Systematic Cluster Build Up by the Reaction of $[Os_3H(X)(CO)_9(MeCN)]$ (X = SR or NHMe; R = Me, Et, or Ph) with $[OsH_2(CO)_4]$

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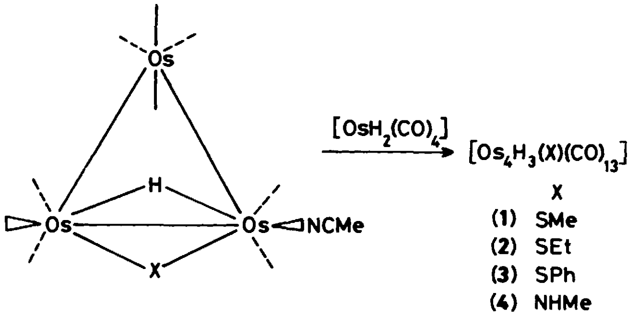
$[OsH_2(CO)_4]$ reacts with the acetonitrile derivatives $[Os_3H(SR)(CO)_9(MeCN)]$ (R = Me, Et, or Ph) and $[Os_3H(NHMe)(CO)_9(MeCN)]$ to form the tetranuclear clusters $[Os_4H_3(SR)(CO)_{13}]$ and $[Os_4H_3(NHMe)(CO)_{13}]$ respectively. The cluster $[Os_4H_3(OPh)(CO)_{12}(MeCN)]$ can be formed by treatment of $[Os_3H(OPh)(CO)_{10}]$ with 2.2 equivalents of Me_3NO followed by $[OsH_2(CO)_4]$. This cluster reacts with $P(OMe)_3$ to form $[Os_4H_3(OPh)(CO)_{12}\{P(OMe)_3\}]$. All compounds were characterised by i.r., ^1H n.m.r., and mass spectroscopy.

In a recent paper[1] we reported the synthesis of the compounds $[Os_4H_3X(CO)_{13}]$ (X = Cl, Br, or I) and $[Os_4H_3(OR)(CO)_{13}]$ (R = Me or Ph) from the reactions of $[Os_3H(X)(CO)_9(NMe_3)]$ and $[Os_3H(OR)(CO)_9(MeCN)]$ with $[OsH_2(CO)_4]$. We now report an extension to this system to include the preparation of the compounds $[Os_4H_3(SR)(CO)_{13}]$ [R = Me (**1**), Et (**2**), or Ph (**3**)], and $[Os_4H_3(NHMe)(CO)_{13}]$ (**4**). Full experimental details for all reactions are now included.



Scheme. Preparation of the new tetranuclear Os_4 clusters

Results and Discussion

As with the previously reported reactions,[1] the acetonitrile complexes $[Os_3H(SR)(CO)_9(MeCN)]$ (R = Me, Et, or Ph)[2] and $[Os_3H(NHMe)(CO)_9(MeCN)]$[3] react rapidly with $[OsH_2(CO)_4]$ to produce compounds (**1**)—(**4**) (Scheme). In the four reactions one of the major products also isolated was the compound $[Os_3H(SR)(CO)_{10}]$ or $[Os_3H(NHMe)(CO)_{10}]$, respectively. These compounds are presumably formed from CO attack on the acetonitrile derivatives, the CO being produced *in situ* from decomposition products. The i.r. and ^1H n.m.r. spectroscopic data (Tables 1 and 2) for the new compounds are similar to those for the compounds already reported suggesting that they have similar structures.[1]

A 400-MHz ^1H n.m.r. spectrum of compound (**2**) revealed a complicated signal for the CH_2 protons of the ethyl group. As is shown in Figure 1, the difference in substituents on the osmium atoms to which the sulphur atom is attached makes the sulphur atom a chiral centre. Therefore, the nuclei H′ and H″ give different signals in the ^1H n.m.r. spectrum, both of which are doublets of quartets. This arises from coupling with the CH_3 group (J_{HH} 6.7 Hz) and with each other ($J_{H'H''}$ = 12.5 Hz).

