Selective Formation of Positional Isomers of Substituted μ_3-Benzynes in Triosmium Clusters by degrading Aryldimethylarsines

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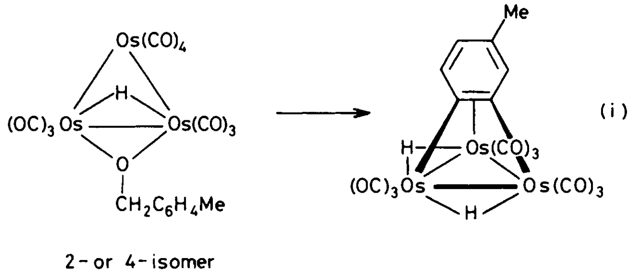
The cluster $[Os_3(CO)_{11}\{AsMe_2(C_6H_4Me\text{-}2)\}]$ in refluxing octane gave the unexpected positional isomer of the methylbenzyne cluster $[Os_3H(CO)_9(AsMe_2)(\mu_3\text{-}C_6H_3Me\text{-}4)]$. Similarly the isomeric clusters $[Os_3(CO)_{11}L]$ [L = (2- or 4-methoxyphenyl)dimethylarsine] both gave the 3-methoxybenzyne cluster $[Os_3H(CO)_9(AsMe_2)(\mu_3\text{-}C_6H_3OMe\text{-}3)]$. A mechanism involving hydrogen-atom transfer between metal and μ_3-benzyne with phenyl intermediates is proposed to account for these migration reactions. The complexes $[Os_3H(CO)_9(AsMe_2)(\mu_3\text{-}C_6H_3R)]$ (R = 4-Me or 3-MeO) exist in solution as rapidly interconverting mixtures of isomers at room temperature which give separate ^{1}H n.m.r. signals at low temperatures. The rapidly interconverting isomers differ in the relative arrangements of the C_6H_3R and the hydride ligands and not by positional isomerism of the benzyne ligands.

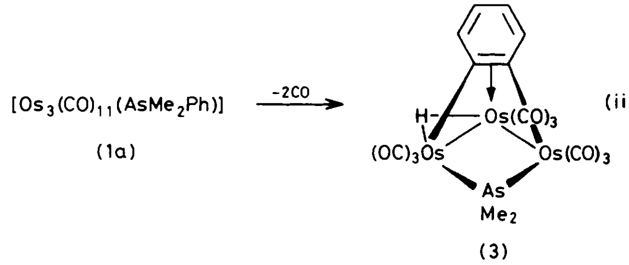
We have already mentioned briefly that in reaction (i) the positional isomer found does not necessarily correspond directly with the isomeric form of the starting benzyl alcohol.[1] Formation of the benzyne derivative



shown from 2-methylbenzyl alcohol requires a loss of the group CH_2O (possibly as CO and H_2) and a hydrogen-migration reaction at the aromatic ring. We now report that the position of substitution of the ring in μ_3-substituted benzynes does not depend upon whether the precursor is 1,2- or 1,4-disubstituted, and suggest a reversible equilibrium between hydrido-benzyne and phenyl clusters to account for this.

RESULTS AND DISCUSSION

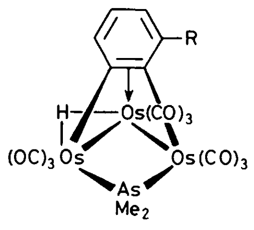
Reaction of $[Os_3(CO)_{12}]$ with tertiary phosphines or arsines L in refluxing toluene gives the simple substitution compounds $[Os_3(CO)_{11}L]$, (1), and $[Os_3(CO)_{10}L_2]$, (2), and only traces of the trisubstituted clusters are obtained if an excess of L is not used.[2,3] At higher temperatures such as in refluxing octane (125 °C), ligand cleavage in these compounds occurs as shown in reaction (ii) for $AsMe_2Ph$.[4] The *X*-ray structure of (3) shows that there are two Os–Os bonds and the benzyne ligand is bound through two σ bonds and with a η^2 co-ordination to the third osmium atom.[5] There have been two oxidative-addition reactions involving an As–C and an *ortho*-C–H cleavage. With H, $AsMe_2$, and C_6H_4 as 1e-, 3e-, and 4e-donating ligands respectively, the presence of two Os–Os bonds can be simply understood in terms of the 18-electron rule. Cleavages of phenyl-phosphines or -arsines to give μ_3-C_6H_4 complexes appears to be a general type of reaction,[6-8] and, since benzyne complexes may also be formed directly from benzene at metal clusters,[9] a study of their chemistry seemed important. As part of their study we set out to obtain specifically substituted μ_3-benzynes using specifically substituted phenylarsines. Thus, 2-substituted phenylarsines should give 3-substituted benzyne clusters such as (4) or (5), 4-substituted phenylarsines should give 4-substituted benzyne clusters such as (6) or (7), while 3-substituted phenylarsines could give either positional isomer.

