Synthesis of Novel Metal–Chalcogen Mixed Clusters by the Reactions of 1,2,3,4,5-Tetrachalcogenastannolanes with $Os_3(CO)_{12}$: The First Examples of Transition-Metal Complexes Bridged by Stannanethione and Stannaneselone

Norihiro Tokitoh, Yasusuke Matsuhashi, and Renji Okazaki*

Department of Chemistry, Faculty of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

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*Summary: Novel, tin-containing transition-metal–chalcogen mixed clusters **2**, **3**, and **4** have been synthesized by the complexation of overcrowded diaryl-substituted 1,2,3,4,5-tetrachalcogenastannolanes, $Tb(Tip)SnY_4$ (**1a**, Y = S; **1b**, Y = Se; Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl), with $Os_3(CO)_{12}$. The molecular structures of clusters **2a** and **2b**, which are the first examples of binuclear osmium complexes bridged by stannanethione and stannaneselone ligands, were successfully determined by X-ray crystallographic analysis.*

The synthesis and structural characterization of transition-metal cluster compounds have been an active area of research for the past few decades.[1] Considerable interest has been focused particularly on the chemistry of clusters with chalcogen atoms in the framework, i.e. metal–chalcogen mixed clusters,[2] since the structural diversity of chalcogen ligands is remarkably greater than that of triorganophosphines, the most widely used class of ligands in modern coordination chemistry. However, there have been very limited numbers of examples of metal–chalcogen mixed clusters incorporating both transition and main-group metals, probably due to the limitation of synthetic methodology.[3]

We have recently succeeded in the synthesis of novel tin-containing cyclic polychalcogenides, 1,2,3,4,5-tetrachalcogenastannolanes $Tb(Tip)SnY_4$ (**1**; Tip = 2,4,6-triisopropylphenyl; Y = S, Se),[4] by taking advantage of a new steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tb in this paper).[5] We report herein the novel synthesis of tin-containing transition-metal–chalcogen mixed clusters by the complexation of **1** with $Os_3(CO)_{12}$, which leads to the first isolation and characterization of binuclear transition-metal complexes of a stannanethione and a stannaneselone. We also describe the X-ray crystallographic structure analysis of these triosmium complexes bridged by a stannanethione and a stannaneselone.

