[As(p\text{-tolyl})_3]$, was reported to give a 70% yield of the cluster $Os_3(\mu_3\text{-}AsC_6H_4Me\text{-}p)(\mu_3,\eta^2\text{-}C_6H_3Me)(CO)_9$ (**2a**) [3]. This cluster is structurally interesting in at least two aspects: (i) it possesses a μ_3-arsenidyne moiety, and (ii) the C_6H_3Me moiety is in a rather uncommon μ_3,η^2 perpendicular (⊥) bonding mode. Our original intention was to carry out a similar thermolysis of the cluster $Os_3(CO)_{11}(AsPh_3)$ (**1**) with the expectation that it would lead to either $Os_3(\mu_3\text{-}AsPh)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9$ (**2**) or $Os_3(\mu\text{-}H)(\mu\text{-}AsPh_2)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9$ (**3**).

2. Results and discussion

The thermolysis of **1** in refluxing nonane for 40 min gave four major products: **2**, **3**, $Os_3(\mu\text{-}AsPh_2)_2(\mu_3,\eta^2\text{-}C_6H_4)(CO)_7$ (**4**) and $Os_3(\mu_3\text{-}AsPh)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_8(AsPh_3)$ (**5**) (Scheme 1). The X-ray structures of all four products have been determined (Figs. 1–4, Table 1) and some relevant bond parameters are collected in Table 2.

The isolation of these four products from the thermolysis is rather unexpected, as the result with the *p*-tolyl analogue would seem to suggest that **2** should be the major species; the work of Deeming and coworkers [2] implied that **3** would likely be formed only in substantial amount by replacement of two of the aryls on arsenic by methyl groups. Furthermore, clusters analogous to **4** and **5** were only reported for the thermolysis of the disubstituted analogue of **1** [2,3]. However, as has been suggested, loss of $AsPh_3$ is probably quite facile and in competition with CO loss during the thermolysis of **1** [2b]; that may account for the formation of **4** and **5**, which may also be regarded as derivatives of **3** and **2**, respectively.

The structures of the *p*-tolyl analogues of **2** and **5**, viz. **2a** and **5a**, respectively, have been reported [3]. Since **5** (or **5a**) is an arsine-substituted derivative of **2** (or **2a**), one may expect to be able to make a comparison between them and obtain some information on the effect of arsine substitution on structural parameters. For instance, it appears that arsine substitution lengthens the Os(1)–C(1) bond (mean of 2.34(1) Å in **2** versus 2.406(6) Å in **5**) and shortens the Os(1)–Os(2) bond (mean of 2.822(1) Å in **2** versus 2.8089(4) Å in **5**); the former is not apparent in a comparison of **2a** with **5a**

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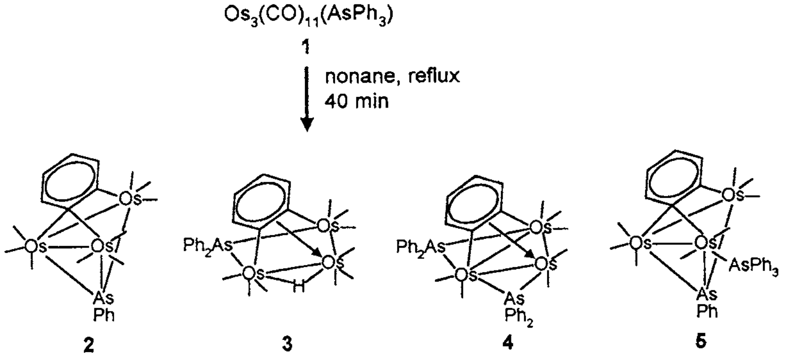

Scheme 1. Thermolysis of **1** in refluxing nonane.

because of the large estimated e.s.d.s associated with the bond parameters in **5a**. Similarly, the structure of the AsMe$_2$ analogue of **3**, viz. $Os_3(\mu\text{-}H)(\mu\text{-}AsMe_2)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9$ (**3a**), has also been reported [4]. The bond parameters in **3** and **3a** are quite similar; the major statistically significant difference is in the longer Os–Os bond lengths (2.946(4) Å and 2.9268(5) Å in **3** and **3a**, respectively), which are presumably bridged by the hydride.

