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**Synthesis and X-ray crystal structures
of $\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)$
and $\text{Os}_3(\text{CO})_8(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)\text{As}(p\text{-tol})_3$.
 ^{13}C and ^1H NMR spectroscopic studies**

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Abstract

The clusters $\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)$ (1) and $\text{Os}_3(\text{CO})_8(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)\text{As}(p\text{-tol})_3$ (2) have been isolated from the reaction of $\text{As}(p\text{-tol})_3$ with $\text{Os}_3(\text{CO})_{12-n}(\text{NCMe})_n$ ($n = 1$ and 2 , respectively) in nonane under reflux at 150°C . They have been shown by a combination of ^{13}C and ^1H NMR and X-ray crystallographic methods to contain a benzyne moiety bonded asymmetrically from one carbon to one osmium atom via a σ bond and from a second carbon which forms a bridge between the remaining two osmium atoms of the open Os-triangle.

Introduction

Triosmium clusters containing $\mu_3\text{-C}_6\text{H}_4$ ligands have been reported to be derived from $[\text{Os}_3(\text{CO})_{12}]$ and PMe_2Ph or AsMe_2Ph by C–H and C–As cleavage [1–3]. In this paper we report the synthesis and full structural characterisation of the two new triosmium clusters $\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)$ (1) and $\text{Os}(\text{CO})_8(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)\text{As}(p\text{-tol})_3$ (2), which also contains such benzyne units. Both 2D and correlation ^{13}C (^1H) NMR techniques have been used to interpret the NMR spectra in the aromatic region.

Experimental

All manipulations were performed under N₂, by standard Schlenk and vacuum-line techniques. Solvents were distilled prior to use under N₂ from the appropriate drying agents.

Routine separation of the products was performed by thin layer chromatography, on commercially prepared glass plates precoated to 0.25 mm thickness with Merck Kieselgel 60, or D.C. Fertlignplatten Aluminium oxide F₂₅₄ (type T) as supplied by Merck.

IR spectra were recorded as solution spectra on a Perkin Elmer 983 grating spectrometer or a Perkin Elmer 1710 Fourier Transform spectrometer, using a 0.5 mm CaF₂ cell. NMR spectra were recorded on Bruker WM 250 HZ or Bruker AM400 FT spectrometers, with internal ²H locks. Mass spectra were recorded on AEI MS 902 or Kratos AEI MS 890 spectrometer.

OsO₄ was supplied by Johnson-Matthey and used for the synthesis of Os₃(CO)₁₂ by the method previously described [4]. Amine oxide was obtained as the dihydrate and purified by Dean-Stark and sublimation techniques. The complexes Os₃(CO)₁₁(NCMe) [5] and Os₃(CO)₁₀(NCMe)₂ [5] and As(*p*-tol)₃ [6] were prepared by published methods.

(i) Synthesis of Os₃(CO)₉(μ₃-C₆H₃CH₃)(μ₃-AsC₆H₄CH₃)

Os₃(CO)₁₁(NCMe) (50 mg) was dissolved in 15 cm³ of distilled nonane in a three necked flask equipped with a N₂ inlet and a reflux condenser. The ligand As(*p*-tol)₃ (20.7 mg) was added under a N₂ flow. The mixture was heated under reflux at 150 °C for 4 h during which there was a colour change from yellow to brown. The solvent was then removed in vacuo and the residue redissolved in 5 cm³ of dichloromethane and chromatographed on TLC plates with CH₂Cl₂/hexane as eluent to give a yellow air-stable compound Os₃(CO)₉(μ₃-C₆H₃CH₃)(μ₃-AsC₆H₄CH₃) (1) in ca. 70% yield along with HOs₃(CO)₉As(*p*-tol)₂ in low yield. X-ray quality crystals of 1 were obtained from CH₂Cl₂/hexane by slow diffusion at room temperature.

(ii) Synthesis of Os₃(CO)₈(μ₃-C₆H₃CH₃)(μ₃-AsC₆H₄CH₃)As(*p*-tol)₃

Thermolysis of Os₃(CO)₁₀(NCMe)₂ (50 mg) and As(*p*-tol)₃ (40.8 mg) in nonane under reflux for 4 h under N₂ was accompanied by a colour change from yellow to brown. The solvent was then removed in vacuo. Preparative TLC with dichloromethane/hexane as eluent afforded two bands of yellow and orange products with similar R_f values. Further purification of the compound by fractional crystallisation gave a fairly pure orange compound Os₃(CO)₈(μ₃-C₆H₃CH₃)(μ₃-AsC₆H₄CH₃)As(*p*-tol)₃ (2) in low yield. X-ray quality single crystals were obtained by slow evaporation of a hexane solution at room temperature.