The ^1H n.m.r. spectrum for compound (**4**) gave further evidence for the assignment of the bridging hydrides in these tetranuclear compounds. Compounds of the type $[Os_3H(NHMe)(CO)_9L]$ [where L = CO or $P(OMe)_3$ and is attached to one of the bridgehead osmium atoms] all exhibit coupling between the NH hydrogen and the metal hydride (J_{HH} *ca.* 2 Hz).[3] For the compound $[Os_4H_3(NHMe)(CO)_{13}]$ (**4**) the three high-field metal–hydride signals were δ −9.25 (s), −12.49 (t, J_{HH} 1.5), and −16.25 (d, J_{HH} 1.5 Hz). Decoupling experiments showed that irradiating the resonance at δ −16.25 reduced the triplet at δ −12.49 to a doublet. Irradiation at the NH proton

Table 1. Infrared and mass spectroscopic data for the new compounds

Compound	$\nu(CO)/cm^{-1}$ [a]	*m/e*
$[Os_4H_3(OH)(CO)_{13}]$	2 131w, 2 106m, 2 076s, 2 058m (sh), 2 051vs, 2 025s, 2 015s, 2 007m (sh), 1 996m, 1 949w	1 152
(1) $[Os_4H_3(SMe)(CO)_{13}]$	2 129mw, 2 106m, 2 069s, 2 052s, 2 028m, 2 024m (sh), 2 015s, 2 003m, 1 994m, 1 967w, 1 953mw	1 182
(2) $[Os_4H_3(SEt)(CO)_{13}]$	2 119mw, 2 106m, 2 068s, 2 051s, 2 031m (sh), 2 028m, 2 023m, 2 014s, 2 003m, 1 993m, 1 966w, 1 952w	1 196
(3) $[Os_4H_3(SPh)(CO)_{13}]$	2 129mw, 2 107m, 2 071s, 2 051vs, 2 040mw, 2 020m, 2 022ms, 2 014ms, 2 002m, 1 994m, 1 994m, 1 955w br	1 244
(4) $[Os_4H_3(NHMe)(CO)_{13}]$	2 124mw, 2 101m, 2 069s, 2 053s, 2 035s, 2 029ms, 2 020ms (sh), 2 016s, 2 004ms, 1 992s, 1 950m	1 165
(5) $[Os_4H_3(OPh)(CO)_{12}(MeCN)]$	2 110w, 2 094m, 2 057s, 2 025s, 2 018vs, 2 006m, 1 982w, 1 967w, 1 944w, 1 926vw	1 200[b]
(6) $[Os_4H_3(OPh)(CO)_{12}\{P(OMe)_3\}]$	2 119m, 2 103m, 2 053ms, 2 040s, 2 023s, 2 012s, 1 995vw, 1 977vw, 1 959m, 1 943m	1 324

[a] In cyclohexane. [b] Corresponds to $[Os_4H_3(OPh)(CO)_{12}]$.

Table 2. ^1H N.m.r. data ($CDCl_3$) for the new compounds (δ p.p.m. relative to $SiMe_4$; J values in Hz)

Compound	Hydrides			Others
	H^A	H^B	H^C	
(1) $[Os_4H_3(SMe)(CO)_{13}]$	−9.64	−17.03	−14.01	2.18 (s, 3 H)
(2) $[Os_4H_3(SEt)(CO)_{13}]$	−9.58	−17.15 (d) $J_{H^BH^C}$ 1.3	−14.03 (d)	1.31 (+, 3 H, CH^D_3) 1.92 (dq, 1 H, CH^EH) 2.61 (dq, 1 H, CHH^F) $J_{H^DH^E} = J_{H^DH^F} = 6.7$; $J_{H^EH^F} = 12.5$
(3) $[Os_4H_3(SPh)(CO)_{13}]$	−9.46 J_{OsH} 39.9	−16.72 (d) J_{OsH} unresolved $J_{H^BH^C}$ 1.8	−13.82 (d) J_{OsH} 52.6, 30.8	7.26 (m, 5 H)
(4) $[Os_4H_3(NHMe)(CO)_{13}]$	−9.25	−16.25 (d) $J_{H^BH^C}$ 1.5	−12.49 (t) $J_{H^CH^D}$ 1.5	3.14 (d, 3 H) J_{HH^D} 6 2.90 (br, NH^D)
(6) $[Os_4H_3(OPh)(CO)_{12}\{P(OMe)_3\}]$	−9.2	−13.6 (d) J_{PH} 3.8	−10.6 (d) J_{PH} 6.6	3.51 (d, 9 H) J_{PH} 11 6.9 (m, 5 H)
(5) $[Os_4H_3(OPh)(CO)_{12}(MeCN)]$	−11.4	−9.3 $J_{H^BH^C}$ 2.3	−8.0	2.09 (s, 3 H) 6.56 (d, 2 H) J_{HH} 7.5 6.79 (t, 1 H) J_{HH} 7.2 7.12 (dt, 5 H)

