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Higher Nuclearity Clusters Containing Osmium and Tin Atoms. Synthesis and Structure of $[(OC)_3Os(SnMe_2)]_3$, $Os_4(SnMe_2)_4(CO)_{14}$, and $Os_4(\mu_3\text{-}O)_2(SnMe_2)_4(CO)_{14}$

Weng Kee Leong, Frederick W. B. Einstein, and Roland K. Pomeroy*

Department of Chemistry, Simon Fraser University,
Burnaby, British Columbia, Canada V5A 1S6

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Pyrolysis of $[(OC)_4Os(SnMe_2)]_2$ **(1)** at 170 °C gave $[(OC)_3Os(SnMe_2)]_3$ **(2)** as the major product. The structure of **2** reveals a planar triangulated (raftlike) Os_3Sn_3 unit ($\bar{6}$ crystallographic symmetry, with Os−Os = 2.974(1) Å and Os−Sn = 2.667(1) and 2.673(1) Å). UV irradiation of **1** in hexane provided the yellow, insoluble $Os_4(SnMe_2)_4(CO)_{14}$ **(3)**. The structure of **3** shows an essentially planar Os_4Sn_4 skeleton comprised of a central rhomboidal Os_2Sn_2 unit with each Os atom part of two outer Os_2Sn triangles. The Os−Sn bonds of the Os_2Sn_2 unit at 2.760(1) and 2.780(1) Å are significantly longer than the corresponding bonds of the Os_2Sn groups (2.678(1) and 2.727(1) Å); the Os−Os bonds in **3** are long at 3.0414(5) Å. From the treatment of **1** in solution with Me_3NO, $Os_4(\mu_3\text{-}O)_2(SnMe_2)_4(CO)_{14}$ **(4)** was isolated in low yield. The structure of **4** has a central six-membered $(OsOSn)_2$ ring to which are fused two OsOSnOs rings such that each outer ring shares a common OsO edge with the central ring. The outer rings of **4** are planar, but the central ring has a boat conformation.

Introduction

The carbonyl cluster chemistry of osmium is more extensive than for any other transition metal.[1] For example, there are 13 stable neutral binary carbonyls of osmium now known,[2] whereas at most four neutral binary carbonyls are known for each of the other transition metals (ruthenium forms $Ru(CO)_5$[3] and $Ru_2(CO)_9$[4] (both of which are unstable), $Ru_3(CO)_{12}$, and the little-studied polymeric $[Ru(CO)_4]_n$[5]). Of the binary carbonyls of osmium, we have reported the synthesis and structure of $Os_4(CO)_{15}$.[6] This cluster has an unusual planar kite structure with adjacent long and short peripheral Os−Os bonds, which we have rationalized in terms of three-center, two-electron bonds, so as to give bond orders of 0.5 and 1.5 for the peripheral metal−metal bonds.[6] More recent molecular orbital calculations by Mealli and Proserpio, however, do not support this view.[7]

We have initiated a program into the synthesis of clusters in which some of the $Os(CO)_4$ fragments in known clusters are replaced by ER_2 units (E = Si, Ge, Sn, Pb; R = organic group, H, halide). Here we report our initial foray in this area, namely, attempts to synthesize the analogue of $Os_4(CO)_{15}$ in which the two wingtip $Os(CO)_4$ groupings are replaced by $SnMe_2$ units (i.e., $Os_2(SnMe_2)(CO)_7$). Iron compounds of formula $Fe_2(ER_2)_2(CO)_7$ have been reported.[8] They have a geometry similar to that of $Fe_2(CO)_9$, with ER_2 units replacing two of the three bridging carbonyls.[8] Bridging carbonyl ligands in osmium carbonyl cluster chemistry are rare, however, and it was believed that $Os_2(SnMe_2)_2(CO)_7$, if it could be prepared, might not contain a bridging carbonyl. Although we have been unable to achieve the synthesis of the target molecule, three novel higher nuclearity clusters containing Os and Sn atoms have been synthesized and are reported here.

Experimental Section

Standard Schlenk techniques were employed in the syntheses. Solvents were rigorously dried and stored under nitrogen before use. The precursor compounds $Os_3(CO)_{12}$ and Me_2SnCl_2 were obtained from commercial sources. The compound $[(OC)_4Os(SnMe_2)]_2$ **(1)** was prepared from $Na_2Os(CO)_4$ and Me_2SnCl_2 by the literature method.[9] An external, medium-pressure mercury discharge lamp (200 W, Hanovia Model 654 A36) contained in a water-cooled quartz jacket was employed in the UV irradiation experiment; there was ~5 cm between the UV source and the edge of the reaction vessel. Infrared spectra were obtained with a Perkin-Elmer 983 spectrometer. NMR spectra were recorded on a Bruker SY-100 or WM400 spectrometer. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

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Table 1. Summary of Crystal Data and Details of Intensity Collection for $[(OC)_4Os(SnMe_2)]_2$ (1), $[(OC)_3Os(SnMe_2)]_3$ (2), $Os_4(SnMe_2)_4(CO)_{14}$ (3), and $Os_4(\mu_3\text{-}O)(SnMe_2)_4(CO)_{14}\cdot C_7H_8$ ($4\cdot C_7H_8$)

	1	2	3	4
formula	$C_{12}H_{12}O_8Os_2Sn_2$	$C_{15}H_{18}O_9Os_3Sn_3$	$C_{22}H_{24}O_{14}Os_4Sn_4$	$C_{29}H_{32}O_{16}Os_4Sn_4$
fw	902.00	1268.96	1748.0	1872.1
cryst syst	monoclinic	hexagonal	monoclinic	monoclinic
space group	$P2_1/n$	$P6_3/m$	$P2_1/n$	$P2/a$
a, Å	9.1465(13)	11.007(2)	9.668(2)	13.895(2)
b, Å	11.9544(16)		17.825(2)	12.550(2)
c, Å	9.8120(10)	12.818(2)	11.203(1)	14.053(2)
β, deg	95.592(10)		105.05(1)	113.56(1)
V, Å^3	1067.8(2)	1345.0(4)	1864.4(4)	2246.3(6)
2θ range of unit cell, deg	30.0−37.0	29.8−39.1	32.0−40.0	40.0−50.0
Z	2	2	2	2
D_{calc}, g cm^{-3}	2.806	3.134	3.114	2.768
μ(Mo Kα), cm^{-1}	142.29	169.27	162.89	135.32
cryst size, mm	0.09 × 0.06 × 0.09	0.09 × 0.12 × 0.13	0.14 × 0.08 × 0.07	0.23 x 0.16 × 0.05
transmission coeff	0.324−0.462	0.196−0.333	0.357−0.545	0.156−0.706
scan range (2θ), deg	4.0−45.0	2.0−50.0	4.0−48.0	4.0−50.0
scan width (ω), deg	$0.90 + 0.35 \tan \theta$	$0.85 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$	$0.85 + 0.35 \tan \theta$
scan rate (ω), deg min^{-1}	0.659−3.30	0.785−3.296	0.75−3.30	0.96−1.30
no. of unique rflns	1386	818	2914	3942
no. of obsd rflns^a	1034	635	2338	3078
no. of params	89	54	169	200
R^b	0.024	0.022	0.022	0.040
$R_w{}^c$	0.026	0.023	0.024	0.042
instrument instability factor (k)	0.00009	0.00005	0.00005	0.00007
extinction	0.179(14)	0.415(15)	0.072(12)	0.083(19)
largest shift/esd in final ls cycle	0.02	0.01	0.11	0.07
largest positive/negative residual electron density in final diff map, e Å^{-3}	0.55/−0.43(12)	0.60/−0.49(11)	1.0/−0.6(2)	1.8/−1.3(3)
GOF^d	1.3	1.5	1.3	2.2
F(000)	799.76	1102.53	1543.53	1675.51

