Thermal Degradation of Dimethylvinylarsine in Triosmium Clusters to give Bridging Vinyl, Vinylidene, and Acetylene Ligands

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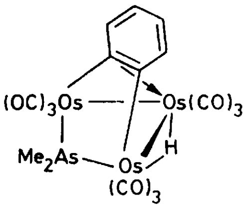
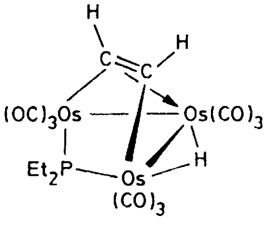
From the thermal decarbonylation of $[Os_3(CO)_{11}\{AsMe_2(CH{=}CH_2)\}]$ in refluxing hydrocarbon solvents the new clusters $[Os_3(CO)_{10}(CH{=}CH_2)(AsMe_2)]$, $[Os_3H(CO)_9(C{=}CH_2)(AsMe_2)]$, and $[Os_3H(CO)_9(CH{=}CH)(AsMe_2)]$ have been isolated and shown to be formed successively. The isomerisation of the μ_3-vinylidene to the μ_3-acetylene complex is the first example of this. Structures and dynamic behaviour are discussed mainly on the basis of ^1H n.m.r. data.

THE compound $[Os_3(CO)_{11}(PMe_2Ph)]$ thermally decarbonylates to give $[Os_3H(CO)_9(C_6H_4)(PMe_2)]$ and the $AsMe_2Ph$ complex behaves similarly.[1] The crystal structure of the arsenic compound shows it to contain only two Os–Os bonds as in (1) and as predicted by electron counting.[2] We observed no intermediates in these reactions to show whether the P–C or As–C bonds were cleaved before or after the *ortho*-C–H bond. An alkyne analogue of the μ_3-C_6H_4 clusters was prepared from PEt_3. Dehydrogenation of the thermally derived cluster $[Os_3H_2(CO)_9(Et_2PCCH_3)]$ [3] using $[CPh_3][BF_4]$ to abstract a hydride ion followed by deprotonation gave $[Os_3H(CO)_9(Et_2PC{=}CH_2)]$.[4] Thermal rearrangement finally gave $[Os_3H(CO)_9(CH{=}CH)(PEt_2)]$, structure (2), the direct analogue of $[Os_3H(CO)_9(C_6H_4)(EMe_2)]$ (E = P or As). One would imagine that the C_2H_2 cluster might be more directly synthesised from $AsMe_2(CH{=}CH_2)$ and we now report that this is so, but interestingly we have identified two intermediates in the conversion of $[Os_3(CO)_{11}\{AsMe_2(CH{=}CH_2)\}]$ into $[Os_3H(CO)_9(CH{=}CH)(AsMe_2)]$ which indicate at least one fragmentation route.



(1)



(2)

RESULTS

Syntheses.—The complexes $[Os_3(CO)_{12-x}\{AsMe_2(CH{=}CH_2)\}_x]$ (x = 1—3) were prepared by direct reaction of $[Os_3(CO)_{12}]$ with the arsine in a sealed tube because of the arsine's volatility. In no case is the alkene co-ordinated (see n.m.r. data for x = 1 in Table). Initially we found that the decarbonylation of $[Os_3(CO)_{11}\{AsMe_2(CH{=}CH_2)\}]$ in refluxing octane gave a mixture from which it was difficult to separate any pure products, but by careful selection of solvents and monitoring the i.r. spectra of reaction solutions we were able to carry out separately the conversions shown in Scheme 1. The two colourless hydrides give a single band in thin-layer chromatography (t.l.c.) on SiO_2. The front of the band contained the final product and the rear the intermediate hydride. Separation was possible but very tedious. It was better to obtain the intermediate hydride after a short time in refluxing octane, to isolate it, and then to isomerise it completely in refluxing nonane to the more stable isomeric hydride. All complexes gave good analytical results and simple ^1H n.m.r. spectra.