The crystal data and details of the structural determination for both 1 and 2 are listed in Table 1. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by use of Mo-K_α radiation. Direct methods allowed location of the Os-atoms and the remaining atoms were located by difference Fourier synthesis. Absorption correction was made by the Walker and Stuart method [7] once complete structural models were obtained and all atoms refined isotropically. For 1 all the atoms except those of H were treated anisotropically,

Table 1
Crystal data and details of measurements for **1** and **2**^a

Formula	C ₂₃ H ₁₃ AsO ₉ Os ₃	C ₄₃ H ₃₄ As ₂ O ₈ Os ₃
<i>M</i>	1078.9	1398.4
Crystal size (mm)	0.15 × 0.20 × 0.10	0.10 × 0.20 × 0.10
System	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	13.178(8)	11.584(8)
<i>b</i> (Å)	11.71(1)	19.670(3)
<i>c</i> (Å)	16.787(6)	19.149(8)
β (°)	98.41(4)	102.95(5)
<i>U</i> (Å ³)	2562.6	4252.3
<i>z</i>	4	4
<i>F</i> (000)	1936	2670
<i>D</i> _c (g cm ⁻³)	2.80	2.18
λ (Mo- <i>K</i> _α) (Å)	0.71069	
μ (Mo- <i>K</i> _α) (cm ⁻¹)	155.5	101.4
Diffractometer	Enraf-Nonius CAD4	
Scan mode	$\omega/2\theta$	
θ -range (°)	2.5–25	
ω -scan width (°)	0.8	1.0
Requested counting		
$\sigma(I)/I$	0.02	0.02
Prescan rate (min ⁻¹)	5	5
Prescan acceptance		
$\sigma(I)/I$	0.5	0.5
Maximum scan time (S)	120	100
Octants explored	± <i>h</i> , + <i>k</i> , + <i>l</i>	
Measured reflections	3763	4609
Unique observed reflections	3638	2979
Absorption correction		
min and max values	0.76 1.17	0.48 1.69
<i>R</i> , <i>R</i> _w , <i>S</i>	0.028, 0.029, 3.9	0.087, 0.093, 4.14
<i>K</i> , <i>g</i>	4.5, 0.0002	3.54, 0.0016

^a Absorption correction was applied by the Walker and Stuart method. $R_w = \Sigma[(F_o - F_c)w^{1/2}]/\Sigma(F_o w^{1/2})$, where $w = k/[\sigma(F) + |g|F^2]$.

with different isotropic thermal parameters for the H(benzyl) and H(methyl) atoms (0.04(8), and 0.18(4) Å², respectively). These latter atoms were placed in calculated positions (C–H 1.08 Å) and refined “riding” on their corresponding C-atoms. In the case of **2** only the Os and As atoms could be treated anisotropically owing to the rather poor quality of the diffraction data. As for **1** two single thermal parameters were used for the two kinds of H-atoms (0.13(4), 0.28(9) Å², respectively). Residual peaks were lower than 0.5 e⁻Å³ in **1** and ca. 1.5 e⁻Å³ in **2** and were mainly close to the heavy atoms. For all calculations the SHELX 76 [8] package of crystallographic programs were used. Fractional atomic coordinates for non-hydrogen atoms are listed in Tables 2 and 3 for **1** and **2** respectively. Lists of hydrogen atom coordinates, thermal parameters, and structure factors are available from the authors.

Table 2

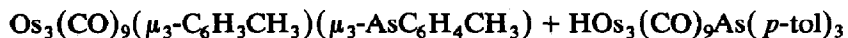
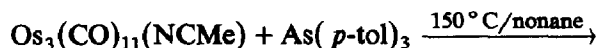
Fractional atomic coordinates for non-hydrogen atoms in **1**

Atom	x	y	z
Os(1)	0.95983(2)	0.17013(3)	0.85738(2)
Os(2)	0.84886(2)	0.21142(3)	0.70429(2)
Os(3)	1.03019(2)	0.31060(3)	0.64783(2)
As	1.03446(6)	0.14602(7)	0.73407(5)
C(1)	1.0643(6)	0.2314(7)	0.9365(5)
O(1)	1.1252(5)	0.2707(6)	0.9826(4)
C(2)	0.8508(6)	0.1729(8)	0.9233(5)
O(2)	0.7896(5)	0.1691(6)	0.9634(4)
C(3)	0.9912(7)	0.0180(8)	0.8903(5)
O(3)	1.0112(6)	-0.0711(6)	0.9113(4)
C(4)	0.7783(7)	0.3290(8)	0.6419(6)
O(4)	0.7356(6)	0.4015(6)	0.6062(5)
C(5)	0.8238(6)	0.0969(8)	0.6218(5)
O(5)	0.8124(5)	0.0286(7)	0.5731(4)
C(6)	0.7372(6)	0.1699(8)	0.7568(6)
O(6)	0.6649(5)	0.1455(8)	0.7853(4)
C(7)	0.9678(7)	0.4401(8)	0.5927(5)
O(7)	0.9281(5)	0.5193(6)	0.5631(4)
C(8)	1.1675(7)	0.3605(8)	0.6506(5)
O(8)	1.2498(5)	0.3903(7)	0.6517(5)
C(9)	1.0369(8)	0.2185(8)	0.5518(6)
O(9)	1.0404(7)	0.1610(7)	0.4989(5)
C(10)	0.9211(6)	0.3404(6)	0.7887(5)
C(11)	1.0049(6)	0.3888(6)	0.7567(4)
C(12)	1.0518(6)	0.4869(6)	0.7938(5)
C(13)	1.0187(6)	0.5361(7)	0.859
C(14)	0.9319(6)	0.4940(7)	0.887
C(15)	0.8828(6)	0.3995(6)	0.851
C(16)	1.0746(8)	0.6389(8)	0.899
C(17)	1.0729(6)	-0.0032(7)	0.699
C(18)	1.0198(6)	-0.1020(7)	0.712
C(19)	1.0535(7)	-0.2052(7)	0.687
C(20)	1.1402(6)	-0.2127(7)	0.650
C(21)	1.1912(6)	-0.1156(7)	0.637
C(22)	1.1577(6)	-0.0104(8)	0.660
C(23)	1.1753(8)	-0.3268(8)	0.624

