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# Reactions of 1,2,3,4,5-Tetrachalcogenastannolanes with Group 6 and 8 Transition-Metal Carbonyls: Formation of Novel Transition-Metal Complexes Bridged by Stannanethiones and Stannaneselones

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The reactions of the 1,2,3,4,5-tetrachalcogenastannolanes Tb(Tip)Sn$Y_4$ (**1**: **1a**, Y = S; **1b**, Y = Se) with $W(CO)_5$·THF and $M_3(CO)_{12}$ (M = Ru, Os) are reported. Stannolane **1a** reacted with $W(CO)_5$·THF to produce Tb(Tip)Sn$S_4$·$W(CO)_5$ (**2**) in 40% yield, which was analyzed crystallographically. The structure of **2** contains an octahedral tungsten unit, the THF ligand of $W(CO)_5$·THF being replaced by a tetrathiastannolane ring at a position $\beta$ to tin. While triruthenium complexes $(\mu_3\text{-Y})_3(\mu_2\text{-Y})Ru_3(CO)_7$[Tb(Tip)Sn] (**4**: **4a**, Y = S; **4b**, Y = Se) and diruthenium complexes $(\mu_3\text{-Y})_2Ru_2(CO)_6$[Tb(Tip)Sn] (**5**: **5a**, Y = S; **5b**, Y = Se) were isolated from the reaction of **1** with $Ru_3(CO)_{12}$, the reactions of **1** with $Os_3(CO)_{12}$ afforded triosmium complexes $(\mu_3\text{-Y})_3Os_3(CO)_7$[Tb(Tip)Sn] (**8**: Y = S, Se) together with triosmium complexes $(\mu_3\text{-Y})_3(\mu_2\text{-Y})Os_3(CO)_7$[Tb(Tip)Sn] (**9a**, Y = S) and diosmium complexes $(\mu_3\text{-Y})_2Os_2(CO)_6$[Tb(Tip)Sn] (**10**, Y = S, Se). The structures of **4b**, **5a**, and **8** were characterized crystallographically. The isolation of **5** and **10**, which have interesting and strained quadracyclic Sn$Y_2M_2$ (M = Ru, Os) ring systems, was considered to be due to steric protection against polymerization by bulky Tb and Tip ligands. The complexes **4** and **9** contain three triply bridging chalcogen ligands in a cluster of three ruthenium or osmium atoms which have only one Ru−Ru or Os−Os bond. The complexes **8** are regarded as binuclear osmium complexes bridged by a stannanethione and a stannaneselone, though the bond lengths between tin and chalcogen were elongated to those for single bonds and the angles around the tin atom were slightly spread out on account of the complexation of osmium. The possible reaction mechanism is also proposed.

## Introduction

The synthesis and structural characterization of transition-metal cluster compounds have been an active area of research for the past few decades,[1] since there has been much interest in transition-metal cluster compounds as a possible source for a new class of homogeneous catalysts.[2] Polynuclear coordination and metal−metal bond cleavage and formation processes may serve as new means for the activation of small molecules.[3] Considerable interest has been focused particularly on the chemistry of such clusters with chalcogen atoms in the framework, i.e. metal−chalcogen mixed clusters,[4] since the structural diversity of chalcogen ligands is remarkably greater than that of triorganophosphines, the most widely used ligand class in modern coordination chemistry. For example, studies on the reaction of transition-metal clusters with cyclic thioethers have been widely explored,[5] because of the importance of the hydrodesulfurization process.[6]

Meanwhile, transition-metal complexes are known to stabilize thermodynamically unstable species such as thio-, seleno- and telluroaldehydes by coordination to C−chalcogen (S, Se, Te) double bonds.[7,8]

Moreover, Satgé et al.[9] recently reported the formation of the dimetallacycle $[(t\text{-BuCp})_2\text{Zr}{-}\text{S}{-}\text{Ge(Me)}_2(o\text{-}C_6H_4)]$ by the insertion of the reactive species of the monomer dialkylgermanethione ($Me_2Ge{=}S$) into the Zr−C bond of the transient benzyne−zirconocene com-

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pound thermally produced from bis($\eta^5$-*tert*-butylcyclopentadienyl)diphenylzirconium, $(t\text{-BuCp})_2ZrPh_2$.

We have previously reported the successful 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), by taking advantage of the 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group (denoted the Tb group hereafter), a new steric protection group, and the formation of stannanethione and stannaneselone by dechalcogenation of **1** with trivalent phosphorus reagents.[10] Because transition-metal complexes such as $M_3(CO)_{12}$ (M = Ru, Os) are known to have a particularly high chalcogenophilic property and react with elemental sulfur and selenium, leading to the formation of chalcogen-ligand clusters, $M_3(CO)_9(Y)_2$ (M = Ru, Os; Y = S, Se),[11] it seemed to be reasonable that tetrachalcogenastannolanes **1** would undergo dechalcogenation by transition-metal carbonyl complexes, resulting in the formation of stannanethione and stannaneselone and they would be subsequently stabilized by coordination of a transition-metal cluster with the chalcogen ligands.

There have been very few examples of metal–chalcogen mixed clusters incorporating both transition and main-group metals so far, probably due to the limitation of synthetic methodology.[8c,12] We wish to describe in this paper the novel synthesis of tin-containing transition-metal–chalcogen mixed clusters by the complexation of **1** with group 6 and group 8 metal carbonyl complexes, which leads to the first isolation and characterization of binuclear transition-metal complexes of stannanethione and stannaneselone.[13]

## Results and Discussion

### 1. Reaction of a Tetrathiastannolane with $W(CO)_6$ and Structure of the Product.

Since group 6 metal carbonyls such as $M(CO)_6$ (M = Mo, W) are known to act as homogeneous desulfurization reagents[14] and to chelate with thio- and selenocarbonyl compounds in an $\eta^1$ or $\eta^2$ form as mentioned above, we first examined the reaction of tetrathiastannolane **1a** with $W(CO)_6$. We chose a THF complex of $W(CO)_5$ as a transition-metal source, because **1a** did not react with $W(CO)_6$ even in refluxing THF. To a THF solution of $W(CO)_5{\cdot}THF$, prepared by irradiation of $W(CO)_6$ in THF, was added tetrathiastannolane **1a** at room temperature. The major product (isolated in 40% yield) was characterized as $Tb(Tip)SnS_4{\cdot}W(CO)_5$ (**2**) on the basis of its infrared and $^1H$ NMR spectra, elemental analysis, and X-ray crystallographic analysis (Scheme 1). An ORTEP diagram and selected bond lengths and angles of **2** are shown in Figure 1 and Table 1.

The infrared spectrum in the carbonyl region shows absorptions at 2080 (m), 1990 (w), 1950 (vs), and 1930 (s, sh) $cm^{-1}$. This is similar to the spectra of the molecules $[(OC)_5W(SCR_2)]$ (R = aryl; $SCR_2$ = thiocamphor, adamanthanethione)[15] and $[(OC)_5W(SH_2)]$.[16] The similarity of the $^1H$ NMR spectrum of **2** to that of tetrathiastannolane **1a** suggested that there is little difference in conformation of their tetrathiastannolane rings. As shown in Figure 1, the molecular structure of **2** is that with simple replacement of the THF ligand by the tetrathiastannolane unit through the complexation of the $\beta$-sulfur atom toward the tungsten atom. In the obtained octahedral tungsten complex **2**, the bond length of W(1)–S(2) is 2.519(9) Å, which is slightly shorter than those of the previously reported octahedral

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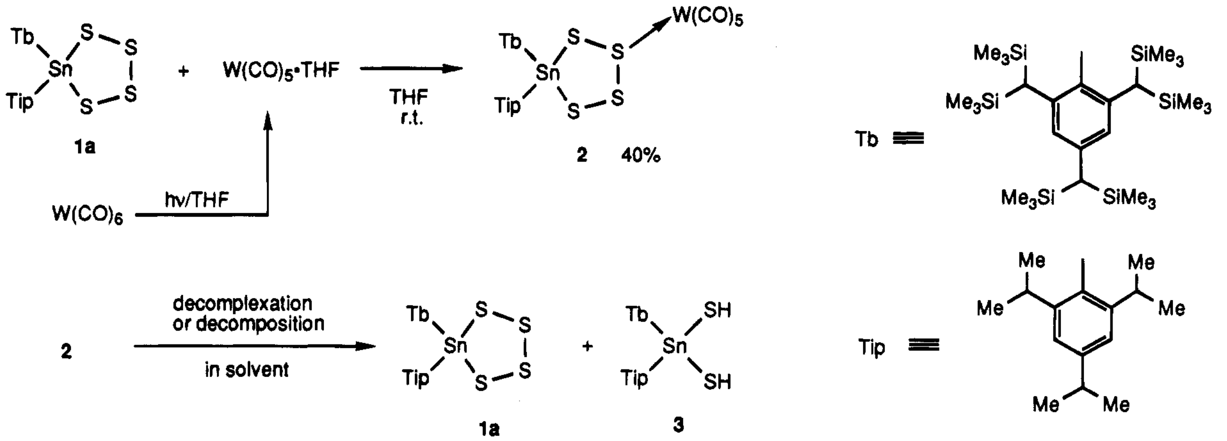
**Scheme 1**