Structure.—In refluxing heptane solution the complex $[Os_3(CO)_{11}\{AsMe_2(CH{=}CH_2)\}]$ gives a non-hydridic derivative (3) by loss of a single CO ligand. The vinyl group has remained intact (^1H n.m.r. evidence) while the chemical shifts indicate that it must be co-ordinated in a η^2 manner. Structure (3a) is the simplest to envisage and relates to $[Os_3(CO)_{10}(S\text{-}trans\text{-}CH_2{=}CHCH{=}CH_2)]$, for example.[5] However, the chemical shifts for the vinyl group have the same wide spread as those for the μ-vinyl in $[Os_3H(CO)_{10}(CH{=}CH_2)]$.[6] Indeed the chemical shifts and coupling constants are so similar (Table) that we believe that the As–C bond is cleaved in (3) so that $AsMe_2$ and $CH{=}CH_2$ are both μ-three-electron donors as in structures (3b) and (3c). The crystals of (3) that we grew were unsuitable for a single-crystal X-ray analysis.

Further decarbonylation of (3) in refluxing oxtane gave $[Os_3H(CO)_9(C{=}CH_2)(AsMe_2)]$ (4) which isomerises to $[Os_3H(CO)_9(CH{=}CH)(AsMe_2)]$ (5) at 150 °C in refluxing nonane. Complex (5) has the structure shown. We deduce this from the similarity of the ν(CO) spectra for (1) and (5) (Figure), compound (1) having the known crystal structure shown. The C_2H_2 ligand in (5) is asymmetric and gives a sharp ^1H n.m.r. AB quartet at −45 °C, but exchange of the ends of

$$\begin{tikzcd}
{[Os_3(CO)_{11}\{AsMe_2(CH{=}CH_2)\}]} \arrow[r, "-CO", "96\ ^\circ C"'] & {\underset{(3)}{[Os_3(CO)_{10}(CH{=}CH_2)(AsMe_2)]}} \arrow[d, "-CO"', "125\ ^\circ C"] \\
{\underset{(5)}{[Os_3H(CO)_9(CH{=}CH)(AsMe_2)]}} & {\underset{(4)}{[Os_3H(CO)_9(C{=}CH_2)(AsMe_2)]}} \arrow[l, "\text{Isomerisation}"', "150\ ^\circ C"]
\end{tikzcd}$$

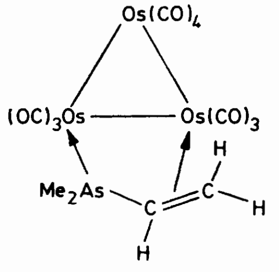
SCHEME 1

Infrared (cm^{-1}) and ^1H n.m.r. data [a]

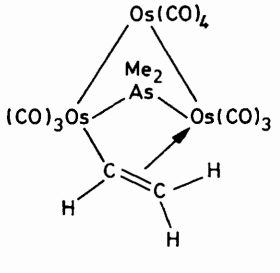
Compound	$\nu(CO)$ [b]	Chemical shifts (δ)			J/Hz
		OsH	$AsMe_2$	Vinylic CH	
$AsMe_2(CH=CH_2)$ [c]			1.00	5.57 (dd), 5.77 (dd), 6.59 (dd)	18.4, 11.5, 1.8
$[Os_3(CO)_{11}\{AsMe_2(CH=CH_2)\}]$	2 109w, 2 055m, 2 033m, 2 020vs, 2 002w, 1 989m, 1 972m, 1 966w, 1 957w		1.80	5.63 (dd), 5.85 (d), 6.46 (d)	17.7, 11.2
$[Os_3(CO)_{10}\{AsMe_2(CH=CH_2)\}_2]$	2 087m, 2 028s, 2 013s, 2 002vs, 1 964s, 1 959s, 1 943m, 1 935m				
(3) $[Os_3(CO)_{10}(CH=CH_2)(AsMe_2)]$	2 102m, 2 063vs, 2 034s, 2 030s, 2 016vs, 2 007m, 1 996m, 1 990 (sh), 1 980m, 1 964m, 1 956m		1.52 1.93	3.99 (dd), 6.02 (dd), 7.46 (dd)	15.0, 9.3, 1.4
$[Os_3H(CO)_{10}(CH=CH_2)]$ [d]		−19.38 (dd)		3.40 (dd), 4.98 (dt), 7.58 (ddd)	14.9, 9.7, 2.2
(4) $[Os_3H(CO)_9(C=CH_2)(AsMe_2)]$	2 093w, 2 070s, 2 048s, 2 015s, 2 008s, 2 003s, 1 994m, 1 977m	−13.81	1.49 1.66	3.29 (m),[e] 5.98 (m) [e]	
(5) $[Os_3H(CO)_9(CH=CH)(AsMe_2)]$	2 096w, 2 072s, 2 047s, 2 018m, 2 012s, 1 994m, 1 982w, 1 972m	−19.19	1.40 1.96	10.03 (d),[f] 10.52 (d),[f]	9.2

