Mode of attachment of the triply-bridging C_6H_4 ligand in open triosmium clusters: crystal structures and fluxionality of the clusters $[Os_3(PMe)(C_6H_4)(CO)_8L]$ (L = CO or PEt$_3$)

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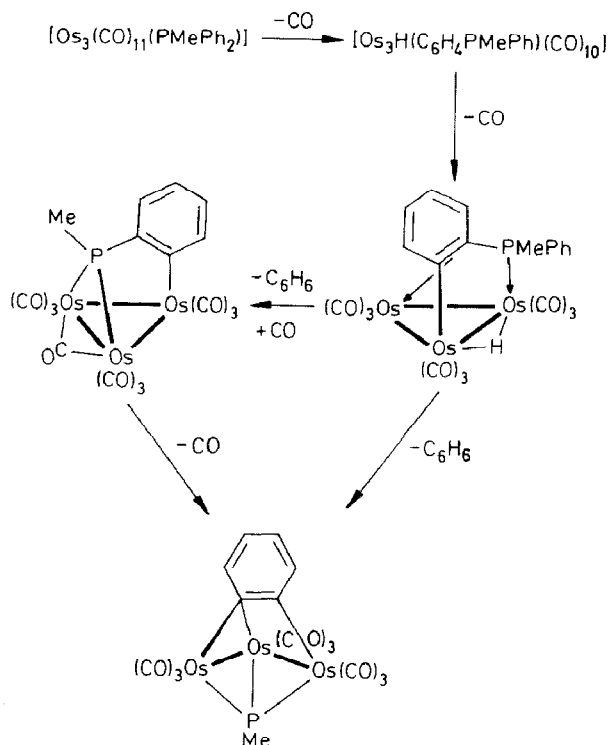*Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (U.K.)*

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Abstract

The cluster $[Os_3(PMe)(C_6H_4)(CO)_9]$ (1) reacts with phosphorus(III) ligands L [PEt$_3$, PCy$_3$, or P(OMe)$_3$] to give the substitution products $[Os_3(PMe)(C_6H_4)-(CO)_{9-x}L_x]$, clusters 2 ($x = 1$) and 3 ($x = 2$). The crystal structures of 1 and 2 (L = PEt$_3$) are compared with that previously reported for $[Os_3(PEt)(C_6H_4)(CO)_9]$; each has two Os-Os bonds and one non-bonding Os · · · Os distance (3.982(1), 4.014(1), and 4.008(2) Å, respectively, for the three compounds). A μ_3-PMe or PEt group caps one face of the Os$_3$ triangle and the opposite one is capped by a μ_3-C$_6$H$_4$ ligand coordinated through σ-Os–C bonds to two mutually bonded Os atoms and does not span the open Os · · · Os edge by σ-bonds as in other cases such as $[Os_3H(AsMe_2)(C_6H_4)(CO)_9]$. Bonding to the third Os atom through one carbon atom involves π-orbitals predominantly, and there is evidence against an alkylidene component in the bridging such as was considered previously. The C_6H_4 ligand is rapidly mobile in 1, and in one of the two isomers of 2 with the ligand L at the central Os atom. The fluxionality is substantially suppressed when L is coordinated at a terminal Os atom as in the isomer of $[Os_3(PMe)(C_6H_4)(CO)_8(PEt_3)]$ whose structure was established crystallographically. The movement of the non-bonded Os · · · Os edge around the metal triangle does occur, but is slow.

Introduction

Evans et al. reported that the treatment of the simple phosphine substituted compounds $[Os_3(CO)_{11}(PRPh_2)]$ (R = Me, Et, or Ph) in refluxing nonane gave moderate yields of the benzyne (*ortho*-phenylene) compounds $[Os_3(PR)(C_6H_4)-$

[Os$_3$(CO)$_{11}$(PMePh$_2$)] $\xrightarrow{-CO}$ [Os$_3$H(C$_6$H$_4$PMePh)(CO)$_{10}$]

$-CO$

Me
P
(CO)$_3$Os—Os(CO)$_3$
O^C—Os
(CO)$_3$

$-C_6H_6$ / $+CO$

PMePh
(CO)$_3$Os—Os(CO)$_3$
Os—H
(CO)$_3$

$-CO$

$-C_6H_6$

(CO)$_3$Os—Os$^{(C}$$^{O)_3}$—Os(CO)$_3$
P
Me

Scheme 1

(CO)$_9$] [1]. By carrying out the reaction with R = Me at lower temperatures we were able to isolate (and so determine the structures) of two intermediates, [Os$_3$H(C$_6$H$_4$PMePh)(CO)$_9$] and [Os$_3$(PMeC$_6$H$_4$)(CO)$_{10}$], and to establish the route to [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_9$] cluster 1, shown in Scheme 1 [2]. The crystal structure of [Os$_3$(PEt)(C$_6$H$_4$)(CO)$_9$] [1] contains only two Os–Os bonds and the C$_6$H$_4$ is in a previously unobserved geometric arrangement. Previously, C$_6$H$_4$ in trinuclear clusters had been found as a four-electron donor in form **A** as in [Os$_3$(PPh$_2$)$_2$(C$_6$H$_4$)(CO)$_7$] [3] or form **B** as in [Os$_3$H(AsMe$_2$)(C$_6$H$_4$)(CO)$_9$] [4], rationalised as involving two σ-M–C bonds and an η^2-attachment to the third metal atom. See ref. 5 for other Os$_3$ examples. The C$_6$H$_4$ ligand in [Os$_3$(PEt)(C$_6$H$_4$)(CO)$_9$] is, however, bonded to two Os atoms through one carbon atom and to only one osmium atom through the other. Description **C**, with a three-centre two-electron bond linking the bridging carbon atom, would require the ligand to be a two-electron donor, and three Os–Os bonds would be expected. The distance between the two Os-bonded carbon atoms was found to be 1.53(5) Å, close to a single bond length and favouring a very significant contribution from the di-alkylidene form **D** which as a four-electron donor would require two Os–Os bonds as found. Evans et al. described the ligand as an *ortho*-phenylene with contributions from both **C** and **D**. More recently a related arsine derivative [Os$_3$(AsC$_6$H$_4$Me)(C$_6$H$_3$Me)(CO)$_9$] has been described [6].