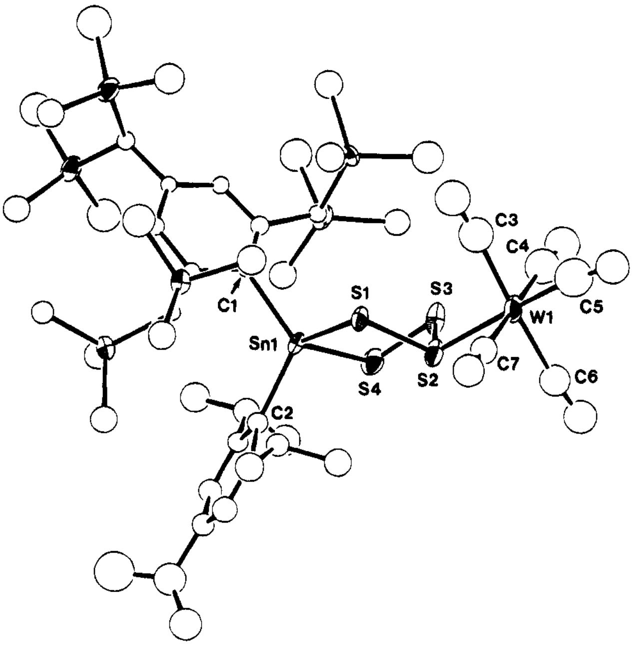


**Figure 1.** ORTEP drawing of Tb(Tip)SnS$_4$W(CO)$_5$ (**2**) with thermal ellipsoid plot (30% probability).

**Table 1. Selected Bond Lengths and Bond Angles for 2**

| | | | |
|---|---|---|---|
| A. Bond Lengths (Å) | | | |
| W(1)−S(2) | 2.519(9) | Sn(1)−C(2) | 2.11(3) |
| Sn(1)−S(1) | 2.474(8) | W(1)−C(3) | 2.06(4) |
| S(1)−S(2) | 2.09(1) | W(1)−C(4) | 1.91(5) |
| S(2)−S(3) | 2.04(1) | W(1)−C(5) | 1.89(5) |
| S(3)−S(4) | 2.00(1) | W(1)−C(6) | 2.03(4) |
| Sn(1)−S(4) | 2.496(7) | W(1)−C(7) | 2.00(4) |
| Sn(1)−C(1) | 2.17(2) | | |
| B. Bond Angles (deg) | | | |
| W(1)−S(2)−S(1) | 108.2(4) | C(2)−Sn(1)−S(4) | 99.2(7) |
| W(1)−S(2)−S(3) | 107.0(4) | Sn(1)−S(1)−S(2) | 100.1(4) |
| C(1)−Sn(1)−C(2) | 118.1(9) | S(1)−S(2)−S(3) | 101.0(4) |
| C(1)−Sn(1)−S(1) | 103.9(6) | S(2)−S(3)−S(4) | 100.7(5) |
| C(1)−Sn(1)−S(4) | 119.6(6) | S(3)−S(4)−Sn(1) | 101.1(4) |
| C(2)−Sn(1)−S(1) | 120.5(8) | S(4)−Sn(1)−S(1) | 93.9(3) |

tungsten complexes containing sulfur ligands where the W−S distances vary from 2.55 to 2.58 Å.[17] The tungsten complex **2** was stable in the air at room temperature or in hexane at low temperature but rather labile in other organic solvents, undergoing cleavage of the W−S bond or extrusion of two sulfur atoms from the tetrathiastannolane ring to provide tetrathiastannolane **1** and dimercaptostannane **3** (Scheme 1). The tungsten complex **2** is the first example of a polysulfido complex of group 6 metals and is considered to be an intermediate in the desulfurization process from polysulfides.

In the reaction of tetraselenastannolane Tb(Tip)SnSe$_4$ (**1b**) with W(CO)$_5$·THF under conditions similar to those for tetrathiastannolane **1a**, Tb(Tip)SnSe$_4$·W(CO)$_5$ was detected by $^1$H NMR in the crude mixture but could not be isolated on account of its instability.

**2. Reaction of Tetrachalcogenastannolanes with Ru$_3$(CO)$_{12}$.** When 1,2,3,4,5-tetrathiastannolane **1a** was treated with an equimolar amount of Ru$_3$(CO)$_{12}$ in toluene at 80 °C for 10 h, two types of tin-containing ruthenium-sulfur mixed clusters **4a** and **5a** were obtained in 50 and 11% yields, respectively. The reaction of 1,2,3,4,5-tetraselenastannolane **1b** with Ru$_3$(CO)$_{12}$ under similar conditions also provided the analogous selenium complexes **4b** (21%) and **5b** (10%) along with diselenadistannetane **6b** (9%), whose formation was explained in terms of dimerization of the stannaneselone Tb(Tip)Sn=Se (Scheme 2).

Complexes **4** and **5** showed satisfactory spectral and analytical data, and the molecular structures of **4b** and **5a** were definitively determined by X-ray crystallographic analysis. The various spectral and physical data for **4** and **5** are summarized in Table 6 (see Experimental Section), and the ORTEP diagrams and selected bond lengths and angles of **4b** and **5a** are shown in Figures 2 and 3 and Tables 2 and 3.

Infrared spectra in the carbonyl region of **5** were similar to those of the molecules [Ru(CO)$_3$YPh]$_2$ (Y = S, Se)[18] and CH$_2$S$_2$Fe$_2$(CO)$_6$ (**7**).[19] The structure of **5** displays an interesting quadracyclic SnS$_2$Ru$_2$ ring system similar to a normal "butterfly" structure[20] such as that for (CH$_3$)$_2$SnS$_2$Fe$_2$(CO)$_6$, except for the addition of a bridging in tin group instead of a bridging methylene group in **7** that serves to pin back the sulfur atoms. The

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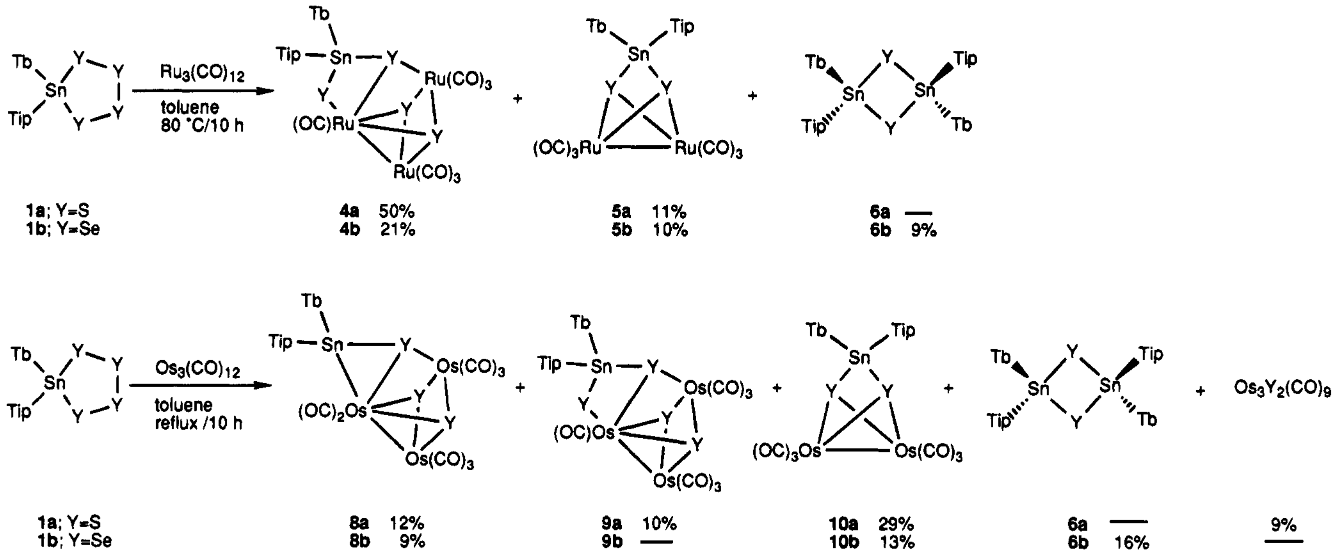
**Scheme 2**



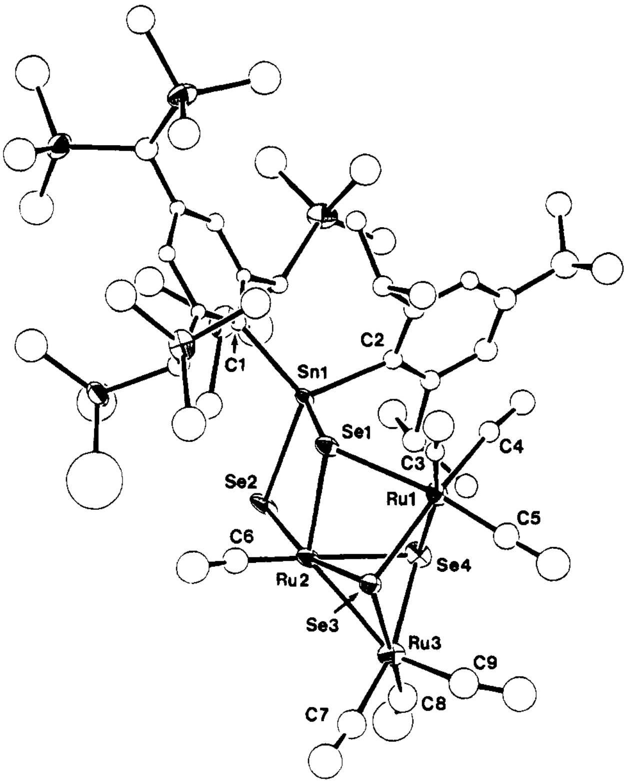
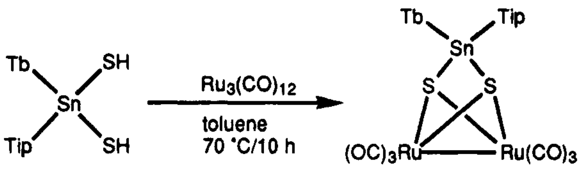


**Figure 2.** ORTEP drawing of Tb(Tip)$SnSe_4Ru_3(CO)_7$ (**4b**) with thermal ellipsoid plot (30% probability).

dihedral angle between the basal planes of the two distorted square pyramids is 64.5° (63.7° in **7**).

The two ruthenium atoms are displaced 0.436 Å for Ru(1) and 0.384 Å for Ru(2) (0.35 Å in **7**) from their respective basal planes in the direction of the axial carbonyl groups. Although the gross structural features are almost similar to those of **7**, on account of the presence of the two bulky aryl groups there are some interesting consequences. The S(1)–Sn(1)–S(2) bridging angle is 78.62(6)°, in contrast to the C(1)–Sn(1)–C(2) angle, which is 135.5(2)° due to steric repulsion between the Tb and Tip groups. This strain is also reflected in the bond lengths of **5a**. The Ru–Ru bond length of 2.637 Å is shorter than the average Ru–Ru bond lengths (2.854 Å for $Ru_3(CO)_{12}$[21]).

While diiron hexacarbonyls containing chalcogen ligands ($Fe_2(CO)_6(YR)_2$; Y = S, Se, and Te) have been widely explored,[22] chalcogen-containing diruthenium complexes are scarcely known because of their facile polymerization to $[Ru_2(CO)_2(YR)_2]_n$.[23] The successful isolation and noticeable stability of **5** in the present study suggest that the combination of the bulky Tb and Tip groups effectively protects these highly strained molecules against polymerization. Complex **5a** was alternatively synthesized in good yield by the reaction of dimercaptostannane Tb(Tip)$Sn(SH)_2$ (**3**) with $Ru_3(CO)_{12}$ (eq 1).



