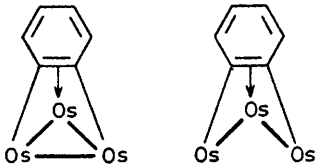
Solution Behaviour of Some Benzyne Complexes of Osmium and the *X*-Ray Crystal Structure of μ_3-Benzyne-1,1,1,2,2,2,3,3,3-nonacarbonyl-μ-dimethylarsino-μ-hydrido-triosmium(2*Os*–*Os*)

By **Antony J. Deeming** * and **Ian P. Rothwell**, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ
Michael B. Hursthouse * and **J. D. Julius Backer-Dirks**, Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

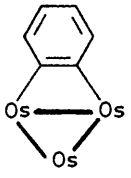
Variable-temperature ^1H and ^{13}C n.m.r. analysis of $[Os_3(C_6H_4)(AsMe_2)_2(CO)_7]$ and its $C_6H_3Pr^i$ analogue has confirmed that one CO ligand rapidly transfers between two Os atoms and that opposite faces of the μ_3-C_6H_4 ligand interchange during two distinct fast intramolecular processes. The *X*-ray crystal structure of $[Os_3(C_6H_4)(AsMe_2)(CO)_9H]$ has been determined. The crystals are triclinic, space group $P\bar{1}$, with a = 9.302(3), b = 9.398(6), c = 15.063(7) Å, α = 101.87(4), β = 72.64(3), γ = 117.48(3)°, and Z = 2 and the structure has been refined to R = 0.0518 for 3 029 observed reflections. The compound contains a triangle of Os atoms joined by two Os–Os bonds with a $AsMe_2$ group bridging the two non-bonded metal atoms. The C_6H_4 ligand is triply bridging the metal atoms with two σ Os–C bonds and a η^2-linkage. The hydride ligand was not located but its position inferred from the structure. Variable-temperature n.m.r. studies of this complex and its $C_6H_3Pr^i$ analogue show that the presence of only two Os–Os bonds does not interfere with the interchange of C_6H_4 ligand faces as indicated by the coalescence of the diastereotopic methyl signals of the Pr^i group.

TRIOSMIUM complexes containing μ_3-C_6H_4 ligands have been derived from $[Os_3(CO)_{12}]$ and PMe_2Ph or $AsMe_2Ph$ by C–H and C–As cleavage.[1] Typical of these complexes are $[Os_3(C_6H_4)(AsMe_2)_2(CO)_7]$, (1), and $[Os_3(C_6H_4)(AsMe_2)(CO)_9H]$, (2). The structure of (1) is clearly assigned by direct comparison with that of the PPh_2 analogue which has been determined by *X*-ray methods.[2] Complex (1) contains a four-electron-donor benzyne ligand with bonding best described by structure (I). There are two

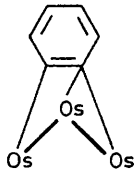


(I)

(II)



(III)



(IV)

more electrons associated with the $Os_3(C_6H_4)$ framework of (2) than with that of (1) and because of this we suggested earlier [1] that (2) contains a two-electron-donor C_6H_4 ligand attached with a different geometry (III) to the Os_3 triangle. The *X*-ray structure of (2) which we now report shows this to be incorrect since the extra two electrons have resulted in a cluster with only two Os–Os bonds (II) while the C_6H_4–metal bonding in (1) and (2) proves rather to be very similar. Another outstanding problem relates to the movements of the C_6H_4 groups with respect to the Os_3 triangles leading to n.m.r. coalescences. Largely on circumstantial grounds we proposed that the ligand flips while rotating so that opposite faces of the C_6 ring successively interchange. We can now provide n.m.r. evidence for this by use of isopropyl-substituted rings as derived from $AsMe_2(C_6H_4Pr^i\text{-}4)$. Carbon-13 n.m.r. evidence for the migration of one CO group between metal atoms in (1) to substantiate an earlier proposal is also presented.

RESULTS AND DISCUSSION

Solution Behaviour of $[Os_3(\mu_3\text{-}C_6H_4)(AsMe_2)_2(CO)_7]$, *Complex* (1).—The two mechanisms in Figure 1 were proposed to account for changes in ^1H n.m.r. spectra with temperature.[1] The faster process (*a*) leads to a time-averaged plane of symmetry and equivalent $AsMe_2$ groups and could not be frozen out even at −110 °C. Process (*a*) does not lead to the symmetrisation of the C_6H_4 ligand which is only observed at higher temperatures by process (*b*). Both mechanisms require rotation/flipping of the C_6H_4 rings and CO transfer between Os atoms, neither of which was established in our earlier report.[1] The ^{13}C n.m.r. spectrum of (1) (Table 1) at −60 °C is consistent with process (*a*) occurring very rapidly and (*b*) much more slowly. At this temperature five signals for the C_6H_4 ligand were observed (intensity ratio 2 : 1 : 1 : 1 : 1 with one accidental coincidence) corresponding to the ABXY ^1H n.m.r. spectrum for the C_6H_4 ligand at the same temperature. Even though the C_6H_4 ligand appears asymmetric, the $AsMe_2$ groups appear equivalent (two ^{13}C signals only) and five CO signals (intensity ratio 2 : 1 : 2 : 1 : 1) are observed (Figure 2). Since all seven CO ligands are different, the signals of intensity 2 must be due to the D,D′ and E,E′ pairs exchanging by process (*a*) which generates a time-averaged plane of symmetry. This is evidence that the carbonyl group F rapidly transfers between Os(2) and Os(3) but without itself interchanging with D,D′, E, or E′. The signal at

