$[Os_3(CO)_{12}Cl(SnCl_2)\{cpM(CO)_3\}]$: Heteropentametallic Chain Cluster Complexes with no Bridging Ligands (cp = η^5-cyclopentadienyl; M = Mo or W)

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The title compounds have been prepared in high yields by the reactions of $Na[cpM(CO)_3]$ with $[Os_3(CO)_{12}Cl(SnCl_3)]$ (cp = η^5-C_5H_5) and the tungsten compound has been shown, by *X*-ray crystallography, to contain a pentametallic chain held together only by metal–metal bonds.

There is considerable current interest in the chemistry of heteronuclear cluster compounds.[1] In many of these clusters, the metal atoms are held together by metal–metal bonds in a closed polyhedral array.[2,3] Chain clusters are a growing class of compounds but the majority have a chain of metal atoms held together, at least in part, by bridging ligands.[4] Thus, chelating group 15 donor ligands have been used to hold chains together as in the Ir_2Rh cluster $[Ir_2Rh(\mu\text{-}CO)_2(CO)_3(\mu\text{-}Cl)\{\mu\text{-}(Ph_2PCH_2)_2AsPh\}_2(BPh_4)_2]$[5] and an eleven heterometal atom chain with bridging carbyne ligands has recently been described.[6] Heteronuclear chain clusters held together *only* by metal–metal bonds have been prepared and structurally characterized as in $[Re_2Pt(CO)_{12}]$ for example;[7] there are few such compounds that have been fully characterized with a chain of more than three metal atoms. Chain cluster compounds may have novel properties as unidimensional conductors or as precursors to metal polymers.

Some years ago,[8] we reported the high yield synthesis and characterization of the compound $[Os_3(CO)_{12}Cl(SnCl_3)]$, which we believed to have a 4-membered heterobimetallic chain, formed by opening of the Os_3 triangle of $[Os_3(CO)_{12}]$ (reaction 1). Reaction of $[Os_3(CO)_{12}Cl(SnCl_3)]$ with $Na[cpM(CO)_3]$ (cp = η^5-C_5H_5) gives high yields (*ca.* 80%) of fine yellow needles of (**1**) or (**2**) as the only isolable products[†] (reaction 2).

$$[Os_3(CO)_{12}] + SnCl_4 \rightarrow [Os_3(CO)_{12}Cl(SnCl_3)] \quad (1)$$

$$[Os_3(CO)_{12}Cl(SnCl_3)] + Na[cpM(CO)_3] \rightarrow [Os_3(CO)_{12}Cl(SnCl_2)\{cpM(CO)_3\}] + NaCl \quad (2)$$

(**1**) M = Mo
(**2**) M = W

Compound (**2**) has been reported previously by Gubin and co-workers[9] although their characterisation data was limited to microanalysis and IR in the ν(CO) region. The additional spectroscopic data that we have now obtained supports the formulation $[Os_3(CO)_{12}Cl(SnCl_2)\{cpW(CO)_3\}]$ proposed for compound (**2**) by Gubin and co-workers but not their structure. The IR spectra in the ν(CO) region for (**1**), (**2**), and $[Os_3(CO)_{12}Cl(SnCl_3)]$ are very similar. These spectra are, however, significantly different to the IR spectra of the carbonyl halides $[Os_3(CO)_{12}X_2]$ whose structures have been determined for X = Cl[10] and X = I[11] and shown to contain a linear Os–Os–Os backbone with X groups occupying equatorial positions on the terminal osmium atoms. Thus the structures of (**1**) and (**2**) may be different to that of $[Os_3(CO)_{12}X_2]$ (X = Cl or I). To resolve this, we have now determined the structure of (**2**) by *X*-ray crystallography.[‡] The structure is depicted in Figure 1 and shows that the triosmium backbone is linear with a chlorine atom occupying