^{a} $I_o > 2.5\sigma(I_o)$. ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$, $w = 1/(\sigma^2(F_o) + k|F_o|^2)$. ^{d} GOF $= [\Sigma w(|F_o| - |F_c|)^2/(\text{degrees of freedom})]^{1/2}$.

Preparation of $[(OC)_3Os(SnMe_2)]_3$ (2). A Carius tube (fitted with a Teflon valve) with $[(OC)_4Os(SnMe_2)]_2$ (**1**; 55 mg, 0.061 mmol) in hexane (10.0 mL) was cooled to −196 °C and evacuated. The solution was degassed with three freeze−pump−thaw cycles; the vessel and its contents were heated at 170 °C for 3 days, during which time the solution changed from pale yellow to golden yellow. The tube was cooled and the solution transferred to a Schlenk flask; the solvent was removed on the vacuum line and the residue extracted with hexane (3 × 2 mL) and toluene (5 and 3 mL). The combined hexane extracts and combined toluene extracts were each subjected to chromatography on silica and gave the same three bands. The first band yielded $[(OC)_3Os(SnMe_2)]_3$ (**2**) (total yield 22 mg, 22%). The analytical sample of **2** was obtained by recrystallization from toluene. As such, two forms of yellow crystals of **2** were obtained: long needles that contained 0.5 molecule of toluene (confirmed by ^{1}H NMR spectroscopy) and hexagonal prisms that did not contain solvent (by X-ray crystallography). IR (hexane): ν(CO) 2043 (m), 2009.5 (s), 1978 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.99 (J_{SnH} = 43.0, 44.4 Hz). Anal. Calcd for $C_{15}H_{18}O_9Os_3Sn_3\cdot 0.5C_7H_8$: C, 16.90; H, 1.69. Found: C, 17.11; H, 1.63.

The constituents of the second (red) and third (yellow) bands that yielded only trace amounts (~2 mg) of material were not identified.

Preparation of $Os_4(SnMe_2)_4(CO)_{14}$ (3). A Pyrex Carius tube fitted with a Teflon valve and containing **1** (220 mg, 0.244 mmol) in hexane (8.0 mL) was evacuated at −196 °C and the solution degassed with two freeze−pump−thaw cycles. The solution was subjected to UV photolysis for 14 h; the initially pale yellow solution turned golden yellow, and a precipitate formed during the course of the photolysis. An IR spectrum of the supernatant solution at this stage showed major peaks due to unreacted **1** and very weak bands at 2085, 1969, and 1953 cm^{-1}. The yellow precipitate was washed with hexane and dried on the vacuum line to afford analytically pure $Os_4(SnMe_2)_4(CO)_{14}$ (65 mg, 30%). IR (CH_2Cl_2): ν(CO) 2089.5 (m), 2019 (s), 1994.5 (m, sh), 1964.5 (w) cm^{-1}. IR (Nujol): ν(CO) 2084 (ms), 2031 (m), 2005 (s), 1989 (ms), 1979.5 (ms), 1968 (w), 1957 (ms) cm^{-1}. Anal. Calcd for $C_{22}H_{24}O_{14}Os_4Sn_4$: C, 15.12; H, 1.38. Found: C, 15.30; H, 1.41. Compound **3** is only sparingly soluble in warm CH_2Cl_2 and $CHCl_3$.

Preparation of $Os_4(\mu_3\text{-}O)_2(SnMe_2)_4(CO)_{14}$ (4). To a solution of **1** (184 mg, 0.204 mmol) in CH_2Cl_2 (15.0 mL) at −5 °C was added dropwise, over ca. 30 min, a solution of freshly sublimed Me_3NO (31 mg, 0.41 mmol) in CH_3CN (15.0 mL). The solution rapidly turned a deeper yellow. The solution was stirred for 60 min following the addition, after which it was quickly filtered through a short column of silica (~1 × 2.5 cm between layers of Celite); the column was washed with CH_2Cl_2 (2 × 5 mL). The CH_2Cl_2 solutions were combined and evaporated to dryness on the vacuum line. The residue was extracted with hexane (4 × 5 mL). The combined hexane extracts were filtered, concentrated, and cooled to −20 °C to afford a precipitate consisting of a yellow powder (identified by its IR spectrum as **1**) along with some orange crystals. The latter were separated by hand and recrystallized from toluene to afford yellow crystals of **4** (estimated yield 10%) as the toluene solvate (presence confirmed by X-ray crystallography) along with colorless blocks of **1**, which were again separated by hand. Compound **4**: IR (hexane) ν(CO) 2088 (w), 2044.5 (m), 2021 (s), 2012 (vs) 2002 (s), 1968.5 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70, 0.58. Anal. Calcd for $C_{22}H_{24}O_{16}Os_4Sn_4\cdot C_7H_8$: C, 18.61; H, 1.72. Found: C, 18.48; H, 1.67.