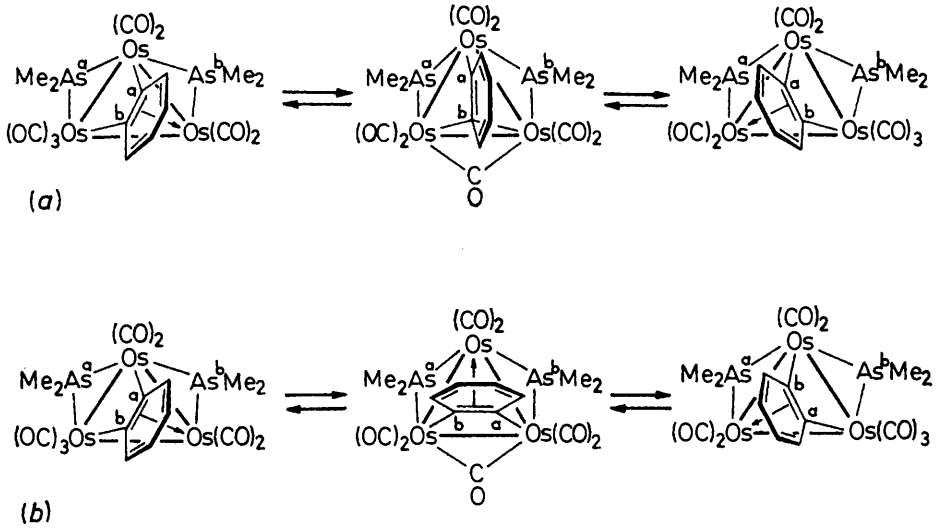


FIGURE 1 Two rapid intramolecular processes proposed for $[Os_3(C_6H_4)(AsMe_2)_2(CO)_7]$, (1)

δ 177.4 was assigned to the migrating group F only on the basis of coalescence behaviour at higher temperatures. Thus above −60 °C three of the five CO signals broaden and coalesce to give signals of intensities 1 : 5 : 1 at room temperature; the signals remaining sharp throughout (δ 181.3 and 184.3 at 27 °C) are then assigned to groups G and I. The transfer of carbonyl F between Os(2) and Os(3) coupled with a localised axial–equatorial exchange at Os(2) would account for the complete exchange of D,D′, E,E′, and F. Also as can be seen from Figure 2 the C_6H_4 ligand becomes effectively symmetrical in this temperature range as observed in the ^1H n.m.r. spectrum.

The other main feature of our proposed mechanisms apart from the CO migration is the rotation/flip of the C_6H_4 ligand. To test whether the opposite faces of the C_6H_4 ligand are interchanging or not, that is to test the flipping mechanism, we chose to introduce the diastereotopic isopropyl group. From 4-isopropylphenyldimethylarsine, we synthesised $[Os_3(C_6H_3Pr^i)(AsMe_2)(CO)_9H]$, (3), and $[Os_3(C_6H_3Pr^i)(AsMe_2)_2(CO)_7]$, (4). The Pr^i groups are positioned furthest from the osmium atoms. The n.m.r. spectra are slightly more complicated but easily interpreted in terms of isomers, complex (4) showing equal abundances of (4a) and (4b) at −60 °C (see Tables 1 and 2). The isomers are in

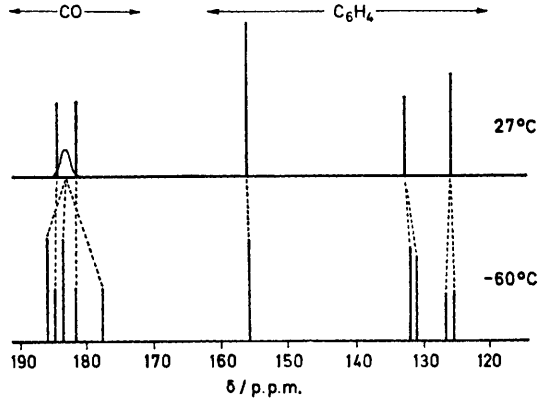


FIGURE 2 Carbon-13 n.m.r. spectra for compound (1) in $CDCl_3$ (diagramatic representation)

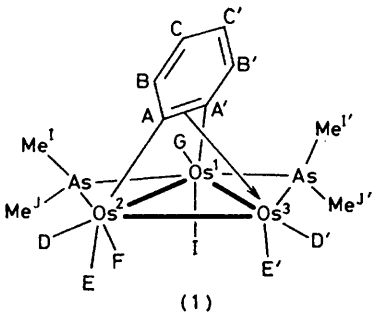
equilibrium by process (*b*), but not by (*a*). Thus at −60 °C twelve ^{13}C signals for the C_6 rings of the two isomers coalesce in pairs to six signals at room tempera-

TABLE 1

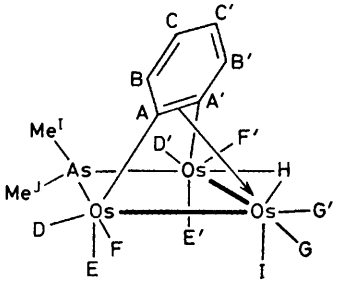
Carbon-13 n.m.r. data for compounds (1)—(4) [a]