Results and discussion

(i) The reaction of $Os_3(CO)_{11}(NCMe)$ with $As(p\text{-tol})_3$

The acetonitrile cluster $Os_3(CO)_{11}(NCMe)$ reacts with $As(p\text{-tol})_3$ (1/1 equiv.) in nonane under reflux to give the air stable product **1** in ca. 70% yield, together with a much lower yield of $HOs_3(CO)_9As(p\text{-tol})_2$.



Spectroscopic techniques were used for the structural characterisation of compound **1**. EI-MS and FAB-MS data are consistent with the trinuclear formulation

Table 3. Fractional atomic coordinates for non-hydrogen atoms in **2**.

Atom	x	y	z
Os(2)	0.46418(17)	0.19725(8)	0.48976(11)
Os(1)	0.69130(16)	0.17116(8)	0.46993(10)
Os(3)	0.54403(18)	0.31606(9)	0.57976(10)
As(2)	0.9032(4)	0.1910(2)	0.5048(3)
As(1)	0.6124(4)	0.2861(2)	0.4743(3)
C(1)	0.6891(29)	0.1717(15)	0.3800(18)
O(1)	0.6708(32)	0.1723(16)	0.3141(21)
C(2)	0.7055(37)	0.0786(21)	0.4631(24)
O(2)	0.7147(30)	0.0186(17)	0.4554(19)
C(3)	0.3515(50)	0.2400(26)	0.4231(30)
O(3)	0.2792(34)	0.2680(18)	0.3803(21)
C(4)	0.3688(63)	0.1783(31)	0.5614(38)
O(4)	0.3047(45)	0.1709(22)	0.5919(28)
C(5)	0.4402(38)	0.1115(22)	0.4453(25)
O(5)	0.4372(28)	0.0578(16)	0.4257(17)
C(6)	0.4555(41)	0.3878(23)	0.5300(26)
O(6)	0.3775(37)	0.4249(19)	0.4936(22)
C(7)	0.6518(45)	0.3753(23)	0.6369(28)
O(7)	0.7273(35)	0.4088(18)	0.6686(21)
C(8)	0.4546(43)	0.3044(22)	0.6485(28)
O(8)	0.3996(32)	0.2972(17)	0.6955(20)
C(9)	0.6130(49)	0.1787(27)	0.5702(31)
C(10)	0.6465(30)	0.2291(16)	0.6241(19)
C(11)	0.7295(38)	0.2210(20)	0.6895(24)
C(12)	0.7674(47)	0.1521(25)	0.7120(31)
C(13)	0.7242(36)	0.1011(20)	0.6649(24)
C(14)	0.6488(45)	0.1080(24)	0.6004(29)
C(15)	0.8371(48)	0.1434(25)	0.7846(30)
C(16)	0.5744(33)	0.3457(18)	0.3971(21)
C(17)	0.5934(33)	0.4147(18)	0.4040(22)
C(18)	0.5606(49)	0.4602(28)	0.3508(33)
C(19)	0.5054(38)	0.4385(20)	0.2825(25)
C(20)	0.4870(46)	0.3713(26)	0.2708(31)
C(21)	0.5260(36)	0.3253(20)	0.3273(24)
C(22)	0.4669(47)	0.4859(26)	0.2167(28)
C(23)	0.9845(38)	0.1506(21)	0.5949(24)
C(24)	0.9783(48)	0.0794(27)	0.6004(32)
C(25)	1.0436(45)	0.0523(25)	0.6649(30)
C(26)	1.1062(46)	0.0918(26)	0.7207(31)
C(27)	1.1205(45)	0.1616(24)	0.7077(29)
C(28)	1.0521(45)	0.1879(24)	0.6449(29)
C(29)	1.1678(43)	0.0625(24)	0.7912(26)
C(30)	0.9921(37)	0.1570(19)	0.4336(23)
C(31)	0.9950(49)	0.1876(25)	0.3677(31)
C(32)	1.0168(51)	0.1694(27)	0.3129(33)
C(33)	1.1079(37)	0.1209(20)	0.3306(24)
C(34)	1.1342(38)	0.0949(20)	0.3998(25)
C(35)	1.0748(36)	0.1131(19)	0.4501(24)
C(36)	1.1628(50)	0.1029(27)	0.2722(31)
C(37)	0.9615(42)	0.2834(23)	0.5276(26)
C(38)	0.9140(47)	0.3266(25)	0.5695(30)
C(39)	0.9570(44)	0.3908(24)	0.5877(27)
C(40)	1.0494(48)	0.4103(26)	0.5588(31)
C(41)	1.1158(62)	0.3699(32)	0.5162(39)
C(42)	1.0535(52)	0.3045(29)	0.4947(33)
C(43)	1.1144(50)	0.4796(26)	0.5817(31)