**3** **5a** 67% (1)

The complex $(\mu_3\text{-Se})_3(\mu_2\text{-Se})Ru_3(CO)_7$[Tb(Tip)Sn] (**4b**) contains three ruthenium atoms, only two of which are mutually bonded with Ru(2)–Ru(3) = 2.785(6) Å, which is slightly shorter than the average Ru–Ru bond lengths. The Ru(1)···Ru(2) and Ru(1)···Ru(3) distances of 3.351 and 3.764 Å, respectively, are approximately 0.6 Å longer than normal Ru–Ru bonds and imply little or no direct metal–metal bonding. The molecule **4b** is held by three $\mu_3$-bridging and one $\mu_2$-bridging inorganic selenide ligands. The two inorganic selenide ligands, Se(3) and Se(4), are bound to all three ruthenium atoms. The ligands Se(3) and Se(4) are displaced at almost equal distances from each ruthenium atom (2.475(7)–2.570(7) Å). The framework of this cluster is substantially similar to that of $Os_3Se_2(CO)_9$, which has been shown to contain a triangle of metal atoms with one long

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[22] (a) Hieber, W.; Spacu, P. *Z. Anorg. Allg. Chem.* **1937**, *233*, 353. (b) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 1663. (c) De Beer, J. A.; Haines, R. J. *J. Organomet. Chem.* **1970**, *24*, 757. (d) Farmery, K.; Kilner, M. *J. Chem. Soc. A* **1970**, 634. (e) Alper, H.; Chan, A. S. K. *J. Am. Chem. Soc.* **1973**, *95*, 4905.

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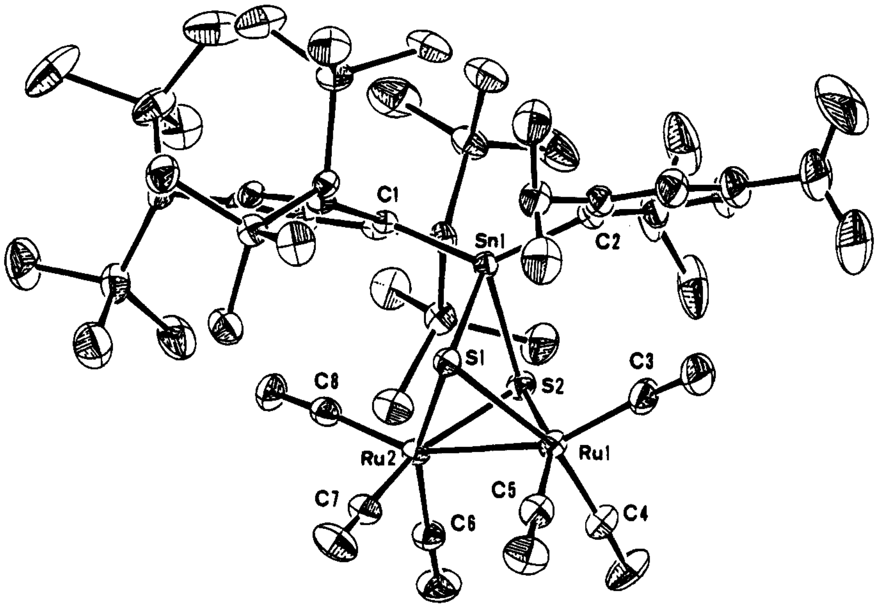

**Figure 3.** ORTEP drawing of Tb(Tip)$SnS_2Ru_2(CO)_6$ (**5a**) with thermal ellipsoid plot (30% probability).

**Table 2. Selected Bond Lengths and Bond Angles for 4b**

| | | | |
|---|---|---|---|
| | A. Bond Lengths (Å) | | |
| Sn(1)–Se(1) | 2.640(6) | Ru(3)–Se(4) | 2.504(7) |
| Sn(1)–Se(2) | 2.517(6) | C(1)–Sn(1) | 2.18(4) |
| Ru(1)–Se(1) | 2.602(6) | C(2)–Sn(1) | 2.17(4) |
| Ru(1)–Se(3) | 2.551(6) | Ru(1)–C(3) | 1.86(5) |
| Ru(1)–Se(4) | 2.568(7) | Ru(1)–C(4) | 2.01(5) |
| Ru(2)–Ru(3) | 2.784(6) | Ru(1)–C(5) | 1.80(5) |
| Ru(2)–Se(1) | 2.574(6) | Ru(2)–C(6) | 1.87(6) |
| Ru(2)–Se(2) | 2.558(7) | Ru(3)–C(7) | 1.99(6) |
| Ru(2)–Se(3) | 2.536(6) | Ru(3)–C(8) | 1.93(6) |
| Ru(2)–Se(4) | 2.567(7) | Ru(3)–C(9) | 1.74(6) |
| Ru(3)–Se(3) | 2.475(7) | | |
| Ru(1)···Ru(2) | 3.351 | Ru(1)···Ru(3) | 3.764 |
| | B. Bond Angles (deg) | | |
| Se(1)–Sn(1)–Se(2) | 86.3(2) | Se(2)–Ru(2)–Se(3) | 164.6(2) |
| Se(1)–Sn(1)–C(1) | 118(1) | Se(2)–Ru(2)–Se(4) | 92.5(2) |
| Se(1)–Sn(1)–C(2) | 104(1) | Se(3)–Ru(2)–Se(4) | 78.6(2) |
| Se(2)–Sn(1)–C(1) | 116(1) | Ru(2)–Ru(3)–Se(3) | 57.3(2) |
| Se(2)–Sn(1)–C(2) | 126(1) | Ru(2)–Ru(3)–Se(4) | 57.8(2) |
| C(1)–Sn(1)–C(2) | 106(1) | Se(3)–Ru(3)–Se(4) | 81.0(2) |
| Se(1)–Ru(1)–Se(3) | 79.5(2) | Sn(1)–Se(1)–Ru(1) | 115.9(2) |
| Se(1)–Ru(1)–Se(4) | 86.8(2) | Sn(1)–Se(1)–Ru(2) | 90.5(2) |
| Se(3)–Ru(1)–Se(4) | 78.3(2) | Ru(1)–Se(1)–Ru(2) | 80.7(2) |
| Ru(3)–Ru(2)–Se(1) | 124.7(2) | Sn(1)–Se(2)–Ru(2) | 93.7(2) |
| Ru(3)–Ru(2)–Se(2) | 129.0(2) | Ru(1)–Se(3)–Ru(2) | 82.4(2) |
| Ru(3)–Ru(2)–Se(3) | 55.2(2) | Ru(1)–Se(3)–Ru(3) | 97.0(2) |
| Ru(3)–Ru(2)–Se(4) | 55.6(2) | Ru(2)–Se(3)–Ru(3) | 67.5(2) |
| Se(1)–Ru(2)–Se(2) | 86.8(2) | Ru(1)–Se(4)–Ru(2) | 81.5(2) |
| Se(1)–Ru(2)–Se(3) | 80.3(2) | Ru(1)–Se(4)–Ru(3) | 95.8(2) |
| Se(1)–Ru(2)–Se(4) | 87.4(2) | Ru(2)–Se(4)–Ru(3) | 66.6(2) |

**Table 3. Selected Bond Lengths and Bond Angles for 5a**

| | | | |
|---|---|---|---|
| | A. Bond Lengths (Å) | | |
| Sn(1)–S(1) | 2.462(2) | Ru(1)–Ru(2) | 2.637(2) |
| Sn(1)–S(2) | 2.454(2) | Ru(1)–C(3) | 1.943(7) |
| Sn(1)–C(1) | 2.188(5) | Ru(1)–C(4) | 1.890(7) |
| Sn(1)–C(2) | 2.195(5) | Ru(1)–C(5) | 1.882(8) |
| Ru(1)–S(1) | 2.446(2) | Ru(2)–C(6) | 1.917(7) |
| Ru(1)–S(2) | 2.431(2) | Ru(2)–C(7) | 1.886(7) |
| Ru(2)–S(1) | 2.415(2) | Ru(2)–C(8) | 1.924(7) |
| Ru(2)–S(2) | 2.432(2) | | |
| | B. Bond Angles (deg) | | |
| S(1)–Sn(1)–S(2) | 78.62(6) | Ru(1)–Ru(2)–S(2) | 57.15(6) |
| S(1)–Sn(1)–C(1) | 109.3(1) | S(1)–Ru(1)–S(2) | 79.37(6) |
| S(1)–Sn(1)–C(2) | 105.0(2) | S(1)–Ru(2)–S(2) | 79.97(7) |
| S(2)–Sn(1)–C(1) | 106.5(1) | Sn(1)–S(1)–Ru(1) | 90.47(6) |
| S(2)–Sn(1)–C(2) | 107.3(2) | Sn(1)–S(1)–Ru(2) | 91.06(7) |
| C(1)–Sn(1)–C(2) | 135.5(2) | Ru(1)–S(1)–Ru(2) | 65.72(5) |
| Ru(2)–Ru(1)–S(1) | 56.58(5) | Sn(1)–S(2)–Ru(1) | 91.00(6) |
| Ru(2)–Ru(1)–S(2) | 57.17(5) | Sn(1)–S(2)–Ru(2) | 90.85(7) |
| Ru(1)–Ru(2)–S(1) | 57.71(5) | Ru(1)–S(2)–Ru(2) | 65.68(6) |

nonbonding edge (Os–Os = 3.791(1) Å) and Se atoms capping the triangle on both sides to give a trigonal-bipyramidal cluster geometry.[11b,c] In the cluster **4b**, the Tb(Tip)$SnSe_2$ ligand can be regarded as coordinating to two nonbonding ruthenium atoms (Ru(1) and Ru(2)) in the complex $Ru_3Se_2(CO)_9$, resulting in the cleavage of the Ru(1)–Ru(3) bond and the release of two carbonyl ligands attached to the Ru(2) atom. As shown in Table 6, in the $^{119}Sn$ NMR of these complexes there appeared two signals. This suggests that these complexes exist as a mixture of two isomers in solution as in the case of triosmium complexes **8a,b**. The presence of the two isomers was also supported by $^1H$ and $^{13}C$ NMR spectra. The structural features of **8a,b** will be described later.