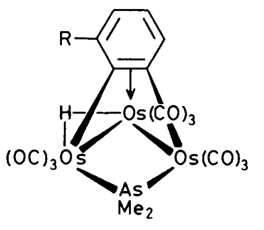


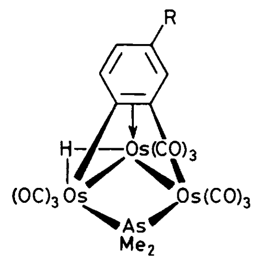
$$[Os_3(CO)_{11}\{AsMe_2(C_6H_4R)\}] \xrightarrow{-2CO} [Os_3H(CO)_9(AsMe_2)(C_6H_3R)] \quad \text{(iii)}$$

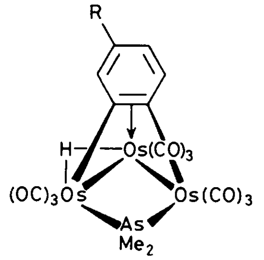
(1b ; R = 2-Me)
(1c ; R = 2-MeO)
(1d ; R = 4-MeO)

In practice, however, thermolysis (refluxing octane, 125 °C) of $[Os_3(CO)_{11}\{AsMe_2(C_6H_4Me\text{-}2)\}]$ gave only one isomer of $[Os_3H(CO)_9(AsMe_2)(\mu_3\text{-}C_6H_3Me)]$, the unexpected 4-substituted compound (6). Furthermore, a similar thermolysis of either the 2- or the 4-isomer of $[Os_3(CO)_{11}\{AsMe_2(C_6H_4OMe)\}]$ gave the same isomer (5) of $[Os_3H(CO)_9(AsMe_2)(\mu_3\text{-}C_6H_3OMe)]$ in each case. No evidence for the alternative isomers (4) or (7) was obtained. The direct structural analogy between (5), (6), and compound (3) of known molecular structure is apparent by comparing data in Table 1 with those for (3).[3] The substitution patterns of (5) and (6) were readily determined from the ^{1}H n.m.r. spectra in the aromatic region (δ 6—9) at room temperature (see Table 2). Since the coalescence temperatures for the


(4a ; R = Me)
(5a ; R = OMe)


(4b ; R = Me)
(5b ; R = OMe)


(6a ; R = Me)
(7a ; R = OMe)


(6b ; R = Me)
(7b ; R = OMe)

interconversion of (5a) with (5b) and of (6a) with (6b) are below room temperature, single sets of C_6H_3R resonances were obtained at normal temperatures. It may be that conjugative interaction of the OMe group with the aromatic ring favours isomer (5) over (7), there being an unfavourable competition between the 4-MeO group in (7) and the metal for the arene lowest unoccupied molecular orbital (l.u.m.o.) that would be involved in π bonding between Os and the η^2-arene. Whatever the reason for the isomer preferences, we would favour an electronic rather than a steric explanation since there would be less crowding in (7) than in the observed isomer (5).

