Systematic Synthesis of Tetranuclear Osmium Clusters by the Reaction of Trinuclear Clusters with $[OsH_2(CO)_4]$; Crystal Structure of $[Os_4H_3Br(CO)_{13}]$†

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The complex $[OsH_2(CO)_4]$ reacts with the clusters $[Os_3(CO)_{12-n}(MeCN)_n]$ (n = 1 or 2) to afford the tetranuclear species $[Os_4H_2(CO)_{15}]$ (**1**) and $[Os_4H_2(CO)_{14}(MeCN)]$ (**2**), respectively. The pyrolysis of $[Os_4H_2(CO)_{14}(MeCN)]$ (**2**) leads to the formation of $[Os_4H_2(CO)_{13}]$ *via* the intermediate $[Os_4H_2(CO)_{14}]$. The acetonitrile ligand of complex (**2**) is readily displaced by $P(OMe)_3$ to give $[Os_4H_2(CO)_{14}\{P(OMe)_3\}]$ (**3**) along with small quantities of $[Os_3(CO)_{10}\{P(OMe)_3\}_2]$ and $[Os_3(CO)_9\{P(OMe)_3\}_3]$. With PPh_3 the reaction is so slow that fragmentation occurs and the only product isolated is $[Os_3(CO)_{10}(PPh_3)_2]$. The hydride-coupling reaction also occurs between $[OsH_2(CO)_4]$ and $[Os_3H(X)(CO)_9(NMe_3)]$ (X = Cl, Br, or I) and the complexes obtained [(**4**)—(**6**) respectively] have been fully characterised. These complexes decompose in solution *via* loss of HX to afford $[Os_4H_2(CO)_{13}]$. The reaction between $[Os_3H(OR)(CO)_9(MeCN)]$ and $[OsH_2(CO)_4]$ proceeds smoothly for R = Me (**7**) or Ph (**8**) but for R = H the major product isolated is $[Os_3H(OH)(CO)_{10}]$. All the products were characterised by i.r., ^1H and ^{13}C n.m.r. spectroscopy and structural assignments made. The structure of the cluster $[Os_4H_3Br(CO)_{13}]$ (**5**) was confirmed by an X-ray analysis and shown to consist of an Os_3 triangle with a pendant $OsH(CO)_4$ unit coordinated to it. One edge of the triangle is bridged by both a hydride and a bromide ligand while another edge is bridged by a hydride.

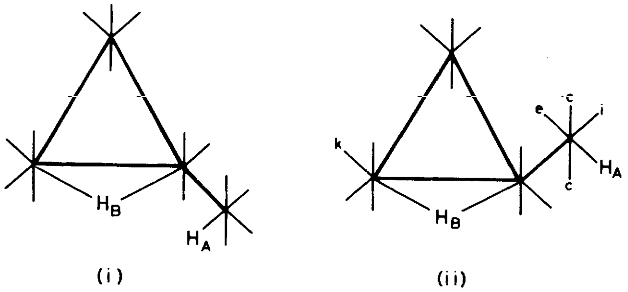
The propensity of low-valent osmium carbonyl complexes for forming cluster species is well established,[1] examples of nuclearities ranging from three to eleven being known. Such species display a variety of geometries and reactivities, and the synthetic control of cluster nuclearity is an essential precursor to detailed studies.

The most widely used synthetic method for increasing nuclearity has been the pyrolysis reaction, during which metal–carbon bonds are broken and new metal–metal bonds formed.[2] Varying degrees of selectivity can be attained by introducing ligands other than CO, the pyrolysis of $[Os_3(CO)_{11}L]$ producing numerous pentanuclear species for L = $P(OMe)_3$,[3] substituted hexanuclear species for L = RNC[4] and high yields of $[Os_{10}C(CO)_{24}]^{2-}$ for L = py (pyridine).[5] Although these pyrolyses are easily performed, the large number of products and general lack of control over the course of the reaction are major limiting factors, and alternative pathways would obviously be desirable.

Chini and co-workers[6] have shown how redox condensations can be used systematically to build anionic clusters of the cobalt and nickel triads, and Hayward and Shapley[7] have adapted this approach to osmium and ruthenium. Some mixed rhenium–osmium[8–11] and tungsten–osmium[12] clusters have recently been prepared by a 'metal-hydride coupling' reaction. We present here a straightforward method for the stepwise build-up of osmium clusters by the reaction of $[OsH_2(CO)_4]$ with trinuclear osmium clusters containing MeCN or NMe_3 ligands. These results have been published in part in a communication.[13]

Results and Discussion

The reaction of $[OsH_2(CO)_4]$ with $[Os_3(CO)_{11}(MeCN)]$ proceeds rapidly and smoothly to produce high yields of $[Os_4H_2(CO)_{15}]$ (**1**). The ^1H n.m.r. spectrum of complex (**1**) exhibits two resonances due to the hydride ligands (Table 1). Observation of ^{187}Os satellites[14] (^{187}Os, $I = \frac{1}{2}$, 1.6%) reveals only one $^1J(OsH)$ for H_A (δ −9.6) and two for H_B (δ −19.3), consistent with terminal and bridging hydride environments respectively (Figure 1). The $^{13}C-\{^1H\}$ n.m.r. spectrum of complex (**1**) is shown in Figure 2 and displays four resonances of relative intensity two, and seven of intensity one due to the carbonyl ligands (Table 2). The pattern is fully consistent with an 'equatorially spiked triangle' arrangement of metal atoms (Figure 1). Selective decoupling at the hydride H_B allows unambiguous assignment of resonances c, e, and i to the $OsH(CO)_4$ group since they all exhibit coupling to H_A (Figures 1 and 2). Decoupling at H_A was, however, less conclusive, since only resonance (k) broadened compared with the $^{13}C-\{^1H\}$ spectrum. This would suggest only one CO ligand coupled to H_B, and therefore structure (ii) in Figure 1 where H_B has only one *trans* carbonyl. However, since literature data on the magnitude of $^2J(CH)$ in such systems are limited, structure (i) cannot be ruled out. In addition, an X-ray structural analysis of the related $[Os_3ReH(CO)_{15}(MeCN)]$ has suggested a *cis* arrangement of hydride and $Re(CO)_5$ moieties[11] [Figure 3(ii)]. Complex (**1**) has so far proved to be too unstable for an X-ray structural analysis.



(i) (ii)

Figure 1. Possible structures for $[Os_4H_2(CO)_{15}]$ (**1**)

The reaction of $[OsH_2(CO)_4]$ with $[Os_3(CO)_{10}(MeCN)_2]$ is

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† 1,2-μ-Bromo-1,1,2,2,2,3,3,3,3-nonacarbonyl-1,2;1,3-di-μ-hydrido-1-tetracarbonylhydrido-osmio-*triangulo*-triosmium.