**3. Reaction of Tetrachalcogenastannolanes with $Os_3(CO)_{12}$.** The reaction of tetrathiastannolane **1a** with $Os_3(CO)_{12}$ gave the three types of osmium complexes **8a**, **9a**, and **10a** together with $Os_3S_2(CO)_9$ under reaction conditions (in refluxing toluene) more vigorous than those for the complexation with $Ru_3(CO)_{12}$. The products **9a** and **10a** were found to be the analogs of the ruthenium complexes **4a** and **5a** on the basis of the spectroscopic similarity. The reaction of **1b** with $Os_3(CO)_{12}$ did not proceed in toluene at 80 °C either, but in refluxing toluene it afforded the crimson complex **8b** (9%), whose spectroscopic data resembled those for complex **8a**, together with diosmium complex **10b** (13%) and stannaneselone dimer **6b** (16%) (Scheme 2).

All the complexes showed satisfactory spectral and analytical data. Determinations of the molecular structures of the complexes **9** and **10** were based on the close resemblance of their spectral data to those for the analogous ruthenium complexes **4b** and **5a**, the structures of which were established by X-ray crystallographic analysis. The molecular structures of **8a,b** were definitively determined by X-ray crystallographic analysis. Their ORTEP diagrams and selected bond lengths and angles are shown in Figures 4 and 5 and Tables 4 and 5; physical and spectral data for **8**–**10** are summarized in Tables 7 and 8 (see Experimental Section).

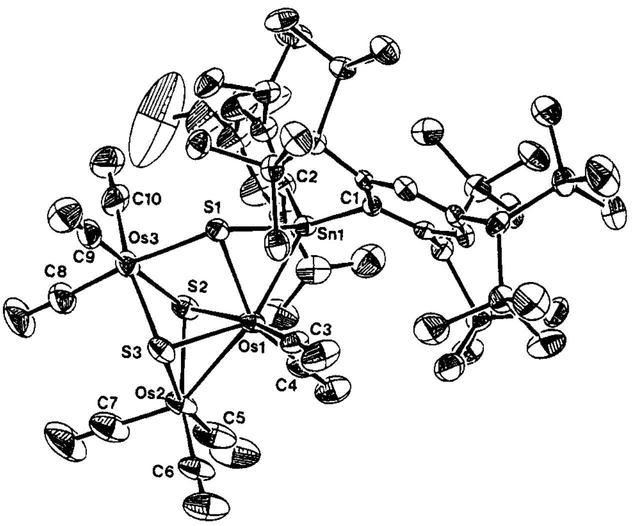

**Figure 4.** ORTEP drawing of Tb(Tip)SnSOs$_3$(CO)$_8$S$_2$ (**8a**) with thermal ellipsoid plot (30% probability).

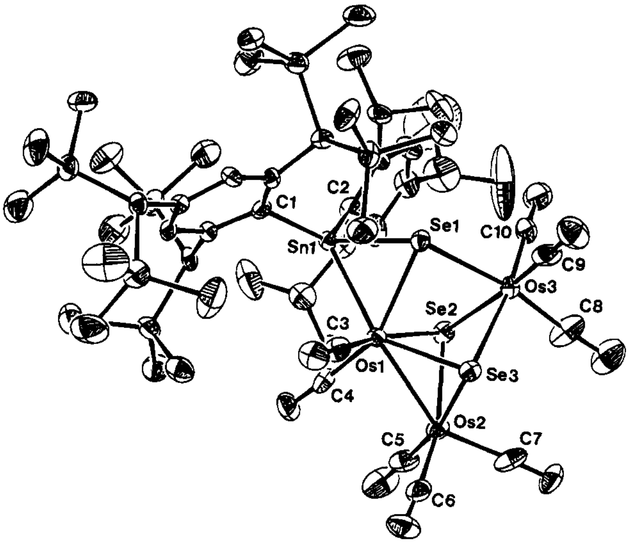

**Figure 5.** ORTEP drawing of Tb(Tip)SnSeOs$_3$(CO)$_8$Se$_2$ (**8b**) with thermal ellipsoid plot (30% probability).

**8a,b** both contain eight terminal carbonyl groups distributed in such a way that Os(2) and Os(3) have three each and Os(1) has two. The infrared spectra in the carbonyl region show absorptions at 2102 (m), 2082 (s), 2009 (br vs), and 1942 (w) cm$^{-1}$ for **8a** and 2096 (m), 2078 (s), 2015 (s), 2002 (vs), 1990 (s), 1937 (w), and 1920 (w) cm$^{-1}$ for **8b**, which are similar to those for Os$_3$Y$_2$(CO)$_9$ (Y = S, Se).[11b,c] There are two triply bridging inorganic sulfide and selenide ligands with bonding distances to the metal atoms ranging from 2.445 to 2.491 Å in **8a** and from 2.513 to 2.582 Å in **8b**. The complex **8** contains three osmium atoms with one osmium–osmium bond; Os(1)–Os(2) = 2.745(1) Å in **8a** and 2.793(2) Å in **8b**, which are shorter than the normal osmium–osmium bonds (e.g., in Os$_3$(CO)$_{12}$, Os–Os = 2.877(3) Å[24]). The long distances Os(1)···Os(3) and Os(2)···Os(3) at 3.258(3) and 3.657(3) Å in **8a** and 3.386(2) and 3.815(2) Å in **8b** preclude any significant metal–metal bonding. As shown in Figures 4 and 5, the two ipso carbons C(1) and C(2) bound to the tin atom lie at almost equal distances from the plane that contains Sn(1)–S(1)–Os(1) (2.0162 and 1.9081 Å for C(1) and C(2) in **8a**, respectively) and Sn(1)–Se(1)–Os(1) (1.9578 and 1.9635 Å for C(1) and C(2) in **8b**, respectively). The bond angle C(1)–Sn(1)–C(2) is 128.7(3)° in **8a** and 127.7(8)° in **8b**, the values of which are slightly spread from the ideal angle for the carbonyl compound (i.e., 120°) and are remarkably larger than that of the ruthenium complex **4b** (106°). Furthermore, the tin atom was found to lie out of the plane containing C(1)–C(2)–S(1) and C(1)–C(2)–Se(1) at a distance of 0.56 Å for **8a** and 0.59 Å for **8b** as a result of complexation. The coupling constant between tin and selenium in **8b** is significant ($^1J_{Sn-Se}$ = 1025 Hz), being much larger than those for single-boded tin–selenium clusters ($^1J_{Sn-Se}$: **4b**, 484 Hz; **5b**, 601 Hz; **10b**, 512 Hz) and attributable to a π-bond character between tin and selenium.[25] The bond lengths between Sn(1) and Y(1) (Y = S, Se), however, are indicative of the corresponding tin–chalcogen single bonds (2.489(3) Å for **8a** and 2.608(3) Å for **8b**).[26] Although there might be some other interpretations as to the coordination state of these

**Table 4. Selected Bond Lengths (Å) for 8**

| 8a | | 8b | |
|---|---|---|---|
| Sn(1)–S(1) | 2.489(3) | Sn(1)–Se(1) | 2.608(3) |
| Sn(1)–Os(1) | 2.662(2) | Sn(1)–Os(1) | 2.672(2) |
| Os(1)–S(1) | 2.491(3) | Os(1)–Se(1) | 2.606(3) |
| Os(1)–S(2) | 2.453(3) | Os(1)–Se(2) | 2.582(2) |
| Os(1)–S(3) | 2.445(3) | Os(1)–Se(3) | 2.566(3) |
| Os(1)–Os(2) | 2.745(3) | Os(1)–Os(2) | 2.793(2) |
| Os(2)–S(2) | 2.419(3) | Os(2)–Se(2) | 2.538(3) |
| Os(2)–S(3) | 2.388(3) | Os(2)–Se(3) | 2.513(3) |
| Os(3)–S(1) | 2.480(3) | Os(3)–Se(1) | 2.605(2) |
| Os(3)–S(2) | 2.431(3) | Os(3)–Se(2) | 2.545(3) |
| Os(3)–S(3) | 2.458(4) | Os(3)–Se(3) | 2.574(3) |
| Sn(1)–C(1) | 2.193(8) | Sn(1)–C(1) | 2.18(2) |
| Sn(1)–C(2) | 2.165(9) | Sn(1)–C(2) | 2.18(2) |
| Os(1)–C(3) | 1.88(1) | Os(1)–C(3) | 1.87(3) |
| Os(1)–C(4) | 1.89(1) | Os(1)–C(4) | 1.90(2) |
| Os(2)–C(5) | 1.90(2) | Os(2)–C(5) | 1.85(3) |
| Os(2)–C(6) | 1.90(1) | Os(2)–C(6) | 1.93(3) |
| Os(2)–C(7) | 1.87(2) | Os(2)–C(7) | 1.94(3) |
| Os(3)–C(8) | 1.87(1) | Os(3)–C(8) | 1.81(3) |
| Os(3)–C(9) | 1.90(1) | Os(3)–C(9) | 1.81(4) |
| Os(3)–C(10) | 1.94(2) | Os(3)–C(10) | 1.86(3) |
| Os(1)···Os(3) | 3.258(3) | Os(1)···Os(3) | 3.386(2) |
| Os(2)···Os(3) | 3.657(3) | Os(2)···Os(3) | 3.815(2) |

**Table 5. Selected Angles (deg) for 8**

| 8a | | 8b | |
|---|---|---|---|
| C(1)–Sn(1)–C(2) | 128.7(3) | C(1)–Sn(1)–C(2) | 127.7(8) |
| C(1)–Sn(1)–S(1) | 104.2(3) | C(1)–Sn(1)–Se(1) | 105.5(6) |
| C(1)–Sn(1)–Os(1) | 113.0(2) | C(1)–Sn(1)–Os(1) | 116.2(6) |
| C(2)–Sn(1)–S(1) | 108.8(3) | C(2)–Sn(1)–Se(1) | 106.7(6) |
| C(2)–Sn(1)–Os(1) | 117.6(2) | C(2)–Sn(1)–Os(1) | 115.6(5) |
| Sn(1)–Os(1)–S(1) | 57.65(8) | Sn(1)–Os(1)–Se(1) | 59.21(7) |
| S(1)–Sn(1)–Os(1) | 57.73(7) | Se(1)–Sn(1)–Os(1) | 59.13(7) |
| Sn(1)–S(1)–Os(1) | 64.63(8) | Sn(1)–Se(1)–Os(1) | 61.66(7) |
| Sn(1)–S(1)–Os(3) | 120.1(1) | Sn(1)–Se(1)–Os(3) | 118.4(1) |
| Sn(1)–Os(1)–Os(2) | 144.29(4) | Sn(1)–Os(1)–Os(2) | 144.16(5) |
| Sn(1)–Os(1)–S(2) | 91.45(8) | Sn(1)–Os(1)–Se(2) | 91.38(7) |
| Sn(1)–Os(1)–S(3) | 136.52(8) | Sn(1)–Os(1)–Se(3) | 138.58(8) |
| Os(1)–S(1)–Os(3) | 81.91(9) | Os(1)–Se(1)–Os(3) | 81.06(7) |