Complex	θ_c/°C	C_6H_3R (R = H or Pr^i) resonances A,A′	B,B′	C,C′	$AsMe_2$ resonances	CO resonances D,D′	E,E′	F	G,I
(1)	27	← 132.8 →	← 156.0 →	← 126.2 →	17.6, 19.6	←	182.0	→	181.2, 183.9
	−60	131.6, 132.6	← 155.9 →	125.0, 127.0	17.4, 19.3	183.3,	185.4,	177.4	181.3, 184.3
(4) [b]	27	127.1, 134.8	152.4, 156.5	126.1, 147.2	17.5, 19.5	←	182.0	→	181.4, 184.0
	−50	127.3, 126.8	152.6, 152.2	125.3, 126.9	17.3, 19.2	183.5,	185.2,	177.5	181.5, 184.5
		134.4, 133.8	156.6, 156.3	145.9, 147.5	19.4		185.8,	177.8	184.3
(2)	120	← 157.9 →	← 143 →	← 126.7 →	12.4, 14.4	178.9,	175.9,	175.5,	172.4
	−40	153.0 162.8	126.0, 158.5	124.7, 128.1	12.1, 13.4	183.9,	181.9,	178.6,	176.0, 174.6,
						173.9,	172.7,	172.4,	168.9
(3) [c]	27				12.5, 14.0				
	−45	148.7, 163.4	121.6, 161.1	124.3, 148.1	12.2, 13.2	184.2,	182.2,	178.8,	176.4 174.7,
						174.1,	172.9,	172.7,	169.0

[a] Recorded in $CDCl_3$. [b] Isopropyl signals at δ 23.5 and 33.7 at 27 °C and δ 23.6 and 33.5 at −50 °C. [c] Isopropyl signals at 23.4 (br) and 33.7 at 27 °C and δ 23.9, 22.9, and 33.7 at −45 °C; minor absorptions which are probably due to the other isomer are not reported. Ring carbon and CO resonances at 27 °C are too broad to be observed and higher temperatures were not used.

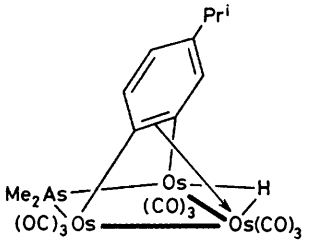


(1)

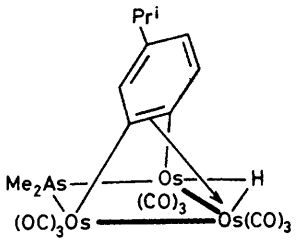


(2)

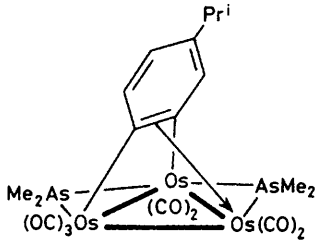
ture. Signals for isomers (4a) and (4b) were not resolved for the $AsMe_2$ and Pr^i groups and are only partly resolved for the CO groups. This is reasonable since the equal abundances for (4a) and (4b) indicate that the substituent coalescence rather than accidental coincidence because clearly separated ^{13}C and ^1H signals are observed in the frozen-out spectra of (3) (see later). Thus we have



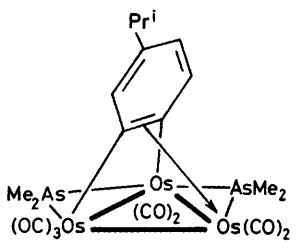
(3a)



(3b)



(4a)

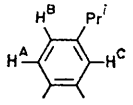


(4b)

evidence that in process (*a*) the opposite faces of the organic ring are interchanging. The C_6H_4 ligand is initially tilted with respect to the Os_3 plane (*ca.* 77° in structures studied crystallographically [2,3]) and for both processes

TABLE 2

Hydrogen-1 n.m.r. data for $C_6H_3Pr^i$ complexes (3) and (4) [a]



Complex	θ_c/°C	$C_6H_3Pr^i$ resonances			Pr^i resonances		$AsMe_2$ resonances
		H^C	H^B	H^A	CH	CH_3	
(4)	27	7.10 (d) [1.8]	6.42 (dd)	7.24 (d) [8.0]	2.42 (m)	1.01 (d) [6.3]	1.69 (s) 2.23 (s)
	−60	7.00 (br) 7.19 (br)	6.37 (br d) 6.50 (br d)	7.32 (d) 7.12 (d) [7.5]	2.40 (br)	1.00 (br d)	1.70 (s) 2.24 (s)
(3) [b]	27	8.51 (br)	6.70 (br d)	8.84 (br d)	2.41 (m)	1.22 (d) [7.0]	1.39 (s) 1.94 (s)
	−60 Major isomer	8.40 (br d) [2.0]	6.69 (dd)	9.01 (d) [9.5]	2.41 (br)	1.27 (d) 1.15 (d)	1.40 (s) 1.95 (s)
	Minor isomer	8.85 (br)	6.98 (dd)	8.55 (d) [7.8]	*c*	*c*	*c*

[a] *J* Values (Hz) in square brackets; br = broad, d = doublet, s = singlet, m = multiplet. Spectra recorded in $CDCl_3$ at 100 MHz; chemical shifts downfield from $SiMe_4$. [b] Metal hydride signal −17.17 (s) at all temperatures. [c] Signals due to minor isomer obscured.

effects of the Pr^i group on the ligand–metal bonding are minimal.

The most important mechanistic result comes from considering the Pr^i signals. A static molecule, (4a) or (4b), would be chiral with no plane of symmetry through the arene ring; the methyl groups of the Pr^i substituent would be diastereotopic. Even when process (*b*) has been frozen out (−60 °C) coalesced signals for the Pr^i group are observed so that the faster process (*a*) must lead to a time-averaged plane of symmetry through the C_6 ring. A single set of $CHMe_2$ resonances is due to (*a*) and (*b*) it must pass through a vertical orientation as it rotates, finally readopting a tilted configuration with the opposite ligand face towards the metal. This relates to the behaviour of μ_3-alkyne ligands as shown by the coalescence of the H^a and H^b signals for the indyne complex $[Os_3(C_9H_6)(CO)_9H_2]$ (Figure 3) which was also interpreted in terms of a rotation/flipping mechanism.[4] Since the faster process (*a*) leads to interchange of the C_6H_4 faces we cannot show that this also occurs for (*b*), although we assume that the movements of the C_6H_4 ligand with respect to the metal atoms are similar in both

cases. Before we consider the dynamic behaviour of (2) we will describe its *X*-ray structure.