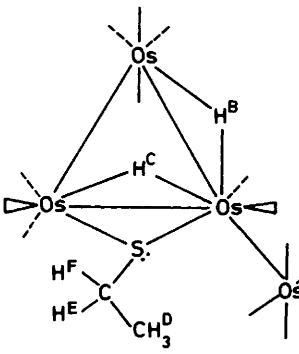


Figure 1. Structure of $[Os_4H_3(SEt)(CO)_{13}]$ (2) showing the equivalent hydrogen nuclei H′ and H″. The metal hydrides are labelled for reference with the ^1H n.m.r. data

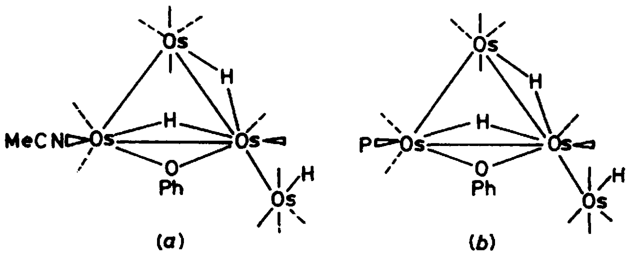


Figure 2. Proposed structure for (*a*) $[Os_4H_3(OPh)(CO)_{12}(MeCN)]$ (5) and (*b*) $[Os_4H_3(OPh)(CO)_{12}\{P(OMe)_3\}]$ (6)

resonance also reduced this triplet to a doublet without any effect on the other hydride signals. This suggests that the hydride with the resonance at δ −12.49 is the hydride bridging the osmium–osmium bond also bridged by the NHMe group. This is consistent with the assignment of the hydride resonances based on the ^{13}C n.m.r. study of $[Os_4H_3Br(CO)_{13}]$.[1]

When $[Os_3H(OPh)(CO)_{10}]$ is treated, in MeCN, with 2.2 equivalents of Me_3NO followed by reaction with $[OsH_2(CO)_4]$, the compound $[Os_4H_3(OPh)(CO)_{12}(MeCN)]$ (5) is formed in moderate yield (36%). Mass spectroscopy of this compound gives *m*/*e* = 1 200 as the highest mass ion, which corresponds to a stoicheiometry of the compound $[Os_4H_3(OPh)(CO)_{12}]$. However, the non-observance of the parent ion is common with compounds containing labile ligands such as MeCN. Elemental analysis shows the formulation as above to be correct.

Compound (5) reacts with $P(OMe)_3$ to give $[Os_3H(OPh)(CO)_9\{P(OMe)_3\}]$[2] and the expected compound $[Os_4H_3(OPh)(CO)_{12}\{P(OMe)_3\}]$ (6). Spectroscopic data are given in Table 1 and reasonable structures consistent with these data are shown in Figure 2. The phosphorus–hydrogen coupling constants for (6) may suggest that both bridging hydrides are attached to the osmium atom which also has the $P(OMe)_3$ ligand bound to it. However, $^3J_{PH}$ coupling constants of the magnitude *ca.* 3 Hz have been observed previously (*cf.* $[Os_3H(SMe)(CO)_9\{P(OMe)_3\}]$[2] and $[Os_3H_2(CO)_{10}\{P(OPh)_3\}]$[4]).

In conclusion this work again emphasises the versatility of the reaction of $[OsH_2(CO)_4]$ with clusters containing labile ligands to give a controlled synthesis of larger clusters.