We do not know the mechanism of hydrogen transfer to obtain (5) from $AsMe_2(C_6H_4OMe\text{-}4)$ or (6) from $AsMe_2(C_6H_4Me\text{-}2)$. As in so many transition-metal organometallic reactions a reversible transfer of hydrogen atoms between metal and carbon atoms would seem most obvious. Thus, if there were a reversible reaction transforming the hydrido-μ_3-benzyne compound into a short-lived phenyl compound as in equation (iv), the benzyne

$$[Os_3H(CO)_9(AsMe_2)(C_6H_3R)] \rightleftharpoons [Os_3(CO)_9(AsMe_2)(C_6H_4R)] \quad \text{(iv)}$$

ligand could interchange the metal-bound carbon atoms

TABLE 1

Infrared ν(CO) data (cm^{-1}) from cyclohexane solutions

Solutions	
(1b) $[Os_3(CO)_{11}\{AsMe_2(C_6H_4Me\text{-}2)\}]$	2 108w, 2 055m, 2 032m, 2 020vs, 2 002w, 1 989mw, 1 970mw, 1 953w
(2b) $[Os_3(CO)_{10}\{AsMe_2(C_6H_4Me\text{-}2)\}_2]$	2 085m, 2 037s, 2 020s, 2 002vs, 1 962s, 1 941m
(1c) $[Os_3(CO)_{11}\{AsMe_2(C_6H_4OMe\text{-}2)\}]$	2 106m, 2 052s, 2 032s, 2 016vs, 2 000w, 1 998m, 1 986s, 1 956w
(2c) $[Os_3(CO)_{10}\{AsMe_2(C_6H_4OMe\text{-}2)\}_2]$	2 083m, 2 025s, 2 010s, 1 998vs, 1 990 (sh), 1 957s, 1 940w, 1 934w
(1d) $[Os_3(CO)_{11}\{AsMe_2(C_6H_4OMe\text{-}4)\}]$	2 106m, 2 053s, 2 032s, 2 017vs, 2 001w, 1 998m, 1 968s, 1 956w
(2d) $[Os_3(CO)_{10}\{AsMe_2(C_6H_4OMe\text{-}4)\}_2]$	2 082m, 2 024s, 2 009s, 1 997vs, 1 989 (sh), 1 956s, 1 940w, 1 933w
(5) $[Os_3H(CO)_9(AsMe_2)(C_6H_3OMe\text{-}3)]$	2 092m, 2 069s, 2 041s, 2 036 (sh), 2 019m, 2 008s, 2 002 (sh), 1 986m, 1 976w, 1 966m
(6) $[Os_3H(CO)_9(AsMe_2)(C_6H_3Me\text{-}4)]$	2 092m, 2 070s, 2 042s, 2 037w (sh), 2 015w (sh), 2 011s, 2 003m, 1 987m, 1 977m, 1 968m

TABLE 2

^{1}H N.m.r. data [a] for compounds of type $[Os_3H(CO)_9(AsMe_2)(C_6H_3R)]$

Compd.	R	θ$_c$/°C	Isomer [b]	AsMe$_2$	OMe/Me	3-H	4-H	5-H	6-H	Os–H
(3)	H	−50		1.36 (s), 1.95 (s)		9.12	7.10	6.80	8.65	−17.00 (s)
(5) [c]	3-OMe	−30	A	1.12 (s), 1.85 (s)	3.80 (s)	—	6.30 (d) (7.3)	7.09 (t) (7.5)	8.12 (d) (8.0)	−17.33 (s)
		−30	B				6.49 (d) (8.0)	6.87 (br)	8.67 (d) (8.0)	−17.02 (s)
		22	A, B	1.26 (s), 1.90 (s)	3.84 (s)	—	6.37 (d) (7.8)	7.05 (t) (7.8)	8.25 (d) (8.0)	−17.17 (s)
(6) [d]	4-Me	−50	A	1.37 (s), 1.95 (s)	2.30 (s)	8.36 (s)	—	6.63 (dd) (8.6, 1.7)	8.95 (d) (8.3)	−17.08 (s)
		−50	B	1.36 (s), 1.94 (s)	2.36 (s)	8.80 (s)	—	6.87 (dd) (8.5, 1.8)	8.50 (d) (8.3)	−17.11 (s)
		60	A, B	1.39 (s), 1.97 (s)	2.34 (s)	8.51 (s)	—	6.71 (dd) (8.5, 1.7)	8.78 (d) (8.0)	−16.95 (s)

[a] Recorded at 200 MHz, chemical shifts (δ) with coupling constants given in parentheses. [b] Isomer A is the most abundant; A : B = 14 : 1 for (5) and 2 : 1 for (6). [c] In $CDCl_2$. [d] In $CDCl_3$.

to adopt the most stable positional isomeric form. We are now attempting selective deuteriation of these benzyne complexes to define the hydrogen transfers implicit in this mechanism.