X-Ray Structure of $[Os_3(C_6H_4)(AsMe_2)(CO)_9H]$, *Complex* (2).—This complex relates closely with $[Os_3(C_6H_4)(PPh_2)(CO)_7(PPh_3)H]$ [3] except that it has two extra

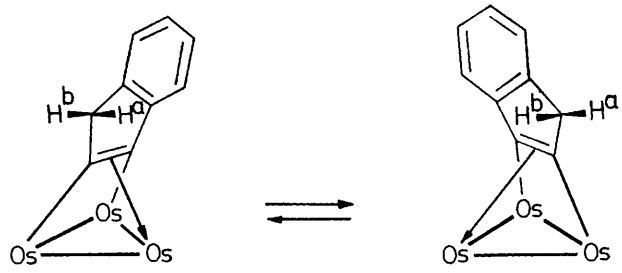


FIGURE 3 Rotation/flipping mechanism proposed for $[Os_3(C_9H_6)(CO)_9H_2]$ [4]

electrons for metal–ligand and/or metal–metal bonding by virtue of an extra two-electron-donor ligand. One would expect there to be one less Os–Os bond in (2) or for the C_6H_4 ligand to be a two-electron rather than a four-electron donor. In either case the complexes should be structurally different, so the *X*-ray structure of (2) was determined for comparison with that of $[Os_3(C_6H_4)(PPh_2)(CO)_7(PPh_3)H]$. The molecular structure is shown in Figure 4, atom co-ordinates are given in Table 3, and

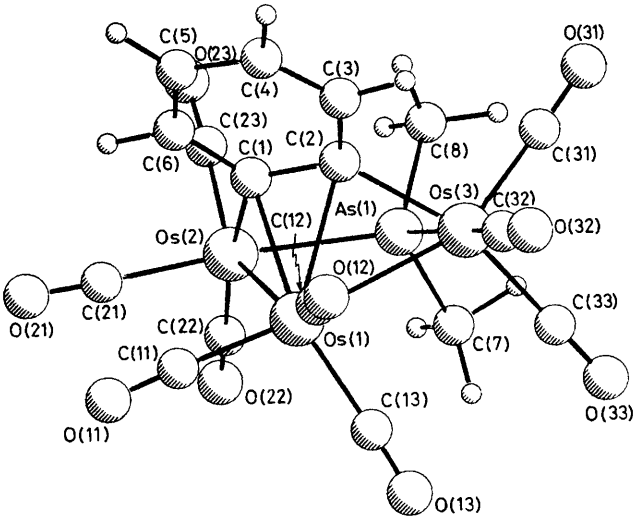


FIGURE 4 *X*-Ray molecular structure of $[Os_3(C_6H_4)(AsMe_2)(CO)_9H]$, (2)

selected bond lengths and angles given in Tables 4 and 5 respectively. Anistropic temperature factors and lists of observed and calculated structure factors are given in Supplementary Publication No. SUP 23066 (15 pp.).*

The osmium–osmium distances of 2.839(4), 2.946(4), and 3.929(5) and the wide Os(3)Os(1)Os(2) angle of 85.5° clearly show that Os(1)–Os(2) and Os(1)–Os(3) are the only metal–metal bonds. The $AsMe_2$ ligand forms a

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 3

Atom co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Os(1)	8 747(1)	2 298(1)	6 722(1)
Os(2)	6 412(1)	−1 079(1)	7 051(1)
Os(3)	6 131(1)	3 047(1)	7 903(1)
As(1)	4 396(2)	136(2)	7 593(1)
C(1)	7 843(14)	829(16)	7 982(8)
C(2)	7 575(15)	2 242(14)	8 364(8)
C(3)	8 407(20)	3 173(21)	9 066(10)
C(4)	9 465(20)	2 811(21)	9 335(10)
C(5)	9 698(20)	1 446(20)	9 004(11)
C(6)	8 920(18)	527(18)	8 331(9)
C(7)	3 096(21)	−285(21)	6 694(14)
C(8)	2 644(20)	−866(23)	8 659(14)
C(11)	10 492(16)	1 686(19)	6 016(9)
C(12)	10 406(18)	4 289(18)	7 032(11)
C(13)	8 434(20)	3 169(21)	5 769(11)
C(21)	8 135(16)	−1 857(16)	6 536(9)
C(22)	5 213(17)	−2 498(17)	6 122(10)
C(23)	5 195(16)	−2 512(20)	8 002(12)
C(31)	4 606(19)	3 133(19)	9 024(10)
C(32)	7 683(20)	5 236(21)	8 095(10)
C(33)	5 161(22)	3 596(22)	7 106(12)
O(11)	11 516(15)	1 327(17)	5 574(8)
O(12)	11 472(14)	5 517(16)	7 211(10)
O(13)	8 256(15)	3 588(18)	5 212(9)
O(21)	9 050(14)	−2 394(15)	6 252(8)
O(22)	4 534(15)	−3 330(16)	5 585(8)
O(23)	4 500(17)	−3 432(16)	8 570(8)
O(31)	3 671(15)	3 161(18)	9 721(8)
O(32)	8 556(16)	6 598(13)	8 238(8)
O(33)	4 527(20)	3 827(19)	6 659(11)
H(3)	8 203(20)	4 217(21)	9 404(10)
H(4)	10 152(20)	3 640(21)	9 834(10)
H(5)	10 460(20)	1 127(20)	9 269(11)
H(6)	9 135(18)	−524(18)	8 030(9)
H(7A)	3 525(21)	330(21)	6 069(14)
H(7B)	2 227(21)	105(21)	7 204(14)
H(7C)	2 485(21)	−1 568(21)	6 528(14)
H(8A)	3 247(20)	−611(23)	9 222(14)
H(8B)	2 127(20)	−2 144(23)	8 464(14)
H(8C)	1 657(20)	−475(23)	8 883(14)