Supplementary data available (No. SUP 56131, 4 pp.): thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Proton n.m.r. data ($CDCl_3$); δ in p.p.m. relative to $SiMe_4$, J values in Hz

Compound	H_A	H_B	H_C	Other
(**1**) $[Os_4H_2(CO)_{15}]$	−9.6 ^1J(OsH) = 37.5	−19.3 ^1J(OsH) = 25.5, 36.0		
(**2**) $[Os_4H_2(CO)_{14}(MeCN)]$	−9.7 (1 H) ^1J(OsH) = 38.5	−17.2 (1 H) ^1J(OsH) unresolved		2.5 (3 H)
(**3**) $[Os_4H_2(CO)_{14}\{P(OMe)_3\}]$	−9.7 (1 H)	−20.1 (1 H) J(PH) = 12.0		3.8 (9 H) J(PH) = 12.0
(**4**) $[Os_4H_3Cl(CO)_{13}]$	−9.5	−14.8 $J(H_BH_C)$ = 2	−12.0	
(**5**) $[Os_4H_3Br(CO)_{13}]$	−9.4 J(OsH) = 37.6	−15.3 J(OsH) = 40.3, 30.3 $J(H_BH_C)$ = 2	−12.6 J(OsH) = 55.5, 33.5	
(**6**) $[Os_4H_3I(CO)_{13}]$	−9.4 J(OsH) = 39.3	−16.4 J(OsH) = 39.8, 29.8 $J(H_BH_C)$ = 2	−13.6 J(OsH) = 54.7, 32.4	
(**7**) $[Os_4H_3(OMe)(CO)_{13}]$	−9.5 (1 H) J(OsH) = 39.7	−14.2 (1 H) J(OsH) = 40.9, 31.5 $J(H_AH_B)$ = 0.6, $J(H_BH_C)$ = 2.0	−10.8 (1 H) J(OsH) = 56.7, 36.9	3.9 (3 H)
(**8**) $[Os_4H_3(OPh)(CO)_{13}]$	−9.3 (1 H)	−13.4 (1 H) $J(H_BH_C)$ unresolved	−10.2 (1 H)	6.81 (3 H) 7.14 [d, J(HH) = 7.0] (2 H)

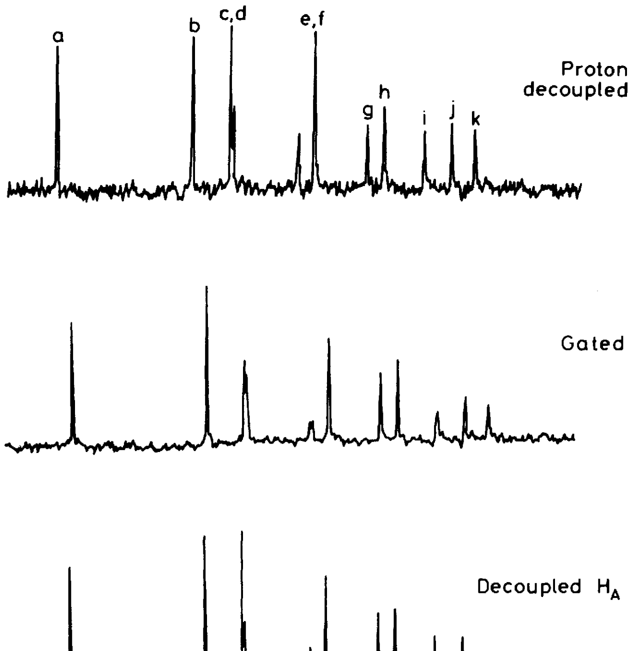


Figure 2. $^{13}C-\{^1H\}$ N.m.r. spectrum of $[Os_4H_2(CO)_{15}]$ (**1**)

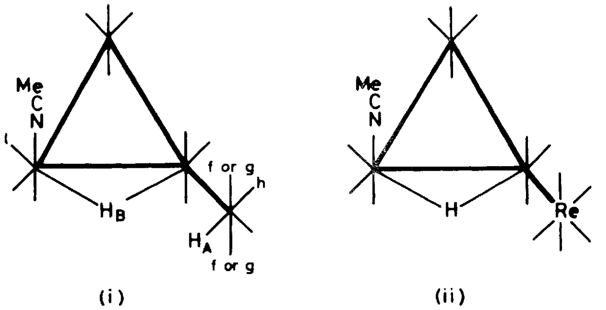


Figure 3. Probable structure of $[Os_4H_2(CO)_{14}(MeCN)]$ (**2**) (i), and the structure of $[Os_3ReH(CO)_{15}(MeCN)]$ (ii)

also smooth and rapid and results in the formation of $[Os_4H_2(CO)_{14}(MeCN)]$ (**2**). The ^1H n.m.r. spectrum of complex (**2**) exhibits two hydride resonances of similar chemical shifts to those of (**1**), ^{187}Os coupling being resolved only for the terminal hydride (Table 1). The $^{13}C-\{^1H\}$ n.m.r. spectrum of (**2**) exhibits fourteen resonances of equal intensity due to the carbonyl ligands as well as those due to the acetonitrile ligand (Table 2). Although poor solubility prevented the observation of selectively decoupled ^{13}C n.m.r. spectra, an overnight accumulation did provide a fully proton-coupled spectrum revealing ^2J(CH) coupling on resonances f, g, h, and l. A tentative assignment of those resonances based on comparison of chemical shifts and ^2J(CH) with complex (**1**) is given in Figure 3.

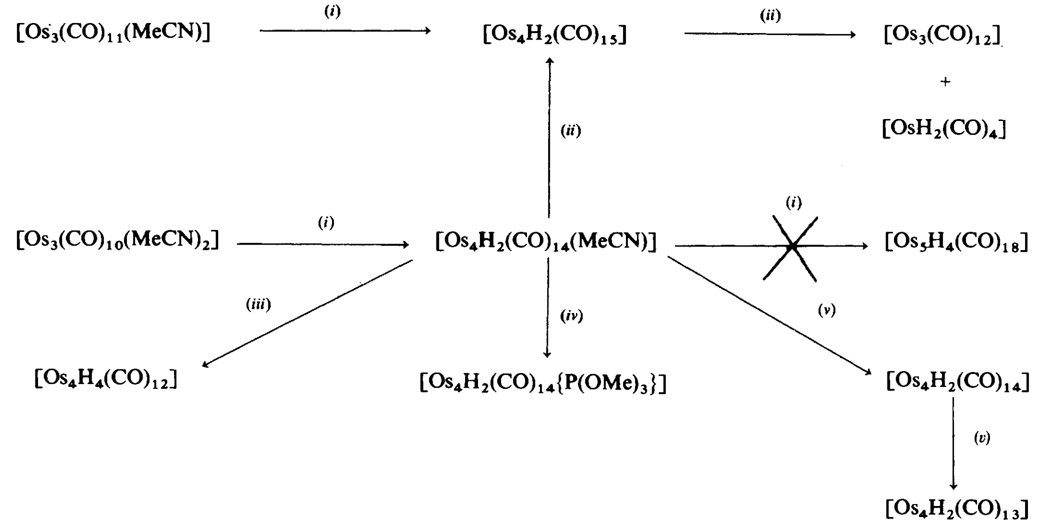
The above data are also consistent with an 'equatorially spiked triangle' arrangement of metal atoms for complex (**2**) [Figure 3(i)], but from the n.m.r. data alone it is not possible to deduce the relative positions of the bridging hydride, MeCN, and $OsH(CO)_4$ groups. It is probable, however, that the structure of (**2**) is similar to that of $[Os_3ReH(CO)_{15}(MeCN)]$,[11] in which the $OsH(CO)_4$ group of (**2**) is replaced by the isoelectronic $Re(CO)_5$ group [Figure 3(ii)].