[a] Recorded in $CDCl_3$ at 27 °C unless stated otherwise. [b] Recorded in cyclohexane. [c] Ref. 9. [d] N.m.r. data from ref. 6 for comparison. [e] Poorly resolved dd with J *ca.* 1—2 Hz; probably *gem*-coupling plus coupling to hydride unresolved for the hydride itself. [f] Sharp AB quartet at −45 °C coalesces around −13 °C to give a broad singlet at δ 10.35 at 27 °C.

the ligand leads to coalescence (T_c −13 °C). For $[Os_3H(CO)_9(\mu_3-C_6H_3Pr^i)(AsMe_2)]$ we have shown that the μ_3 ligand must move with respect to the Os_3 triangle, interchanging the faces of the aryne ligand,[2] and presumably the acetylene complex behaves similarly. In cluster (1) the long, and presumably non-bonding, Os–Os distance can be spanned by the C_6H_4 ligand and presumably the CH=CH ligand can do likewise. The intermediate hydride (4) contains the $C=CH_2$ ligand ($J_{gem} < 2$ Hz) which is likely to be bound in a μ_3 manner as in $[Os_3H_2(CO)_9(C=CH_2)]$. Furthermore the $\nu(CO)$ spectra of (4) and (5) are so similar (Figure) that we believe they have the same basic geometry, that is (4) has the structure shown. The vinylidene ligand must span the long Os–Os distance and presumably with a single carbon atom, but the consequences of this on the Os–C–Os bond angle of the bridge cannot be assessed as again we have not obtained crystals suitable for structure determination.* Whereas cluster (5) is fluxional, (4) is not. Two sharply resolved $C=CH_2$ signals are observed in the ^1H n.m.r.



(3a)



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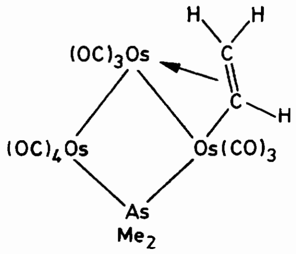

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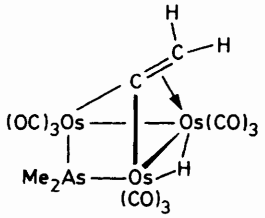

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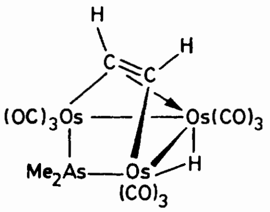


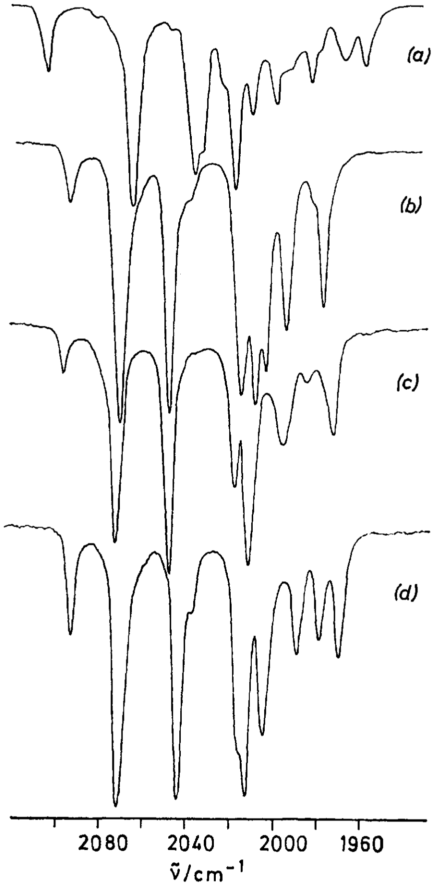
(5)