Cluster **4** is the first of its kind that has been structurally characterised; the most closely related structure is that of $Os_3(\mu\text{-}H)_2(\mu\text{-}AsMe_2)_2(CO)_8$ (**4a**) [5]. Cluster **4** has the benzyne in a $\mu_3,\eta^2,\|$ bonding mode. The Os$_3$As$_2$ core is a slightly puckered 'raft'; the dihedral angle between the Os(1)Os(2)As(4) and the Os(1)Os(2)Os(3) planes is 167.0°, and that between the Os(1)Os(3)As(5) and the Os(1)Os(2)Os(3) plane is 157.6°. This is in sharp contrast to that of **4a**, in which the AsMe$_2$ units clearly lie out of the plane of the Os$_3$ unit, one above and one below; the corresponding dihedral angles are 67.8° and 112.4°. The Os(1)–Os(3) bond length, at 2.7737(4) Å, is the shortest observed in any osmium–Group 15 cluster to date [6]. Another notable structural feature of **4** is the presence of a semibridging carbonyl; the Os(1)···C(33) distance is 2.72(1) Å and the ∠Os(3)C(33)O(33) is 165.9(8)°, compared with the analogous Os(1)···C(31) distance of 3.48(1) Å and ∠Os(3)C(33)O(33) of 177(1)° in **3**. This is a relatively uncommon feature in osmium cluster chemistry.

The $\mu_3,\eta^2,\perp$ bonding mode of the aryl ring in **2a** and **5a** has been discussed at length [3]. The unusual bonding mode has been ascribed to two σ-type Os–C bonds and a π interaction between one of the osmium atoms with a molecular orbital of the aryl ring. In support of this, two structural points were brought up: (i) the almost orthogonality of one of the Os–C bonding vectors with the aryl ring plane (97° and 98° for **2a** and **5a**, respectively), and (ii) lengthening of the two C–C bonds from the μ_2-C in the aryl rings (mean of 1.42(1) Å and 1.45(6) Å, in **2a** and **5a**, respectively) compared with the other C–C bond lengths of the ring (mean of 1.38(1) Å and 1.39(6) Å, in **2a** and **5a**, respectively). Examination of the structural parameters for **2** and **5** shows that the corresponding Os–C bonding vectors (Os(11)–C(101) and Os(21)–C(201) for the two crystallographically distinct molecules in **2**, and Os(1)–C(1) in **5**) deviate quite significantly from being orthogonal to the $\mu_3,\eta^2,\perp$-C$_6$H$_4$ ring planes (69.0°, 70.3° and 60.7°, respectively). In fact, these angles are not very different from the corresponding ones observed in **3** and **4**, which have $\mu_3,\eta^2,\|$-C$_6$H$_4$ rings; the dihedral angle between the

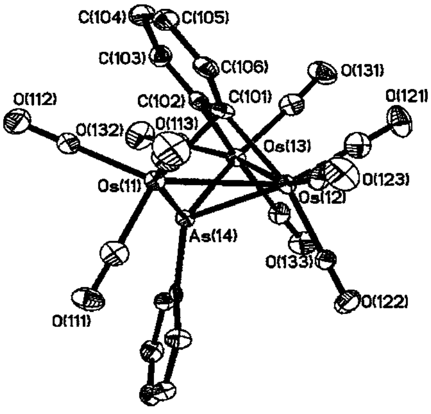

Fig. 1. ORTEP diagram (50% thermal ellipsoids) for cluster **2** (H atoms omitted).

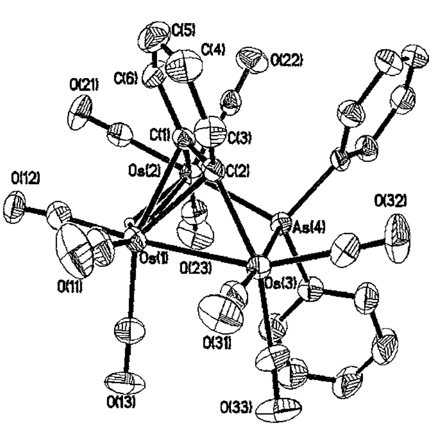

Fig. 2. ORTEP diagram (50% thermal ellipsoids) for cluster **3** (organic H atoms omitted).