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with excess of $[OsH_2(CO)_4]$ or of $[Os_4H_2(CO)_{14}(MeCN)]$ with $[OsH_2(CO)_4]$ does not result in the formation of any pentanuclear species (Scheme 1). This is in contrast to the analogous reactions with $[ReH(CO)_5]$ where Os_3Re_2 species are readily formed (Scheme 2).[8,9] There are, however, a number of similarities in the general reactivities of $[Os_3ReH(CO)_{15}(MeCN)]$ and $[Os_4H_2(CO)_{14}(MeCN)]$. Carbon monoxide will displace the acetonitrile ligand from both, although for the homonuclear osmium species prolonged reaction results in fragmentation to

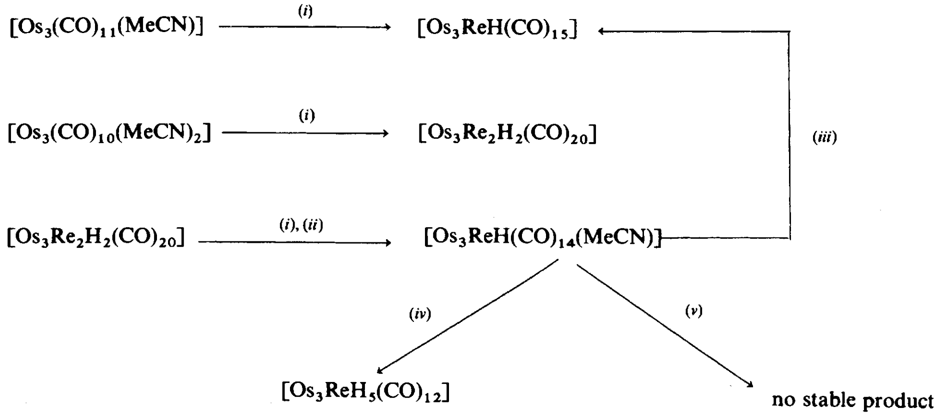
Table 2. ^{13}C N.m.r. data; δ/p.p.m. relative to $SiMe_4$, *J* in Hz

Compound	CO ligands	Other
$[Os_4H_2(CO)_{15}]$	194.5 (2 C), 184.8 (2 C), 182.2 [2 C, $J(CH_A)$ = 6.0], 182.0 (1 C), 177.4 [1 C, $J(CH_A)$ = 17.9], 176.2 (2 C), 175.5 (1 C), 171.2 (1 C), 168.2 [1 C, $J(CH_A)$ = 4.3], 166.3 (1 C), 164.6 [1 C, $J(CH_B)$ = 9.2]	
$[Os_4H_2(CO)_{14}(MeCN)]$	197.0 (1 C), 194.5 (1 C), 187.2 (1 C), 184.7 (1 C), 182.0 (1 C), 181.5 [1 C, *J*(CH) = 5], 181.3 [1 C, *J*(CH) = 5], 176.7 [1 C, *J*(CH) = 22], 175.3 (1 C), 172.8 (1 C), 172.7 (1 C), 170.5 [1 C, *J*(CH) = 14], 169.9 (1 C), 167.5 (1 C)	127.4, 4.4
$[Os_4H_2(CO)_{14}\{P(OMe)_3\}]$	194.9 (2 C), 184.6 (2 C), 181.6 [2 C, *J*(PC) = 11.6], 181.2 [2 C, *J*(CH) = 7.6], 180.4 (1 C), 176.5 [1 C, *J*(CH) = 18.2], 172.1 (1 C), 171.4 (1 C), 168.4 (1 C), 167.7 [1 C, *J*(CH) = 4.9]	30.1
$[Os_4H_3Br(CO)_{13}]$	179.9 [1 C, *J*(CH) = 8.4], 179.4 [2 C, $J(CH_A)$ = 7.4], 179.1 (1 C), 175.5 [1 C, $J(CH_A)$ = 16.1], 174.9 (1 C), 174.8 [1 C, $J(CH_B)$ = 4.1], 171.1 [1 C, $J(CH_B)$ = 3.7], 170.7 [1 C, $J(CH_C)$ = 13.2], 168.7 [1 C, $J(CH_B)$ = 10.9], 165.9 [1 C, $J(CH_A)$ = 5.1], 165.4 (1 C), 164.7 [1 C, $J(CH_B)$ = 3.5]	

For the purpose of the text the resonances listed are labelled a, b, c, *etc.* in sequence.



Scheme 1. Reactions of homonuclear tetranuclear osmium species. (*i*) $[OsH_2(CO)_4]$; (*ii*) CO; (*iii*) H_2; (*iv*) $P(OMe)_3$; (*v*) warm



Scheme 2. Reactions of heteronuclear Os_3Re species. (*i*) $[ReH(CO)_5]$; (*ii*) MeCN; (*iii*) CO; (*iv*) H_2; (*v*) heat

$[Os_3(CO)_{12}]$ and $[OsH_2(CO)_4]$ by cleavage to the 'spiked' bond. Both systems will also react with hydrogen, the homonuclear species adding one molecule of hydrogen whereas the mixed-metal species adds two (Scheme 2).[9] The products of these reactions, $[Os_4H_4(CO)_{12}]$ and $[Os_3ReH_5(CO)_{12}]$, however, both exhibit closed tetrahedral geometries.[9,15]

An interesting contrast between the homo- and heteronuclear species is to be found upon pyrolysis. Heating $[Os_4H_2(CO)_{14}(MeCN)]$ in toluene results in the rapid formation of an orange solution. An orange band can be isolated by t.l.c., but the i.r. spectrum is dependent upon the length of time of the pyrolysis and indicated a mixture of two compounds. The limiting product was identified as $[Os_4H_2(CO)_{13}]$ and mass spectral studies of the intermediate mixture revealed the presence of $[Os_4H_2(CO)_{14}]$.

The homonuclear osmium species thus exhibits a sequential loss of 2e$^-$ donor ligands (MeCN then CO) and formation of new metal–metal bonds with consequent closing of the cluster (Figure 4). The tetrahedral geometry of $[Os_4H_2(CO)_{13}]$ has recently been confirmed,[16] but we have so far been unsuccessful

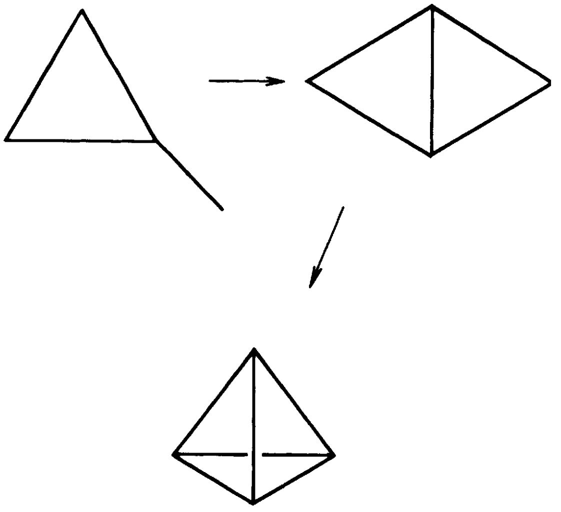


Figure 4. The sequential loss of ligands from $[Os_4H_2(CO)_{14}(MeCN)]$ (2)

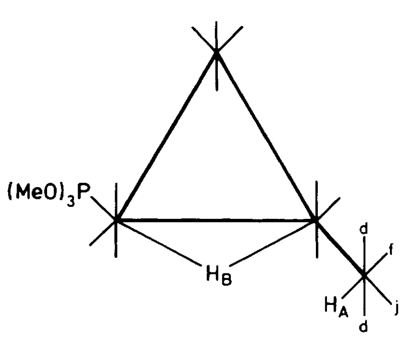
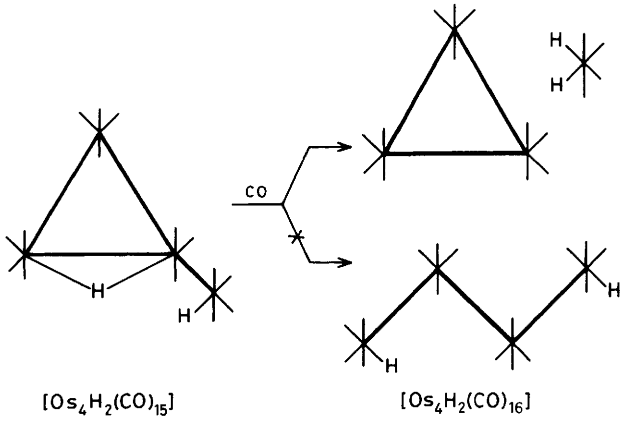


Figure 5. Proposed structure of $[Os_4H_2(CO)_{14}\{P(OMe)_3\}]$ (3)