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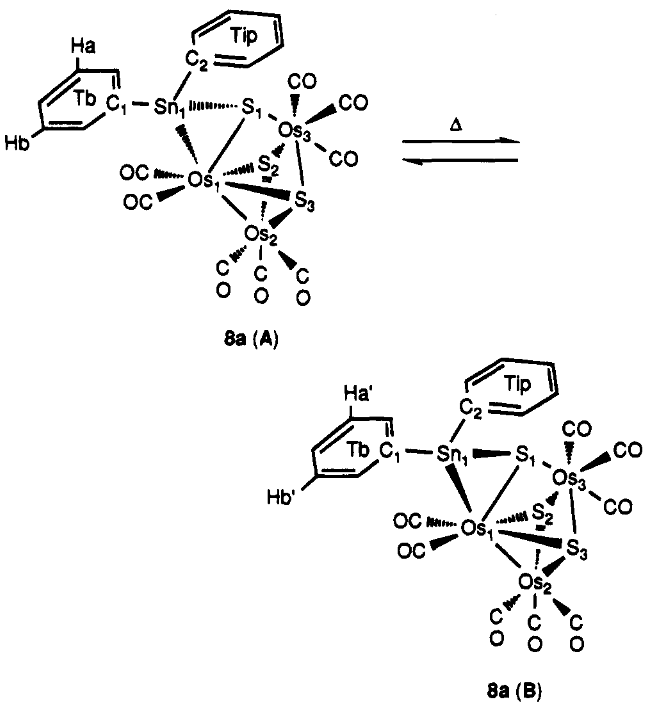
(24) Churchill, M. R.; Deboer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(25) Satgé et al. reported the increase of the $^1J_{Sn-P}$ value in the formation of stannaphosphenes R$_2$Sn=PAr from single-bonded tin–phosphorus compounds: Couret, C.; Escudié, J.; Satgé, J.; Raharinirina, A.; Andriamizaka, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 8280.

(26) The lengths of the tin–sulfur and tin–selenium single bonds in oligomeric dialkyltin sulfides and selenides are reportedly 2.40–2.48 Å for Sn–S and 2.53–2.55 Å for Sn–Se. 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.

**Scheme 3**



metal–chalcogen mixed clusters, one can regard the complexes **8a,b** as binuclear osmium complexes bridged by a stannanethione and a stannaneselone, Tb(Tip)-Sn=Y (Y = S, Se). To our knowledge, **8a,b** represent the first examples of transition-metal complexes of a stannanethione and a stannaneselone.

There have been some reports on such binuclear complexes of their carbon analogs thioketone and selenoketone (or thioaldehyde and selenoaldehyde).[8] 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(1) Å).[8d]

Of particular note among the structural features of these new cluster complexes is a dynamic process, as revealed by the NMR data for **8a,b**. Thus, the $^1$H, $^{13}$C, and $^{119}$Sn NMR spectra of complexes **8a,b** in $CDCl_3$ at room temperature showed two sets of signals (approximately 1:1 intensity 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 3). This phenomenon was also proved by the fact that there were observed in 2D NOESY NMR the cross peaks between $H_a$, $H_a'$ (at 6.63 and 6.50 ppm) and $H_b$, $H_b'$ (at 6.54 and 6.40 ppm) at room temperature, respectively (Scheme 3 and Figure 6).

In the $^{13}$C NMR spectra of **8a**, 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 peaks at 169.27, 172.34, 174.54, and 175.08 ppm were about twice that of the others (Figure 7). The $^1$H and $^{13}$C NMR spectra of **8a** in toluene-$d_8$ showed the coalescence of the signals at 97 °C, suggesting a wagging across the pseudosymmetry plane or even more extensive migration of the Tb(Tip)Sn group at this temperature (Figure 8). Similarly, those of **4** and **8b** also showed the coalescence of the signals at elevated temperature (57 °C for **4** and 97 °C for **8b**).

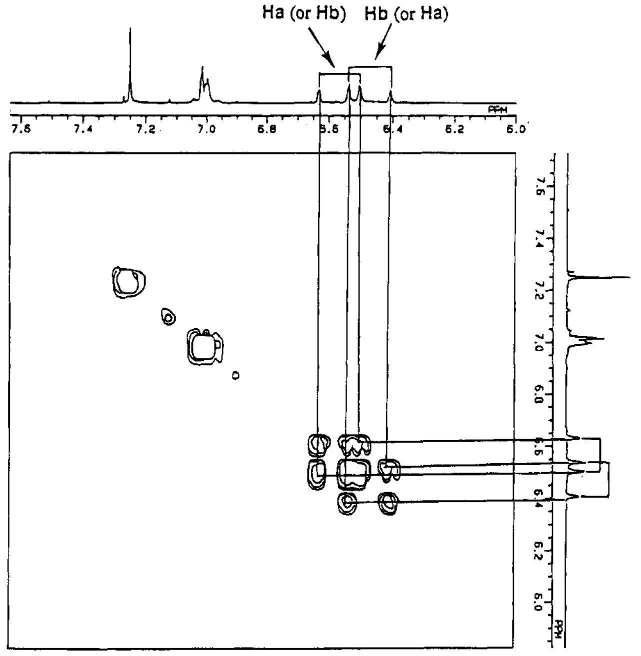


**Figure 6.** 2D NOESY NMR for $Tb(Tip)SnSOs_3(CO)_8S_2$ (**8a**) in the range 6.00–7.60 ppm.

### 4. Plausible Mechanism for the Formation of the Transition-Metal Complexes 4, 5, and 8–10.

The initial step of the reaction of tetrachalcogenastannolane **1a** or **1b** with $M_3(CO)_{12}$ is considered to be the formation of $M_3(\mu_3\text{-}Y)_2(CO)_9$ (**11**: Y = S, Se) (Scheme 4), which has been reported previously as a product in the reaction of $M_3(CO)_{12}$ with elemental sulfur and selenium, because cyclic polychalcogenides are known as good chalcogen sources. In fact, $Os_3(\mu_3\text{-}S)_2(CO)_9$ was isolated through the reaction of the tetrathiastannolane **1a** with $Os_3(CO)_{12}$. The thermal degradation of the trinuclear metal complex **11** and capture of chalcogen from **A** would afford the dinuclear complex $M_2(\mu_3\text{-}Y_2)(CO)_6$ (**12**). This proposed mechanism is consistent with the fact that reaction of $S_8$ with $Fe_3(CO)_{12}$ at 50 °C gave a 50% yield of a mixture of $Fe_2(CO)_6S_2$ and $Fe_3(CO)_9S_2$.[27] The reactive species of stannylene **B** produced through the reaction readily reacts with dinuclear complex **12** to afford **5** and **10**, since stannylenes are known to readily react with disulfides to result in the formation of products of insertion into the S–S bond.[28] While the relatively stable intermediate $Tb(Tip)SnY_2$ (**A**) inserts into trinuclear complex **11** at 80 °C to afford **4** or **9**, $Tb(Tip)SnY_2$ (**A**) releases a chalcogen atom in refluxing toluene to form a stannanethione and a stannaneselone (**C**), which then undergo complexation with trinuclear metal complex **11** to afford **8**. Since no thermal interconversion among **8–10** was observed under the reaction conditions (refluxing in toluene), it can be ruled out that the clusters obtained here are kinetically related.

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[28] Neumann, W. P.; Schwarz, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 812.

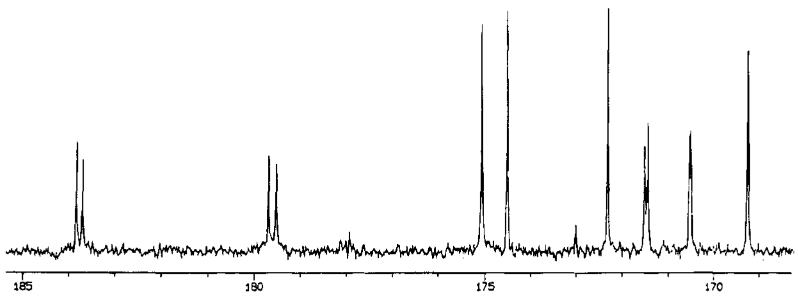

**Figure 7.** $^{13}$C NMR for the carbonyl region of Tb(Tip)$SnSOs_3(CO)_8S_2$ (**8a**) in $CDCl_3$ at room temperature.

**Figure 8.** Variable-temperature $^{13}$C NMR for the carbonyl region of Tb(Tip)$SnSOs_3(CO)_8S_2$ (**8a**) in toluene-$d_8$.

Furthermore, the starting material Tb(Tip)$SnS_4$ (**1a**) did not decompose thermally under the reaction conditions.

## Experimental Section

**General Procedure.** All melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl before use. All reactions were carried out under an argon atmosphere unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with JAI gel 1H and 2H columns (Japan Analytical Industry) with chloroform as solvent. Dry column chromatography (DCC) was performed with ISN silica DCC 60A. Flash column chromatography (FCC) was carried out with Fuji Davison BW-300. Preparative thin-layer chromatography was carried out with Merck Kieselgel 60 PF254 (Art. No. 7747). The $^1$H NMR (500 and 400 MHz), $^{13}$C NMR (125 and 100 MHz), and $^{119}$Sn NMR spectra (149 MHz) were measured in $CDCl_3$ or $C_6D_5CD_3$ with a Bruker AM-500 or JEOL GX-400 spectrometer using $CHCl_3$, $C_6H_5CH_3$ or $Me_4Sn$ as an internal standard. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