TABLE 4

Bond lengths (Å) with estimated standard deviations in parentheses

Os(2)–Os(1)	2.946(4)	C(7)–As(1)	1.941(26)
Os(3)–Os(1)	2.839(4)	C(8)–As(1)	1.940(19)
C(1)–Os(1)	2.296(15)	C(2)–C(1)	1.436(22)
C(2)–Os(1)	2.388(14)	C(6)–C(1)	1.413(28)
C(11)–Os(1)	1.917(18)	C(3)–C(2)	1.401(21)
C(12)–Os(1)	1.873(15)	C(4)–C(3)	1.361(33)
C(13)–Os(1)	1.941(24)	C(5)–C(4)	1.367(29)
Os(3)–Os(2)	3.929(5)	C(6)–C(5)	1.341(23)
As(1)–Os(2)	2.483(4)	O(11)–C(11)	1.136(22)
C(1)–Os(2)	2.198(13)	O(12)–C(12)	1.167(18)
C(21)–Os(2)	1.953(19)	O(13)–C(13)	1.079(29)
C(22)–Os(2)	1.942(16)	O(21)–C(21)	1.119(24)
C(23)–Os(2)	1.888(19)	O(22)–C(22)	1.119(19)
As(1)–Os(3)	2.482(3)	O(23)–C(23)	1.164(23)
C(2)–Os(3)	2.138(19)	O(31)–C(31)	1.150(19)
C(31)–Os(3)	1.869(16)	O(32)–C(32)	1.173(19)
C(32)–Os(3)	1.914(17)	O(33)–C(33)	1.124(34)
C(33)–Os(3)	1.962(27)		

symmetrical bridge between the non-bonded Os(2) and Os(3) atoms. Since there are only two Os–Os bonds, one can predict from the 18-electron rule that the C_6H_4 should be a four-electron donor. This is consistent with its observed mode of attachment which is best interpreted as involving two σ bonds Os(2)–C(1) and Os(3)–C(2) and a η^2 linkage between C(1), C(2), and Os(1). The bonding

TABLE 5

Bond angles (°) with estimated standard deviations in parentheses

Os(3)–Os(1)–Os(2)	85.5(1)	C(31)–Os(3)–Os(2)	117.2(8)
C(1)–Os(1)–Os(2)	47.6(3)	C(32)–Os(3)–Os(2)	135.8(5)
C(11)–Os(1)–Os(2)	91.4(5)	C(33)–Os(3)–Os(2)	112.5(6)
C(12)–Os(1)–Os(2)	152.3(6)	C(2)–Os(3)–As(1)	84.5(4)
C(13)–Os(1)–Os(2)	115.0(5)	C(31)–Os(3)–As(1)	91.3(5)
C(1)–Os(1)–Os(3)	76.0(5)	C(32)–Os(3)–As(1)	173.5(6)
C(11)–Os(1)–Os(3)	174.7(5)	C(33)–Os(3)–As(1)	90.8(6)
C(12)–Os(1)–Os(3)	93.0(6)	C(31)–Os(3)–C(2)	100.1(8)
C(13)–Os(1)–Os(3)	84.3(6)	C(32)–Os(3)–C(2)	90.3(9)
C(11)–Os(1)–C(1)	98.8(7)	C(33)–Os(3)–C(2)	162.4(6)
C(12)–Os(1)–C(1)	105.2(7)	C(32)–Os(3)–C(31)	93.4(7)
C(13)–Os(1)–C(1)	154.1(6)	C(33)–Os(3)–C(31)	96.9(9)
C(12)–Os(1)–C(11)	87.7(8)	C(33)–Os(3)–C(32)	93.0(9)
C(13)–Os(1)–C(11)	100.9(8)	Os(3)–As(1)–Os(2)	104.6(2)
C(13)–Os(1)–C(12)	92.3(9)	C(7)–As(1)–Os(2)	112.6(7)
Os(3)–Os(2)–Os(1)	46.1(1)	C(8)–As(1)–Os(2)	112.2(9)
As(1)–Os(2)–Os(1)	81.1(1)	C(7)–As(1)–Os(3)	112.8(6)
C(1)–Os(2)–Os(1)	50.5(4)	C(8)–As(1)–Os(3)	114.1(6)
C(21)–Os(2)–Os(1)	93.7(4)	C(8)–As(1)–C(7)	100.8(9)
C(22)–Os(2)–Os(1)	121.1(5)	Os(2)–C(1)–Os(1)	81.9(5)
C(23)–Os(2)–Os(1)	142.5(5)	C(2)–C(1)–Os(1)	75.7(9)
C(1)–Os(2)–Os(3)	54.3(4)	C(6)–C(1)–Os(1)	123.0(9)
C(21)–Os(2)–Os(3)	138.2(3)	C(2)–C(1)–Os(2)	124.2(12)
C(22)–Os(2)–Os(3)	118.9(5)	C(6)–C(1)–Os(2)	117.3(11)
C(23)–Os(2)–Os(3)	110.2(6)	C(6)–C(1)–C(2)	117.8(12)
C(1)–Os(2)–As(1)	85.2(5)	C(1)–C(2)–Os(3)	125.2(10)
C(21)–Os(2)–As(1)	174.0(4)	C(3)–C(2)–Os(3)	119.2(14)
C(22)–Os(2)–As(1)	90.9(6)	C(3)–C(2)–C(1)	115.5(17)
C(23)–Os(2)–As(1)	90.1(7)	C(4)–C(3)–C(2)	122.4(18)
C(21)–Os(2)–C(1)	93.8(6)	C(5)–C(4)–C(3)	123:1(16)
C(22)–Os(2)–C(1)	171.2(6)	C(6)–C(5)–C(4)	115.9(21)
C(23)–Os(2)–C(1)	92.7(7)	C(5)–C(6)–C(1)	125.1(18)
C(22)–Os(2)–C(21)	89.2(7)	O(11)–C(11)–Os(1)	178.0(15)
C(23)–Os(2)–C(21)	95.9(8)	O(12)–C(12)–Os(1)	178.2(16)
C(23)–Os(2)–C(22)	95.2(7)	O(13)–C(13)–Os(1)	176.5(17)
Os(2)–Os(3)–Os(1)	48.4	O(21)–C(21)–Os(2)	175.8(11)
As(1)–Os(3)–Os(1)	83.3	O(22)–C(22)–Os(2)	178.9(18)
C(2)–Os(3)–Os(1)	55.2(4)	O(23)–C(23)–Os(2)	176.6(17)
C(31)–Os(3)–Os(1)	155.1(7)	O(31)–C(31)–Os(3)	178.5(19)
C(32)–Os(3)–Os(1)	90.6(6)	O(32)–C(32)–Os(3)	176.2(17)
C(33)–Os(3)–Os(1)	107.5(6)	O(33)–C(33)–Os(3)	176.0(14)
As(1)–Os(3)–Os(2)	37.7		