Scheme 3. Fragmentation of 'spiked triangle' Os_4 species

in obtaining crystals of $[Os_4H_2(CO)_{14}]$ suitable for *X*-ray studies. In comparison, pyrolysis of $[Os_3ReH(CO)_{15}(MeCN)]$ was reported to yield 'no stable products',[9] although the more condensed species $[Os_3ReH(CO)_{15}]$ is known.[17,18]

The acetonitrile ligand of complex (2) is readily displaced by $2e^-$ phosphorus-donor ligands, reaction with $P(OMe)_3$ proceeding rapidly to yield $[Os_4H_2(CO)_{14}\{P(OMe)_3\}]$ (3). ^1H N.m.r. studies on complex (3) indicated one terminal hydride and one bridging hydride coupled to the phosphite ligand [^2J(PH) = 12 Hz, Table 1]. An equatorial site for the phosphite ligand was confirmed by ^{13}C n.m.r. studies which revealed four

Table 3. Infrared spectroscopic data (cm^{-1}) for new complexes

Compound	
$[Os_4H_2(CO)_{15}]^a$	2 106m, 2 075s, 2 054s, 2 040w, 2 028w (sh), 2 019m, 2 010m, 2 001m, 1 991w
$[Os_4H_2(CO)_{14}(MeCN)]^b$	2 113w, 2 085s, 2 059s, 2 039w, 2 027m (sh), 2 017m,br, 2 001m,br, 1 971w
$[Os_4H_2(CO)_{14}\{P(OMe)_3\}]^c$	2 094m, 2 060m, 2 047w, 2 030s, 2 013m,br, 2 004 (sh), 1 984w
$[Os_4H_3Cl(CO)_{13}]^d$	2 133w, 2 111m, 2 082s, 2 065m (sh), 2 055vs, 2 034m, 2 026s, 2 019s, 1 998m, 1 960w (sh), 1 955w
$[Os_4H_3Br(CO)_{13}]^d$	2 133w, 2 111m, 2 081s, 2 065m (sh), 2 055vs, 2 033m, 2 026s, 2 018s, 1 996m, 1 959w, 1 955w (sh)
$[Os_4H_3I(CO)_{13}]^d$	2 131w, 2 110m, 2 078s, 2 065m (sh), 2 054vs, 2 032m, 2 026s, 2 018s, 1 994m, 1 958w, 1 954w (sh)
$[Os_4H_3(OMe)(CO)_{13}]^d$	2 130w, 2 107m, 2 074s, 2 057s, 2 050vs, 2 028m, 2 023ms, 2 014s, 1 995m, 1 963w, 1 950w
$[Os_4H_3(OPh)(CO)_{13}]$	2 130w, 2 108m, 2 077s, 2 055m (sh), 2 051vs, 2 029m (sh), 2 024s, 2 016s, 2 007m, 1 995m, 1 950w,br

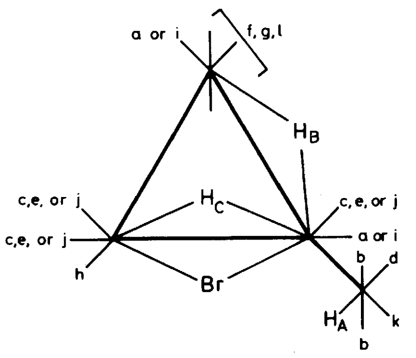
[a] In hexane. [b] In thf. [c] In dichloromethane. [d] In cyclohexane.

resonances of intensity two, and six of intensity one due to the carbonyl ligands (Table 2). Selectively decoupled ^{13}C n.m.r. spectra could not be obtained, but on overnight accumulation did provide a fully proton-coupled ^{13}C spectrum, which revealed ^2J(CH) coupling on resonances d, f, and j. Their magnitudes are similar to those of the $OsH(CO)_4$ groups in complexes (1) and (2) and we propose similar assignments (Figure 5), although the *cis* arrangement of bridging hydride and $OsH(CO)_4$ groups cannot be unambiguously established.

Also isolated from the reaction of $P(OMe)_3$ with complex (2) were small quantities of $[Os_3(CO)_{10}\{P(OMe)_3\}_2]$ and $[Os_3(CO)_9\{P(OMe)_3\}_3]$, indicating that cluster fragmentation also occurs with phosphite ligands. Reaction of (2) with PPh_3 is so slow that the fragmentation reactions compete more effectively, the only product isolated being $[Os_3(CO)_{10}(PPh_3)_2]$. The preferential cleavage of the 'spiked' Os–Os bond over one of the Os–Os bonds of the triangle is notable since the 'linear' cluster $[Os_4H_2(CO)_{16}]$, with three metal–metal bonds, is known (Scheme 3).[19]

We have recently developed synthetic procedures for the formation of $[Os_3H(X)(CO)_9L]$ (X = Cl, Br, I, OMe, OH, or OPh; L = MeCN or NMe_3),[20] and the hydride-coupling reaction can be extended to these systems. While for the formation of $[Os_3H(X)(CO)_9(NMe_3)]$ the relative order of yields is Cl > Br > I, for the formation of the final product $[Os_4H_3X(CO)_{13}]$ both yields and stability are in the reverse order. Infrared spectra for all three species, $[Os_4H_3X(CO)_{13}]$ [X = Cl (4), Br (5), or I (6)] are very similar, suggesting that they are all isostructural (Table 3).

Proton n.m.r. studies on complex (5) revealed three resonances due to the hydride ligands (Table 1), H_A exhibiting a single ^1J(OsH) satellite coupling and H_B and H_C [coupled, J(HH) = 2 Hz] each displaying two ^1J(OsH) couplings (Table 1) consistent with H_A being terminal and H_B and H_C bridging (Figure 6). Carbon-13 n.m.r. studies provided further confirmation of the structure shown and unambiguous assignment of H_B and H_C. The ^{13}C-$\{^1H\}$ spectrum of complex (5) exhibited one resonance of intensity two and eleven of intensity one (Figure 7). Selectively decoupled ^{13}C n.m.r. spectra showed resonances b, d, and k coupled to H_A, allowing their assignment to the $OsH(CO)_4$ group, resonance h coupled to H_C, and a, f, g, i, and l coupled to H_B (Table 2). Resonance h can



δ/p.p.m.	J(CH)/Hz			Assignment
	H_A	H_B	H_C	
179.91		8.36		a
179.41	7.37			b
179.05				c
175.48	16.14			d
174.92				e
174.78		4.09		f
171.09		3.65		g
170.65			13.18	h
168.66	5.12	10.89		i
165.95				j
165.36				k
164.72		3.51		l

Figure 6. Structure of $[Os_4H_3Br(CO)_{13}]$ (**5**) and ^{13}C n.m.r. assignment

therefore be assigned to the carbonyl *trans* to H_C of the $Os(CO)_3$ group of the triangle, and a and i [with the larger values of $J(OsH_B)$] to the carbonyls *trans* to H_B on the $Os(CO)_4$ and $Os(CO)_2$ groups (Figure 6).