Experimental

The compound $[OsH_2(CO)_4]$ was prepared by the method of Moss and Graham[5] and used as a dilute solution in heptane. The compounds $[Os_3H(X)(CO)_9(NMe_3)]$ (X = Cl, Br, or I),[6] $[Os_3H(OR)(CO)_9(MeCN)]$ (R = H, Me, or Ph),[2] $[Os_3H(SR)(CO)_9(MeCN)]$ (R = Me, Et, or Ph),[2] and $[Os_3H(NHMe)(CO)_9(MeCN)]$[3] were prepared by previously reported methods.

Reaction of $[Os_3H(X)(CO)_9(NMe_3)]$ (X = Cl, Br, *or* I) *with* $[OsH_2(CO)_4]$.—In each case the $[Os_3H(X)(CO)_9(NMe_3)]$ was used as a solid as prepared from $[Os_3H(X)(CO)_{10}]$ without purification. This made little difference to the products obtained when compared with the reaction of the purified starting materials. $[OsH_2(CO)_4]$ in heptane (1 cm^3, *ca.* 5 mg cm^{-3}) was added to $[Os_3H(Cl)(CO)_9(NMe_3)]$ {prepared from 20 mg $[Os_3H(Cl)(CO)_{10}]$} and the reaction mixture heated gently (50 °C) for 15 min until the reaction was complete (as monitored by i.r. spectroscopy and spot t.l.c.). Chromatography using hexane as eluant separated the products, which were (in decreasing order of R_f) $[Os_3H_2(CO)_{10}]$ (trace), $[Os_3H(Cl)$-

$(CO)_{10}]$ (6 mg, 30%), $[Os_4H_2(CO)_{13}]$ (5 mg, 20%), and $[Os_4H_3Cl(CO)_{13}]$ (7 mg, 27%).

Reaction of $[Os_3H(Br)(CO)_9(NMe_3)]$ with $[OsH_2(CO)_4]$ was carried out in a similar manner except CH_2Cl_2–heptane (30:70%) was used as the solvent. Yields of products: $[Os_3H_2(CO)_{10}]$ (trace), $[Os_3H(Br)(CO)_{10}]$ (11%), $[Os_4H_2(CO)_{13}]$ (10%), and $[Os_4H_3Br(CO)_{13}]$ (40%). For the preparation of $[Os_4H_3I(CO)_{13}]$ no heat is required (yield 25%). Only traces of $[Os_3H_2(CO)_{10}]$ and $[Os_3H(I)(CO)_{10}]$ were observed.

Reaction of $[Os_3H(OR)(CO)_9(MeCN)]$ (R = H, Me, *or* Ph) *with* $[OsH_2(CO)_4]$.—The solution from the reaction of $[Os_3H(OMe)(CO)_{10}]$ (23 mg) with Me_3NO–MeCN was filtered through silica and the solvent removed *in vacuo*. To this impure $[Os_3H(OMe)(CO)_9(MeCN)]$, $[OsH_2(CO)_4]$ in heptane (1 cm^3) was added followed by CH_2Cl_2 (10 cm^3). On addition of the CH_2Cl_2, the acetonitrile derivative dissolves, the solution turns emerald green, and then gradually reverts back to yellow. This emerald green colour is not obtained if any trace of MeCN is present. The reaction mixture was stirred for 15 min and then the solvent removed under vacuum. Chromatography using CH_2Cl_2–hexane (30:70) as eluant isolated the compound $[Os_4H_3(OMe)(CO)_{13}]$ (12.2 mg, 40%). $[Os_3H(OMe)(CO)_{10}]$ (12%) was isolated as a minor faster eluting compound.

The reaction to produce $[Os_4H_3(OPh)(CO)_{13}]$ proceeds in a similar manner except the initial colour change is to red which then reverts to yellow. Compounds isolated in decreasing order of R_f were $[Os_3H_2(CO)_{10}]$ (trace), $[Os_4H_3(OPh)(CO)_{13}]$ (27%), $[Os_3H(OPh)(CO)_9(MeCN)]$ (trace), $[Os_4H_3(OPh)(CO)_{12}(MeCN)]$ (10%) (Found: C, 20.00; H, 1.60; N, 0.80. Calc. for $C_{20}H_{11}NO_{13}Os_4$: C, 19.45; H, 0.75; N, 1.15%). Yields are calculated from the amount of $[Os_3H(OPh)(CO)_{10}]$ starting material used. Reaction of $[Os_3H(OH)(CO)_9(MeCN)]$ with $[OsH_2(CO)_4]$ results in similar colour changes as above. However, only traces of $[Os_4H_3(OH)(CO)_{13}]$ are formed. $[Os_3H(OH)(CO)_{10}]$ (40% recovered) and decomposition products are the major compounds produced.