**Reaction of Tetrathiastannolane 1a with $W(CO)_5$·THF.** To a THF solution (30 mL) of $W(CO)_5$·THF, prepared by irradiation of a THF solution of tungsten hexacarbonyl (422 mg, 12 mmol) for 2 h with a high-pressure mercury lamp under ice cooling, was added a THF solution (10 mL) of tetrathiastannolane **1a** (300 mg, 0.30 mmol) at room temperature, and the solution was stirred at ambient temperature for 10 h. After removal of the solvent, the residue was separated with GPLC to afford a fraction containing Tb and Tip substituents which was washed with a small amount of cold hexane. Precipitates were filtered to afford {5-[2,4,6-tris(bis(trimethylsilyl)methyl)phenyl]-5-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetrathiastannolan-2-yl}pentacarbonyltungsten (**2**; 157 mg, 40%) as yellow crystals. The filtrate was chromatographed with PTLC (hexane) to give **1a** (34 mg) and [2,4,6-tris(bis(trimethylsilyl)methyl)phenyl](2,4,6-triisopropylphenyl)dimercaptostannane (**3**; 21 mg, 8%). **2**: yellow crystals; mp 175–176 °C; IR (KBr) $\nu_{C-O}$ 2080, 1990, 1950, 1930 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.01 (s, 36H), 0.03 (s, 18H), 1.21 (d, $J$ = 6.9 Hz, 6H), 1.21 (br s, 12H), 1.34 (s, 1H), 1.64 (s, 1H), 1.66 (s, 1H), 2.84 (sept, $J$ = 6.9 Hz, 1H), 3.30 (br s, 2H), 6.38 (s, 1H), 6.51 (s, 1H), 7.07 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.83 (q), 1.78 (q), 23.84 (q), 23.85 (q), 30.90 (d), 32.20 (d), 32.87 (d), 34.31 (d), 40.30 (br d), 123.02 (d), 123.19 (d), 128.29 (d), 138.52 (s), 142.76 (s), 146.56 (s), 151.39 (s), 151.69 (s), 153.38 (s), 195.83 (s, $^1J_{W-C}$ = 64.6 Hz), 199.89 (s). Anal. Calcd for $C_{47}H_{82}O_5S_4Si_6SnW$: C, 42.56; H, 6.23; S, 9.66. Found: C, 42.26; H, 6.27; S, 9.63.

**Thermal Reaction of 1a with $Ru_3(CO)_{12}$.** A mixture of tetrathiastannolane **1a** (500 mg, 0.50 mmol) and triruthenium dodecacarbonyl (319 mg, 0.50 mmol) in 30 mL of toluene was heated to 80 °C for 10 h, during which time the disappearance of **1a** was monitored by TLC. After removal of the solvent, the residue was subjected to flash column chromatography (20% $CH_2Cl_2$–80% hexane) to afford the dark green triruthenium complex **4a** (374 mg, 50%) and the yellow diruthenium complex **5a** (72 mg, 11%). Both **4a** and **5a** were recrystallized from ethanol–chloroform. **4a**: dark green crystals; $^1$H NMR ($CDCl_3$ at 57 °C) $\delta$ −0.26 (s, 9H), 0.08 (br s, 9H), 0.09 (br s, 9H), 0.14 (s, 9H), 0.31 (s, 9H), 0.41 (s, 9H), 0.83 (d, $J$ = 6.3 Hz, 3H), 1.14 (d, $J$ = 6.9 Hz, 3H), 1.15 (d, $J$ = 6.9 Hz, 3H), 1.19 (d, $J$ = 6.4 Hz, 3H), 1.28 (s, 1H), 1.34 (d, $J$ = 6.4 Hz, 3H), 1.36 (s, 1H), 1.37 (d, $J$ = 6.4 Hz, 3H), 2.62 (br s, 1H), 2.76 (sept, $J$ = 6.9 Hz, 1H), 3.70 (s, 1H), 4.96 (br s, 1H), 6.38 (br s, 1H), 6.47 (br s, 1H), 6.86 (s, 1H), 7.06 (s, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 1.11 (br q), 2.28 (br q), 2.51 (br q), 23.77 (q), 23.79 (q), 24.56 (br q), 26.08 (q), 27.18 (q), 29.11 (q), 30.73 (d), 31.34 (d), 31.55 (d), 32.86 (d), 34.47 (d), 37.52 (d), 123.66 (d), 123.90 (d), 128.51 (br d), 129.97 (br d), 144.05 (s), 145.02 (s), 146.39 (s), 148.97 (s), 151.12 (s), 151.28 (s), 153.07 (s), 158.88 (s), 183.21 (s), 183.61 (s), 183.80 (s), 188.73 (s), 189.40 (s), 192.00 (s), 197.27 (s). Anal. Calcd for $C_{49}H_{82}O_7Ru_3S_4Si_6Sn{\cdot}H_2O$: C, 38.72; H, 5.57; S, 8.43. Found: C, 38.51; H, 5.15; S, 8.40. For UV/vis, IR, and $^{119}$Sn NMR spectra, see Table 6. **5a**: yellow crystals; mp 210 °C dec; $^1$H NMR ($CDCl_3$) $\delta$ 0.02 (s, 18H), 0.11 (s, 18H), 0.32 (s, 18H), 1.25 (d, $J$ = 6.9 Hz, 6H), 1.31 (d, $J$ = 6.5 Hz, 6H), 1.42 (s, 1H), 1.50 (d, $J$ = 6.5 Hz, 6H), 1.57 (br s, 2H), 2.82 (br s, 2H), 2.88 (sept, $J$ = 6.9 Hz, 1H), 6.49 (br s, 2H), 7.11 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 1.05 (br q), 1.74 (br q), 2.51 (br q), 23.72 (q), 26.97 (q), 27.12 (q), 30.70 (d), 33.82 (d), 34.14 (d), 38.37 (br d), 124.85 (d), 129.77 (br d), 144.64 (s), 145.10 (s), 146.21 (s), 149.45 (s), 151.59 (s), 154.05 (s), 186.01 (br s), 188.59 (s), 196.54 (s). Anal. Calcd for $C_{48}H_{82}O_6Ru_2S_2Si_6Sn$: C, 44.05; H, 6.32; S, 4.90. Found: C, 43.68; H, 6.01; S, 5.31. For UV/vis, IR, and $^{119}$Sn NMR spectra, see Table 6.

**Scheme 4**

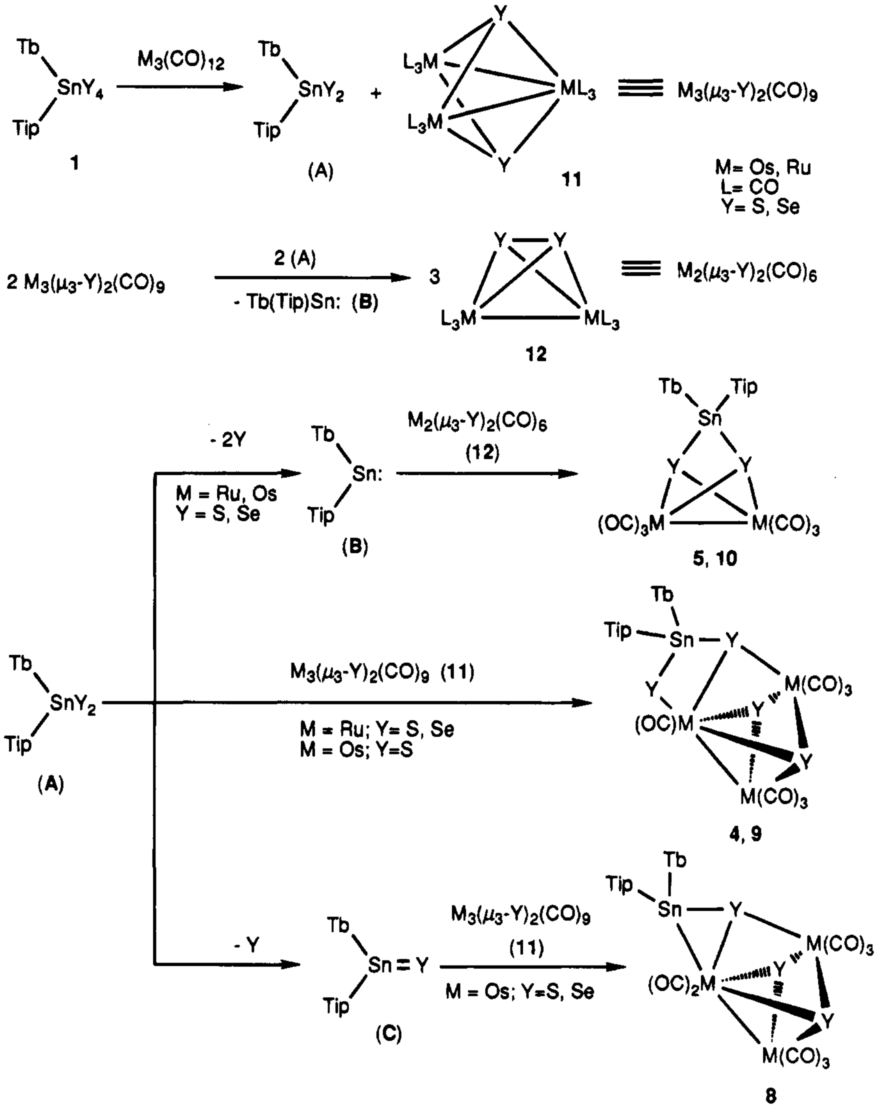

**Table 6. Physical and Spectral Data for 4 and 5**

| | Tb(Tip)SnS$_4$Ru$_3$(CO)$_7$ (**4a**) | Tb(Tip)SnSe$_4$Ru$_3$(CO)$_7$ (**4b**) | Tb(Tip)SnS$_2$Ru$_2$(CO)$_6$ (**5a**) | Tb(Tip)SnSe$_2$Ru$_2$(CO)$_6$ (**5b**) |
|---|---|---|---|---|
| color of cryst | dark green | yellowish brown | yellow | yellowish orange |
| mp, °C | 140 dec | 185 dec | 210 dec | 208 dec |
| UV/vis (hexane), nm ($\epsilon$) | 230 (92 500), 256 (50 300), 300 (22 300), 609 (900) | 232 (49 500), 260 (21 200), 310 (19 600), 504 (1380), 556 (670) | 229 (75 800), 265 (27 800), 294 (12 500), 340 (5300) | 234 (52 100), 263 (25 800), 306 (9550), 358 (3480) |
| IR (KBr) $\nu_{C=O}$, cm$^{-1}$ | 2110 (m), 2094 (s), 2044 (br vs), 1964 (w), 1950 (w) | 2104 (m), 2088 (vs), 2030 (br vs), 2015 (s sh), 1942 (m) | 2079 (s), 2048 (s), 2002 (br vs) | 2075 (s), 2046 (s), 2000 (br vs) |
| $^{119}$Sn NMR, $\delta$ (CDCl$_3$, Me$_4$Sn) | 110, 106 | −84, −86[a] ($^1J_{Sn-Se}$ = 484 Hz) | 255 | 84 ($^1J_{Sn-Se}$ = 601 Hz) |

[a] Both signals have the same $^1J_{Sn-Se}$ value.

