Tin–Osmium Cluster Formation with a Monomeric Tin(II) Alkyl: The Formation, Crystal Structure and Reactivity of $[Os_3(\mu\text{-}H)SnR(CO)_{10}]$, a formal Stannyne Complex of the Osmium Triangle $\{R = C(SiMe_3)_2C_5H_4N\text{-}2\}$

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The monomeric tin(II) species SnR_2 $\{R = C(SiMe_3)_2C_5H_4N\text{-}2\}$ reacts with $[Os_3(H)_2(CO)_{10}]$ in hexane to give $[Os_3(\mu\text{-}H)SnR(CO)_{10}]$ **1** quantitatively; **1** is the first formal stannyne complex of the triosmium nucleus, in which the picoline nitrogen is coordinated to the tin atom, and which is itself also reactive, being a potential precursor to high nuclearity SnOs clusters.

In an extensive series of papers Stone and coworkers have described complexes with bridging carbene or carbyne ligands.[1] We now report the first bridging stannyne complex, derived by cleavage of an R group from the stannylene (stannanediyl) precursor, $[SnR_2]$.[2]

Addition of the stannylene to $[Os_3(H)_2(CO)_{10})]$ in hexane at room temperature leads quantitatively to the formation of $[Os_3(\mu\text{-}H)SnR(CO)_{10}]$ **1**,† with cleavage of one of the stannylene R-groups. Fig. 1 shows the molecular structure, together with selected bond lengths and angles, derived from a single crystal‡ grown anaerobically in hexane at −25 °C to prevent reaction (see below), and worked up rapidly at low temperature.

Without mechanistic implications, one of the originally bridging hydrogen atoms of $[Os_3(H)_2(CO)_{10}]$ has cleaved an R group from the tin atom of the stannylene, to give SnR, which then replaces the H-atom bridging the same Os–Os vector, *trans* to the remaining H. The N-atom of the remaining

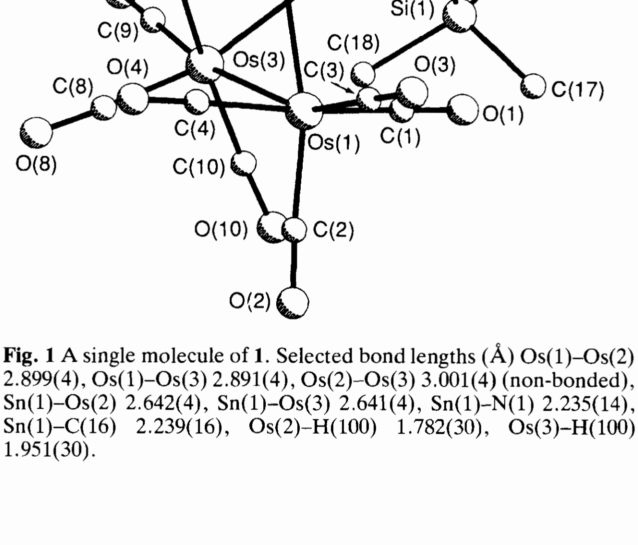

Fig. 1 A single molecule of **1**. Selected bond lengths (Å) Os(1)–Os(2) 2.899(4), Os(1)–Os(3) 2.891(4), Os(2)–Os(3) 3.001(4) (non-bonded), Sn(1)–Os(2) 2.642(4), Sn(1)–Os(3) 2.641(4), Sn(1)–N(1) 2.235(14), Sn(1)–C(16) 2.239(16), Os(2)–H(100) 1.782(30), Os(3)–H(100) 1.951(30).

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† Compound **1** is an air-stable, diamagnetic orange solid, decomp. 205 °C under Ar; decomp. 145 °C in air. Satisfactory elemental analysis (C,H,N) was obtained on material after recrystallisation from hexane. IR (CsI disc) ν(CO) 2084s, 2025s, 2007s, 1980s, 1963s, 1950(sh) cm^{-1}.

‡ *Crystal data* for **1**: $C_{22}H_{23}NO_{10}Os_3Si_2Sn$, M 1206.892, monoclinic, space group $P2_1/n$, (alternative orientation of $P2_1/c$, no. 14), $Z = 4$, $D_c = 2.499$ g cm^{-3}, $a = 10.796(3)$, $b = 19.296(1)$, $c = 15.396(2)$ Å, $\beta = 90.016(6)°$, $U = 3207.2(6)$ Å^3 (by least-squares refinement of the setting angles of 25 reflections, $15° < \theta < 18°$), $\lambda = 0.71069$ Å, $F(000) = 2191$, μ(Mo-Kα) = 122.08 cm^{-1}. 6053 reflections were measured ($1 < \theta < 22°$) using a single crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm on an Enraf-Nonius CAD-4 diffractometer (Mo radiation, graphite monochromator, ω-2θ scans). After a decay and empirical absorption correction the data merged to give 4157 unique reflections (merging $R = 0.0906$), of these 3721 had $|F_{obs}| \geq 4\sigma |F_{obs}|$. The structure was solved by the Patterson routines of SHELXS and refined by full-matrix least-squares analysis to $R = 0.0432$. The heavy atoms were refined anisotropically and the hydrogens (with the exception of the bridging hydride) were placed geometrically. The weighting scheme was refined to give a flat analysis of variance ($R_w = 0.0467$).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

R-group remains coordinated to the tin atom in the product. In terms of electron counting, the $Os_3(CO)_{10}$ moiety in **1** has a cve (cluster valence electron) count of 44, and requires four electrons. These are clearly provided, one by the hydrogen and three by the RSn group, as demanded by its formulation as a stannyne ligand. This is also in agreement with the series of structurally related species $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}X)]$, in which X is invariably a three-electron donor.[3]

Noteworthy points concerning the structure are (*i*) the short Sn–Os distances [2.641(12) and 2.642(14) Å] compared with normal bridging Sn groups on Os_3 triangles {*e.g.*, 2.737(av) for the four Sn–Os bonds in $[Os_3(CO)_{10}(\mu\text{-}SnR_2)_2]$, where R = $CH(SiMe_3)_2$}.[4] This is further support for the stannyne formulation; as is (*ii*) the shortening (by 0.20 Å) of the Sn–N distance on coordination, associated with the greater Lewis acid character of the tin atom in the complex,[5] (*iii*) the long Os(2)–Os(3) separation resulting from the formal replacement of the one-electron H-ligand with the three-electron RSn ligand [changing from 2.680(2) Å in the dihydride,[6] to 3.001(4) Å in the present compound]; and (*iv*) the symmetrical nature of the tin bridge. It is interesting, however that the doubly bridged Os–Os distance in $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}SEt)]$, in which the SEt ligand is also a formal three-electron donor is that of a typical single bond (2.863 Å), in contrast with the present, essentially non-bonding separation.

Further chemical interest in **1** derives from its reactivity. Thus, though it is stable in the crystalline state, in solution it rapidly loses a further molecule of RH, giving rise to an associated osmium–tin species, which we are currently examining as a source of high nuclearity tin–osmium cluster species. This reactivity, has precluded any useful information from NMR spectra for **1**, except to confirm its diamagnetism.

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