with respect to the metal atoms is essentially symmetrical and as shown in (II).

The hydride ligand observed in the ^{1}H n.m.r. spectrum was not located in this crystal-structure determination. Although Os(2) and Os(3) are essentially equivalent with respect to the C_6H_4 and $AsMe_2$ ligands there is far from being a molecular plane of symmetry. Thus Os(2)–Os(1) is longer by 0.107 Å than Os(3)–Os(1) and is believed to accommodate the bridging hydride. Furthermore, the three carbonyl ligands at Os(1) are very asymmetrically arranged with only C(11)O(11) occupying an equatorial position. It appears that while remaining approximately at right angles to each other, these three carbonyl ligands have twisted to make space for the hydride to bridge Os(1)–Os(2). Thus the angles C(22)Os(2)Os(1) and C(13)Os(1)Os(2) (121 and 115.0° respectively) are much greater than C(33)Os(3)Os(1) and C(13)Os(1)Os(3) (107.5 and 84.3° respectively). These wide angles associated with the Os(1)–Os(2) bond make space for the hydride to be along this bond below the Os_3 plane opposite the C(1) atom of the C_6H_4 ligand.

The major structural features of compound (2) and $[Os_3(C_6H_4)(PPh_2)(CO)_7(PPh_3)H]$ are compared in Figure 5. Surprisingly (2) and its phosphorus analogue show no tendency to thermally decarbonylate to form the third Os–Os bond present in $[Os_3(C_6H_4)(PPh_2)(CO)_7(PPh_3)H]$. It is remarkable that the structures of these compounds are so similar in spite of the different number of Os–Os bonds and that the 18-electron rule operates so well. Compounds (2), $[Os_3(C_6H_4)(\mu\text{-}CH{=}NPh)(CO)_8H_3]$,[5] and $[Os_3(C_6H_4)(PEt)(CO)_9]$[6] all require a two-electron-donating C_6H_4 if they are to maintain three

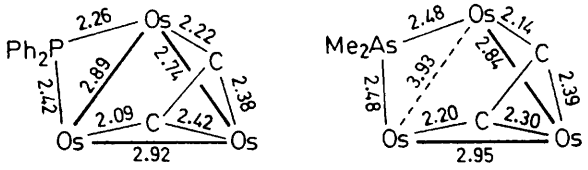


FIGURE 5 A comparison of the cluster skeletons of $[Os_3(C_6H_4)(PPh_2)(CO)_7(PPh_3)H]$ and of compound (2); only the co-ordinated atoms of the C_6H_4 ligands are shown (bond lengths in Å)

metal–metal bonds. In (2), as shown, metal–metal bond cleavage allows the C_6H_4 ligand to be a four-electron donor (II), in $[Os_3(C_6H_4)(CH{=}NPh)(CO)_8H_3]$ the C_6H_4 is a μ two-electron donor (III), while in $[Os_3(C_6H_4)(PEt)(CO)_9]$ there are two Os–Os bonds but the C_6H_4 is very unusually bound (IV) and possibly is behaving as a four-electron donor while also a μ_3 ligand. The bonding modes (I) to (IV) emphasise the interesting structural variations to be found for arynes and alkynes in clusters.