We have investigated such systems further by determining crystal structures of [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_9$] and [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_8$(PEt$_3$)] and by examining the fluxionality of the substituted compounds, and conclude that **E** is the best description for the μ_3-C$_6$H$_4$ system.

(A)   (B)   (C)   (D)   (E)
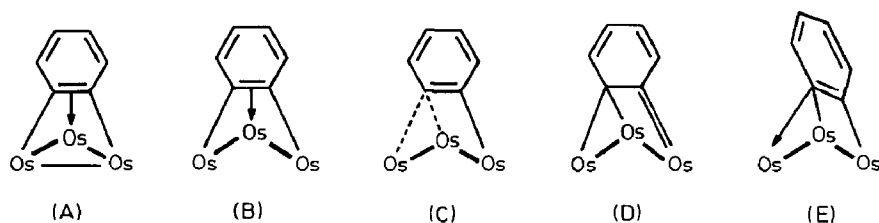
Results and discussion

Syntheses

Compound **1** was prepared as previously reported [1], and reaction of **1** with PEt$_3$ or P(OMe)$_3$ (ligands L) in refluxing octane gave a mixture of the mono- and di-substituted compounds [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_8$L] (**2**) and [Os$_3$(PMe)(C$_6$H$_4$)-(CO)$_7$L$_2$] (**3**), which were separated by TLC. The corresponding reaction with tricyclohexylphosphine (PCy$_3$) gave only the mono-substituted compound. Each of the substituted compounds exists as a mixture of a major and a minor isomer, which were not separable by TLC except that in one case we were able to isolate essentially pure isomeric samples in low quantity. Thus TLC of [Os$_3$(PMe)(C$_6$H$_4$)-(CO)$_8$(PEt$_3$)] (**2a**) on SiO$_2$ with a 9/1 mixture by volume of petroleum ether (b.p. 60–80°C) and dichloromethane gave a single yellow band, and this was cut into two and each half rechromatographed separately. The top part of the top band after rechromatography and lower part of the other were highly enriched isomerically with only traces of the other isomer detected by ^{1}H NMR. These isomers of **2a** in CDCl$_3$ solution did not undergo interconversion during 120 h in the dark, but in daylight were reconverted to the original mixture within hours. We managed to obtain a few crystals of the major isomer of **2a** for an X-ray structural determination.

Crystal structures of the clusters [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_9$] (1) and [Os$_3$(PMe)(C$_6$H$_4$)-(CO)$_8$(PEt$_3$)] (2a)

The reported structure of the PEt-analogue of **1** has some very interesting features, as indicated in the Introduction [1]. We determined the structure of **1** to see if these features persist and the structure of **2a** to establish the PEt$_3$ substitution position in the major isomer and to see the effect of phosphine substitution on the C$_6$H$_4$ coordination. The molecular structure of **1** is shown in Fig. 1 and that of **2a** in Fig. 2, and selected bond lengths and angles of both compounds are listed in Table 1. Crystallographic data are given in Table 2 and atomic coordinates in Tables 3 and 4. There are crystallographic differences between the PMe cluster **1**, which is monoclinic, and its PEt analogue which is triclinic, but their molecular structures are entirely equivalent except in minor detail. The reported structure of the PEt compound was not particularly well-refined ($R = 0.079$) and the esd's are large; the refinement for **1** was marginally better ($R = 0.056$), allowing a better assessment of the geometry of the C$_6$H$_4$ ligand and its coordination.

We have confirmed that the C$_6$H$_4$ ligand is unusually bonded, with C(2) bonded only to Os(3) while C(1) bridges Os(1) and Os(2). Regarding the previously
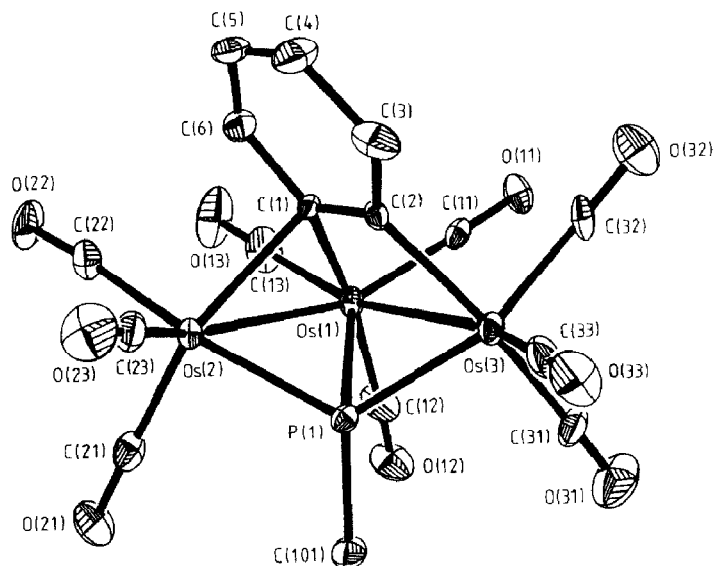
Fig. 1. Molecular structure of the *ortho*-phenylene cluster [Os₃(PMe)(C₆H₄)(CO)₉] (1).