On standing in solution these clusters decompose *via* loss of HX (in the order X = Cl > Br > I) to yield $[Os_4H_2(CO)_{13}]$, rather than by loss of $2e^-$ donor CO ligands to yield the known species $[Os_4H_3X(CO)_{12}]$ (Scheme 4).[21] This facile loss of HX has hitherto not been observed for osmium cluster species, but has been observed for pentanuclear ruthenium cluster species.[22]

In order to establish the exact stereochemistry of the $[Os_4H_3X(CO)_{13}]$ clusters and confirm the n.m.r. assignments the *X*-ray analysis of the bromine complex (**5**) was undertaken. The molecular structure of $[Os_4H_3Br(CO)_{13}]$ (**5**) is shown in Figure 8, while the associated bond lengths and angles are presented in Table 4. The Os(1),Os(2),Os(3) atoms define an irregular triangle one edge of which [Os(1)–Os(2)] is bridged symmetrically by Br and H(12). The $Os(4)(CO)_4H$ unit is pendant on Os(1) giving the spiked triangular metal framework geometry. All thirteen carbonyl ligands are terminal. Os(1) carries two of these groups and Os(2) three groups, while both Os(3) and Os(4) carry four each. Os(4) also carries a terminal hydride ligand while the remaining hydride H(13) bridges the Os(1)–Os(3) edge. The hydride positions were not located directly in the *X*-ray analysis but were placed in the positions shown in Figure 8 using the potential-energy calculation method developed by Orpen[23] with the terminal Os–H distance set at 1.61 Å and the bridging Os–H distances set at 1.85 Å. The assignments of the bridging hydrides along the Os(1)–Os(2) and Os(1)–Os(3) edges are confirmed by the lengthening of these edges compared to the unbridged Os(2)–Os(3) edge, and by the bending back of the equatorial carbonyl ligands from the edges; the average *cis* Os–Os–C angle for the Os(1)–Os(2) and Os(1)–Os(3) edge is 113(3)° compared to an average of 91(2)° for the Os(2)–Os(3) edge.

If it is assumed that the bridging bromine ligand acts as a three-electron donor and each hydride as a one-electron donor,

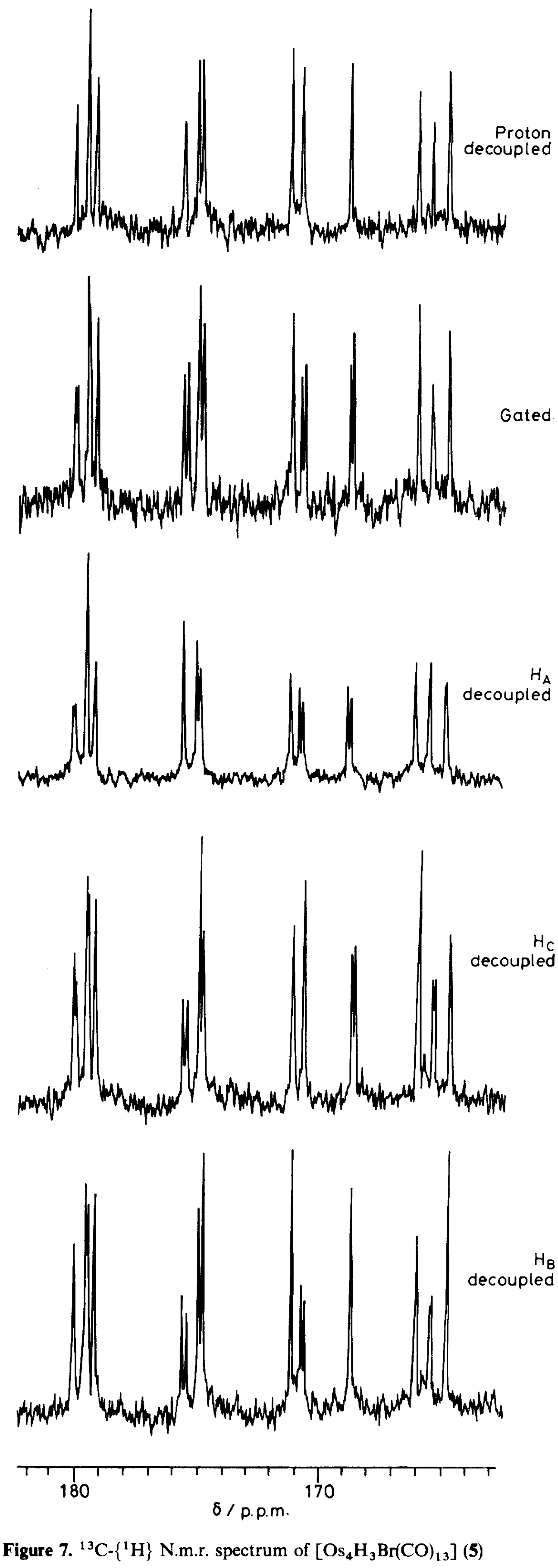
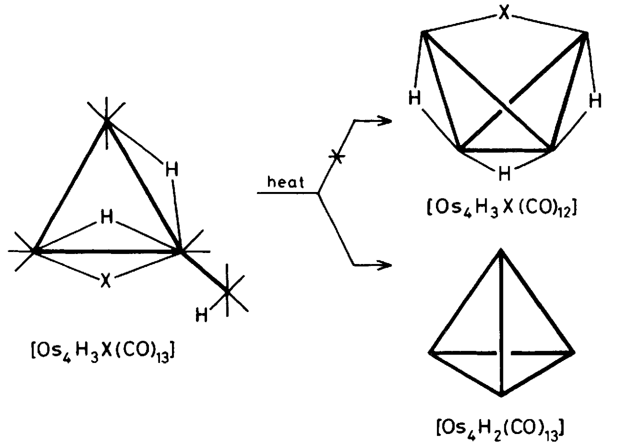


Figure 7. $^{13}C-\{^1H\}$ N.m.r. spectrum of $[Os_4H_3Br(CO)_{13}]$ (**5**)

Table 4. Bond lengths (Å) and angles (°) for $[Os_4H_3Br(CO)_{13}]$

Os(2)–Os(1)	2.873(2)	C(42)–Os(4)	1.989(20)	Os(3)–Os(1)	3.075(2)	C(43)–Os(4)	1.935(17)
Os(4)–Os(1)	2.895(2)	C(44)–Os(4)	1.891(18)	Br–Os(1)	2.595(3)	O(11)–C(11)	1.132(16)
C(11)–Os(1)	1.885(16)	O(12)–C(12)	1.117(18)	C(12)–Os(1)	1.862(17)	O(21)–C(21)	1.134(17)
Os(3)–Os(2)	2.857(2)	O(22)–C(22)	1.142(19)	Br–Os(2)	2.591(3)	O(23)–C(23)	1.157(19)
C(21)–Os(2)	1.935(16)	O(31)–C(31)	1.104(15)	C(22)–Os(2)	1.888(19)	O(32)–C(32)	1.138(19)
C(23)–Os(2)	1.898(17)	O(33)–C(33)	1.135(19)	C(31)–Os(3)	1.944(14)	O(34)–C(34)	1.139(18)
C(32)–Os(3)	1.939(18)	O(41)–C(41)	1.133(16)	C(33)–Os(3)	1.957(19)	O(42)–C(42)	1.117(20)
C(34)–Os(3)	1.970(18)	O(43)–C(43)	1.127(17)	C(41)–Os(4)	1.921(15)	O(44)–C(44)	1.140(18)