**Preparation of Dimercaptostannane 3.** To a THF solution (50 mL) of tetrathiastannolane **1a** (500 mg, 0.50 mmol) was added LiB(C$_2$H$_5$)$_3$H (1 M in THF, 3 mL, 0.30 mmol) at room temperature, and the solution was stirred at room temperature for 2 h. After evaporation of the solvent, the residue was separated with flash column chromatography (hexane) to provide [2,4,6-tris(bis(trimethylsilyl)methyl)phenyl]-(2,4,6-triisopropylphenyl)dimercaptostannane (**3**; 302 mg, 64%) as white crystals, which was recrystallized from ethanol–chloroform. **3**: white crystals; mp 203–205 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 0.02 (s, 18H), 0.05 (s, 18H), 0.07 (s, 18H), 0.67 (s, 2H), 1.22 (d, $J$ = 6.7 Hz, 6H), 1.29 (d, $J$ = 6.4 Hz, 12H), 1.32 (s, 1H), 2.10 (br s, 1H), 2.37 (br s, 1H), 2.85 (sept, $J$ = 6.7 Hz, 1H), 3.32 (sept, $J$ = 6.4 Hz, 2H), 6.31 (br s, 1H), 6.45 (br s, 1H), 7.04 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 0.84 (q), 1.44 (q), 1.69 (q), 23.89 (q), 26.30 (br q), 30.38 (d), 31.01 (d), 31.26 (d), 34.25 (d), 36.73 (d), 122.46 (d), 122.80 (d), 127.70 (d), 137.57 (s), 141.19 (s), 145.07 (s), 150.94 (s), 151.26 (s), 154.19 (s). Anal. Calcd for C$_{42}$H$_{84}$S$_2$Si$_6$Sn: C, 53.64; H, 9.00; S, 6.82. Found: C, 53.40; H, 8.72; S, 6.39.

**Thermal Reaction of 3 with Ru$_3$(CO)$_{12}$.** A mixture of dimercaptostannane **3** (100 mg, 0.11 mmol) and triruthenium dodecacarbonyl (135 mg, 0.22 mmol) in 10 mL of toluene was heated at 70 °C for 10 h. After removal of the solvent, the residue was subjected to flash column chromatography (hex-

**Table 7. Physical and Spectral Data for 8**

| | Tb(Tip)$SnSOs_3(CO)_8S_2$ (**8a**) | Tb(Tip)$SnSeOs_3(CO)_8Se_2$ (**8b**) |
|---|---|---|
| color of cryst | reddish yellow | crimson |
| mp, °C | 90–92 | 188–192 |
| UV/vis (hexane), nm ($\epsilon$) | 231 (32 700), 306 (6150), 346 (4230) | 230 (159 200), 314 (35 200), 363 (23 900) |
| IR (KBr), $\nu_{C=O}$, cm$^{-1}$ | 2102 (m), 2082 (s), 2009 (br vs), 1942 (w) | 2096 (m), 2078 (s), 2015 (s), 2002 (vs), 1990 (s), 1937 (w), 1920 (w) |
| $^{119}$Sn NMR, $\delta$ ($CDCl_3$, $Me_4Sn$) | −117, −123 | −113, −120[a] ($^1J_{Sn-Se}$ = 1025 Hz) |

[a] Both signals have the same $^1J_{Sn-Se}$ value.

**Table 8. Physical and Spectral Data for 9 and 10**

| | Tb(Tip)$SnS_4Os_3(CO)_7$ (**9a**) | Tb(Tip)$SnS_2Os_2(CO)_6$ (**10a**) | Tb(Tip)$SnSe_2Os_2(CO)_6$ (**10b**) |
|---|---|---|---|
| color of cryst | red | pale yellow | yellow |
| mp, °C | 240 dec | 285 dec | 285 dec |
| UV/vis (hexane), nm ($\epsilon$) | 229 (62 400), 280 (18 100), 393 (2230), 534 (1020) | 232 (41 900), 265 (15 400), 304 (5390), 338 (2510) | 230 (222 000), 264 (16 700), 319 (4890) |
| IR (KBr), $\nu_{C=O}$, cm$^{-1}$ | 2108 (m), 2090 (s), 2029 (br vs), 1947 (w) | 2077 (s), 2044 (s), 1988 (br vs) | 2073 (s), 2042 (s), 1986 (br vs) |
| $^{119}$Sn NMR, $\delta$ ($CDCl_3$, $Me_4Sn$) | 96, 92 | 289 | 116 ($^1J_{Sn-Se}$ = 512 Hz) |

ane) followed by further purification with GPLC to afford diruthenium complex **5a** (91 mg, 67%).

**Thermal Reaction of 1b with $Ru_3(CO)_{12}$.** A mixture of tetraselenastannolane **1b** (1.00 g, 0.84 mmol) and triruthenium dodecacarbonyl (537 mg, 0.84 mmol) in 50 mL of toluene was heated at 80 °C for 10 h. After removal of the solvent, the residue was subjected to flash column chromatography (hexane to 20% $CH_2Cl_2$–80% hexane) to afford the yellowish brown triruthenium complex **4b** (299 mg, 21%) and the yellowish orange diruthenium complex **5b** (120 mg, 10%) together with *trans*-1,3,2,4-diselenadistannetane **6b**[10] (73 mg, 9%). Both **4b** and **5b** were recrystallized from ethanol–chloroform. **4b**: yellowish brown crystals; mp 185 °C dec; $^1$H NMR ($CDCl_3$ at 57 °C) $\delta$ −0.25 (s, 9H), 0.07 (br s, 18H), 0.12 (s, 9H), 0.35 (s, 9H), 0.41 (s, 9H), 0.78 (d, $J$ = 6.3 Hz, 3H), 1.13 (d, $J$ = 6.7 Hz, 3H), 1.14 (d, $J$ = 6.8 Hz, 6H), 1.27 (s, 1H), 1.37 (d, $J$ = 6.7 Hz, 3H), 1.38 (s, 1H), 1.39 (d, $J$ = 6.7 Hz, 3H), 2.57 (br s, 1H), 2.75 (sept, $J$ = 6.8 Hz, 1H), 3.71 (s, 1H), 4.91 (br s, 1H), 6.28 (br s, 1H), 6.54 (br s, 1H), 6.83 (s, 1H), 7.01 (s, 1H); $^{13}$C NMR ($CDCl_3$ at 57 °C) $\delta$ 1.04 (br q), 2.32 (br q), 2.54 (q), 23.79 (q), 25.04 (q), 26.03 (q), 27.17 (q), 28.77 (q), 30.77 (br d), 32.54 (br d), 33.16 (d), 34.44 (d), 37.92 (d), 123.79 (d), 123.99 (d), 128.70 (br d), 129.61 (br d), 142.21 (s), 142.56 (s), 144.20 (s), 146.10 (s), 148.60 (s), 151.06 (s), 152.56 (s), 155.99 (s), 181.40 (s), 182.68 (s), 183.16 (s), 183.30 (s), 188.19 (s), 191.59 (s), 197.29 (s). Anal. Calcd for $C_{49}H_{82}O_7Ru_3Se_4Si_6Sn{\cdot}2H_2O$: C, 34.11; H, 5.02; Se, 18.30. Found: C, 34.00; H, 4.59; Se, 18.01. For UV/vis, IR, and $^{119}$Sn NMR spectra, see Table 6. **5b**: yellowish orange crystals; mp 208 °C dec; $^1$H NMR ($CDCl_3$) $\delta$ 0.02 (s, 18H), 0.11 (s, 18H), 0.35 (s, 18H), 1.24 (d, $J$ = 6.9 Hz, 6H), 1.29 (d, $J$ = 6.4 Hz, 6H), 1.41 (s, 1H), 1.53 (d, $J$ = 6.4 Hz, 6H), 1.58 (br s, 2H), 2.81 (br s, 2H), 2.87 (sept, $J$ = 6.9 Hz, 1H), 6.46 (br s, 2H), 7.05 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.94 (br q), 1.71 (br q), 2.77 (br q), 23.70 (q), 26.92 (q), 27.46 (q), 30.68 (d), 33.97 (d), 34.08 (d), 38.40 (br d), 124.61 (d), 129.49 (br d), 141.02 (s), 143.26 (s), 145.01 (s), 149.31 (s), 151.45 (s), 153.71 (s), 190.81 (br s), 195.24 (br s), 195.81 (br s). Anal. Calcd for $C_{48}H_{82}O_6Ru_2Se_2Si_6Sn$: C, 41.07; H, 5.89; Se, 11.23. Found: C, 40.78; H, 5.65; Se, 11.10. For UV/vis, IR, and $^{119}$Sn NMR spectra, see Table 6.