Solution Behaviour of $[Os_3(\mu_3\text{-}C_6H_4)(AsMe_2)(CO)_9H]$, *Complex* (2).—The C_6H_4 ligand in (2) shows greater asymmetry in the ^{1}H n.m.r. spectrum than in (1). Indeed, the asymmetry in the ^{13}C n.m.r. spectrum is so enormous (compare Figures 2 and 6) that before the

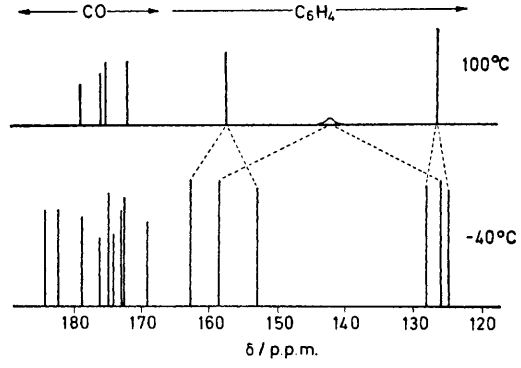


FIGURE 6 Carbon-13 n.m.r. spectra of compound (2) in $CDCl_3$ (diagramatic representation)

X-ray structure was available we believed that the C_6H_4 ligand in (2) was co-ordinated quite differently to that in (1). The process observed in spectra recorded between −60 °C and 27 °C, Figure 6, which effectively symmetrises the C_6H_4 ligand could be a simple reversible hydride migration from the Os(1)–Os(2) to the Os(1)–Os(3) edge with some angular reorganisation of carbonyl ligands, especially at Os(1), to generate a time-averaged plane of symmetry. However, the simultaneous broadening and collapse of all nine ^{13}C signals of the CO groups

on warming from −40 to +40 °C is inconsistent with this, since a pairwise coalescence of eight signals (D,D'; E,E'; F,F'; G,G') would leave the signal due to I unaffected. Studies on complex (3) $[Os_3(C_6H_3Pr^i)(AsMe_2)(CO)_9H]$ have also shown that a simple hydride migration alone cannot account for the observations. At −60 °C isomers (3a) and (3b) are observed in intensity ratio 1 : 4, but we could not tell which was the major isomer, while at 27 °C the spectrum is the average for the two isomers, Figure 7. Their interconversion by a hydride shift alone cannot explain the simultaneous

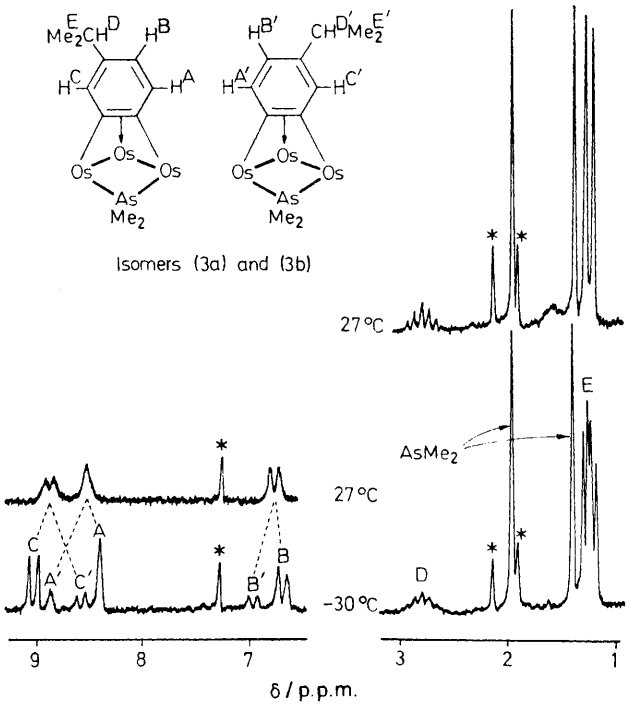


FIGURE 7 Proton n.m.r. spectra for $[Os_3(C_6H_3Pr^i)(AsMe_2)(CO)_9H]$, (3), in $CDCl_3$; an asterisk indicates solvent or impurity absorptions

generation of a time-averaged plane of symmetry through the C_6 ring. Thus the two $CHMe_2$ doublets (^1H n.m.r.) and singlets (^{13}C n.m.r.) at −60 °C for the major isomer have coalesced at 27 °C. The diastereotopic Me groups can only exchange if the $Os_3(C_6H_4)$ framework is dynamic. Again a rotation/flipping mechanism could account for this. The presence of only two Os–Os bonds does not significantly affect the motion of the $Os_3(C_6H_4)$ group of atoms.

It was stated above that hydride migration could not account for the ^{13}C n.m.r. spectra, but neither can a C_6H_4 rotation on its own. Thus the nine separate ^{13}C (carbonyl) signals all broaden and coalesce together to give four signals at 100 °C, Figure 5. These are roughly equal in intensity and we believe they should have intensities 2 : 3 : 2 : 2. The mean shifts of these peaks weighted in this way before and after coalescence are δ 175.9 and 175.7 respectively. We suggest that, as well as movements of the C_6H_4 and H ligands, a localised axial–equatorial exchange of CO groups at Os(1) gives rise to the coalesced signal of intensity 3 while the three other coalesced signals are due to the six remaining CO groups in symmetry related pairs. For complex (2), CO migration between osmium atoms is not required as for (1).

EXPERIMENTAL

Preparation of Compounds.—Compounds (1) and (2) were prepared as reported earlier.[1]

4-*Isopropylphenyldimethylarsine.* Bromine (0.25 mol) was added slowly over 30 min to a mixture of isopropylbenzene (60 g, 0.5 mol) and iron granules (1 g). Addition of water and straightforward work-up gave 1-bromo-4-isopropylbenzene (40 g, b.p. 220—222 °C at atmospheric pressure). In dry anaerobic conditions $AsMe_2I$ (17 g) was slowly added to a Grignard reagent prepared from this bromide (15 g) and magnesium (1.8 g) in diethyl ether. Hydrolysis and work-up gave the product as a colourless liquid (8 g, b.p. 224 °C at atmospheric pressure), slightly contaminated with the parent bromo-compound.