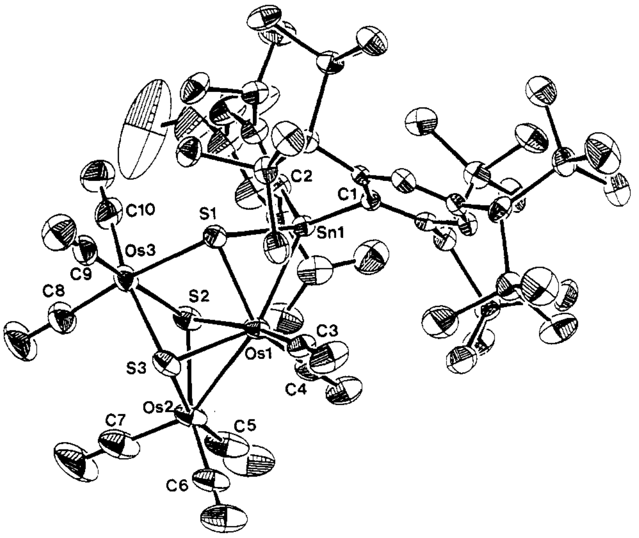

Figure 1. ORTEP drawing of $Tb(Tip)SnS_3Os_3(CO)_8$ (**2a**) with thermal ellipsoid plots (30% probability). Selected bond lengths (Å) and angles (deg): Sn(1)–S(1) = 2.489(3), Sn(1)–Os(1) = 2.662(2), Os(1)–S(1) = 2.491(3), Os(1)–S(2) = 2.453(3), Os(1)–S(3) = 2.445(3), Os(1)–Os(2) = 2.745(1), Os(2)–S(2) = 2.419(3), Os(2)–S(3) = 2.388(3), Os(3)–S(1) = 2.480(3), Os(3)–S(2) = 2.431(3), Os(3)–S(3) = 2.458(4), Sn(1)–C(1) = 2.193(8), Sn(1)–C(2) = 2.165(9), Os(1)–C(3) = 1.88(1), Os(1)–C(4) = 1.89(1), Os(2)–C(5) = 1.90(2), Os(2)–C(6) = 1.90(1), Os(2)–C(7) = 1.87(2), Os(3)–C(8) = 1.87(1), Os(3)–C(9) = 1.90(1), Os(3)–C(10) = 1.94(2); C(1)–Sn(1)–C(2) = 128.7(3), C(1)–Sn(1)–S(1) = 104.2(3), C(1)–Sn(1)–Os(1) = 113.0(2), C(2)–Sn(1)–S(1) = 108.8(3), C(2)–Sn(1)–Os(1) = 117.6(2), Sn(1)–Os(1)–S(1) = 57.65(8), S(1)–Sn(1)–Os(1) = 57.73(7), Sn(1)–S(1)–Os(1) = 64.63(8), Sn(1)–S(1)–Os(3) = 120.1(1), Sn(1)–Os(1)–Os(2) = 144.29(4), Sn(1)–Os(1)–S(2) = 91.45(8), Sn(1)–Os(1)–S(3) = 136.52(8), Os(1)–S(1)–Os(3) = 81.91(9). Extra distances (Å): Os(1)···Os(3) = 3.258(3), Os(2)···Os(3) = 3.657(3).

When 1,2,3,4,5-tetrathiastannolane **1a** was treated with an equimolar amount of $Os_3(CO)_{12}$ in refluxing toluene for 10 h, three types of tin-containing osmium–sulfur mixed clusters, **2a**, **3a**, and **4a**, were obtained in 21, 13, and 24% yields, respectively.[6] The reaction of $Tb(Tip)SnSe_4$ (**1b**) with $Os_3(CO)_{12}$ under similar conditions also gave analogous selenium complexes **2b** (9%) and **4b** (13%) together

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(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980. (b) Adams, R. D.; Selegue, J. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 4, p 967. (c) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1. (d) *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapters 3 and 5. (e) Adams, R. D. *Polyhedron* **1985**, *4*, 2003 and references cited therein.

(2) (a) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. (b) Gysling, H. J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1986; Chapter 18.

(3) (a) Seyferth, D.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 508. (b) Seyferth, D.; Henderson, R. S.; Gallagher, M. K. *J. Organomet. Chem.* **1980**, *193*, C75. (c) Adams, R. D.; Katahira, D. A. *Organometallics* **1982**, *1*, 460. (d) Cardin, C. J.; Cardin, D. J.; Power, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 505. (e) Viswanathan, N.; Morrison, E. D.; Geoffroy, G. L.; Geib, S. J.; Rheingold, A. L. *Inorg. Chem.* **1986**, *25*, 3100.

(4) (a) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *Tetrahedron Lett.* **1991**, *32*, 6151. (b) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351. See also: Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047.

(5) (a) Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1987**, 2293. (b) Okazaki, R.; Unno, M.; Inamoto, N.; Yamamoto, G. *Chem. Lett.* **1989**, 493. (c) Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1989**, 791.