considered forms **C** and **D**, we can say that there is no detectable contribution from **D** based on C–C bond lengths in the ring which are in the range 1.36(3) to 1.45(3) Å for cluster **1** and 1.36(3) to 1.44(2) Å for **2a**, within the normal ranges expected for arene rings. We regard the length of 1.53(3) Å observed for the PEt compound for the bond corresponding to C(1)–C(2) in **1** and **2a** to be an artifact of the structure determination and not an indication of a significant reduction in bond order for this carbon–carbon bond. In fact we believe that neither **C** nor **D** is a good representation of the C₆H₄ coordination. Both forms would seem to require that the C₆ ring
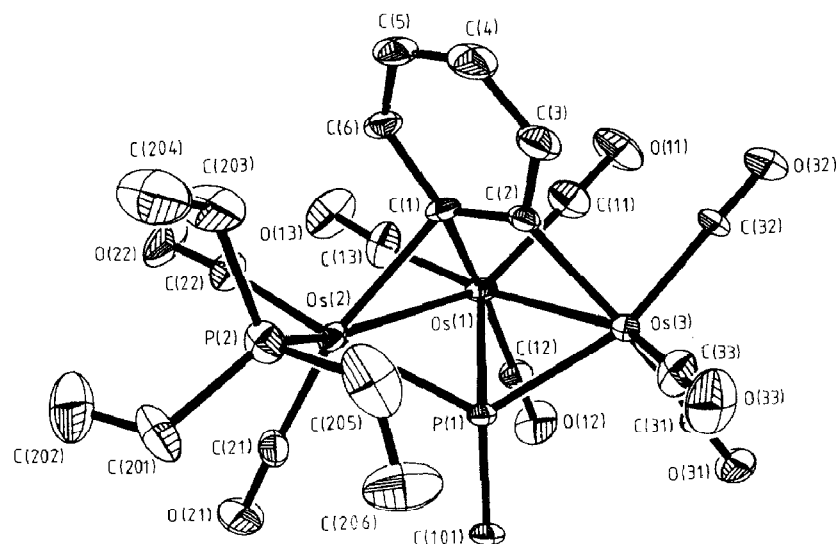

Fig. 2. Molecular structure of the phosphine-substituted derivative of **1**, [Os₃(PMe)(C₆H₄)(CO)₈(PEt₃)] (**2a**).

Table 1

Selected bond lengths (Å) and angles (°) for the clusters [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_9$], cluster **1** and [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_8$(PEt$_3$)], cluster **2a**

	Cluster **1**	Cluster **2a**
Os(1)–Os(2)	2.782(1)	2.795(1)
Os(1)–Os(3)	2.917(1)	2.890(1)
Os(1)–P(1)	2.402(4)	2.417(3)
Os(2)–P(1)	2.331(4)	2.321(3)
Os(3)–P(1)	2.300(4)	2.314(4)
P(1)–C(101)	1.85(2)	1.82(2)
Os(3)–C(2)	2.13(2)	2.13(1)
Os(1)–C(1)	2.17(2)	2.17(1)
Os(2)–C(1)	2.32(2)	2.33(2)
C(1)–C(2)	1.39(2)	1.44(2)
C(2)–C(3)	1.44(3)	1.42(2)
C(3)–C(4)	1.43(3)	1.36(3)
C(4)–C(5)	1.36(3)	1.40(3)
C(5)–C(6)	1.45(3)	1.40(2)
C(6)–C(1)	1.42(2)	1.43(2)
Os(2)–P(2)		2.328(4)
P(2)–C(201)		1.77(2)
P(2)–C(203)		1.90(2)
P(2)–C(205)		1.89(3)
Range of CO lengths	1.11(2)–1.16(2)	1.10(2)–1.16(2)
Average CO length	1.139	1.127
Range of Os–CO lengths	1.85(2)–1.95(2)	1.84(2)–1.95(2)
Average Os–CO	1.905	1.913
Os(3)–Os(1)–Os(2)	88.6(1)	89.8(1)
C(1)–Os(1)–Os(2)	54.3(4)	54.3(4)
C(1)–Os(1)–Os(3)	68.6(4)	70.9(4)
C(1)–Os(1)–P(1)	77.6(4)	78.1(4)
P(1)–Os(1)–Os(2)	52.8(1)	52.3(1)
P(1)–Os(1)–Os(3)	50.1(1)	50.8(1)
C(1)–Os(2)–Os(1)	49.4(4)	49.0(3)
C(1)–Os(2)–P(1)	76.3(4)	76.9(3)
P(1)–Os(2)–Os(1)	55.2(1)	55.4(1)
P(2)–Os(2)–Os(1)		146.3(1)
P(2)–Os(2)–C(1)		101.8(4)
P(2)–Os(2)–P(1)		107.6(1)
C(2)–Os(3)–Os(1)	69.9(4)	69.3(4)
C(2)–Os(3)–P(1)	79.7(4)	82.0(4)
P(1)–Os(3)–Os(1)	53.2(1)	54.0(1)
Os(2)–C(1)–Os(1)	76.3(5)	76.7(5)
C(2)–C(1)–Os(1)	111 (1)	106.6(9)
C(2)–C(1)–Os(2)	109 (1)	114.1(9)
C(6)–C(1)–Os(1)	129 (1)	130 (1)
C(6)–C(1)–Os(2)	97 (1)	104 (1)
C(6)–C(1)–C(2)	119 (2)	117 (1)
C(3)–C(2)–Os(3)	126 (1)	127 (1)
C(1)–C(2)–Os(3)	111 (1)	112.3(9)
C(1)–C(2)–C(3)	122 (2)	120 (1)
C(4)–C(3)–C(2)	118 (2)	120 (2)
C(5)–C(4)–C(3)	121 (2)	122 (2)
C(6)–C(5)–C(4)	121 (2)	119 (2)
C(1)–C(6)–C(5)	119 (2)	121 (2)

(continued)

Table 1 (continued)

	Cluster **1**	Cluster **2a**
Os(2)–P(1)–Os(1)	72.0(1)	72.3(1)
Os(3)–P(1)–Os(1)	76.6(1)	75.3(1)
Os(3)–P(1)–Os(2)	118.6(2)	120.0(1)
C(101)–P(1)–Os(1)	118.9(7)	120.3(6)
C(101)–P(1)–Os(2)	119.5(6)	119.4(5)
C(101)–P(1)–Os(3)	121.8(6)	120.5(5)

be approximately perpendicular to the Os_3 plane in order to maintain a geometry at C(1) as close as possible to tetrahedral. Figure 3 shows how the C_6 rings are tilted with respect to the Os_3 planes in these compounds. In **1** the C(1)–Os(1) and C(2)–Os(3) bonds have the expected length for σ-bonds (2.17(2) and 2.13(3) Å, respectively). The Os(2)–C(1) direction can be seen to be roughly orthogonal to the