$[Os_3(CO)_{12-x}L_x]$ [x = 1, 2, or 3; L = $AsMe_2(C_6H_4Pr^i$-4)]. A solution of $[Os_3(CO)_{12}]$ (1.0 g) and the arsine L (1.0 cm³) in toluene (30 cm³) was heated under reflux for 2.5 h. Removal of solvent and t.l.c. (silica) separation of the residue gave the products $[Os_3(CO)_{11}L]$ as yellow *crystals* (0.57 g) (Found: C, 24.7; H, 1.7. $C_{22}H_{17}AsO_{11}Os_3$ requires C, 23.95; H, 1.55%), ν(CO) (cyclohexane) at 2 109, 2 054, 2 033, 2 020, 2 003, 1 989, and 1 969 cm⁻¹, and $[Os_3(CO)_{10}L_2]$ as orange *crystals* (0.31 g) (Found: C, 29.15; H, 2.3. $C_{32}H_{34}As_2O_{10}Os_3$ requires C, 29.6; H, 2.65%), ν(CO) (cyclohexane) at 2 085, 2 026, 2 010, 2 002, 1 963, 1 958, and 1 940 cm⁻¹. A third band gave a red oily solid (*ca.* 0.10 g) containing mainly $[Os_3(CO)_9L_3]$, which was not fully characterised.

$[Os_3(C_6H_3Pr^i)(AsMe_2)(CO)_9H]$ (3). A solution of $[Os_3(CO)_{11}L]$ (0.57 g; see above) in octane was heated under reflux for 3 h. Thin-layer chromatography (silica) of the residue after removal of solvent gave complex (3) as red *crystals* (0.27 g) (Found: C, 22.5; H, 1.25. $C_{20}H_{17}AsO_9Os_3$ requires C, 22.95; H, 1.65%); ν(CO) (cyclohexane) at 2 092, 2 071, 2 042, 2 011, 2 003, 1 986, 1 976, and 1 967 cm⁻¹.

$[Os_3(C_6H_3Pr^i)(AsMe_2)_2(CO)_7]$ (4). To achieve the best possible yield of (4), the combined $[Os_3(CO)_{10}L_2]$ (0.57 g) and $[Os_3(CO)_9L_3]$ (0.1 g) fractions were heated under reflux in n-nonane solution for 3 h. Work-up as above gave complex (4) as red *crystals* (0.130 g) (Found: C, 21.1; H, 2.05. $C_{20}H_{22}As_2O_7Os_3$ requires C, 21.95; H, 2.05%); ν(CO) (cyclohexane) at 2 053, 2 007, 1 994, 1 987, 1 951, and 1 935 cm⁻¹. The i.r. spectra of the $C_6H_3Pr^i$ complexes are almost indistinguishable around 2 000 cm⁻¹ from those of the analogous C_6H_4 complexes.[1]

X-*Ray Structure Determination of* $[Os_3(C_6H_4)(AsMe_2)(CO)_9H]$, *Compound* (2).—*Crystal data.* $C_{17}H_{11}AsO_9Os_3$, M = 1 004.79, Triclinic, a = 9.302(3), b = 9.398(6), c = 15.063(7) Å, α = 101.87(4), β = 72.64(3), γ = 117.48(3)°, U = 1 111.4 Å³, space group $P\bar{1}$, D_m > 2.96 g cm⁻³, Z = 2, D_c = 3.00 g cm⁻³, $F(000)$ = 891.86, μ(Cu-K_α) = 314.35 cm⁻¹, λ = 1.541 8 Å.

Data collection. A CAD4 diffractometer was employed. Intensities were measured in the range 3.0 ⩽ θ ⩽ 60.0° using Cu-K_α radiation and a ω—2θ scan procedure, scan width ω = 0.8 + 0.15 tan θ. Reflections were measured for ± h, k, ± l, with a maximum measuring time of 90 s.

The crystal dimensions and morphology were 0.1 {001} × 0.2 {101} × 0.375 {$\bar{1}1\bar{2}$} × 0.45 {$01\bar{1}$} mm. A total of 3 392 reflections was measured, of which 3 306 were unique. 3 029 Reflections having $I > 3\sigma(I)$ were considered observed and corrected for absorption.

Structure solution and refinement. The positions of the osmium atoms were found from the best E map. Anisotropic temperature factors were used for all non-hydrogen atoms, with the hydrogen-atom parameters fixed; $U_{iso.}$ 0.1072 Å^2 for the H atoms on the ring and 0.1112 Å^2 for those on CH_3. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.0008\ (F_o)^2]$. Refinement converged to a final R of 0.0518 and a weighted R of 0.0542. The programs and computers used for the calculations and the scattering factor data were as in ref. 7.

We thank Johnson Matthey for a loan of OsO_4, and the S.R.C. for a research studentship (for I.P.R.) and for other financial support.

[1/027 *Received*, 8*th January*, 1981]

REFERENCES

[1] A. J. Deeming, R. E. Kimber, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1973, 2589.
[2] G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford, and R. S. Nyholm, *J. Organomet. Chem.*, 1972, **40**, C70.
[3] C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J. Chem. Soc., Chem. Commun.*, 1972, 87.
[4] A. J. Deeming, *J. Organomet. Chem.*, 1978, **150**, 123.
[5] R. D. Adams and N. M. Golembeski, *J. Organomet. Chem.*, 1979, **172**, 239.
[6] S. C. Brown, J. Evans, and L. E. Smart, *J. Chem. Soc., Chem. Commun.*, 1980, 1021.
[7] M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.