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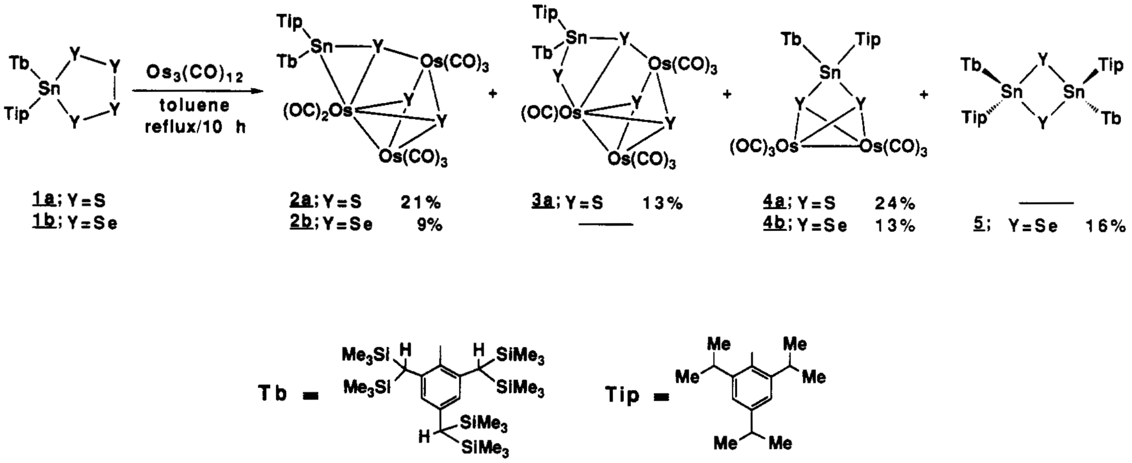
Scheme I



with the 1,3,2,4-diselenadistannetane derivative **5** (16%) (Scheme I).

All the products here obtained were stable enough to be separated by thin-layer chromatography on silica gel and showed satisfactory spectral and analytical data.[7] Of the newly obtained osmium complexes, the molecular structures of **2a** and **2b** were definitively determined by X-ray crystallographic analysis. An ORTEP drawing of **2a** is shown in Figure 1 together with its selected interatomic bond lengths and angles.[8]

As shown in Figure 1, two metal-to-metal bonds, i.e. Sn(1)–Os(1) and Os(1)–Os(2), are clearly present, while the Os(3) atom is connected to the other metal atoms by means of the three bridging sulfur atoms. The bond length between Sn(1) and S(1) atoms (2.489(3) Å) is indicative of the corresponding tin–sulfur single bond.[9] Although there might be some interpretations as to the coordination state of these metal–chalcogen mixed clusters, one can regard the complex **2a** as a binuclear osmium complex formally bridged by a stannanethione, Tb(Tip)Sn=S. The molecular structure of complex **2b** is virtually the same as that of **2a**.[10] To our knowledge, **2a** and **2b** represent the first examples of transition-metal complexes bridged by stannanethione and stannaneselone ligands.

There have been some reports on such binuclear complexes of their carbon analogues, thioketone and selenoketone (or thioaldehyde and selenoaldehyde).[11] For example, the selenium-bridged transition-metal complexes $[(\eta^5\text{-}C_5H_5)Mn(CO)_2]_2Se_n$ (n = 1, 2) are readily converted by diazomethane into a binuclear complex with a selenoformaldehyde bridge, $(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_4(CH_2{=}Se)$, the crystallographic structure analysis of which also showed a distinct elongation of the bridging C–Se bond up to a single-bond length (1.900(11) Å).[11d]

Of particular note among the structural features of these new cluter complexes is a dynamic process, as revealed by the NMR data for **2a** and **2b**.[7] Thus, the ^{1}H and ^{13}C NMR spectra of complex **2a** in $CDCl_3$ at room temperature showed two sets of signals (approximately 1:1 intensity

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(6) Since no thermal interconversion among **2**, **3**, and **4** was observed under the reaction conditions (refluxing in toluene for 10 h), it can be ruled out that the clusters here obtained are kinetically related. Furthermore, we have found that the starting material Tb(Tip)SnS_4 (**1a**) did not decompose thermally under the reaction conditions. The detailed mechanism for the formation of these unique metal–chalcogen mixed clusters will be described in a full paper.