X-ray Analysis of 1−4. Crystals suitable for X-ray crystallography were obtained by recrystallization from the following solvents: hexane (**1**), toluene (**2**, **4**), and chloroform (**3**). (The nonsolvated form of **2** was used in the X-ray study.) In each case a crystal was mounted, in air, on an Enraf-Nonius diffractometer and intensity data were collected with the use of graphite-monochromated Mo Kα radiation. The final unit cell was determined from 25 well-centered high-angle reflections that were widely scattered in reciprocal space. Two intensity standards were measured at intervals of 60 min of X-ray exposure time. Absorption corrections were made with either a Gaussian numerical integration (checked against

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Table 2. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (Å^2) for $[(OC)_4Os(SnMe_2)]_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)	occ
Os(1)	0.58782(5)	0.54045(3)	0.20953(4)	0.0516	0.8921(7)
Sn(1)	0.32878(8)	0.53075(6)	0.03883(7)	0.0517	0.8921(7)
O(11)	0.615(1)	0.7739(6)	0.0824(9)	0.0879	0.8921(7)
O(12)	0.401(1)	0.6141(9)	0.4375(9)	0.1060	0.8921(7)
O(13)	0.536(1)	0.2895(6)	0.2451(8)	0.0851	0.8921(7)
O(14)	0.903(1)	0.5388(7)	0.355(1)	0.1029	0.8921(7)
C(11)	0.603(1)	0.687(1)	0.131(1)	0.067(3)	0.8921(7)
C(12)	0.475(1)	0.589(1)	0.353(1)	0.074(3)	0.8921(7)
C(13)	0.554(1)	0.382(1)	0.232(1)	0.060(3)	0.8921(7)
C(14)	0.785(1)	0.538(1)	0.301(1)	0.072(3)	0.8921(7)
C(1)	0.228(1)	0.6938(9)	0.027(1)	0.084(4)	0.8921(7)
C(2)	0.176(1)	0.421(1)	0.123(1)	0.103(4)	0.8921(7)
Os(10)	0.3516(4)	0.4955(3)	0.1616(4)	0.0517	0.1079(7)
Sn(10)	0.6139(7)	0.5871(5)	0.0961(6)	0.0516	0.1079(7)
O(111)	0.5433(4)	0.2946(3)	0.2578(4)	0.08(2)	0.1079(7)
O(112)	0.4019(4)	0.6261(3)	0.4326(4)	0.08(2)	0.1079(7)
O(113)	0.2122(4)	0.6907(3)	-0.0062(4)	0.08(2)	0.1079(7)
O(114)	0.0597(4)	0.3737(3)	0.1849(4)	0.08(2)	0.1079(7)
C(111)	0.4722(4)	0.3687(3)	0.2219(4)	0.067(3)	0.1079(7)
C(112)	0.3829(4)	0.5774(3)	0.3355(4)	0.074(3)	0.1079(7)
C(113)	0.2678(4)	0.6229(3)	0.0556(4)	0.060(3)	0.1079(7)
C(114)	0.1712(4)	0.4189(3)	0.1720(4)	0.072(3)	0.1079(7)
C(101)	0.7912(7)	0.5368(5)	0.2412(6)	0.084(4)	0.1079(7)
C(102)	0.6036(7)	0.7692(5)	0.1050(6)	0.103(4)	0.1079(7)

Table 3. Bond Lengths (Å) and Selected Bond Angles (deg) for $[(OC)_4Os(SnMe_2)]_2$ (1)

Bond Lengths

Os(1)−Sn(1)	2.768(1)	Sn(1)−C(1)	2.15(1)
Os(1′)−Sn(1)	2.758(1)	Os(1)−C(14)	1.93(1)
Os(1)−C(11)	1.93(1)	Sn(1)−C(2)	2.14(1)
Os(1)−C(12)	1.92(1)	C−O	1.13(1)−1.16(1)
Os(1)−C(13)	1.93(1)		

Bond Angles

Sn(1)−Os(1)−Sn(1′)	75.32(3)	Os(1)−Sn(1)−C(1)	109.3(3)
C(12)−Os(1)−C(14)	101.9(5)	Os(1′)- Sn(1)−C(1)	112.6(3)
C(11)−Os(1)−C(13)	162.8(5)	Os(1)−Sn(1)−C(2)	110.1(4)
Sn(1)−Os(1)−C(14)	170.0(4)	Os(1′)−Sn(1)−C(2)	113.5(4)
Sn(1′)−Os(1)−C(14)	94.7(4)	C(1) −Sn(1)−C(2)	106.5(5)
Os(1)−Sn(1)−Os(1′)	104.68(3)	Os(1)−C(11)−O(11)	178.3(11)

Table 4. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (Å^2) for $[(OC)_3Os(SnMe_2)]_3$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Os(1)	0.54047(4)	0.38156(4)	0.2500	0.0385
Sn(1)	0.75249(6)	0.64566(7)	0.2500	0.0420
O(11)	0.3212(9)	0.4699(9)	0.2500	0.0915
O(12)	0.5365(5)	0.3841(5)	0.0110(5)	0.0738
C(1)	0.7879(8)	0.7757(8)	0.1162(7)	0.0682
C(11)	0.404(1)	0.437(1)	0.2500	0.0665
C(12)	0.5396(7)	0.3819(7)	0.0985(8)	0.0533

Table 5. Bond Lengths (Å) and Selected Bond Angles (deg) for $[(OC)_3Os(SnMe_2)]_3$ (2)

Bond Lengths

Os(1)−Os(1′)	2.974(1)	Os(1)−C(12)	1.94(1)
Os(1)−Sn(1)	2.667(1)	Sn(1)−C(1)	2.141(7)
Os(1′)−Sn(1)	2.673(1)	C(11)−O(11)	1.14(1)
Os(1)−C(11)	1.88(1)	C(12)−O(12)	1.12(1)

Bond Angles

Sn(1)−Os(1)−Sn(1′)	172.31(2)	Os(1)−Sn(1)−Os(1′)	67.69(2)
Sn(1)−Os(1)−C(11)	94.7(3)	Os(1)−Sn(1)−C(1)	119.8(2)
Sn(1)−Os(1)−C(12)	90.0(2)	Os(1)−Sn(1)−C(1′)	119.9(2)
Sn(1)−Os(1)−C(12)	90.0(2)	C(1) −Sn(1)−C(1′)	106.4(5)
C(11)−Os(1)−C(12)	89.6(2)		