for **1**, for which the microanalytical data (C 25.41 and H 1.02%) are consistent with the structural characterisation. The ^1H NMR spectrum of compound **1** exhibits signals at δ 2.02(s,CH₃), 2.42(s,CH₃), 6.66(d,H⁴), 7.19(s,H⁶), 7.29(d,As-tol), 7.55(d,As-tol), 8.01(d,H³) (Fig. 1a). The assignment of the ^1H NMR spectrum follows from the coupling pattern, while complete assignment of the ^{13}C NMR spectrum was based on coordination of one bond and long range reverse $^{13}\text{C}\{^1\text{H}\}$ correlation experiments (Fig. 1b).

When the correlation experiment is set up to detect connections through long-range couplings, the resulting spectra will generally contain cross peaks for two and three-bond connections, including those to quaternary carbons. However by this method it was possible to evaluate the $J(\text{C}-\text{H})$ coupling constant as $J(\text{H}^4-\text{C}^4)$ 141.54, $J(\text{H}^5-\text{C}^6)$ 161.54 and $J(\text{H}^3-\text{C}^3)$ 157.86 Hz for compound **1**.

The benzyne carbon atoms exhibit similar chemical shifts with, however, a significant upfield chemical shift for C¹, which may be associated with a partial loss of alkyne character due to the unusual coordination of C¹-C² ring carbons. Alternatively, anisotropic shielding due to M_2C_2 currents [9] may lead to the upfield shifts and this would be consistent with the anomalously short T_1 value, measured by an inversion recovery sequence, for the ring carbons. Spin lattice relaxation values for the other quaternary ring carbon, which do not show NOE enhancement, are markedly longer Table 4.

(ii) *The reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with $\text{As}(p\text{-tol})_3$*

The reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with $\text{As}(p\text{-tol})_3$ gave a mixture of isomers of $\text{Os}_3(\text{CO})_8\text{As}(p\text{-tol})_2\text{As}(p\text{-tol})_3$.

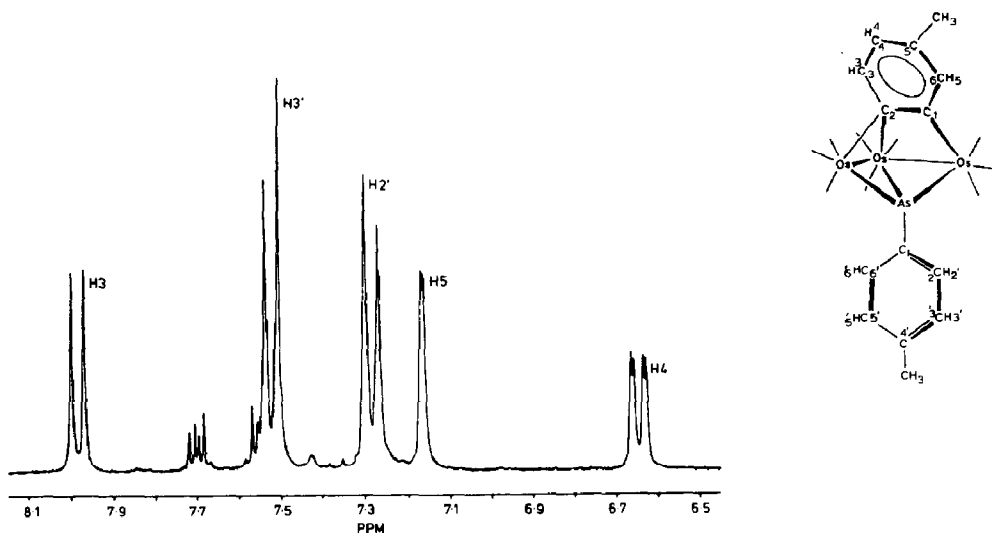
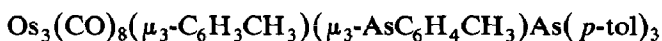
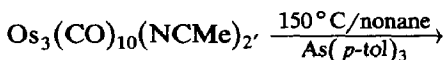


Fig. 1a. $^1\text{H}-^{13}\text{C}$ correlation (normal) for $\text{Os}_3(\text{CO})_8(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)\text{As}(p\text{-tol})_3$.