Table 2

Crystallographic data for $[Os_3(PMe)(C_6H_4)(CO)_9]$, cluster **1**, and for $[Os_3(PMe)(C_6H_4)(CO)_8(PEt_3)]$, cluster **2a**

	1	**2a**
Formula	$C_{16}H_7O_9Os_3P$	$C_{21}H_{22}O_8Os_3P_2$
M (g mol^{-1})	944.79	1034.94
Size (mm^3)	0.3 × 0.1 × 0.05	0.4 × 0.4 × 0.4 × 0.2 [a]
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	13.957(6)	9.378(2)
b (Å)	8.771(3)	10.581(2)
c (Å)	17.023(4)	14.492(3)
α (°)	90	96.78(2)
β (°)	94.77(3)	92.29(2)
γ (°)	90	107.65(2)
V (Å^3)	2077(1)	1356(1)
Z	4	2
D_c (g cm^{-3})	3.02	2.53
λ(Mo-K_a) (Å)	0.71073	0.71073
μ(Mo-K_a) (cm^{-1})	184.17	141.56
$F(000)$	1671	940
2θ range (°)	$4 \geq 2\theta \geq 50$	$5 \geq 2\theta \geq 50$
hkl range	$0,0,-21 \rightarrow 17,11,21$	$0,-13,-18 \rightarrow 12,13,18$
Total no. data	4127	5116
No. unique data	3691	4798
Rejection criteria	$F_o \leq 3\sigma(F_o)$	$F_o \leq 6\sigma(F_o)$
No. refns used in refinement	2969	3922
No. parameters in refinement	262	307
R [b]	0.056	0.054
R_w	0.044	0.055
g in weighting scheme $1/[\sigma^2(F)+gF^2]$	0.00010	0.00142
Max height in final diff. Fourier (eÅ^{-3})	2.3	2.6
Largest shift/esd in final cycle	0.002	0.002

[a] Triangular prism of thickness 0.2 mm. [b] $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$.

Table 3

Fractional atomic coordinates ($\times 10^4$) for the cluster [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_9$] (1)

	x	y	z
Os(1)	1870(1)	1028(1)	3073(1)
Os(2)	2743(1)	951(1)	1663(1)
Os(3)	2937(1)	−1719(1)	3561(1)
P(1)	3501(3)	328(5)	2892(3)
C(101)	4490(14)	1548(22)	3328(12)
C(1)	1686(10)	−750(19)	2183(8)
C(2)	2192(11)	−2052(18)	2431(9)
C(3)	2084(14)	−3469(24)	2010(14)
C(4)	1447(16)	−3494(30)	1308(14)
C(5)	923(15)	−2240(30)	1073(12)
C(6)	1014(12)	−826(25)	1513(12)
C(11)	1062(12)	139(19)	3807(10)
C(12)	2363(14)	2540(22)	3805(13)
C(13)	926(16)	2346(26)	2539(14)
C(21)	3589(15)	2551(21)	1595(12)
C(22)	1810(13)	1922(24)	908(12)
C(23)	3365(14)	−270(24)	948(11)
C(31)	3477(15)	−968(27)	4569(12)
C(32)	1969(15)	−2960(21)	3980(11)
C(33)	3805(14)	−3332(25)	3491(14)
O(11)	550(9)	−323(15)	4250(8)
O(12)	2706(12)	3441(19)	4204(10)
O(21)	4103(12)	3576(18)	1571(11)
O(22)	1301(11)	2560(20)	474(9)
O(23)	3765(12)	−980(20)	518(10)
O(33)	4354(10)	−4305(17)	3421(11)
O(32)	1386(12)	−3730(19)	4208(11)
O(31)	3787(16)	−504(21)	5142(12)
O(13)	356(13)	3054(24)	2198(10)

organic ring and the distance (2.32(2) Å) is longer and as expected for a π-interaction. The atom Os(2) is within bonding distance only of atom C(1) of the ring, and therefore we propose that Os(1) and Os(3) are σ-bonded to the ring and that there is an interaction through the π-orbitals to Os(2) through just the one carbon atom, unlike the situation in **A** and **B** in which the π-orbitals contribute to a normal η^2-bonding to the unique metal atom. The Os–C distances, Os(2)–C(6) (2.87 Å) and Os(2)–C(2) (3.07 Å), are both too long to be considered as direct bonds. Clearly it is possible to mix the σ- and π-orbitals in such systems, and the above description implying a complete separation is an extreme case, but essentially correct, we believe.

The PEt$_3$ compound has essentially the same geometric features except that the ring is less tilted with respect to the metal plane (Fig. 3) and the Os(2)–C(1) direction is further from perpendicular to the organic ring. This could be the result of steric repulsion between the ortho-phenylene and the PEt$_3$ ligand or there could be greater π-back-bonding from Os(2) to the organic ring with the phosphine coordinated. The Os(2)–C(1) distance is the same in both compounds and we prefer a steric explanation. As we shall show in the next section these systems are fluxional and distortion of the C$_6$H$_4$ coordination is expected to require very little energy.