Table 6. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (Å^2) for $Os_4(SnMe_2)_4(CO)_{14}$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Os(1)	1.02359(4)	0.32479(2)	0.38549(3)	0.0389
Os(2)	0.99253(3)	0.42968(2)	0.16599(3)	0.0308
Sn(1)	1.23932(6)	0.35853(3)	0.28569(5)	0.0395
Sn(2)	1.16434(6)	0.47662(3)	0.01839(5)	0.0376
O(11)	1.1447(8)	0.4602(4)	0.5498(6)	0.0765
O(12)	0.7180(8)	0.3271(5)	0.4195(8)	0.0769
O(13)	0.9633(9)	0.1938(4)	0.1989(6)	0.0816
O(14)	1.1632(8)	0.2194(4)	0.5961(6)	0.0724
O(21)	1.1137(8)	0.5708(3)	0.3139(6)	0.0674
O(22)	0.6940(6)	0.4398(3)	0.2121(6)	0.0502
O(23)	0.9319(7)	0.3019(4)	0.0233(6)	0.0622
C(1)	1.412(1)	0.4234(6)	0.3966(8)	0.0679
C(2)	1.331(1)	0.2726(6)	0.1972(9)	0.0685
C(3)	1.348(1)	0.5426(6)	0.1136(8)	0.0650
C(4)	1.242(1)	0.3884(5)	-0.080(1)	0.0627
C(11)	1.096(1)	0.4098(5)	0.4903(9)	0.056(2)
C(12)	0.829(1)	0.3291(5)	0.4030(9)	0.061(3)
C(13)	0.982(1)	0.2419(5)	0.2686(9)	0.060(3)
C(14)	1.111(1)	0.2579(5)	0.5159(9)	0.059(2)
C(21)	1.0679(9)	0.5177(5)	0.2599(8)	0.044(2)
C(22)	0.8071(9)	0.4334(4)	0.1991(7)	0.041(2)
C(23)	0.9517(9)	0.3485(4)	0.0488(8)	0.045(2)

φ-scan measurements).[10] Data reduction included corrections for intensity scale variation and for Lorentz and polarization effects.

The positions of the Os atoms were determined by direct methods or from Patterson maps. Subsequent electron density difference syntheses revealed the remaining non-hydrogen atoms. Hydrogen atoms were generally not located and were placed in calculated positions (C−H distance 0.96 Å) and given isotropic temperature factors 10% larger than the thermal parameter of the carbon atom to which they were attached. The coordinates of carbon atoms with attached hydrogen atoms were linked so that the derived coordinates included contributions from derivatives from the appropriate atom sites. For all cases an extinction parameter was required in the assignment. Unit weights were employed initially, but at the final stage of each refinement a weighting scheme, based on counting statistics, was adopted for which $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. Comments on individual structure determinations follow this section. Complex scattering factors for neutral atoms[11] were employed in the calculation of structure factors. The programs used for data reduction, structural solution, and initial refinement were from the NRCVAX[12] crystal structure system. The program suite CRYSTALS[13] was employed in the final refinement. All computations were carried out on a MicroVAX-11 computer. Crystallographic data are summarized in Table 1. Final fractional coordinates for the non-hydrogen atoms of **1**−**4** are given in Tables 2, 4, 6, and 8, respectively, and bond length and angle data are in Tables 3, 5, 7, and 9, respectively.

Compound 1. The two intensity standards showed steady decay (20−30%) with time. There was a half-molecule in the asymmetric unit. The final model had the Os, Sn, and O atoms anisotropic. Two large residual peaks were found in the difference map, which were interpreted as disordered Os and Sn atoms; these were located such that the Os and Sn atom positions were interchanged, with the plane of the disordered molecule tilted with respect to the main molecule. The disorder was modeled with a complete, partial-occupancy molecule as follows: the Os and Sn atoms (of the disordered molecule) were given anisotropic temperature factors, which were linked to the corresponding Sn and Os atoms, respectively, of the ordered molecule. The O atoms were given one common isotropic temperature factor, with the isotropic temperature factors of the C atoms linked to their counterparts in the main molecule. The $Os(CO)_4$ and $SnMe_2$ fragments were

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Table 7. Bond Lengths (Å) and Selected Bond Angles (deg) for $Os_4(SnMe_2)_4(CO)_{14}$ (3)

Bond Lengths			
Os(1)−Os(2)	3.0414(5)	Sn(1)−C(1)	2.14(1)
Os(1)−Sn(1)	2.678(1)	Sn(1)−C(2)	2.14(1)
Os(2)−Sn(1)	2.727(1)	Sn(2)−C(3)	2.16(1)
Os(2)−Sn(2)	2.760(1)	Sn(2)−C(4)	2.16(1)
Os(2)−Sn(2′)	2.780(1)	Os(2)−C(21)	1.92(1)
Os(1)−C(11)	1.93(1)	Os(2)−C(22)	1.92(1)
Os(1)−C(12)	1.94(1)	Os(2)−C(23)	1.93(1)
Os(1)−C(13)	1.95(1)	C−O	1.14(1)−1.15(1)
Os(1)−C(14)	1.91(1)		
Bond Angles			
Os(1)−Os(2)−Sn(1)	55.00(2)	Os(2)−Os(1)−Sn(1)	56.53(2)
Os(1)−Os(2)−Sn(2)	136.24(2)	Sn(2)−Os(2)−Sn(2′)	70.72(2)
C(11)−Os(1)−C(13)	169.2(4)	C(12)−Os(1)−C(14)	101.3(4)
C(21)−Os(2)−C(22)	96.1(3)	C(21)−Os(2)−C(23)	165.4(4)
C(22)−Os(2)−C(23)	96.9(3)	Os(1)−Sn(1)−Os(2)	68.47(2)
Os(1)−Sn(1)−C(1)	117.0(3)	Os(2)−Sn(1)−C(1)	119.0(3)
Os(1)−Sn(1)−C(2)	119.6(3)	Os(2)−Sn(1)−C(2)	121.3(3)
C(1) −Sn(1)−C(2)	107.5(4)	Os(2)−Sn(2)−Os(2′)	109.28(2)
Os(2)−Sn(2)−C(3)	114.4(3)	Os(2′)- Sn(2)−C(3)	105.0(2
Os(2)−Sn(2)−C(4)	115.3(3)	Os(2′)- Sn(2)−C(4)	104.5(3)
C(3) −Sn(2)−C(4)	107.4(4)		