* *Note added at proof*: The structure of $[Os_3H(CO)_9(C=C=CPh_2)(OH)]$ has recently been determined (S. Aime, A. J. Deeming, J. D. J. Backer-Dirks, and M. B. Hursthouse, unpublished results). It is similar to (4) except that OH replaces $AsMe_2$ and $C=C=CPh_2$ replaces $C=CH_2$, however the terminal C atom of $C=C=CPh_2$ spans a metal-metal bonded pair of Os atoms. This compound and (4) have similar i.r. spectra and are very likely directly related in structure.

spectrum of (4) at 35 °C. This is consistent with but not evidence for a ready rotation of alkynes and arynes with respect to the Os_3 triangles but a rigid Os_3–vinylidene arrangement.

DISCUSSION

It appears to be particular fortuitous that two intermediates have been observed in this reaction but not in the related thermolysis of $[Os_3(CO)_{11}(AsMe_2Ph)]$.[1] It seems probable that As–C cleavage has preceded C–H bond cleavage assuming that our interpretation of the structure of $[Os_3(CO)_{10}(CH{=}CH_2)(AsMe_2)]$ (3) is correct. This is not the only course available. For example, a triosmium cluster derived using PPh_3 contains the ligand $PPh_2C_6H_4$ in which case *ortho*-metallation has occurred first.[7]



Infrared spectra of (*a*) $[Os_3(CO)_{10}(CH{=}CH_2)(AsMe_2)]$ (3), (*b*) $[Os_3H(CO)_9(C{=}CH_2)(AsMe_2)]$ (4), (*c*) $[Os_3H(CO)_9(CH{=}CH)(AsMe_2)]$ (5), and (*d*) $[Os_3H(CO)_9(C_6H_4)(AsMe_2)]$ (1) in cyclohexane

To our knowledge this is the first report of the interconversion of isomers containing μ_3-C=CH_2 and μ_3-CH=CH respectively. This isomerisation is related to the conversion of $[Fe_3H(CO)_9(MeC{=}NH)]$ into $[Fe_3H(CO)_9(MeCH{=}N)]$.[8] The simplest mechanism is a direct 1,2-hydrogen-atom shift but hydrogen-atom transfer between carbon and metal atoms is more likely; Scheme 2 shows two distinct routes (1) and (2) to the latter. Route (1) is *via* what is presumed to be the intermediate in the formation of compound (4) from (3). We favour route (1) over (2) on intuitive rather than experimental evidence.

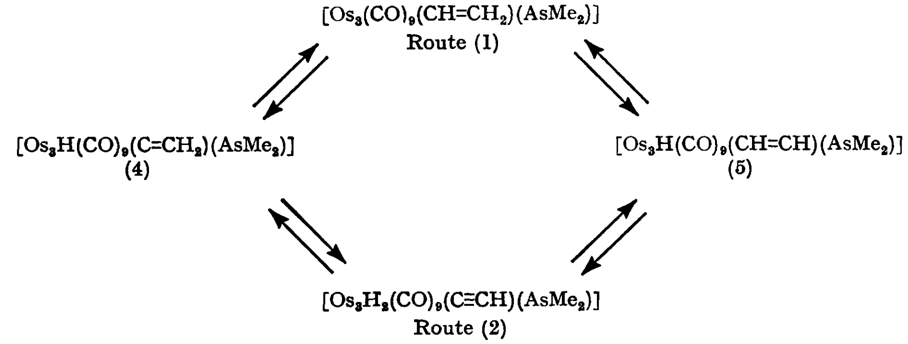
EXPERIMENTAL

The dimethylvinylarsine was prepared from $Sn(CH{=}CH_2)_4$ by a reported method.[9]