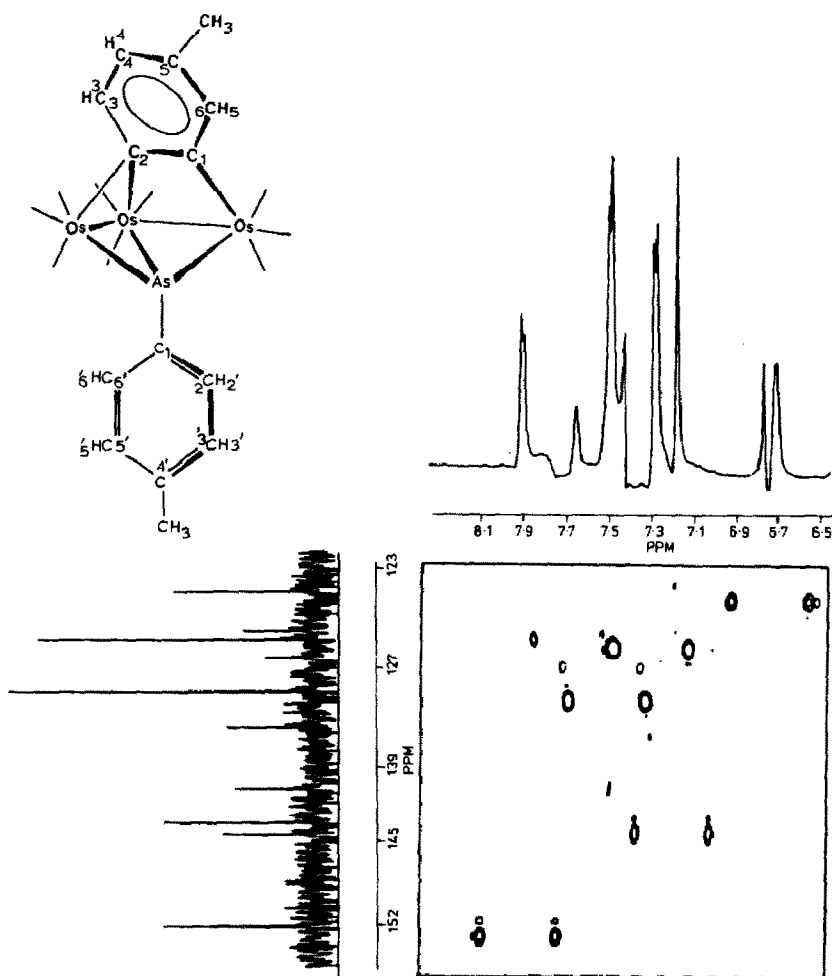


Fig. 1b. ^1H - ^{13}C correlation for $\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)$.

The ^1H NMR spectrum exhibits signals at δ 2.25 (s, CH_3), 2.52 (d, CH_3), 6.93 (d), 7.07 (m), 7.12 (d), 7.23 (d) and 7.74 (d); the aromatic region is shown in Fig. 2. It is difficult to separate and identify the isomeric contribution from the complicated set of resonances observed in the aromatic region. In the ^1H - ^1H COSY (Fig. 2) diagram, connectivity data suggest that three types of tolyl ligands are present, in keeping with the formulation of the compound as $\text{Os}_3(\text{CO})_8(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)\text{As}(p\text{-tol})_3$. Two AX patterns, a and b, are identified, as well as an AB pattern c, and a smaller AX pair d, attributed to a minor isomer. The second order pattern c derives from a coordination mode of the tolyl ligand in which the chemical shifts of the ring protons are quite similar and arises from an unusual environment for the ligand. Alternatively, in a less probable solution, the AXAB pattern, ac, may refer to the same tolyl ligand and result from a highly asymmetric environment of the *p*-tolyl substituent, reflected in the chemical shift and coupling shift and coupling pattern, and consistent with the like ligand representation shown in Fig. 3.

Table 4

The ^1H and ^{13}C NMR spectroscopic data for the cluster $\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)$ as obtained from AM 400 FT spectrometer

$^1\text{H}/\delta$, ppm assignment	6.66 d H^4	7.19 s H^5	7.29 d $\text{H}^2\text{H}^6/\text{H}^3\text{H}^5$	7.55 d $\text{H}^7\text{H}^5/\text{H}^2\text{H}^6$	8.01 d H^3
$^{13}\text{C}/\delta$, ppm assignment $T_1(+0.01\text{s})$	108.4 C^1	129.7 $\text{C}^{2'}$	133.8 $\text{C}^{3'}$	144.1 $\text{C}^{4'}$	145.0 C^5
	125.9 C^4	136.6 $\text{C}^{1'}$	141.4 $\text{C}^{4'}$	152.3 C^3	178.9 CO
					181.2 CO