Table 8. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (Å) for $Os_4(\mu_3\text{-}O)(SnMe_2)_4(CO)_{14}$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)	occ
Os(1)	0.40715(4)	0.18024(4)	0.24854(4)	0.0459	
Os(2)	0.38972(4)	0.26702(4)	0.43765(4)	0.0390	
Sn(1)	0.20311(6)	0.20582(7)	0.20598(7)	0.0443	
Sn(2)	0.38846(6)	0.34108(7)	0.61493(7)	0.0414	
O(1)	0.2225(5)	0.2667(6)	0.3466(6)	0.0416	
O(11)	0.3799(9)	-0.0383(8)	0.3306(9)	0.0798	
O(12)	0.6489(8)	0.1747(9)	0.349(1)	0.0824	
O(13)	0.3917(9)	0.4142(8)	0.1747(9)	0.0784	
O(14)	0.3768(9)	0.0946(9)	0.0363(9)	0.0762	
O(21)	0.3709(8)	0.0486(7)	0.5286(8)	0.0697	
O(22)	0.6241(7)	0.2597(8)	0.5455(9)	0.0709	
O(23)	0.4010(7)	0.5042(7)	0.3820(8)	0.0632	
C(11)	0.390(1)	0.042(1)	0.303(1)	0.0561	
C(12)	0.560(1)	0.178(1)	0.316(1)	0.0724	
C(13)	0.397(1)	0.329(1)	0.205(1)	0.0594	
C(14)	0.386(1)	0.125(1)	0.115(1)	0.0574	
C(21)	0.378(1)	0.128(1)	0.491(1)	0.0517	
C(22)	0.5364(9)	0.261(1)	0.507(1)	0.0482	
C(23)	0.3959(9)	0.415(1)	0.401(1)	0.0478	
C(1)	0.105(1)	0.070(1)	0.191(1)	0.0658	
C(2)	0.126(1)	0.328(1)	0.100(1)	0.0739	
C(3)	0.5298(9)	0.299(1)	0.745(1)	0.0632	
C(4)	0.361(1)	0.508(1)	0.638(1)	0.0607	
C(51)	0.750(4)	0.370(2)	0.000(4)	0.068(6)	0.26(1)
C(52)	0.717(3)	0.279(2)	0.057(3)	0.068(6)	0.26(1)
C(53)	0.750(4)	0.179(2)	0.000(4)	0.068(6)	0.26(1)
C(54)	0.797(4)	0.170(2)	-0.033(4)	0.068(6)	0.26(1)
C(55)	0.825(3)	0.262(3)	-0.071(3)	0.068(6)	0.26(1)
C(56)	0.800(4)	0.362(2)	-0.046(4)	0.068(6)	0.26(1)
C(57)	0.658(4)	0.288(4)	0.126(4)	0.111(6)	0.26(1)
C(61)	0.776(4)	0.386(2)	-0.035(4)	0.068(6)	0.24(1)
C(62)	0.730(4)	0.335(2)	0.025(3)	0.068(6)	0.24(1)
C(63)	0.719(3)	0.225(2)	0.019(3)	0.068(6)	0.24(1)
C(64)	0.753(3)	0.166(2)	-0.045(3)	0.068(6)	0.24(1)
C(65)	0.799(3)	0.217(3)	-0.104(3)	0.068(6)	0.24(1)
C(66)	0.810(3)	0.327(3)	-0.099(3)	0.068(6)	0.24(1)
C(67)	0.669(4)	0.169(4)	0.084(4)	0.111(6)	0.24(1)

Table 9. Bond Lengths (Å) and Selected Bond Angles (deg) for $Os_4(\mu_3\text{-}O)(SnMe_2)_4(CO)_{14}$ (4)

Bond Lengths			
Os(1)−Os(2)	2.9702(8)	Os(2)−Sn(2)	2.666(1)
Os(1)−Sn(1)	2.673(1)	Os(2)−O(1)	2.158(7)
Os(1)−C(11)	1.96(1)	Sn(2)−O(1)	2.051(7)
Os(1)−C(12)	1.95(2)	Sn(1)−C(1)	2.14(1)
Os(1)−C(13)	1.95(2)	Sn(1)−C(2)	2.11(1)
Os(1)−C(14)	1.92(2)	Sn(1)−O(1)	2.034(8)
Os(2)−C(21)	1.93(1)	Sn(2)−C(3)	2.15(1)
Os(2)−C(22)	1.88(1)	Sn(2)−C(4)	2.17(1)
Os(2)−C(23)	1.93(1)	C−O	1.10(1)−1.15(1)
Bond Angles			
Os(2)−Os(1)−Sn(1)	72.40(3)	C(21)−Os(2)−C(22)	90.4(5)
C(11)−Os(1)−C(13)	165.7(6)	C(21)−Os(2)−C(23)	171.0(6)
C(12)−Os(1)−C(14)	100.4(6)	C(22)−Os(2)−C(23)	91.2(5)
Os(1)−Sn(1)−O(1)	96.4(2)	Os(2)−Sn(2)−O(1′)	112.0(2)
Os(1)−Sn(1)−C(1)	120.2(4)	Os(2)−Sn(2)−C(3)	111.2(4)
Os(1)−Sn(1)−C(2)	116.2(4)	Os(2)−Sn(2)−C(4)	122.9(4)
O(1) −Sn(1)−C(1)	103.1(4)	O(1′) −Sn(2)−C(3)	101.1(4)
O(1) −Sn(1)−C(2)	104.3(5)	O(1′) −Sn(2)−C(4)	101.7(4)
C(1) −Sn(1)−C(2)	112.5(6)	C(3) −Sn(2)−C(4)	105.6(5)
Os(1)−Os(2)−Sn(2)	175.89(3)	Os(2)−O(1) −Sn(1)	105.7(3)
Os(1)−Os(2)−O(1)	85.5(2)	Os(2)−O(1) −Sn(2′)	126.0(4)
Sn(2)−Os(2)−O(1)	98.5(2)	Sn(1)−O(1) −Sn(2′)	127.3(4)

refined as rigid groups by linking their coordinate shifts. Finally, the total occupancy was constrained to be 1.

Compound 2. The intensity standards showed random variations in the range ±1%. All non-hydrogen atoms were anisotropic in the final model.

Compound 3. The two intensity standards showed random variation (±2%) over the period of data collection. In the final model, anisotropic thermal parameters were used for all the non-hydrogen atoms, except the carbonyl carbon atoms, where isotropic thermal parameters were employed.

Compound 4. A thin platelike crystal was used in the study. Data collection was initially carried out in bisecting geometry; data for $\theta > 15°$ were collected with the azimuth position corresponding to minimum absorption. The two intensity standards showed a regular 30% decrease over the period of data collection. A toluene molecule was disordered about the crystallographic 2-fold axis, with the methyl group off it. The toluene molecule was modeled with isotropic carbon and hydrogen atoms, with the phenyl ring carbons regularized to a hexagon of side 1.39 Å; the C and H atoms were given a common temperature factor for each atom type. These solvent molecules were refined as rigid groups pivoted at the ring centers by dummy atoms. The two partial occupancy molecules had their total occupancy constrained to fill the site completely (i.e. 0.5). All non-hydrogen atoms of the cluster molecule had anisotropic thermal parameters in the final model.