(7) The spectral and analytical data for **2a** are listed as an example: reddish yellow crystals; mp 90–92 °C; ^{1}H NMR (toluene-d_8, 400 MHz at 97 °C) δ 0.02 (br s, 9H), 0.11 (s, 9H), 0.12 (s, 9H), 0.28 (br s, 18H), 0.32 (s, 9H), 1.12 (d, J = 7.0 Hz, 6H), 1.23 (d, J = 6.7 Hz, 3H), 1.41 (d, J = 6.7 Hz, 3H), 1.44 (s, 1H), 1.54 (d, J = 6.4 Hz, 3H), 1.58 (d, J = 6.4 Hz, 3H), 1.84 (br s, 1H), 2.70 (sept, J = 7.0 Hz, 1H), 2.97 (br s, 1H), 3.43 (sept, J = 6.4 Hz, 1H), 3.69 (sept, J = 6.7 Hz, 1H), 6.60 (br s, 1H), 6.72 (br s, 1H), 7.05 (s, 1H), 7.06 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.86 (q × 2), 1.24 (q), 1.28 (q), 1.34 (q × 2), 1.69 (q), 1.73 (q), 1.76 (q), 2.14 (q), 2.78 (q), 2.97 (q), 23.41 (q), 23.45 (q), 24.18 (q), 24.21 (q), 25.48 (q × 2), 26.87 (q × 2), 28.98 (q), 29.39 (q), 30.18 (q), 30.84 (q), 34.12 (d × 2), 34.46 (d), 34.62 (d), 35.07 (d), 36.51 (d), 39.20 (d), 39.53 (d), 41.05 (d), 41.34 (d), 122.41 (d), 122.60 (d), 122.80 (d), 122.86 (d), 123.08 (d), 123.31 (d), 128.43 (d), 128.61 (d), 141.02 (s), 141.07 (s), 143.83 (s), 143.96 (s), 144.40 (s), 144.49 (s), 149.58 (s), 149.63 (s), 150.56 (s × 3), 150.69 (s), 153.51 (s × 2), 153.84 (s), 153.87 (s), 169.27 (s × 2), 170.53 (s), 170.56 (s), 171.48 (s), 171.53 (s), 172.34 (s × 2), 174.54 (s × 2), 175.08 (s × 2), 179.55 (s), 179.71 (s), 183.72 (s), 183.84 (s); IR (KBr) $\nu_{C=O}$ 2102, 2082, 2009, 1942 cm^{-1}; UV–vis (hexane) λ_{max} 231 (ϵ 32 100), 306 (6040), 346 (4150) nm. Anal. Calcd for $C_{50}H_{82}O_8Os_3S_3Si_6Sn$: C, 34.02; H, 4.68; S, 5.45. Found: C, 33.92; H, 4.45; S, 5.80. The ^{1}H and ^{13}C NMR spectra of **2a** in $CDCl_3$ at room temperature showed two sets of signals (approximately 1:1 intensity ratio) due to the existence of two geometric isomers. In the ^{13}C NMR spectra the 12 peaks appearing in the range from 169.27 to 183.84 ppm were assigned as those of the carbonyl carbons, where the intensities of the peaks at 169.27, 172.34, 174.54, and 175.08 ppm were about twice that of the others. For the ^{1}H NMR data were shown the chemical shifts of coalesced signals observed in toluene-d_8 at 97 °C, while for the ^{13}C NMR data were listed the chemical shifts of the two sets of signals in $CDCl_3$ at room temperature because of the complexity of the coalesced spectrum in toluene-d_8 at 97 °C resulting from inevitable overlap with the signals of the solvent. Experimental details are described in the supplementary material together with the physical properties of **2b** and **3–5**. Determinations of the molecular structures of the complexes **3a**, **4a**, and **4b** were based on the X-ray crystallographic analysis of the analogous ruthenium complexes, Tb(Tip)$SnSe_4Ru_3(CO)_7$ and Tb(Tip)$SnS_2Ru_2(CO)_6$, and the close resemblance of their spectral data to those for **3a**, **4a**, and **4b**, the details of which will be described elsewhere.