Os(3)–Os(1)–Os(2)	57.3(1)	C(33)–Os(3)–Os(1)	95.1(4)	Os(4)–Os(1)–Os(2)	147.0(1)	C(32)–Os(3)–C(31)	96.6(6)
Os(4)–Os(1)–Os(3)	108.6(1)	C(33)–Os(3)–C(31)	89.9(7)	Br–Os(1)–Os(2)	56.3(1)	C(33)–Os(3)–Os(2)	84.8(5)
Br–Os(1)–Os(3)	83.5(1)	C(34)–Os(3)–Os(1)	82.0(4)	Br–Os(1)–Os(4)	94.7(1)	C(33)–Os(3)–C(32)	94.4(7)
C(11)–Os(1)–Os(2)	109.0(5)	C(34)–Os(3)–C(31)	89.9(7)	C(11)–Os(1)–Os(3)	166.0(5)	C(34)–Os(3)–Os(2)	89.4(4)
C(11)–Os(1)–Os(4)	84.4(5)	C(34)–Os(3)–C(33)	174.2(7)	C(11)–Os(1)–Br	90.3(5)	C(34)–Os(3)–C(32)	91.3(6)
C(12)–Os(1)–Os(2)	120.1(5)	C(42)–Os(4)–Os(1)	87.4(4)	C(12)–Os(1)–Os(3)	94.3(4)	C(41)–Os(4)–Os(1)	85.6(5)
C(12)–Os(1)–Os(4)	88.6(5)	C(43)–Os(4)–Os(1)	84.8(5)	C(12)–Os(1)–Br	176.4(5)	C(42)–Os(4)–C(41)	95.3(6)
C(12)–Os(1)–C(11)	91.2(7)	C(43)–Os(4)–C(42)	95.4(6)	Os(3)–Os(2)–Os(1)	64.9(1)	C(43)–Os(4)–C(41)	165.2(7)
Br–Os(2)–Os(1)	56.4(1)	C(44)–Os(4)–C(41)	94.8(7)	Br–Os(2)–Os(3)	88.1(1)	C(44)–Os(4)–Os(1)	176.3(6)
C(21)–Os(2)–Os(1)	142.0(5)	C(44)–Os(4)–C(43)	94.1(7)	C(21)–Os(2)–Os(3)	94.3(5)	C(44)–Os(4)–C(42)	96.2(7)
C(21)–Os(2)–Br	93.6(5)	O(11)–C(11)–Os(1)	179.3(15)	C(22)–Os(2)–Os(1)	115.0(5)	Os(2)–Br(1)–Os(1)	67.3(1)
C(22)–Os(2)–Os(3)	87.8(6)	O(21)–C(21)–Os(2)	179.6(11)	C(22)–Os(2)–Br	171.5(5)	O(12)–C(12)–Os(1)	178.1(14)
C(22)–Os(2)–C(21)	94.2(6)	O(23)–C(23)–Os(2)	174.8(14)	C(23)–Os(2)–Os(1)	106.3(4)	O(22)–C(22)–Os(2)	177.1(17)
C(23)–Os(2)–Os(3)	169.2(4)	O(32)–C(32)–Os(3)	179.0(13)	C(23)–Os(2)–Br	91.9(5)	O(31)–C(31)–Os(3)	178.1(15)
C(23)–Os(2)–C(21)	96.4(6)	O(34)–C(34)–Os(3)	177.2(14)	C(23)–Os(2)–C(22)	90.8(7)	O(33)–C(33)–Os(3)	175.9(12)
Os(2)–Os(3)–Os(1)	57.8(1)	O(42)–C(42)–Os(4)	178.4(17)	C(31)–Os(3)–Os(1)	147.7(5)	O(41)–C(41)–Os(4)	177.2(15)
C(31)–Os(3)–Os(2)	91.1(5)	O(44)–C(44)–Os(4)	175.5(16)	C(32)–Os(3)–Os(1)	114.7(4)	O(43)–C(43)–Os(4)	176.6(16)
C(32)–Os(3)–Os(2)	172.3(4)						



Scheme 4. Loss of HX from $[Os_4H_3X(CO)_{13}]$ to form $[Os_4H_2(CO)_{13}]$

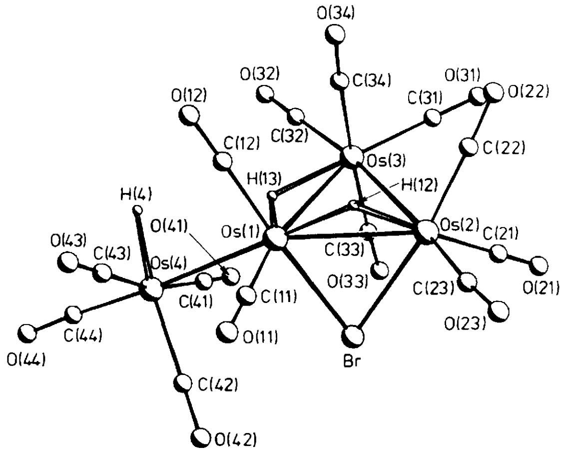


Figure 8. Molecular structure of $[Os_4H_3Br(CO)_{13}]$ (5) including the atom numbering scheme

electron-counting schemes indicate that each metal atom obeys the 18-electron rule, and the cluster as a whole is a 64-electron species consistent with the existence of four formal metal–metal bonds. In this way the spiked Os_4 structure may be derived from the electron-precise Os_4 tetrahedral geometry, where there are six metal–metal bonds, by passing through the open 'butterfly' metal arrangement, containing five metal–metal bonds, and is the result of the formal addition of two electron pairs to the *closo* structure. The tetrametal spiked geometry is an alternative metal arrangement for 64-electron systems to the rectangle observed in $[Ir_4(CO)_8\{C_2(CO_2Me)_2\}_4]$[24] or the rhomboidal arrangement in $[Os_4(CO)_{12}(CS)S]$.[25] The metal arrangement adopted is dependent on the number and the relative bridging characteristics of the ligands present.

The structure of $[Os_4H_3Br(CO)_{13}]$ may be compared to that of $[Os_3(\mu\text{-H})(\mu\text{-Br})(CO)_{10}]$,[26] and may be considered as derived from it by the replacement of the pseudo-equatorial carbonyl ligands on one of the Os atoms involved in bridge bonding by a $OsH(CO)_4$ group. In order to maintain the electron count an additional hydride is placed on the Os–Os edge adjacent to the pendant $OsH(CO)_4$ group. It is the orientation and relative position of the spike which is one of the most interesting features of the structure. The Os(4) atom lies on the same side of the Os_3 triangle as the Br atom, their respective distances from the Os_3 plane being 1.51 and 2.08 Å. It is perhaps slightly surprising that two bulky groups should lie on the same side of the molecule, however an examination of the intramolecular constants shows no steric crowding. The geometry around the Os(4) atom is close to octahedral, and the orientation of the $OsH(CO)_4$ group is such that the carbonyl ligands are staggered with respect to those bonded to Os(1) as evidenced by the torsion angles C(11)–Os(1)–Os(4)–C(42) 52.1° and C(12)–Os(1)–Os(4)–C(43) 47.8°. This orientation places the terminal hydride close to the plane passing through the Os_3 triangle and H(13) and the H(13) ··· H(4) distance of 2.68 Å is greater than the sum of the hydrogen van der Waals radii. A carbonyl group in the position occupied by the terminal hydride would induce considerable steric strain on the system. It is probable that it is the position of the terminal hydride which plays an important role in determining the position and orientation of the $OsH(CO)_4$ group once its co-ordination to Os(1) has been achieved. The hydride H(4) is also in a location where it is approximately *trans* to the bromine atom.

The Os(1)–Os(2) edge in $[Os_4H_3Br(CO)_{13}]$ (**5**), which is bridged by both the bromide and a hydride, is similar in length to the values of 2.851(1) and 2.876(1) Å for the equivalent bonds in the two independent molecules in $[Os_3HBr(CO)_{10}]$.[26] The Os–Br bond lengths [average 2.593(2) Å] and the Os–Br–Os angle in complex (**5**) are also similar to the related parameters in $[Os_3HBr(CO)_{10}]$;[26] in the latter the average Os–Br length and the Os–Br–Os angle are 2.587(3) Å and 66.9(7)°, respectively. The dihedral angle between the Os_3 and Os_2Br planes in (**5**) (105.5°) is similar to the average value of 110.1° in $[Os_3HBr(CO)_{10}]$.[26] This suggests that the replacement of a carbonyl group by an $OsH(CO)_4$ unit has little effect on the bonding in the Os(μ-H)(μ-Br)Os unit. The orientation of the carbonyls on Os(2) in complex (**5**) is also similar to that in $[Os_3HBr(CO)_{10}]$.[26]

