Metal Cluster Expansion by Addition of Low-valent Group 4B Reagents: Crystal and Molecular Structure of $[Os_3SnH_2(CO)_{10}\{CH(SiMe_3)_2\}_2]$; a Compound with Hydrogen Bridging Osmium and Tin

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Cluster expansion of $[Os_3H_2(CO)_{10}]$ with $[SnR_2]$ [R = $CH(SiMe_3)_2$] takes place in high yield to give $[Os_3SnH_2(CO)_{10}R_2]$, the first 'closed' triosmium–main-group metal cluster to be structurally characterized; a novel feature is the presence of a hydrogen atom bridging the tin atom and one of the osmium atoms.

We report the formation of a compound having an unexpected hydrogen bridge between tin and osmium during the addition of a low-valent main-group compound to the $[Os_3H_2(CO)_{10}]$ cluster. One objective of our work on clusters has been the synthesis of mixed main-group and transition-metal compounds. We now show that main-group metals can be incorporated into transition-metal clusters *via* low-valent derivatives in a controlled reaction under mild conditions. Reaction (1) takes place at room temperature in hexane to give, after work up, orange crystals of the tetranuclear complex in 85% (isolated) yield. The product has been characterized by elemental analysis, i.r.† and n.m.r. spectroscopy, and a full single-crystal *X*-ray structure analysis,‡ see Figure 1.

$$[SnR_2] + [Os_3H_2(CO)_{10}] \xrightarrow[R = CH(SiMe_3)_2]{} [Os_3SnH_2(CO)_{10}R_2] \tag{1}$$

This is the first 'closed' tin–triosmium cluster to be structurally characterized, although a number of 'open' compounds have been described.[1—3] Indeed to our knowledge, no similar complex containing a main-group metal has been structurally studied.[4] The geometry is shown in Figure 1, and salient bond lengths and angles are given in Figure 2. As can be seen, the metal framework is that of a planar *arachno*-molecule (7 skeletal electron pairs) with the bulky alkyl groups bonded essentially perpendicular to this plane. The most interesting feature of the new compound is the presence of a hydrogen atom bridging the tin atom and Os(2).

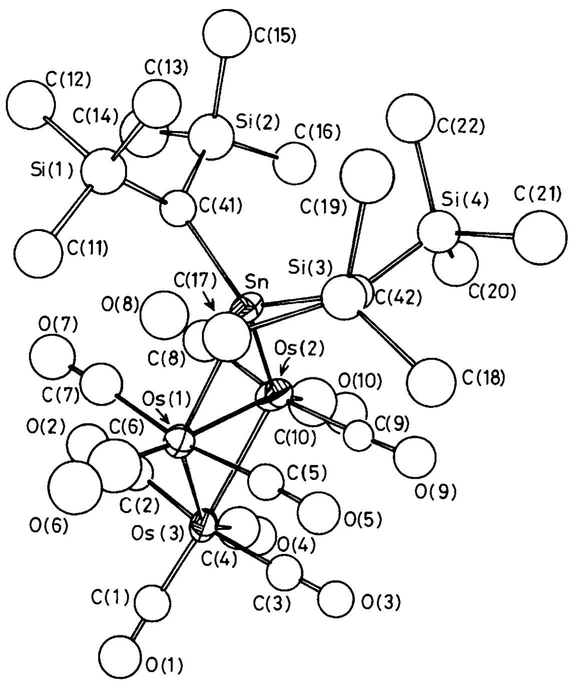

Figure 1. A perspective view of the molecule including the atom numbering scheme. Bridging hydrogen atoms are not shown.

There are three pieces of evidence for this: (i) the long Os(2)–Sn bonding, (ii) the opening of the Sn–Os(2)–C(10) angle, and (iii) the presence of tin-117 and -119 satellites on one of the hydride resonances in the ^1H n.m.r. spectrum. With regard to (i) the marked asymmetry of the Os(1)–Os(2)–Sn triangle [Sn–Os(1) 2.645(3), Sn–Os(2) 2.855(3) Å], and particularly the abnormal lengthening of the Sn–Os(2) distance {previous literature values are 2.712(1) and 2.711(1) Å in *trans*-$[(Ph_3Sn)_2Os(CO)_4]$,[1] 2.531—2.600 Å in $(NMe_4)_4[OsCl(SnCl_3)_5]$,[2] and 2.653(1) Å in $[HOs_3(\mu_3S)(\mu_3,\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)]$[3]}, point strongly to the hydrogen bridge. The lengthening compared to Os(1)–Sn is 0.21 Å, whereas Os(1)–Os(3), also hydrogen bridged, is 0.05 Å longer than Os(2)–Os(3).

The irregular alignment of the CO groups around the three osmium atoms, point (ii) (see Figure 2), provides further evidence for the two hydride locations, one bridging Os(1) and Os(3), and a second bonded to Os(2) and *trans* to Os(3). The presence of a terminal hydrogen on Os(2), however, would not cause the abnormal lengthening observed. (Neither hydrogen is directly detectable in the final difference map.)