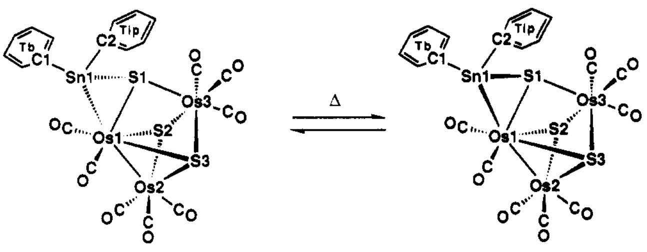
(8) Crystal and experimental data for **2a**: $C_{50}H_{82}O_8Os_3S_3Si_6Sn$, fw = 1765.18, crystal size (mm) 0.40 × 0.30 × 0.65, triclinic, space group $P\bar{1}$, a = 13.31(1) Å, b = 24.069(4) Å, c = 12.051(3) Å, α = 94.57(2)°, β = 113.75(3)°, γ = 99.58(5)°, V = 3438(4) Å^3, Z = 2, D_c = 1.705 g/cm^3, R = 0.043 (R_w = 0.043). The data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å); μ = 61.24 cm^{-1}. Of the 16 566 reflections collected, 15 885 were unique ($2\theta < 55°$). The structure was solved by direct methods, and the final cycle of full-matrix least-squares refinement was based on 7663 observed reflections ($I > 3\sigma(I)$) and 640 variable parameters.

(9) The lengths of the tin–sulfur single bonds in the oligomeric dialkyltin sulfides are reportedly 2.40–2.48 Å. See: (a) Menzebach, B.; Bleckmann, P. *J. Organomet. Chem.* **1975**, *91*, 291. (b) Jacobsen, H.-J.; Krebs, B. *J. Organomet. Chem.* **1977**, *136*, 333. (c) Puff, H.; Gattermeyer, R.; Hundt, R.; Zimmer, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 547.

(10) The ORTEP drawing and crystallographic data for **2b** are described in the supplementary material together with tables of bond lengths, angles, and thermal and positional parameters.

(11) (a) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546. (b) *Organometallics* **1982**, *1*, 240. (c) Herrmann, W. A.; Weichmann, J.; Serrano, R.; Blechshmitt, K.; Pfisterer, H.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 314. (d) Herberhold, M.; Ehrenreich, W.; Bühlmeyer, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 315. (e) Paul, W.; Werner, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 316. (f) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1983**, *244*, C53. (g) Herrmann, W.; Rohrmann, J.; Schäfer, A. *J. Organomet. Chem.* **1984**, *265*, C1. (h) Herberhold, M.; Jellen, W.; Murray, H. H. *J. Organomet. Chem.* **1984**, *270*, 65. (i) Werner, H.; Paul, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 58. (j) Adams, R. D.; Bain, J. E.; Tasi, M. *Organometallics* **1986**, *5*, 1920. See also ref 3c.

Scheme II



2a(A) 2a(B)

ratio) most likely due to the existence of two geometric isomers generated by the bending of the Tb(Tip)Sn unit relative to the pseudosymmetry plane which bisects the Os_3S_3 cluster and the asymmetric substitution on the tin atom by the two different aryl groups (Scheme II). The ^1H and ^{13}C NMR spectra of **2a** in toluene-d_8 showed the coalescence of the signals at 97 °C, suggesting a wagging across this plane or even more extensive migration of the Tb(Tip)Sn group at this temperature.

In summary, we have found a new approach to unique metal–chalcogen mixed clusters with both main-group and transition metals starting from tetrachalcogenametallolanes 1. Above all, the formation of the osmium complexes **2a** and **2b** is noteworthy as the first examples of transition-metal complexes bridged by a stannanethione and a stannaneselone, which are among a novel class of double-bond compounds between heavier main-group elements of current interest.

Further investigation on the reaction mechanism for the formation of the new tin-containing metal complexes and their reactivities is now in progress.

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Supplementary Material Available: Text giving experimental details for the preparation of **2**–**5** and their spectral and analytical data and crystallographic data with tables of bond lengths, angles, and thermal and positional parameters for **2a** and **2b** (100 pages). Ordering information is given on any current masthead page.

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