The Os(2)–Os(3) unbridged bond in $[Os_4H_3Br(CO)_{13}]$ (**5**) is only slightly longer than the average distance of 2.843(2) Å for the unbridged Os–Os bonds in $[Os_3HBr(CO)_{10}]$,[25] while these distances in both complexes are significantly shorter than the average value of 2.877(3) Å for an Os–Os bond in the parent binary carbonyl, $[Os_3(CO)_{12}]$.[27] The hydride-bridged Os(1)–Os(3) distance is *ca.* 0.2 Å longer than in $[Os_3(CO)_{12}]$, and somewhat longer than the hydride-bridged bond length of 2.989(1) Å in $[Os_3H_2(CO)_{11}]$.[27] However, hydride-bridged Os–Os bonds of over 3 Å have been observed in several tetranuclear clusters.[21] The Os(1)–Os(4) bond length is also slightly longer than the Os–Os distance in $[Os_3(CO)_{12}]$.[27] This bond is shorter than the equivalent Os–Re distances in the mixed-metal cluster $[Os_3ReH(CO)_{15}(MeCN)]$ [2.959(1) Å] where the $Re(CO)_5$ group takes up the spiked position.[11]

The carbonyl groups are all essentially linear and none shows a deviation of more than 4σ from linearity. Although the estimated standard deviations on the carbonyl distances are too high to make an accurate assessment of the bonding in these ligands the Os–C distances follow the generally accepted trends for different *trans* groups competing for back donation from the same set of metal orbitals. The longest Os–C bonds [average 1.96(3) Å] in the triangular Os_3 unit are associated with the two axial carbonyls on Os(3). The equatorial carbonyl Os–C bond lengths of Os(3) [average 1.94(2) Å] are longer than those *trans* to the Os–Os bonds on Os(1) and Os(2) [average 1.89(3) Å]. The Os–C distances *trans* to the bridging bromine atom [average 1.88(2) Å] are significantly shorter than the carbonyl Os–C distance *trans* to the bridging hydride H(12). For Os(4) the longest Os–C distance is *trans* to the terminal hydride while the shortest is *trans* to the Os(1)–Os(4) bond. The average carbonyl C–O distance is 1.13 Å.

Reaction of $[Os_3H(OR)(CO)_9(MeCN)]$ with $[OsH_2(CO)_4]$ proceeds smoothly for R = Me and Ph but not for R = H. In the latter case the major product isolated was $[Os_3H(OH)(CO)_{10}]$. Spectral data for the alkoxide species $[Os_4H_3(OR)(CO)_{13}]$ [R = Me (**7**) or Ph (**8**)] are similar to those for the halide species (Tables 1 and 3) suggesting similar structures. It is interesting to note that with the compound $[Os_4H_3(OMe)(CO)_{13}]$ a small coupling (0.6 Hz) was resolved between the terminal hydride H_A and the bridging hydride H_B.

The mechanism of the 'hydride-coupling' reaction is, as yet, not fully understood. There are two probable pathways: initial formation of an M···H–M′ three-centre bond or initial dissociation of the mononuclear species to form a nucleophilic carbonylate anion. The former [mechanism (a)] should be facilitated by hydridic HML_n species and the latter [mechanism (b)] by acidity. To date, all 'hydride-coupling' reactions with trinuclear osmium species have involved reasonably acidic mononuclear fragments;[28] *e.g.* $[ReH(CO)_5]$, $[OsH_2(CO)_4]$, $[WH(\eta\text{-}C_5H_5)(CO)_3]$. Furthermore, we have found that $[OsH_2(CO)_2(PPh_3)_2]$ will not couple with $[Os_3(CO)_{11}(MeCN)]$, even in refluxing tetrahydrofuran. These data would suggest that mechanism (b) dominates in these systems. However, there are cases where the coupling apparently involves neutral species, such as in the formation of $[Os_2H_2(CO)_8]$[29] and $[Re_2MnH(CO)_{14}]$.[30] Clearly, more work is required to distinguish between these, or other, pathways.

Experimental

None of the compounds reported here is air-sensitive, but all reactions were carried out under an atmosphere of dry nitrogen to exclude moisture. Although not air-sensitive, all new compounds reported decompose slowly at room temperature in solution and in the solid state; however, they are sufficiently stable to handle for several hours before repurification is required. Products were separated in the air by thin-layer chromatography (t.l.c.) with plates coated with 0.25 mm of Merck Kieselgel 60 F_{254}. All solvents were dried over appropriate reagents and distilled prior to use.

Proton, ^{13}C, and ^{31}P n.m.r. data were obtained on Bruker WM 250, WH 400 or Varian XL100 instruments at 20 °C using deuteriated solvents as lock and reference ($SiMe_4$, $\delta = 0$), except for the ^{31}P n.m.r. spectra, where an insert containing $C_6D_5CD_3$ as lock and 1% trimethyl phosphate as reference (downfield positive) were used. Infrared spectra were recorded on a Perkin-Elmer 257 instrument between 2 140 and 1 600 cm^{-1} using CO(g) as calibrant. Mass spectra were obtained on a AEI MS12 spectrometer with *ca.* 70 eV (1.12×10^{-17} J) ionizing potential at 100—150 °C. Tris(perfluoroheptyl)-*s*-triazine was used as reference.

The compounds $[Os_3(CO)_{11}(MeCN)]$, $[Os_3(CO)_{10}(MeCN)_2]$, and $[Os_3H(X)(CO)_{10}]$ (X = Cl, Br, I, OH, OMe, or OPh) were prepared by the literature methods.[31] The complex $[OsH_2(CO)_4]$ was prepared by the method of Moss and Graham[19] and was stored under N_2 at −20 °C as a dilute solution in heptane (*ca.* 5 mg cm^{-3}). An approximate concentration can be estimated by reaction with CBr_4 and weighing the precipitated $[OsBr_2(CO)_4]$.[19]

Preparations.—All of the compounds reported here, with the exception of $[Os_4H_2(CO)_{14}\{P(OMe)_3\}]$, were prepared by

Table 5. Analytical data for new compounds

		Microanalysis (%)[b,c]		
Compound	M[a,b]	C	H	N
$[Os_4H_2(CO)_{15}]$	1 190	15.3	0.15	0.00
	(1 190)	(15.25)	(0.15)	(0.00)
$[Os_4H_2(CO)_{14}(MeCN)]$	1 162[d]	15.95	0.45	1.20
	(1 203)	(16.1)	(0.40)	(1.15)
$[Os_4H_2(CO)_{14}\{P(OMe)_3\}]$	1 286	16.05	0.90	0.00
	(1 286)	(16.0)	(0.70)	(0.00)
$[Os_4H_3Cl(CO)_{13}]$	1 170			
	(1 170)			
$[Os_4H_3Br(CO)_{13}]$	1 215			
	(1 215)			
$[Os_4H_3I(CO)_{13}]$	1 262			
	(1 262)			
$[Os_4H_3(OMe)(CO)_{13}]$	1 166			
	(1 166)			
$[Os_4H_3(OPh)(CO)_{13}]$	1 228			
	(1 228)			

[a] For ^{192}Os. [b] Calculated values in parentheses. [c] By Mr. D. Flory of this laboratory. [d] Corresponds to $Os_4H_2(CO)_{14}$.