The 360 MHz ^1H n.m.r. spectrum in perdeuteriotoluene shows high-field peaks due to the bridging hydrogens at δ −9.2 and −9.5. The higher-field resonance shows coupling to the tin-117 and -119 isotopes, *J* 258.7 and 298.0 Hz. The presence of this coupling, taken with the co-ordination of the tin to two Os and two C atoms rules out a terminal Sn–H, and unambiguously establishes the Os–H–Sn bridge. Furthermore, these values are substantially lower than in tin(IV)

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† I.r. (KBr disc, $\nu_{CO} \pm 5$ cm^{-1}) 2124(s), 2072(s), 2036(s), 2017(s), 1984(s), 1980(s), and 1962(s).

‡ A single crystal of $[Os_3SnH_2(CO)_{10}\{CH(SiMe_3)_2\}_2]$ with dimensions 0.3 × 0.2 × 0.2 mm was grown from n-hexane at −20 °C. *Crystal data:* $C_{24}H_{40}O_{10}Os_3Si_4Sn$, $M = 1290.21$, monoclinic, space group $P2_1/c$, $a = 9.617$, $b = 21.342$, $c = 19.461$ Å, $\beta = 102.31°$, $U = 3902.4$ Å^3, $Z = 4$, $D_c = 2.195$ g cm^{-3}, $D_m = 2.11$ g cm^{-3}. A total of 3553 unique reflections for which $2 < \theta < 20°$ were measured on an Enraf-Nonius CAD 3 diffractometer using ω–2θ scans and Mo-K_α radiation for which $\lambda = 0.71069$ Å. The structure was solved using MULTAN (G. Germain, P. Main, and M. M. Woolfson, MULTAN 78) and was refined with 1686 reflections for which $F_o > 2\sigma(F_o)$ using full-matrix least-squares in the SHELX system (G. M. Sheldrick, SHELX 76). At the present stage of refinement, $R = 4.84$ and $R' = 5.40\%$ and no absorption correction has been applied. Anisotropic temperature factors have been used for the Os and Sn atoms only. All hydrogen atoms apart from the bridging ones were included in calculated positions in the final refinement. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

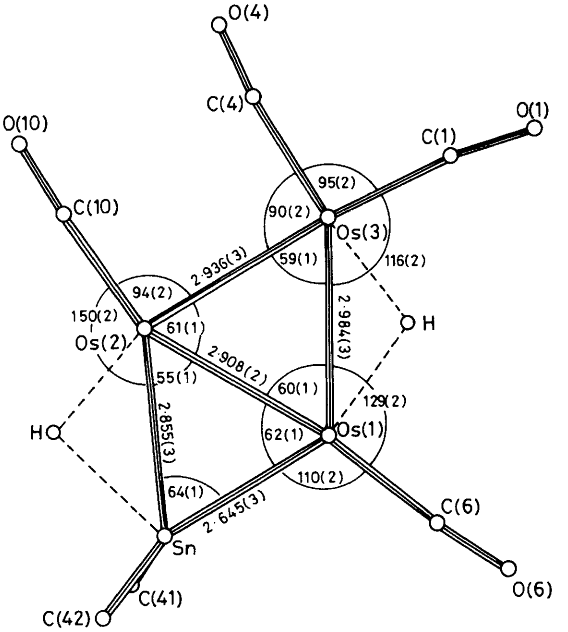

Figure 2. Projection of part of the molecule onto the Os(1)–Os(2)–Os(3) plane to show the geometry of this plane with bond lengths (Å) and bond angles (°). Only the carbonyl positions lying in the plane are shown, with others and the organic ligands on Sn being omitted for clarity. Os(1), Os(2), Os(3), and Sn are essentially coplanar (r.m.s.d. 0.0162). Bonds to the two bridging hydrogen atoms are indicated by dotted lines.

hydrides, as would be expected from the presence of the two electropositive osmium atoms bonded to tin, the five co-ordination of the tin atom, and the weaker bridging (as opposed to covalent 2-electron) tin–hydrogen interaction. (In addition, weaker bands at δ −17.3 and −17.5 are observed, and attributed to an isomer, which is formed on thermal rearrangement of the complex.)

The synthesis, which gives good yields and occurs under mild conditions, offers some useful features. Retention of the hydride ligands allows for further reactions, and the presence of the $CH(SiMe_3)_2$ ligands confers a solubility which will be of particular significance for clusters of higher nuclearity. The heating of this cluster to *ca.* 90 °C in heptane or toluene effects conversion into a second Os–Sn cluster, at present not fully characterised, but which retains the metal hydrides.

We thank Professor M. F. Lappert (for the 360 MHz spectrum), Cork County Council for a grant (to J. M. P.), and Johnson-Matthey for generous loans of osmium.

Received, 20th January 1984; Com. 079

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