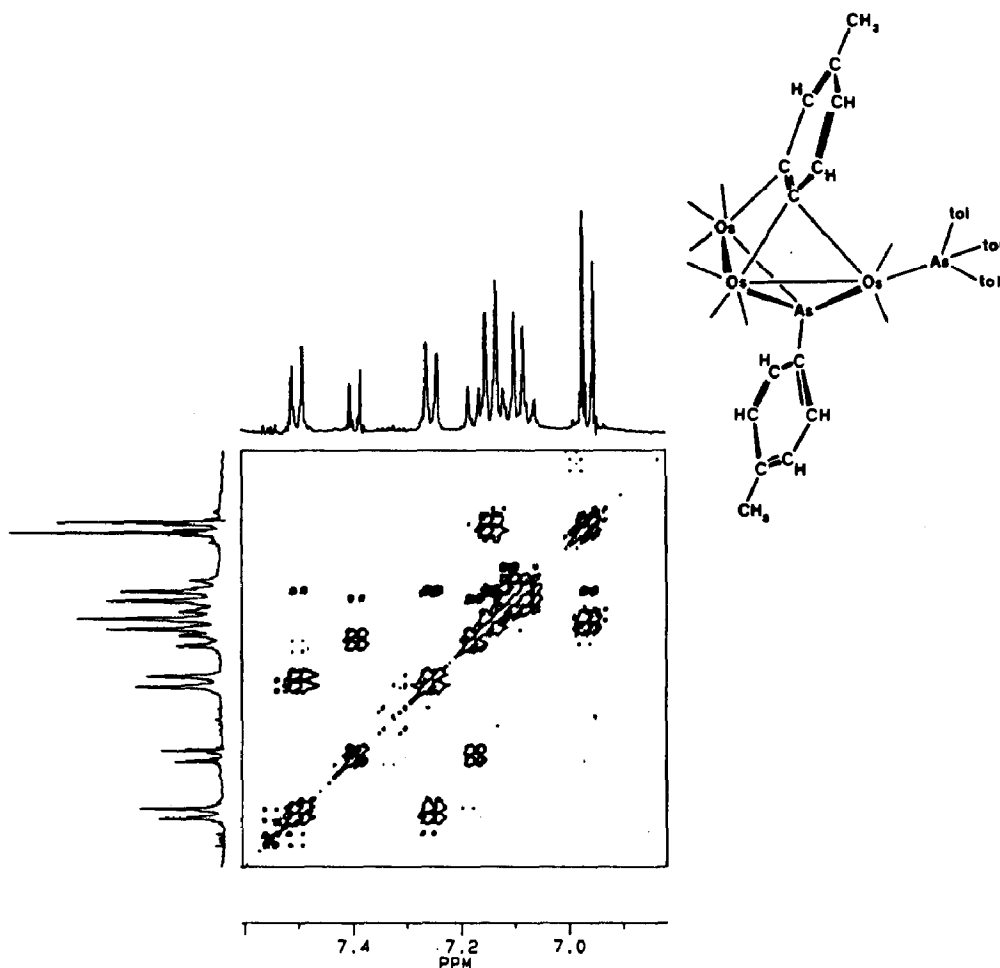


Fig. 2. ^1H - ^1H COSY of $\text{Os}_3(\text{CO})_8(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{AsC}_6\text{H}_4\text{CH}_3)\text{As}(p\text{-tol})_3$.

Complete structural elucidation was carried out for the more thermodynamically stable isomer by single crystal X-ray crystallography.

The molecular structures of **1** and **2** are closely related and will be considered together. A comparison of relevant bond distance and angles in Table 5. The two molecules are shown in Figs. 4 and 5 together with the relevant atom labelling. The metal atom framework consists of an "open" triangle of Os-atoms (Os–Os open edge 4.110(1) and 4.131(1)Å, Os(1)–Os(2)–Os(3) 91.4(1), 92.5(1)°, respectively) which bear on opposite sides a $\mu_3\text{-As}(p\text{-tol})$ and a $\mu_3\text{-C}_6\text{H}_3\text{CH}_3$ ligand. In **2** one CO group on Os(1) is formally replaced by an $\text{As}(p\text{-tol})_3$ ligand. The remaining two

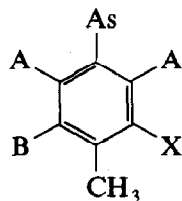


Fig. 3. Possible ligand representation for $\text{Os}_3(\text{CO})_8(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)\text{As}(p\text{-tol})_3$.

Table 5

Comparison of relevant bond distances (Å) and angles (°) in **1** and **2**

1		2	
Os(1)–Os(2)	2.807(1)	Os(1)–Os(2)	2.789(3)
Os(2)–Os(3)	2.936(1)	Os(2)–Os(3)	2.928(2)
Os(1)–As	2.435(1)	Os(1)–As(1)	2.447(4)
Os(2)–As	2.542(1)	Os(2)–As(1)	2.513(5)
Os(3)–As	2.406(1)	Os(3)–As(1)	2.403(5)
Os(1)–C(10)	2.323(8)	Os(1)–C(9)	2.31(6)
Os(2)–C(10)	2.191(8)	Os(2)–C(9)	2.07(6)
Os(3)–C(11)	2.113(8)	Os(3)–C(10)	2.15(3)
C(10)–C(11)	1.42(1)	C(9)–C(10)	1.42(6)
C(11)–C(12)	1.41(1)	C(10)–C(11)	1.41(5)
C(12)–C(13)	1.37(1)	C(11)–C(12)	1.46(6)
C(13)–C(14)	1.39(1)	C(12)–C(13)	1.37(6)
C(14)–C(15)	1.38(1)	C(13)–C(14)	1.35(6)
C(10)–C(15)	1.42(1)	C(14)–C(9)	1.53(7)
C(13)–C(16)	1.51(1)	C(12)–C(15)	1.45(7)
As–C(17)	1.933(8)	As(1)–C(16)	1.86(4)
		As(2)–C(23)	1.94(5)
		As(2)–C(30)	2.00(4)
		As(2)–C(37)	1.95(5)
C(17)–C(18)	1.39(1)	C(16)–C(17)	1.38(5)
C(18)–C(19)	1.38(1)	C(17)–C(18)	1.34(6)
C(19)–C(20)	1.38(1)	C(18)–C(19)	1.39(6)
C(20)–C(21)	1.36(1)	C(19)–C(20)	1.35(6)
C(21)–C(22)	1.39(1)	C(20)–C(21)	1.41(6)
C(17)–C(22)	1.38(1)	C(16)–C(21)	1.39(5)
C(20)–C(23)	1.50(1)	C(19)–C(22)	1.55(6)
mean Os–C	2.209	mean Os–C	2.177
mean C–O	1.43	mean C–O	1.17
Os(1)–Os(2)–Os(3)	91.4(1)	Os(1)–Os(2)–Os(3)	92.5(1)
Os(1)–As–C(17)	121.2(2)	Os(1)–As(1)–C(16)	125(1)
Os(2)–As–C(17)	120.0(2)	Os(2)–As(1)–C(16)	119(1)
Os(3)–As–C(17)	121.7(2)	Os(3)–As(1)–C(16)	117(1)
		Os(2)–Os(1)–As(2)	149.3(1)
Os(1)–C(10)–Os(2)	76.8(2)	Os(1)–C(9)–Os(2)	79(2)
Os(2)–C(10)–C(11)	108.6(5)	Os(2)–C(9)–C(10)	118(4)
Os(3)–C(11)–C(10)	112.7(5)	Os(3)–C(10)–C(9)	103(3)
C(10)–C(11)–C(12)	118.4(7)	C(9)–C(10)–C(11)	126(4)
C(11)–C(12)–C(13)	121.9(8)	C(10)–C(11)–C(12)	118(4)
C(12)–C(13)–C(14)	120.0(7)	C(11)–C(12)–C(13)	116(5)
C(13)–C(14)–C(15)	119.4(8)	C(12)–C(13)–C(14)	127(5)
C(14)–C(15)–C(10)	121.7(8)	C(13)–C(14)–C(9)	120(5)
C(15)–C(10)–C(11)	118.1(7)	C(14)–C(9)–C(10)	111(5)