Action of Dimethylvinylarsine on $[Os_3(CO)_{12}]$.—A sealed glass tube containing the metal carbonyl (1.0 g) and the arsine (1.0 g) in toluene (40 cm^3) under nitrogen was heated at 145 °C for 3 h. The solvent was removed under vacuum and the residue chromatographed on preparative t.l.c. (SiO_2) plates eluting with light petroleum (b.p. 40—60 ° C)–dichloromethane (*ca.* 1 : 5 v/v) to give three main bands which gave $[Os_3(CO)_{11}\{AsMe_2(CH{=}CH_2)\}]$ (0.35 g) as yellow crystals (Found: C, 17.8; H, 0.95. $C_{13}H_9AsO_{11}Os_3$ requires C, 17.8; H, 0.90%), $[Os_3(CO)_{10}\{AsMe_2(CH{=}CH_2)\}_2]$ (0.52 g) as orange crystals (Found: C, 19.55; H, 1.65. $C_{18}H_{18}As_2O_{10}Os_3$ requires C, 19.4; H, 1.60%), and $[Os_3(CO)_9\{AsMe_2(CH{=}CH_2)\}_3]$ (0.17 g) as orange crystals (Found: C, 20.7; H, 2.20. $C_{21}H_{27}As_3O_9Os_3$ requires C, 20.7; H, 2.25%).

Thermolyses.—$[Os_3(CO)_{11}\{AsMe_2(CH{=}CH_2)\}]$. A solution of the undecacarbonyl (0.270 g) in heptane (20 cm^3) was heated under reflux for 20 h under nitrogen. After removal of the solvent the residue was chromatographed (SiO_2), eluting with pentane, to give unreacted undecacarbonyl (0.082 g) and $[Os_3(CO)_{10}(CH{=}CH_2)(AsMe_2)]$ (0.100 g) as yellow crystals. Another band gave a rather impure sample of $[Os_3H(CO)_9(C{=}CH_2)(AsMe_2)]$ (0.060 g) which was discarded.

$[Os_3(CO)_{10}(CH{=}CH_2)(AsMe_2)]$. A solution of this complex (0.080 g) in octane (20 cm^3) was refluxed under nitrogen



SCHEME 2

for 2 h. Chromatographic work-up gave the complex $[Os_3H(CO)_9(C{=}CH_2)(AsMe_2)]$ as a colourless solid (0.061 g) (Found: C, 16.65; H, 0.90. $C_{11}H_9AsO_9Os_3$ requires C, 16.35; H, 0.95%).

$[Os_3H(CO)_9(C{=}CH_2)(AsMe_2)]$. A solution of this complex (0.170 g) in nonane (20 cm^3) was refluxed under nitrogen for 2 h. Small but distinct changes in the i.r. spectrum around 2 000 cm^{-1} occurred but it was difficult to judge the extent of reaction. Removal of the solvent and chromatography of the residue on SiO_2, eluting with pentane, gave a band which was shown to be an inseparable mixture of starting material and product. This mixture was thermolysed further in refluxing nonane for 2 h by which time there was no remaining starting material and chromatographic work-up gave pure $[Os_3H(CO)_9(CH{=}CH)(AsMe_2)]$ (0.103 g) as a colourless solid (Found: C, 16.75; H, 1.00. $C_{11}H_9AsO_9Os_3$ requires C, 16.35; H, 0.95%).

$[Os_3(CO)_{10}\{AsMe_2(CH{=}CH_2)\}_2]$. The decacarbonyl (0.400 g) in octane (40 cm^3) sealed in a glass tube was heated at 155 °C for 8 h. Removal of solvent and chromatographic work-up gave starting material (0.210 g), $[Os_3(CO)_{11}\{AsMe_2(CH{=}CH_2)\}]$ (0.05 g), and $[Os_3H(CO)_9(C{=}CH_2)(AsMe_2)]$ (0.109 g), together with other unidentified products.

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