We have already described the rapid interconversion of isomers such as (6a) and (6b) (but where R = Pr^i).[5] Although these are formally related by a migration of the hydride from one Os–Os bond to the other, their interconversion seems to require motion of the C_6H_3R ligand with respect to the Os_3 triangle as evidenced by the exchange of the diastereotopic methyl groups of the Pr^i derivative. Compounds (5) and (6) also exist as mixtures of two isomers which give frozen-out spectra only below -10 °C. The relative abundances of (6a) and (6b) at -30 °C is around 2.1 : 1.0 although which isomer predominates is unknown. As might be expected when the ring substituent is adjacent to the metal as in (5) there is greater discrimination of the isomers which have relative abundances around 14 : 1 at -30 °C. Table 2 gives ^1H n.m.r. data for each of the isomers and shows that the coalesced spectra correspond well enough with the weighted average of the frozen-out spectra, bearing in mind that the isomeric abundances might be temperature dependent.

EXPERIMENTAL

Preparation of Aryldimethylarsines.—(*2-Methoxyphenyl*)*dimethylarsine*. This compound has been prepared previously from 2-lithiomethoxybenzene,[10] but we have prepared it from the Grignard reagent derived from 2-bromomethoxybenzene which was reacted with iododimethylarsine in diethyl ether. It was distilled as a colourless liquid (75% yield), b.p. 72—73 °C (0.9 mmHg), lit.,[6] 70—72 °C (1 mmHg).* ^1H N.m.r. ($CDCl_3$): δ 1.18 (s) ($AsMe_2$), 3.80 (s) (MeO), and 6.7—7.4 (m) (C_6H_4).

(*4-Methoxyphenyl*)*dimethylarsine*. This was similarly obtained as a colourless liquid. ^1H N.m.r. (neat): δ 1.25 (s) ($AsMe_2$), 3.77 (s) (MeO), 7.00 (m) and 7.58 (m) (C_6H_4).

(*2-Methylphenyl*)*dimethylarsine*. This was also similarly prepared as a colourless liquid. ^1H N.m.r. ($CDCl_3$): δ 1.10 (s) ($AsMe_2$), 2.40 (s) (Me), and 6.95—7.40 (m) (C_6H_4).

Preparation of Cluster Compounds.—*Substitution of* $[Os_3(CO)_{12}]$ *by* (*2-methylphenyl*)*dimethylarsine*. A solution of $[Os_3(CO)_{12}]$ (0.70 g) and $AsMe_2(C_6H_4Me\text{-}2)$ (0.20 g) in toluene (30 cm^3) was heated under reflux for 4 h. Removal of solvent and thin-layer chromatography (t.l.c.) (SiO_2) of the residue, eluting with pentane–diethyl ether (4 : 1 by volume), gave the monosubstituted cluster $[Os_3(CO)_{11}\{AsMe_2(C_6H_4Me\text{-}2)\}]$, (1b), as yellow crystals (0.53 g) (Found: C, 22.8; H, 1.5. $C_{20}H_{13}AsO_{11}Os_3$ requires C, 22.35; H, 1.2%) and the disubstituted cluster $[Os_3(CO)_{10}\{AsMe_2(C_6H_4Me\text{-}2)\}_2]$, (2b), as orange crystals (0.15 g) (Found: C, 28.0; H, 2.1. $C_{28}H_{26}As_2O_{10}Os_3$ requires C, 27.05; H, 2.1%).