Table 4

Fractional atomic coordinates ($\times 10^4$) for the cluster [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_8$(PEt$_3$)] (2a)

	x	y	z
Os(1)	2865(1)	4241(1)	8303(1)
Os(2)	−60(1)	2569(1)	8393(1)
Os(3)	2288(1)	4116(1)	6315(1)
C(11)	4869(22)	4316(21)	7937(13)
O(11)	6013(16)	4396(19)	7740(11)
C(12)	3306(19)	6127(16)	8680(11)
O(12)	3506(19)	7217(12)	8861(10)
C(13)	3112(21)	3814(17)	9539(13)
O(13)	3323(20)	3510(17)	10247(9)
C(21)	−1286(20)	3419(17)	8974(12)
O(21)	−2021(20)	3993(16)	9341(10)
C(22)	90(23)	1783(18)	9507(12)
O(22)	86(22)	1377(17)	10196(10)
C(31)	2816(19)	6022(18)	6253(12)
O(31)	3173(15)	7130(12)	6247(10)
C(32)	4107(22)	3913(19)	5850(13)
O(32)	5199(20)	3862(18)	5597(13)
C(33)	1057(20)	3557(17)	5177(13)
O(33)	309(20)	3205(18)	4494(10)
C(1)	1979(16)	2164(13)	7685(10)
C(2)	1902(16)	2157(14)	6691(10)
C(3)	1839(22)	972(20)	6092(12)
C(4)	1889(25)	−139(19)	6454(17)
C(5)	2073(23)	−149(17)	7417(14)
C(6)	2101(19)	985(17)	8025(13)
P(1)	608(4)	4219(3)	7427(2)
C(101)	−100(19)	5643(16)	7606(12)
P(2)	−2066(5)	830(5)	7623(3)
C(201)	−3872(26)	674(27)	8015(18)
C(202)	−3921(33)	444(27)	9004(19)
C(203)	−1787(29)	−872(19)	7633(22)
C(204)	−2996(32)	−2023(29)	7214(26)
C(205)	−2299(29)	963(34)	6343(16)
C(206)	−2878(40)	1942(35)	6144(23)
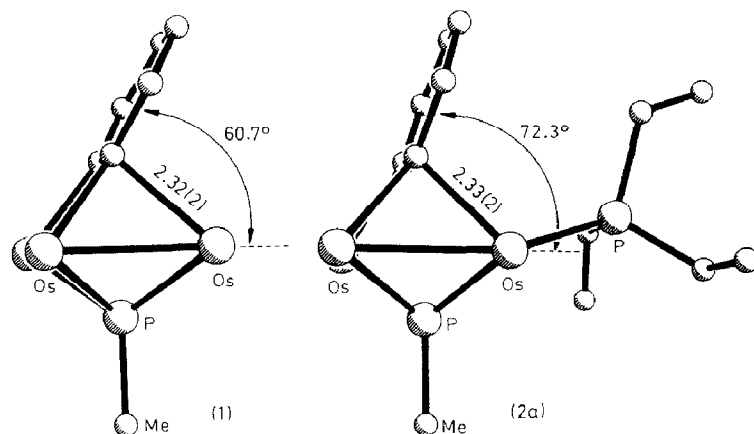
Fig. 3. Views in the plane of the C$_6$H$_4$ rings of compounds 1 and 2a showing the relative dispositions of the Os atoms with respect to the rings.
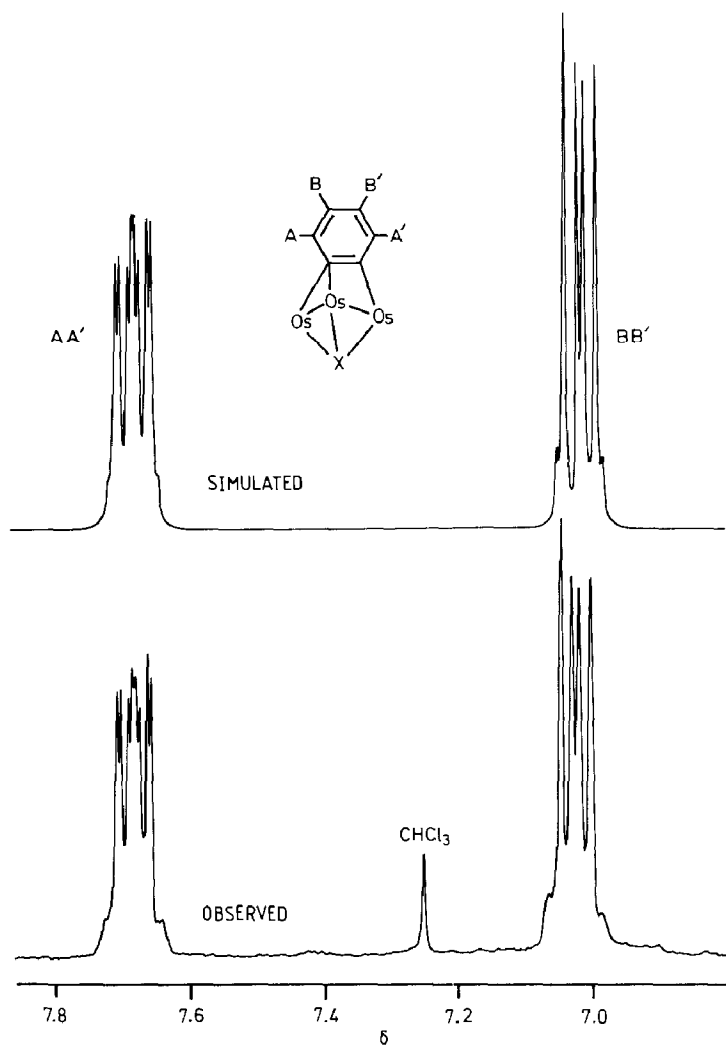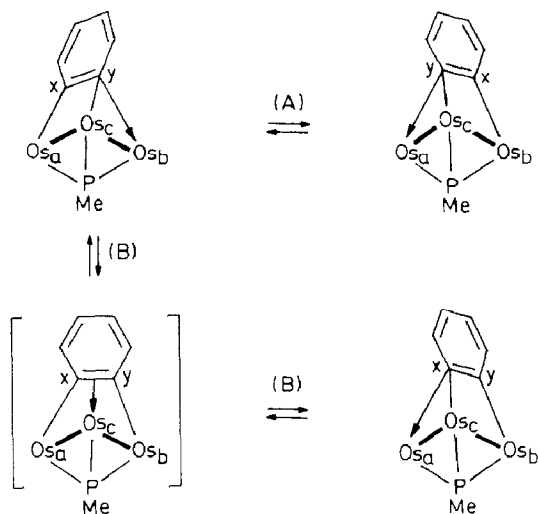
Fig. 4. Observed and simulated spectra for compound **1** recorded at room temperature in $CDCl_3$ at 200 MHz. The simulation was on the basis of $J(AB) = J(A'B') = 7.2$ Hz, $J(AB') = J(A'B) = 2.0$ Hz, $J(BB') = 5.8$ Hz, $J(AA') = 0$ Hz, $J(AX) = J(A'X) = 1.2$ Hz.