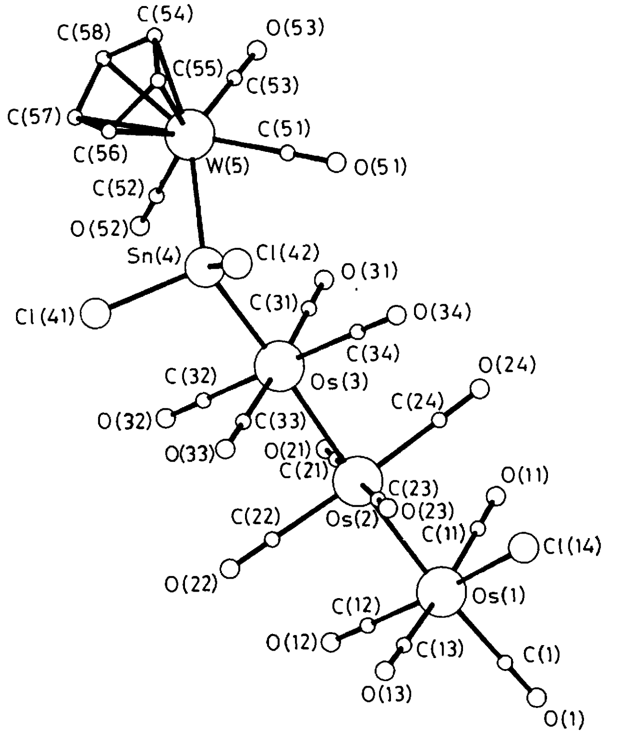

Figure 1. A view of the structure of (**2**), $[Os_3(CO)_{12}Cl(SnCl_2)\{cpW(CO)_3\}]$. Selected bond lengths (Å) and angles (°) (estimated standard deviations in the least significant digit is given in parenthesis): Os(1)–Os(2) 2.862(4), Os(2)–Os(3) 2.907(4), Os(3)–Sn 2.636(6), Sn–W 2.756(7), Os–Cl 2.394(24); Os(1)–Os(2)–Os(3) 175.9(2), Os(2)–Os(3)–Sn 175.8(2), Os(3)–Sn–W 132.8(2).

[†] Satisfactory microanalytical data were obtained for (**1**) and (**2**). For (**1**): m.p. 168—174 °C; IR ν(CO) (CH_2Cl_2) 2144m, 2112m, 2060s, 2034vs, 1994m, 1951w, 1913m; (Nujol) ν(SnCl) 300s; ν(OsCl) 292sh; ν(SnMo) 170w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.68(s). For (**2**): m.p. 156—161 °C; IR ν(CO) (CH_2Cl_2) 2144m, 2112m, 2060s, 2035vs, 1995m, 1941w, 1905m; (Nujol) ν(SnCl) 300s; ν(OsCl) 294sh; ν(SnW) 164s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.78(s); ^{119}Sn NMR ($CDCl_3$) δ 75.8(s) p.p.m. (relative to $SnMe_4$) with ^{183}W satellites [$^1J(^{119}Sn\text{–}^{183}W)$ 384 Hz].

[‡] *Crystal data* for (**2**): $C_{20}H_5O_{15}Cl_3Os_3SnW \cdot 1/2CH_2Cl_2$, *M* = 1507.22, triclinic, space group $P\bar{1}$, *a* = 8.50(1), *b* = 13.368(9), *c* = 18.311(12) Å, α = 110.74(4), β = 92.93(3), γ = 103.82(4)°, *U* = 1769 Å^3, μ(Mo-K_α) = 151.2 cm^{-1}. Data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation. The data were corrected for Lorentz polarization and absorption effects. Full-matrix least-squares refinement of 212 parameters gave *R* = 0.109, R_w = 0.113 for 2436 unique reflections. Crystal with dimensions 0.05 × 0.08 × 0.10 mm used for *X*-ray work. Yellow plates, grown from toluene/CH_2Cl_2 with great difficulty. The high value of the *R* factor is attributed to the poor quality of the crystal. Residual electron density $-4.9 \leqslant \Delta_p \leqslant 6.0$ eÅ^{-3}. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

an equatorial site on one of the terminal osmium atoms. The $SnCl_2[cpW(CO)_3]$ group, however, occupies an axial position on the other terminal osmium, thus making a linear Os_3Sn chain. With the tungsten bonded to tin, this makes a heteropentametallic chain, Os_3SnW, with no bridging ligands. Since the IR spectrum of $[Os_3(CO)_{12}Cl(SnCl_3)]$ in the ν(CO) region is almost identical to that of (**1**) and (**2**) [apart from the ν(CO) of the $cpM(CO)_3$ units], we believe that this compound has a similar structure with a linear Os_3 unit and Cl occupying an equatorial position and $SnCl_3$ occupying an axial position on the terminal osmiums, *i.e.*, (*eq*)-$ClOs(CO)_4Os(CO)_4Os(CO)_4$(*ax*)-$(SnCl_3)$. Main group trichloro substituents thus appear to prefer axial positions in Os_3 chains since in $[Os_3(CO)_{12}(SiCl_3)_2]$, the $SiCl_3$ groups both occupy axial positions.[12] It is interesting to note that the metal–metal bond lengths in (**2**) are normal, Os–Os 2.862(4) and 2.907(4) Å {*cf.* Os–Os in $[Os_3(CO)_{12}Cl_2]$ is 2.893(1) Å[10] and in $[Os_3(CO)_{12}]$ 2.877(3) Å[13]}. The length of Os–Sn in (**2**) is 2.636(6) Å (which lies in the range of 2.64–2.87 Å observed for a number of compounds with Os–Sn bonds[14]) and that of Sn–W of 2.756(7) Å is in the range observed for other compounds with Sn–W bonds.[14] Thus it would appear that there are no bonding constraints for forming long transition metal chains, particularly when they are interspersed with main group metal atoms. We are currently investigating the synthesis of longer chain compounds as well as examining the properties and reactivity of these novel compounds.

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