Thermolysis of $[Os_3(CO)_{11}\{AsMe_2(C_6H_4Me\text{-}2)\}]$. A solution of the arsine complex (1b) (0.50 g) in n-octane was heated under reflux for 1.5 h. The solvent was removed under vacuum and the residue separated by t.l.c. (SiO_2) to give $[Os_3H(CO)_9(AsMe_2)(C_6H_3Me\text{-}4)]$, (6), as yellow crystals (0.22 g) (Found: C, 21.6; H, 1.3. $C_{18}H_{13}AsO_9Os_3$ requires C, 21.2; H, 1.3%).

Substitution of $[Os_3(CO)_{12}]$ *by* (*2-methoxyphenyl*)*dimethylarsine*. A solution of $[Os_3(CO)_{12}]$ (0.54 g) and $AsMe_2(C_6H_4OMe\text{-}2)$ (0.11 cm^3) in toluene (30 cm^3) was heated under reflux for 2.5 h. The solvent was removed under vacuum and the residue separated by t.l.c. (SiO_2) eluting with pentane–diethyl ether (2 : 1 by volume) to give the monosubstituted complex $[Os_3(CO)_{11}\{AsMe_2(C_6H_4OMe\text{-}2)\}]$, (1c), as yellow crystals (0.27 g) (Found: C, 22.2; H, 1.3. $C_{20}H_{13}AsO_{12}Os_3$ requires C, 22.0; H, 1.2%) and the disubstituted complex $[Os_3(CO)_{10}\{AsMe_2(C_6H_4OMe\text{-}2)\}_2]$, (2c), as orange crystals (0.16 g) (Found: C, 27.0; H, 1.95. $C_{28}H_{26}As_2O_{12}Os_3$ requires C, 26.4; H, 2.05%).

Thermolysis of $[Os_3(CO)_{11}\{AsMe_2(C_6H_4OMe\text{-}2)\}]$. A solution of the arsine compound (1c) (0.25 g) in octane was heated under reflux for 2 h. Removal of the solvent and t.l.c. (SiO_2) of the residue, eluting with pentane–diethyl ether (2.1 by volume), gave $[Os_3H(CO)_9(AsMe_2)(C_6H_3OMe\text{-}3)]$, (5), as yellow crystals (0.17 g) (Found: C, 21.2; H, 1.3. $C_{18}H_{13}AsO_{10}Os_3$ requires C, 20.9; H, 1.25%).

Substitution of $[Os_3(CO)_{12}]$ *by* (*4-methoxyphenyl*)*dimethylarsine*. A solution of $[Os_3(CO)_{12}]$ (0.50 g) and $AsMe_2(C_6H_4OMe\text{-}4)$ (0.11 cm^3) in octane (25 cm^3) was heated under reflux for 1.5 h. Removal of the solvent under vacuum and t.l.c. (SiO_2) of the residue, eluting with pentane–diethyl ether (2.1 by volume), gave the monosubstituted compound $[Os_3(CO)_{11}\{AsMe_2(C_6H_4OMe\text{-}4)\}]$, (1d), as yellow crystals (0.23 g) (Found: C, 22.6; H, 1.2. $C_{20}H_{13}AsO_{12}Os_3$ requires C, 22.0; H, 1.2%) and $[Os_3(CO)_{10}\{AsMe_2(C_6H_4OMe\text{-}4)\}_2]$, (2d), as orange crystals (0.18 g) (Found: C, 26.5; H, 1.95. $C_{28}H_{26}As_2O_{12}Os_3$ requires C, 26.4; H, 2.05%).

Thermolysis of $[Os_3(CO)_{11}\{AsMe_2(C_6H_4OMe\text{-}4)\}]$. A solution of the arsine complex (1d) (0.22 g) in octane was heated under reflux for 2 h. Removal of the solvent and t.l.c. (SiO_2) of the residue, eluting with pentane–diethyl ether (2 : 1 by volume), gave $[Os_3H(CO)_9(AsMe_2)(C_6H_3OMe\text{-}3)]$, (5), as yellow crystals (0.19 g) (Found: C, 21.2; H, 1.3). This compound is spectroscopically identical with that formed from (1c) above.

We thank Johnson Matthey Ltd. for a generous loan of OsO_4, the S.E.R.C. for financial support, and Mr. C. R. Cooksey for synthesising some of the aryldimethylarsines.

[1/1849 *Received*, *27th November*, 1981]

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.