Results and Discussion

$[(OC)_4Os(SnMe_2)]_2$ (1). The cluster **1** was prepared, in only moderate yield, by the standard methodology shown in eq 1.[9,14] In order to compare Os−Sn bond

$$Os_3(CO)_{12} \xrightarrow{Na/NH_3(l)} [Os(CO)_4]^{2-} \xrightarrow{Me_2SnCl_2,\ THF} [(OC)_4(SnMe_2)]_2 \qquad (1)$$

1

lengths with lengths in the higher nuclearity clusters described below, the structure of **1** was determined. Unfortunately, as for the Fe analogue,[15] the structure was disordered and therefore of somewhat low quality. A view of **1** is shown in Figure 1. Unlike $Os_4(CO)_{16}$[16] (to which **1** is an isolobal analogue), the tetrametallic core of **1** is planar. Most unbridged Os−Sn bonds reported in the literature are in the range 2.653(1)−

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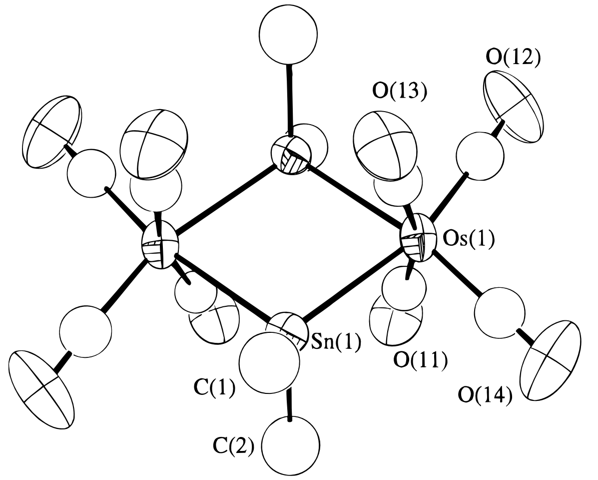


Figure 1. Molecular structure of $[(OC)_4Os(SnMe_2)]_2$ (**1**).

2.726(5) Å,[17] but in $Os_3(SnR_2)(CO)_{10}$, where R is the bulky $CH(SiMe_3)_2$ substituent, the Os−Sn distances are in the range 2.727(7)−2.753(7) Å.[18] Some exceptionally long Os−Sn bonds (2.816(1)−2.873(3) Å) have also been reported.[19] The Os−Sn bond lengths in **1** at 2.758(1) and 2.767(1) Å are therefore longer than normal. The Os−Sn lengths in the Os_2Sn_2 unit of $Os_4(SnMe_2)_4(CO)_{14}$, described below, are also long.

The axial carbonyls in **1** show a marked leaning toward the $SnMe_2$ groups: the C(11)−Os(1)−C(13) angle is 162.8(5)°. We have observed the same leaning in the crystal structures of related compounds: for example, $[(OC)_4Os(GeMe_2)]_2$[20] and $Os_2(SnMe_2)_2(CO)_7(PMe_3)$.[21] It is also found in $[(OC)_4Fe(SnMe_2)]_2$[15] and mononuclear derivatives such as *cis*-$Fe(CO)_4(SiMe_3)_2$[22a] and *cis*-$Fe(CO)_4(SnPh_3)_2$,[22b] but it is not as pronounced as in *cis*-$Ru(CO)_4(GeCl_3)_2$.[22c] Given this wide occurrence, we believe this leaning can be attributed to an inherent electronic effect rather than packing forces.[23] The EMe_3 (E = Si, Sn) ligands are known to be strong σ-donor but poor π-acceptor ligands[24] (in much the same way as PMe_3), whereas the corresponding ECl_3 groups are strong π-acceptor ligands.[24,25] In pseudooctahedral complexes with two cis-orientated EMe_2 (or EMe_3 ligands) there would be buildup of π-electron density in the region of these ligands. It would therefore be expected that the axial carbonyls would lean toward these regions in order to maximize overlap of this electron density with the appropriate π^* molecular orbitals on the axial carbonyls as shown in Chart 1. This argument is somewhat different from those used previously where the leaning is attributed to interaction of the π^* MO's on the carbonyls with the filled M−L σ bonds (where L is a weak π-acceptor ligand).[26]

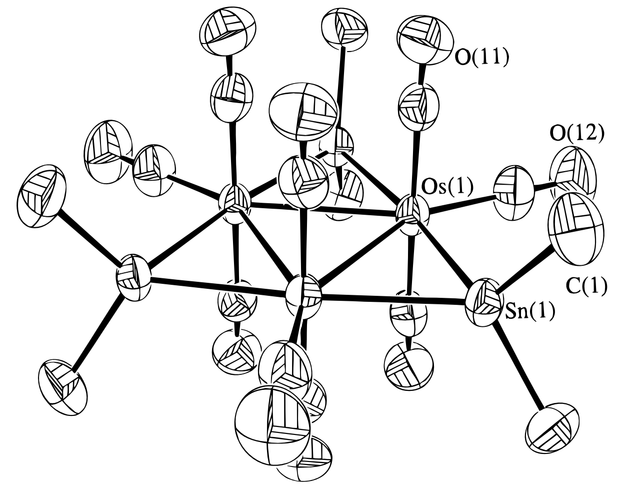
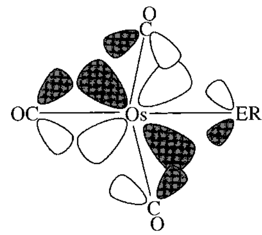


Figure 2. Molecular structure of $[(OC)_3Os(SnMe_2)]_3$ (**2**).

Chart 1



The three most common methods of removing a carbonyl ligand from a complex is by pyrolysis, UV photolysis, and oxidation to CO_2 by Me_3NO (or some other reagent). The use of these three methods to remove a carbonyl ligand from **1** and a description of the resulting products is now described.