Table 1
Crystal data for clusters **2**–**5**

Compound	**2**	**3**	**4**	**5**
Colour	Red	Orange	Red	Orange
Crystal dimensions (mm^3)	0.40 × 0.40 × 0.24	0.28 × 0.26 × 0.25	0.13 × 0.10 × 0.08	0.26 × 0.16 × 0.09
Empirical formula	$C_{21}H_9AsO_9Os_3$	$C_{27}H_{15}AsO_9Os_3$	$C_{37}H_{24}As_2O_7Os_3 \cdot 0.5CH_2Cl_2$	$C_{38}H_{24}As_2O_8Os_3 \cdot 0.5CH_2Cl_2$
Formula weight	1050.80	1128.91	1343.46	1371.47
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$	*Pcca*	*C*2/*c*	$P\bar{1}$
a (Å)	8.9970(1)	35.6726(6)	17.7009(3)	10.9584(3)
b (Å)	15.7332(1)	10.2100(2)	11.0998(2)	12.0629(3)
c (Å)	17.3937(2)	15.7995(2)	38.3661(1)	14.6713(4)
α (°)	92.170(1)	90	90	86.069(1)
β (°)	91.920(1)	90	95.124(1)	89.000(1)
γ (°)	106.336(1)	90	90	89.931(1)
Volume (Å^{-3})	2358.51(4)	5754.45(17)	7507.91(19)	1934.54(9)
Z	4	8	8	2
μ (mm^{-1})	17.564	14.407	11.997	11.645
Reflections collected	17 691	44 357	47 811	17 733
Independent reflections (R_{int})	11 154 (0.0390)	7295 (0.0706)	9366 (0.0447)	9204 (0.0343)
Completeness (%) to (2θ°)	86.2 (58.66)	92.1 (58.74)	89.2 (59.02)	88.1 (58.36)
Final R [$I>2\sigma(I)$]	0.0379	0.0513	0.0469	0.0380
wR_2 (all data)	0.0988	0.1083	0.0732	0.0932

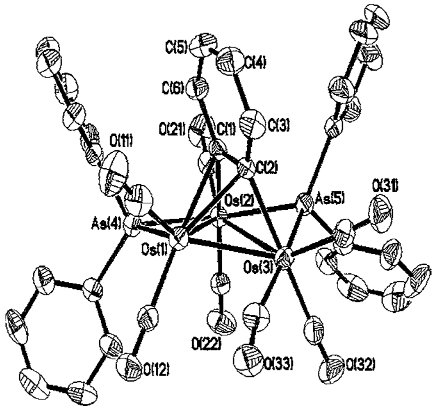

Fig. 3. ORTEP diagram (50% thermal ellipsoids) for cluster **4** (H atoms omitted).

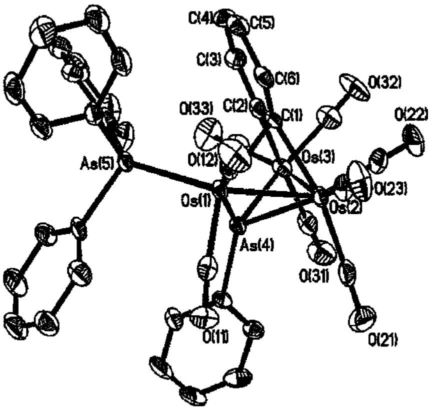

Fig. 4. ORTEP diagram (50% thermal ellipsoids) for cluster **5** (H atoms omitted).