Fluxionality involving C_6H_4 rotation

Evans et al. have described the fluxional behaviour of the compounds of type $[Os_3(PR)(C_6H_4)(CO)_9]$ and shown that the ^1H NMR spectrum of the C_6H_4 ring at room temperature is the AA'BB' part of an AA'BB'X spectrum where X is ^{31}P [1]. Figure 4 shows how this spectrum may be simulated. This spectrum requires the *ortho*-phenylene to be symmetrical and this can be achieved if the molecular structure in the crystal is fluxional in solution. This spectrum is essentially the same at $-90°C$ and Evans et al. have shown that the the terminal Os atoms are still apparently equivalent by a fluxional process even at $-132°C$. They considered that it is the aryne rock process **A** that exchanges Os_a and Os_b, but in addition to this, or instead of it, there must be another process leading to exchange of C_x with C_y (Scheme 2). Process **B** could account for this. The symmetrical intermediate with C_x and C_y spanning the open edge would be structurally analogous to alkyne com-

pounds such as $[Fe_3(PR)(PhC_2H)(CO)_9]$ [7]. It has been shown that there is no detectable exchange between the CO ligands at Os_c and those at the other metal atoms, and therefore Os_c must remain unique during the fluxionality. Processes **A** and **B** together amount to total rotation of the C_6H_4 at the metal surface, although **B** alone is enough to exchange of C_x with C_y and Os_a with Os_b.

We initially replaced CO by phosphines to make the terminal metal atoms inequivalent, and thereby lower the rate of this very rapid *ortho*-phenylene rotation to make it accessible by observing coalescence effects. If Os_a could be made intrinsically different from Os_b (by phosphine substitution, for example), neither process **A** nor **B** on its own would lead to symmetrisation of the C_6H_4 ligand but a combination of the two processes would. The cluster $[Os_3(PMe)(C_6H_4)(CO)_8(PEt_3)]$ (**2a**) exists as two isomers which are interconverted photochemically but not at room temperature in the dark (see above). Figure 5 shows ^1H NMR spectra of the mixture in the C_6H_4 region and Fig. 6 shows the proposed structures. The major isomer which corresponds to the crystal structure shows an ABCD spectrum for C_6H_4, which indicates that complete ligand rotation (**A** and **B** together) has been suppressed, as predicted. As the temperature is raised to $70°C$ broadening occurs and coalescence is approached. We believe that this coalescence is good evidence for the relatively slow operation of processes **A** and **B** together. We think that it is most likely that process **B** will in general have the lower barrier, and that process **A** is rate-limiting in this case, although we have no experimental evidence for this.

Although the major isomer of **2a** is slowly fluxional the minor isomer gives an AA'BB' spectrum (marked ★ in the $10°C$ spectrum of Fig. 5; no coupling to ^{31}P detected) indicating rapid exchange. Since we have argued that substitution at a terminal Os atom suppresses exchange, we propose that this minor isomer has PEt_3 at either an axial or equatorial site of the central atom Os_c. If the PEt_3 is axial, process **B** would be degenerate and on its own would lead to rapid C_6H_4 exchange. If there is equatorial substitution, then movement of PEt_3 between the two equatorial sites will be necessary for exchange. In $[Os_3(PEt)(C_6H_4)(CO)_9]$ exchange of the three CO ligands at Os_c gives ^{13}C NMR coalescence between -100 and $-132°C$ [1]. PEt_3 site exchange at the same Os atom could also be very fast.
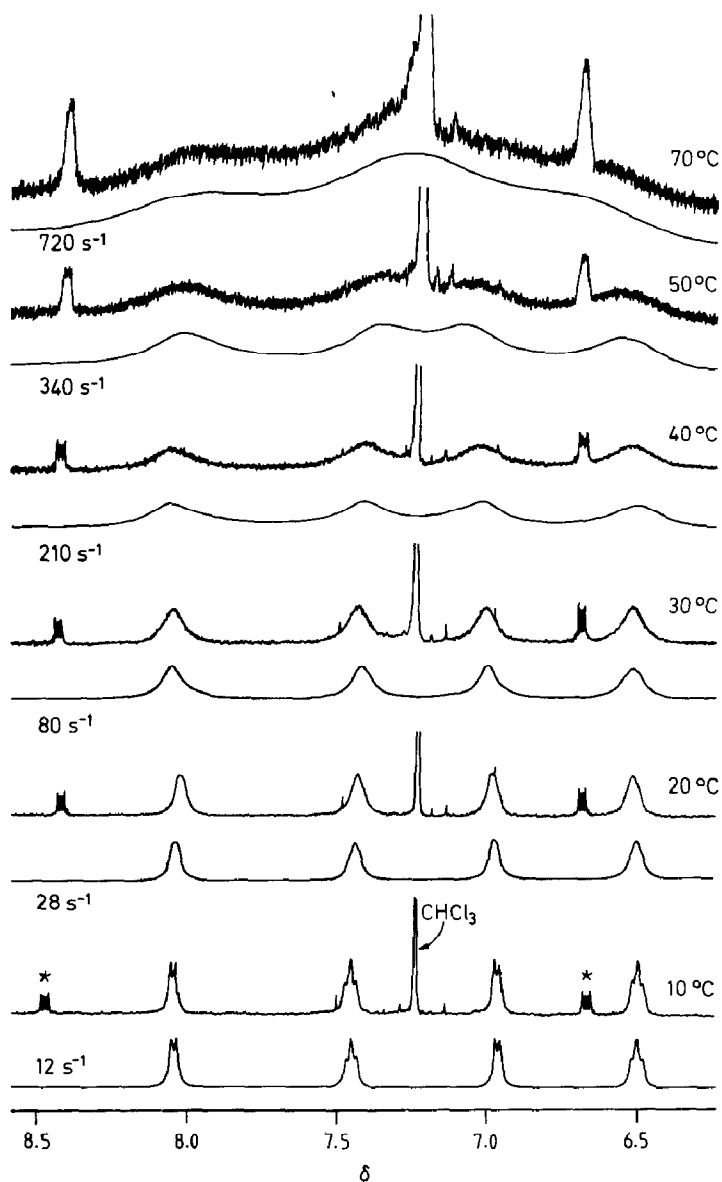
Fig. 5. Observed and simulated 400 MHz ^{1}H NMR spectra for [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_8$(PEt$_3$)] (2a) in CDCl$_3$. The major isomer corresponding the the crystal structure gives the ABCD spectrum that has been simulated. The minor isomer gives the AA'BB' spectrum marked ★.