$[(OC)_3Os(SnMe_2)]_3$ (2). Pyrolysis of **1** in hexane in an evacuated sealed Carius tube at 170 °C for 3 days afforded $[(OC)_3Os(SnMe_2)]_3$ (**2**) in 22% yield; other minor products in the reaction were not identified (eq 2). The

$$\mathbf{1} \xrightarrow[22\%]{170\ °C,\ 3\ days} \underset{\mathbf{2}}{[(OC)_3Os(SnMe_2)]_3} \qquad (2)$$

structure of **2** (Figure 2) reveals a planar, raftlike Os_3Sn_3 core similar to that found for $[(OC)_3M(GeMe_2)]_3$ (M = Ru,[27] Os[20,28]); the molecules are constrained by their crystallographic site symmetry ($\bar{6}$) to be planar. The structure of **1** may also be compared to those of $Os_5(\mu\text{-}CO)(CO)_{17}$[2b,c] and $Os_6(CO)_{17}[P(OMe)_3]_4$,[29] which also have planar triangulated metal skeletons. The structure of $Os_6(CO)_{21}$, to which **2** is an isolobal analogue, has not been determined but presumably has an Os_6 raft nucleus.[30]

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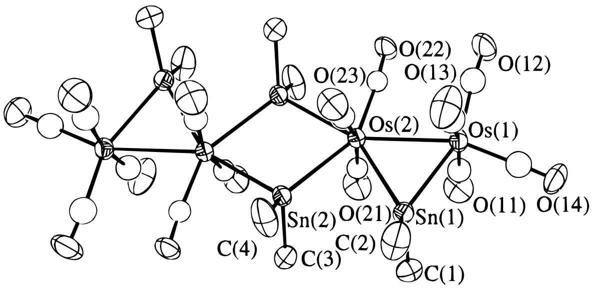


Figure 3. Molecular structure of $Os_4(SnMe_2)_4(CO)_{14}$ (**3**).

The conversion of **1**, with its four-membered Os_2Sn_2 ring, to **2** upon pyrolysis is consistent with the polyhedral skeletal electron pair theory (PSEPT) view that metal clusters are most stable when comprised of triangular (rather than square) metal units.[31] The thermal stability of **1** is, however, quite remarkable when it is compared to the stability of $Os_4(CO)_{16}$ (which decomposes in solution at room temperature to $Os_3(CO)_{12}$).[16]

The Os−Sn bond lengths in **2** at 2.667(1) and 2.673(1) Å are within the normal range, mentioned above, for such bonds. The Os−Os bond lengths (each at 2.974(1) Å) are long: osmium−osmium distances in open, low-nuclearity clusters are usually compared to 2.877(3) Å, the average Os−Os bond length in $Os_3(CO)_{12}$.[32] In $Os_5(\mu\text{-}CO)(CO)_{17}$ the metal−metal bond lengths lie in the range 2.847(1) Å ($Os(\mu\text{-}CO)Os$) to 2.892(1) Å,[2b] whereas in $Os_6(CO)_{17}[P(OMe)_3]_4$ the range is 2.834(2)−2.909(2) Å.[29]

$Os_4(SnMe_2)_4(CO)_{14}$ (3). The UV irradiation of **1** in hexane afforded **3** as a yellow precipitate (eq 3). The

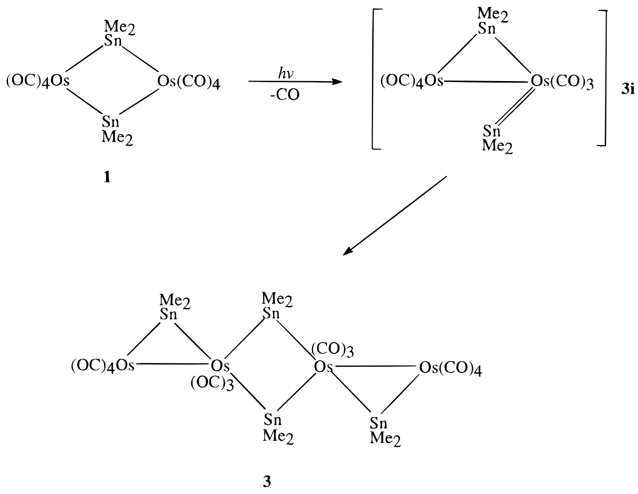
$$\mathbf{1} \xrightarrow[30\text{‰}]{h\nu} \underset{\mathbf{3}}{Os_4(SnMe_2)_4(CO)_{14}} \qquad (3)$$

precipitation of the product onto the walls of the reaction vessel eventually prevented efficient passage of UV light to the reaction solution, and therefore the reaction was stopped after about 30% conversion of **1** to **3**.

The crystal structure of **3** shows (Figure 3) an Os_4Sn_4 skeleton comprised of a rhomboidal Os_2Sn_2 unit, with each Os atom part of two outer Os_2Sn triangles. The molecule has a center of symmetry with the eight metal atoms essentially in a plane (the dihedral angle between the Os(1)Sn(1)Os(1′)Sn(1′) and Os(1)Os(2)Sn(2) planes is 3.5°). The Os−Sn bonds of the metal triangles are, at 2.678(1) and 2.727(1) Å, similar to the Os−Sn lengths in **2** which, as mentioned previously, are in the normal range for Os−Sn lengths reported in the literature. On the other hand, the Os−Sn bonds of the rhomboid are significantly longer at 2.760(1) and 2.780(1) Å and are similar to the corresponding lengths in **1**.

Ring strain in homonuclear cage and cluster compounds of Si, Ge, and Sn are significantly less than in the corresponding C compounds.[32] Nevertheless, the other structural parameters for the Os_2Sn triangle in **3** might be taken to indicate ring strain. The Os(1)−Sn(1)−Os(2) angle is 68.47(2)°, a major distortion from the tetrahedral value; the corresponding angle in the Os_2Sn_2 rhomboid is 109.28(2)°. The Os(1)−Os(2) bond length of 3.0414(5) Å is exceptionally long for an unbridged Os−Os bond of a trinuclear fragment (recall that the average Os−Os distance in $Os_3(CO)_{12}$ is 2.877(3) Å).

Scheme 1



The formation of **3** from **1** could be envisaged to proceed via the stannylene derivative $(OC)_4Os(SnMe_2)Os(SnMe_2)(CO)_3$ **(3i)** as shown in Scheme 1. As a reviewer has pointed out, there must be a cis to trans rearrangement of the tin ligands about the $Os(CO)_3$ unit in **3i** before dimerization to give **3**. The proposed intermediate **3i** may be considered a resonance form of $Os_2(SnMe_2)(CO)_7$, the original target molecule analogous to $Os_4(CO)_{15}$. It is perhaps relevant to mention here that ethylene readily undergoes reversible dissociation from $Os_2(\mu\text{-}C_2H_4)(CO)_8$.[34] In other words, 2 + 2 cycloadditions can occur readily if one of the moieties is based on a transition metal. Furthermore, the iron analogue of **1**, $[(OC)_4Fe(SnMe_2)]_2$, readily yields the stannylene-like derivatives $Fe(CO)_4(SnMe_2L)$ (L = weak Lewis base),[35] and the iron analogue of **3i** has been proposed as an intermediate in the rearrangement of $Fe_2(SnR_2)_2(\mu\text{-}CO)(CO)_6$ compounds.[8b]

The reaction depicted in eq 3 and Scheme 1 is easily reversed by treating **3** in solution at 65 °C with 1 atm of carbon monoxide. We have also found that treatment of a solution of **3** at room temperature with PMe_3 readily affords $Os_2(SnMe_2)_2(CO)_7(PMe_3)$, the derivative of **1**, in which one of the equatorial carbonyls has been replaced by the phosphine.[21] Although we have not studied the substitution of **2** by PMe_3, we have found that the germanium analogue of **2**, $[Os(CO)_3(GeMe_2)]_3$, does not readily undergo substitution with PMe_3 until 120 °C.