Table 6. Atom co-ordinates (× 10^4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	4 064(1)	780(1)	2 559(1)
Os(2)	6 439(1)	−197(1)	3 702(1)
Os(3)	7 211(1)	1 325(1)	2 884(1)
Os(4)	2 429(1)	1 259(1)	734(1)
Br	4 935(1)	−706(1)	2 105(1)
C(11)	2 334(15)	254(11)	2 590(10)
O(11)	1 289(10)	−54(9)	2 609(8)
C(12)	3 534(15)	1 843(11)	2 952(12)
O(12)	3 179(12)	2 476(9)	3 175(10)
C(21)	8 117(16)	−858(10)	3 678(11)
O(21)	9 103(10)	−1 246(9)	3 670(10)
C(22)	7 352(16)	321(13)	4 834(12)
O(22)	7 917(12)	644(10)	5 500(8)
C(23)	5 631(14)	−1 077(11)	4 260(11)
O(23)	5 235(12)	−1 613(9)	4 654(10)
C(31)	9 205(15)	1 214(11)	3 623(12)
O(31)	10 325(12)	1 134(9)	4 057(9)
C(32)	7 469(14)	2 356(11)	2 223(11)
O(32)	7 640(12)	2 958(9)	1 835(10)
C(33)	7 559(13)	498(12)	2 012(13)
O(33)	7 846(11)	31(9)	1 526(8)
C(34)	6 814(14)	2 053(10)	3 827(11)
O(34)	6 624(12)	2 454(9)	4 397(9)
C(41)	4 214(15)	1 141(11)	467(11)
O(41)	5 248(11)	1 097(9)	283(8)
C(42)	1 881(13)	4(13)	530(11)
O(42)	1 580(11)	−700(9)	397(9)
C(43)	932(16)	1 560(11)	1 259(11)
O(43)	35(12)	1 765(9)	1 531(9)
C(44)	1 379(17)	1 649(12)	−434(13)
O(44)	680(12)	1 843(10)	−1 139(9)

stirring a slight excess of [$OsH_2(CO)_4$] with the appropriate trinuclear cluster in dichloromethane {except for [$Os_4H_2(CO)_{14}(MeCN)$], where tetrahydrofuran was employed}. The reaction was monitored by i.r. spectroscopy and t.l.c. and on completion (*ca.* 15—30 min) solvent and excess of [$OsH_2(CO)_4$] were removed under vacuum. The residue was dissolved in a small volume of dichloromethane and the products isolated by t.l.c. Infrared, mass spectroscopic, and microanalytical data are given in Tables 3 and 5.

[$Os_4H_2(CO)_{14}\{P(OMe)_3\}$]. The complex [$Os_4H_2(CO)_{14}(MeCN)$] (43 mg, 0.04 mmol) in dichloromethane (20 cm^3) was stirred with a solution (4 cm^3) of $P(OMe)_3$ in dichloromethane (*ca.* 6 mg cm^{-3}). The reaction was monitored by i.r. spectroscopy and t.l.c. and on completion the volume of solvent was reduced and products separated by t.l.c. to yield [$Os_4H_2(CO)_{14}\{P(OMe)_3\}$] in 62% yield. Also isolated were small quantities of [$Os_3(CO)_{10}\{P(OMe)_3\}_2$] and [$Os_3(CO)_9\{P(OMe)_3\}_3$].

Crystal Structure Determination of [$Os_4H_3Br(CO)_{13}$].—A suitable crystal was mounted on a glass fibre with epoxy-resin.

Crystal data. $C_{13}H_3BrO_{13}Os_4$, M = 1 207.85, monoclinic, a = 9.771(2), b = 15.264(3), c = 15.558(4) Å, β = 107.74(2)°, U = 2 210.1 Å^3 (by constrained least-squares refinement on diffractometer angles for 50 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/c$ (no. 14), Z = 4, D_c = 3.63 g cm^{-3}, $F(000)$ = 2 096. Yellow plates. Crystal dimensions (distance to faces from centre): 0.112 (100,$\bar{1}$00) × 0.025 (010,0$\bar{1}$0) × 0.023 mm (001,00$\bar{1}$), μ(Mo-K_α) = 247.57 cm^{-1}.

Data collection and processing.[32] Stoe-Siemens diffractometer, ω–θ mode with scan width 0.06°, 24 steps in scan, scan time 0.5—2.0 s per step, graphite-monochromated Mo-K_α radiation; 7 329 reflections measured ($5.0 \leqslant 2\theta \leqslant 47.5°$, $+h, \pm k, \pm l$), 3 371 unique [merging R = 0.030 after absorption correction (maximum, minimum transmission factors 0.30, 0.02)] giving 2 721 with $F > 4\sigma(F)$. No appreciable variation in intensity.

Structure analysis and refinement. Direct methods (Os and Br) followed by Fourier difference techniques. Full-matrix least-squares refinement with all non-hydrogen atoms assigned anisotropic thermal parameters. The weighting scheme $w = 2.3666/[\sigma^2(F_o) + 0.000\,196|F_o|^2]$ gave satisfactory agreement analyses. Final R and R' 0.040 and 0.033. The structure was solved and refined using SHELX 76[33] and scattering factors were taken from ref. 34. Final atomic co-ordinates are listed in Table 6.

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References

1 B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 225.
2 C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 2606.
3 J. M. Fernandez, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1981, 2250.
4 M. J. Mays and P. D. Gavens, *J. Organomet. Chem.*, 1979, **177**, 443.
5 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 224.
6 P. Chini, *J. Organomet. Chem.*, 1980, **200**, 37; P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, 1976, **14**, 285.
7 C-M. T. Hayward and J. R. Shapley, *Inorg. Chem.*, 1982, **21**, 3816.
8 J. R. Shapley, G. A. Pearson, M. Taichikawa, G. E. Schmidt, M. R. Churchill, and F. J. Hollander, *J. Am. Chem. Soc.*, 1977, **99**, 8064.
9 M. R. Churchill, F. J. Hollander, R. A. Lashewycz, G. A. Pearson, and J. R. Shapley, *J. Am. Chem. Soc.*, 1981, **103**, 2430.
10 M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1978, **17**, 3546.
11 M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1981, **20**, 4124.
12 M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1979, **18**, 1612.
13 E. J. Ditzel, H. D. Holden, B. F. G. Johnson, J. Lewis, A. J. Sanders, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 1373.
14 E. C. Constable, B. F. G. Johnson, J. Lewis, G. N. Pain, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 754.
15 B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *Acta Crystallogr., Sect. B*, 1981, **37**, 1728.
16 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, P. R. Raithby, R. Sorrell, M. J. Taylor, and M. McPartlin, unpublished work.
17 J. Knight and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1972, 1022.
18 M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1977, **16**, 2493.
19 J. R. Moss and W. A. G. Graham, *Inorg. Chem.*, 1977, **16**, 75.
20 E. J. Ditzel, B. F. G. Johnson, and J. Lewis, unpublished work.
21 B. F. G. Johnson, J. Lewis, P. R. Raithby, K. Wong, and K. D. Rouse, *J. Chem. Soc., Dalton Trans.*, 1980, 1248; B. F. G. Johnson J. Lewis, P. R. Raithby, and C. Zuccaro, *ibid.*, p. 716; B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, P. R. Raithby, and K. H. Whitmire, *ibid.*, 1983, 1339.
22 I. A. Oxton, D. B. Powell, D. H. Farrar, B. F. G. Johnson, J. Lewis, and J. N. Nicholls, *Inorg. Chem.*, 1981, **20**, 4302; B. F. G. Johnson, J. Lewis, J. N. Nicholls, J. Puga, and K. H. Whitmire, *J. Chem. Soc., Dalton Trans.*, 1983, 787.

23 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2059.
24 P. F. Heveldt, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1978, 340.
25 P. V. Broadhurst, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1982, 1641.
26 M. R. Churchill and R. G. Lashewycz, *Inorg. Chem.*, 1979, **18**, 3261.
27 M. R. Churchill and B. G. De Boer, *Inorg. Chem.*, 1977, **16**, 878.
28 R. F. Jordan and J. R. Norton, *J. Am. Chem. Soc.*, 1982, **104**, 1255.
29 J. Evans and J. R. Norton, *J. Am. Chem. Soc.*, 1974, **96**, 7577.
30 H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Am. Chem. Soc.*, 1967, **89**, 2775.
31 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.
32 R. J. Goudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby, and W. Clegg, *Acta Crystallogr., Sect. B*, 1982, **38**, 2689; W. Clegg, *Acta Crystallogr., Sect. A*, 1983, **39**, 170.
33 SHELX 76, Crystal Structure Solving Package, G. M. Sheldrick, Cambridge, 1976.
34 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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