The ^{1}H NMR spectrum for clusters 2 with ligands PEt$_3$, PCy$_3$, and P(OMe)$_3$ are all very similar, showing a major ABCD pattern and a minor AA'BB' pattern. The abundances of the two isomers are very similar in each case. In the tricyclohexyl case the spectrum of the freshly prepared and isolated compound showed only the major isomer, and only after standing for several days did the minor very fluxional isomer appear. The major isomer of the PCy$_3$ complex is slightly more rapidly fluxional than the PEt$_3$ one, and that of the P(OMe)$_3$ complex even more so. Activation energies obtained from line-shape analyses are: PEt$_3$, $E_a = (65 \pm 3)$: PCy$_3$, $E_a = (63 \pm 6)$; P(OMe)$_3$, $E_a = (51 \pm 2)$ kJ mol^{-1}.
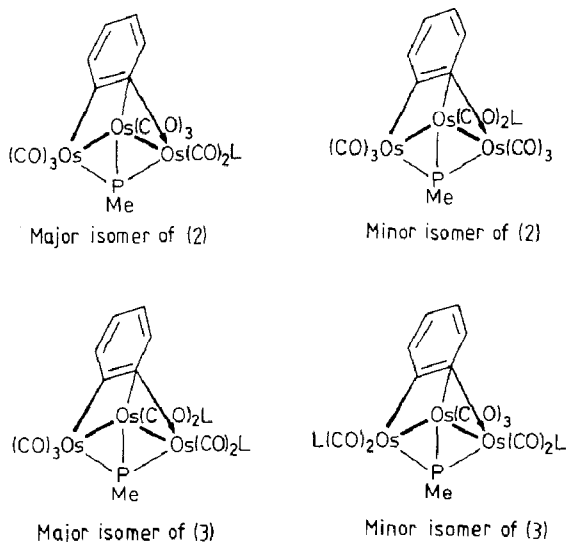
Fig. 6. Proposed geometries of the major and minor isomers of compounds 2 and 3.

The disubstituted compound $[Os_3(PMe)(C_6H_4)(CO)_7L_2]$ (3) (L = PEt$_3$ or P(OMe)$_3$) also exist as isomeric mixtures. In each case the major isomer shows an ABCD ^1H NMR spectrum for the C_6H_4 ligand which does not alter up to 60°C while the minor isomer gives an AA'BB' spectrum and is therefore fluxional. We propose the structures shown in Fig. 6.

Structural comparison of 1 with related ruthenium compounds

Thermolysis of $[Ru_3(CO)_{11}(PPh_3)]$ in toluene does not give $[Ru_3(PPh)(C_6H_4)(CO)_9]$ analogous to the osmium system but the compounds $[Ru_3(PPh_2)_2(C_6H_4)(CO)_7]$, $[Ru_4(PPh)(C_6H_4)(CO)_{11}]$, and $[Ru_5(PPh)(C_6H_4)(CO)_{13}]$ are formed instead [8]. Clearly the trinuclear product is that expected if some phosphine transfer leads to clusters containing two PPh_3 but the tetra- and penta-nuclear compounds are formally derived by the successive additions of $Ru(CO)_2$ units to the as yet unknown species $[Ru_3(PPh)(C_6H_4)(CO)_9]$. We attempted to add $Os(CO)_2$ or $Ru(CO)_2$ units to cluster 1 by its reaction with $[Os_3(CO)_{12}]$ in refluxing decane or
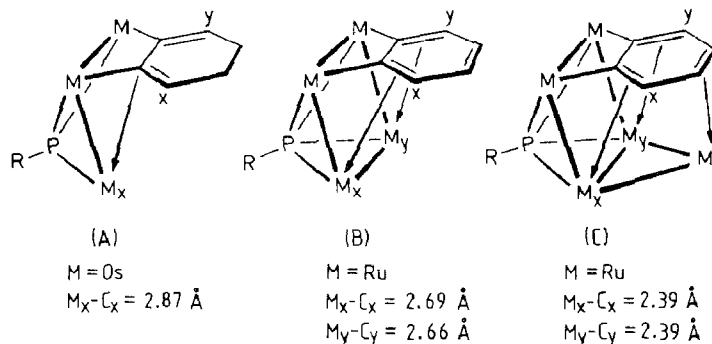
Fig. 7. Structures of **A** $[Os_3(PMe)(C_6H_4)(CO)_9]$, **B** $[Ru_4(PPh)(C_6H_4)(CO)_{11}]$ and **C** $[Ru_5(PPh)(C_6H_4)-(CO)_{13}]$ with the CO ligands omitted.

with $[Ru_3(CO)_{12}]$ in refluxing xylene but in neither case did we obtain products. The structural relation between the M_3, M_4, and M_5 compounds is interesting. Figure 7 shows a representation of the compounds which clearly demonstrates the series in which the C_6H_4 ligands donates four, six, and eight electrons respectively. As the arene is increasingly tied to the metal atoms as more are added, the 3- and 6-carbon atoms are closer to the metal atoms as shown in Fig. 7. In **A** and **B** the extent of direct bonding to the β-carbon atoms is slight, but in **C** both the α- and β-carbon atoms are strongly bonded to the metal atoms.