**Thermal Reaction of 1a with $Os_3(CO)_{12}$.** A mixture of tetrathiastannolane **1a** (599 mg, 0.60 mmol) and triosmium dodecacarbonyl (542 mg, 0.60 mmol) in 30 mL of toluene was heated under reflux for 10 h. After removal of the solvent, the residue was subjected to GPLC and DCC (hexane) to give the reddish yellow triosmium complex **8a** (127 mg, 12%), the red triosmium complex **9a** (105 mg, 10%), and the yellow diosmium complex **10a** (257 mg, 29%). **8a**, **9a**, and **10a** were all recrystallized from ethanol–chloroform. **8a**:[29] reddish yellow crystals; mp 90–92 °C; $^1$H NMR (toluene-$d_8$ at 97 °C, 400 MHz) $\delta$ 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) $\delta$ 0.86 (q), 1.24 (q), 1.28 (q), 1.34 (q), 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), 25.32 (q), 25.48 (q × 2), 26.87 (q), 28.98 (q), 29.39 (q), 30.18 (d), 30.84 (d), 34.12 (d), 34.46 (d), 34.62 (d), 35.07 (d), 36.51 (d), 39.20 (d), 39.53 (d), 41.05 (d), 41.39 (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 × 2), 150.69 (s), 153.51 (s), 153.84 (s), 153.87 (s), 169.27 (s), 170.53 (s), 170.56 (s), 171.48 (s), 171.53 (s), 172.34 (s), 174.54 (s), 175.08 (s), 179.55 (s), 179.71 (s), 183.72 (s), 183.84 (s). 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. For UV/vis, IR, and $^{119}$Sn NMR spectra, see Table 7. **9a**: red crystals; mp 240 °C dec; $^1$H NMR ($CDCl_3$ at 57 °C) $\delta$ −0.25 (s, 9H), 0.08 (br s, 18H), 0.13 (s, 9H), 0.31 (s, 9H), 0.41 (s, 9H), 0.84 (d, $J$ = 6.3 Hz, 3H), 1.15 (d, $J$ = 6.9 Hz, 3H), 1.16 (d, $J$ = 6.9 Hz, 3H), 1.20 (d, $J$ = 6.4 Hz, 3H), 1.27 (s, 1H), 1.29 (s, 1H), 1.34 (d, $J$ = 6.5 Hz, 6H), 2.57 (br s, 1H), 2.77 (sept, $J$ = 6.9 Hz, 1H), 3.52 (s, 1H), 4.92 (br s, 1H), 6.39 (br s, 1H), 6.49 (br s, 1H), 6.88 (s, 1H), 7.07 (s, 1H); $^{13}$C NMR ($CDCl_3$ at 57 °C, 100 MHz) $\delta$ 1.15 (br q), 2.23 (br q), 2.39 (q), 2.54 (q), 23.63 (q), 24.31 (br q), 26.11 (q), 27.13 (q), 29.11 (q), 30.76 (d), 31.45 (br d), 32.86 (br d), 34.47 (d), 37.53 (d), 123.79 (d), 124.03 (d), 128.64 (br d), 130.14 (br d), 144.34 (s), 145.34 (s), 147.03 (br s), 148.88 (br s), 150.98 (br s), 151.61 (s), 152.95 (s), 156.72 (s), 168.45 (s), 169.20 (s), 169.61 (s), 169.67 (s), 172.35 (s), 173.07 (s), 175.56 (s). Anal. Calcd for $C_{49}H_{82}O_7Os_3S_4Si_6Sn$: C, 33.26; H, 4.67; S, 7.25. Found: C, 33.05; H, 4.49; S, 7.31. For UV/vis, IR, and $^{119}$Sn NMR spectra, see Table 8. **10a**: yellow crystals; mp 285 °C dec; $^1$H NMR ($CDCl_3$) $\delta$ 0.02 (s, 18H), 0.11 (s, 18H), 0.33 (s, 18H), 1.25 (d, $J$ = 6.9 Hz, 6H), 1.31 (d, $J$ = 6.4 Hz, 6H), 1.42 (s, 1H), 1.45 (br s, 2H), 1.50 (d, $J$ = 6.4 Hz, 6H), 2.75 (br s, 2H), 2.88 (sept, $J$ = 6.9 Hz, 1H), 6.50 (br s, 2H), 7.12 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.91 (br q), 1.76 (br q), 2.49 (br q), 23.70 (q), 27.08 (q), 27.11 (q), 30.79 (d),

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[29] For the $^1$H NMR data the chemical shifts of coalesced signals observed in toluene-$d_8$ at 97 °C are shown, while for the $^{13}$C NMR data the chemical shifts of the two sets of signals in $CDCl_3$ at room temperature are listed, 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.

**Table 9. Crystal Data for 2, 4b, 5a, and 8a,b**

| | **2** | **4b** | **5a** | **8a** | **8b** |
|---|---|---|---|---|---|
| cryst syst | monoclinic | triclinic | triclinic | triclinic | triclinic |
| space group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 17.34(5) | 15.578(4) | 14.017(1) | 13.31(1) | 16.821(5) |
| $b$, Å | 11.09(1) | 23.123(5) | 18.80(1) | 24.069(4) | 18.260(6) |
| $c$, Å | 32.985(5) | 10.195(2) | 12.925(6) | 12.051(3) | 13.508(4) |
| $\alpha$, deg | | 98.16(2) | 108.76(4) | 94.57(2) | 106.22(3) |
| $\beta$, deg | | 98.11(2) | 90.06(4) | 113.75(3) | 107.09(2) |
| $\gamma$, deg | | 94.51(2) | 78.69(4) | 99.58(5) | 75.37(3) |
| $V$, Å$^3$ | 6327 | 3581(1) | 3155(3) | 3438(4) | 3721(3) |
| $Z$ | 4 | 2 | 2 | 2 | 2 |
| $D_c$, g cm$^{-3}$ | 1.392 | 1.584 | 1.387 | 1.705 | 1.701 |
| $R$ | 0.068 | 0.106 | 0.036 | 0.043 | 0.068 |
| $R_w$ | 0.064 | 0.126 | 0.037 | 0.043 | 0.086 |

33.68 (d), 34.18 (d), 38.01 (br d), 125.36 (d), 130.07 (br d), 145.21 (s), 145.54 (s), 146.64 (s), 149.37 (s), 151.89 (s), 154.26 (s), 169.93 (s), 172.24 (s), 178.15 (s). Anal. Calcd for $C_{48}H_{82}O_6Os_2S_2Si_6Sn$: C, 38.77; H, 5.56; S, 4.31. Found: C, 38.51; H, 5.41; S, 3.91. For UV/vis, IR, and $^{119}$Sn NMR spectra, see Table 8.

**Thermal Reaction of 1b with $Os_3(CO)_{12}$.** A mixture of tetraselenastannolane **1b** (200 mg, 0.17 mmol) and triosmium dodecacarbonyl (157 mg, 0.17 mmol) in 20 mL of toluene was heated under reflux for 10 h. After removal of the solvent, the residue was subjected to PTLC (hexane) to afford the crimson triosmium complex **8b** (28 mg, 9%) and the yellow diosmium complex **10b** (34 mg, 13%) along with diselenadistannetane **6b** (26 mg, 16%). Both **8b** and **10b** were recrystallized from ethanol–chloroform. **8b**:[29] crimson crystals; mp 188–192 °C; $^1$H NMR (toluene-$d_8$ at 77 °C) $\delta$ 0.09 (br s, 9H), 0.165 (s, 9H), 0.172 (s, 9H), 0.34 (br s, 27H), 1.18 (d, $J$ = 6.9 Hz, 6H), 1.27 (d, $J$ = 6.4 Hz, 3H), 1.49 (d, $J$ = 6.7 H, 3H), 1.50 (s, 1H), 1.56 (d, $J$ = 6.5 Hz, 3H), 1.61 (d, $J$ = 6.4 Hz, 3H), 1.98 (br s, 1H), 2.76 (sept, $J$ = 6.9 Hz, 1H), 3.17 (br s, 1H), 3.54 (br s, 1H), 3.77 (br s, 1H), 6.73 (br s, 2H), 7.10 (s, 1H), 7.11 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 0.99 (q), 1.19 (q), 1.26 (q), 1.65 (q), 1.67 (q), 1.85 (q), 2.30 (q), 2.81 (q), 2.96 (q), 23.63 (q), 24.05 (q), 25.46 (q), 25.49 (q), 25.89 (q), 26.14 (q), 26.60 (q), 26.78 (q), 28.76 (q), 29.24 (q), 30.11 (d), 30.82 (d), 34.13 (d), 34.22 (d), 35.07 (d), 35.21 (d), 35.67 (d), 38.40 (d), 38.88 (d), 41.43 (d), 41.81 (d), 122.58 (d), 122.61 (d), 122.73 (d), 122.83 (d), 123.24 (d), 123.41 (d), 128.57 (d), 128.84 (d), 140.80 (s), 140.97 (s), 143.67 (s), 143.67 (s), 143.77 (s), 147.33 (s), 147.47 (s), 149.98 (s), 150.04 (s), 150.39 (s), 150.43 (s), 150.98 (s), 151.25 (s), 153.26 (s), 153.29 (s), 153.44 (s), 153.48 (s), 167.74 (s), 167.81 (s), 169.58 (s), 169.62 (s), 170.83 (s), 170.89 (s), 171.18 (s), 173.99 (s), 176.74 (s), 177.30 (s), 177.49 (s), 178.76 (s), 178.89 (s). Anal. Calcd for $C_{50}H_{82}O_8Os_3Se_3Si_6Sn$: C, 31.50; H, 4.34. Found: C, 31.53; H, 4.18. For UV/vis, IR, and $^{119}$Sn NMR spectra, see Table 7. **10b**: yellow crystals; mp 285 °C dec; $^1$H NMR (CDCl$_3$) $\delta$ 0.02 (s, 18H), 0.11 (s, 18H), 0.35 (s, 18H), 1.25 (d, $J$ = 6.9 Hz, 6H), 1.30 (d, $J$ = 6.4 Hz, 6H), 1.41 (s, 1H), 1.44 (br s, 2H), 1.55 (d $J$ = 6.4 Hz, 6H), 2.73 (br s, 2H), 2.88 (sept, $J$ = 6.9 Hz, 1H), 6.46 (br s, 2H), 7.07 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 1.24 (br q), 1.63 (br q), 2.77 (br q), 23.69 (q), 27.04 (q), 27.39 (q), 30.78 (d), 33.74 (d), 34.13 (d), 38.15 (br d), 125.13 (d), 130.12 (br d), 141.95 (s), 144.02 (s), 145.40 (s), 149.20 (s), 151.73 (s), 153.92 (s), 171.62 (s), 173.93 (s), 177.50 (s). Anal. Calcd for $C_{48}H_{82}O_6Os_2Se_2Si_6Sn$: C, 36.47; H, 5.27; Se, 9.99. Found: C, 36.41; H, 5.07; Se, 10.19. For UV/vis, IR, and $^{119}$Sn NMR spectra, see Table 8.

**Crystal and Experimental Data for 2, 4b, 5a, and 8a,b.**[30] The intensity data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å), and the structures were solved by direct methods for **2**, **4b**, and **8a,b** and by a combination of the Patterson method and direct methods for **5a**. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp. The non-hydrogen atoms were defined anisotropically for **5a** and **8a,b** and either anisotropically or isotropically for **2** and **4b**, and all hydrogen atoms were located by calculation. The final cycle of full-matrix least-squares refinement was based on 2584 (for **2**), 3899 (for **4b**), 6856 (for **5a**), 7663 (for **8a**), and 8395 (for **8b**) observed reflections ($I > 3.00\sigma(I)$) and 317 (for **2**), 355 (for **4b**), 586 (for **5a**), and 640 (for **8a,b**) variable parameters, respectively. Crystal data for all molecules are summarized in Table 9.

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**Supplementary Material Available:** Figures giving full atom labeling and tables giving crystal data, atomic coordinates, temperature factors, bond lengths and angles, and torsion angles for **2**, **4b**, **5a**, and **8a,b** (204 pages). Ordering information is given on any current masthead page.

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[30] All the crystallographic data with tables of thermal and positional parameters for **8a,b** have already been deposited as the supplementary material of the preliminary communication.[13]