$Os_4(\mu_3\text{-}O)_2(SnMe_2)_4(CO)_{14}$ (4). When the reaction of **1** in CH_3CN/CH_2Cl_2 with 2 equiv of Me_3NO was monitored by infrared spectroscopy, it was apparent that several products were formed. IR absorptions were seen to grow at different rates, some of which diminished in intensity as the reaction progressed. The only product that could be isolated (in ~10% yield) was $Os_4(\mu_3\text{-}O)_2(SnMe_2)_4(CO)_{14}$ **(4)**, as a yellow crystalline solid

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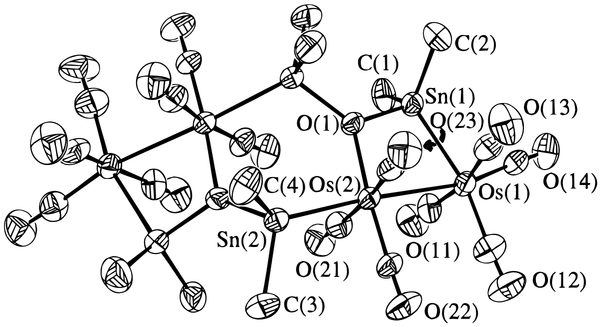

Figure 4. Molecular structure of $Os_4(\mu_3\text{-}O)_2(SnMe_2)_4(CO)_{14}$ (**4**).

(eq 4).

$$\mathbf{1} + \mathrm{Me_3NO} \xrightarrow[10\%]{} \underset{\mathbf{4}}{\mathrm{Os_4(\mu_3\text{-}O)_2(SnMe_2)_4(CO)_{14}}} \qquad (4)$$

The X-ray crystal structure of **4** reveals the configuration shown in Figure 4. Cluster **4** may be considered as derived from **3** by the addition of two oxygens atoms so as to expand the original three- and four-membered rings into four- and six-membered rings, respectively. (It has been found that treatment of **3** with Me_3NO does not yield **4** under the same conditions.) In the solid state, **4** has a crystallographic 2-fold axis that passes through the center of the $Os_2Sn_2O_2$ ring. The four-membered rings are essentially planar; the dihedral angle between the Os(2)O(1)Sn(1) and Os(2)Os(1)Sn(1) planes is 1.5°. The central ring, however, has a boat conformation; the dihedral angle between the Os(2)Sn(2)O(1′) and O(1)Os(2)O(1′)Os(2′) planes is 46.4°. The non-carbonyl oxygen atoms are planar three-coordinate, and the coordination of the $OOsSn_2$ group is similar to that of OSn_3 units observed previously;[23,36] the O-Sn(1) and O−Sn(2) lengths are 2.049(7) and 2.031(8) Å, respectively. The Os(1)−Os(2) bond length in **4** at 2.9706(8) Å, although somewhat long for an Os−Os single bond, is nevertheless significantly shorter than the Os−Os bond in **3**. The Os−Sn lengths in **4** of 2.666(1) Å (Os(1)-Sn(1)) and 2.673(1) Å (Os(2)-Sn(2)) are typical of Os−Sn single bonds. The Os(1)-O(1) distance of 2.165(7) Å in **4** may be compared to 2.06(2) Å, the Os−O length in $Os_4(\mu_3\text{-}O)_4(CO)_{12}$,[37] and 2.06(2) and 2.07(2) Å, the corresponding distances in $Os_6(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_{18}$.[38]

Conclusions. In transition-metal carbonyl cluster compounds containing main-group elements (i.e., other than CO), the question arises as to whether the main-group element is best considered as part of a simple ligand or whether it is an essential part of the metal cluster framework. For example, in compounds such as $Os_3(CO)_{11}(PR_3)$[39] and $Os_4(CO)_{13}(PMe_3)$[40] the phosphine is acting as a simple ligand, whereas in clusters such as $Ru_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)(CO)_{10}$[41] and $M_4(\mu_4\text{-}Bi)_2(CO)_{12}$ (M = Ru,[42] Os[43]) the group 15 atom is essentially part of the cluster framework as required by PSEPT. There are, however, molecules where the bonding of the main-group element is intermediate and consequently the bonding is ambiguous. Examples of molecules in this category are $Ru_4(\mu\text{-}PPh_2)_2(CO)_{13}$[44] and $M_4(\mu_3\text{-}PPh)(CO)_{13}$[45] (M = Ru, Os). Some of the clusters of this type, as in $Ru_4(\mu\text{-}PPh_2)(CO)_{13}$, $Ru_4(\mu\text{-}PPh_2)_4(CO)_{14}$,[44] and $Os_4(\mu_3\text{-}S)_2(CO)_{12}$,[46] have unusual metal−metal interactions.[7]

Of the clusters described in this study, we believe, given its thermal stability, short Os−Sn bonds, and resemblance to $Os_6(CO)_{19}$, that in cluster **2** the $SnMe_2$ vertices of the deltahedral Os_2Sn units are probably best considered as part of the cluster framework. The central rhomboidal Os_2Sn_2 polygon present in **1** and **3** resembles the Os_4 skeleton in $Os_4(CO)_{16}$, which, as mentioned previously, is unstable in solution at room temperature with respect to $Os_3(CO)_{12}$.[16] We therefore believe that the four-membered Os_2Sn_2 rings in **1**, **3**, and **4** have at best only partial metal cluster character. This is in agreement with the view of PSEPT that triangular metal units are more stable than rhomboidal units.

The structural motifs exhibited by clusters containing group 8 and group 14 metal atoms are numerous.[23,47] The fused-ring systems found in **3** and **4** are, nevertheless, unprecedented and further illustrate the structural diversity of this class of clusters.

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Supporting Information Available: Tables of hydrogen atom coordinates and anisotropic temperature factors for **1**−**4** (8 pages). Ordering information is given on any current masthead page.

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