Table 2
Selected bond lengths (Å) for clusters **2**–**5**

	2[a]	**3**	**4**	**5**
Os(1)–Os(2)	2.8208(4); 2.8222(4)	2.9268(5)	2.8109(4)	2.8089(4)
Os(1)–Os(3)	–	2.8397(5)	2.7737(4)	–
Os(2)–Os(3)	2.9572(4); 2.9607(5)	–	–	2.9728(4)
Os(1)–As(4)	2.4532(8); 2.4464(9)	–	2.3821(8)	2.4739(7)
Os(2)–As(4)	2.5278(8); 2.5364(9)	2.4950(10)	2.4489(8); 2.4204(8)[b]	2.5730(7)
Os(3)–As(4)	2.4079(8); 2.4132(9)	2.4869(10)	2.4891(8)[c]	2.4312(7)
Os(1)–C(1)	2.339(8); 2.344(9)	2.310(9)	2.369(7)	2.406(6)
Os(2)–C(1)	2.162(9); 2.175(8)	2.172(9)	2.151(7)	2.175(7)
Os(3)–C(2)	2.113(8); 2.111(8)	2.129(9)	2.172(7)	2.126(7)
Os(1)–C(2)	–	2.371(9)	2.279(7)	–
C(1)–C(2)	1.455(11); 1.411(12)	1.434(13)	1.430(10)	1.441(9)
C(2)–C(3)	1.384(12); 1.396(11)	1.457(13)	1.400(10)	1.390(10)
C(3)–C(4)	1.428(14); 1.408(13)	1.331(16)	1.384(11)	1.384(10)
C(4)–C(5)	1.401(14); 1.393(14)	1.415(17)	1.399(12)	1.392(10)
C(5)–C(6)	1.371(13); 1.371(13)	1.367(16)	1.358(10)	1.396(10)
C(6)–C(1)	1.424(12); 1.440(12)	1.453(13)	1.434(10)	1.422(9)

[a] Two molecules in the asymmetric unit.

[b] Os(2)–As(5).

[c] Os(3)–As(5).

Os(1)C(1)C(2) plane and the C_6H_4 ring plane is 58.2° and 61.0° for **3** and **4**, respectively. Although the C–C bond lengths around the C_6H_4 rings in **2** and **5** show, on the whole, the trend observed in **2a** and **5a**, there are some (notably the C(3)–C(4) bond in **2**) that do not. In our mind, these observations indicate that the $\parallel$ and $\perp$ modes of the μ_3,η^2-C_6H_4 ring probably do not represent significantly different involvements of the molecular orbitals of the ring.

A comparison of the structures discussed here indicates that the $\mu_3,\eta^2,\perp$ bonding mode for the C_6H_3R (R = H or Me) ring is associated with a μ_3-AsR group, whereas the more common $\mu_3,\eta^2,\parallel$ bonding mode is associated with the μ_2-AsR_2 group; this observation has also been made elsewhere [7]. In both bonding modes, the aryne cluster may be regarded as a phenylene complex, i.e. an $Os_2(\eta^2$-$C_6H_3R)$ group, with a further two-electron donation to the third osmium. This is reflected in one of the Os–C distances being significantly longer than the other two in the $\perp$ case (ranges of 2.31–2.41 Å and 2.07–2.19 Å, respectively, for **2**, **2a**, **5**, and for **5a**), and the longer Os–C distances to the unique Os atom compared with the other two in the $\parallel$ case (ranges of 2.28–2.39 Å and 2.13–2.20 Å, respectively, for **3**, **3a** and **4**). A phenylene may be expected to place some strain on the Os–Os bond on which it straddles, causing lengthening of the bond as a result of the geometrical constraint placed by the sp^2 hybridisation at the ring carbon atoms. This is observed to be so in the clusters discussed here, as the phenylene-bridged bonds are all above ca. 2.928 Å, whereas the other Os–Os bonds are all below ca. 2.840 Å (except for the hydride-bridged bond in **3**). The difference between the two bonding modes may thus be regarded as a reflection of the symmetry or asymmetry of the aryne in its interaction with the third osmium.

However, although the bonding interaction between an aryne and a metal cluster does not appear to have been studied with theoretical tools, it seems reasonable to expect that it may be adequately described by the better-studied alkyne–cluster interaction [8]. In that system, increased π back-bonding from the metal cluster to the alkyne/aryne is expected to favour the $\perp$ mode. In the clusters with a μ_2-AsR_2 group, the aryne is trans to a number of carbonyl ligands, which compete for back-bonding electron density from the same metal orbitals. On the other hand, in the clusters containing a μ_3-AsR group, the carbonyls that are trans to the aryne are replaced by the weaker π-acceptor μ_3-AsR group. It may, therefore, be argued that the latter situation results in enhanced back-bonding into the aryne, thus accounting for the observed difference in the aryne bonding mode.