Preparation of $[Os_4H_3(SR)(CO)_{13}]$ (R = Me, Et, *or* Ph).—$[OsH_2(CO)_4]$ in heptane (1 cm^3) was added to $[Os_3H(SPh)(CO)_9(MeCN)]$ (25 mg) and then CH_2Cl_2 (10 cm^3) was added. The reaction was stirred for 30 min, with monitoring by spot t.l.c. followed by removal of the solvent. Thin layer chromatography [CH_2Cl_2–hexane (30:70 v/v)] resulted in the isolation of $[Os_4H_3(SPh)(CO)_{13}]$ (15 mg, 47%) as the major band (Found: C, 18.40; H, 0.85. Calc. for $C_{19}H_8O_{13}Os_4S$: C, 18.45; H, 0.73%). Minor amounts of $[Os_3H(SPh)(CO)_{10}]$ were also isolated. The reactions to prepare $[Os_4H_3(SMe)(CO)_{13}]$ and $[Os_4H_3(SEt)(CO)_{13}]$ were carried out in a similar manner. Typically yields for the tetranuclear species $[Os_4H_3(SR)(CO)_{13}]$ were 25—30%, while 50% of the compound $[Os_3H(SR)(CO)_{10}]$ was recovered.

Preparation of $[Os_4H_3(NHMe)(CO)_{13}]$.—$[OsH_2(CO)_4]$ in heptane (1 cm^3) was added to $[Os_3H(NHMe)(CO)_9(MeCN)]$ (26 mg) and then CH_2Cl_2 (10 cm^3) was added. The reaction mixture was stirred for *ca.* 30 min with monitoring by i.r. spectroscopy. The solvent was removed *in vacuo* and the residue plated using CH_2Cl_2–hexane (30:70) as eluant. The two major compounds produced were $[Os_3H(NHMe)(CO)_{10}]$ (10 mg, 39%) and $[Os_4H_3(NHMe)(CO)_{13}]$ (11 mg, 32%).

Preparation of $[Os_4H_3(OPh)(CO)_{12}(MeCN)]$ *and* $[Os_4H_3(OPh)(CO)_{12}\{P(OMe)_3\}]$.—$[Os_3H(OPh)(CO)_{10}]$ (50 mg) was dissolved in MeCN (25 cm^3) and 2.2 molar equivalents of Me_3NO (8.6 mg) added. The reaction mixture was stirred for 15 min, and then filtered through silica. The solvent was removed under vacuum and $[OsH_2(CO)_4]$ in heptane (2 cm^3) followed by CH_2Cl_2 (10 cm^3) was added to the residue. The solution turned from yellow to red on addition of CH_2Cl_2, followed by a gradual change to orange on stirring. After *ca.* 10 min the mixture was chromatographed [CH_2Cl_2–hexane (30:70)] to yield $[Os_4H_3(OPh)(CO)_{12}(MeCN)]$ (23.2 mg, 36%). Also isolated were traces of $[Os_4H_3(OPh)(CO)_{13}]$ and $[Os_3H(OPh)(CO)_9(MeCN)]$.

$[Os_4H_3(OPh)(CO)_{12}(MeCN)]$ (20 mg) was dissolved in cyclohexane (20 cm^3) and $P(OMe)_3$ (1 drop) added. The solution was heated gently (60 °C) until i.r. spectroscopy indicated that reaction had occurred. The solvent was removed under vacuum and the residue chromatographed using CH_2Cl_2–hexane (30:70) as eluant. Compounds isolated were $[Os_3H(OPh)(CO)_9\{P(OMe)_3\}]$ (8 mg) and $[Os_4H_3(OPh)(CO)_{12}\{P(OMe)_3\}]$ (5 mg, 23%).

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