Os atoms bear three terminal carbonyls each. The two pairs of Os–Os bonds have different lengths, being longer in **1** than in **2** (2.807(1), 2.936(1) compared with 2.789(3), 2.928(2) Å). The three Os– μ_3 –As bonds are also unequal, ranging from 2.406(1) to 2.542(1) Å in **1** and from 2.403(5) to 2.513(4) Å in **2**, the long bond involving the interaction with the central Os-atom (Os(2)). Interestingly, the terminal Os–As distance in **2** (2.427(5) Å) does not differ substantially from the average

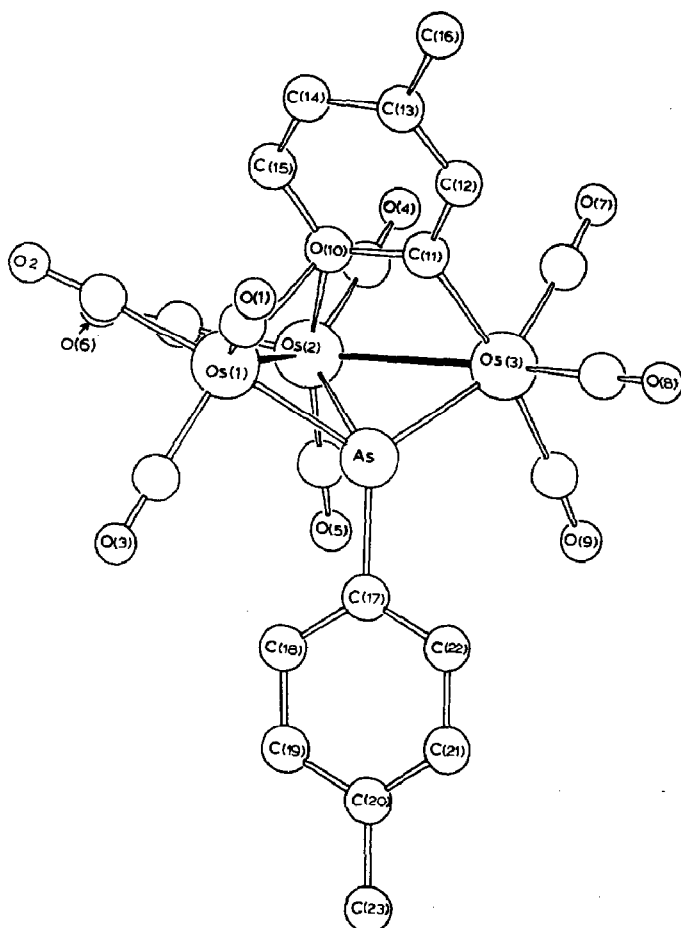


Fig. 4. X-ray structure of $\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_5\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)$.