3. Experimental

All reactions and manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried, distilled, and kept under nitrogen prior to use. Thin-layer chromatography (TLC) separation was carried out on Merck 20 × 20 cm^2 plates coated with silica gel 60 of 0.25 mm thickness. Routine NMR spectra were recorded as $CDCl_3$ solutions on a Bruker ACF300 NMR spectrometer and IR spectra as hexane solutions in solutions cell with 0.1 mm pathlengths and NaCl windows. FAB mass spectra were obtained on a Finnigan MAT95XL-T spectrometer with an *m*-nitrobenzyl alcohol matrix. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. Cluster **1** was prepared from the reaction of $AsPh_3$ with $Os_3(CO)_{11}(CH_3CN)$.

3.1. Thermolysis of 1

Cluster **1** (112 mg, 95 mmol) was refluxed in nonane (20 ml) until the colour of the solution changed from bright yellow to orange (ca. 40 min). Removal of the solvent and volatiles in vacuo and TLC separation (hexane/CH_2Cl_2, 95/5, v/v as mobile phase) of the residue gave five major bands, in order of elution as follows: $Os_3(\mu_3$-AsPh$)(\mu_3,\eta^2$-$C_6H_4)(CO)_9$ (**2**) (yield: 22 mg, 22%), $Os_3(\mu$-H$)(\mu$-$AsPh_2)(\mu_3,\eta^2$-$C_6H_4)(CO)_9$ (**3**) (yield: 21 mg, 20%), unreacted **1**, $Os_3(\mu$-$AsPh_2)_2(\mu_3,\eta^2$-$C_6H_4)(CO)_7$ (**4**) (yield: 13 mg, 11%) and $Os_3(\mu_3$-AsPh$)(\mu_3,\eta^2$-$C_6H_4)(CO)_8(AsPh_3)$ (**5**) (yield: 16 mg, 13%).

3.2. Analytical data

Analytical data for **2**. Found: C, 24.38; H, 0.99. Calc. for $C_{21}H_9AsO_9Os_3$: C, 24.00; H, 0.86%. *ν*(CO): 2066vs, 2043s, 2012s, 2006ms, 1996m, 1991m, 1982w, 1973w cm^{-1}; δ_H 7.7–7.1 (m, Ph); $M^+ = 1049.6$ (observed), 1052 (calculated).

Analytical data for **3**. Found: C, 28.72; H, 1.45. Calc. for $C_{27}H_{15}AsO_9Os_3$: C, 28.73; H, 1.34%. *ν*(CO, hexane): 2095w, 2073vs, 2046s, 2036w, 2023m, 2013m, 2005m, 1989w, 1972w cm^{-1}; δ_H 7.6–7.0 (m, Ph), −15.5 (s, OsHOs); $M^+ = 1129.8$ (observed), 1130 (calculated).

Analytical data for **4**. Found: C, 34.28; H, 1.85. Calc. for $C_{37}H_{24}As_2O_7Os_3$: C, 34.16; H, 1.86%. *ν*(CO, hexane): 2055m, 2006m, 1994sh, 1990vs, 1948m,br cm^{-1}; δ_H 7.6–7.3 (m, Ph); $M^+ = 1301.9$ (observed), 1302 (calculated).

Analytical data for **5**. Found: C, 33.64; H, 1.73. Calc. for $C_{38}H_{24}As_2O_8Os_3 \cdot \frac{1}{2}CH_2Cl_2$: C, 33.72; H, 1.84%. *ν*(CO, hexane): 2071s, 2039vs, 2007vs,br, 1975mw, 1963mw, 1943w cm^{-1}; δ_H 7.5–7.1 (m, Ph); $M^+ = 1329.8$ (observed), 1330 (calculated).

The presence of CH_2Cl_2 in the crystals of **4** and **5** were confirmed by ^{1}H-NMR.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 151648–151651. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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