Experimental

The cluster $[Os_3(CO)_{11}(PMePh_2)]$ was prepared in good yield by treating $[Os_3(CO)_{11}(MeCN)]$ with $PMePh_2$ in dichloromethane at room temperature [9].

Synthesis of [Os₃(PMe)(C₆H₄)(CO)₉], cluster (1)

By use of the method described by Evans et al. [1], a solution of $[Os_3(CO)_{11}(PMePh_2)]$ (0.420 g) in nonane (40 cm^3) was heated under reflux for 3 h, then reduced to dryness under vacuum and the residue chromatographed (TLC (SiO_2), eluant: light petroleum (b.p. 30–40 °C)/CH_2Cl_2, 9/1 v/v). The major yellow band which moved fastest was collected, and the remaining material was extracted and and treated in refluxing nonane for 3 h, then chromatographed as above to give more of the main yellow band. The combined yellow bands were extracted with dichloromethane, to yield compound **1** as yellow crystals (0.371 g, 82%) from hexane. Spectral data: ν(CO) (hexane): 2085w, 2061vs, 2047w(sh), 2040vs, 2008s, 2004s, 1989s, 1981m(sh), 1976vw cm^{-1}: ^{1}H NMR: δ 7.61(m, C_6H_4), 7.00 (m, C_6H_4) (see Fig. 1), 2.96 (d, PCH_3, J(PH) 7.6 Hz).

Syntheses of substitution derivatives of cluster (1)

Triethylphosphine. A solution of cluster **1** (0.100 g) and PEt_3 (0.0125 cm^3) in octane (40 cm^3) was refluxed for 20 min after which the IR spectrum showed that a reaction had substantially occurred. The solution was reduced to dryness under reduced pressure and the residue separated by preparative TLC [SiO_2: eluant: petroleum ether (b.p. 40–60 °C)/dichloromethane, 9/1 v/v]. Four bands were obtained, and yielded: cluster **1** (0.0197 g), $[Os_3(PMe)(C_6H_4)(CO)_8(PEt_3)]$ **(2a)** (0.053 g, 48%) as yellow crystals shown by ^{1}H NMR to be an isomeric mixture (ν(CO) (hexane): 2967s, 2049vw, 2034vs, 2004vs, 1997s, 1972w, 1964m, 1940w cm^{-1}), $[Os_3(PMe)(C_6H_4)(CO)_7(PEt_3)_2]$ cluster **(3a)** (0.012 g, 11%) as orange crystals (also an isomeric mixture) (ν(CO) (hexane): 2067w, 2063(sh), 2050(sh), 2044m, 2037m, 1997vs, 1978s, 1972s, 1962m, 1956m, 1950(sh), 1938m, 1929w, 1918m cm^{-1}), and an unidentified purple band (0.002 g).

Tricyclohexylphosphine. A similar reaction of cluster **1** (0.041 g) with PCy_3 (0.007 g) gave one yellow TLC band which was characterised as an isomeric mixture of $[Os_3(PMe)(C_6H_4)(CO)_8(PCy_3)]$ **(2b)** (0.0156 g, 30%) (ν(CO) (hexane): 2066vs, 2035vs, 2002vs, 1996s, 1971m, 1963m, 1936m cm^{-1}).

Trimethylphosphite. A similar reaction of cluster **1** (0.050 g) and $P(OMe)_3$ (0.007 cm^3) but with 1 h reflux gave an isomeric mixture of $[Os_3(PMe)(C_6H_4)(CO)_8\{P(OMe)_3\}]$ **(2c)** (0.0117 g, 22%) as a mustard-coloured solid (ν(CO) (hexane): 2069s, 2049m, 2037vs, 2013s, 2000vs, 1990m, 1981m, 1974m, 1966m cm^{-1}), and

[Os$_3$(PMe)(C$_6$H$_4$)(CO)$_7${P(OMe)$_3$}$_2$] (3c) 0.0065, 11%) also as a mustard-coloured solid as an isomeric mixture (ν(CO) (hexane): 2052m, 2014vs, 1999(sh), 1991s, 1975m, 1965s, 1956(sh), 1953(sh), 1944w cm^{-1}).

Crystal structure determinations for [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_9$] (1) and for [Os$_3$(PMe)(C$_6$H$_4$)(CO)$_8$(PEt$_3$)] (2a)

Yellow crystals of clusters 1 and 2a were obtained by evaporation of solution in light petroleum (b.p. 30 40°C). Unit cell parameters were obtained by least-squares fits of 26 reflections in the 2θ range 19 to 35° for cluster 1 and 24 reflections in the 2θ range 12 to 30° for cluster 2a using a Nicolet R3m/v diffractometer operating at room temperature with graphite-monochromated Mo-K_α radiation. Crystal data and details of the data collection, structure solution, and refinement are given in Table 2. Data were collected by the ω–2θ scan mode and measured intensities were corrected for a small decay based on the intensities of three standard reflections measured periodically throughout the data collection, for Lorentz and polarisation effects, and empirically for absorption using the azimuthal scan method.

The Os atoms were located by direct methods (SHELXTL PLUS [10]) and the structure was refined by least-squares full-matrix methods and difference Fourier synthesis. All non-hydrogen atoms were located and refined anisotropically and hydrogen atoms were not included in the model. Atomic coordinates are given in Table 3 for cluster 1 and in Table 4 for cluster 2a.

Acknowledgements

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