Os- μ_3 -As distance (2.454(5) Å). The main feature revealed by the structural determination of 1 and 2 is the coordination of $\mu_3\text{-(C}_6\text{H}_5\text{CH}_3)$ ligand, which uses two of its C-atoms to bind to the three metal centres. A similar coordination mode was observed for the (C_6H_4) ligand in $[\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_4)(\mu_3\text{-PC}_2\text{H}_5)]$ [3], which contains essentially the same metal atom framework supported by a $\mu_3\text{-PC}_2\text{H}_5$ ligand underneath the coordination plane of the benzyne fragment. As previously noted, the nature of the bonding interaction between the organic moiety in 1 and 2 and the corresponding benzyne ligand in this latter species is somewhat problematical. If the $\mu_3\text{-As}(p\text{-tol})$ ligand is regarded as a four electron donor, then in order to make a total of 50 electrons for an electron-precise open triangle, the $\mu_3\text{-(C}_6\text{H}_5\text{CH}_3)$ ligand is required to supply four electron to the cluster orbitals. In the benzyne species the contribution of two non-equivalent (4 electron or 2 electron donation) ligand-to-cluster interactions was invoked. On the basis of the structural evidences (see Scheme 1) we suggest that the bonding mode may be better described as the result of two σ -interactions (Os(2)-C(10), Os(3)-C(11) in 1, Os(2)-C(9), Os(3)-C(10) in 2) and of a π -interaction between Os(1) and a molecular orbital of appropriate symmetry of the $\text{C}_6\text{H}_5\text{CH}_3$ ligand (see Scheme 1). Such an interaction is not

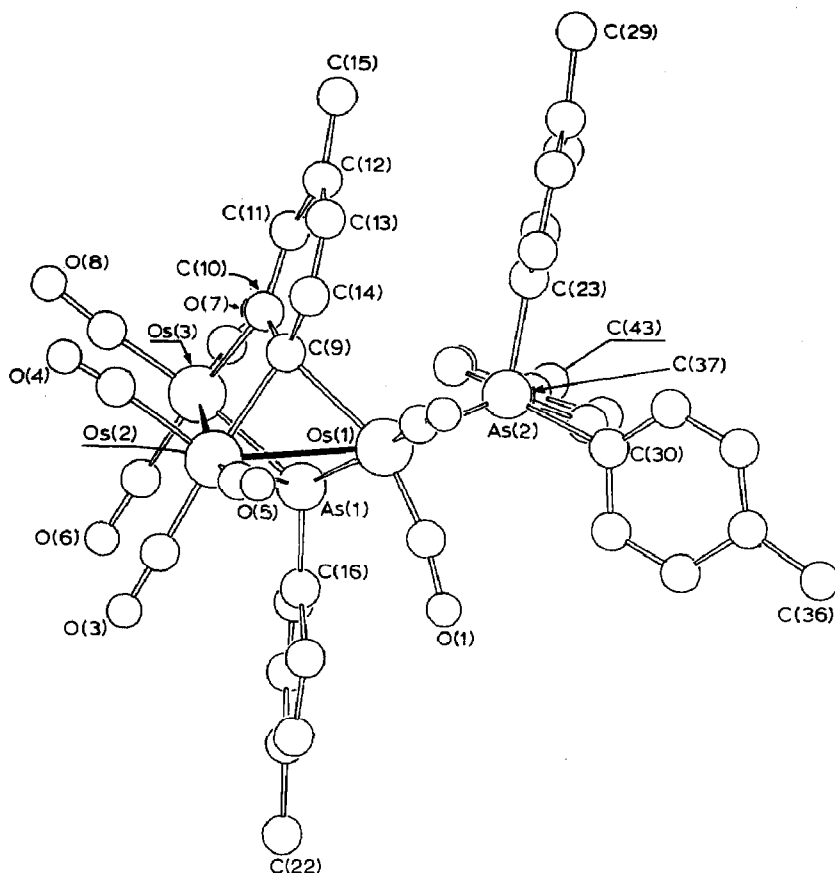
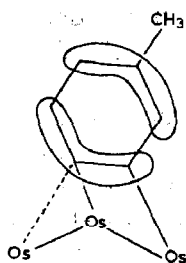


Fig. 5. X-ray structure of $\text{Os}_3(\text{CO})_8(\mu_3\text{-C}_6\text{H}_3\text{CH}_3)(\mu_3\text{-AsC}_6\text{H}_4\text{CH}_3)\text{-As}(p\text{-tol})_3$.

directed towards the mid-point of a C–C bond in the ligand, but towards the C-atom (C(10) and C(9), respectively) of the ring, the Os–C bonding axis being almost orthogonal (97 and 98° , respectively) to the ligand plane. The lengthening of the C–C bonds involving the metal bound carbon atoms (mean $1.42(1)$ in **1** and $1.45(6)$ Å in **2**) relative to the other C-atoms of the ring (mean $1.38(1)$, $1.39(6)$ Å) clearly shows that the bonding interaction is delocalised over a molecular orbital of the ligand. It should also be noted that the π Os–C interaction is much longer than the two σ -interactions ($\text{Os}(1)\text{-C}(10)$ $2.323(8)$ in **1**, $\text{Os}(1)\text{-C}(9)$ $2.31(6)$ in **2**, $\text{Os}(2)\text{-C}(10)$ $2.191(8)$, $\text{Os}(3)\text{-C}(11)$ $2.113(8)$ in **1**, $\text{Os}(2)\text{-C}(9)$ $2.07(3)$, $\text{Os}(3)\text{-C}(10)$ $2.15(3)$



Scheme 1

Å in 2. A similar bond length distribution was observed in $\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_4)(\mu_3\text{-PC}_2\text{H}_5)$ [3]. The osmium-carbonyl distances fall within the expected range for neutral Os-cluster species.

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